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Research article

Efficacy of yellow gypsum application on mitigating arsenic bioavailability in groundnut and *Boro*-rice grown under arsenic contaminated soil

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A B S T R A C T

Agricultural soils naturally enriched with Arsenic (As) represent a significant global human health risk. In the present investigation, a series of pot experiments were conducted to study the efficacy of three levels of Yellow Gypsum (YG) application on bioavailability of As to *kharif* groundnut followed by *boro*-rice grown under 17 different levels of soil As contamination for two consecutive years. The results revealed that application of YG @ 60 kg ha^{-1} effectuated the lowest soil As content and the highest percent decline in soil extractable As at pegging (9.42 mg kg^{-1} and 9.81%) and harvesting (8.81 mg kg^{-1} and 11.85%) in groundnut, maximum tillering (7.52 mg kg^{-1} and 16.95%) and harvesting (6.77 mg kg^{-1} and 19.85%) in *boro*-rice respectively. It was also observed that irrespective of its level, the extractable As content of soil decreased significantly ($P < 0.05$) with increasing dosage of YG. Increase in YG dose effectuated a significant ($P < 0.05$) increasing trend and increase in As content in soil indicated a decreasing trend of Ca:As, Fe:As and S:As ratios which pointed out the potentiality of YG for reducing As bio-availability in contaminated soils and thus could be a good option for mitigating the risk of As contamination in food chain.

1. Introduction

Arsenic (As), a toxic metalloid and a class-I carcinogen, exists in the environment in different inorganic and organic forms ranking twentieth in abundance of elements in the earth's crust, fourteenth in seawater and twelfth in human body [1]. Available literature suggests while weathering of rocks containing As, combustion of coal, and smelting of metal ores constitute the geogenic source of As contamination in soil system, anthropological sources include application of As-based pesticides, wood preservation by chromated copper arsenate (CCA) and mining activities [2]. Human suffering from As toxicity through very high degree of As contamination of ground water has been reported in Bangladesh followed by West Bengal in India and around 20 countries across the globe including Argentina, Chile, Finland, Hungary, Mexico, Nepal, China etc. [3]. The first report of As contamination of groundwater in India was recorded in the states of Haryana, Punjab, Himachal Pradesh, Uttar Pradesh and other parts of northern India during 1976 [4] and later [5] but the highest among different states of India was reported in the lower Gangetic Plains of West Bengal in 1984 [6]. The As concentration in groundwater in India ranges between 50 and 1600 $\mu g l^{-1}$ is several orders of magnitude higher than the maximum

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acceptable concentration (MAC) set by WHO (10 μgl^{-1}) [3]. The problem arising out of drinking the contaminated groundwater is further aggravated due to its extensive usage (85–90%) for irrigating crop fields [7]. Ccontinuous and indiscriminate use of As contaminated groundwater may lead to a build-up of this toxic element in soils, in turn triggering its entry into the food chain. Build-up of As in soils can also pose a significant risk to quality of ground water used for drinking and irrigating crop fields; adversely affect plant growth, animal health, food safety and ultimately human health [8,9]. Allowing entry of both arsenate and arsenite efficiently, Rice can accumulate 10 folds' higher amount of As in grain compared to other cereal crops [10] and among different agricultural crops is rated the greatest contributor towards inorganic As uptake through food [11]. Elevated level of As in rice grain [12,13] have been reported from paddy fields irrigated with As contaminated water. Recent reports in the literature suggested definite link between As exposure from rice and risks of hypertension and cancer in As-affected populations in Bihar (India), England, Wales [14,15] and Beijing [16].

In Legumes rate of translocation of As is low resulting in in its accumulation mainly in leaves, and thus indicates that it can be translocated via phloem to the grain. As expected for a non-hyperaccumulator plant in groundnut also most of the As absorbed is observed in roots [17,18]. Systematic research on As concentration in edible parts of peanuts grown under different edaphic condition are lacking. Recycling/recovery/management of solid waste (SW) including those generated in iron and steel making industry vis-à-vis their adverse environmental impact has received much public attention in recent years. Value addition of these wastes for agricultural use and reducing their quantum has attracted attention of the global scientific community. One such value-added product containing quite good amount of essential plant nutrients is YG, prepared from treatment of 60 mesh Linz-Donawitz slag (LD slag) (steel slag obtained from the Linz-Donawitz making process) with sulphuric acid followed by neutralization [19]. Cations and anions mutually influence their behavior in soil environment [20] and calcium and magnesium being the most important cations in soil environmental can influence the behavior of important anions, such as As (As), in a complex manner as both precipitation and adsorption equilibriums are potentially important. Application of calcium to soil increases sorption of Ca^{2+} leading to increased positive charge of the adsorption surface and thereby increase anion sorption [21]. The significance of YG in agricultural use because of its potential as an excellent replacement for common gypsum and better plant nutritional values in terms of sulphur, calcium, phosphorus, iron and silica. It also contains traces of micro-nutrients like manganese, copper, boron, nickel, molybdenum, etc. The content of heavy metal and other hazardous metals are quite below the limit set by toxicity characteristic leaching procedure (TCLP) for the product of similar nature such as phospho gypsum [22]. Day by day arsenic content in soil is increasing by various agricultural practices and leading to arsenic build-up in soil and causing treat to human health and ecosystem. It is also every important to recycle the industrial hazardous and non-hazardous to conserve natural resources and for go green earth. Hence, we have focused on how extent management of industrial solid waste (Yellow Gypsum) and reducing the soil extractable arsenic in this study. This study focused on reducing the As bioavailability to the plants under different degree of induced As contamination in pots using YG as an amendment.

2. Material and methods

2.1. Experiment and treatment details

Bulk surface soil (0–0.15 m) was collected from rice fields of Panchpota area of Nadia district, West Bengal, in Eastern India. The bulk soil was dried in shade and ground to pass through 2 mm sieve. A 5 kg portion of the processed soil was filled in a series of earthen pots (20 cm diameter) to which graded levels of As ranging between 0 and 24.0 mg kg^{-1} (Table 1) were added through As salt of sodium (sodium arsenite $NaAsO_2$) and allowed to equilibrate for one month. After equilibration, the final Extractable Arsenic concentration ranging between 12.2 and 22.8 mgkg^{-1} soil was achieved (Table 1). Groundnut (TG-51) was grown during *kharif (Rainy)*

Table 1
Olsen extractable Arsenic content in experimental pots.

Treatments	Amount of Arsenic Added to the Soil (mg kg^{-1})	Olsen Extractable Arsenic Content (mg kg^{-1}) After Equilibration
T_0	0	12.20^{q}
T_1	1.5	14.80^{p}
T_2	3.0	15.20^{o}
T_3	4.5	15.40^{n}
T_4	6.0	15.80^{m}
T_5	7.5	16.90^{l}
T_6	9.0	17.30^{k}
T_7	10.5	17.80^{j}
T_8	12.0	18.60^{i}
T_9	13.5	19.40^{h}
T_{10}	15.0	19.50^{g}
T_{11}	16.5	19.60^{f}
T_{12}	18.0	20.90^{e}
T_{13}	19.5	21.00^{d}
T_{14}	21.0	21.20^{c}
T_{15}	22.5	21.60^{b}
T_{16}	24.0	22.80^{a}

SEm ± 0.019.
LSD ($P < 0.05$) 0.052.

season followed by Rice (Shatabdi: IET-4786) during *boro* (dry) season in these pots. Three levels of YG amendments viz., 0, 30 and 60 kgha^{-1} were also applied to these treated soils. The experiment was laid out in a Completely Randomized Design and replicated thrice. The physicochemical properties and element content of Yellow Gypsum were provided in Supplementary Material Table S1.

2.2. Initial soil characteristics

The initial properties of As spiked soil in the 17 pots after equilibration and before sowing of groundnut crop were analysed for extractable (Olsen's Extractant) As content, pH, S, Ca, Fe and Mn following standard protocols. While the extractable As content of the soil under different levels of As treatment varied between 12.20 and 22.80 mg kg^{-1} (Table 1); the pH, S, Ca, Fe and Mn content varied between 7.23 and 7.35; 45.97–46.11 mg kg^{-1}; 2.45–2.58 cmol (P^{+}) kg^{-1}; 50.93–51.32 mg kg^{-1} and 22.97–23.14 mg kg^{-1}, respectively (Fig. 1).

2.3. Fertilizer and amendment application

Three levels of YG *i.e.,* 0 kg ha^{-1}, 30 kg ha^{-1} and 60 kg ha^{-1} were applied to the pots two weeks before sowing or transplanting of crop and left for equilibration. Groundnut crop was fertilized with recommended doses of chemical fertilizer (N: P_2O_5: K_2O: 25:50:50 kg ha^{-1}) and *boro*-rice with recommended dose of chemical fertilizer (N:P_2O_5:K_2O: 120:60:60 kg ha^{-1}) through urea, single super phosphate and muriate of potash uniformly to all the treatments. Full dose of P and K and half dose of N were applied 7 days before Sowing in groundnut and transplanting in rice, the remaining one-half of N was applied during flowering stage in groundnut and maximum tillering stage of rice.

2.4. Soil sampling

Groundnut (*cv. TG-51*) was sown during kharif season using three seeds per pot. Similarly, thirty days old rice seedlings (*cv. Shatabdi: IET 4786*) were transplanted during *boro* season using three rice hills (two seedlings per hill) per pot. Soil samples were collected at 45 days after sowing and transplanting and during harvest of each crop for recording observations in groundnut and rice crop, respectively.

2.5. Determination of extractable soil arsenic

Accurately weighed 2.5 g of soil was shaken for 30 min with 50 ml 0.5 M $NaHCO_3$ (pH-8.5) to which 1 spoonful of activated charcoal was added and filtered using Whatman no. 42 filter paper in a polythene bottle. A 10 ml portion of the filtrate was taken in 50 ml volumetric flask and 1 ml each of 5% ascorbic acid and 5 % potassium iodide were added to it. Then it was kept for 45 min and finally volume was made up using 10 % HCl. Finally, readings were taken in FIAS-flame technique using hydride generator (sodium borohydride) in Atomic Absorption Spectrophotometer (AAS) [Model: PerkinElmer Pinnacle 900F) as proposed by Ref. [23].

2.6. Determination of soil parameters

Soil pH was estimated following method proposed by Jackson [24], Available Sulphur by Williams and Steinbergs [25],

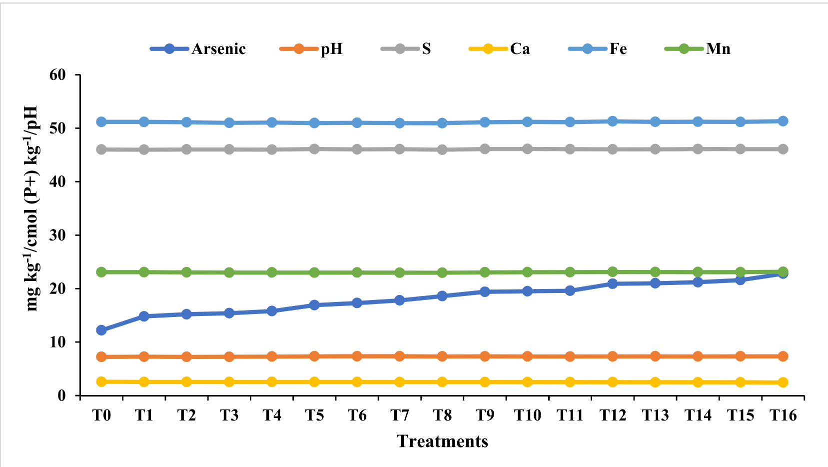

Fig. 1. Initial chemical properties of the experimental soil (Extractable Arsenic, Soil pH, Extractable Sulphur, Extractable Calcium, Extractable Iron, Extractable Manganese) (*Treatments (Spiked As Conc. (ppm) in pots):* T_0*-0,* T_1*-1.5,* T_2*-3.0,* T_3*-4.5,* T_4*-6.0,* T_5*-7.5,* T_6*-9.0,* T_7*-10.5,* T_8*-12.0,* T_9*-13.5,* T_{10}*-15.0,* T_{11}*-16.5,* T_{12}*-18.0,* T_{13}*-19.5,* T_{14}*-21.0,* T_{15}*-22.5,* T_{16}*-24.0*).

Table 2
Effect of Yellow Gypsum on Soil Extractable Arsenic (mg kg^{-1}) under different arsenic concentration treatments at different stages of Groundnut and *Boro*-rice crop.

Treatment	Soil extractable Arsenic (mg kg^{-1})															
	Groundnut								*Boro*-rice							
	Pegging				Harvest				Maximum Tillering				Harvest			
	Y_0	Y_{30}	Y_{60}	Mean (T)	Y_0	Y_{30}	Y_{60}	Mean (T)	Y_0	Y_{30}	Y_{60}	Mean (T)	Y_0	Y_{30}	Y_{60}	Mean (T)
T_0	11.44	10.68	9.42	**10.51**^{m}	11.30	10.35	8.81	**10.15**^{l}	10.92	9.66	7.52	**9.36**^{k}	10.72	9.25	6.77	**8.91**^{k}
T_1	13.97	13.24	11.98	**13.06**^{l}	13.82	12.91	11.37	**12.70**^{k}	13.39	12.18	10.03	**11.87**^{j}	13.19	11.76	9.28	**11.41**^{j}
T_2	14.36	13.62	12.37	**13.45**^{k}	14.21	13.29	11.76	**13.08**^{j}	13.77	12.55	10.41	**12.24**^{ij}	13.57	12.14	9.66	**11.79**^{ij}
T_3	14.55	13.82	12.56	**13.64**^{k}	14.40	13.48	11.95	**13.28j**	13.96	12.75	10.60	**12.43**^{hi}	13.76	12.33	9.84	**11.97**^{hi}
T_4	14.94	14.20	12.94	**14.03**^{j}	14.79	13.87	12.33	**13.66**^{i}	14.34	13.13	10.98	**12.81**^{h}	14.14	12.70	10.22	**12.35**^{h}
T_5	16.05	15.40	14.20	**15.22**^{i}	15.90	15.09	13.64	**14.88**^{h}	15.45	14.37	12.34	**14.05**^{g}	15.27	14.00	11.67	**13.64**^{g}
T_6	16.44	15.79	14.59	**15.61**^{h}	16.29	15.48	14.02	**15.26**^{g}	15.83	14.75	12.72	**14.43**^{g}	15.65	14.38	12.04	**14.02**^{g}
T_7	16.93	16.27	15.07	**16.09**^{g}	16.78	15.96	14.50	**15.75**^{f}	16.31	15.22	13.19	**14.91**^{f}	16.12	14.85	12.51	**14.49**^{f}
T_8	17.75	17.12	15.98	**16.95**^{f}	17.61	16.85	15.48	**16.65**^{e}	17.15	16.12	14.20	**15.82**^{e}	16.96	15.76	13.53	**15.42**^{e}
T_9	18.57	18.02	16.98	**17.86**^{e}	18.43	17.79	16.56	**17.59**^{d}	17.98	17.10	15.34	**16.81**^{d}	17.81	16.78	14.75	**16.45**^{d}
T_{10}	18.67	18.12	17.08	**17.95**^{e}	18.53	17.88	16.66	**17.69**^{d}	18.08	17.20	15.44	**16.90**^{d}	17.90	16.87	14.85	**16.54**^{d}
T_{11}	18.76	18.21	17.17	**18.05**^{e}	18.63	17.98	16.75	**17.79**^{d}	18.17	17.29	15.53	**17.00**^{d}	18.00	16.96	14.94	**16.63**^{d}
T_{12}	20.07	19.61	18.66	**19.45**^{d}	19.95	19.42	18.33	**19.23**^{c}	19.48	18.78	17.16	**18.47**^{c}	19.33	18.49	16.66	**18.16**^{c}
T_{13}	20.17	19.71	18.76	**19.55**^{cd}	20.05	19.51	18.42	**19.33**^{c}	19.58	18.87	17.25	**18.57**^{c}	19.43	18.58	16.75	**18.25**^{c}
T_{14}	20.36	19.90	18.95	**19.74**^{c}	20.24	19.71	18.62	**19.52**^{c}	19.77	19.06	17.44	**18.76**^{bc}	19.61	18.77	16.94	**18.44**^{bc}
T_{15}	20.75	20.29	19.34	**20.13**^{b}	20.63	20.09	19.00	**19.90**^{b}	20.15	19.44	17.82	**19.14**^{b}	20.00	19.15	17.31	**18.82**^{b}
T_{16}	21.96	21.55	20.69	**21.40**^{a}	21.84	21.38	20.42	**21.22**^{a}	21.36	20.75	19.29	**20.47**^{a}	21.21	20.51	18.86	**20.19**^{a}
Mean (Y)	**17.40**^{a}	**16.80**^{b}	**15.69**^{c}		**17.26**^{a}	**16.53**^{b}	**15.21**^{c}		**16.80**^{a}	**15.84**^{b}	**13.96**^{c}		**16.63**^{a}	**15.49**^{b}	**13.33**^{c}	
Range	**12.54**				**13.03**				**13.84**				**14.44**			
	LSD (*P* < *0.05*)	**SEm ±**	**SE(d)**		**LSD (*P* < *0.05*)**	**SEm ±**	**SE(d)**		**LSD (*P* < *0.05*)**	**SEm ±**	**SE(d)**		**LSD (*P* < *0.05*)**	**SEm ±**	**SE(d)**	
T	0.07	0.03	0.04		0.07	0.02	0.04		0.10	0.04	0.05		0.1	0.04	0.05	
Y	0.03	0.01	0.02		0.03	0.01	0.02		0.04	0.02	0.02		0.04	0.02	0.02	
T*Y	0.16	0.04	0.06		0.12	0.04	0.06		0.18	0.06	0.09		0.2	0.06	0.09	

(Treatments (Spiked As Conc. (ppm) in pots): T_0-0, T_1-1.5, T_2-3.0, T_3-4.5, T_4-6.0, T_5-7.5, T_6-9.0, T_7-10.5, T_8-12.0, T_9-13.5, T_{10}-15.0, T_{11}-16.5, T_{12}-18.0, T_{13}-19.5, T_{14}-21.0, T_{15}-22.5, T_{16}-24.0); numbers followed by different letters indicate significant differences at P < 00.05 (otherwise statistically at par). NS: non-significant (P > 00.05).

Exchangeable Calcium by David method [26], DTPA extractable Iron and Manganese by Lindsay and Norvell [27].

2.6.1. Ca:As, Fe:As and S:As ratios in soil

Elements concentration ratios were calculated as

$$\text{Ca : As ratio} = \frac{\textit{Concentration of Exchangeable Calcium in soil}}{\textit{Concentration of Extractable Arsenic in soil}}$$

$$\text{Fe : As ratio} = \frac{\textit{Concentration} \text{ of DTPA Extractable Iron in soil}}{\text{Concentration of Extractable Arsenic in soil}}$$

$$\text{S : As ratio} = \frac{\textit{Concentration} \text{ of Available Sulphur in soil}}{\text{Concentration of Extractable Arsenic in soil}}$$

2.6.2. Pecentage (%) change calculations in soil

Pecentage (%) change calculations in soil were calculated as

$$\text{Pecentage (\%)}\ \textit{change over control} = \frac{\textit{Mean of the stage} - \textit{Mean of the control}\ (Y0)}{\textit{Mean of the control}\ (Y0)} X\ 100$$

$$\text{Pecentage (\%)}\ \textit{change over Initial} = \frac{\textit{Mean of the stage} - \textit{Mean of the initial content}}{\textit{Mean of the initial content}} X\ 100$$

$$\text{Pecentage (\%) change over control} = \frac{\text{Mean of the stage} - \text{Mean of the control } (Y_0)}{\text{Mean of the control } (Y_0)} \text{X } 100$$

$$\text{Pecentage (\%) change over Initial} = \frac{\text{Mean of the stage} - \text{Mean of the initial content}}{} \text{X } 100$$

$$\text{Pecentage (\%) change in Arsenic} = \frac{\text{Mean Extractable As at particular season (or) stage of the crop} - \text{Mean Extractable As at initial set up of experiment}}{\text{Mean Extractable As at initial set up of experiment}} \text{X } 100$$

2.7. Statistical analysis

All statistical analyses were carried out using SPSS (SPSS 7.5, 1997) and R software. All measured variables were statistically analysed following methods meant for Factorial Completely Randomized Design (CRD). Duncan's multiple range test (DMRT) at 5% was followed to compare the treatment means. Factorial CRD analysis was done using OPSTAT software (created by O.P. Sheoran, CCS HAU, Hissar, Haryana) to assess the bioavailability of As at different growth stages of groundnut and *boro-rice*. Data pooled over two seasons in respective crops have been presented. Correlation Matrix (Pearson Correlation Coefficient) was prepared to understand the interrelationship among different soil and plant parameters of the component crops of the sequence. The data generated was further analysed using Regression and Path Analysis to arrive at specific conclusions.

3. Results

3.1. Effect of addition of different doses of yellow gypsum on extractable arsenic (mg kg^{-1}) in soil

Application of YG exerted a significant ($P < 0.05$) effect on extractable As in soil under both the crops. The extractable As content varied between 11.44 to 21.96 and 11.30–21.84 mg kg^{-1} (Y_0), 10.68 to 21.55 and 10.35–21.38 mg kg^{-1} (Y_{30}) and 9.42 to 20.69 and 8.81–20.42 mg kg^{-1} (Y_{60}) at pegging and harvest stage of groundnut, respectively (Table 2). Irrespective of dosage of YG, the lowest mean soil extractable As was observed in treatment T_0 (10.51, 10.15 mg kg^{-1}) and the highest was observed in treatments T_{16} (21.40, 21.22 mg kg^{-1}) during pegging and harvest stages of groundnut in general. Bioavailability of As significantly ($P < 0.05$) decreased with increasing dosage of YG irrespective of the level of As contamination in the experimental soil. Application of 60 kg YG ha^{-1} (Y_{60}) effectuated the lowest soil extractable As (15.69, 15.21 mg kg^{-1}) followed by application of 30 kg YG ha^{-1} (Y_{30}) (16.80, 16.53 mg kg^{-1}) and the highest extractable As (17.40, 17.26 mg kg^{-1}) content of soil were recorded under the control where no YG was applied (Y_0) during pegging and harvest stages of groundnut, respectively (Table 2).

Similarly, in *boro*-rice, the extractable As content of soil ranged between 10.92 to 21.36 and 10.72–21.21 mg kg^{-1} (Y_0), 9.66 to 20.75 and 9.25–20.51 mg kg^{-1} (Y_{30}), 7.52 to 19.29 and 6.77–18.86 mg kg^{-1} (Y_{60}) during maximum tillering and harvest stages, respectively (Table 2). The lowest mean soil extractable As was observed in treatment T_0 (9.36, 20.47 mg kg^{-1}) and the highest was observed in treatments T_{16} (8.91, 20.19 mg kg^{-1}) during maximum tillering and harvest stages of rice in general. Irrespective of the level of As contamination the bioavailability of As decreased significantly ($P < 0.05$) with increasing dosage of YG application in the experimental soil. The lowest soil extractable As (13.96, 13.33 mg kg^{-1}) was recorded under application of 60 kg YG ha^{-1} (Y_{60}) followed by application of 30 kg YG ha^{-1} (Y_{30}) (15.84, 15.49 mg kg^{-1}) and the highest extractable As (16.80, 16.63 mg kg^{-1}) was recorded under the control pots (Y_0) during maximum tillering and harvest stages of rice, respectively (Table 2).

Irrespective of the level of As contamination, a significant decreasing trend ($P < 0.05$) in the mean extractable As content with increasing dosage of YG application was observed in all the soils. The highest decline in soil extractable As with respect to the control (Y_0) was observed under T_0Y_{60} (17.66, 22.0, 31.15, 36.88%) and the lowest in $T_{16}Y_{30}$ (1.87, 2.11, 2.84, 3.31 %) during pegging and harvest stages of groundnut; maximum tillering and harvest stages of *boro*-rice, respectively.

Irrespective of treatments, the mean extractable As content showed a decreasing trend with increase in dosage of YG. The highest decline in soil extractable As with respect to the control (Y_0) was observed under Y_{60} (9.81, 11.85, 16.95, 19.85%) and also with respect to the initial As content (13.96, 16.58, 23.46 and 26.92%) (Fig. 2) followed by Y_{30} and the lowest in Y_0 at pegging and harvest stages of groundnut; maximum tillering and harvest stages of *boro*-rice, respectively.

Time scale of application had a prominent effect on As bioavailability. In our study we have started with *kharif* groundnut crop followed by *boro*-rice and repeated twice. In four seasons of experiment highest percent decline in As was observed in season-IV *i.e.* at boro-rice harvest (12.23% (Y_0), 20.67% (Y_{30}) and 36.46% (Y_{60}). The trend of decline in As availability by application of YG followed the order Season-I < Season-II < Season-III < Season-IV. Percent decline in As bioavailability with respect to initial As content was the highest with application of 60 kg YG ha^{-1} (Y_{60}) (7.40, 17.38, 25.77 and 36.46%) followed by Y_{30} and the lowest in Y_0 (Fig. 3).

3.2. Effect of Yellow Gypsum application on soil pH

The pH of the experimental soil increased from the initial value under both groundnut and *boro*-rice at harvest. Under groundnut crop the highest soil pH (7.53) was recorded in T_5 as well as in T_{15} and the lowest (7.50) was in T_{10}. Under *boro*-rice, however, the highest soil pH (7.39) was recorded in T_1 and the lowest (7.35) was recorded in T_8 (Fig. 4(*a*)). Submergence under *boro*-rice effectuated decline in soil pH compared to groundnut crop but it never dropped below the initial value. Irrespective of the level of contamination, application of YG resulted significant ($P < 0.05$) increase in soil pH under both the crops and the highest soil pH (7.54 and 7.40) was observed under Y_{60} while the lowest (7.48 and 7.34) under Y_0 in groundnut and *boro*-rice, respectively (Fig. 4(*b*)).

3.3. Effect yellow gypsum application on Ca:As, Fe:As and S:As ratios in soil

In the present investigation, an uniform level of recommended dose chemical fertilizers (RDF) to the soil in all the pots and three levels of YG (0, 30 and 60 kg ha^{-1}) in the designated pots were applied. The Ca:As, Fe:As and S:As ratio were calculated during the harvest stage of each crop. Application of YG exerted a significant ($P < 0.05$) effect on the Ca:As, Fe:As and S:As ratios in the soil under groundnut and boro-rice. An increaseing trend in Ca:As, Fe:As and S:As ratios with increasing dose of YG could be observed in both the crops. Arsenic content in soil also exerted a significant ($P < 0.05$) influence on Ca:As, Fe:As and S:As ratios also. Increase in As content of soil led to a decreasing trend in Ca:As, Fe:As and S:As ratios [Fig. 5(a), 6&7]. The Ca:As ratio ranged between 19.9 to 57.4 and 19.1 to 71.5 in groundnut (Table 3) and *boro*-rice (Table 4), respectively [Fig. 5(*a*)]. Irrespective of treatment, the highest Ca:As ratio was observed in Y_{60} (33.8 and 37.9) followed by Y_{30} (29.7 and 30.3) and the lowest was observed in Y_0 (26.8 and 26.1) in groundnut and *boro*-rice [Fig. 5(*b*) and Tables 3 and 4], respectively. Application of YG resulted in a significant ($P < 0.05$) change in the Fe:As and S:As

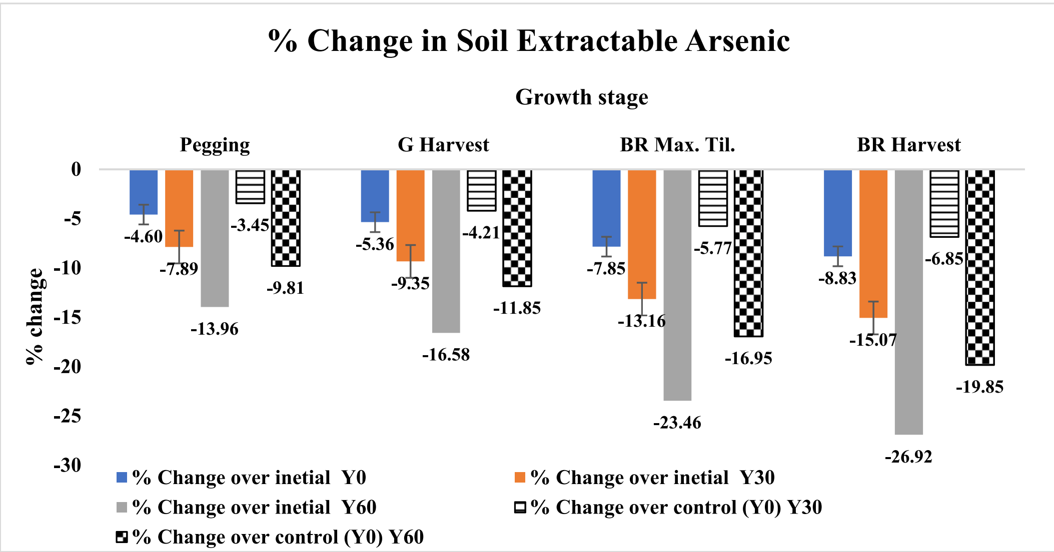

Fig. 2. Percent change in soil extractable arsenic during different growth stages of groundnut and Boro-rice by addition of various doses of yellow gypsum (Y_0- No Yellow Gypsum application, Y_{30}- Yellow Gypsum@30 kg ha^{-1}, Y_{60}- Yellow Gypsum@60 kg ha^{-1}).

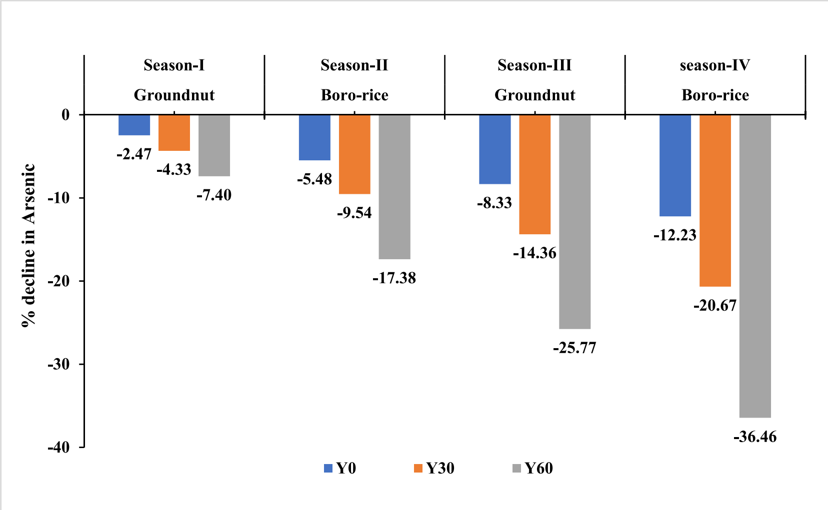

Fig. 3. Effect of time scale of application on arsenic availability (Y_0- No Yellow Gypsum application, Y_{30}- Yellow Gypsum@30 kg ha^{-1}, Y_{60}- Yellow Gypsum@60 kg ha^{-1}).

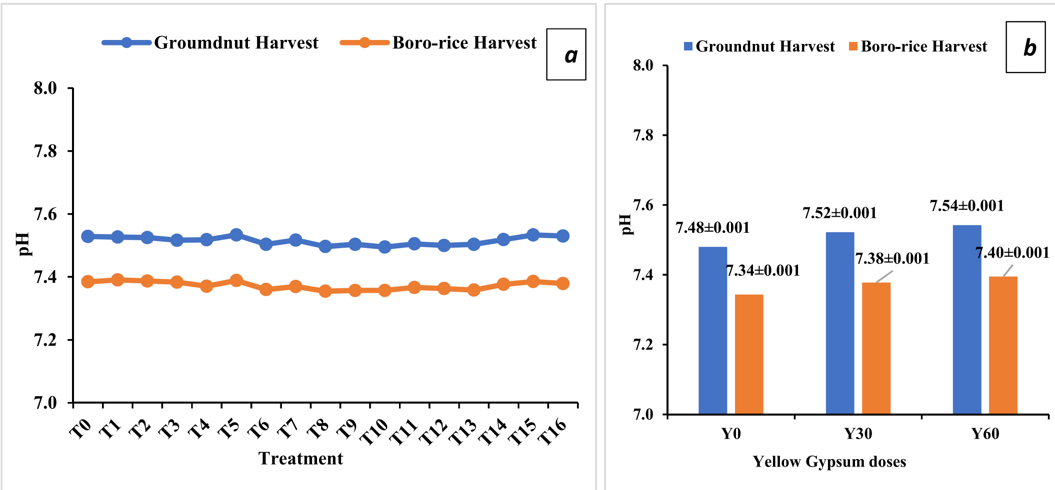

Fig. 4. a) pH changes in arsenic treatments; b) Effect of Yellow Gypsum application on pH in arsenic contaminated soil (Treatments (Spiked As Conc. (ppm) in pots): T_0-0, T_1-1.5, T_2-3.0, T_3-4.5, T_4-6.0, T_5-7.5, T_6-9.0, T_7-10.5, T_8-12.0, T_9-13.5, T_{10}-15.0, T_{11}-16.5, T_{12}-18.0, T_{13}-19.5, T_{14}-21.0, T_{15}-22.5, T_{16}-24.0; Y_0- No Yellow Gypsum application, Y_{30}- Yellow Gypsum@30 kg ha^{-1}, Y_{60}- Yellow Gypsum@60 kg ha^{-1}).

ratio in groundnut and boro-rice. While the Fe:As and S:As ratios under Groundnut crop ranged between of 2.1–5.6 and 1.7 to 5.0 (Table 3) under *boro*-rice these ratios varied between 1.9 to 7.0 and 1.5 to 6.3 (Table 4) (Figs. 6 and 7). The highest Fe:As (3.4 and 3.8) and S:As ratio (3.0 and 3.4) were recorded under application of 60 kg YG ha^{-1} (Y_{60}) followed by Y_{30} (Fe:As ratio of 3.0 and 3.0 and S:As ratio of 2.5 and 2.5) and the lowest in Y_0 (Fe:As ratio of 2.8 and 2.5 and S:As ratio of 2.2 and 2.0) in groundnut and *boro*-rice respectively (Fig. 8 and Tables 3 and 4).

3.4. Screening of soil parameters affecting arsenic availability in soil

The generated data was further analysed to ascertain the interrelation among the extractable As content of soil and other soil parameters using Simple Pearson's correlation [28]. A Stepwise regression analysis [29] was also performed taking extractable soil As content as the dependent variable and other soil parameters as independent variables. Predictors influencing the dependent variable have been identified within the probability limits ($F \leq 0.01$to ≤ 0.05) have been listed in the model summery table. The Durbin-Watson value of 1.910 in groundnut and 1.958 in *boro*-rice indicates that the model needed no auto-correction throughout the process.

Careful appraisal of the Pearson's correlation coefficient values (Table 5) indicated significant ($P < 0.01$) influence of application of YG on the relationship among the As content of soil and other soil parameters. Under groundnut crop the extractable As content of soil

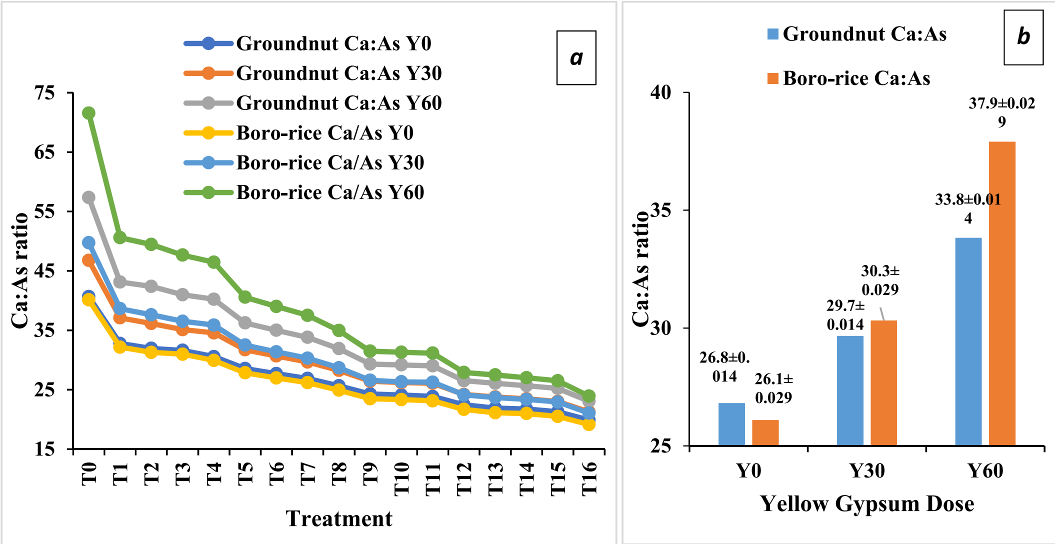

Fig. 5. a) Effect of Arsenic on Ca:As ratios in treatments; b) Effect of Yellow Gypsum application on Ca:As ratio in arsenic contaminated soil (Treatments (Spiked As Conc. (ppm) in pots): T_0-0, T_1-1.5, T_2-3.0, T_3-4.5, T_4-6.0, T_5-7.5, T_6-9.0, T_7-10.5, T_8-12.0, T_9-13.5, T_{10}-15.0, T_{11}-16.5, T_{12}-18.0, T_{13}-19.5, T_{14}-21.0, T_{15}-22.5, T_{16}-24.0; Y_0- No Yellow Gypsum application, Y_{30}- Yellow Gypsum@30 kg ha^{-1}, Y_{60}- Yellow Gypsum@60 kg ha^{-1}).

Table 3
Effect of Yellow Gypsum application on Soil Ca:As, Fe:As and S:As ratios under different arsenic concentration treatments of Groundnut.

Treatment	Groundnut											
	Ca:As				Fe:As				S:As			
	Y_0	Y_{30}	Y_{60}	Mean (T)	Y_0	Y_{30}	Y_{60}	Mean (T)	Y_0	Y_{30}	Y_{60}	Mean (T)
$\mathbf{T_0}$	40.7	46.8	57.4	$\mathbf{47.6^{a}}$	4.1	4.6	5.6	$\mathbf{4.7^{a}}$	3.3	3.9	5.0	$\mathbf{4.0^{a}}$
$\mathbf{T_1}$	32.8	37.1	43.1	$\mathbf{37.3^{b}}$	3.4	3.7	4.4	$\mathbf{3.8^{b}}$	2.7	3.1	3.8	$\mathbf{3.2^{b}}$
$\mathbf{T_2}$	31.9	36.1	42.4	$\mathbf{36.5^{b}}$	3.3	3.6	4.2	$\mathbf{3.7^{b}}$	2.6	3.0	3.7	$\mathbf{3.1^{b}}$
$\mathbf{T_3}$	31.6	35.1	41.0	$\mathbf{35.6^{b}}$	3.2	3.5	4.1	$\mathbf{3.6^{b}}$	2.6	3.0	3.7	$\mathbf{3.0^{b}}$
$\mathbf{T_4}$	30.6	34.6	40.2	$\mathbf{34.8^{b}}$	3.1	3.5	4.0	$\mathbf{3.5^{b}}$	2.5	2.9	3.5	$\mathbf{3.0^{bc}}$
$\mathbf{T_5}$	28.6	31.7	36.2	$\mathbf{32.0^{c}}$	2.9	3.2	3.6	$\mathbf{3.2^{c}}$	2.4	2.7	3.2	$\mathbf{2.7^{cd}}$
$\mathbf{T_6}$	27.7	30.7	35.0	$\mathbf{30.9^{cd}}$	2.8	3.1	3.5	$\mathbf{3.1^{cd}}$	2.3	2.6	3.1	$\mathbf{2.6^{de}}$
$\mathbf{T_7}$	26.9	29.7	33.8	$\mathbf{29.9^{cd}}$	2.7	3.0	3.4	$\mathbf{3.0^{cd}}$	2.2	2.5	3.0	$\mathbf{2.6^{def}}$
$\mathbf{T_8}$	25.6	28.2	31.9	$\mathbf{28.5^{de}}$	2.6	2.8	3.2	$\mathbf{2.9^{de}}$	2.1	2.4	2.8	$\mathbf{2.4^{efg}}$
$\mathbf{T_9}$	24.3	26.4	29.3	$\mathbf{26.6^{ef}}$	2.5	2.7	3.0	$\mathbf{2.7^{ef}}$	2.0	2.3	2.6	$\mathbf{2.3^{fgh}}$
$\mathbf{T_{10}}$	24.1	26.2	29.2	$\mathbf{26.4^{ef}}$	2.5	2.7	3.0	$\mathbf{2.7^{ef}}$	2.0	2.2	2.6	$\mathbf{2.3^{gh}}$
$\mathbf{T_{11}}$	23.9	26.1	29.0	$\mathbf{26.2^{efg}}$	2.5	2.7	3.0	$\mathbf{2.7^{efg}}$	2.0	2.2	2.6	$\mathbf{2.3^{gh}}$
$\mathbf{T_{12}}$	22.5	24.2	26.5	$\mathbf{24.3^{fgh}}$	2.3	2.5	2.7	$\mathbf{2.5^{fgh}}$	1.9	2.1	2.4	$\mathbf{2.1^{hi}}$
$\mathbf{T_{13}}$	21.9	23.8	26.1	$\mathbf{23.9^{fgh}}$	2.3	2.5	2.7	$\mathbf{2.5^{fgh}}$	1.8	2.0	2.3	$\mathbf{2.1^{hi}}$
$\mathbf{T_{14}}$	21.7	23.5	25.7	$\mathbf{23.6^{fgh}}$	2.3	2.4	2.7	$\mathbf{2.5^{fgh}}$	1.8	2.0	2.3	$\mathbf{2.1^{hi}}$
$\mathbf{T_{15}}$	21.3	23.0	25.2	$\mathbf{23.1^{gh}}$	2.2	2.4	2.6	$\mathbf{2.4^{gh}}$	1.8	2.0	2.3	$\mathbf{2.0^{hi}}$
$\mathbf{T_{16}}$	19.9	21.3	23.1	$\mathbf{21.4^{h}}$	2.1	2.2	2.4	$\mathbf{2.3^{h}}$	1.7	1.9	2.1	$\mathbf{1.9^{i}}$
Mean (Y)	$\mathbf{26.8^{c}}$	$\mathbf{29.7^{b}}$	$\mathbf{33.8^{a}}$		$\mathbf{2.8^{c}}$	$\mathbf{3.0^{b}}$	$\mathbf{3.4^{a}}$		$\mathbf{2.2^{c}}$	$\mathbf{2.5^{b}}$	$\mathbf{3.0^{a}}$	
Range	37.5				3.5				3.3			
	LSD (*P* < *0.05*)	**SEm ±**	**SE (d)**		**LSD (*P* < *0.05*)**	**SEm ±**	**SE(d)**		**LSD (*P* < *0.05*)**	**SEm ±**	**SE (d)**	
T	0.09	0.03	0.05		0.013	0.005	0.007		0.02	0.01	0.01	
Y	0.04	0.01	0.02		0.006	0.002	0.003		0.01	0.004	0.01	
T*Y	0.16	0.06	0.08		0.023	0.008	0.011		0.04	0.02	0.02	

(Treatments (Spiked As Conc. (ppm) in pots): T_0-0, T_1-1.5, T_2-3.0, T_3-4.5, T_4-6.0, T_5-7.5, T_6-9.0, T_7-10.5, T_8-12.0, T_9-13.5, T_{10}-15.0, T_{11}-16.5, T_{12}-18.0, T_{13}-19.5, T_{14}-21.0, T_{15}-22.5, T_{16}-24.0); numbers followed by different letters indicate significant differences at $P < 00.05$ (otherwise statistically at par). NS: non-significant ($P > 00.05$).

was significantly negatively correlated with calcium content ($r = -0.603^{**}$) and iron content ($r = -0.246^{**}$) but positively correlated with sulphur content ($r = 0.175^{*}$) (Table 5). Calcium, sulphur, iron and manganese were positively correlated with among themselves but were negatively correlated with soil pH. The above relations suggested that availability of As in soil decreases with increase in Ca, Fe, S and Mn content in soil. The results of Path Analysis also indicated a negative direct effect of soil calcium (−1.83) followed by pH

Table 4
Effect of Yellow Gypsum application on Soil Ca:As, Fe:As and S:As ratios under different arsenic concentration treatments of *Boro*-rice.

Treatment	*Boro*-rice											
	Ca:As				Fe:As				S:As			
	Y_0	Y_{30}	Y_{60}	Mean (T)	Y_0	Y_{30}	Y_{60}	Mean (T)	Y_0	Y_{30}	Y_{60}	Mean (T)
T_0	40.1	49.7	71.5	**51.4**^{a}	3.8	4.8	7.0	**4.9**^{a}	3.0	4.0	6.3	**4.2**^{a}
T_1	32.2	38.6	50.6	**39.4**^{b}	3.1	3.7	5.1	**3.9**^{b}	2.5	3.2	4.6	**3.3**^{b}
T_2	31.3	37.6	49.4	**38.4**^{bc}	3.0	3.6	4.9	**3.7**^{bc}	2.4	3.1	4.4	**3.2**^{bc}
T_3	31.0	36.5	47.7	**37.4**^{bcd}	3.0	3.6	4.8	**3.7**^{bcd}	2.4	3.0	4.3	**3.1**^{bc}
T_4	29.9	35.9	46.5	**36.5**^{bcde}	2.9	3.5	4.6	**3.6**^{bcde}	2.3	2.9	4.2	**3.0**^{bc}
T_5	27.8	32.5	40.6	**33.1**^{cdef}	2.7	3.1	4.0	**3.2**^{cdef}	2.1	2.7	3.7	**2.7**^{bcd}
T_6	27.0	31.4	39.0	**31.9**^{defg}	2.6	3.1	3.9	**3.1**^{def}	2.1	2.6	3.5	**2.7**^{cd}
T_7	26.2	30.3	37.5	**30.8**^{efg}	2.5	3.0	3.8	**3.0**^{efg}	2.0	2.5	3.4	**2.6**^{cde}
T_8	24.9	28.7	35.0	**29.1**^{fgh}	2.4	2.8	3.5	**2.8**^{fgh}	1.9	2.4	3.1	**2.4**^{def}
T_9	23.5	26.6	31.5	**26.9**^{ghi}	2.3	2.6	3.2	**2.7**^{fghi}	1.8	2.2	2.9	**2.3**^{def}
T_{10}	23.3	26.3	31.3	**26.7**^{ghi}	2.3	2.6	3.2	**2.7**^{fghi}	1.8	2.2	2.8	**2.2**^{def}
T_{11}	23.1	26.3	31.2	**26.6**^{ghi}	2.3	2.6	3.2	**2.6**^{fghi}	1.8	2.2	2.8	**2.2**^{def}
T_{12}	21.7	24.1	27.9	**24.4**^{hi}	2.1	2.4	2.8	**2.4**^{ghi}	1.7	2.0	2.5	**2.0**^{ef}
T_{13}	21.1	23.7	27.5	**23.9**^{hi}	2.1	2.4	2.8	**2.4**^{ghi}	1.6	2.0	2.5	**2.0**^{ef}
T_{14}	21.0	23.4	27.0	**23.6**^{hi}	2.1	2.3	2.8	**2.4**^{hi}	1.6	1.9	2.5	**2.0**^{ef}
T_{15}	20.5	22.9	26.5	**23.2**^{hi}	2.0	2.3	2.7	**2.3**^{hi}	1.6	1.9	2.4	**1.9**^{f}
T_{16}	19.1	21.1	23.9	**21.3**^{i}	1.9	2.2	2.5	**2.2**^{i}	1.5	1.8	2.2	**1.8**^{f}
Mean (Y)	**26.1**^{c}	**30.3**^{b}	**37.9**^{a}		**2.5**^{c}	**3.0**^{b}	**3.8**^{a}		**2.0**^{c}	**2.5**^{b}	**3.4**^{a}	
Range	52.4				5.0				4.8			
	LSD (*P* < *0.05*)	**SEm ±**	**SE (d)**		**LSD (*P* < *0.05*)**	**SEm ±**	**SE(d)**		**LSD (*P* < *0.05*)**	**SEm ±**	**SE (d)**	
T	0.19	0.07	0.10		0.013	0.005	0.007		0.03	0.01	0.02	
Y	0.08	0.03	0.04		0.006	0.002	0.003		0.01	0.005	0.01	
T*Y	0.33	0.12	0.17		0.023	0.008	0.011		0.05	0.02	0.03	

(Treatments (Spiked As Conc. (ppm) in pots): T_0-0, T_1-1.5, T_2-3.0, T_3-4.5, T_4-6.0, T_5-7.5, T_6-9.0, T_7-10.5, T_8-12.0, T_9-13.5, T_{10}-15.0, T_{11}-16.5, T_{12}-18.0, T_{13}-19.5, T_{14}-21.0, T_{15}-22.5, T_{16}-24.0); numbers followed by different letters indicate significant differences at $P < 00.05$ (otherwise statistically at par). NS: non-significant ($P > 00.05$).

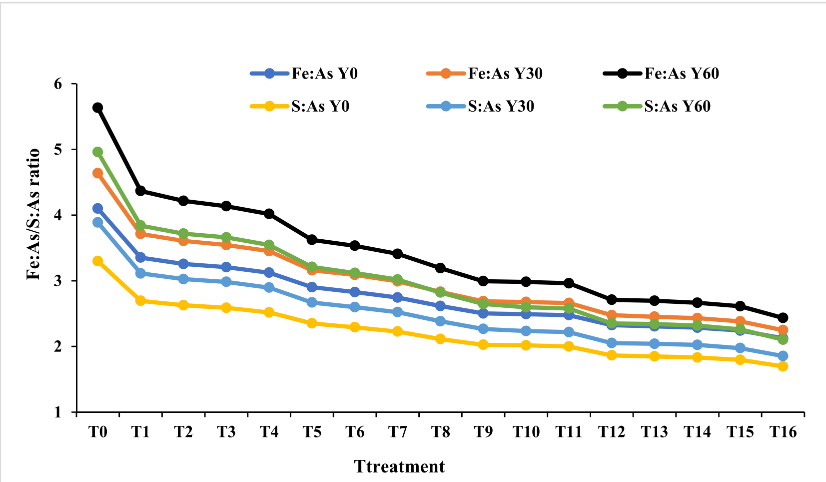

Fig. 6. Effect of Arsenic on Fe:As and S:As ratios in treatments of Groundnut crop
(Treatments (Spiked As Conc. (ppm) in pots): T_0-0, T_1-1.5, T_2-3.0, T_3-4.5, T_4-6.0, T_5-7.5, T_6-9.0, T_7-10.5, T_8-12.0, T_9-13.5, T_{10}-15.0, T_{11}-16.5, T_{12}-18.0, T_{13}-19.5, T_{14}-21.0, T_{15}-22.5, T_{16}-24.0; Y_0- No Yellow Gypsum application, Y_{30}- Yellow Gypsum@30 kg ha^{-1}, Y_{60}- Yellow Gypsum@60 kg ha^{-1}).

(−0.18) and manganese (−0.06) and a positive direct effect of soil iron (+1.28) followed by sulphur (+0.14) content with soil extractable As content (Fig. 9). The residual effect (0.20) thus, indicated that the five-soil parameter included in this study explained 80 per cent variation in soil As content under groundnut crop.

Similarly, soil under rice crop the As content in the soil depicted a negative correlation with calcium content (r = −0.654**), sulphur content (r = −0.460**), iron content (r = −0.372**) and manganese content (r = −0.196*) (Table 6). While calcium, sulphur and iron content had a significant ($P < 0.05$) positive correlation with each other, they exhibited significant negative correlation with

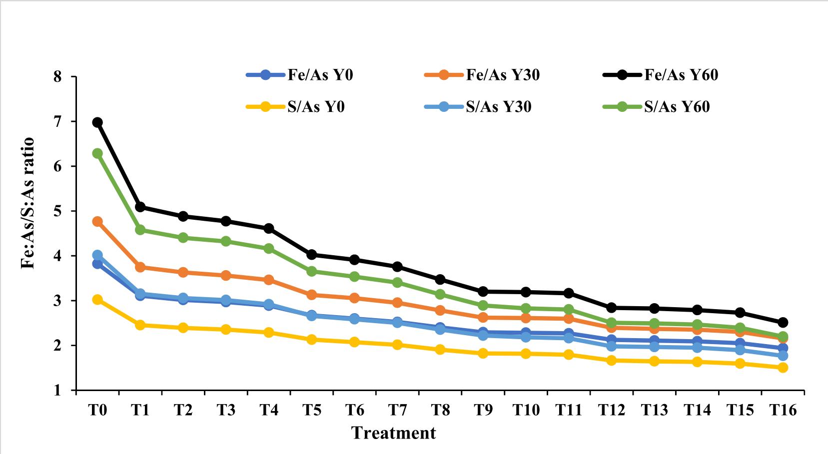

Fig. 7. Effect of Arsenic on Fe:As and S:As ratios in treatments of boro-rice
(Treatments (Spiked As Conc. (ppm) in pots): T_0-0, T_1-1.5, T_2-3.0, T_3-4.5, T_4-6.0, T_5-7.5, T_6-9.0, T_7-10.5, T_8-12.0, T_9-13.5, T_{10}-15.0, T_{11}-16.5, T_{12}-18.0, T_{13}-19.5, T_{14}-21.0, T_{15}-22.5, T_{16}-24.0; Y_0- No Yellow Gypsum application, Y_{30}- Yellow Gypsum@30 kg ha^{-1}, Y_{60}- Yellow Gypsum@60 kg ha^{-1}).

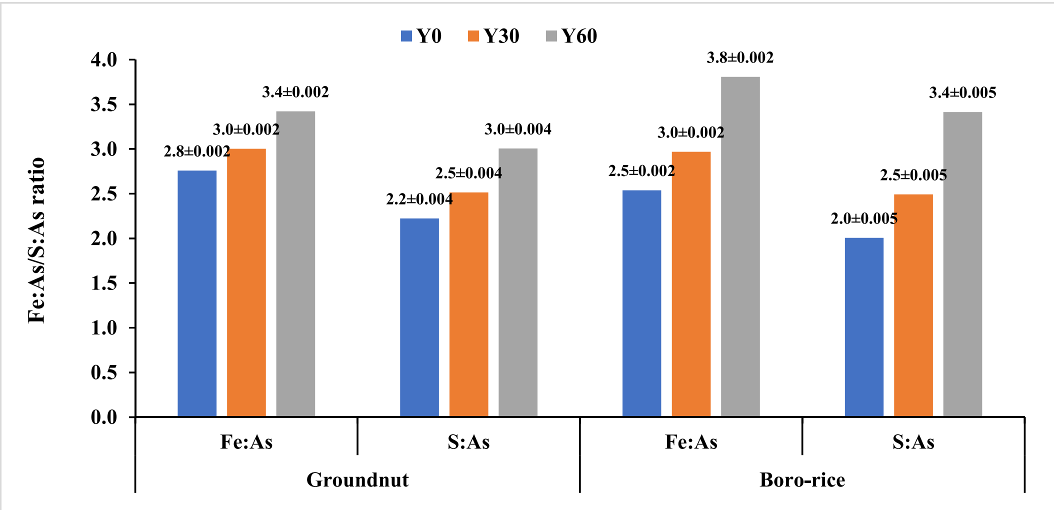

Fig. 8. Effect of Yellow Gypsum application on Fe:As and S:As ratio in arsenic contaminated soil (Y_0- No Yellow Gypsum application, Y_{30}- Yellow Gypsum@30 kg ha^{-1}, Y_{60}- Yellow Gypsum@60 kg ha^{-1}).

Table 5
Correlation coefficient (r) between different soil parameters of Groundnut crop.

	As	pH	S	Fe	Mn	Ca	Mg
As	1						
pH	0.089	1					
S	0.172[b]	−0.364[a]	1				
Fe	−0.246[a]	−0.459[a]	0.497[a]	1			
Mn	−0.108	−0.181[b]	0.425[a]	0.927[a]	1		
Ca	−0.603[a]	−0.491[a]	0.349[a]	0.886[a]	0.723[a]	1	

(As- Arsenic, pH- Soil pH, S- Sulphur, Fe- Iron, Mn- Manganese, Ca- Calcium and Mg- Magnesium; numbers followed by different symbols indicate significant differences ** at $P < 0.01$, * at $P < 0.05$. no symbols: non-significant ($P > 0.05$).
[a] Correlation is significant at the 0.01 level (2-tailed).
[b] Correlation is significant at the 0.05 level (2-tailed).

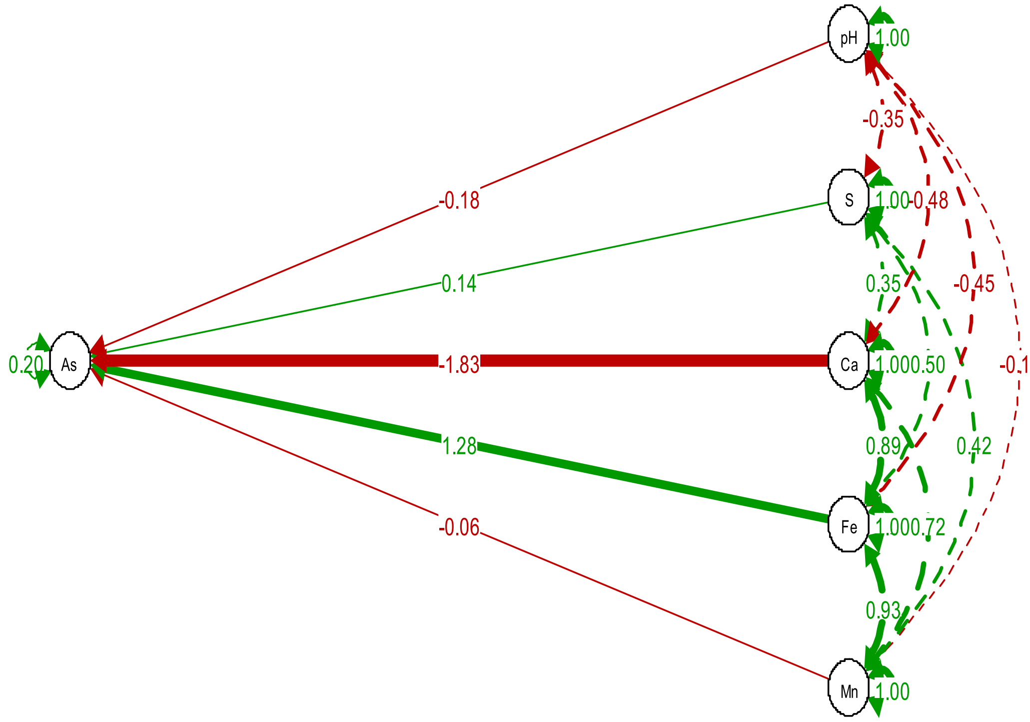

Fig. 9. Path Analysis for soil arsenic of Groundnut crop
(*Red line indicates negative effect and Green line indicates positive effect on arsenic availability, Straight line-direct effect and Dotted line- Indirect effect*) (*As-Arsenic, pH- Soil* pH, *S- Sulphur, Ca- Calcium, Fe- Iron and Mn- Manganese*).

Table 6
Correlation coefficient (r) between different soil parameters of *Boro*-Rice crop.

	As	pH	S	Fe	Mn	Ca
As	1					
pH	0.131	1				
S	−0.460[a]	−0.568[a]	1			
Fe	−0.372[a]	−0.492[a]	0.986[a]	1		
Mn	−0.196[b]	−0.048	0.752[a]	0.837[a]	1	
Ca	−0.654[a]	−0.494[a]	0.949[a]	0.919[a]	0.677[a]	1

(As- Arsenic, pH- Soil pH, S- Sulphur, Fe- Iron, Mn- Manganese, Ca- Calcium and Mg- Magnesium; numbers followed by different symbols indicate significant differences ** at $P < 0.01$, * at $P < 0.05$. no symbols: non-significant ($P > 0.05$).
[a] Correlation is significant at the 0.01 level (2-tailed).
[b] Correlation is significant at the 0.05 level (2-tailed).

soil pH. The above relations suggested that availability of As in soil decreases with increase in Ca, S, Fe and Mn in soil. The results of Path Analysis indicated that soil available sulphur (−3.36) had the highest negative direct effect on soil As content followed by the soil calcium (−1.54), manganese (−0.67) content and soil pH (−0.19), the iron content of soil (+4.79) indicated the highest positive direct effect with soil extractable As content (Fig. 10). The residual effect (0.14) thus indicated that the nine-soil parameters included in this study explained 86 per cent variation in soil As content in soil under *boro*-rice.

In both the crops iron content in soil exerted a negative indirect effect on soil As content through exhibiting a positive effect on Mn (+0.93), Ca (+0.89) and S (+0.50) under groundnut crop (Fig. 9) and S (+0.99), Ca (+0.92) and Mn (+0.84) under *boro*-rice (Fig. 10).

In Regression study soil As concentrations under groundnut crop was treated as dependent variable and Ca and Fe were identified as predictor variables following backward process (Table 7). The Durbin Watson value of 1.910 indicated the viability of the model to fit perfectly with the predictor variables analysed. Similarly, in boro-rice soil Ca, S, Fe and pH were identified as predictor variables with Durbin Watson value of 1.958 indicating the viability of the model to fit perfectly with the predictor variables analysed (Table 8).

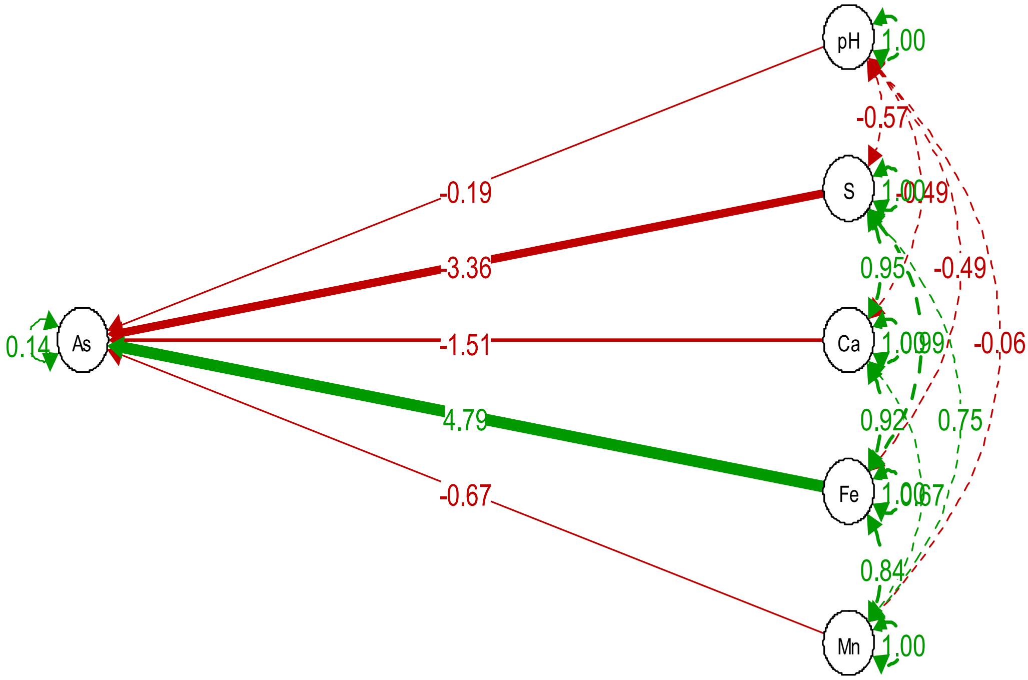

Fig. 10. Path Analysis for soil arsenic of *Boro*-Rice
(*Red line indicates negative effect and Green line indicates positive effect on arsenic availability, Straight line-direct effect and Dotted line- Indirect effect*) (*As-Arsenic, pH- Soil* pH*, S- Sulphur, Ca- Calcium, Fe- Iron and Mn- Manganese*).

Table 7
Summary of the stepwise regression in Groundnut soil.

Model	R	R Square	Adjusted R Square	R Square Change	Durbin Watson
1	0.646[a]	0.417	0.356	0.417	**1.910**
2	0.644[b]	0.414	0.366	−0.003	
3	0.622[c]	0.386	0.35	−0.028	
4	0.608[d]	0.369	0.344	−0.017	

(As- Arsenic, pH- Soil pH, S- Sulphur, Fe- Iron, Mn- Manganese, Ca- Calcium and Mg- Magnesium).
e Dependent Variable: As.
[a] Predictors: (Constant), Ca, pH, S, Fe, Mn.
[b] Predictors: (Constant), Ca, pH, S, Fe.
[c] Predictors: (Constant), Ca, pH, Fe.
[d] Predictors: (Constant), Ca, Fe.

Table 8
Summary for the stepwise regression of *Boro*-Rice soil.

Model	R	R Square	Adjusted R Square	R Square Change	Durbin Watson
1	0.664[a]	0.441	0.383	0.441	**1.958**
2	0.664[b]	0.441	0.396	0.000	

(As- Arsenic, pH- Soil pH, S- Sulphur, Fe- Iron, Mn- Manganese, Ca- Calcium and Mg- Magnesium).
d. Predictors: (Constant), Ca, S, Fe, pH.
e. Dependent Variable: As.
[a] Predictors: (Constant), Ca, S, Mn, Fe, pH.

4. Discussion

A significant ($P < 0.05$) decreasing trend in the mean extractable As content of soil with increasing dosage of YG in all the As spiked treatments was observed. With respect to the control treatment (Y_0) the highest decline in soil extractable As was observed in T_0Y_{60} at pegging (17.66%) and at harvest (22.0%) stages of groundnut crop while in *boro*-rice, the highest decline was observed at the maximum tillering (31.15%) and harvest (36.88%) stages. YG being a good source of Ca, S and oxides of Fe and Mn led to decrease in extractable As content of soil in the present study probably due to a significant ($P < 0.05$) increase in the Ca:As, Fe:As and S:As ratios in soil during the harvest stages of groundnut and *boro*-rice. Calcium inhibits As mobility both in soil and plant maninly due to its immobilization by the formation of low solubility Ca–As precipitates such as $Ca_4(OH)_2(AsO_4)_2 \cdot 4H_2O$ and johnbaumite, $Ca_5(AsO_4)_3(OH)$. Ca–As precipitates. The results of regression study also suggested decrease in the availability of As in soil with increase in Ca, S, Fe and Mn in soil. Increase in Ca:As molar ratios in YG treated soil may increase As immobilization by formation of stable precipitates. The high Ca and sulphur content in YG led to As immobilization by sorption and inclusion in pozzolanic reaction products and formation of Ca–As and S–As precipitates [30]. observed a significant increase in As^{III} and As^{V} immobilization when the Ca:As molar ratios exceeded 1:1 and apparently the effectiveness of both As (III) and As (V) immobilization increased with increasing Ca:As molar ratios.

Yellow Gypsum application significantly ($P < 0.05$) increased soil pH in both groundnut and *boro*-rice crops. Increase in soil pH caused by the gypsum (alkaline amendment), could lead to an increase of metals associated with carbonated fractions [30,31]. Apatite is an effective host because its stability over broad ranges of pH. Each of these precipitates have limited pH ranges within which they exhibit solubility minima. Calcium arsenates are stable at high pH and exhibit lowest equilibrium concentrations of arsenate ion, whereas ferric arsenates *i.e.,* scorodite are stable only at low pH [32]. Beneficial effect of lime addition to As containing wastes in reducing the mobility of dissolved As, through the formation of low solubility calcium arsenate [$Ca_3(AsO_4)_2$] has been reoported in the literature [33]. The mean extractable As over all the treatments decreased with increase in dosage of YG. The highest decline in soil extractable As with respect to the control (Y_0) was observed under Y_{60} at pegging (9.81%) and harvest (11.85%) stages of groundnut crop, and maximum tillering (16.95%) and harvest (19.85%) of *boro*-rice (Fig. 2). This decline could be due to presence of calcium, sulphur (SO_4^{-2}), silicon (SiO_2), iron (Fe_2O_3), phosphorus, manganese (MnO) and magnesium (MgO) in the applied YG [19], which might have interacted with As in soil solution and consequently forming less soluble precipitates with calcium (calcium arsenate), sulphur (As sulphide) and iron (ferric arsenate). Our results are in line with [34] who reported that application of combined amendment (CF) comprising 90% calcium sulphate ($CaSO_4$) and 10% ferric oxide (Fe_2O_3) decreased As concentration in soil by 55.5%–69.3% in contaminated soil. The efficacy of YG, however, exhibited a decreasing trend with increase in As content of soil which may be due to decrease in CA: As, Fe: As and S:As molar ratio in soil. Increase in the dose of YG application showed a significant ($P < 0.05$) increasing trend and the increase in As content in treatments showed a decreasing trend of Ca:As, Fe:As and S:As ratios in both the crops.

Arsenic content in the experimental soil registered a significant ($P < 0.05$) negative correlation with Ca, Fe and Mn content of soil but, sulphur content in groundnut crop had a positive correlation (0.172*) (Table 3) and positive direct effect (+0.14) on As (Fig. 9). Whereas, sulphur content in *boro*-rice soil exhibited and significant ($P < 0.05$) negative correlation (−0.460**) (Table 6) and had the highest negative direct effect (−3.36) on soil As content (Fig. 10). This phenomenon can be explained by the fact that reduction of sulphur (SO_4^{2-}) into sulphide (S^{2-}) under reduced condition of rice soils could have been used as an electron donor in bio reduction of arsenate (As^{V}) to arsenite (As^{III}) [35,36]. The soil with higher inherent sulphate content along with the additional sulphur provided by YG helped in precipitation of As reducing its bioavailability. Arsenate (As^{III}) in the paddy soil solution under reduced soil environment can react with sulphide (S^{2-}) forming precipitate As sulphide (As_2S_3) complex resulting in reduced As bioavailability in soil [37,38]. Iron and sulphur co-precipitation may also result in As immobilization. Furthermore, the mobility of As may decrease because of the formation of $Ca(AsO_4)_2$ and $CaHAsO_3$ precipitates [39,40].

In both the crops, iron content in soil registered a significant ($P < 0.001$) negative correlation (−0.246** and −0.372**) with As content (Tables 5 and 6) and positive direct effect (1.28 and 4.79) on extractable As content of soil but, exhibited negative direct effect through S, Ca and Mn which indicated that iron content in soil indirectly influenced As bioavailability through Ca, S and Mn content in soil (Figs. 9 and 10). Application of YG providing Fe_2O_3 (5.03%) [19] helped in sorption of As on iron oxides or hydroxides and reduced bioavailability of As in soil solution. The bio-availability and behaviour of As in natural system is strongly influenced by its sorption on solid surfaces such as oxides of Mn, Al and Fe [41]. Iron oxides and hydroxides represent the major sink for As sorption in soil [42]. Our results are in agreement with the reports by Ref. [43] who also observed relatively higher effectiveness of application of iron fertilizer in reducing As availability in soil. Appraisal of results (Tables 3 and 4) revealed significant ($P < 0.05$) increase in the Fe:As and S:As ratios with application of YG. Increase in the dose of YG registered an increasing trend and the increase in As content in soil a decreasing trend of Fe:As and S:As ratios. These increase in Fe:As and S:As ratios might have resulted in precipitation or co-precipitation of As on iron and sulphur. Sulphate-reducing conditions often favour As partitioning to the solid phase [44], although the S:Fe and S:Fe:As ratios are critically important in determining whether dissolved concentrations of As are diminished or not [45,46]. Manganese exhibited a negative direct effect on soil As content in groundnut (−0.06) and *boro*-rice crops (−0.67) (Figs. 9 and 10) and application of YG increased the manganese content in soil and a negative correlation with As content of soil under groundnut (−0.108) and boro-rice (−0.196*) (Tables 5 and 6) probably because of reduced bio-availability of As by sorption of arsenite on the surfaces of Mn-Oxide and also facilitating oxidation of arsenite to arsenate. This oxidation reaction As^{III} and MnO_2 transforms the toxic arsenite to a less toxic aqueous arsenate species, which subsequently precipitates with Mn^{2+} as a mixed As–Mn low soluble precipitate. The results corroborated with findings of [47,48]. Time scale of application also had a prominent effect on As bioavailability. The trend of decline in As availability on application of YG followed the order: Season-I < Season-II < Season-III < Season-IV (Fig. 3). Percent decline in As bioavailability with respect to initial As content was the highest (36.46%) with application of 60 kg YG ha^{-1} at the harvest of *boro*-rice which might be due to increase in other essential nutrients like S, Ca, Fe and Mn in soil. Application of YG to soil decreased the adsorption of SO_4^{-2} ion on positively charged sites in soil matrix leading to increase in soil available sulphur [49,50]. Increase in the availability of exchangeable Ca^{2+} due to decomposition of gypsum [51,52] and DTPA extractable Fe and Mn [50,53] in soil helped in sorption of As in soil resulting in the decline in As availability.

5. Conclusion

Findings from this study revealed that YG produced from LD-slag as a by-product of steel industry could be a potential amendment for As contaminated soils. Results of this investigation revealed that YG addition to As contaminated soil was effective in reducing the As bioavailability. Extractable As content in soil decreased significantly ($P < 0.005$) with increasing dosage of YG in all the As treatments.

Irrespective of treatments in both the cropping cycles, compared to the control (Y_0), application of 60 kg YG ha^{-1} recorded highest percentage decline in soil extractable As at pegging and harvest stages of groundnut; and maximum tillering and harvest stages of *boro*-rice. Efficacy of YG decreased with increase in As concentrations in treatment during both the cropping cycles. Increase in the doses of YG had an increasing trend of Ca:As, Fe:As and S:As ratios while the Ca:As, Fe:As and S:As ratios decreased with increase in As content in soil. The trend of decline in As availability by repeated application of YG over the seasons followed the order: Season-I < Season-II < Season-III < Season-IV. Present study indicated that application of 60 kg YG ha^{-1} was the most effective rate for reducing As availability in groundnut and *boro*-rice crop. Further, studies are necessary to evaluate the effect of higher dosage and long-term application of YG on As and heavy metals mitigation potential in different crops.

Data availability statement

All data pertaining to the study is included in this paper.

CRediT authorship contribution statement

Kiran Pilli: Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation. **Prasanta Kumar Patra:** Validation, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. **Subhajit Pal:** Writing – review & editing. **Bishnuprasad Dash:** Writing – review & editing. **Jaison M:** Writing – review & editing. **Pravat Utpal Acharjee:** Writing – review & editing. **Rudra Vinayak:** Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. BSupplementary data

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References

[1] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, Talanta 58 (2002) 201–235, https://doi.org/10.1016/S0039-9140(02)00268-0.
[2] P. Smedley, D. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem. 17 (5) (2002) 517–568, https://doi.org/10.1016/S0883-2927(02)00018-5.
[3] S.K. Sanyal, S.K. Gupta, S.S. Kukal, K. Jeevan Rao, Soil degradation, pollution and amelioration, in: H. Pathak, S.K. Sanyal, P.N. Takkar (Eds.), State of Indian Agriculture-Soil, National Academy of Agricultural Sciences, New Delhi, 2015, pp. 234–266.
[4] D.V. Datta, M.K. Kaul, Arsenic content of tube well water in villages in northern India. A concept of arsenicosis, J. Assoc. Phys. India 24 (1976) 599–604. PMID: 1025145.
[5] S. Srivastava, Y.K. Sharma, Arsenic occurrence and accumulation in soil and water of eastern districts of Uttar Pradesh, India, Environ. Monit. Assess. 185 (6) (2013) 4995–5002.
[6] R. Garai, A. Chakraborty, S. Dey, K. Saha, Chronic arsenic poisoning from tube-well water, J. Indian Med. Assoc. 82 (1984) 34–35. PMID: 6747321.
[7] S.K. Sanyal, S.K.T. Nasar, Arsenic contamination of groundwater in West Bengal (India): build-up in soil-crop systems, in: Analysis and Practice in Water Resources Engineering for Disaster Mitigation, New Age International (P) Limited, Publishers, New Delhi, 2002, pp. 216–222.
[8] P.M. Amaibi, J.A. Entwistle, N. Kennedy, M. Cave, S.J. Kemp, S. Potgieter-Vermaak, J.R. Dean, Mineralogy, solid-phase fractionation and chemical extraction to assess the mobility and availability of arsenic in an urban environment, Appl. Geochem. 100 (2018) 244–257, https://doi.org/10.1016/j.apgeochem.2018.12.0.

[9] A.K. Mensah, B. Marschner, S.M. Shaheen, J. Wang, S.-L. Wang, J. Rinklebe, Arsenic contamination in abandoned and active gold mine spoils in Ghana: geochemical fractionation, speciation, and assessment of the potential human health risk, Environ. Pollut. 261 (2020) 114116, https://doi.org/10.1016/j.envpol.2020.114116.

[10] B. Williams, G. Leung, H. Maiato, A. Wong, Z.X. Li, E.V. Williams, C. Kirkpatrick, C.F. Aquadro, C.L. Rieder, M.L. Goldberg, Mitch - a rapidly evolving component of the Ndc80 kinetochore complex required for correct chromosome segregation in Drosophila, J. Cell Sci. 120 (20) (2007) 3522–3533, https://doi.org/10.1242/jcs.012112.

[11] D. Mondal, D.A. Polya, Rice is a major exposure route for arsenic in Chakdaha block, Nadia district, West Bengal, India: a probabilistic risk assessment, Appl. Geochem. 23 (11) (2008) 2987–2998, https://doi.org/10.1016/j.apgeochem.2008.06.025.

[12] A.A. Meharg, Arsenic in rice. understanding a new disaster for South-East Asia, Trends Plant Sci. 9 (9) (2004) 415–417, https://doi.org/10.1016/j.tplants.2004.07.002.

[13] P.N. Williams, M.R. Islam, E.E. Adomako, A. Raab, S.A. Hossain, Y.G. Zhu, J. Feldmann, A.A. Meharg, Increase in rice grain arsenic for regions of Bangladesh irrigating paddies with elevated arsenic in ground waters, Environ. Sci. Technol. 40 (2006) 4903–4908, https://doi.org/10.1021/es060222i.

[14] L. Xu, D. Mondal, D.A. Polya, Positive Association of Cardiovascular Disease (CVD) with chronic exposure to drinking water arsenic (As) at concentrations below the WHO provisional guideline value: a systematic review and meta-analysis, Int. J. Environ. Res. Publ. Health 17 (7) (2020) 2536, https://doi.org/10.3390/ijerph17072536.

[15] L. Xu, D.A. Polya, Exploratory study of the association in the United Kingdom between hypertension and inorganic arsenic (iAs) intake from rice and rice products, Environ. Geochem. Health 43 (2021) 2505–2538, https://doi.org/10.1007/s10653-020-00573-8.

[16] R. Stone, Food safety: arsenic and paddy rice: a neglected cancer risk? Science 321 (2008) 184–185, https://doi.org/10.1126/science.321.5886.184.

[17] E. Bianucci, A. Godoy, A. Furlan, J.M. Peralta, L.E. Hernández, R.O. Carpena-Ruiz, S. Castro, Arsenic toxicity in soybean alleviated by a symbiotic species of Bradyrhizobium, Symbiosis 74 (3) (2018) 167–176.

[18] J.M. Peralta, C.N. Travaglia, R.A. Gil, A. Furlan, S. Castro, E.C. Bianucci, An Effective Rhizoinoculation Restraints Arsenic Translocation in Peanut and Maize Plants Exposed to a Realistic Groundwater Metalloid Dose. *International Congress and Exhibition: Arsenic In the Environment*, Beijing, P.R. Environmental Arsenic in a Changing World, China, 2018.

[19] S. Ashrit, P.K. Banerjee, R.V. Chatti, V. Rayasam, U.G. Nair, Synthesis and characterization of yellow gypsum from LD slag fines generated in a steel plant, Curr. Sci. 109 (4) (2015) 727–732. http://www.jstor.org/stable/24905733.

[20] W. Stumm, Chemistry of the Solid-Water Interface, Wiley, NewYork, 1992.

[21] E. Smith, R. Naidu, A.M. Alston, Chemistry of inorganic arsenic in soils: II. Effect of phosphorus, sodium, and calcium on arsenic sorption, J. Environ. Qual. 31 (2002) 557, https://doi.org/10.2134/jeq2002.5570.

[22] S. Ashrit, Supriya Sarkar, Rashmi Singh, Sundeep Z. Yadav, Ravikrishna V. Chatti, Characterization of blast furnace flue dust - a multi analytical techniques approach, Metallurgical Research and Technology 117 (6) (2020) 606, https://doi.org/10.1051/metal/2020059.

[23] S. Johnson, W.M. Barnard, Comparative effectiveness of fourteen solutions for extracting arsenic from four western New York soils, Soil Sci. Soc. Am. J. 43 (1979) 304–308.

[24] M.L. Jackson, Soil Chemical Analysis, Prentice hall of India pvt. Ltd., New Dehli, India, 1973.

[25] C.H. Williams, H. Steinbergs, Soil sulfur fractions as chemical indices of available sulphur in some Australian soils, Aust. J. Agric. Res. 10 (1959) 340–352, https://doi.org/10.1071/AR9590340.

[26] D.J. David, The determination of exchangeable sodium, potassium, calcium and magnesium in soils by atomic-absorption spectrophotometry, The Analyst 85 (1012) (1960) 495–503.

[27] W.L. Lindsay, W.A. Norvell, Development of a DTPA soil test for zinc, iron, manganese, and copper, Soil Sci. Soc. Am. J. 42 (1978) 421–428, https://doi.org/10.2136/sssaj1978.03615995004200030009x.

[28] N.J. Gogtay, U.M. Thatte, Principles of correlation analysis, J. Assoc. Phys. India 65 (2017).

[29] K. Wang, Stepwise regression and all possible subsets regression in education, Int. J. Arts Sci. 2 (2016) 60–81.

[30] D.H. Moon, D. Dermatas, N. Menounou, Arsenic immobilization by calcium–arsenic precipitates in lime treated soils, Sci. Total Environ. 330 (1–3) (2004) 171–185, https://doi.org/10.1016/j.scitotenv.2004.03.016.

[31] J. Kim, In-Situ Stabilization of Arsenic-Contaminated Soil Using Industrial By-Products 1–6, https://www.researchgate.net/publication/267256646, 2015.

[32] R.G. Robins, In Mercury and Arsenic Wastes: Removal, Recovery, Treatment and Disposal, in: U.S. Environmental Protection Agency Pollution Technology Review, Noyes Data Corporation, New Jersey, 1992, pp. 63–66, submitted for publication.

[33] J. Bothe, V. James, P.W. Brown, Arsenic immobilization by calcium arsenate formation, Environ. Sci. Technol. 33 (1999) 3806, https://doi.org/10.1021/es980998m.

[34] W. Zhai, W. Zhao, H. Yuan, T. Guo, M.Z. Hashmi, X. Liu, X. Tang, Reduced Cd, Pb, and as accumulation in rice (*Oryza sativa* L.) by a combined amendment of calcium sulfate and ferric oxide, Environ. Sci. Pollut. Control Ser. 27 (2) (2020) 1348–1358, https://doi.org/10.1007/s11356-019-06765-9.

[35] Y. Takahashi, R. Minamikawa, K.H. Hattori, K. Kurishima, N. Kihou, K. Yuita, Arsenic behavior in paddy fields during the cycle of flooded and non-flooded periods, Environ. Sci. Technol. 38 (4) (2004) 1038–1044, https://doi.org/10.1021/es034383n.

[36] J.C. Fisher, D. Wallschläger, B. Planer-Friedrich, A new role for sulfur in arsenic cycling, Environ. Sci. Technol. 42 (2008) 81–85, https://doi.org/10.1021/es0713936.

[37] S. Wu, P. Kuschk, A. Wiessner, J. Müller, R.A. Saad, R. Dong, Sulphur transformations in constructed wetlands for wastewater treatment: a review, Ecol. Eng. 52 (2013) 278–289, https://doi.org/10.1016/j.ecoleng.2012.11.003.

[38] S.L. Saalfield, B.C. Bostick, Changes in iron, sulfur, and arsenic speciation associated with bacterial sulfate reduction in ferrihydrite-rich systems, Environ. Sci. Technol. 43 (2009) 8787–8793, https://doi.org/10.1021/es901651k.

[39] S. Lee, E.Y. Kim, H. Park, In situ stabilization of arsenic and metal contaminated agricultural soil using industrial by-products, Geoderma 161 (2011) 1–7, https://doi.org/10.1016/j.geoderma.2010.11.008.

[40] D. Zhang, Z. Yuan, S. Wang, Incorporation of arsenic into gypsum: relevant to arsenic removal and immobilization process in hydrometallurgical industry, J. Hazard Mater. 300 (2015) 272–280, https://doi.org/10.1016/j.jhazmat.2015.07.015.

[41] L.C. Jones, B.J. Lafferty, D.L. Sparks, Additive and competitive effects of bacteria and Mn oxides on arsenite oxidation kinetics, Environ. Sci. Technol. 46 (12) (2012) 6548–6555, https://doi.org/10.1021/es204252f.

[42] G.P. Warren, B.J. Alloway, N.W. Lepp, B. Singh, F.J. Bochereau, C. Penny, Field trials to assess the uptake of arsenic by vegetables from contaminated soils and soil remediation with iron oxides, Sci. Total Environ. 311 (2003) 19–33.

[43] P. Manomita, N. Bhowmik, B. Bandopadhyay, A. Sharma, Comparison of mercury, lead and arsenic with respect to genotoxic effects on plant systems and the development of genetic tolerance, Environ. Exp. Bot. 52 (3) (2004) 199–223, https://doi.org/10.1016/j.envexpbot.2004.02.009.

[44] J. Buschmann, M. Berg, Impact of sulfate reduction on the scale of arsenic contamination in groundwater of the Mekong, Bengal and Red River deltas, Appl. Geochem. 24 (7) (2009) 1278–1286, https://doi.org/10.1016/j.apgeochem.2009.04.002.

[45] B.D. Kocar, T. Borch, S. Fendorf, Arsenic repartitioning during biogenic sulfidization and transformation of ferrihydrite, Geochem. Cosmochim. Acta 74 (3) (2010) 980–994, https://doi.org/10.1016/j.gca.2009.10.023.

[46] P.A. O'Day, D. Vlassopoulas, R. Root, N. Rivera, The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions, Proc. Natl. Acad. Sci. USA 101 (38) (2004) 13703–13708, https://doi.org/10.1073/pnas.0402775101.

[47] D.W. Oscarson, P.M. Huang, C. Defose, A. Herbillon, Oxidative power of Mn(IV) and Fe(III) oxides with respect to arsenite in terrestrial and aquatic environments, Nature 291 (1981) 50–51, https://doi.org/10.1038/291050a0.

[48] C. Tournassat, L. Charte, D. Bosbach, A. Manceau, Arsenic (III) oxidation by birnessite and precipitation of manganese (II) arsenate, Environ. Sci. Technol. 36 (2002) 493–500, https://doi.org/10.1021/es0109500.

[49] R.P. Soratto, C.A. Crusciol, Dolomite and phosphogypsum surface application effects on annual crops nutrition and yield, Agron. J. 100 (2008) 261–270, https://doi.org/10.2134/agronj2007.0120.
[50] M. Vicensi, C. Lopes, V. Koszalka, R.C. Umburanas, J. Kawakami, C.A. Pott, M.M.L. Muller, Gypsum rates and splitting under no-till: soil fertility, corn performance, accumulated yield and profits, J. Soil Sci. Plant Nutr. (2019) 1–13, https://doi.org/10.1007/s42729-019-00157-1.
[51] N.B. Prakash, P. Dhumgond, S. Venkatesh, T. Chikkaramappa, S. Ashrit, Performance of slag-based gypsum on maize yield and available soil nutrients over commercial gypsum under acidic and neutral soil, Commun. Soil Sci. Plant Anal. 1–19 (2020), https://doi.org/10.1080/00103624.2020.1791161.
[52] M. Laxmanarayanan, B. Nagabovanalli, Prakash, D. Prabhudev, Shruthi, Shrenivas Ashrit, Slag-based gypsum as a source of sulphur, calcium and silicon and its effect on soil fertility and yield and quality of groundnut in southern India, J. Soil Sci. Plant Nutr. (2020), https://doi.org/10.1007/s42729-020-00335-6.
[53] B.H. Niazi, I.M. Salim, M. Ahmad, Use of gypsum to increase fertilizer efficiency on normal soils, Asian J. Plant Sci. 2 (9) (2003) 673–676. https://doi:10.3923/ajps.2003.673.676.