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Remediation of Arsenic Toxicity in the Soil-Plant System by Using Zinc Fertilizers

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Abstract

Availability of soil arsenic (As) and plant As at various levels of zinc (Zn) and As applications were examined. A pot-culture experiment with a leafy vegetable, Kalmi (*Ipomoea aquatica*), on an Inceptisols, was conducted where As was applied with irrigation water at the rates of 0 mg/L (As control), 0.5 mg/L, 1 mg/L and 2 mg/L and Zn was added to the soil as $ZnCl_2$ solution at the rate of 0 mg/L (Zn control), 1 mg/L, 2 mg/L and 3 mg/L during pot preparation. The experiment was conducted in triplicates for 45 days till the plants were grown to maturity. At the end of the experiment the remedial effect of Zn on As toxicity was examined and as such, yield parameters, As and Zn accumulation in Kalmi plants, residual concentrations of As and Zn in soils and plants were measured. It appeared from the present study that there exists an antagonistic relationship between Zn and As *i.e.*, Zn in soils was found to reduce As availability in soils as well as its accumulation in plants, particularly at an elevated application rate of 3 mg/L Zn. The findings could be used as a strategy to mitigate arsenic toxicity in As contaminated soils.

Keywords

Remediation, Arsenic, Soil-Plant System

1. Introduction

Arsenic is a proven potent killing agent. It has been termed as the biggest natural calamity in known human history of the world. Ground water contamination by As has been reported in 20 countries of the world encompassing all the continents [1] but the extent of ground water contamination in Bangladesh is by far the most severe as it covers almost 80% of the country with about 50% of the population at exposure risk of different degrees and the source is mainly geogenic [2].

About 40% of total arable land in Bangladesh is now under irrigation facilities and more than 60% of this irrigation is met from groundwater, most of which is contaminated with As to variable extent [2]. As arsenic contaminated groundwater is being used for irrigation purpose, there is a risk of soil accumulation as well as possible creeping of this toxic element to the food chain through plant uptake and animal consumption [3]. It may cause hazards both in soil environment and in crop quality. Normal level of As in soils is 4 - 8 mg As/kg, but in areas where As contaminated ground water is used for irrigation, the soil As level can reach up to 58 mg As/kg [4].

On the other hand, Zn is an essential micronutrient element for plants [5]. It is reported to involve in some important plant metabolic processes like enzyme activation, especially carbonic anhydrase and enolase [6], protein production [7], growth hormone (especially auxin) formation and chlorophyll formation [8], pollination by pollen tube formation [9] [10] [11] and pigment formation for photosynthesis [12].

As a micronutrient element, Zn is known to interact with some other elements. Some well known interactions are Zn-N [13] [14], Zn-Fe [15], Zn-Mn [16], Zn-Cu, Zn-B [7] and mostly Zn-P which causes "P" induced Zn deficiency [17]. As arsenic (As) and phosphorus (P) are in the same group of periodic table (Group VA) and Zn and P bear an antagonistic relationship, it is assumed that Zn is to show antagonism with As *i.e.,* Zn is expected to depress arsenic (As) concentration in soils as well as in plants. To substantiate the hypothesis, a plant culture experiment was made where kalmishak (*Ipomoea aquatica*) was used as the test plants as it is an available fast growing and widely consumed leafy vegetable.

2. Materials and Methods

Composite soil samples, collected from the surface (0 - 15 cm) of the field of Bangladesh Jute Research Institute (BJRI) of Manikgonj district (23˚52'60"N and 90˚02'12"E), were air-dried, ground and divided into two parts. The first part was passed through a 0.5mm sieve and used for analyzing some physical and chemical parameters of the soil. The soil had a pH of 6.52, silt loam texture, 0.87% organic carbon, 0.09% total nitrogen, 0.10 meq% available potassium, 3.03 mg available phosphorus and 11.17 mg available sulfur/ kg soil. Diethylene-triamine-penta-Acetic acid (DTPA) extractable Zn content of the soil was 1.89 mg/kg and water extractable As content was below the detection limit (0.02 mg/L) of the atomic absorption spectrophotometer (AAS).

Another part of the soil was passed through a 5 mm sieve and put into 48 earthen pots each having 2 kg soils for the pot experimentation. To ensure the optimum growth of Kalmi, the test plant species, Nitrogen (N), Phosphorous (P) and Potassium (K) fertilizers were added at a rate of 260 kg Urea/ha, *i.e.* 0.259 g/2 kg soil; 188 kg TSP/ha, *i.e.* 0.188 g/2 kg soil and 98.5 kg MP/ha, *i.e.* 0.099 g/2 kg soil respectively [18].

The experiment was conducted by following a factorial experiment. Four different doses of Zn (0, 1, 2 and 3 mg/L) and of As (0, 0.5, 1 and 2 mg/L) were selected as treatments. The different rates of Zn were supplied as 300 ml $ZnCl_2$ solution during pot preparation and the doses of As was applied with daily irrigation water. Arsenic solution was prepared by dissolving 80% Na-meta arsenite and 20% Na-arsenate and application of As doses were started after 10 days of germination of Kalmi. The control treatments did not receive either Zn or As. The plants of these pots were irrigated with As free tap water.

Kalmi plants were harvested by uprooting them after 45 days of their growth. Then, after washing and weighing for fresh weight, the samples were cut, oven dried and sieved with 0.2 mm sieve and digested with concentrated nitric acid for further chemical analysis. On the other hand, soil samples, collected from pots after harvesting of plants, were air dried, ground and sieved through a 0.5 mm sieve and extracted with DTPA and distilled water for the analysis of Zn and As respectively.

All the data in the present experiment were statistically analyzed by using Microsoft Excel and MINITAB (version 17) packages. The results of experiment were statistically evaluated in the form of one-way analysis of variance (ANOVA).

3. Results and Discussion

The fresh and dry matter yields of Kalmi as affected by the various combinations of As and Zn treatments are shown in **Table 1** and **Table 2**. The values presented in the tables are averages of three individual replications. There were 5 plants in each pot and the results presented here are in g/100 plant basis.

Table 1 shows that the highest amount of fresh matter was obtained for the treatment combination of $As_{0.5}Zn_0$ and the minimum amount was produced for the treatment $As_{0.5}Zn_3$.

On the other hand, as for the dry matter production, $As_{0.5}Zn_3$ treatment produced the maximum while the minimum amount was obtained for the As_2Zn_1 treatment (**Table 2**). The table also shows that at zero Zn application and zero As application the fresh matter yield was low. With the increase of As dose to 0.5 mg/L, yield was increased and attained the highest value. It could be due to the

Table 1. Fresh matter (g/100 plants) production of Kalmi (*Ipomoea aquatica*) plants at different combinations of As and Zn.

Zn→ / As↓	0 mg/L	1 mg/L	2 mg/L	3 mg/L
0 mg/L	89.5	85.3	139.6	123.5
0.5 mg/L	148	112.2	106.4	76.3
1 mg/L	125.1	101.8	107.9	144.5
2 mg/L	103.3	119.4	85.3	102.7
P value→	**0.136**	**0.534**	**0.065**	**0.010**
Comment	**not significant**	**not significant**	**not significant**	**Significant**

Table 2. Dry weight (g/100 plants) production of Kalmi (*Ipomoea aquatica*) plants at different combinations of As and Zn.

Zn→ / **As↓**	0 mg/L	1 mg/L	2 mg/L	3 mg/L
0 mg/L	6.8	7.2	11.1	10.7
0.5 mg/L	12.3	9.5	8.1	12.7
1 mg/L	10.2	9.5	9.3	8.3
2 mg/L	9.1	6.0	6.3	8.2
P value→	**0.034**	**0.515**	**0.072**	**0.030**
Comment	**significant**	**not significant**	**not significant**	**Significant**

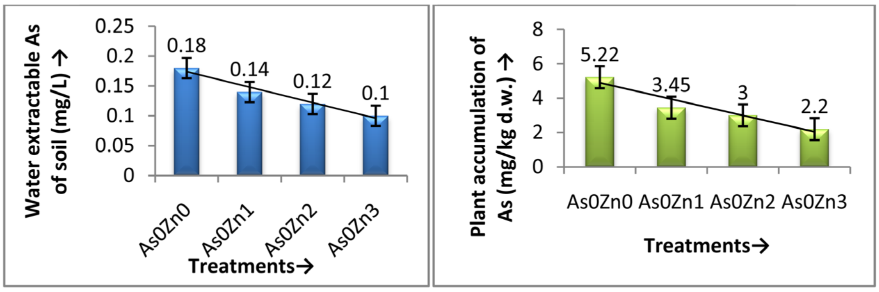
fact that at low concentration of As, the P availability or Fe availability was favored which caused this yield increase. Similar observations were found at low concentration of an antagonistic or otherwise not essential element favor growth with Na for a different crop [19]. It needs to be further mentioned that the fresh matter yield was better than control for all the other treatments.

The analysis of variance (ANOVA) test indicated that the effect of elevated dose of Zn (3 mg/L), on both fresh and dry matter production of Kalmi, over different rates of As application was significant (P value = 0.010 for fresh weight and P value = 0.030 for dry weight production), whereas the effect of other doses of Zn (1 and 2 mg/L) on different levels of As was found to be not significant. On the other hand, when Zn was absent, the dry matter production showed a significant increase with increasing As in the soil indicating the fact that the soil lacked sufficient Zn supply (P value = 0.034).

The results (**Table 1** and **Table 2**) clearly indicate that the higher doses of As caused reduction of yield of Kalmi plants, especially when the dry matter production was reduced. It may be due to the harmful impact of As on plant metabolism as As was also reported as a well-known metabolic inhibitor [20]. Supporting this hypothesis, it was also reported that the higher concentrations of As interfere with metabolic processes and inhibit plant growth, sometimes leading to death [21]. Growth reduction of several plants due to higher doses of arsenic was also reported by [22]. Lower biomass production of plants resulting lower synthesis and lower pigment concentration due to increasing levels of As in plant-soil environment was also reported by [23].

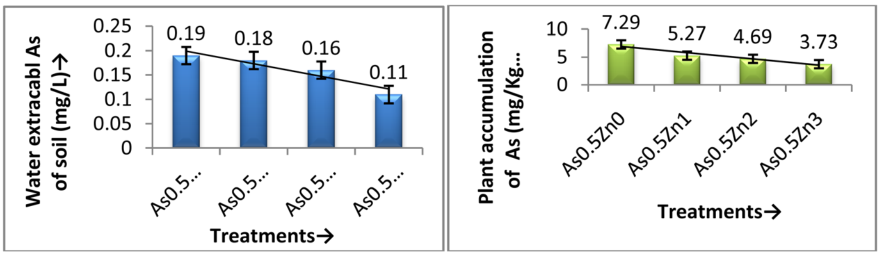
Water extractable As in soils and plant As concentration for different combinations As-Zn treatments are shown (**Figures 1-4**).

It is to be noted that the control treatment where no Zn was added, showed the maximum concentration of As both for soils and plants, but with the increase in Zn level, As was found to be decreased. However, a slight increase in the concentration of As, found in native soil in an absolute control treatment (As_0Zn_0), was found which could be due to the solubilization of some of the total As by the root exudates (usually the organic acids), or it could have been added as an impurity from the P-fertilizer used.



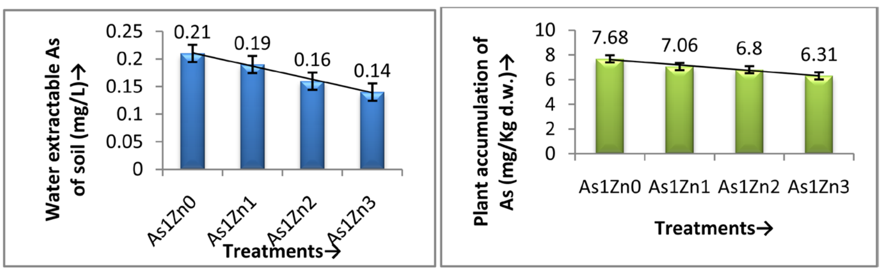
(a) (b)

Figure 1. (a) No As in soils with (b): As in plants at no As in different levels of Zn soil with different levels of Zn.



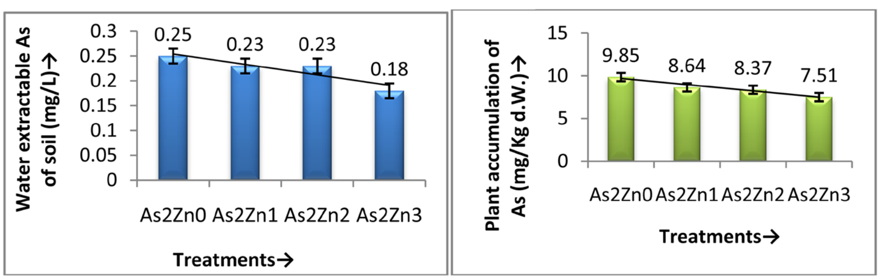
(a) (b)

Figure 2. (a) 0.5 mg/L of As in soils; (b) As in plants at 0.5 mg/L of As in soil with different levels of Zn. with different levels of Zn.



(a) (b)

Figure 3. (a) 1 mg/L of As in soils; (b) As in plants 1 mg/L of As in soil with different levels of Zn. with different levels of Zn.



(a) (b)

Figure 4. (a) 2 mg/L of As in soils; (b) As in plants 2 mg/L of As in soil with different levels of Zn. with different levels of Zn.

With regard to increasing doses of Zn fertilization, it was recorded that the As availability was countered indicating an interacting effect between Zn and As.

Higher doses of Zn was found to decrease the mobility of As (**Figure 1(a)**, **Figure 2(a)**, **Figure 3(a)** and **Figure 4(a)**) in soils as well as the plant Zn concentration (**Figure 1(b)**, **Figure 2(b)**, **Figure 3(b)** and **Figure 4(b)**) under the present experimental condition.

One of the causes of such decrease might be the precipitation or fixation of As as Zn-arsenate, which makes it less mobile and unavailable to plants [24].

$$\text{Arsenate} + \text{ZnCl}_2 \rightarrow \text{Zn} - \text{arsenates} \quad \text{(Insoluble and unavailable to the plant)}$$

This tends to indicate that Zn could alleviate As accumulation in plants. As per the free-ion activity model (FIAM) [25], the uptake of As by kalmi plants was reduced as the free-ion activity or availability of that element was reduced from the surrounding soil solution which is similar to the findings of [26].

This observation also corroborates to the findings that of a similar trend for As-Zn interaction in a submerged soil [27]. Correspondingly, it was reported that the toxicity of arsenic may be reduced by applying sulfates of zinc, iron and aluminum to the soil [28]. An increase in arsenic concentration was correlated with decreasing application of graded levels of Zn as Zn-sulfate was also reported [29].

All the values of water extractable As in soils and plant uptake of As were found to be highly significant (P value < 0.001).

It is evident from the result of the experiment that, higher doses of Zn fertilizers were found to suppress As availability in soils as well as the plant As contents. In this experiment, it was found that among all the doses, the maximum dose of Zn (3 mg/L) had the maximum antagonistic effect on As as it reduced the soil extractable As concentration from 0.25 to 0.18 mg/kg and the plant As concentrations from 9.85 to 7.51 mg/kg dry weight for the maximum Zn dose (3 mg/L).

On that note, it can be suggested that Zn fertilizers, especially $ZnCl_2$, can be used to reduce As toxicity from soils as well as to reduce plant As contents, but of course within the critical limit value of Zn for plants.

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