Chapter

Protecting Rice Grains from Arsenic Toxicity through Cultural Management: Bangladesh Perspective

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Abstract

In 1997, arsenicosis was reported as a result of ingesting arsenic-containing rice grown in arsenic (As)-rich soil, irrigated with high As water from shallow tube wells (STW) and deep tube wells (DTW) in Bangladesh. Of the 4 million ha irrigated fields, 60% were under STW and 15% under DTW waters; almost all were arsenic contaminated in varying quantities since they were used. In the present study, it was determined that irrigation from STW water having 500 μg As/l produced rice grains with 2.56 mg As/kg in a field with initial 3.21 mg/kg soil, leaving 8.27 mg/kg soil compared to pond water irrigation where only roots absorbed 0.105 ± 0.069 mg As/kg leaving ≤2.6 mg/kg soil. About 2.5 mg As/kg soil may be considered a safe level for arsenic-free rice cultivation. Bio-mitigation of the STW water using duckweed (DW) (*Spirodela polyrhiza*) was expensive and disposal in various ways of As-loaded DW produced was hazardous returning arsenic to ecosystems. Alternative to the groundwater (GW), surface water can be made available by constructing rubber dams and converting rivers into surface water reservoirs to overcome the arsenic toxicity and protecting rice and other grains, integrating aquaculture of the DW and *Azolla pinnata* var. *pinnata* for fish and poultry feeds. Permanent solution could be achieved executing "Delta Plan 2100" saying "No to groundwater use for irrigation, let the Arsenic stay in the underground".

Keywords: arsenic toxicity, rice toxicity, groundwater arsenic, soil arsenic, bio-mitigation, *Spirodela polyrhiza*, river reservoirs, rubber dam, Bangladesh

1. Introduction

In Bangladesh, As was discovered in 1993, while doctors and health personnel were dealing with health effects of its contamination in drinking water. Since then, As-contaminated groundwater was found in 44 districts out of which arsenicosis patients were detected in 26 districts, 7 of which were highly affected, and out of 64 districts [1] (**Figure 1**), some districts as a catastrophe affecting human health [1, 2]. Southern districts in particular contained >300 μg As/l in GW, and more than 20% tube wells contain more than 100 μg As/l that are used for irrigation and drinking [3]. The metalloid at low concentration (10–50 μg As/l) in a sandy soil may be more phytotoxic (i.e., available) than much higher levels (200–500 μg As/l) in a heavier clay soil [4]. Arsenic is found everywhere in traces, i.e., in the air, in the ocean and freshwaters (some drinking water supplies), in soil, etc., polluting the environment and causing arsenicosis (melanosis, keratosis, gangrene, chronic ulcer, skin cancer, etc.) in human [1, 5]. Studies also confirmed that a substantial amount of this heavy metal is absorbed by plants [6–9]. The question is how as appeared heavily in soils, drinking, and irrigation waters of Bangladesh? In the 1960s, 4 million hand tube wells (HTW)

Figure 1.
Arsenic-affected areas in Bangladesh based on studies from 1993 to 1996 [1]. Round white spot (within blue) east of mid-region is the study site at Sonargaon.

were installed at a depth of 10–15 m for drinking water without checking arsenic in the aquifers [10]. In the 1970s high-yielding rice variety known as the International Rice Research Institute (IRRI) paddy var. IR8 was introduced in Bangladesh that required huge irrigation, necessitating the installation of STW at a depth of 25–30 m [personal communication Director General, Dr. Md. Shahjahan Kabir of Bangladesh Rice Research Institute, Gazipur, Bangladesh]. For decades DTW have been installed at 100–200 m depth which are also contaminated with arsenic [11]. In Jessore alone, 74 out of 85 DTW tested had an average 210 μg As/l. Of the 4 million ha irrigated fields, 25% used surface water, 60% STW, and 15% DTW waters in Bangladesh [11]. The organic As (oAs) is not but inorganic arsenic (iAs) is toxic to human [12]. Concentration of absorbed arsenic in rice grains of Bangladesh was in toxic level for human consumption [13–15]. It was reported that 1.7–2.55 mg/kg rice grains were found in areas having 15–27 mg As/kg soil [16]. It was also reported that As concentrations in rice grains from flooded soils were 10–15 times higher than aerobically grown (non-flooded) rice, and similarly the concentration of inorganic As (iAs) in the grains from the flooded treatment was 2.6–2.9 fold higher than the non-flooded treatment [15].

Rice is by far the largest food dietary source of iAs for populations not drinking water with elevated As [17]. Arsenic in rice, cowpeas, vegetable crops, peas, snap beans, and sweet corn plants antagonize the uptake of nutrients like N, P, K, S, Ca, Mn, and Z [18–20] and reduced height of rice plants, straw and grain yield, grain per panicle, and the number of field grains per panicle applying 10 mg As/kg soil or above [19–22]. Phosphate replacement by arsenate preventing ATP generation was observed by [4, 7, 23] reducing ATP-dependent N_2 fixation [9]. Human activities like smelting, mining, the use of pesticides, making glasses and ceramics, etc. are responsible for contaminating earth surface [24], which is now a global health issue [25]. However, it has been estimated that about 30 metric ton of arsenic is borne by the biomass of the earth and is assumed to be the 12th most abundant element in the biosphere [26].

Arsenic removal efficiency varies with many conditions, like site-specific chemicals and geographic and economic conditions [27]. There have not been any significant and innovative improvements in the methods for removing arsenic from HTW water in a decade of research for drinking [28]. However, no attempt has so far been taken to remove arsenic from large volume of the contaminated STW waters for using in irrigation. In the present study, an attempt was made to use efficient arsenic-absorbing floating plant *S. polyrhiza* to remove toxic arsenic from STW water in situ for protecting rice grains through cultural management.

2. Materials and methods

Field studies were carried out at Nilkanda Union under P. S. Sonargaon, District Narayanganj, lying between 23°30′ and 23°46′ N and 90°31′ and 90°41′ E (**Figure 1**) [29]. A good number of submerged and exposed soil (rice, wheat, and vegetable fields) and water (STW, HTW, and pond) samples were collected in four replications at a gap of 0.5–1.0 km in the winter and spring seasons and analyzed to determine the amount of As absorbed by different crops and its presence in soils and water sources. Water samples were collected from DTW and STW one from each at village Kachua, under P.S. Kachua, district Chandpur, about 100 km southeast of Sonargaon.

2.1 Selection of plants and cultivation for bioremediation of arsenic

Six strains under three species of *Azolla* (*A. caroliniana* Dh 103; *A. filiculoides* Dh 104; *A. pinnata* var. *pinnata* Dh 111; *A. pinnata* var. *pinnata* Dh 112; *A. pinnata* var. pinnata Dh 113; and *A. filiculoides* Dh 115) and two species of *Spirodela* (*S. polyrhiza* Dh

116 and *S. punctata* Dh 117, Lemnaceae) were considered to select efficient As absorbing floating plants [9] by growing them in the growth room under controlled conditions: continuous light flux of 120 μE/m^2/s from daylight fluorescent tubes and 70–90% relative humidity at 30 ± 1°C. Liquid inorganic nutrient medium Chu 10D-N [30], a modified version of [31], with double the strength of P (3.56 mg/l) and K (9.45 mg/l) for *Azolla* strains, and IRRI medium with NH_4NO_3 as nitrogen source following [32] for species of *Spirodela* were grown in conical flasks of 150 ml capacity containing 50 ml medium adding arsenic trioxide as inorganic As (iAs) source before autoclaving. *S. polyrhiza* and *S. punctata* were grown at much higher arsenic concentrations as the plant is often found to grow in polluted waters and stressed environment [33]. The plants were grown at pH 6.00 [34, 35]. All plant biomasses after 3 days growth were oven dried at 90°C for 24 hour for determining growth and As absorbed [9].

2.2 Determination of nitrogenase activity

Nitrogenase activity in the presence of arsenic was determined by acetylene reduction assay (ARA) technique of [36] and details of the experiment given in [9].

2.3 Chemical analysis

Home-yard ponds and HTW waters were collected in iodized bottles and stored in ice box immediately and then in the laboratory deep freeze. Water quality of the pond and HTW waters is given in **Figure 2**. Whole plants of *Azolla* and *Spirodela*, roots, shoots, and grain samples of rice plant were collected separately and dried at 70°C for 3 days, grounded, and kept in poly-bags till analysis. Arsenic was determined by atomic absorption spectrometer (Shimadzu AA-680/G V-3) after digestion with nitric and perchloric acids at 5:1 ratio in a closed system. Arsenic concentration in brown-rice grains was cross-checked by neutron activation analysis

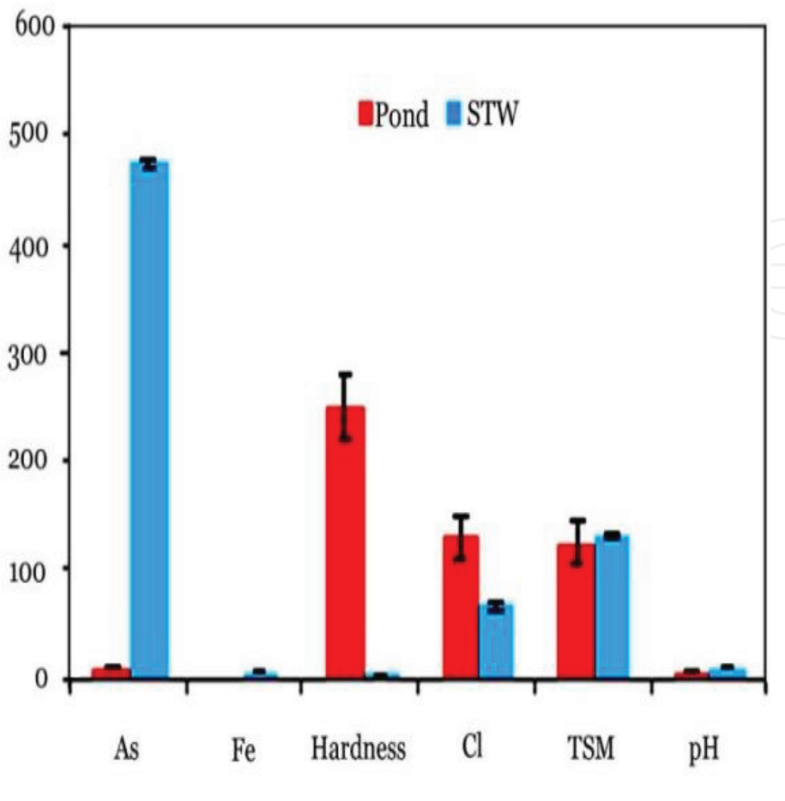

Figure 2.
Water quality of pond (control) and STW (installed 3 years ago) used for growing BR-28 rice in fields. Unit for tAs is μg/l and for others as mg/l. After [43]. n = 5; vertical bars are standard deviations.

(NAA) using 3 MW Research Reactor at Atomic Energy Research Establishment, Saver, Dhaka. PO_4-P in the culture medium was determined following [37].

Soil samples were collected from a depth of 0–5 cm in five replications from each plot on the basis of composite sampling method in [38]. Determinations of various fractions were carried out as described: EC by EC meter in [39]; pH by a microprocessor pH-meter, soil to water ratio was 1:2.5; organic carbon by wet oxidation method; organic matter by multiplying the percentage of organic carbon with conventional Van Bemmelen's factor of 1.74 in [40]; textural classes and particle size distribution by hydrometer method as described in [41, 42], respectively; and As by AAS (Perkin Elmer M-3110, USA) following low temperature sample digestion with HNO_3-HCl mixture at a ratio of 1:3 in volumetric flasks with reflex condenser under a closed system.

2.4 Cultivation of *S. polyrhiza* in a production pond

The DW was cultivated in a 400 m^2 pond adding urea nitrogen, triple super phosphate, and muriate of potash in a solution at the rate of 40, 20, and 10 kg/ha/day, respectively [29]. The fertilizer solution was mixed with the pond water every day just after 10% harvest before noon time. The production was 1 ton/ha/day and 1 kg DW covers about 1 m^2 water.

2.5 Bioremediation of arsenic-contaminated HTW water

Mini-scale bioremediation was carried out in 50 L capacity RCC (cemented) tubs lined with polythene [29]. The tubs were set in the open area of a house having sufficient natural light. Arsenic-contaminated HTW (installed 25 years ago) having 475.5 ± 10.6 μg/l and 6.30 mg/l iron was used. Fresh DW from the cultivation pond was spread onto the tub water to form a complete cover. The amount per tub added was weighed, and the same amount was added after every 24 hours for 6 days. 100 ml surface water, 20 g fresh DW, and sediment from each tub bottom were collected for analysis of As in the samples.

Large-scale bioremediation experiment was carried out in about 1 meter deep, 350 m^2 pond situated near to the experimental rice field [29]. It was filled with arsenic (495 ± 10 μg As/l was considered as 500 μg As/l)-contaminated STW water which appeared reddish brown in color. The STW water had 8.85 mg/l iron. About 350 kg DW was spread over the stored STW water in the pond and divided into eight blocks by bamboos for keeping the plants equally spread for As absorption. After every 2 days, 1.0 kg fresh DW, 100 ml water, and 50 g sediment were collected from each block for chemical analysis and for using as feed for broiler and Bengal goat. All the floating DW was then harvested (kept in a shallow pit for decomposition and used in biogas production). Fresh DW was again spread completely covering the water surface.

2.6 Cultivation of rice

Effects of arsenic on the arsenic toxicity of winter-rice grain of variety BR28 were studied in a farmer's field having silt clay containing sand 4.31%, silt 45.56%, clay 50.13%, pH 6.35, EC 200 μS/cm, iron 0.87%, arsenic 3.21 mg/kg soil, and organic matter 1.85%, in Silmondi and Narailbag soil series at Meghna floodplain [29]. Research plots were 19 × 19 m in five replications arranged in complete randomized block design. NPK fertilizers from urea, TSP, and MP, respectively, were applied at 45, 15, and 40 kg/ha, respectively, to all plots at the time of land preparation other than N. The N was applied at 25 kg/ha 15 days after transplanting (DAT) and 20 kg/ha before flowering. "Boro" rice var. BR28 seedlings of 10 days old were transplanted and irrigated once in a week with pond water as control and 500 μg As/l contaminated STW water that dries up by the end of that week and watered again for the next one week [29].

3. Results and discussion

3.1 Water and soil chemistry

Prevalence of total arsenic (As) in soil and water sources collected from areas at a gap of 0.5–1.0 km in the winter and spring seasons at Sonargaon is given in **Table 1**. Arsenic in pond water was due to seepage and water flow from the household use of As-contaminated HTW. The concentration of iron had direct correlation to the amount of arsenic present. Rice field soils in the areas had highest arsenic ranging from 5.83 to 8.01 mg/kg (due to weekly irrigation about nine times with STW water), followed by wheat (due to broadcast seeding and standing irrigation after 20, 60, and 80 days (before flowering)) and vegetable fields (due to non-standing irrigation two times during dry period). Water from the HTW was found to have 131 ± 0.1 μg As/l (10 years old) to 475.5 ± 10.6 μg As/l (25 years old). Similarly, 1-year-old STW water was found to have 92.2 ± 1.5 μg As/l, while the 3-year-old one had 495.0 ± 10 μg As/l indicating that the older the tube well, the more is the groundwater arsenic indicating tube wells having less than 100 μg As/l in the early 2000s most likely have now increased to several hundred or more.

The water of 1-year-old DTW was with very little or no arsenic, while STW had 150 ± 3.0 μg As/l and has been found to be moderately affected [1] at village Kachua in Meghna floodplain. In Ganges floodplain, there are reports of an average 210 μg As/l in DTW water in many areas of Jessore district and in highly affected areas (**Figure 1**). The most alarming point is that each and every crop had arsenic toxicity for irrigating with GW (**Table 1**). To get a good yield, irrigation is a must and alternative source(s) need to be found out.

Quality of pond and STW waters used in irrigating rice cultivation experiments is shown in **Figure 2**.

3.2 Selection of arsenic removing plants in the laboratory

Six strains of *Azolla* under three species were treated with arsenic trioxide in the laboratory to determine their ability to grow and absorb As, PO_4-P uptake, and

Waters (μg/l for As, mg/l for iron)								Soils (mg/kg)		
DTW		STW		HTW		Pond				
As	Iron	As	Iron	As	Iron	As	Iron	Rice	Wheat	Vege.
3.40 ± 0.90*	0.95*	495 ± 10.00	8.85	250.5 ± 2.08	7.40	9.66 ± 1.16	0.83	7.65	4.42	3.15
		(3 years old)		(15 years old)		9.13 ± 0.31	0. 70	6.39	4.23	2.53
		313 ± 4.00	8.15	131.0 ± 0.10	6.10	3.20 ± 0.20	0. 44	7.88	3.15	1.96
		(2 years old)		(10 years old)		3.11 ± 0.17	0.30	8.01	4.09	4.21
		92.2 ± 1.50	8.10	152.0 ± 3.5	6.30			5.83		3.65
		(1 year old)		(10 years old)				7.48		3.68
		150 ± 3.00*	6.10*	475.5 ± 10.6	7.60					4.02
		(3 years old)		(25 years old)						2.66

**Indicate values of two tube wells from village Kachua P.S. Kachua (moderately affected area).*

Table 1.
Prevalence of arsenic in soils and waters at Sonargaon.

nitrogenase activity (**Figure 3a**–**d**) [9]. *A. pinnata* var. *pinnata* Dh 111, Dh 112, and Dh 113 strains grew well at 100 μg iAs/l. The growth of strains Dh 112 and Dh113 was identical even at 400 μg iAs/l in 3 days (**Figure 3b**). Only *A. pinnata* var. *pinnata* Dh 113 appeared to be suitable for absorption of iAs from 100 μg iAs/l [9]. This was due to the substantial absorption of PO_4-P at 100 μg iAs/l and mild absorption in higher concentrations (**Figure 3c**). *A. pinnata* var. *pinnata* Dh 113 absorbed about 0.0066% arsenic of d. wt. from 100 to 200 μg/l As in 3 days (**Figure 3b**) [9]. Only *A. pinnata* var. *pinnata* Dh 113 appeared to be suitable for absorption of As from 100 μg/l As [43]. The presence of higher amount of PO_4-P in the iAs containing medium (**Figure 3c**) than the control (without iAs) suggests that after three days growth phosphate uptake was limited by plants and replaced by arsenate or competitively absorbed limiting ATP formation, indicated by decreased ATP-dependent nitrogenase activity, which was nil at 400 μg As/l (**Figure 3d**) [9].

S. polyrhiza Dh 116 and *S. punctata* Dh 116 were treated with arsenic trioxide in the laboratory to determine their ability to grow and absorb As and PO_4-P (**Figure 4a**–**c**) [9]. The highest accumulation of 0.0351% iAs on dry wt. basis (**Figure 4b**) was observed in *S. polyrhiza* from 1000 μg iAs/l, and this was due to substantial absorption of PO_4-P from medium containing 1000 μg iAs/l (**Figure 4c**).

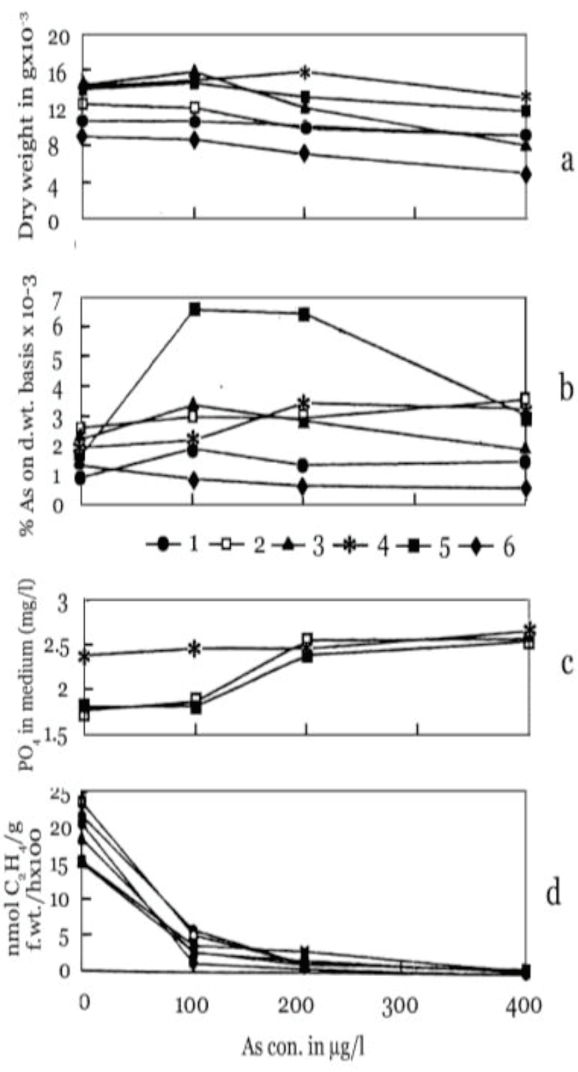

Figure 3.
(a–d) Effects of arsenic trioxide in batch culture under controlled environments measured after 3 days of inoculation: (a) on growth, (b) % accumulation of As, (c) absorption of PO_4-P, and (d) nitrogenase activity by Azolla species/strains—(1) A. caroliniana Dh103, (2) A. filiculoides Dh104, (3) A. pinnata var. pinnata Dh111, (4) A. pinnata var. pinnata Dh112, (5) A. pinnata var. pinnata Dh113, and (6) A. filiculoides Dh115. After [9].

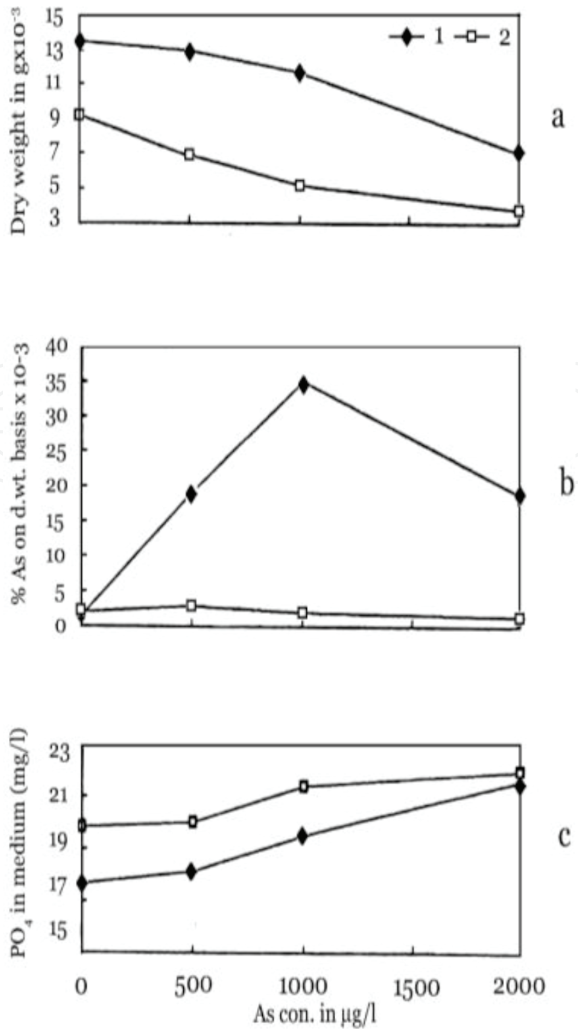

Figure 4.
(a–c) Effects of arsenic trioxide in batch culture under controlled environments measured after 3 days of inoculation: (a) on growth, (b) % accumulation of As, and (c) absorption of PO_4-P by Spirodela—(1) S. polyrhiza Dh116 and (2) S. punctata Dh117. After [9].

Of the eight floating plants tested, *S. polyrhiza* Dh 116 showed the highest absorption capacity to be much higher than *A. pinnata* var. *pinnata* Dh 113 [9].

3.3 Bio-mitigation of As from contaminated STW water using *S. polyrhiza*

3.3.1 Removing As in a mini-scale with the water in cemented tubs

In the laboratory *S. polyrhiza* showed the highest accumulation (0.0351% As on dry wt. basis) among floating plants from 1000 μg/l in 3 days (**Figure 4b**) [9]. Therefore, outdoor experiments were carried out at Sonargaon growing the DW in RCC tubs in 475.5 ± 10.6 μg As/l water and 6.30 mg Fe/l (**Figure 5a**–**c**). The DW absorbed about 295 mg As/kg d. wt. after 24-hour treatment (**Figure 5a**). A substantial amount of As was coagulated with iron (synergistic reaction) from 24 hours to 6 days giving similar curve like absorption of As by DW (**Figure 5b** and **c**).

3.3.2 Removing As in a large-scale keeping the water in a pond

The *S. polyrhiza* Dh 116 absorbed about 295 mg/kg d. wt. after 24 hours in tub experiment and thus could be a good candidate for mitigating As from the contaminated STW water in a large scale (**Figure 6a**–**c**). The 350 m^2 pond contains 350 m^3

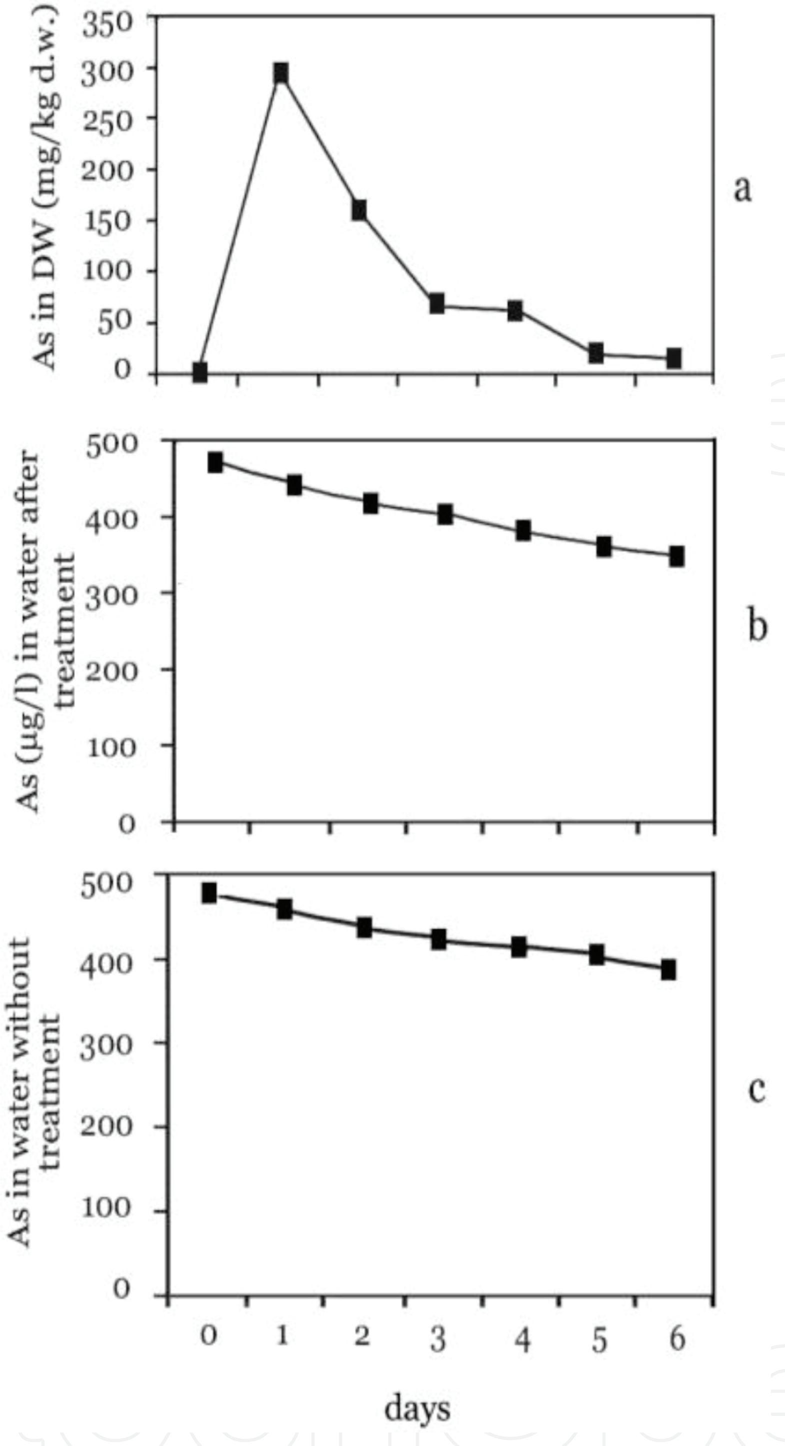

Figure 5.
(a–c) Changes in concentration of 475.5 ± 10.6 µg As/l HTW water after treatment with S. polyrhiza dh 116 in cemented (RCC) tubs.

or 350,000 l water. One liter STW water contains 500 µg As/l. Three hundred fifty thousand liters of water would contain 175 g As from which 157.5 g is to be removed to get 50 µg As/l acceptable level of irrigation water. The DW removed 325 mg As/kg dry DW (**Figure 7a**) with similar iron absorption curve in 2 days (**Figure 7b**). Therefore, 350 kg fresh DW was equal to 20 kg dry DW (5% basis) which could remove 6500 mg or 6.5 g As, and thus to remove 157.5 g arsenic 24-hour treatment means 8.4 ton fresh DW would be needed in 48 days. In each 24 hour, arsenic loaded roots and plant debris, and As and Fe coagulates (synergistic) deposited 63.7 mg As on the pond bottom (**Figure 7d** and **e**), estimated to be about 1.529 g As after treatment. The bioremediation technique is time-consuming and expensive, requiring two ponds and over eight tons As-loaded DW waste.

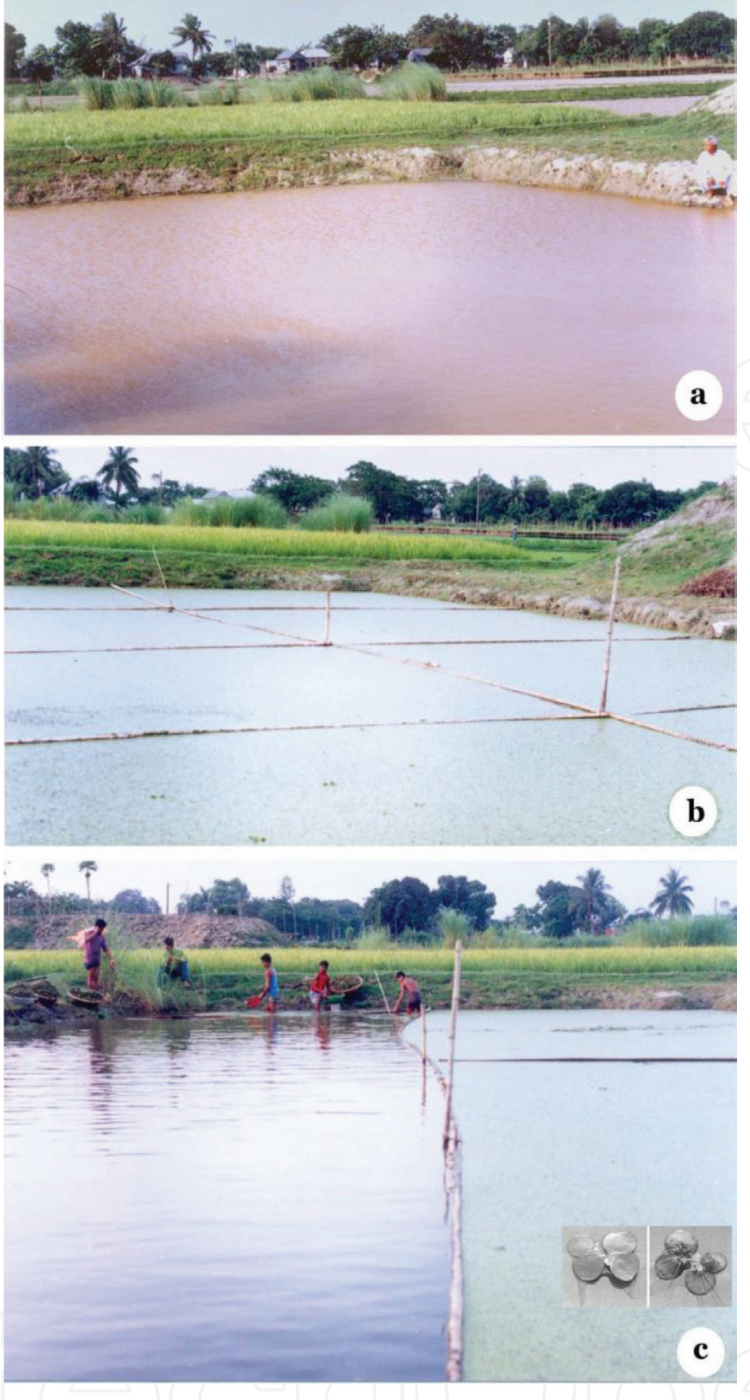

Figure 6.
(a–c) Bioremediation process of arsenic contaminated GW using S. polyrhiza. (a) 500 μg/l As STW water immediately after storage in the pond appeared grayish red colored, (b) a complete cover of the DW on the water, and (c) half of the DW cover removed after 8 days of treatment showing relatively clear water. Inset in "c" shows dorsal and ventral surfaces of the plant.

3.4 Effects of As-contaminated irrigation water on rice cultivation

"Boro" rice BR28 was grown in 500 μg As/l STW water (Section 2.6).

3.4.1 Arsenic in rice-cultivated soil

Arsenic concentration in soils of the experimental plots during rice cultivation is shown in **Figure 8**. Initial soil As was 3.21 mg/kg, increased to 7.51 mg/kg due to low uptake of As during seedling adaptation stage for 7 days irrigation with 500 μg As/l and 8.85 mg Fe/l STW water. During March rapid vegetative growth results in rapid uptake of As, reducing it to 5.50 mg As/kg soil. Further absorption

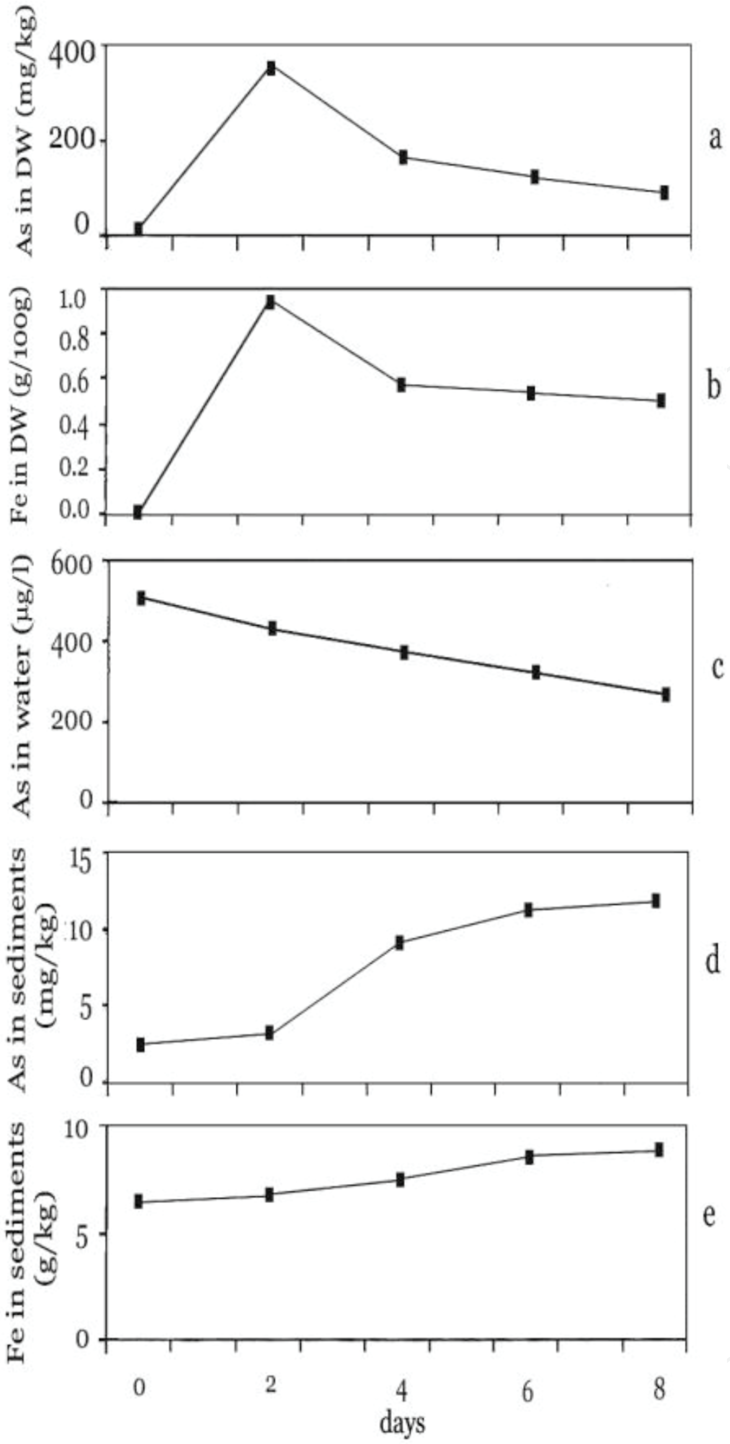

Figure 7.
(a–e) Changes in As (500 µg As/l) and Fe (8.85 mg/l iron) after treating with S. polyrhiza in the treatment pond and natural coagulation.

during panicle initiation, grain formation, and maturation in April reduced As to 4.90 mg/kg soil. Irrigation was stopped after a week creating non-flooded condition when As solubility decreased [15] simultaneously with low or no nutrient uptake by mature plants, increasing As concentration to 8.27 ± 1.35 mg/kg soil during harvest (**Figure 8**). There are reports on the increased soil As for using contaminated GW in rice fields year after year to 1.0 and 1.1 mg/kg soil in Bangladesh [16] and West Bengal [44], respectively.

In irrigated pond water (**Figure 8**), As concentration insignificantly decreases till the day of harvesting, ranging from 1.91 ± 0.26 to 2.6 ± 0.80 mg/kg soil from initial 3.21 mg/kg. Only roots absorbed 0.075–0.156 mg As/kg in the presence of a good amount of As for the growing period (**Figures 8** and **9**). It appears that As absorption in pond water

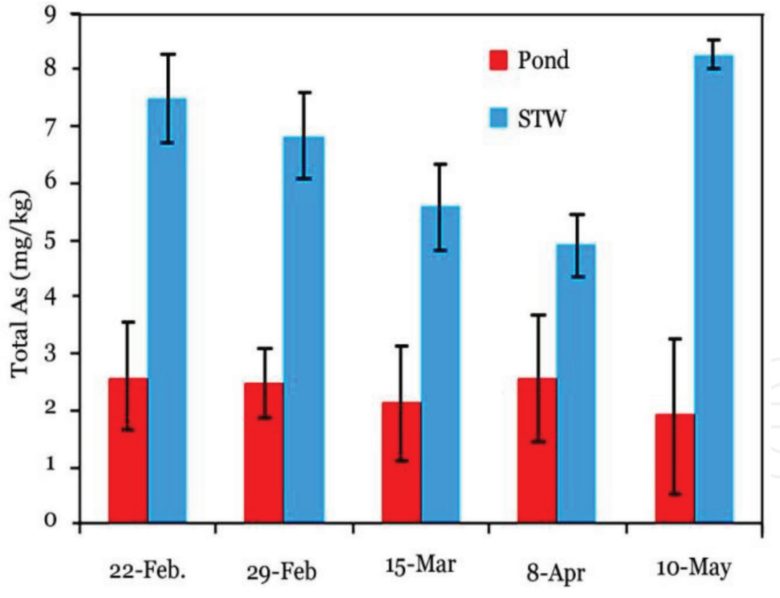

Figure 8.
Arsenic concentration in soils of the experimental plots during rice cultivation transplanted on 15 Feb 2004, irrigated with pond and shallow tube well waters. Initial soil arsenic was 3.21 mg/kg; contaminated pond water had only 9.50 ± 0.50 μg/l, while STW water had 500 μg As/l. Rice crop harvested on 10 may. After [43]. n = 5; vertical bars, standard deviation.

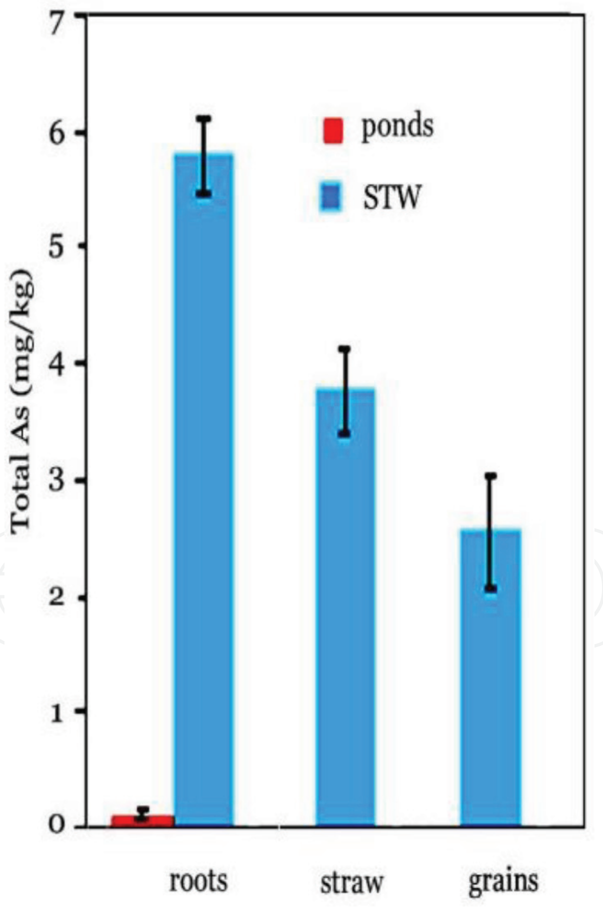

Figure 9.
Arsenic concentration in roots, straw, and brown rice grains of BR 28 at the time of harvest. Initial soil arsenic was 3.21 mg/kg, while pond and shallow tube well waters contained 9.50 ± 0.50 and 476 ± 3 μg/l arsenic, respectively. After [43]. n = 5; ± and vertical bars are standard deviation.

irrigated plots is limited at 2.6 ± 0.80 mg/kg soil. Therefore, 2.5 mg/kg soil could be considered as a safe level for arsenic-free rice cultivation in Bangladesh. The permissible limit for the USA is 5 mg As/kg soil for agricultural use [45].

It has been estimated that Bangladesh clayey soil needs about 1000 l irrigation water/m^2/year (in conservative use) [11]; in other words 2500 l/kg surface water is needed for producing 1 kg rice, considering production of 4.0 ton/ha.

3.4.2 Arsenic distributions/accumulations in rice crops

Arsenic accumulation in the "Boro" rice plant parts was mostly in roots followed by shoots, brown-rice grains (**Figure 9**), and husks. The rice grain contained 2.552 ± 0.507 mg/kg As, similar to adjacent rice field (2.56 ± 0.20 mg/kg) which was determined by neutron activation analysis. The presence of 1.7–1.8 mg/kg rice grains was recorded in areas having 15–27 mg As/kg soil [13]. The high As content in straws found in the present study might affect cattle due to bioaccumulation when consumed, while roots would contribute about 5.7 mg/kg for the next crop. Using pond water as a control in the same field, only roots absorbed o.113 ± 0.054 mg As/kg leaving mean As 2.60 mg/kg soil.

The concentration of absorbed As in rice grains was much above the permissible limit of 1.00 mg/kg [14] for human consumption. It was estimated that elevated inorganic arsenic in rice significantly contributes to dietary arsenic intake in USA [17], which was estimated to be double (80%) in Bangladesh and India, and the rest was dimethyl-arsenate (DMA). Bioavailability of iAs from rice was reported to be high [15]. It was estimated that As concentration in rice would have to be as low as 0.050 mg/kg if consumed at 200 g/d to equate to similar exposure from drinking water at 10 μg/l [18]. Sonargaon rice contain 2.552 ± 0.507 mg As/kg which would have 0.85–1.276 mg iAs per kg rice assuming about 33–50% of As according to [46], while there are reports of 22–42% iAs, and the rest was DMA [15]. This in quantity ranged from 0.561 to 1.072 mg iAs/kg for Bangladesh rice. If the lowest amount 0.561 mg iAs/kg rice grain is considered and equates to permissible limit of 0.050 mg/l water (which would be about 0.250 mg iAs/kg consumed at 200 g/day by a 60 kg adult person), then a person in the study area is consuming double the amount of permissible iAs compared to China's food standard limit of 0.15 mg iAs/kg [38]. Thus estimated high iAs present in the rice grain at Sonargaon can lead to greatly increased exposure to chronic carcinogen.

The presence of arsenic affects PO_4-P absorption from the liquid medium by plants where phosphate is replaced by arsenates and prevents ATP synthesis [6, 9, 23]. Therefore, if the phosphorus, for example, is 50% less than the required amount in a cell, it could be assumed that the required amount of ATP synthesis would not take place affecting physiology, cell division to new cell formation, etc. in any affected organism. The high total arsenic in the soil would affect all the biotic communities including biological N_2-fixing soil bacteria, as is found in *A. pinnata* var. *pinnata* where ATP-dependent nitrogenase activity was severely affected [9].

A Rickshaw (a three-wheeler, non-mechanized) puller in the present study area had melanosis (hyper-pigmentation) or reddish spots, hairs having 3.99 ± 0.21, and nails having 8.90 ± 0.29 mg As/kg identified as "first stage group" [14] drinking 250 μg/l As for 2 years which was 8.42 mg/kg body wt. The lower value (4–8 mg As/kg samples) was due to the release of arsenic by deamination, and the accumulation may be higher in other parts of a body. Piped water from DTW was supplied for 2 years by the NGO Forum in the village of Nilkanda, Sonargaon; still farmers, day laborers, and Rickshaw pullers of many villages show symptoms of arsenicosis. The reason could be retention of arsenic in their body and most likely also eating high arsenic-containing rice, wheat, and vegetables (**Table 1**). The manifestation of the symptom (melanosis) appears to take place after some years of drinking and eating arsenic-contaminated water, rice, vegetables, etc. [17] as indicated by high amount of arsenic in nails and hairs.

3.4.3 Effects of high arsenic on weeds in rice fields

Effects of high arsenic on the occurrence of weeds in the rice field soil were studied. Out of 14 species recorded, six could not grow in the experimental rice field [47]. The Importance Value Index (IVI) indicated that *Alternanthera sessilis*, *Cynodon dactylon*, *Echinochloa colonum*, *Enhydra fluctuans*, *Hedyotis corymbosa*, and *Lippia nodiflora* are very sensitive to arsenic; *Lindernia antipoda* and *Eriocaulon setaceum* were not affected at all, while the growth of *Cyperus rotundus*, *Eclipta alba*, and *Fimbristylis* sp. was enhanced in the presence of arsenic (**Table 2**). The sensitiveness appears to be due to enhanced arsenic absorption by seeds, reduced germination percentage, radical length, and biomass accumulation leading to their death, as seen in seed germination of *Glycine max* at 25 and 100 μM sodium arsenate

Name of weeds	Den.	Freq.	Abun.	Rel. den.	Rel. freq.	Rel. abun.	IVI	H	D
Alternanthera sessilis	0.2 (–)	02 (–)	1.0 (–)	1.96 (–)	3.85 (–)	4.76 (–)	10.57 (–)	3.135 (2.751)	0.865 (0.836)
Cynodon dactylon	0.6 (–)	0.2 (–)	3.0 (–)	5.88 (–)	3.85 (–)	14.28 (–)	24.01 (–)		
Cyperus exaltatus	0.6 (0.4)	0.6 (0.2)	1.0 (2.0)	5.88 (8.33)	11.54 (7.69)	4.76 (14.81)	22.18 (30.83)		
C. rotundus	— (0.2)	— (0.2)	— (1.0)	— (4.16)	— (7.69)	— (7.41)	— (19.26)		
Eclipta alba	— (0.4)	— (0.2	— (1.0)	— (8.33)	— (7.69)	— (7.41)	— (23.43)		
Echinochloa colonum	1.0 (–)	0.4 (–)	2.5 (–)	9.8 (–)	7.69 (–)	11.9 (–)	29.39 (–)		
Enhydra fluctuans	0.6 (–)	0.4 (–)	1.5 (–)	5.88 (–)	7.69 (–)	7.14 (–)	22.71 (–)		
Eriocaulon sp.	2.2 (0.8)	0.8 (0.4)	2.75 (2.0)	21.57 (16.66)	15.38 (15.38)	13.09 (14.81)	50.04 (46.85)		
Fimbristylis sp.	— (0.6)	— (0.4)	— (1.5)	— (12.5)	— (15.38)	— (11.11)	— (38.99)		
Hedyotis corymbosa	0.4 (–)	0.2 (–)	2.0 (–)	3.92 (–)	3.85 (–)	9.52 (–)	17.29 (–)		
Hydrocotyle rotundifolia	0.6 (0.4)	0.6 (0.4)	1.0 (1.0)	5.88 (8.3)	11.54 (15.38	4.76 (7.41)	22.18 (31.12)		
Lindernia antipoda	2.2 (1.4)	0.8 (0.4	2.75 (3.5	21.57 (29.16)	15.38 (15.38)	13.09 (25.92)	50.04 (70.46)		
Lippia nodiflora	0.6 (–)	0.4 (–)	1.5 (–)	5.8 (–)	7.69 (–)	7.17 (–)	20.71 (–)		
Panicum sp.	1.2 (0.6)	0.6 (0.4)	2.0 (1.5)	11.76 (12.5)	11.54 (15.38)	9.54 (11.11)	32.82 (38.99)		

Abbreviations: Den., density; Freq., frequency; Abun., abundance; Rel. den., relative density; Rel. Freq., relative frequency; Rel. Abun., relative abundance. After [47].
Average and standard errors cannot be determined through the abovementioned indices.

Table 2.
Phytosociological analysis, Shannon index (H), Simson's index (D) of diversity of the weeds in plots irrigated with pond water and arsenic-contaminated STW waters.

and sodium arsenite [48]. It was suggested that because of the so-called soil/plant barrier effect, elevated arsenic in soil may well reduce crop production substantially before enhanced food chain accumulation occurred [49].

Of the 4 million ha irrigated crop fields, 75% of fields use 100% GW [10]. A significant amount of arsenic withdrawn from underground remains as soil arsenic. Monsoon rain and flood waters are washing away As which is carried to the estuaries at the end and is being accumulating there year after year. This would affect the marine flora and fauna in the near future [47]. A significant amount of As (0.86 (SE 0.057; CV 34.66) mg As/kg) was absorbed by the leaves of *Sonneratia apetala*, a mangrove plant in three coastal islands of Bangladesh, indicating that groundwater As is being accumulated in the biotic and abiotic components along the coast as well [49, 50].

In 1997 the presence of arsenic in all coastal districts, in different level of toxicities—highly contaminated (Bagerhat and Noakhali), moderately contaminated (Sundarbans and Lakshmipur), and low contaminated (Pirojpur, Patuakhali, Bhola, and Feni)—was reported [1] (**Figure 1**). Various studies showed increased arsenic in all types of tube wells as they become older (**Table 1**), indicating that the toxicity levels seen in the mid-1990s might have increased from low to moderate, moderate to high, or even absence of arsenic in the rest of the districts to low or moderate presence of arsenic in over the last 20 years. However, status of arsenic throughout Bangladesh including sites mentioned in [1] should be thoroughly checked.

3.5 Arsenic toxicity management

There are two methods to manage arsenic toxicity in arsenic-loaded DW: first producing biogas and second using as animal feed.

3.5.1 Use in biogas production

The arsenic-loaded DW can be predigested for 4–5 days in summer months covering in polythene. The predigested 60–70 kg DW and similar amount of cow dung can be charged into a doom-shaped biogas digester buried into the soil. The retention time can be 50 days. Everyday 25 kg *S. polyrhiza* and 10 kg cow dung can be mixed and then added into the digester. The gas contains 63–65% methane compared to 60% by cow dung only. Three m^3 volume of biogas can be produced daily, sufficient for cooking twice by a family with eight members. The slurry containing concentrated arsenic can also best be disposed by making bricks binding/trapping the arsenic for over 100 years [28]. This approach requires additional huge structural investment.

3.5.2 Use as animal feed

S. polyrhiza could be used to feed fish, poultry, and cattle [29]. The fresh duckweed is used directly as fish feed keeping at corners within floating fences of a pond. The fish production was 20% higher than the normal feed (long-term effect of toxicity was not studied). The duckweed powder at 4% mixed with the normal feed of broilers per day caused accumulation of 1.28 μg/l arsenic in the blood that reduced to 0.912 ± 0.386 μg/l after 3 months, while in the same period, 4.67 μg/kg stool gradually decreased to 0.61 μg/kg. Feeding arsenic-loaded duckweed to goat resulted in increased accumulation of As (0.567–1.060 μg/kg) in the blood causing death of kids [28]. Milk had also high As (0.86 μg/l). Thus the use of arsenic-loaded DW produced in the bio-mitigation process as poultry and cattle feeds was highly hazardous [29].

3.5.3 Status of As toxicity management

Bioremediation process for getting As-free GW for irrigation that was tested needs additional huge investment (two ponds, DW production cost, cost of labor, etc.). Moreover, an estimated 1.539 g As will remain in the bottom of the pond after treatment. Disposal of the arsenic-loaded DW to nontoxic level through various uses was hazardous (Section 3.5.2). STW and DTW waters were found to become arsenic contaminated in 2–5 years. Withdrawal of the GW contaminates biosphere permanently, i.e., circulating the element in the nature in a matter of weeks or months affecting biotic components (**Figure 3a**–**d**). Therefore, alternative arsenic-free freshwater sources (about 1000 l/m^2/year equivalent to 2500 l or 2500 kg water/kg arsenic-free rice cultivation in clayey soil) have to be managed for feeding millions of people of Bangladesh on the one hand and saving our biosphere on the other hand. It is possible only by using surface water (Section 3.6.3).

3.6 Current status of arsenic management in Bangladesh

3.6.1 Occurrence and level of arsenic toxicity in Bangladesh

There are 64 districts, out of which 26 were arsenicosis affected in various degrees surveyed between 1993 and 1997 [1] (**Figure 1**): (a) highly affected (>100 patients identified) in 7 districts, (b) moderately affected (>50 patients identified) in 11 districts, (c) less affected (<50 patients identified) in 8 districts, and (d) arsenic contamination present (no patient was identified) in 18 districts. Out of 64 districts, 42 were distributed in four floodplains: (a) Ganges had 26 districts (7 highly affected), (b) Meghna 10 districts (1 highly affected) and (c) Surma-Kushiara 5 districts with arsenic presence but no patients were found, (d) Jamuna 2 districts without any patient, and (e) 2 districts in Madhupur tract (less affected) all due to drinking and consuming arsenic-contaminated GW and food grains/vegetables. Two-thirds of the districts/country was affected with arsenic by the year 1997 [1]. Highly affected Bagerhat and moderately affected major part of Sundarbans south of the Ganges floodplain along the coast are alarming, indicating coastal water pollution. Data on arsenic in irrigation water and paddy soil profiles in Bangladesh [16] and West Bengal [51] indicated a yearly input of 1.0 and 1.1 mg As/kg soil, respectively, in the topsoil (soil density of 1 kg/l). Therefore, distribution of arsenicosis reported in 1997 [1] would be much higher over the last two decades through arsenic toxicity of rice, wheat grains/vegetable, etc. if not by arsenic-contaminated drinking water [17].

Why the Ganges and Meghna floodplains are so much affected with GW arsenic, when Jamuna floodplain with one of the largest and longest river is not? Is it that the GW of the two highly affected floodplains has some link with arsenic mines/industries or there are anthropogenic reasons (dumping the contaminant, deep into the aquifer) in upstream?

3.6.2 Intensity of irrigation

The total area under irrigation in Bangladesh is 4 million ha, and 75% is covered by GW resources: 2.5 m ha via 924,000 STWs (main source of GW As) and 0.6 m ha via 23,000 DTWs [11]. DTW for irrigation is installed at about 100 m depth, and in Jessore alone 74 among 85 DTW used for irrigation had >50 μg As/l arsenic [51]. The rest 25% land is irrigated using surface water of rivers, "Beels," "Haors," etc. In dry season, 3.5 m ha is used for Boro rice, 0.23 m ha for wheat, and 2.7 m ha for other crops. Rajshahi Division has the highest percentage under irrigation which is 39%, followed by Dhaka 27%, Chittagong 13%, Khulna 12%, Sylhet 7%, and Barisal 2% [11]. We must step up the use of surface water from 25% to 100% (Section 3.6.3).

3.6.3 Methods for arsenic's reduction

It has been clearly indicated that As concentrations in rice are increasing over time because of prolonged input of As-contaminated irrigation water, and three options are proposed to free rice grains from toxicity: reduce As-contaminated irrigation water use in rice cultivation, promote cropping patterns, and select/breed rice cultivars that are tolerant to As and have limited uptake of As [11]. As per the first option of limited As-contaminated irrigation water use, there must be alternative sources of huge surface water, e. g., initially forming reservoirs and constructing rubber dams in rivers, and execution of long-term "Delta Plan 2100". Regarding the second option, cropping pattern throughout the country has been established over the decades of testing, while selection/breeding of rice varieties tolerant to As and limited uptake are questionable. It is known that As and P elements are in the same position in the periodic table (chemically similar), and thus the rice cultivar that will not absorb As will not absorb P as well. In the present study, arsenic bio-mitigation of irrigation water tested was not effective, and disposal of wastes was hazardous. As arsenic-contaminated GW produces toxic rice grains and accumulates arsenic in the soil year after year, avoiding the use of GW is the only solution for protecting rice grains from arsenic toxicity, including other organisms. Man might alter the quantities of arsenic in any component of an ecosystem in a localized area but cannot change or stop the natural biological processes that occur [52]. Therefore, an alternative immediate attention is needed to provide enormous volume of As-free irrigation water, and that is through the use of surface waters using river network of Bangladesh (**Figure 10**). Bangladesh is a country of rivers having almost one river in each village. The rivers have to be dredged to get continuous flow of waters from the upstreams, converting the rivers as reservoirs simultaneous with the construction of rubber dams. Several rubber dams have so far been installed in Bangladesh, one of which is at Sonargaon (**Figure 11**). Bangladesh government has the plan to establish **"Ganges Barrage"** to supply freshwater to Ganges floodplain and surroundings including Sundarbans [53]. Huge deposit of sediments in the Ganges River bed has been identified as a major problem (what to do with the sediments) for using the Ganges as a reservoir [personal communication, Rawshan Ali Khan, Project Director of Ganges Barrage Project, Dhaka, Bangladesh].

The National Economic Council (NEC) of Bangladesh has recently approved **"Delta Plan 2100"** the key objective of which is to provide food and water security and fight natural disasters [54]. The theme is "let the rivers flow, let the rivers live." In the first phase, the government will be implementing about 80 projects at an estimated cost of US $ 37 billion by 2030. Out of six goals, Delta goal 3 is "Ensuring sustainable and integrated river systems and estuaries." In a seminar, it has been mentioned that "rivers would be channelized and sediments would be removed." Details are not available regarding what is meant by the "removal." It immediately indicates dumping sediments on to the river banks!

The landmass of Bangladesh has been formed throughout the Pleistocene and up to the present by sediments washed down from the Himalaya Mountains through the Ganges, Jamuna (Brahmaputra), and Meghna Rivers and their numerous tributaries and distributaries [55]. In terms of relative age of the landmass, the region may be divided into four parts: hilly lands of the Tertiary (and older) in the southeast Chittagong and CHT districts, terrace lands of

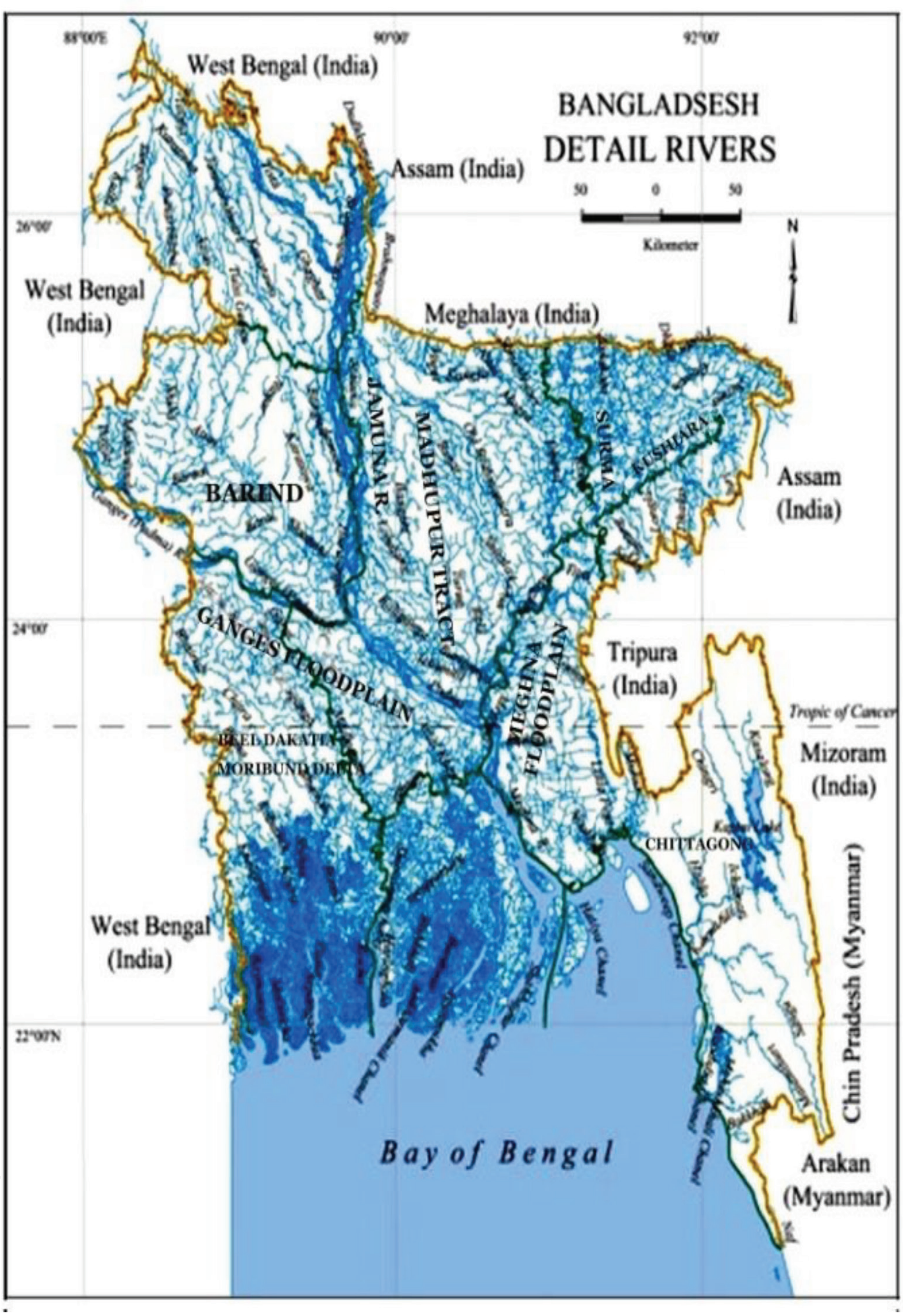

Figure 10.
River network of Bangladesh, where three mighty rivers Ganges, Jamuna (Brahmaputra), and Meghna altogether ended into the bay of Bengal.

Pleistocene in the Barind and Madhupur Jungle, tipper surface of the early Recent in the median eastern part, and the extensive floodplains of the Recent in the rest of the country (Ganges floodplain and southern part of Meghna floodplain) (**Figures 1** and **10**). Geologists believe that in the same way, the present Sundarbans has been established 7000 years ago [56]. From geophysical

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Figure 11.
Rubber dam installed in the old Brahmaputra River at Sonargaon, Bangladesh, in 2003. (a) Showing low water volume in the river bed at noon time, on the north of bridge, and(b) rubber dam inflated (on the left of the bridge) to hold water in the river during afternoon.

changes on the formation of Bangladesh, it is obvious that sediment-loaded river water flow to the Bay of Bengal resulted from extensive floodplains including Sundarbans [56], and any disruption would cause land degradation, which is already done by Farakka Barrage since 1975 [53]. To reclaim environment of all the floodplains, dredging of Ganges, Jamuna, and Meghna River beds along with tributaries and distributaries making them flow round the year is primarily needed and letting the dredged sediments flow along with floodwater during June to October, up to the Bay of Bengal", the way Bengal Delta was formed [53, 56]. The surface water is ideal in the sense that it contains all the nutrient elements in relatively the same proportion (Redfield ratio) for irrigating rice and other crops and protecting crops and biota from arsenic toxicity. Increased surface water would reduce GW salinity in the southwestern Bangladesh and increase productivity in the hinterlands [53]. To get rid of arsenics, protecting surface water is the only environmentally benign option saying "no to groundwater for irrigation, let the arsenic stay in the underground." The water reservoirs may integrate aquaculture of DW and *A. pinnata* var. pinnata for fish and poultry feeds [57].

4. Summary

The arsenics causing arsenicosis in Bangladesh water were first detected in 1993. Presently, many districts of Bangladesh use As-contaminated GW for rice irrigation and an integrated approach within the framework of land degradation has been suggested [11]. Considering the necessity of huge volume of arsenic-free irrigation water, physiography of Bangladesh and three mighty rivers flowing through the Bay of Bengal forming extensive network of rivers within the country, immediate attention must be given to construct rubber dams, convert rivers into freshwater reservoirs to overcome the arsenic toxicity, and protect rice and other grains. The integrated approach described in this manuscript would be environment friendly increasing total crop productivity including aquaculture of duckweeds and A. *pinnata* var. *pinnata* for producing fish and poultry feeds.

Permanent solution could be achieved executing "Delta Plan 2100" saying "No to groundwater use for irrigation, let the Arsenic stay in the underground".

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