App. Envi. Res. 41(1) (2019): 8-21

Applied Environmental Research

Journal homepage : http://www.tci-thaijo.org/index.php/aer

Role of Natural Wetlands in Arsenic Removal from Arsenic-Contaminated Runoff

Vanlop Thathong[1,2], Netnapid Tantamsapya[3,5,*], Chatpet Yossapol[3], Chih-Hsiang Liao[4], Wanpen Wirojanagud[5]

[1] Department of Environmental Science, Faculty of Science and Technology, Loei Rajbhat University, Loei, Thailand
[2] Department of Environmental Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen, Thailand
[3] School of Environmental Engineering, Institutes of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand
[4] Department of Environmental Resources Management, Chia Nan University of Pharmacy and Science, Tainan, Taiwan
[5] Research Center for Environmental and Hazardous Substance Management, Khon Kaen University, Khon Kaen, Thailand
[*] Corresponding author: Email: netnapid@sut.ac.th

Article History
Submitted: 2 September 2018/ Revision received: 23 September 2018/ Accepted: 24 September 2018/ Published online: 20 February 2019

Abstract

This research aims to identify the role of natural wetlands in arsenic (As) removal. Phu Lek wetland in Loei Province, Thailand, was selected as the study area. Monthly samples of water (144), plant (360), and sediment (144) were collected from the wetland for 24 months. As concentration in the surface water at the wetland inlet was 0.85±0.26 mg L^{-1}, and 0.02±0.01 mg L^{-1} at the wetland outlet. It was observed that the As level in water decreased significantly along its flow path, with an As removal efficiency of 98 %. As concentration in the sediment was 89.53-356.22 mg kg^{-1} at the inlet of wetland, but decreased gradually downstream of the water flow. Three dominant emergent plant species were observed in this wetland. As accumulation (0.02-2.37 mg kg^{-1}) was noted in all the parts of the three plant species. As content was the highest in the rootlet (0.00-1.27 mg kg^{-1}) compared to that in foliage (0.00-0.84 mg kg^{-1}), leaf stalk (0.00-1.86 mg kg^{-1}), and rhizome (0.00-2.64 mg kg^{-1}). The level of As in the different vegetation species was in the order *Diplazium esculentum* > *Colocasia esculenta* > *Lasia spinose*. Further, As entrapment in the different plant plants followed the order rootlet > rhizome > foliage > leaf stalk. All the three plant species showed high bioconcentration factors, with values of 0.03-1.28, 0.02-0.93, 0.00-0.84, and 0.00-0.38 at the rootlet, rhizome, foliage, and leaf stalk, respectively, but had low translocation factors (foliage/rootlet: 0.02-0.90 and leaf stalk/rootlet: 0.00-0.44). In summary, As present in the surface water could be effectively removed by the wetland system.

Keywords: Arsenic; Plants; Wetland; Runoff; Gold mine; Loei

Introduction

Arsenic (As) is a naturally occurring element in mineral vein formations and coexists with other elements such as copper, manganese, lead, tin, silver, and gold. Mining of these minerals may cause As contamination in the surrounding areas. Owing to inappropriate mining management, As contamination has been frequently reported in many areas worldwide, including in the Grasberg gold mine (Indonesian Papua), Muruntau gold mine (Uzbekistan), Carlin-Nevada complex (USA), Yanacocha gold mine (northern Peru), Lagunas Norte gold mine (north-central Peru), Lihir gold mine (Papua), Goldstrike (Betze Post) and Cortez gold mines (northwestern Elko), Veladero gold mine (Argentina), and super pit (Kalgoorlie, Western Australia) [1-3].

As contamination caused by gold mining can significantly impact the ecological environment of surrounding regions. The mining of gold-bearing sulfide minerals such as arsenopyrite (FeAsS), which is an As sulfide mineral releases considerable amounts of As into surface waters and even into underground aquifers. This poses a great threat to drinking water sources. Further, water bodies near the mines may be contaminated with cyanide and/or other liquid wastes generated by mining site facilities [4]. In addition, mining wastes such as tailings and waste rock may contain sulfides like pyrite (FeS_2) and FeAsS. Oxidation of these compounds generates acidity leading to the release of As [5-7].

In Thailand, the gold mine located at Wang Saphung District of Loei Province has been identified as a potential source of As contamination in the surrounding areas [8]. Since mining activities in this region started in 2006, the Pollution Control Department of Thailand has been conducting monitoring programs around the mining site. According to reports, As concentrations were 0.003-0.107 mg L^{-1} in surface waters, 0.001-0.130 mg L^{-1} in groundwater, and 28.32-429 mg kg^{-1} in sediment and soil [8-9]. As shown in Figure 1, As monitoring was also carried out along the Phu Lek Creek, a small creek with a natural wetland. This monitoring program reported that the As concentration in the water entering the wetland exceeded the regulatory standard; however, As concentration reduced dramatically downstream, and As level in the outlet of the creek was below the regulatory value. Thus, it is highly likely that the purification mechanism of natural wetlands is capable of As removal. Further, similar findings have been reported by several other researchers [10-11].

In wetland environments, As is primarily retained in sediments or media, rather than being accumulated in plants [12]. As present in wetlands can precipitate and form insoluble sulfide compounds or FeAsS, depending on the redox condition [4, 13-16]. High As removal efficiencies can be achieved through co-precipitation in the presence of sulfate, ferric chloride [16-1], and iron oxide [18]. It should be noted that the bed soil in Phu Lek wetland is characterized as laterite, which is primarily composed of iron oxides. This type of soil can be used to remove As from water with an efficiency of 50-93 % [19-21].

The above-mentioned background information indicates that the wetland of Phu Lek Creek may be capable of retaining As present in the water stream and this As-retaining mechanism needs to be explored. Therefore, the objective of this research is to investigate the role of plants in As removal in a natural wetland located at Phu Lek Creek in Loei Province, Thailand. The results of this study can guide the use of natural wetlands in the study area for As removal. This remediation technique will help reduce cost and solve the problem of As contamination.

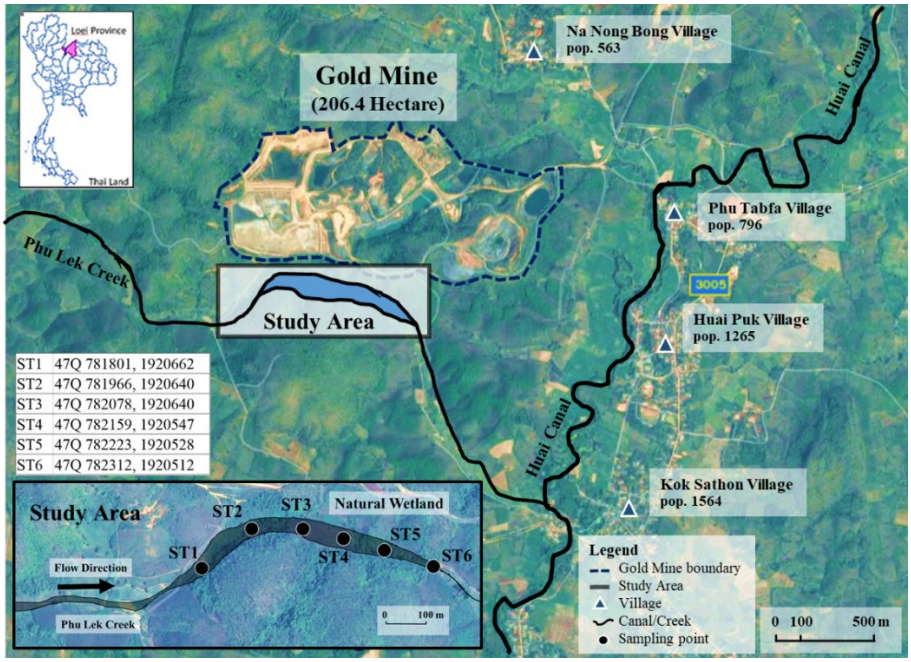

Figure 1 Geographical map of the gold mine and Phu Lek Creek. Population of the nearby villages (2018) and sampling points (ST1-ST6) are indicated.

Materials and methods

1) Site survey

As shown in Figure 1, the studied site, Phu Lek wetland, is located near an inactive old gold mine in Loei Province, Thailand. This mine was operated from 2006 to 2013 as an open-pit mine and for ore dressing. Phu Lek creek runs south to the mining area and occasionally receives As-contaminated runoff [9]. The nearby wetland receives water from two principal streams, a small creek in the northwest and a groundwater spring in the northeast. The wetland is about 640 m long and 10-50 m wide, with a water depth of 0.20-1 m and a total area of approximately 10,000 m^2. During the study period (November 2012 to October 2014), surface water flowed into the wetland throughout the year. Figures 2 and 3 shows vegetation growth and the dominant plant species, respectively, in the wetland. With regards to geological characteristics, the study area is underlain by a sedimentary formation consisting of crystalline limestone, muddy sandstone, carbonaceous siltstone, and shale. This formation is intruded by Early Triassic granodiorite and Late Triassic andesitic dikes. Gold occurs with pyrrhotite ($Fe_{(1-x)}S$), pyrite (FeS_2), and FeAsS, with chalcopyrite ($CuFeS_2$) in the retrograde zone [2, 22].

2) Sampling preparation and analysis

In this study, monthly surface water and plant samples were collected at the sampling points (ST1-ST6) along the creek, as illustrated in Figure 1. The monitoring period was 24 months from November 2012 to October 2014. The parameters analyzed, sample preservation and preparation process, and the analytical methods used in this study are described in the subsequent paragraphs.

- Water samples (1,000 mL) were collected using the grab sampling method from the sampling sites indicated in Figure 1. These samples were acidified with HNO_3 to pH < 2 and stored at 4±0.5 °C prior to analysis for metal concentrations using an inductively coupled plasma optical emission spectrometer (ICP-OES; Optima 2100 DV, Perkin Elmer; USA, APHA, 1998).

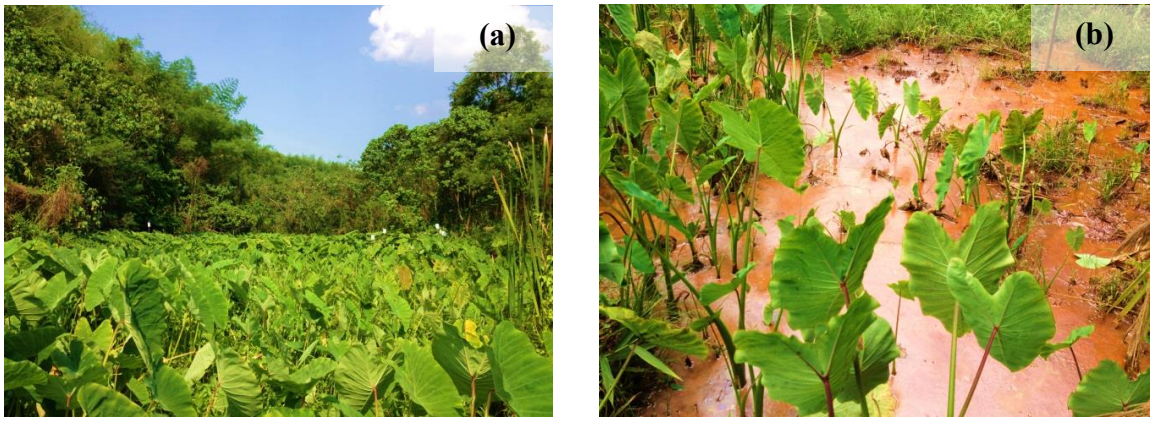

Figure 2 Vegetation at the sampling points: (a) ST1 and (b) ST3 along Phu Lek wetland.

Colocasia esculenta L. Schott
Local name: TARO/BON

Diplazium esculentum R. Swartz
Local name: PHUK KOOD

Lasia spinosa L. Thwaites
Local name: PHUK NHAM

Figure 3 The dominant plant species of Phu Lek wetland.

- Soil samples were collected through core sampling from the soil surface (0-20 cm). The samples were first air-dried and sieved, and then dried in an oven at 105 °C for 24 h. The dried samples were weighed and digested to form a solution with HNO_3 and $HClO_4$ (Italmar OPR) at a ratio of 1:3 (v/v).

- Plant samples were washed to remove clay and sand particles, and subsequently dried in an oven at 105 °C for 24 h to achieve a constant weight. The dry weight of the samples was measured. Dried samples were then ground to a fine powder using a ceramic mortar. The digestion method and chemicals used for plant samples are the same as those used for soil sample digestion.

All the samples were prepared and analyzed in the Science Center Laboratory of Loei Rajabhat University. After digestion of the samples, As and iron (Fe) levels in the solution were analyzed using an ICP-OES (Perkin Elmer, Optima 8000) of the Center for Scientific and Technological Equipment, Suranaree University of Technology. The details of the sampling and analysis methods are listed in Table 1.

As removal efficiency (% RE) from aqueous media was determined using Eq. 1 [16, 23].

$$\% RE = (As_{(inflow)}-As_{(outflow)}/As_{(inflow)})x100 \quad \text{(Eq. 1)}$$

where $As_{(inflow)}$ is inflow As concentration (mg L^{-1}) and $As_{(outflow)}$ is outflow As concentration (mg L^{-1}).

The translocation factor (TF) reflects the ability of plants to translocate As to their aerial parts, such as stems and leaves [24-25]. TF is the ratio of As concentration in above-ground plant tissues (foliage and leaf stalk) to that in plant rootlets and was calculated using Eq. 2 [23].

$$TE = As_{above}/As_{rootlets} \quad \text{(Eq. 2)}$$

where As_{above} is the concentration of As in above-ground plant tissues (total concentration in foliage and leaf stalk; mg kg^{-1} plant dry weight) and $As_{rootlets}$ is the As concentration in the plant rootlets (mg kg^{-1} plant dry weight).

Bioconcentration factor (BCF) reflects the ability of plants to accumulate As. In this study, it was calculated as the ratio of As concentration in the different plant parts (foliage, leaf stalk, rootlets, and rhizome) to As concentration in soil using Eq. 3 [23, 26-28].

$$BCF = (As_{plant}/As_{soil})x100 \quad \text{(Eq. 3)}$$

where As_{plant} represents the total concentration of As in different plant tissues (foliage, leaf stalk, rootlets, and rhizome; mg kg^{-1} plant dry weight) and As_{soil} is the As concentration in soil (mg kg^{-1}).

3) Statistical analysis

All statistical analyses were performed using SPSS v.17.0 (IBM Corp., Armonk, NY, USA). The measured data were expressed as means±standard deviation (SD). Comparisons between groups were performed using t-test and analysis of variance (One way-ANOVA), where $p < 0.05$ is considered statistically significant. Both quality assurance (QA) and quality control (QC) were used in planning, sampling, analysis, and data reporting throughout this study.

Results and discussion

1) As content in water

The creek was found to be contaminated with As and As concentration at its inlet (ST1) was as high as 0.85±0.26 mg L^{-1}. The As-retaining capacity of the wetland was observed to be distance-dependent, as shown in Table 2. As levels in water decreased significantly ($p < 0.05$) downstream of the wetland. Most of the As was removed (84 %) at a distance of 180 m downstream of the water flow path. At the creek outlet (640 m downstream) 98 % of the As had been removed. During the study period of 24 months, the seasonal (dry, rainy, and winter seasons) correlation of As removal was insignificant ($p < 0.05$). Figure 4 shows the As removal efficiencies and concentrations at the inlet and outlet points over the study period. Our findings are similar to those of Schwindaman et al. [29] and Mays and Edwards [30], who reported 40-95 % As removal in wetlands/creeks. Further, the flow of water through the wetland resulted in the removal of 40 %, 53 %, 71 %, and 84 % of TDS, TSS, sulfate, and iron, respectively (Table 2).

Table 1 Methods for sampling and analysis

Monthly samples	Sampling method	Analytical method	
		Parameters	Methods/references
Surface water (n=144)	Grab sampling	Flow rate	Flowmeter, APHA(2012)
		Temperature	Onsite, Thermometer
		pH	Onsite, pH meter, APHA (2012)
		Eh	Onsite, ORP meter, APHA (2012)
		Dissolved Oxygen (DO)	Onsite, DO meter, APHA (2012)
		Electrical Conductivity (EC)	Onsite, EC meter, APHA (2012)
		Total Dissolved Solids (TDS)	Onsite, TDS meter, APHA (2012)
		Total Suspended Solids	Onsite, TSS meter, APHA (2012)
		Dissolved Organic Carbon	UV254, APHA (2012)

Table 1 Methods for sampling and analysis (*continued*)

Monthly samples	Sampling method	Analytical method	
		Parameters	**Methods/references**
	Sampling with quadrats (plots of 10×10 m) four parts: foliage, leaf stalk, rootlet, and rhizome	Sulfates	Turbid metric method APHA (2012)
		Total Fe	ICP-OES, APHA (2012)
		Total As	ICP-OES, APHA (2012)
Plants (n=360)		Total As	Digestion of 1000 mg dry weight of plant sample with 1:3 (v/v) HNO_3:$HClO_4$ (Italmas OPR) ICP-OES, APHA (2012)
Soil (n=144)	Core sampling (0-20 cm)	Total As	Digestion of 1000 mg dry weight of soil with 1:3 (v/v) of HNO_3:$HClO_4$ (Italmas OPR) ICP-OES, APHA (2012)

Table 2 Monthly water characteristics at different sampling points (n=144) within the natural wetland

Parameters	Sampling points (Distance downstream)						
	ST1 (0 m)	**ST2 (180 m)**	**ST3 (290 m)**	**ST4 (400 m)**	**ST5 (490 m)**	**ST6 (640 m)**	**Removal (%)**
Flow rate (m^3 d^{-1})	389.06 ±93.03	-	379.99 ±95.59	-	-	365.44 ±98.16	
Depth of sediment (cm)	81.33 ±11.01	91.95 ±12.90	101.35 ±17.79	90.21 ±17.25	81.78 ±14.78	71.71 ±11.19	-
Temperature (°C)	27.58 ±0.55	27.72 ±0.58	27.65 ±0.41	27.57 ±0.44	27.49 ±0.62	27.44 ±0.52	-
pH	6.29 ±0.64	6.44 ±0.78	6.74 ±0.43	7.30 ±0.50	7.04 ±0.57	7.40 ±0.26	-
Eh (mV)	442.12 ±70.36	491.13 ±53.64	412.29 ±58.78	451.27 ±79.85	293.00 ±6 1.70	364.75 ±73.13	-
DO (mg L^{-1})	3.36 ±0.49	3.64 ±0.60	4.34 ±0.52	4.92 ±0.26	5.04 ±0.61	5.13 ±0.54	-
EC (µmhos cm^{-1})	533.17 ±109.28	451.32 ±85.92	566.74 ±73.83	656.49 ±106.11	378.74 ±53.63	351.11 ±98.22	-
TDS (mg L^{-1})	475.89 ±136.22	273.90 ±43.77	421.17 ±63.99	593.11 ±124.88	313.04 ±72.88	287.26 ±73.80	39.64 ±13.12
TSS (mg L^{-1})	37.97 ±8.43	48.40 ±11.31	51.23 ±10.55	31.51 ±8.20	24.38 ±6.91	17.81 ±7.25	53.09 ±3.11
DOC (mg L^{-1})	3.43 ±1.43	5.50 ±2.43	11.09 ±5.06	8.81 ±3.66	5.07 ±1.29	2.72 ±1.20	-
Sulfates (mg L^{-1})	0.10 ±0.06	0.20 ±0.13	0.24 ±0.14	0.08 ±0.03	0.04 ±0.02	0.02 ±0.01	-
Fe (mg L^{-1})	4.50 ±1.73	3.96 ±2.20	3.75 ±0.77	3.05 ±1.79	1.63 ±0.95	0.73 ±0.66	70.72 ±17.73
As (mg L^{-1})	0.85 ±0.26	0.144 ±0.09	0.100 ±0.07	0.080 ±0.06	0.046 ±0.03	0.017 ±0.01	83.85 ±14.65
As removal efficiency (%)	-	83.85 ±8.36	88.27 ±7.54	90.10 ±8.72	94.45 ±3.70	97.91 ±1.57	98.33 ±1.50

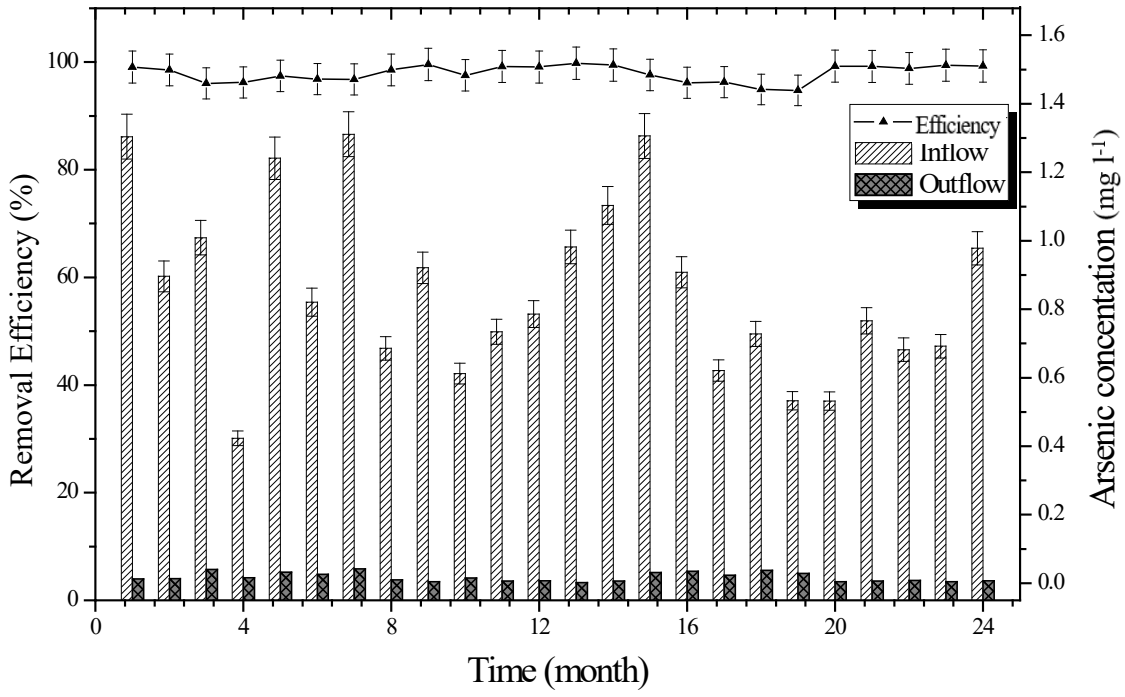

Figure 4 Monitored As concentrations at the inlet and outlet of Phu Lek wetland.

2) Arsenic content in plants

A field survey revealed that the three dominant emergent plant species in Phu Lek wetland are *Diplazium esculentum* R. Swartz, *Colocasia esculenta* L. Schott, and *Lasia spinosa* L. Thwaites (Figure 3). As shown in Table 3, As accumulated in all parts of these three plant species with concentration ranging from 0.04 to 3.23 mg kg^{-1}. This As accumulation level is relatively lower than that of other wetland emergent plants such as species of genus *Pteris, P. longifolia, P. Cretica, P. Umbrosa*, and hyper-accumulator *Pteris,* which has been reported to have an accumulation capacity of 140-190 mg kg^{-1} in some studies [31-33] while Zhao et al. [12] reported a value of 6,200-7,600 mg kg^{-1}. This indicates that the emergent plants found in Phu Lek Creek are not hyper-accumulators. Interestingly, both water flow distance and seasonal changes were not significantly correlated with As content in plants ($p < 0.05$). The mean As accumulation capacity of the three dominant plant species follows the order *Diplazium esculentum* > *Colocasia esculenta* > *Lasia spinose*.

Table 3 shows the As distribution in various parts of the different plant species. As content was the highest in the rootlet (0.25-3.23 mg kg^{-1}) compared to that in foliage (0.17-0.85 mg kg^{-1}), leaf stalk (0.03-1.21 mg kg^{-1}), and rhizome (0.50-2.78 mg kg^{-1}) as shown in Figure 5. The general trend of As content in plants is reported to be rootlet > rhizome > leaf tissue for wetland plants such as *Canna glauca* L., *Colocasia esculenta* L., *Cyperus papyrus* L., *Monochoria vaginalis* (Burm.f.), *Salvinia molesta* D., *Typha angustifolia* L., and *Polypogon monspeliensis* L. [10, 34]; vetiver grasses [14]; Indian rice (*Oryza sativa* L.) [35]; and *Pteris vittata* L. [32]. Table 4 shows the calculated values of BCF and TF. For the three dominant plant species, the BCF values are 0.00-1.28 (rootlet), 0.00-0.93 (rhizome), 0.00-0.84 (foliage), and 0.00-0.38 (leaf stalk); BCF values for rootlet and rhizome are higher than those of foliage and leaf stalk.

Further, the order of mobility as expressed by $BCF_{rootlet}$ was lower than that by $BCF_{rhizome}$, indicating the accumulation of the metal in the plant roots. Plant roots and sludge sediments are the primary sinks for As retention in the rhizosphere [36]. Plants retain heavy metals taken up from soils in their root cells, detoxifying the heavy metals through chelation in the cytoplasm or storing them inside vacuoles [37]. On the other hand, the TF values are relatively low at 0.02-0.90 for rootlet/foliage and 0.00-0.44 for rootlet/leaf stalk. This demonstrates that the three dominant emergent plants in Phu Lek wetland tend to bind As through rhizostabilization and phyto-accumulation. In other words, As translocation from the underground to the aboveground plant parts is higher for foliage than for leaf stalk.

Table 3 Arsenic contents (mg kg^{-1}) in different plant species and in soil

Plant species/ soil sample	Plant part	Sampling points (distance downstream)							BCF	TF
		ST1 (0 m)	ST2 (180 m)	ST3 (290 m)	ST4 (400 m)	ST5 (490 m)	ST6 (640 m)	Mean		
Colocasia esculenta L. Schott	foliage	0.84 ±0.31	0.85 ±0.73	0.84 ±0.71	0.78 ±0.80	0.29 ±0.24	0.21 ±0.22	0.64 ±0.50	0.26	0.34
	leaf stalk	0.05 ±0.03	0.16 ±0.31	0.24 ±0.49	0.37 ±0.82	0.06 ±0.07	0.03 ±0.06	0.15 ±0.30	0.06	0.08
	rootlet	1.43 ±0.62	2.13 ±1.17	2.46 ±1.45	2.84 ±2.39	1.40 ±1.16	1.10 ±0.90	1.89 ±1.28	0.78	-
	rhizome	0.84 ±0.35	0.86 ±0.37	1.01 ±0.76	0.98 ±0.82	0.52 ±0.27	0.50 ±0.56	0.79 ±0.52	0.32	0.42
	average	0.79 ±0.33	1.00 ±0.65	1.14 ±0.85	1.24 ±1.21	0.57 ±0.44	0.46 ±0.44	0.87 ±065.	-	-
Diplazium esculentum R. Swartz	foliage	0.46 ±0.26	0.51 ±0.27	0.74 ±0.49	0.67 ±0.43	0.50 ±0.61	0.32 ±0.31	0.53 ±0.40	0.21	0.22
	leaf stalk	0.59 ±0.46	1.10 ±1.23	1.21 ±1.03	0.96 ±0.86	0.76 ±1.07	0.47 ±0.71	0.85 ±0.89	0.35	0.36
	rootlet	2.55 ±1.59	2.94 ±1.86	3.23 ±2.43	2.78 ±2.60	1.60 ±1.24	1.12 ±1.20	2.37 ±1.82	0.97	-
	rhizome	2.77 ±2.59	2.78 ±3.43	2.72 ±2.96	2.14 ±2.57	1.57 ±2.26	0.95 ±1.56	2.16 ±2.56	0.89	0.91
	average	1.59 ±1.23	1.83 ±1.70	2.00 ±1.70	1.63 ±1.62	1.11 ±1.30	0.72 ±0.95	1.48 ±1.42	-	-
Lasia spinosa L. Thwaites	foliage	*	0.17 ±0.07	0.21 ±0.10	0.18 ±0.10	*	*	0.18 ±003.	0.07	0.64
	leaf stalk	*	0.04 ±0.03	0.06 ±0.04	0.04 ±0.04	*	*	0.04 ±0.02	0.02	0.14
	rootlet	*	0.30 ±0.11	0.25 ±0.15	0.30 ±0.13	*	*	0.28 ±0.07	0.11	-
	rhizome	*	0.21 ±0.06	0.24 ±0.11	0.23 ±0.12	*	*	0.23 ±0.05	0.09	0.82
	average	*	0.18 ±0.13	0.19 ±0.16	0.19 ±0.08	*	*	0.18 ±0.06	-	-
As in soil		356.22 ±82.16	353.20 ±81.33	327.23 ±78.13	200.56 ±45.14	136.04 ±29.24	89.53 ±17.24	243.80 ±41.33	-	-

Note: * means that *Lasia spinosa* L .Thwaites was not present at ST1, ST5, and ST6

Table 4 Bioconcentration factor and translocation factor of arsenic in different plant species (n=144)

Plants Species	Bioconcentration factor (BCF)				Translocation factor (TF)	
	Rootlet	Rhizome	Foliage	Leaf stalk	Foliage/rootlet	Leaf stalk/rootlet
Colocasia esculenta L .Schott	0.04-1.28	0.02-0.34	0.01-0.32	0.00-0.08	0.02-0.90	0.00-0.44
Diplazium esculentum R.Swartz	0.00-1.08	0.00-0.93	0.00-0.34	0.00-0.38	0.03-0.22	0.04-0.36
Lasia spinosa L .Thwaites	0.03-0.21	0.03-0.16	0.02-0.09	0.00-0.02	0.22-0.64	0.02-0.14

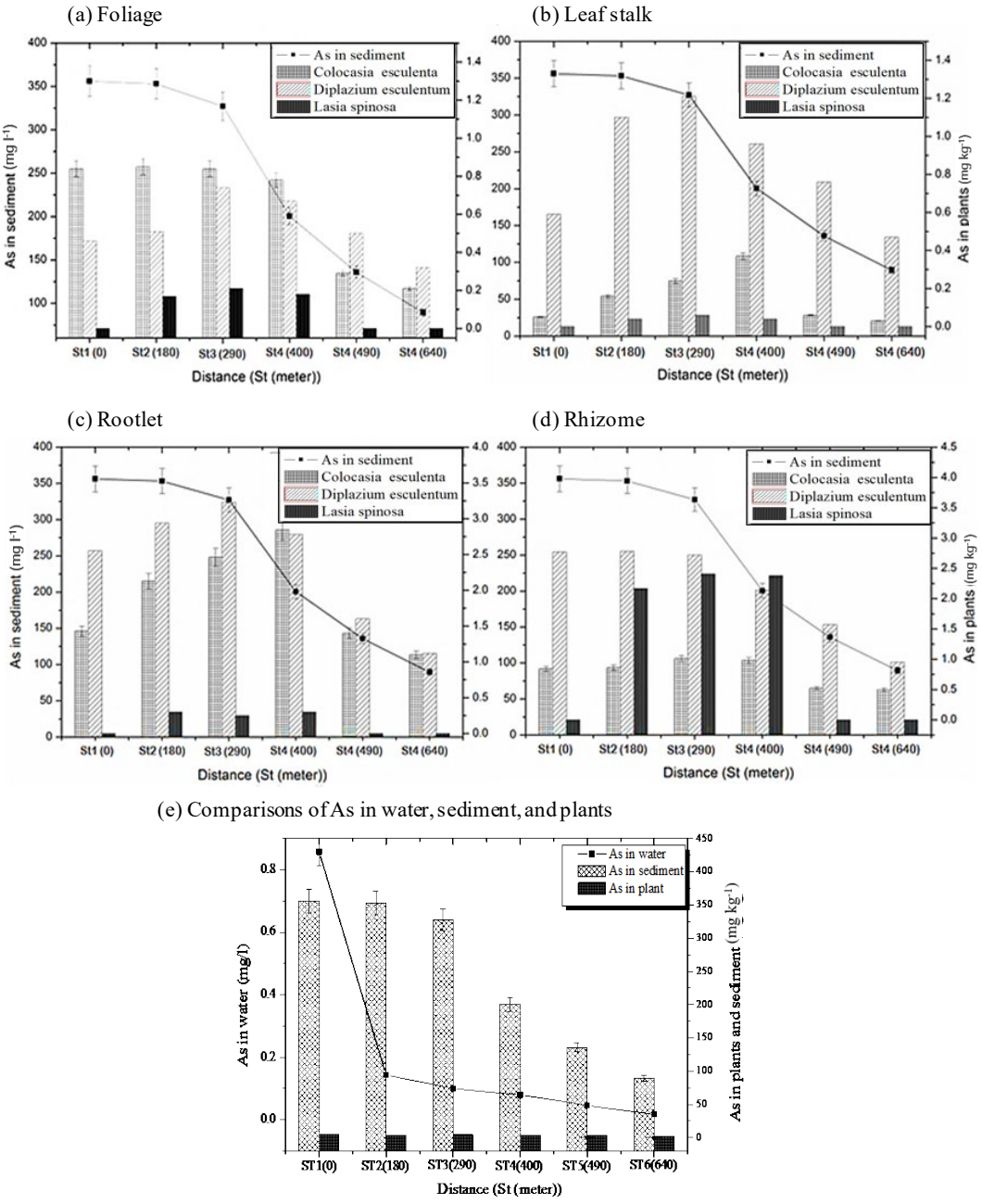

Figure 5 As concentration profiles in water, plants, and sediments along the flow path in the wetland area.

The statistical analyses conducted in this study revealed that As content in soil or in soil/water was not correlated to As content in plants ($p < 0.05$). This is because As accumulation in plants is complex and depends considerably on specific chemical factors and substrates onsite as well as plant physiology besides As concentration in soil [38-39]. The findings of this study indicate that uptake of As by plants is restricted by the precipitation and co-precipitation of arsenic onto laterite soil. Lin et al. [40] reported a similar phenomenon, wherein Fe oxides (iron plaques) formed around the roots of rice plants bound As and reduced its translocation to the aboveground tissues of the plant.

3) Role of natural wetlands in arsenic removal

Figure 6 shows a proposed model of As removal in Phu Lek wetland. When the surface runoff contaminated with As flows into the wetland, the hydrological condition changes. For example, the runoff width may increase from ~10 m to ~50 m while the water depth may decrease from ~1.0 m to ~0.2 m resulting in slower water velocity. As content was the highest at the inlet of the wetland in both water and sediment. Subsequently, it decreased downstream of the water flow. As shown in Figures 2 and 3, the sediment appears to have a rusty color. Laterite soil is known to originate from hematite (Fe_2O_3) and goethite (FeO(OH)) weathering. Previous studies have reported that As can be removed from water via chemical precipitation in the presence of laterite soil [20, 41-43]. Under aerobic conditions, As in water can easily bind with Fe oxide to form a precipitate/co-precipitate, according to the reaction shown in Eqs. 4 and 5 [18, 20].

$$HAsO_2 + O_2 \leftrightarrow HAsO_4 \quad \text{(Eq. 4)}$$

$$H_2AsO_4 + Fe(OH)_3 \leftrightarrow FeAsO_4 + 3H_2O \quad \text{(Eq. 5)}$$

Generally, As can also react to form a precipitate in the presence of sulfate and ferric chloride. However, in the case of Phu Lek wetland, the sediment contains only a low amount of sulfur. Thus, as the sediment of Phu Lek wetland contains a considerable amount of iron, As co-precipitation occurred primarily in the form of $FeAsO_4$.

After the removal of As from water through Fe-bound precipitation (Figure 6A), it was transported from the upper horizon into the lower argillic horizon (Figure 6B). The vertical distribution of As concentration in wetlands is controlled by adsorbent distribution, As deposition, and biogeochemical processes in the wetland soils [44]. Both emergent plant rootlets and rhizomes can stabilize heavy metals around its tissue via rhizostabilization in the presence of rhizospheric microbes [45-46]. In this study, As concentration was found to be the highest at soil bed depths of 0-20 cm. Survey of the wetland field revealed that such a depth falls within the root zone of the dominant emergent plants. Thus, in our study area, rhizostabilization is expected to be the major mechanism. As concentration in sediment around the root zone was in the range of 89.53-356.22 mg kg^{-1} from precipitation/co-precipitation and As adsorption with iron in the sediment (laterite soil). The As precipitate was taken up by the plants and further translocated and accumulated in the rootlet (0.14-2.37 mg kg^{-1}), rhizome (0.79-2.16 mg kg^{-1}), leaf stalk (0.02-0.53 mg kg^{-1}), and foliage (0.09-0.64 mg kg^{-1}) with a lower TF.

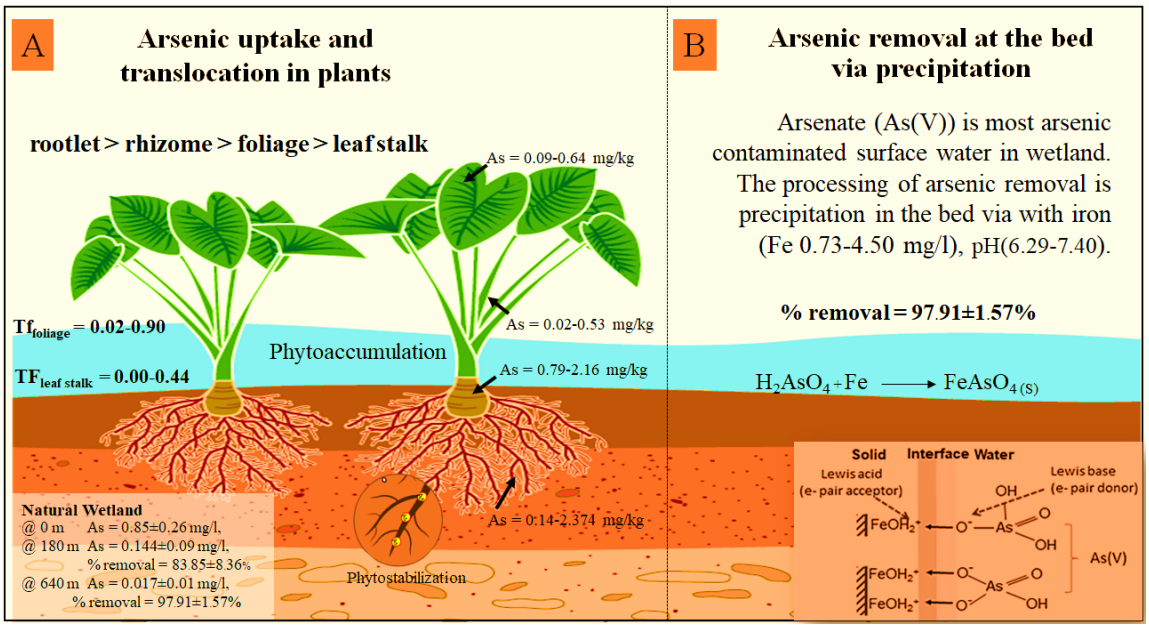

Figure 6 The proposed model for As removal in natural wetlands through a) As uptake and translocation in plants and b) As removal at the bed via precipitation.

Conclusion

In this study, three major mechanisms of As removal from aqueous media in natural wetlands were noted. First, As in surface water was removed primarily at the inlet of the wetland, with an overall removal efficiency of 98 %. Second, As was entrapped at the root zone. Third, As uptake by plants occurred at the rootlet through rhizostabilization. At the inlet of the wetland, As content in surface sediment (0-20 cm) was 89.53-356.22 mg kg^{-1}; this value gradually decreased downstream of the water flow. Three dominant emergent plant species, *Colocasia esculenta* L. Schott, *Diplazium esculentum* R. Swartz, and *Lasia spinosa* L. Thwaites, were noted in the study area. As was present in all parts of these plant species, with mean concentrations in the range of 0.02-2.37 mg kg^{-1}. As levels were higher in the underground parts, with BF values of 0.00-1.28, 0.00-0.93, 0.00-0.84, and 0.00-0.38 in the rootlet, rhizome, foliage, and leaf stalk, respectively. Further, As translocation from the underground to aboveground plant parts is higher for foliage than for leaf stalk.

Acknowledgment

The authors thank the Ministry of Science & Technology, Office of Higher Education Commission (OHEC), and S&T Postgraduate Education and Research Development Office (PERDO) for their financial support towards this research. We would also like to express our sincere gratitude to Loei Rajabhat University, the Environmental Research Institute (ERIC), and the Center of Excellence on Hazardous Substance Management (HSM) at Chulalongkorn University for their invaluable support in terms of facilities and scientific equipment.

References

[1] Nakwanit, S., Visoottiviseth, P., Khokiattiwong, S., Sangchoom, W. Management of arsenic-accumulated waste from constructed wetland treatment of mountain tap-water. Journal of Hazardous Materials, 2011, 185(2-3), 1081-1085.

[2] Yotsawate, S., Phuekvilai, P., Yookongkaew, N. Potential of heavy metal uptake and accumulation in

dominant herbaceous plants around gold mine areas in Pichit Province. Science and Technology, 2017, 25(1) , 110-123.

[3] De Sisto, S.L. Jamieson, H.E., Parsons, M.B. Subsurface variations in arsenic mineralogy and geochemistry following long-term weathering of gold mine tailings. Applied Geochemistry, 2016, 73, 81-97.

[4] Henke, K. Arsenic: Environmental chemistry, health threats and waste treatment. John Wiley & Sons. 2009.

[5] Savage, K.S., Tingle, T.N., O' Day, P.A., Waychunas, G.A., Bird, D.K. Arsenic speciation in pyrite and secondary weathering phases, Mother Lode gold district, Tuolumne County, California. Applied Geochemistry, 2000, 15(8), 1219-1244.

[6] Haffert, L., Craw, D., Pope, J. Climatic and compositional controls on secondary arsenic mineral formation in high-arsenic mine wastes, South Island, New Zealand. New Zealand Journal of Geology and Geophysics, 2010, 53(2-3), 91-101.

[7] Jamieson, H.E., Walker, S.R., Parsons, M.B. Mineralogical characterization of mine waste. Applied Geochemistry, 2015, 57, 85-105.

[8] Weerasiri, T., Wirojanagud, W., Srisatit, T. Localized profile of arsenic in soil and water in the area around gold mine. Current World Environment, 2013, 8(2), 231-240.

[9] Pollution Control Department (PCD). Monitoring report environmental quality surrounding gold mine at Wong Sa Pung, Loei Province. Ministry of Natural Resources and Environment, Thailand, 2012

[10] Ye, Z.H., Lin, Z.Q., Whiting, S.N., de Souza, M.P., Terry, N. Possible use of constructed wetland to remove selenocyanate, arsenic, and boron from electric utility wastewater. Chemosphere, 2003, 52(9), 1571-1579.

[11] Rodgers Jr, J.H., Castle, J.W. Constructed wetland systems for efficient and effective treatment of contaminated waters for reuse. Environmental Geosciences, 2008, 15(1), 1-8.

[12] Zhao, F.J., Dunham, S.J., McGrath, S.P., Arsenic hyperaccumulation by different fern species. New Phytologist, 2002, 156 (1), 27-31.

[13] Buddhawong, S., Kuschk, P., Mattusch, J., Wiessner, A., Stottmeister, U. Removal of arsenic and zinc using different laboratory model wetland systems. Engineering in Life Sciences, 2005, 5(3), 247-252.

[14] Singhakant, C., Koottatep, T., Satayavivad, J. Enhanced arsenic removals through plant interactions in subsurface-flow constructed wetlands. Journal of Environmental Science and Health Part A, Toxic/Hazardous Substance and Environmental Engineering, 2009, 44(2), 163-169.

[15] Wilkin, R.T., Ford, R.G. Arsenic solid-phase partitioning in reducing sediments of a contaminated wetland. Chemical Geology, 2006, 228(1-3), 156-174.

[16] Lizama, A.K., Fletcher, T.D., Sun, G. Removal processes for arsenic in constructed wetlands. Chemosphere, 2011, 84(8), 1032-1043.

[17] National Rivers Authority. 1992. River corridor surveys: Methods and procedures. Conservation technical handbook No.1: NRA, Bristol. DOI: 10.1002/(SICI)1099-0755(199807/08)8:4<455::AID-AQC284>3.0.CO;2-7

[18] Su, C., Puls, R.W. Arsenate and arsenite removal by zerovalent iron: Kinetics, redox, transformation, and implications for in situ groundwater remediation.

Environmental Science and Technology, 2001, 35(7), 1487-1492.

[19] Sharmin, N. Arsenic removal processes on trial in Bangladesh. Technologies for arsenic removal from drinking water. Edited by Ahmed, M.F., Ali, M.A., Adeel, Z. Bangladesh University of Engineering and Technology, Dhaka-The United Nations University, Tokyo, 2001, 23-30.

[20] Ramaswami, A., Tawachsupa, S., Isleyen, M. Batch-mixed iron treatment of high arsenic waters. Water Research, 2001, 35(18), 4474-4479.

[21] Canales, R.M., Guan, H., Bestland, E., Hutson, J., Simmons, C.T. Particle-size effects on dissolved arsenic adsorption to an Australian laterite. Environmental Earth Sciences, 2012, 68(8), 2301-2312.

[22] Rhine, E.D., Onesios, K.M., Serfes, M.E., Reinfelder, J.R., Young, L.Y. Arsenic transformation and mobilization from minerals by the arsenite oxidizing strain WAO. Environmental Science and Technology, 2008, 42(5), 1423-1429.

[23] Thathong, V. Treatment of arsenic in gold mine runoff using constructed wetland containing laterite soil and taro (Colocasia esculenta L. schott). Doctor of Philosophy Thesis in Environmental Engineering, Graduate School, Khon Kaen University. (2018).

[24] Marchiol, L., Assolari, S., Sacco, P., Zerbi, G. Phytoextraction of heavy metals by canola (Brassica napus) and radish (Raphanus sativus) grown on multicontaminated soil. Environmental Pollution, 2004, 132(1), 21-27.

[25] Wang, X., Ma, L.Q., Rathinasabapathi, B., Liu, Y., Zeng, G. Uptake and translocation of arsenite and arsenate by Pteris vittata L.: Effects of silicon, boron and mercury. Environmental and Experimental Botany, 2010, 68(2), 222-229.

[26] Liu, C.W., Chen, Y.Y., Kao, Y.H., Maji, S.K. Bioaccumulation and translocation of arsenic in the ecosystem of the Guandu Wetland, Taiwan. Wetlands, 2014, 34(1), 129-140.

[27] MacFarlane, G.R., Koller, C.E., Blomberg, S.P. Accumulation and partitioning of heavy metals in mangroves: a synthesis of field-based studies. Chemosphere, 2007, 69(9), 1454-1464.

[28] Wu, G.R., Hong, H.L., Yan, C.L., Arsenic accumulation and translocation in mangrove (Aegiceras corniculatum L.) grown in arsenic contaminated soils. International Journal of Environmental Research and Public Health, 2015, 12(7), 7244-7253.

[29] Schwindaman, J.P., Castle, J.W., Rodgers Jr, J.H., Fate and distribution of arsenic in a process-designed pilot-scale constructed wetland treatment system. Ecological Engineering, 2014, 68, 251-259.

[30] Mays, P.A., Edwards, G.S. Comparison of heavy metal accumulation in a natural wetland and constructed wetlands receiving acid mine drainage. Ecological Engineering, 2001, 16(4), 487-500.

[31] Ma, L.Q., Komar, K.M., Tu, C., Zhang, W., Cai, Y., Kennelley, E.D. A fern that hyperaccumulates arsenic. Nature, 2001, 409(6820), 579.

[32] Kertulis-Tartar, G.M., Ma, L.Q., Tu, C., Chirenje, T. Phytoremediation of an arsenic-contaminated site using Pteris vittata L.: A two-year study. International Journal of Phytoremediation, 2006, 8(4), 311-322 .

[33] Gumaelius, L., Lahner, B., Salt, D.E., Banks, J.A. Arsenic hyperaccumulation in gametophytes of Pteris vittata. A new model system for analysis of arsenic hyperaccumulation. Plant Physiology, 2004, 136(2), 3198-3208.

[34] Bindu, T., Sylas, V.P., Mahesh, M., Rakesh, P.S., Ramasamy, E.V. Pollutant removal from domestic wastewater with Taro (Colocasia esculenta) planted in a subsurface flow system. Ecological Engineering, 2008, 33(1), 68-82.

[35] Dwivedi, S., Tripathi, R.D., Srivastava, S., Singh, R., Kumar, A., Tripathi, P., Tuli, R. Arsenic affects mineral nutrients in grains of various Indian rice (Oryza sativa L.) genotypes grown on arsenic-contaminated soils of West Bengal. Protoplasma, 2010, 245(1-4), 113-124.

[36] Rahman, K.Z., Wiessnes, A., Kuschk, P., van Afferden, M., Mattusch, J., Muller, R.A. Removal and fate of arsenic in the rhizosphere of *Juncus* effusus treating artificial wastewater in laboratory-scale constructed wetlands. Ecological Engineering, 2014, 69, 93-105.

[37] Soriano-Disla, J.M., Gómez, I., Navarro -Pedreño, J., Jordán, M.M. The transfer of heavy metals to barley plants from soils amended with sewage sludge with different heavy metal burdens. Journal of Soils and Sediments, 2014, 14(4), 687-696.

[38] Khan, A., Khan, S., Khan, M.A., Qamar, Z., Waqas, M. The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: A review. Environmental Science and Pollution Research, 2015, 22(18), 13772-13799.

[39] Karimi, N., Alavi, M. Arsenic contamination and accumulation in soil, groundwater and wild plant species from Qorveh County, Iran. Biharean Biology, 2016, 10(2), 69-73.

[40] Lin, S.C., Chang, T.K., Huang, W.D., Lur, H.S., Shyu, G.S. Accumulation of arsenic in rice plant: A study of an arsenic-contaminated site in Taiwan, Paddy and Water Environment, 2015, 13(1), 11-18.

[41] Larsson, M., Leiss, A., Bhattacharya, P., Jacks, G. , Chtterjee, D. Arseniferous groundwater in the Bengal Delta Plains: Appraisal of the low cost remediation techniques . In International Conference on Arsenic in Bangladesh Groundwater : World' s greatest arsenic calamity, USA, 1999, 27-28.

[42] Viraraghavan, T. , Subramanian, K.S., Aruldoss, J.A. Arsenic in drinking water problems and solutions. Water Science and Technology, 1999, 40(2), 69-76.

[43] Maiti, A., DasGupta, S., Basu, J.K., De, S. Adsorption of arsenite using natural laterite as adsorbent. Separation and Purification Technology, 2007, 5(3), 350-359.

[44] Lin, C., Wang, J., Cheng, H., Ouyang, W. Arsenic profile distribution of the wetland argialbolls in the Sanjiang plain of northeastern China. Scientific Reports, 2015, 5, 10766.

[45] Faulwetter, J.L., Gagnon, V. , Sundberg, C., Chazarenc, F., Burr, M.D., Brisson, J., Stein, O.R. Microbial processes influencing performance of treatment wetlands: A review. Ecological Engineering, 2009, 35(6), 987-1004.

[46] Kumar, S.S., Kadier, A. , Malyan, S.K., Ahmad, A. Bishnoi, N.R. Phyto-remediation and rhizoremediation: Uptake, mobilization and sequestration of heavy metals by plants. In Plant-microbe interactions in agro-ecological perspectives, 2017, 367-394.