

Article

# Hydrogeochemistry of Groundwater and Arsenic Adsorption Characteristics of Subsurface Sediments in an Alluvial Plain, SW Taiwan

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**Abstract:** Many studies were conducted to investigate arsenic mobilization in different alluvial plains worldwide. However, due to the unique endemic disease associated with arsenic (As) contamination in Taiwan, a recent research was re-initiated to understand the transport behavior of arsenic in a localized alluvial plain. A comprehensive approach towards arsenic mobility, binding, and chemical speciation was applied to correlate groundwater hydrogeochemistry with parameters of the sediments that affected the As fate and transport. The groundwater belongs to a Na-Ca-HCO<sub>3</sub> type with moderate reducing to oxidizing conditions (redox potential = −192 to 8 mV). Groundwater As concentration in the region ranged from 8.89 to 1131 µg/L with a mean of 343 ± 297 µg/L, while the As content in the core sediments varied from 0.80 to 22.8 mg/kg with a mean of 9.9 ± 6.2 mg/kg. A significant correlation was found between As and Fe, Mn, or organic matter, as well as other elements such as Ni, Cu, Zn, and Co in the core sediments. Sequential extraction analysis indicated that the organic matter and Fe/Mn oxyhydroxides were the major binding pools of As. Batch adsorption experiments showed that the sediments had slightly higher affinity for As(III) than for As(V) under near neutral pH conditions and the As adsorption capacity increased as the contents of Fe oxyhydroxides as well as the organic matter increased.

**Keywords:** adsorption; alluvial aquifers; arsenic; speciation; sequential extraction

## 1. Introduction

High arsenic (As) concentrations of natural origin are often found in groundwater of alluvial aquifers in different parts of the world. Such As-enriched aquifers also exist in the coastal Chianan Plain of southwestern Taiwan. This region is unique for its endemic cases of a peripheral vascular disease (i.e., gangrene), known as Blackfoot Disease (BFD), since 1960s [1]. The occurrence of BFD was strongly correlated with the direct ingestion of groundwater containing, on average, 671 ± 149 µg/L total dissolved As [2]. Several works addressed their heterogeneous distribution in the alluvial aquifers of the Chianan Plain and a number of geogenic sources and release mechanisms of As were reported in this region [3–5]. Among them, reductive dissolution of As-bound Fe/Mn oxyhydroxides in organic-rich sediments was considered as one of the major processes [4–6]. Other processes, like

pyrite oxidation and siderite dissolution were also responsible for high As in Taiwan [7]. Chemical weathering of As-rich silicate minerals such as biotite in the Western Foothill Belt of the Central Mountain Range of Taiwan might also be one of the sources of As contamination in the Chianan Plain [8,9].

Spatial variation of As distribution in Chianan plain was controlled by local hydrogeological factors [9]. However, vertical distribution of As did not reflect any significant correlation with the depth [4–6]; arsenic in different solid phases and its associated release processes were mainly responsible for such As enrichment. However, in-depth cross sectional studies on subsurface sediments are limited, which may make it difficult to elucidate the characteristics of solid phase As uptake and its release mechanism. Although the arsenic-laden groundwater is no longer used for drink water purpose, it is still used in fishery of the region. Thus, developing a cost-effective method to remove arsenic from water remains as a challenge.

Sequential extraction may help in explaining partitioning of As in different solid phases in subsurface sediments as well as identifying the chemical speciation of As. Arsenic in solid phases was generally the result of chemisorption of As(V) or As(III) on soil colloid surfaces, mainly Fe oxide/hydroxides [10], in addition to be retained by minerals like biotite, goethite, and ferrihydrite [11]. In calcareous sediments, As could be adsorbed on carbonate minerals [10]. Different affinities of As(III) and As(V) can influence the extent of their adsorption on sediment constituents, which in turn affects the As concentrations in natural water [12]. Iron oxides have positive surface charges possessing high capability to adsorb negative-charged arsenate (e.g.,  $\text{H}_2\text{AsO}_4^-$ , and  $\text{AsO}_4^{3-}$ ) in water, whereas reduced As in the form of uncharged complex (e.g.,  $\text{H}_3\text{AsO}_3$ ) is less adsorbed by oxides and other minerals. Thus, As(III) is more mobile than other As species. For these reasons, chemical speciation analysis of sediment samples is essential to identify the forms of As present along the soil profile, which helps understand its transport, fate, and availability in natural systems.

The major objectives of this study are to: (i) understand the distribution of As in groundwater and core sediments; (ii) study the distribution of As among various hosting solids, metal-sediment interactions (mainly Mn and Fe), and As speciation in sediments; (iii) elucidate the adsorption characteristics of arsenic speciation in aquifers; and (iv) understand the binding, mobility, and fate of As in the As-enriched aquifer.

## 2. Materials and Methods

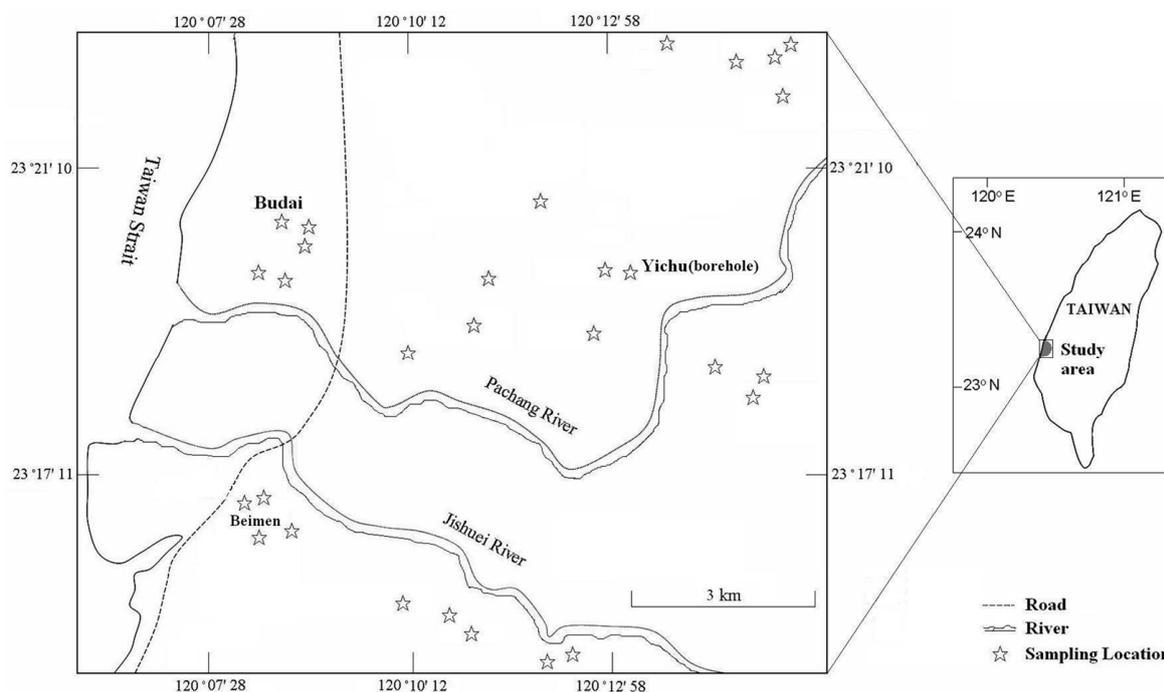
### 2.1. Geologic Setting

The alluvial Chianan Plain is located in the southwestern part of Taiwan (Figure 1) with an area of 2400 km<sup>2</sup>. It is surrounded by the Peikang River in the north, the Ernjen River in the south, the Western Foothill Belt of the Central Mountain Range in the east, and the Taiwan Strait in the west. Subsurface sediments of this coastal plain were deposited during the Quaternary period in a deltaic environment where the groundwater was reducing in nature [4,5,13]. The plain is covered by alluvial deposits originating from the Western Foothill Belt of the Central Mountain Range through erosion and fluvial transport [6,9]. The sediments deposited into the plain are fine-grained clastic, while the subsurface water is highly saline, especially near the coastal areas. The sediments, deposited in shallow to deep sea environments, locally known as the Gutingkeng Formation at a depth of 100 to 280 m, often contain high amounts of organic ooze and humic acids [14]. Detailed local geological and hydrogeological setting was reported elsewhere [9].

### 2.2. Drilling and Sediment Collection

One borehole was drilled to a depth of 200 m in the town of Yichu in southwestern Taiwan. The site is located in the transition zone between the BFD-affected area and the non-affected area (Figure 1). The core sediments were sampled using a split-spoon sampler with rotary drill rigs at

various depths and were immediately sealed in zipper packets and preserved in an anaerobic chamber for speciation analysis.



**Figure 1.** Study area of the Chianan Plain in southwestern Taiwan, which includes the drilling site at Yichu. The locations of the groundwater sampling points are also marked.

### 2.3. Core Sediments Characterization

The particle size distribution was analyzed using the pipette method [15]. The specific surface area (SSA) and cation exchange capacity (CEC) were determined by the methylene blue method. The total organic carbon (TOC) was measured using a LECO carbon analyzer after the sediments were first treated with 2 mol/L  $H_2SO_4$  to remove free inorganic carbonates. The trace elements of core sediment were analyzed using ICP-MS version (Agilent 7500 cs, Santa Clara, CA, USA).

### 2.4. Groundwater Sampling and Analysis

Twenty-nine samples of groundwater were collected from the surrounding areas near the drilling site. Temperature, pH, electrical conductivity, salinity, total dissolved solids (TDS), and uncorrected oxidation-reduction potential (ORP) were measured on site using portable instruments. Groundwater samples were acidified with  $HNO_3$  or  $HCl$  to pH 2 for major cations and As speciation analyses and un-acidified for major anion analyses. The major cations of  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ , and  $NH_4^+$  and major anions of  $Cl^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $SO_4^{2-}$ , and  $F^-$  were analyzed with an ion chromatograph (Dionex, Suonyvale, CA, USA) using external calibration (accuracy:  $\pm 6\%$ ; precision:  $\pm 5\%$ ). Alkalinity and phosphate were analyzed spectrophotometrically. Dissolved organic carbon (DOC) was analyzed using a carbon analyzer (Analytikjena Multi N/C 2100, Überlingen, Germany). Elemental composition was measured using ICP-MS (Agilent 7500 cs). Arsenic speciation was performed with the HG-AFS technique using the Millennium Excalibur system PSA 10.055 (PSA Analytical Ltd., Kent, UK) with a detection limit of  $1 \mu g/L$ .

### 2.5. Sequential Extraction Procedures

Sequential extraction of As was intended to determine the content of As bounded on different solid phases: (1) water soluble; (2) clay and carbonate; (3) Mn oxyhydroxides; (4) Fe oxyhydroxides;

and (5) organic matter and sulfides in As-enriched sediments [16]. For all extraction 2 g of sediment and 16 mL of extraction solution was used. The sediments were mixed with 1 mol/L  $MgCl_2$  for 1 h in extraction (1). For extraction (2), 1 mol/L sodium acetate/acetic acid buffered at pH 4.5 was mixed with the residues from extraction (1) for 15 h. For extraction (3), residues from extraction (2) was extracted with 40 mL of 0.04 mol/L hydroxylamine hydrochloride in 25% acetic acid at 95 °C for 5 h. For extraction (4), 100 mL of 0.2 mol/L oxylate + 0.2 mol/L oxalic acid was used for extractions of residues from extraction (3) and the extraction lasted for 4 h in the dark. For extraction (5), 6 mL of 0.02 N  $HNO_3$  and 10 mL of 30%  $H_2O_2$  were mixed with the residues from extraction (4) and heated to 85 °C for 2 h. The amounts of the residual fraction of As were computed as the difference between bulk concentration (determined by Aqua Regia total digestion) and the sum of leachable fractions.

### 2.6. Arsenic Speciation

The As speciation analyses were determined using the method by Georiadis [17]. A mild extraction media of phosphate solution [18] and sodium diethyldithiocarbamate trihydrate (NaDDC) were used as extractants. The supernatant solution was filtered through a 0.45  $\mu m$  PVDF Acrodisc<sup>®</sup> syringe (Pall Corp., Port Washington, NY, USA) filter into a 2 mL HPLC vial and was immediately analyzed using the HG-AFS technique with the Millennium Excalibur system.

### 2.7. Batch Study for As Adsorption

Samples of fine particles with relatively high As contents were selected for further adsorption experiments to determine the As adsorption capacity. To each 50 mL centrifuge tube, 1 g of sediments and 10 mL of As(V) or As(III) solution made from  $Na_2HAsO_4 \cdot 7H_2O$  or  $NaAsO_2$  at concentrations of 0.1, 0.4, 0.6, 0.8, 1.2, 1.6, and 2.0 mM were mixed for 24 h on a shaker table. No background electrolyte was added. The solution pH was between 7.6 and 8.8, under which the As(V) was in  $HAsO_4^{2-}$  form while As(III) was in  $H_3AsO_3$  form, and the pH was not maintained. After centrifugation, the As concentrations in the supernatants were measured and the amount of As adsorbed were determined by the differences between the initial and the equilibrium As concentrations. The adsorption data were fitted to the Langmuir adsorption isotherm and the As adsorption capacity was then calculated.

## 3. Results and Discussion

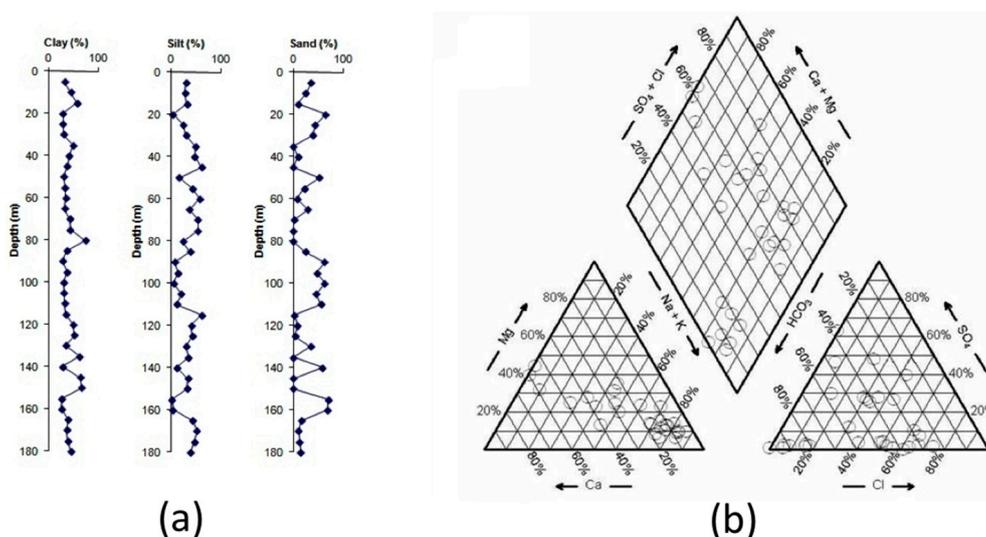
### 3.1. Chemical Characterization of Sediments

A total of 38 core sediment samples at various depths down to 200 m were analyzed for their physico-chemical characteristics, particle size distribution and bulk geochemical (major ions and trace elements) composition. The average clay percentage was predominantly higher than that of sand and silt throughout the entire core, with the highest value (74%) at 85 m (Figure 2a). Overall, the percentage of sand was slightly decreased with depth, whereas the percentage of silt was about the same throughout the entire depth of the core, exhibiting a slight increasing trend with depth for clays. The sediments at alluvial Chianan Plain at various depths were similar to those of the Bengal Delta Plain [5,6].

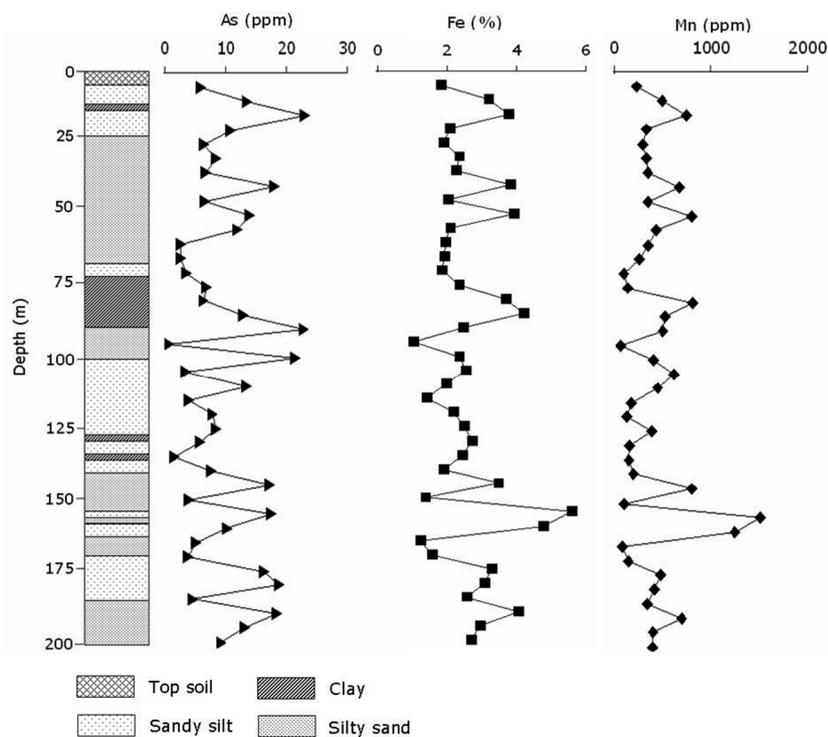
The Yichu core sediments were reddish brown to gray in color with alteration of light and dark sediments along the entire depth. The gray color of the subsurface sediments suggested reduced environment in these aquifers, and the adsorbed As could be released to the groundwater via reductive dissolution of Fe/Mn oxyhydroxides [19]. This suggested potential release of the adsorbed As if the geochemical parameters such as pH and ORP changed.

The elemental composition of the Yichu core sediments is presented in Table 1. The As, Fe, and Mn contents showed a large variation with depth (Figure 3), ranging from 0.80 to 22.8 mg/kg (mean  $9.9 \pm 6.2$  mg/kg), 1.0% to 5.6% (mean  $2.6\% \pm 1.0\%$ ), and 69 to 1511 mg/kg (mean  $429 \pm 306$  mg/kg), respectively. Highest levels of As were found at depths of 15, 40, 90, 100, 180, and 190 m. Regression analysis between As and other elements and TOC (Figure 4) showed positive correlations. For Fe, Mn,

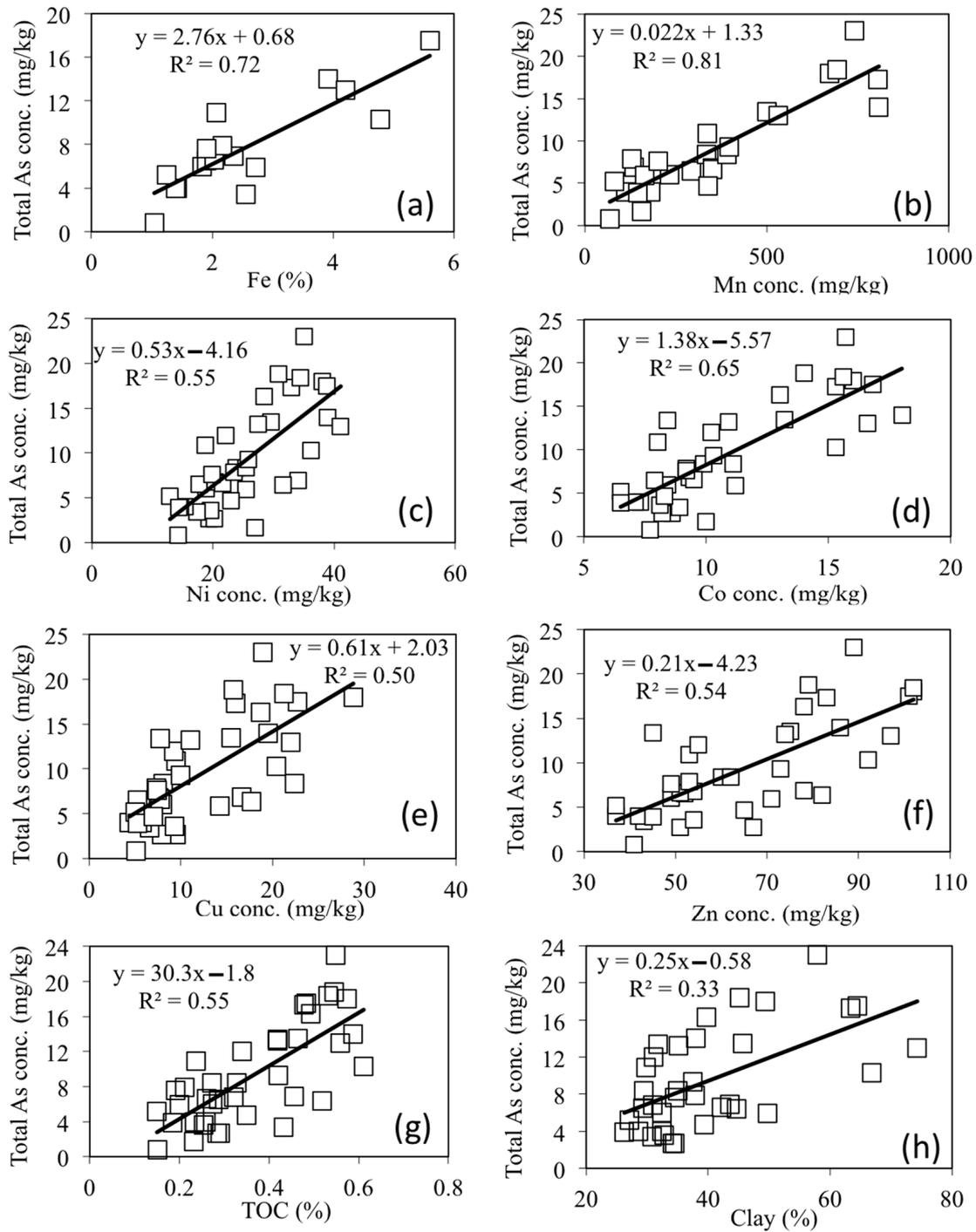
and TOC, the correlations were  $R^2 = 0.72, 0.81,$  and  $0.55,$  respectively, with  $p < 0.05,$  suggesting their strong association. Positive correlations between As and Fe ( $R^2 = 0.65, p < 0.05,$ ) or Mn ( $R^2 = 0.42, p < 0.05,$ ) were also observed in a previous study of sediments collected from an adjacent Budai area (Figure 1), which indicates that Fe and Mn in the sediments could be in the form of adsorbed phases on fine-grain (clay size) mineral surfaces [20]. Positive correlations were also found between As and Ni ( $R^2 = 0.55, p < 0.05,$ ) or Co ( $R^2 = 0.65, p < 0.05,$ ) for siderophile, and between As and Cu ( $R^2 = 0.50, p < 0.05,$ ) or Zn ( $R^2 = 0.54, p < 0.05,$ ) for chalcophile, indicating that sulfide solids may serve as local sinks for As under sulfate-reducing conditions.



**Figure 2.** Variation of percentages of sand, silt, and clay with depth for the core sediments (a). Piper diagram showing the ionic constituents of the groundwater samples collected from the Chianan Plain (b).



**Figure 3.** Lithology of Yichu drilled borehole along with variations in As, Fe, and Mn content with depth.



**Figure 4.** Correlation between total arsenic concentration with: Fe (a); Mn (b); Ni (c); Co (d); Cu (e); Zn (f); TOC (g); and clay content (h) for the core sediments of Yichu.

**Table 1.** Elemental composition of core sediment samples of Yichu, Chianan Plain.

Sample Depth (m)	As (mg/kg)	Fe (%)	Mn (mg/kg)	Ni (mg/kg)	Co (mg/kg)	Pb (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Ca (%)	Al (%)	P (%)	Mg (%)	K (%)	NH <sub>4</sub> (mg/kg)	Cl <sup>-</sup> (mg/kg)	NO <sub>3</sub> <sup>-</sup> (mg/kg)	HCO <sub>3</sub> <sup>-</sup> (mg/kg)
5	6	1.83	234	18.8	8.4	9.1	49	8	NA	NA	NA	NA	NA	2.29	0.41	105.4	57.42
10	13.5	3.19	500	29.6	13.2	18.1	75	15.5	0.41	1.09	0.036	0.43	0.18	2.04	2.56	6.98	115.0
15	23	3.77	742	35.1	15.7	22.3	89	18.9	0.93	1.56	0.045	0.8	0.2	3.47	0.81	10.65	63.82
20	10.9	2.07	337	18.7	8	12	53	9.5	1.05	1.71	0.049	0.92	0.2	2.58	0.62	16.92	64.49
25	6.5	1.9	294	17.7	7.9	8.3	52	5.3	0.74	0.95	0.032	0.48	0.12	2.51	0.35	6.07	67.97
30	8.4	2.35	334	23.8	9.9	11.1	60	8.1	0.75	0.98	0.031	0.52	0.12	2.99	1.27	0.776	81.91
35	6.8	2.26	351	20.4	9.3	11	54	7.6	0.82	1.16	0.038	0.62	0.13	3.36	1.11	0.745	77.33
40	18	3.81	672	38.1	16	28.2	102	28.8	0.9	1.08	0.042	0.62	0.13	3.81	11.29	0.454	134.2
45	6.6	2.03	351	21.6	9.5	12.2	51	7.7	1.23	1.8	0.049	1.05	0.17	BDL	9.04	0.217	92.42
50	14	3.92	808	38.9	18	21.9	86	19.5	1.01	0.99	0.069	0.62	0.13	5.66	7.54	0.195	50.54
55	12	2.1	431	22.1	10.2	11.5	55	9.2	1.2	1.83	0.052	1.07	0.21	7.90	3.57	31.67	71.16
60	2.7	1.96	354	19.4	8.6	10.4	51	9.5	1.09	1	0.035	0.63	0.13	7.90	6.26	1.857	83.47
65	2.7	1.92	262	20.2	8.2	10.3	67	7.9	0.93	1.04	0.043	0.55	0.17	3.39	1.84	41.11	65.74
70	3.6	1.86	99	19.6	8.1	8.6	54	9.3	0.8	0.98	0.036	0.52	0.12	3.65	0.34	4.29	81.33
75	6.9	2.36	136	34	17.4	18.4	78	16.6	0.12	1.05	0.036	0.37	0.14	10.73	1.15	189.3	81.33
80	6.4	3.69	815	31.6	14	18.8	82	17.7	0.18	1.44	0.043	0.51	0.13	2.78	0.71	82.06	86.42
85	13	4.21	531	41.1	16.6	21.8	97	22	0.57	1.68	0.055	0.71	0.14	5.61	0.76	74.12	36.6
90	22.8	2.46	504	21.9	10.4	12.1	57	10	0.67	2.03	0.046	0.96	0.18	2.72	0.33	73.09	34.31
95	0.8	1.04	69	14.2	7.7	8.4	41	5.1	0.1	1.25	0.038	0.36	0.15	5.27	0.64	5.45	31.47
100	21.5	2.35	411	21.1	9.8	12	52	8.5	0.07	0.58	0.013	0.19	0.1	3.09	0.58	0.184	76.45
105	3.4	2.55	622	17.4	8.9	9.9	43	6.6	0.14	1.22	0.051	0.33	0.14	3.21	0.39	3.113	75.08
110	13.4	1.98	448	18.7	8.4	10.3	45	7.7	0.17	0.88	0.026	0.29	0.12	2.99	0.23	59.77	87.39
115	4	1.42	181	15.4	7.3	8.1	42	5.8	0.45	0.85	0.025	0.38	0.11	6.45	0.32	77.08	129.62
120	7.9	2.17	129	23.4	9.2	11.3	53	7.3	0.36	0.78	0.022	0.33	0.12	4.6	0.18	60.81	17.08
125	8.4	2.48	391	25.5	11.1	12.3	62	22.4	0.11	0.99	0.032	0.42	0.13	1.59	0.32	76.34	34.56
130	5.9	2.72	164	25.5	11.2	13.4	71	14.2	0.82	1.22	0.045	0.56	0.14	1.58	0.31	32.26	130.1
135	1.7	2.43	157	26.9	10	16.1	85	13.3	0.08	1.54	0.038	0.47	0.17	2.22	0.23	18.02	45.75
140	7.6	1.91	203	19.9	9.2	12	49	7.4	0.12	1.45	0.026	0.55	0.15	2.56	0.32	34.06	41.37
145	17.3	3.47	805	32.9	15.3	19.1	83	16	0.12	0.95	0.034	0.37	0.12	4.89	0.34	10.53	128.7
150	4	1.39	112	14.6	7.1	8	37	4.4	1.12	1.59	0.048	0.83	0.14	2.41	0.16	6.89	82.59
155	17.5	5.6	1511	38.8	16.8	24.5	101	22.7	0.08	0.69	0.027	0.27	0.1	3.24	0.24	3.71	30.84
160	10.3	4.78	1248	36.2	15.3	26.3	92	20.4	1.73	1.9	0.125	0.91	0.17	7.38	0.07	5.384	BDL
165	5.2	1.24	82	12.9	6.5	6.5	37	5	0.98	1.81	0.102	0.88	0.17	1.99	0.15	4.148	97.6
170	3.9	1.58	146	14.4	6.5	7.4	45	5.3	0.05	0.69	0.013	0.25	0.1	63.46	3.53	3.415	106.5
175	16.3	3.27	478	28.5	13	20.1	78	18.7	0.22	0.83	0.02	0.34	0.1	81.35	8.05	6.05	76.68
180	18.8	3.08	422	30.8	14	18	79	15.7	0.95	1.5	0.044	0.8	0.14	64.42	4.11	3.191	57.51
185	4.7	2.57	338	23	8.3	11.6	65	7	0.91	1.44	0.042	0.8	0.13	53.68	4.29	11.79	75.08
190	18.4	4.05	694	34.4	15.6	33.5	102	21.2	0.75	1.33	0.038	0.7	0.15	2.29	0.40	105.4	57.42
195	13.2	2.95	400	27.4	10.9	17.4	74	11	1.07	1.97	0.05	1.08	0.19	2.04	2.56	6.98	115.0
200	9.3	2.7	398	25.8	10.3	15.7	73	10	0.87	1.46	0.047	0.77	0.17	3.47	0.81	10.65	63.82
Min	0.80	1.04	69	12.9	6.5	6.5	37.0	4.4	0.05	0.58	0.013	0.19	0.10	0	0.07	0.184	0
Max	22.8	5.60	1511	41.1	18.0	33.5	102	28.8	1.73	2.03	0.125	1.08	0.21	81.4	11.3	189.3	134.2
Mean	9.93	2.64	429.1	25.0	11.0	14.7	65.5	12.2	0.63	1.26	0.042	0.60	0.14	9.94	1.96	29.78	72.6
STD	6.20	1.00	306.6	7.82	3.4	6.36	19.3	6.29	0.44	0.39	0.020	0.25	0.03	19.2	2.79	40.99	31.8
Median	8.15	2.40	372.5	23.2	9.95	12.0	61.0	9.50	0.75	1.22	0.038	0.55	0.14	3.30	0.63	8.76	75.1

### 3.2. Hydrogeochemistry and Occurrences of As in Groundwater

The physico-chemical characteristics of the groundwater collected from the alluvial Chianan Plain are presented in Tables 2 and 3 ( $n = 29$ ). The hydrochemical properties of the groundwater in the neighboring areas of the drilling site exhibited considerable variations in a range of well depth from 3 m to 313 m, i.e., water temperature (18.1 to 32.3 °C; mean  $25.6 \pm 2.86$  °C), pH (7.05 to 8.34; mean  $7.64 \pm 0.35$ ), EC (0.85 to 67.9 mS/cm; mean  $4.32 \pm 12.3$  mS/cm), salinity (0.2‰ to 46.2‰; mean  $2.46 \pm 8.44$  ‰), TDS (408 to 2750 mg/L; mean  $998 \pm 678$  mg/L), DOC (11.3 to 204 mg/L, mean =  $107 \pm 52.2$  mg/L), and ORP (−192 to 8 mV; mean  $-107 \pm 49.2$  mV). The alkalinity ranged from 154 to 340 mg/L (mean  $183 \pm 31.5$  mg/L).

Among the major anions, chloride ranged from <0.1 to 332 mg/L (mean  $103 \pm 91.4$  mg/L), and nitrate varied from 3.50 to 7.80 mg/L (mean  $4.60 \pm 1.80$  mg/L). Elevated levels of sulfate were observed up to 385 mg/L (mean  $17.1 \pm 70.8$  mg/L). Fluoride was mostly absent with the exception of four locations showing the maximum at 3.16 mg/L. Similarly, nitrite was only found in six sites (mean  $105 \pm 261$  mg/L). Phosphate showed a meager variation between <0.1 to 6.08 mg/L (mean  $1.91 \pm 1.40$  mg/L). Among the major cations,  $\text{Na}^+$  was found to vary within 1.41 to 871 mg/L (mean  $320 \pm 224$  mg/L).  $\text{NH}_4^+$  was observed at five sites (mean  $3.81 \pm 7.32$  mg/L). Other cations  $\text{K}^+$  (3.34 to 59.8 mg/L; mean  $15.4 \pm 12.2$  mg/L),  $\text{Mg}^{2+}$  (7.37 to 105 mg/L; mean  $49.9 \pm 28.6$  mg/L) and  $\text{Ca}^{2+}$  (11.7 to 531 mg/L; mean  $103 \pm 102$  mg/L) also varied considerably. The general water type was found to be an Na-Cl type as observed from the Piper diagram (Figure 2b). The major cation  $\text{Ca}^{2+}$  may derive from carbonate minerals such as calcite and dolomite, while  $\text{Mg}^{2+}$  may originate from biotite, chlorite, and carbonate minerals, and  $\text{K}^+$  may derive from orthoclase and clay minerals [21].

The As(III) and As(V) concentrations ranged from 0.62 to 954  $\mu\text{g/L}$  (mean  $209 \pm 242$   $\mu\text{g/L}$ ) and from 0.23 to 318  $\mu\text{g/L}$  (mean  $84.6 \pm 94.9$   $\mu\text{g/L}$ ), respectively (Table 3), among the 29 groundwater wells. Only a few samples contained arsenic concentrations within the WHO standard of <10  $\mu\text{g/L}$ , and most of the groundwater samples contained concentrations higher than 100  $\mu\text{g/L}$ .

### 3.3. Solid Phase Partitioning of As and Speciation

Figure 5 shows the fraction of extractable and non-extractable solid phase As at different depths. The relative proportion of different As pools did not show much depth variation. The percentage of leachable As did not vary much until at a depth of 110 m. Only a small fraction (0.03% to 2.17%) of As was present in the water soluble/leachable form and clay/carbonate bound fraction (0.01% to 1.43%). Similarly, the exchangeable of As accounted for 4% in the sediments of Zhalong wetland in Northeastern China ([22]. Among the various extractable pools, the organic matter (0.90%–51.4%) and Fe/Mn-oxyhydroxides were found to be the major binding phases (1.08%–51.1% bound to Mn-oxyhydroxide, and 0.58%–25.5% to Fe-oxyhydroxides). These results confirmed that the As in the sediments interacted with the Fe/Mn phases via adsorption. The amounts of As in the sodium pyrophosphate and 0.1 M hydroxylamine extracts were found to be higher among various extractable pools, suggesting that organic matter and Mn-oxyhydroxides are the dominant hosts of solid phase As. A general trend of increasing As bound to organic matter was observed below a depth of 130 m, whereas As bound to Mn-oxyhydroxide was uniform until a depth of 150 m, and thereafter it increased markedly. The majority of the As fractions is bound to the recalcitrant fraction. The percentage of non-extractable As was uniformly high and ranged widely between 41.4% and 96.8%, suggesting that most As was associated with residual phases of crystalline sulfides, except at a depth of 135 m where the non-leachable fraction was only 1.60%. In a similar study, 88%–91% of the total As concentration was found associated with residual fraction in mariculture sediments from Dongshan Bay in China across from Taiwan Strait [23].

**Table 2.** Physico-chemical characteristics of groundwater samples ( $n = 29$ ) collected from Yichu, Chianan plain, southwestern Taiwan.

Sample Location	Latitude/Longitude	Depth (m)	Temp (°C)	EC (mS/cm)	TDS (mg/L)	Salinity (‰)	pH	ORP (mV)	DOC (mg/L)
Beimen 2B	N 23°17'23.4"/E 120°8'57.8"	60	24.8	67.9	OFL	46.2	7.1	−128	23
Yenshui 2	N 23°18'4"/E 120°15'12"	23	20.9	1.2	575	0.4	7.83	−158	26.4
Yichu (house)	N 23°19'52.3"/E 120°13'27.2"	20	24.7	3.08	1481	1.5	7.23	−108	17.
Lucao1B (rice field)	N 23°24'59.9"/E 120°17'50.6"	13	18.1	1.52	727	0.6	7.54	−54	11.3
Lucao1A (house)	N 23°24'59"/E 120°17'51"	30	24.3	1.79	857	0.7	7.54	−118	19.6
Liujiiao2	N 23°30'27.3"/E 120°16'19.1"	67	24.9	1.044	501	0.3	7.31	−148	13.7
Budai-Shinwen	N 23°20'22"/E 120°7'57.9"	313	24.7	1.15	554	0.4	7.63	−140	158
Budai-3	N 23°20'29.7"/E 120°9'37"	233	32.3	0.97	463	0.3	8.25	−96	129
Beimen CN 9	N 23°18'33.3"/E 120°8'45.7"	100	31.7	1.67	799	0.7	8.1	−72	157
Beimen-Jinhu	N 23°18'26"/E 120°9'8.2"	300	28.5	1.42	682	0.5	7.44	−139	159
Beimen 2A	N 23°30'27.6"/E 120°16'19"	277	24.7	1.86	893	0.8	7.33	−144	163
Yenshui 3	N 23°18'6.7"/E 120°15'11.1"	23	24.7	1.56	751	0.6	7.92	−158	119
Yenshui 1	N 23°18'2.4"/E 120°14'57.2"	23	24.7	1.37	657	0.5	8.12	−133	124
Beimen 1	N 23°17'23.3"/E 120°5'41.2"	200	26.4	1.43	684	0.5	7.68	−149	205
Budai 5	N 23°22'56.8"/E 120°9'49.6"	200	24.5	0.86	410	0.2	8.34	8	97.7
Budai 4	N 23° 19'37.8"/E 120° 9'3.2"	300	23.9	3.55	1704	1.8	7.76	−100	141
Hsuechia 2	N 23°13'46.1"/E 120°10'4.3"	3	21.4	5.47	2626	2.9	7.38	−96	105
Siaying 3	N 23°14'14.7"/E 120°14'21.7"	233	27.5	0.85	408	0.2	8.13	−17	111
Siaying 1	N 23°14'7.9"/E 120°14'40"	150	25	3.37	1619	1.7	7.05	−27	103
Yichu 5	N 23°19'59.7"/E 120°13'11.6"	20	26.1	1.57	751	0.6	7.24	−119	125
Yichu 6	N 23°19'29.7"/E 120°12'48.1"	20	25.1	2.32	1116	1	7.5	−102	142
Yichu 7	N 23°18'55.5"/E 120°10'5.8"	72	29.1	1.13	545	0.4	8.1	−192	136
Yichu 8	N 23°18'57.1"/E 120°10'25.6"	143	25.2	5.44	2750	2.9	7.9	−10	138
Lucao 3	N 23°22'40.4"/E 120°16'51.8"	4.5	27.8	1.10	531	0.3	7.3	−91	87
Lucao 4	N 23°23'15.1"/E 120°17'39.2"	83	26.5	1.49	716	0.6	7.84	−148	101
Lucao 5	N 23°23'25.3"/E 120°17'20.4"	300	26.3	2.08	998	0.9	7.63	−153	98.3
Hsuechia 3	N 23°17'7.5"/E 120°11'6.7"	67	27.8	0.96	462	0.2	7.65	−72	122
Hsuechia 4	N 23°16'22.2"/E 120°9'36.2"	5	24.1	5.05	2610	2.7	7.34	−113	155
Hsuechia 5	N 23°14'39.6"/E 120°9'14.7"	7	27.1	2.24	1076	1	7.59	−118	115
	Min	3	18.1	0.85	408	0.2	7.05	−192	11.3
	Max	313	32.3	67.9	2750	46.2	8.34	8	204
	Mean	113	25.6	4.32	998	2.46	7.64	−107	107
	STD	110	2.86	12.3	678	8.44	0.35	49.2	52.2
	Median	67	25	1.56	739	0.6	7.63	−118	119

**Table 3.** Hydrochemical characteristics of groundwater samples ( $n = 29$ ) collected from Yichu, Chianan plain, southwestern Taiwan.

Sample Location	Alkalinity (mg/L)	F (mg/L)	Cl (mg/L)	NO <sub>2</sub> (mg/L)	NO <sub>3</sub> (mg/L)	SO <sub>4</sub> (mg/L)	Na (mg/L)	NH <sub>4</sub> (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	PO <sub>4</sub> (mg/L)	As(III) (µg/L)	As(V) (µg/L)	Fe (µg/L)	Mn (µg/L)
Beimen 2B	184	2.89	332	0.00	8.17	10.4	582	0.00	26.2	51.4	66	3.00	102	224	18,809	32.3
Yenshui 2	182	2.85	57.0	0.00	7.70	29.1	138	2.3	17.9	63	64.7	3.17	560	184	3725	91.0
Yichu (house)	190	3.16	269	0.00	7.76	336	277	0.00	20.1	88.1	236	0.44	102	10.5	8338	160
Lucao1B (rice field)	188	2.88	89.7	0.00	8.28	90.7	1.41	0.00	3.34	71.2	144	1.20	4.95	3.94	4879	75.9
Lucao 1A (house)	185	2.86	108	0.00	0.00	111	1.71	0.00	3.4	70.7	176	2.60	41.1	5.23	28	1.19
Litujiao 2	175	2.97	24.9	0.00	7.66	72.3	75.9	0.00	3.63	37.7	121	1.09	89.8	5.03	12,129	237
Budai- Shinwen	185	0.00	171	0.00	3.50	0.00	422	0.00	4.56	24.8	34.8	2.18	604	100	1271	30.3
Budai-3	177	0.00	9.85	0.00	0.00	3.33	223	10.1	8.25	12.8	16.2	3.92	654	64.4	533	40.7
Beimen CN 9	173	0.00	104	0.00	3.35	11.4	391	0.00	16.9	23	11.7	6.08	212	40.6	365	58.9
Beimen-Jinhu	180	0.00	137	0.00	3.36	3.11	362	28.3	6.88	31.4	42.3	1.86	356	184	4033	32.9
Beimen 2A	172	0.00	116	0.00	3.39	5.88	332	24.3	5.71	35.5	74.5	3.00	158	220	3537	28.0
Yenshui 3	177	0.00	76.8	0.00	0.00	86.8	194	4.45	20	77.2	102	1.82	954	177	2994	27.6
Yenshui 1	176	0.00	70.2	0.00	2.91	8.85	245	0.00	32.7	45.8	26.4	2.22	274	41.6	466	25.5
Beimen 1	340	0.00	12.4	1.29	3.79	3.16	333	0.00	3.66	12.6	33.8	4.16	372	161	2326	28.9
Budai 5	157	0.00	17.6	1.13	4.63	4.71	170	0.00	6.56	7.37	33.4	1.42	1.96	319	381	17.6
Budai 4	166	0.00	212	473	3.89	11.4	622	0.00	13.3	51.5	98.7	1.72	24.5	285	5832	28.7
Hsuechia 2	175	0.00	0.00	859	3.72	234	698	0.00	14.7	106	531	0.00	10.3	3.22	10,260	2609
Siaying 3	154	0.00	5.94	0.00	3.65	3.55	191	5.84	10.7	13.6	26.8	1.38	57.9	10.2	519	70.1
Siaying 1	171	0.00	0.00	207	385	0.95	531	0.00	8.55	32	112	2.43	190	9.15	12,093	263
Yichu 5	183	0.00	73.2	0.00	3.71	92.7	151	2.66	16.1	70.4	161	0.21	94.2	12.9	9385	107
Yichu 6	192	0.00	96.3	0.00	3.6	262	300	0.00	32.2	86.7	163	1.31	49.8	6.60	7022	1047
Yichu 7	182	0.00	23.4	0.00	3.49	3.43	259	11.8	12.8	16.2	17.9	2.89	305	104	1062	85.8
Yichu 8	189	0.00	258	539	4.46	39.8	816	0.00	29.9	77.1	59.9	1.91	0.62	96.1	956	17.5
Lucao 3	163	0.00	14.6	0.00	0.00	128	34	0.00	6.02	66.2	203	0.00	22.9	1.36	14,508	1957
Lucao 4	177	0.00	112	0.00	3.67	12.9	295	0.00	18.8	27.9	37.7	2.92	188	51.9	3428	87.9
Lucao 5	177	0.00	187	0.00	3.87	5.45	273	12.4	19.4	58.9	68.6	1.04	57.8	18.2	5389	192
Hsuechia 3	176	0.00	19.7	0.00	3.64	3.14	194	8.46	7.81	20.2	42	1.04	510	112	5281	161
Hsuechia 4	181	0.00	226	965	4.66	51.9	872	0.00	59.9	103	130	0.14	34.1	3.68	12,104	359
Hsuechia 5	179	0.00	155	0.00	3.83	126	316	0.00	18.9	66.2	157	0.34	34.8	0.23	10,965	339
Min	154	0.00	0.00	0.00	0.00	0.00	1.41	0.00	3.34	7.37	11.7	0.00	0.62	0.23	28.1	1.19
Max	340	3.16	332	965	385	335	871	28.2	59.8	105	531	6.08	954	318	18,809	2609
Mean	183	0.61	103	105	17.1	60.4	320	3.81	15.4	49.9	103	1.91	209	84.6	5607	283
SD	31.5	1.21	91.4	261	70.8	86.6	224	7.32	12.2	28.6	102	1.40	242	94.9	5046	595
Median	177	0	89.8	0	3.71	11.4	276	0	13.3	51.4	68.5	1.82	102	41.5	4033	75.9

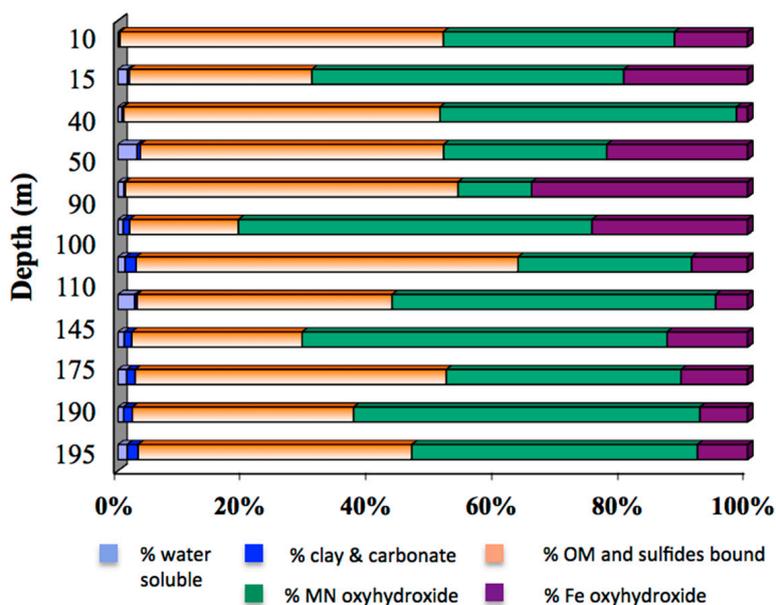


Figure 5. Percentage of sequentially extracted As phases at different depths where As was found in high concentrations.

The predominant species in the Yichu core sediments was As(III) (Figure 6). The As(III) ranged from  $0.9 \pm 0.2$  to  $14 \pm 0.78 \mu\text{g/kg}$ , whereas As(V) ranged from  $0.13 \pm 0.06$  to  $6.48 \pm 0.63 \mu\text{g/kg}$ . It is well known that As(V) is reduced to As(III) under reducing conditions. Due to the lack of negative charged for arsenite under near neutral pH condition, its affinity to iron and manganese oxides is much weaker than As(V), and can be released into water [24]. In addition, due to the weak binding, 92%–99% of As(III) could be extracted under subcritical conditions [25].

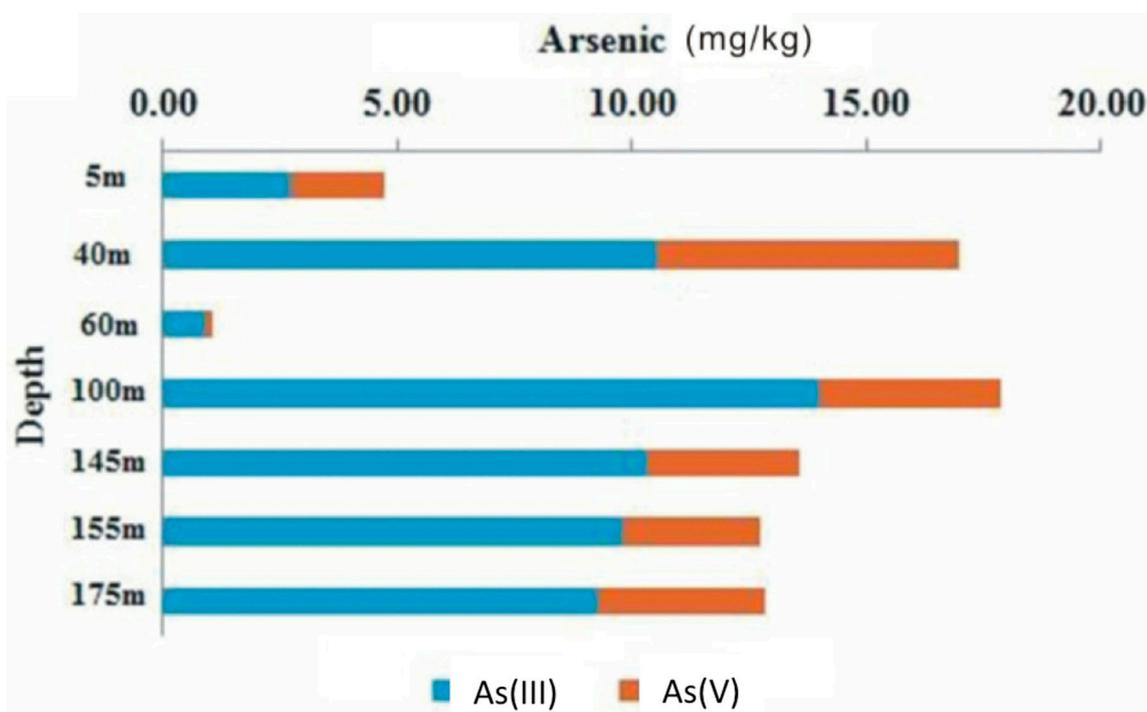


Figure 6. Arsenic speciation of the Yichu core sediment.

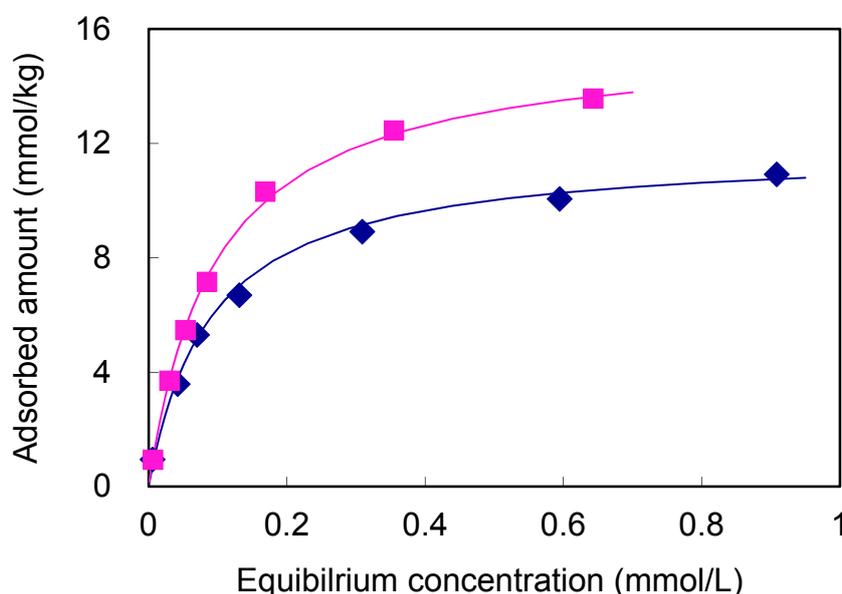
### 3.4. Adsorption Characteristics of Arsenic in Sediment and Its Implication on Mobilization

A characteristic adsorption isotherm was observed when the adsorption of As(III) and As(V) was plotted against the equilibrium As concentration at an equilibrium pH of 7.5 (Figure 7). Overall, a slightly high As(III) adsorption on these sediments were observed. This finding is similar to the trend observed in the Budai core sediments of the Chianan Plain [20] and agrees well with the As speciation analyses of the core samples (Figure 6). Adsorption of As(III) on ferrihydrite was considerably faster than that of As(V) at pH 7 to 8 [26]. Multiple linear regression analyses showed the following results:

$$\text{As(V)} = 0.03 \text{ Clay} - 0.01 \text{ Mn} + 0.48 \text{ Fe} + 3.52 \text{ TOC} + 7.01 \text{ SSA} - 54.51 \text{ CEC}, \text{ adjusted } R^2 = 0.99$$

$$\text{As(III)} = -0.04 \text{ Clay} + 0.002 \text{ Mn} + 1.17 \text{ Fe} + 18.5 \text{ TOC} + 6.19 \text{ SSA} - 48.08 \text{ CEC}, \text{ adjusted } R^2 = 0.99$$

They suggest positive correlation with Fe, TOC, SSA, and negative correlation with CEC, confirming the observations for correlations between As contents and elements concentrations in these core sediment samples ( $n = 40$ ) (Figure 4).



**Figure 7.** A typical As(III) (■) and As(V) (◆) adsorption isotherm with the lines of the Langmuir fits to the observed data.

Due to the strong adsorption of As(V) and As(III) onto organic matters, they are likely to remain in soils for a long time, especially in fine-textured soils with high Fe content [27]. Similar results were observed for estuarine sediments in SW Taiwan [28] and in the sediments of silty clay and silty sand of the Yun-Lin Plain, Taiwan [29].

The groundwater contained low levels of sulfate, indicating that oxidation of pyrite may not be the likely source of As. The element image analyses showed no correlation between pyrite and As contents [30]. Thus, reductive dissolution of As-contained ferric iron under anaerobic conditions is suggested to be a major mobilizing force for As release to the groundwater of the Chianan Plain. Although no such correlation has been observed between As and bicarbonate concentration, high As groundwater usually contains relatively elevated concentrations of bicarbonate in the Chianan Plain aquifer. This may result in desorption of As oxyanions under the competitive sorption effect of elevated concentrations of bicarbonate [31].

#### 4. Conclusions

The hydrogeochemical characteristics of groundwater and subsurface sediments and the adsorption characteristics of arsenic speciation in aquifers were investigated in the As-enriched areas of the Chianan Plain in southwestern Taiwan. The concentration of aqueous As was strongly depth-dependent, with the maximum at 1131 µg/L. Redox-sensitive parameters were closely related to bicarbonate and electrical conductivity. Dissolved As was significantly correlated with Fe contents, suggesting that the Fe-bearing phases is likely to be a sink of As. The aquifer sediments were characterized with higher clay content and alkaline pH and were enriched with organic matter, which bears a positive correlation with As content at different depths under consideration. In core samples, As, Fe, and Mn exhibited strong depth dependence, suggesting reductive dissolution to be a major mobilizing force for As under moderately reducing conditions. Sequential separation showed that the organic matter and Fe/Mn-oxyhydroxides are the major binding phases of As. The speciation analyses showed dominance of As(III) over As(V) in the sediment samples under consideration. Arsenic adsorption on the sediments followed the Langmuir adsorption isotherm with a higher adsorption capacity for As(III) than for As(V), confirming the major adsorbed species was As(III) in the sediments.

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#### References

1. Tseng, W.-P. Effects and dose-response relationships of skin cancer and blackfoot disease with arsenic. *Environ. Health Perspect.* **1977**, *19*, 109–119. [[CrossRef](#)] [[PubMed](#)]
2. Chen, S.-L.; Dzeng, S.R.; Yang, M.-H. Arsenic species in groundwaters of Blackfoot Disease area, Taiwan. *Environ. Sci. Technol.* **1994**, *28*, 877–881. [[CrossRef](#)] [[PubMed](#)]
3. Chen, C.C. Accumulation and Release of Arsenic in Sediments from Hsindong and Jinhu in Chianan Plain, Taiwan. Master's Thesis, Department of Geosciences, National Taiwan University, Taipei, Taiwan, 2003.
4. Wang, S.-W.; Liu, C.-W.; Jang, C.-S. Factors responsible for high arsenic concentrations in two groundwater catchments in Taiwan. *Appl. Geochem.* **2007**, *22*, 460–476. [[CrossRef](#)]
5. Nath, B.; Jean, J.-S.; Lee, M.-K.; Yang, H.-J.; Liu, C.-C. Geochemistry of high arsenic groundwater in Chia-Nan plain, Southwestern Taiwan: Possible sources and reactive transport of arsenic. *J. Contam. Hydrol.* **2008**, *99*, 85–96. [[CrossRef](#)] [[PubMed](#)]
6. Reza, R.A.H.M.; Jean, J.-S.; Yang, H.-J.; Lee, M.-K.; Hsu, H.-F.; Liu, C.-C.; Lee, Y.-C.; Bundschuh, J.; Lin, K.-H.; Lee, C.-Y. A comparative study on arsenic and humic substances in alluvial aquifers of Bengal delta plain (NW Bangladesh), Chianan plain (SW Taiwan) and Lanyang plain (NE Taiwan): Implication of arsenic mobilization mechanisms. *Environ. Geochem. Health* **2011**, *33*, 235–258. [[CrossRef](#)] [[PubMed](#)]
7. Lin, Y.-B.; Lin, Y.-P.; Liu, C.-W.; Tan, Y.-C. Mapping of spatial multi-scale sources of arsenic variation in groundwater on Chia-Nan floodplain of Taiwan. *Sci. Total Environ.* **2006**, *370*, 168–181. [[CrossRef](#)] [[PubMed](#)]
8. Saunders, J.A.; Lee, M.-K.; Uddin, A.S.; Mohammad, S.; Wilkin, R.; Fayek, M.; Korte, N. Natural arsenic contamination of Holocene alluvial aquifers by linked glaciation, weathering, and microbial processes. *Geochem. Geophys. Geosyst.* **2005**, *6*, 1–7. [[CrossRef](#)]
9. Sengupta, S.; Sracek, O.; Jean, J.-S.; Lu, H.-Y.; Wang, C.-H.; Palcsu, L.; Liu, C.-C.; Jen, C.-H.; Bhattacharya, P. Spatial variation of groundwater arsenic distribution in Chianan Plain, SW Taiwan: Role of local hydrogeological factors and geothermal sources. *J. Hydrol.* **2014**, *518*, 393–409. [[CrossRef](#)]
10. Sadiq, M. Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. *Water Air Soil Pollut.* **1997**, *93*, 117–136. [[CrossRef](#)]

11. Keon, N.E.; Swartz, C.H.; Brabander, D.J.; Harvey, C.; Hemond, H.F. Validation of an arsenic sequential extraction method for evaluating mobility in sediment. *Environ. Sci. Technol.* **2001**, *35*, 2778–2784. [[CrossRef](#)] [[PubMed](#)]
12. O'day, P.A.; Vlassopoulos, D.; Root, R.; Rivera, N. The influence of sulfur and iron on dissolved arsenic concentrations in the shallow subsurface under changing redox conditions. *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 13703–13708. [[CrossRef](#)] [[PubMed](#)]
13. Lu, K.-L.; Liu, C.-W.; Wang, S.-W.; Jang, C.-S.; Lin, K.-H.; Vivian-Liao, H.-C.; Liao, C.-M.; Chang, F.-J. Assessing the characteristics of groundwater quality of arsenic contaminated aquifers in the blackfoot disease endemic area. *J. Hazard. Mater.* **2011**, *185*, 1458–1466. [[CrossRef](#)] [[PubMed](#)]
14. Yu, X. Humic acids from endemic arsenicosis areas in Inner Mongolia and from the Blackfoot-disease areas in Taiwan: A comparative study. *Environ. Geochem. Health* **2001**, *23*, 27–42.
15. Gee, G.W.; Or, D. Particle-size analysis. In *Soil Science Society of America Book Series: Methods of Soil Analysis. Part 4. Physical Methods*; Dane, J.H., Topp, G.C., Eds.; Soil Science Society of America: Madison, WI, USA, 2002; Volume 5, pp. 255–293.
16. Matera, V.; Le Hecho, I.; Laboudigue, A.; Thomas, P.; Tellier, S.; Astruc, M. A methodological approach for the identification of arsenic bearing phases in polluted soils. *Environ. Pollut.* **2003**, *126*, 51–64. [[CrossRef](#)]
17. Georgiadis, M.; Cai, Y.; Solo-Gabriele, H.M. Extraction of arsenate and arsenite species from soils and sediments. *Environ. Pollut.* **2006**, *141*, 22–29. [[CrossRef](#)] [[PubMed](#)]
18. Loeppert, R.H.; Jain, A.; El-Haleem, M.A.A.; Biswas, B.K. Quantity and speciation of arsenic in soils by chemical extraction. In *Biogeochemistry of Environmentally Important Trace Elements*; Cai, Y., Braids, O.C., Eds.; American Chemical Society: Washington, DC, USA, 2002; p. 436.
19. McArthur, J.M.; Banerjee, D.M.; Hudson-Edwards, K.A.; Mishra, R.; Purohit, R.; Ravenscroft, P.; Cronin, A.; Howarth, R.J.; Chatterjee, A.; Talukder, T.; et al. Natural organic matter in sedimentary basins and its relation to arsenic in anoxic ground water: The example of West Bengal and its worldwide implications. *Appl. Geochem.* **2004**, *19*, 1255–1293. [[CrossRef](#)]
20. Li, Z.; Hong, H.; Jean, J.-S.; Koski, A.J.; Liu, C.-C.; Reza, S.A.H.M.; Randolph, J.J.; Kurdas, S.R.; Friend, J.H.; Antinucci, S.J. Characterization on arsenic sorption and mobility of the sediments of Chia-Nan Plain, where Blackfoot disease occurred. *Environ. Earth Sci.* **2011**, *64*, 823–831. [[CrossRef](#)]
21. Jeong, C.H. Effect of land use and urbanization on hydrochemistry and contamination of groundwater from Taejon area, Korea. *J. Hydrol.* **2001**, *253*, 194–210. [[CrossRef](#)]
22. Luo, J.; Ye, Y.; Gao, Z.; Wang, Y.; Wang, W. Trace element (Pb, Cd, and As) contamination in the sediments and organisms in Zhalong Wetland, Northeastern China. *Soil Sediment Contam. Int. J.* **2016**, *25*, 395–407. [[CrossRef](#)]
23. Du, Y.; Meng, F.; Fu, W.; Wang, Z. Distribution, speciation and bioaccumulation of Hg and As in mariculture sediments from Dongshan Bay, China. *Soil Sediment Contam. Int. J.* **2016**, *25*, 489–504. [[CrossRef](#)]
24. Acharya, S.K.; Lahiri, S.; Raymahashay, B.C.; Bhowmik, A. Arsenic toxicity of groundwater in parts of the Bengal basin in India and Bangladesh: The role of quarternary stratigraphy and holocene sea-level fluctuation. *Environ. Geol.* **2000**, *39*, 1127–1137. [[CrossRef](#)]
25. Oh, S.Y.; Yoon, M.K. Chemical extraction of arsenic and heavy metals from contaminated soils under high temperature and pressure conditions in abandoned mines in South Korea. *Soil Sediment Contam. Int. J.* **2015**, *24*, 423–436. [[CrossRef](#)]
26. Klaus, P.R.; Jain, A.; Loeppert, R.H. Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* **1998**, *32*, 344–349.
27. Woolson, E.A. Emission, cycling and effects of arsenic in soil ecosystems. In *Biological and Environmental Effects of Arsenic*; Fowler, B.A., Ed.; Elsevier Science Publisher B.V.: Amsterdam, The Netherlands; New York, NY, USA; Oxford, UK, 1983; pp. 51–120.
28. Hung, J.-J.; Lu, C.-C.; Huh, C.-A.; Lin, J.-T. Geochemical controls on distributions and speciation of As and Hg in sediments along the Gaoping (Kaoping) Estuary–Canyon system off southwestern Taiwan. *J. Mar. Syst.* **2009**, *76*, 479–495. [[CrossRef](#)]
29. Liu, C.-W.; Lin, K.-H.; Kuo, Y.-M. Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan. *Sci. Total Environ.* **2003**, *313*, 77–89. [[CrossRef](#)]

30. Hong, H.; Yin, K.; Lai, X.; Du, Y.; Li, Z.; Jean, J.-S. Occurrence of Arsenic in Mudstone of the Endemic Blackfoot Disease Region, Taiwan. In *Arsenic in Geosphere and Human Diseases*; Taylor & Francis Group: London, UK, 2010; pp. 556–557.
31. Stollenwerk, K.G.; Breit, G.N.; Welch, A.H.; Yount, J.C.; Whitney, J.W.; Foster, A.L.; Uddin, M.N.; Majumder, R.K.; Ahmed, N. Arsenic attenuation by oxidized aquifer sediments in Bangladesh. *Sci. Total Environ.* **2007**. [[CrossRef](#)] [[PubMed](#)]



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