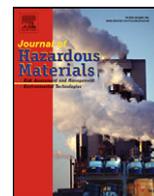




Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Assessing the characteristics of groundwater quality of arsenic contaminated aquifers in the blackfoot disease endemic area

Kuang-Liang Lu^a, Chen-Wuing Liu^{a,*}, Sheng-Wei Wang^a, Cheng-Shin Jang^b, Kao-Hung Lin^c, Vivian Hsiu-Chuan Liao^a, Chung-Min Liao^a, Fi-John Chang^a

^a Department of Bioenvironmental Systems Engineering, National Taiwan University, Taipei 106, Taiwan, ROC

^b Department of Leisure and Recreation Management, Kainan University, Taoyuan 338, Taiwan, ROC

^c Sustainable Environment Research Center, National Chen Kung University, Tainan 701, Taiwan, ROC

ARTICLE INFO

Article history:

Received 26 June 2010

Received in revised form 17 October 2010

Accepted 19 October 2010

Available online xxx

Keywords:

Blackfoot disease endemic area

Arsenic

Groundwater

Redox couples approach

Multivariate statistical techniques

ABSTRACT

Redox couples approach and multivariate statistical techniques, including factor analysis, cluster analysis and discriminant analysis, were applied to evaluate and to interpret the complex groundwater quality in the blackfoot disease endemic area, Taiwan. Most groundwater samples were characterized as Na–Ca–HCO₃ with HCO₃⁻ as the dominant anion. Total arsenic (As) concentration, predominantly as As³⁺, ranged from <1.0 to 562.7 μg/L. The patterns of measured reducing potential were consistent with those values calculated from As couple, revealing the in situ environment enhanced the accumulation of As concentration in the groundwater. Factor analysis proposed a four-factor model, comprising salination, reductive dissolution of Fe/Mn oxyhydroxides, As reduction and chemical potential factor, and explained 89.94% of total variance in groundwater. Furthermore, two factors, reductive dissolution of Fe/Mn oxyhydroxides and As reduction, suggested that the decoupled reductive processes accounted for high As concentration in this area. Cluster analysis was adopted to spatially categorize the sampled wells into three main clusters and characterized by the factor scores of the four-factor model. Two-parameter (pH and Eh) model derived from discriminant analysis can be used for preliminary assessment to determine whether the As concentration exceeds 10 μg/L with simple field measurements in this area.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Coastal aquifers have been reported to be vulnerable to arsenic (As) contamination, especially in south Asia [1,2]. Literature studies have extensively documented that the intake of As-polluted water poses the health hazards to humans, such as skin lesions and cancers occurring in both internal and external bodies [3]. Severe As contamination in groundwater, particularly in Bangladesh, resulted in developing millions of cases of arsenicosis and thousands of As-attributable excess deaths annually [4]. The mechanisms of As partitioning to the aqueous phase are complex and often intimately involve with the geochemical cycling of Fe oxyhydroxides and sulfide minerals as well as ligand displacement [1,2,5]. In addition, the mixing of groundwater and saline water further complicates the hydrogeochemical processes in coastal aquifer [6].

In Taiwan, As-contaminated aquifers typically existed in the coastal plains where was deposited in the young quaternary deltaic environment and groundwater was under reducing condition. The

most well-known region, blackfoot disease (BFD) area, located in the Chianan Plain and a total of 2758 BFD patients were reported before 1997. A neighboring region, the Choushui River alluvial fan, mainly in the southern part, high As groundwater was observed in the shallow aquifer near the sea shore [7,8]. Generally, these two regions were delineated as the BFD endemic area. The enrichment of aqueous As in this area was generally attributed to the reducing process, involved with the dissolution of As-bearing Fe oxyhydroxides [8]. Furthermore, groundwater salination was severe and dominated the local groundwater characteristics. At present, it is increasingly recognized that a transition from aerobic to anaerobic conditions, involving with the concurrent reduction of Fe³⁺ and As⁵⁺, influenced the mobilization of As in groundwater [1,2,5]. However, qualitative descriptions concerning distribution and release of As in the subsurface environment of the BFD endemic area required further study.

Multivariate statistical methods are widely adopted to assess the properties of water quality. The application is valuable for evidencing temporal and spatial variations caused by nature and anthropogenic factors. The dimensionality reduction of the large water quality data set facilitates the interpretation of the complex hydrochemical processes for the identification of pollution

* Corresponding author. Tel.: +886 2 2362 6480; fax: +886 2 2363 9557.

E-mail addresses: cwliu@ntu.edu.tw, lcw@gwater.aged.ntu.edu.tw (C.-W. Liu).

sources and influential factors [7–11]. The purpose of this study was to characterize the As-contaminated groundwater quality of the BFD endemic area by redox couples approach and multivariate statistical analyses. In situ Eh values were compared with the theoretically calculated values of various redox couples (i.e. N, Fe, As and S) to systematically define the redox state of high As groundwater. Multivariate statistical methods, including factor analysis (FA), cluster analysis (CA) and discriminant analysis (DA), were applied to explore main hydrogeochemical structure and to determine the key indicative parameters that were responsible for spatial variations of As in groundwater. In addition, the scores of various wells, obtained from DA function, were further adopted to spatially categorize the groundwater into safe ($As \leq 10 \mu\text{g/L}$) and contaminated ($As > 10 \mu\text{g/L}$) zones and then verified with the distribution of measured As concentrations. This was the first study focused on the hydrogeochemical properties of As in the BFD endemic area which covered both the BFD area of the Chianan Plain and the littoral area of the southern Choushui River alluvial fan.

2. Materials and methods

2.1. Study area

The BFD endemic area, including the littoral area of the southern Choushui River alluvial fan and BFD area in the Chianan Plain, located in the southwestern part of Taiwan and accounted for the coverage of 437.59 km² (Fig. 1). The littoral area of the Choushui River alluvial fan was in the distal-fan, comprising three aquifers and aquitards, respectively, based on hydrogeological classification to a depth of around 300 m [12]. Furthermore, according to C¹⁴ dating [13], the uppermost sequence was deposited 3–9 ka ago during the Holocene transgression followed by 35–50 ka ago in the middle sequence and 80–120 ka ago in the lowest sequence. For Chianan Plain, although the hydrogeological profiles exhibit no clear layer structure, it can be roughly divided into five aquifers via the geological ages and specific depth intervals. Aquifer 1 was mostly formed in the Holocene, and the deposits in aquifers 2–5 were classified as Miocene to Pleistocene. More relevant information could be referred herein [8].

2.2. Sampling and field measurements

A total of 33 monitoring wells from 11 hydrological stations were included whereas 23 groundwater samples (7 hydrological stations) collected from the southern Choushui River alluvial fan and the rest from the Chianan Plain at different depths (33.1–306.5 m) in December 2008 (Fig. 1 and Table 1). Notably, a hydrological station comprises several nested wells with different depths to monitor the respective aquifer. The field sampling methods used the NIEA code W103.52B set by the Taiwan Environment Protection Administration. At least 3 wellbore volumes of groundwater were pumped before sampling. Dissolved oxygen (DO), temperature, pH, electrical conductivity (EC) and electrical potential (Eh) were measured in a flow-through cell every 5 min during well purging. Cell sensors were calibrated in the field before measuring any of these parameters [14]. Water samples were collected until DO, pH and EC stabilized. After purging, a probe (MiniSonde, USA), which is 5 cm in diameter and 70 cm in length, including a data logger, a circulator and 5 sensors for DO, temperature, EC, pH and Eh measurements, was lowered down to the screen position of the well and remained there for at least 10 min before parameters of water quality were read [15]. Water samples for metal and other ionic concentration measurements were filtrated with 0.45 μm nylon filters and acidified with various acids for specific analysis [14]. Additionally, to preserve the native As species,

groundwater samples were pre-treated following Gallagher et al. [16] during sampling. Samples were then kept in ice boxes and delivered to the laboratory within 24 h. Analytical results of As species were further compared with that reported by Chen et al. [17] with the addition of H₂SO₄ for preservation.

2.3. Laboratory analyses

Dissolved ions concentrations were determined by conventional methods. The concentrations of major anions (Cl⁻, NO₃⁻ and SO₄²⁻) and cations (Na⁺, K⁺, Ca²⁺, Mg²⁺ and NH₄⁺) in groundwater samples were analyzed by Dionex DX-120 ion chromatography. Trace elements (Fe and Mn) were measured with inductively coupled plasma and atomic emission spectrometry (ICP-OES) (Varian, VISTA-MPX).

Ferrous (Fe²⁺) concentrations were measured colorimetrically using the ferrozine method [18]. The difference between total Fe and Fe²⁺ concentrations equals to Fe³⁺ concentrations. Four major As species, As(III), As(V), MMA and DMA, were separated using an anion column (Phenomenex, Nucleosil, 10 μm , 250 mm \times 4.6 mm), connected with an high performance liquid chromatography (HPLC) (Perkin Elmer, Series 200), which was interfaced to an electro-thermal atomic absorption spectrometer (AAS) (Perkin-Elmer, AA 200) and a hydride generation (HG) system (Perkin-Elmer, FIAS 100) [19]. The recovery rate of As(III) and As(V) yielded 100.7 \pm 3.8% and 97.2 \pm 4.0%, respectively. Hydrogen sulfide was measured by spectrophotometer (Thermo, GENESYS 10 VIS) following methylene blue method, detected the adsorption at 664 nm. Total alkalinity was determined by acid titration using methyl-orange. Dissolved organic carbon (DOC) was measured using the high temperature combustion method [14].

2.4. Redox potential calculations

In nature waters, there are numerous elements that participate in different redox reactions such as N, Fe, As, S and C. Theoretically, the redox potential calculated from the activity ratio of different redox couples using the appropriate NERNST-equations should yield identical redox potentials, if the chemical components are in the thermodynamic equilibrium [20]. It is therefore critically important for such calculations that the concentrations of both redox partners are well above the detection limits. Due to the absence of detected methane concentration, this study adopted N, Fe, As and S species for redox couple calculations. For N species, the nitrate/ammonia-couple is used to calculate $p\varepsilon$:

$$p\varepsilon = 14.9 - \frac{5}{4} \text{pH} + \log \frac{[\text{NO}_3^-]}{[\text{NH}_4^+]} \quad (1)$$

In natural waters with normal pH the $p\varepsilon$ may be calculated based on Fe(II) by Eq. (2) [20]:

$$p\varepsilon = 16.5 - 3\text{pH} + \log[\text{Fe}^{2+}] \quad (2)$$

Cherry et al. [21] introduced the calculation of redox potential from the concentrations of As(III) and As(V).

$$p\varepsilon = 11 - \frac{3}{2} \text{pH} + \frac{1}{2} \log \frac{[\text{H}_2\text{AsO}_4^-]}{[\text{H}_3\text{AsO}_3]} \quad \text{for } \text{pH} < 7 \quad (3)$$

$$p\varepsilon = 14.5 - 2\text{pH} + \frac{1}{2} \log \frac{[\text{HAsO}_4^{2-}]}{[\text{H}_3\text{AsO}_3]} \quad \text{for } \text{pH} > 7 \quad (4)$$

Under reducing conditions sulfate is reduced to sulfide. The redox potential may be calculated with the NERNST-equations:

$$p\varepsilon = 5.12 - \frac{5}{4} \text{pH} + \frac{1}{8} \log \frac{[\text{SO}_4^{2-}]}{[\text{H}_2\text{S}]} \quad \text{for } \text{pH} < 7 \quad (5)$$

Table 1
Hydrochemical compositions of groundwater samples in the southern Choushui River alluvial fan and Chianan Plain.

No.	Depth (m)	T (°C)	pH	EC ($\mu\text{S}/\text{cm}$)	Eh (mV)	Na ⁺ (mg/L)	K ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Fe ²⁺ (mg/L)	Fe ³⁺ (mg/L)	Mn (mg/L)	As ³⁺ ($\mu\text{g}/\text{L}$)	As ⁵⁺ ($\mu\text{g}/\text{L}$)	Cl ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	NH ₄ ⁺ (mg/L)	HCO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Sulfide (mg/L)	DOC (mg/L)
1-1	124.9	26.2	7.6	399	-99	28.4	2.1	67.4	10.2	0.3	<0.1	0.1	7.2	<1.0	1.5	<0.03	1.7	262	25.2	0.02	1.5
1-2	227.3	30.8	7.8	380	-126	56.8	1.6	31.8	3.8	<0.1	<0.1	<0.04	<1.0	<1.0	3.0	<0.03	0.4	300	3.5	0.02	1.3
2-1	51.3	25.6	7.1	6450	-155	6460.0	265.0	452	761.0	34.7	17.7	2.5	297.1	53.7	18400.0	<0.03	6.5	227	1810.0	0.02	4.3
2-2	105.4	25.9	7.4	1602	-107	260.0	24.8	43.5	42.2	0.4	<0.1	0.2	19.1	<1.0	375.0	<0.03	4.6	381	21.4	0.02	3.9
2-3	202.7	30.1	7.6	405	-120	58.8	1.8	28.3	3.8	1.7	0.6	0.1	6.8	<1.0	5.5	<0.03	0.4	305	2.8	0.02	0.4
2-4	285.0	31.9	7.9	413	-147	62.0	1.6	24.5	3.0	<0.1	<0.1	0.1	6.4	<1.0	11.9	<0.03	0.4	299	4.2	0.02	0.6
3-1	56.0	25.3	7.4	908	-131	104.0	21.6	36.3	31.0	0.7	0.1	0.2	539.7	<1.0	42.7	<0.03	0.2	264	59.5	0.03	3.2
3-2	121.6	27.1	7.4	154	-144	50.2	1.5	38.8	6.3	0.7	0.1	0.1	53.1	<1.0	6.0	<0.03	0.7	320	3.7	0.01	1.0
3-3	169.7	28.2	7.3	429	-127	48.9	1.3	36.0	3.5	<0.1	<0.1	0.2	21.3	<1.0	7.9	<0.03	0.6	288	1.6	0.01	0.8
3-4	225.1	29.0	7.4	455	-134	45.5	1.5	41.6	5.8	0.1	<0.1	0.1	15.3	<1.0	16.4	<0.03	0.4	281	6.7	0.02	0.7
4-1	33.1	26.4	6.9	1526	-81	96.1	7.6	268.0	163.0	12.5	6.2	0.5	72.8	27.5	64.0	<0.03	4.1	837	660.0	0.02	0.4
4-2	85.4	26.0	7.4	368	-80	31.4	1.7	59.6	11.2	1.5	0.4	0.2	1.8	<1.0	4.5	<0.03	1.0	312	11.1	0.01	1.3
4-3	134.7	27.3	7.3	332	-96	45.3	1.4	42.4	6.8	<0.1	<0.1	0.1	15.3	<1.0	3.0	<0.03	0.6	282	6.5	0.01	1.1
4-4	182.2	28.2	7.4	336	-112	43.2	1.2	36.3	5.3	<0.1	<0.1	0.2	2.2	<1.0	5.0	<0.03	0.6	259	7.4	0.01	1.1
4-5	266.7	30.0	7.6	344	-120	48.7	1.5	43.7	6.5	<0.1	<0.1	0.1	9.9	<1.0	7.4	<0.03	0.3	254	10.3	0.02	1.0
5-1	66.3	25.4	7.0	2070	-110	384.0	38.6	91.3	96.8	6.7	3.6	0.7	407.8	<1.0	814.0	0.2	8.8	430	95.6	0.02	3.0
5-2	152.5	27.6	7.3	560	-149	57.5	1.8	44.0	6.3	<0.1	<0.1	0.1	73.8	<1.0	45.7	<0.03	0.6	300	7.2	0.04	1.5
6-1	56.3	25.9	7.2	15,000	-178	6080.0	277.0	235.0	725.0	5.2	2.4	0.1	89.8	<1.0	11200.0	0.1	11.0	393	1520.0	0.02	2.9
6-2	146.0	27.9	7.4	1127	-179	158.0	4.2	79.9	18.6	1.9	0.7	0.2	97.8	<1.0	243.0	<0.03	0.9	302	30.0	1.36	1.4
7-1	98.1	25.9	7.3	6290	-144	2160.0	85.9	43.1	167.0	1.9	0.9	0.1	44.1	<1.0	3670.0	<0.03	8.9	605	287.0	0.02	5.2
7-2	174.7	29.6	7.5	502	-149	80.1	2.4	20.8	4.8	<0.1	<0.1	0.1	23.3	<1.0	18.4	<0.03	0.7	324	25.9	0.02	2.2
7-3	221.3	29.6	7.6	1517	-148	283.0	10.0	24.7	21.0	<0.1	<0.1	0.1	32.5	<1.0	332.0	<0.03	1.2	340	32.6	0.02	2.6
7-4	263.0	30.8	7.5	478	-147	84.0	2.5	13.5	4.7	<0.1	<0.1	<0.04	7.9	<1.0	3.0	<0.03	0.9	342	2.2	0.01	2.3
8-1	90.7	27.1	7.3	1050	-123	222.0	5.7	23.7	13.5	1.8	0.8	<0.04	373.9	<1.0	133.0	<0.03	2.0	551	7.9	0.02	4.2
8-2	167.0	29.6	7.6	559	-166	115.0	4.6	13.7	9.1	0.2	<0.1	0.1	136.5	<1.0	2.5	<0.03	1.5	432	3.2	0.02	3.4
8-3	246.8	31.0	7.6	514	-152	101.0	3.3	15.3	7.0	<0.1	<0.1	<0.04	71.5	<1.0	2.5	<0.03	0.9	384	2.6	0.02	3.1
8-4	306.5	31.9	7.7	537	-168	112.0	3.0	13.7	5.7	<0.1	<0.1	<0.04	74.8	<1.0	<1.4	<0.03	1.4	395	3.7	0.02	3.2
9-1	41.0	25.5	7.1	1023	-144	239.0	16.8	15.5	26.2	0.5	0.1	<0.04	499.0	<1.0	99.3	0.1	5.9	670	30.9	0.02	9.4
9-2	176.0	28.6	7.2	600	-121	134.0	5.2	18.3	10.2	2.7	1.2	0.2	149.3	<1.0	<1.4	0.1	1.9	515	8.9	0.02	5.1
10-1	76.0	27.2	7.2	2000	-124	694.0	13.3	43.2	46.0	3.8	1.9	<0.04	562.7	<1.0	754.0	0.1	11.7	814	0.2	0.02	7.9
10-2	117.0	29.3	7.8	999	-150	230.0	8.1	10.9	12.8	<0.1	<0.1	<0.04	519.7	33.7	106.0	<0.03	4.3	617	5.9	0.03	6.8
11-1	80.0	26.2	7.2	2000	-122	704.0	14.8	58.5	59.4	4.5	2.2	0.2	527.7	<1.0	973.0	0.1	7.8	641	0.1	0.02	13.8
11-2	204.0	29.2	7.3	967	-157	222.0	9.1	33.8	25.4	1.9	0.8	0.3	298.6	<1.0	188.0	<0.03	4.4	486	6.8	0.01	5.8

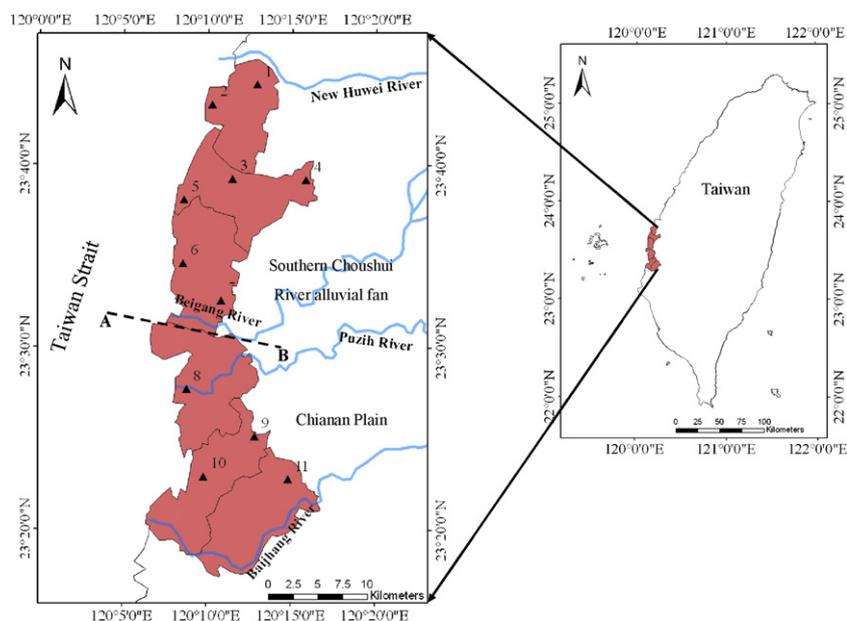


Fig. 1. Study area and location of groundwater sampling stations. Solid triangles represented the hydrogeological stations. Line A–B geographically divided the southern Choushui River alluvial fan and the Chianan Plain.

$$p\varepsilon = 4.25 - \frac{9}{8}\text{pH} + \frac{1}{8} \log \frac{[\text{SO}_4^{2-}]}{[\text{HS}^-]} \quad \text{for } \text{pH} > 7 \quad (6)$$

Furthermore, the conversion between Eh and $p\varepsilon$ was performed by the following equation:

$$\text{Eh} = \frac{2.3RT}{F} p\varepsilon \quad (7)$$

where $F=1$ faraday (=96,490 C/mol); R =gas constant (=8.314 J/mol K); and T =temperature in K.

2.5. Multivariate analysis

2.5.1. Factor analysis (FA)

Factor analysis (FA) yields the general relationship between measured chemical variables by elucidating the multivariate patterns that may help to classify the original data. The geochemical interpretation of factors may provide insight of the main processes that govern the distribution of hydrochemical variables. In this study, only factors with eigenvalues that exceed one are retained for analyses [22].

2.5.2. Cluster analysis (CA)

Cluster analysis (CA) uses an analysis of variance approach to measure a distance between variable clusters, attempting to minimize the sum of squares of any two clusters that could be formed at each step. Hydrochemical data with similar properties are clustered in a group. To avoid misclassifications arising from the different order of magnitude of the variables, the variance for each variable is standardized. The Ward's method is used to carry out CA [23]. In this study, eighteen hydrochemical parameters, including T, pH, EC, Eh, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} , Mn, As^{3+} , As^{5+} , Cl^- , NH_4^+ , HCO_3^- , SO_4^{2-} and DOC concentrations, are considered to evaluate the characteristics of the groundwater by FA and CA.

2.5.3. Discriminant analysis (DA)

Stepwise DA is employed to establish the discrimination model with hydrochemical parameters of groundwater between groups step-by-step [23]. This study partitions groundwater into two groups in advance based on the Taiwan drinking water standard of As concentration (10 $\mu\text{g/L}$). Scores of each sites, calculated by

substituting standardized values of hydrochemical parameters to the discriminant functions, represent the tendency of classification, i.e. the group with $\text{As} \leq 10 \mu\text{g/L}$ has relative high scores in contrast to the group with $\text{As} > 10 \mu\text{g/L}$ in this study. This work used SPSS to perform FA, CA and DA [24].

3. Results and discussion

3.1. Hydrochemistry of groundwater

3.1.1. General hydrochemistry

Hydrochemical data of 33 analyzed groundwater samples were summarized in Table 1. Groundwater pH was predominantly as mildly alkaline ($\text{pH} > 7$) and reducing in nature. Electrical conductivity varied widely from 154 to 15,000 $\mu\text{S/cm}$ and the highest value occurred at shallow aquifer in the southern Choushui River alluvial fan, sample 6-1. According to the classification of Piper diagram, type II water ($n=15$) were prevailing in this area followed by types IV ($n=9$), I ($n=8$) and III ($n=1$) waters (Fig. 2). Type II water was likely caused by the deposition of fine particles (silty sand and clay) in the coastal area, leading to slow flow rate and the formation of stagnant groundwater [25]. Seawater intrusion resulted in the existence of saline water type (type IV), particularly in the shallow aquifer, whereas the source in the deeper aquifer could be attributed to the mixing of the ancient seawater. Furthermore, type IV samples contained higher As concentration ($>10 \mu\text{g/L}$). Most of the samples were Na–Ca– HCO_3 type with HCO_3^- as the dominant anion, except for type IV samples with Cl^- .

Ammonia ion (NH_4^+) was the major N-species, spreading from 0.2 to 11.7 mg/L, which can be ascribed to either the short of recharge or the depletion by bacterial mediated reactions [26]. For iron, dominant species was Fe^{2+} , ranging from <0.1 to 34.7 mg/L with the average of 2.6 mg/L. Furthermore, Fe^{3+} concentrations spanned in the narrow range but varied concurrently with Fe^{2+} . Under reducing conditions, concentration of Mn was also high, reaching up to 2.5 mg/L. The spatial pattern of SO_4^{2-} was consistent with areal distribution of saline samples with the maximum value of 1810.0 mg/L in sample 2-1 which also contained the highest concentration of Cl^- . In addition, sulfide concentrations were generally less than 0.05 mg/L with the highest concentration of 1.36 mg/L in

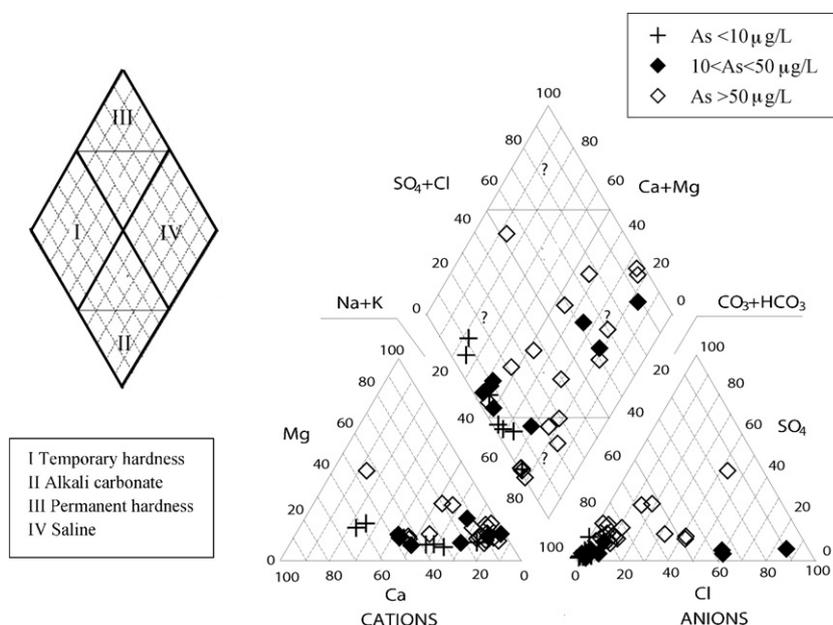


Fig. 2. Piper plot of sampled groundwaters in the southern Choushui River alluvial fan and Chianan Plain.

sample 6-2 where the lowest Eh was also measured. Concentrations of HCO_3^- were high and spread in the range of 227–837 mg/L. Dissolved organic carbon concentrations spanned from 0.4–13.8 mg/L. In addition to the dissolution of the carbonate, dissolved organic carbon may be an active source for HCO_3^- in groundwater [27].

3.1.2. Distribution of As species and redox potential calculation

Analysis of groundwater samples yielded a range of As concentrations (<1.0–562.7 $\mu\text{g/L}$), dominated by As^{3+} (accounted for 73–100% of total As), with 76% of the selected samples exceeding the Taiwan drinking water standard of As concentrations (10 $\mu\text{g/L}$) (Table 1, Fig. 3). No organic forms of As species (MMA and DMA) were detected. Comparing with $\text{As}^{3+}/\text{As}^{5+}$ ratio (2.6) reported by Chen et al. [17], a relative high ratio in this study was observed as the result of non-detected As^{5+} in the most water samples. The cause was partially attributed to different pretreatment methods on samples. The predominance of As^{3+} was in agreement with the reduced geochemical environment of the water (Table 1). Only two samples, 2-2 and 10-2, contained higher As^{5+} concentrations. The coexistence of As^{3+} and As^{5+} under generally reducing conditions may be due to the slow reduction kinetics of As^{5+} released during the reductive dissolution of Fe oxyhydroxides [28]. Arsenite may also be converted to arsenate by reacting with an oxidant. According to analytical data, only sample 1-2 contained non-detectable As concentration and located in the northern part of the study area where low As concentration was reported in this area [8]. Additionally, groundwater samples collected from the Chianan Plain contained higher As levels than those in the southern Choushui River alluvial fan [8].

Vertical profile of the As_{tot} concentrations (sum of As^{3+} and As^{5+}) showed that high As concentration samples existed within depth from 30 to 80 m and 80 to 200 m in the southern Choushui River alluvial fan and the Chianan Plain, respectively (Fig. 3a) [8]. Although high levels of As_{tot} , Fe_{tot} (sum of Fe^{2+} and Fe^{3+}) and Mn concentrations occurred in the shallow depth (<100 m) (Fig. 3a–c), no significant correlations were observed between As with Fe and Mn. The approximate tendency of DOC and HCO_3^- was observed (Fig. 3d and e) and correlated significantly ($r^2 = 0.41$, $p < 0.05$), suggesting that the degradation of organic matter resulted in generation of DOC and high HCO_3^- in the groundwater and caus-

ing subsequent redox reaction [29]. Distinct correlations between As_{tot} with DOC ($r^2 = 0.58$, $p < 0.05$), HCO_3^- ($r^2 = 0.32$, $p < 0.05$) and NH_4^+ ($r^2 = 0.30$, $p < 0.05$) supported the mobilization of As in the groundwater pertaining to anoxic environment as the result of biodegrading of organic matter [30,31]. High SO_4^{2-} concentrations in the shallow depth (less than 100 m) could be subject to intrusion of seawater in the littoral area (Fig. 3). Poor correlation between As and SO_4^{2-} indicated that As was not directly mobilized by the dissolution sulfide minerals such as arsenopyrite [2].

The measured Eh value usually yielded an accuracy within ± 50 mV [20]. Alternatively, we can measure the major redox couples as indicators to determine the redox status of the water by using the NERNST equation [32]. In general, without influence by oxygen, the redox values calculated from the Fe and As couples were consistent and also found herein (Fig. 4). Regardless of the positive values calculated from N species, the in situ negative Eh values fell within the values calculated from Fe/As and S couples, revealing the in situ redox gradient moved from Fe/As-reducing toward S-reducing environment as evidenced by the detection of sulfide concentration (Fig. 4). Further, the distribution patterns of in situ measurements were consistent with those values calculated via As couple (data not shown), indicating that local hydrogeochemical condition may be in favor of the enrichment of As in the groundwater. Cherry et al. [21] indicated that the As(III)–As(V) couple is an useful tool in the assessment of the redox status of the in situ hydrogeochemical conditions as it is responding to the natural $p\text{-E}$ -condition fast enough to give a representative indication of them. In spite of the presence of sulfide concentration in all collected samples, the relatively high negative values calculated from S redox couple could be pertaining to the slow equilibration of this system as well as high sulfate concentration resulted from the seawater intrusion as described above.

3.2. Factor and cluster analyses

A four-factor model was determined by FA of which their percentage of variance and cumulative percentage of variance explained 89.94% of the total variance in the data set. The terms, “strong”, “moderate”, and “weak” as applied to factor loadings, referred to absolute loading values of >0.75, 0.75–0.5 and 0.5–0.3,

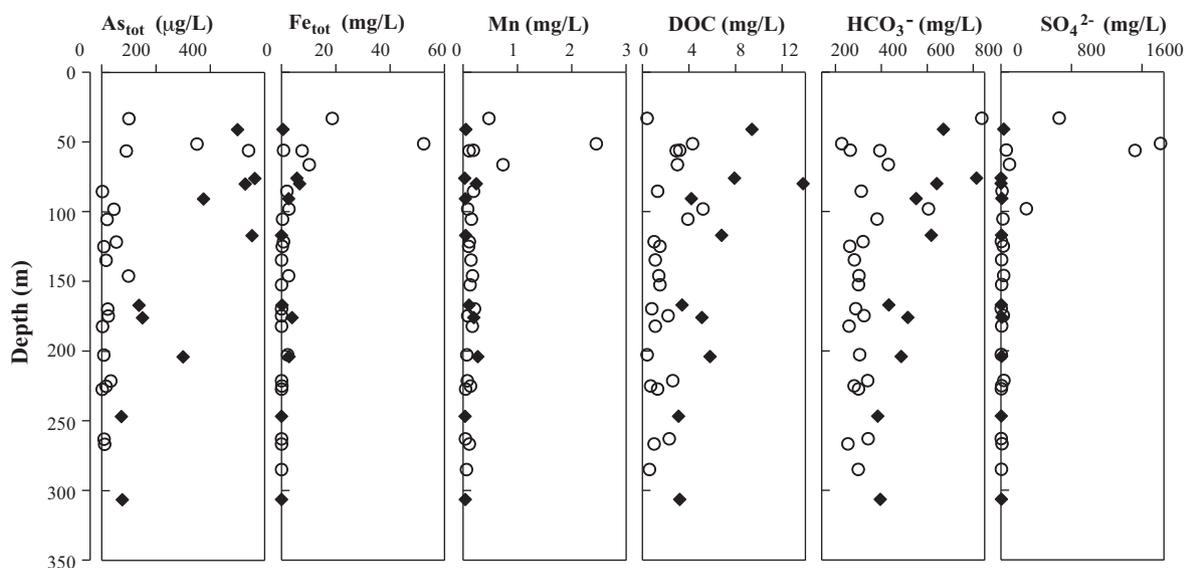


Fig. 3. Profiles of the distribution of As and other solutes in groundwater with depth. Solid diamond and hollow circle separately represented samples taken from the Chianan Plain and southern Choushui River alluvial fan. As_{tot} and Fe_{tot} represented the total concentrations of As (As^{3+} and As^{5+}) and Fe (Fe^{2+} and Fe^{3+}) species, respectively.

respectively, presented the loading of the varimax rotation factor matrix for the four-factor model. This study selected absolute factor loadings of over 0.7 to evaluate the relationships between the factors and hydrochemical data. Factor 1, which comprised strong positive loading on EC, Na^+ , K^+ , Mg^{2+} , Cl^- and SO_4^{2-} , accounted for 32.02% of the total variance. The areal distribution of factor score of factor 1 had high and positive values at the shallow depth in the southern Choushui River alluvial fan. These hydrochemical items were the dominant solutes in the seawater and significantly correlated. Groundwater salination in this area was mainly attributed to the sea water intrusion caused by over-pumping and partially caused by residence of ancient seawater [33,34]. Thus, factor 1 was denoted as the salination factor.

The second factor accounted for 29.87% of the total variance and showed high loadings on Ca^{2+} , Fe^{2+} , Fe^{3+} , Mn and As^{5+} . The close correspondence between the aqueous As and Ca suggested that dissolution of calcite accompanied the release of As, driven by CO_2 generated from the microbial respiration process [35]. In contrast to As^{3+} , As^{5+} was preferred to be the dominant host of As

species onto the surface of Fe/Mn oxyhydroxides [2]. The presence of dissolved Fe species, Mn and As^{5+} in the factor 2 were consistent with the mechanism of reductive dissolution of Fe/Mn oxyhydroxides via respiration of organic matter, with congruent release of associated adsorbed and coprecipitated As [35,36]. This factor was denoted as the reductive dissolution of Fe/Mn oxyhydroxides.

Factor 3 explained 16.76% of the total variance with strong loadings of As^{3+} , HCO_3^- and DOC. Many studies indicated that microbial activities accelerated the diagenetic processes, involving mobilization of As from sediment with high organic matters [37,38]. In addition to the indirect pathway of reductive dissolution of Fe/Mn oxyhydroxides, direct transformation between As species (i.e. As^{5+} to As^{3+}) also enhanced the mobility of As in the groundwater [2,39]. With regard to the significant relation between aqueous Fe and As(V) but the predominant As species as As(III) in the groundwater, the As-rich groundwater in this area was postulated as a decoupled processes, combined with Fe/Mn and As reduction. Islam et al. [40] indicated that the decoupled reduction of Fe(III) and As(V) may, therefore, reflect adaptation of the respiratory pathway in the microorganisms and the capacity for arsenic release was critically limited by the availability of electron donor in the sediments. Such characterizations observed herein supported the formation of reducing environment triggering the redox couples, i.e. N, Fe/Mn, As, S and C reacted orderly. Accordingly, As was released in groundwater due to the favorable reducing condition and this reduction was coupled to the microbial degradation of organic matter.

Factor 4 explained 11.30% of the total variance. It exhibited high positive loadings on T and pH, and negative loading on Eh. The formation of reducing environment could increase pH followed by the decreasing Eh. Hence, this factor denoted as the chemical potential factor [41] which governed the chemical reactions of As in the hydrogeo-environment.

Cluster analysis was adopted to spatially explain the similarity of the groundwater quality among wells and depicted a dendrogram, composing of three major clusters. Results of grouped samples identified by CA were then compared with the common properties determined by FA. Cluster 1 comprised 20 samples (wells number 1-1, 1-2, 2-2 to 2-4, 3-2 to 3-4, 4-2 to 4-5, 5-2, 6-2, 7-2 to 7-4 and 8-2 to 8-4) with mean scores among the four factors were the dominant cluster and typified the groundwater quality in the BFD endemic area. Cluster 2 contained 11 samples (wells number 3-1,

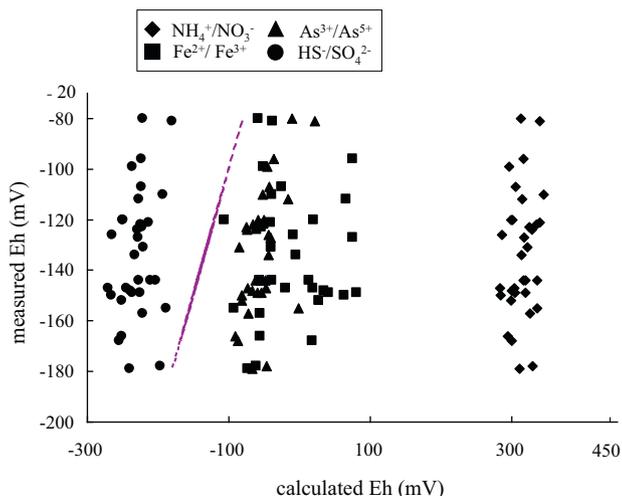


Fig. 4. Comparison of field measured Eh values with calculated Eh values using different redox couples. Solid line represented the in situ measured Eh values.

4-1, 5-1, 7-1, 8-1, 9-1, 9-2, 10-1, 10-2, 11-1 and 11-2) with high score values in factors 3 and 4, representing the groundwater with higher As concentrations in the shallow depth. Only two samples (wells number 2-1 and 6-1) were categorized as cluster 3. Cluster 3 had high score values in factors 3 and 4 and also had extremely high score values in factor 1, indicating the groundwater under both As-contaminated and severe salination conditions.

3.3. Discriminant analysis

Stepwise DA was carried out to derive the discriminant function which was applied to spatially delineate the groundwater into safe ($\leq 10 \mu\text{g/L}$) and contaminated ($>10 \mu\text{g/L}$) zones. All measured hydrochemical parameters, exclusive of As species, were considered to construct the discriminant function model. The derived discriminant function was as follow:

$$\text{DA Function} = 1.216\text{pH} + 0.983\text{Eh} - 0.03 \quad (8)$$

Hydrochemical parameters pH and Eh, the fourth factor determined by the FA in section 3.2, were identified as the key parameters in the discriminant function. The correct classification rate is 87.9% using the developed discriminant function (Table 2).

Table 2
Comparison of the correctness of the predicted results with field measurements.

		Field measurement	
		As conc. $\leq 10 \mu\text{g/L}$	As conc. $>10 \mu\text{g/L}$
Predicted Result	As conc. $\leq 10 \mu\text{g/L}$	7	1
	As conc. $>10 \mu\text{g/L}$	3	22

Seven and twenty-two groundwater samples characterized by $\leq 10 \mu\text{g/L}$ and $>10 \mu\text{g/L}$ As concentration, respectively, were classified correctly. One and three samples with As concentration $\leq 10 \mu\text{g/L}$ and $>10 \mu\text{g/L}$, respectively, were misclassified by the discriminant function model.

The discriminant scores of each groundwater samples were acquired from its standardized values of hydrochemical parameters and discriminant function. The score distributions at four layers, including 0–80 m, 80–160 m, 160–230 m and >230 m, were spatially mapped (Fig. 5a) and compared with the measured total As concentration of the corresponding layers in the BFD endemic area (Fig. 5b). The scores of safe sample sites possessed high pH and Eh features were significantly larger than those from con-

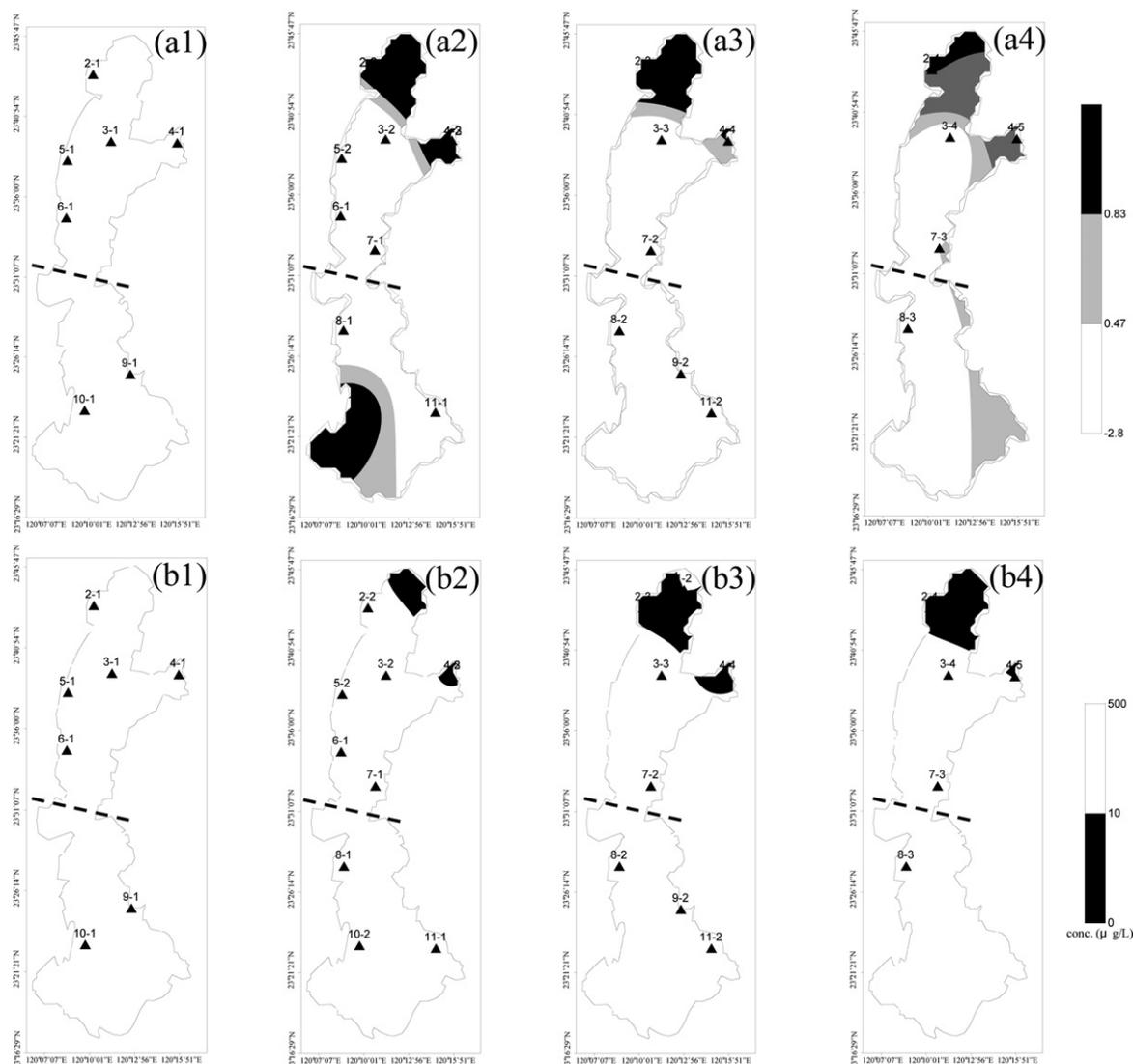


Fig. 5. Spatial distribution of DA scores and total As concentration (in $\mu\text{g/L}$) at different layers in the BFD endemic area. (a) DA scores, (b) total As concentration. 1–4 denote the layer 1 (0–80 m), layer 2 (80–160 m), layer 3 (160–230 m) and layer 4 (>230 m), respectively. Dotted line defined the boundary between the southern Choushui River alluvial fan and the Chianan Plain. Triangle symbol represented sampled wells.

taminated sample sites. In addition, the DA scores spread from -2.80 to 2.39 with a transition zone of scores range from 0.47 to 0.83 separated the contaminated (scores between -2.80 and 0.47) and safe (scores between 0.83 and 2.39) zones. Basically, except layers 2 (80 – 160 m) and 4 (>230 m), the zonations delineated by scores of discriminant function model were similar with the distribution of measured As concentrations (Fig. 5). The grey transition zone provided a smooth transitive area between contaminated and safe zones which accounted for the uncertainty of the discriminant function in delineating the contaminated and safe zones (Fig. 5). Moreover, the derived discriminant function can be used as a screening model to assess whether the As concentration is above or below $10 \mu\text{g/L}$ without measurement of As concentration in apriori.

4. Conclusions

We assessed the spatial variations in groundwater quality of the BFD endemic area in Taiwan. Local groundwaters were under moderate to strong reducing conditions with 76% samples exceeding $10 \mu\text{g/L}$ in As. We have showed that the redox potential distribution of in situ measurements was consistent with those values computed from As couple and enhanced the formation of high As groundwater. Factor analysis revealed that the major geochemical process is pertaining to reductive dissolution of As-bearing Fe/Mn oxyhydroxides in this area. We further derived a two-parameter (pH and Eh) model which yielded highly correct assignments to classify samples with $\text{As} \leq 10 \mu\text{g/L}$ and $>10 \mu\text{g/L}$. Generally, if the groundwater is acidic and under reduced condition, the arsenic concentration will exceed $10 \mu\text{g/L}$ and vice versa. This technique is readily applicable to pre-determine whether the As concentration exceeds $10 \mu\text{g/L}$ threshold value in the study site using simple in situ measured parameters. Moreover, it correctly delineated the As-contaminated zone among different depths and provided useful information for effectively implementing the safe use of groundwater and formulating an optimal groundwater monitoring plan.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financially supporting this research under Contract No. NSC-95-2313-B-002-050-MY3.

References

- [1] R.T. Nickson, J.M. McArthur, W.G. Burgess, K.M. Ahmed, P. Ravenscroft, M. Rahman, Arsenic poisoning of Bangladesh groundwater, *Nature* 395 (1998) 338.
- [2] P.L. Smedley, D.G. Kinniburgh, A review of the source, behavior, and distribution of arsenic in nature water, *Appl. Geochem.* 17 (2002) 517–568.
- [3] A.H. Smith, P.A. Lopipero, M.N. Bates, C.M. Steinmaus, Arsenic epidemiology and drinking water standards, *Science* 296 (2002) 2145–2146.
- [4] W.H. Yu, C.M. Harvey, C.F. Harvey, Arsenic in groundwater in Bangladesh: a geostatistical and epidemiological framework for evaluating the death effects and potential remedies, *Water Resour. Res.* 39 (2003) 1146.
- [5] M.A. Halim, R.K. Majumder, S.A. Nessa, Y. Hiroshiro, M.J. Uddin, J. Shimada, K. Jinno, Hydrogeochemistry and arsenic contamination of groundwater in the Ganges Delta Plain, Bangladesh, *J. Hazard. Mater.* 16 (2009) 1335–1345.
- [6] W.S. Moore, The subterranean estuary: a reaction zone of groundwater and seawater, *Mar. Chem.* 65 (1999) 111–125.
- [7] C.W. Liu, K.H. Lin, Y.M. Kuo, Application of factor analysis in the assessment of groundwater quality in a blackfoot disease area in Taiwan, *Sci. Total Environ.* 313 (2003) 77–89.
- [8] S.W. Wang, C.W. Liu, C.S. Jang, Factors responsible for high arsenic concentrations in two groundwater catchments in Taiwan, *Appl. Geochem.* 22 (2007) 460–467.
- [9] A. Kouras, I. Katsoyiannis, A. Voutsas, Distribution of arsenic in groundwater in the area of Chalkidiki, Northern Greece, *J. Hazard. Mater.* 147 (2007) 890–899.
- [10] A.K. Krishna, M. Satyanarayanan, P.K. Govil, Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: a case study from Patancheru, Medak District, Andhra Pradesh, India, *J. Hazard. Mater.* 167 (2009) 366–373.
- [11] Y.M. Kuo, F.J. Chang, Dynamic factor analysis for evaluating groundwater arsenic trends, *J. Environ. Qual.* 39 (2010) 176–184.
- [12] Central Geological Survey, Project of groundwater monitoring network in Taiwan during first stage—research report of Chou-Shui River alluvial fan, Water Resources Bureau, Taiwan, 1999.
- [13] C.Y. Huang, Foraminiferal analysis and stratigraphic correlation on the sub-surface geology of the Choushuichi alluvial fan, in: Conf. on Groundwater and Hydrogeology of Choushui River Alluvial Fan, Taipei, Taiwan, February 8–9, Water Resources Bureau, Taipei, 1996, pp. 55–66.
- [14] APHA (American Public Health Association), Standard Methods for the Examination of Water and Waste Water, 20th ed., APHA, American Water Works Association, and Water Pollution Control Federation, Washington, DC, 1998.
- [15] W.F. Chen, T.K. Liu, Dissolved oxygen and nitrate of groundwater in Choushui Fan-Delta, western Taiwan, *Environ. Geol.* 44 (2003) 731–737.
- [16] P.A. Gallagher, C.A. Schwegel, A. Parks, B.M. Gamble, L. Wymmer, J.T. Creed, Preservation of As(III) and As(V) in drinking water supply samples from across the United States using EDTA and acetic acid as a means of minimizing iron-arsenic coprecipitation, *Environ. Sci. Technol.* 38 (2004) 2919–2927.
- [17] S.L. Chen, S.R. Dzung, M.H. Yang, K.H. Chlu, G.M. Shieh, C.M. Wai, Arsenic species in groundwaters of the blackfoot disease area, Taiwan, *Environ. Sci. Technol.* 28 (1994) 877–881.
- [18] D.R. Lovley, E.J.P. Phillips, Rapid assay for microbially reducible ferric iron in aquatic sediments, *Appl. Environ. Microbiol.* 153 (1987) 1536–1540.
- [19] Y.K. Huang, K.H. Lin, H.W. Chen, C.C. Chang, C.W. Liu, M.H. Yang, Y.M. Hsueh, As species contents at aquaculture farm and in farmed mouthbreeder (*Oreochromis mossambicus*) in BFD hyperendemic areas, *Food Chem. Toxicol.* 41 (2003) 1491–1500.
- [20] M. Kolling, Comparison of different methods for redox potential determination in nature waters, in: J. Schuring, H.D. Schulz, W.R. Fischer, J. Bottcher, W.H.M. Duijnsveld (Eds.), *Redox-Fundamentals, Processes and Applications*, Springer, New York, 2000, pp. 42–54.
- [21] J.A. Cherry, A.U. Shaik, D.E. Tallmann, R.V. Nicholson, Arsenic species as an indicator of redox conditions in groundwater, *J. Hydrol.* 43 (1979) 373–392.
- [22] R.A. Reymont, K.H. Joreskog, *Applied Factor Analysis in the Natural Sciences*, Cambridge University Press, New York, 1993.
- [23] S. Sharma, *Applied Multivariate Techniques*, Wiley & Sons, New York, 1996.
- [24] SPSS Inc., *SPSS BASE 8.0—Application Guide*, SPSS Inc., Chicago, USA, 1998.
- [25] M.A. Halim, R.K. Majumder, S.A. Nessa, K. Oda, Y. Hiroshiro, B.B. Saha, S.M. Hossain, S.K.A. Latif, M.A. Islam, K. Jinno, Groundwater contamination with arsenic in Sherajdikhan, Bangladesh: geochemical and hydrological implications, *Environ. Geol.* 58 (2009) 73–84.
- [26] V.S. Chauhan, R.T. Nickson, D. Chauhan, L. Iyengar, N. Sankaramakrishnan, Ground water geochemistry of Ballia district, Uttar Pradesh, India and mechanism of arsenic release, *Chemosphere* 75 (2009) 83–91.
- [27] P.L. Smedley, M. Zhang, G. Zhang, Z. Luo, Mobilization of arsenic and other trace elements in fluvio-lacustrine aquifers of the Huhhot Basin, Inner Mongolia, *Appl. Geochem.* 18 (2003) 1453–1477.
- [28] K.G. Stollenwerk, G.N. Breit, A.H. Welch, J.C. Yount, J.W. Whitney, A.L. Foster, M.N. Uddin, R.K. Majumder, N. Ahmed, Arsenic attenuation by oxidized aquifer sediments in Bangladesh, *Sci. Total Environ.* 379 (2007) 133–150.
- [29] R. Artinger, G. Buckau, S. Geyer, P. Fritz, M. Wolf, J.I. Kim, Characterization of groundwater humic substances: influence of sedimentary organic carbon, *Appl. Geochem.* 15 (2000) 97–116.
- [30] M.A. Hasan, K.M. Ahmed, O. Sracek, P. Bhattacharya, M. von Bromssen, S. Broms, J. Fogelstrom, M.L. Mazumder, G. Jacks, Arsenic in shallow groundwater of Bangladesh: investigations from three different physiographic settings, *Hydrogeol. J.* 15 (2007) 1507–1522.
- [31] J.M. McArthur, P. Ravenscroft, S. Safiulla, M.F. Thirlwall, Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh, *Water Resour. Res.* 37 (2001) 109–117.
- [32] W. Stumm, Interpretation and measurement of redox intensity in natural waters, *Schweiz. Z. Hydrol.* 46 (1984) 291–296.
- [33] Y.B. Lin, Y.P. Lin, C.W. Liu, Y.C. Tan, Mapping of spatial multi-scale sources of arsenic variation in groundwater on ChiaNan Floodplain of Taiwan, *Sci. Total Environ.* 370 (2006) 168–181.
- [34] C.W. Liu, K.H. Lin, S.Z. Chen, C.S. Jang, Aquifer salinization in the Yun-Lin Coastal Area, Taiwan, *J. Am. Water Res. Assoc.* 39 (2003) 817–827.
- [35] C.F. Harvey, C.H. Swartz, A.B.M. Badruzzaman, N. Keon-Blute, V. Niedan, D. Brabander, P.M. Oates, K.N. Ashfaq, S. Islam, H.F. Hemond, M.F. Ahmed, Arsenic mobility and groundwater extraction in Bangladesh, *Science* 298 (2002) 1602–1606.
- [36] B.D. Kocar, M.L. Polizzotto, S.G. Benner, S.C. Ying, M. Ung, K. Ouch, S. Samreth, B. Suy, K. Phan, M. Sampson, S. Fendorf, Integrated biogeochemical and hydrologic processes driving arsenic release from shallow sediments to groundwaters of Mekong delta, *Appl. Geochem.* 23 (2008) 3059–3071.
- [37] J. Akai, K. Izumi, H. Fukuhara, H. Masuda, S. Nakano, T. Yoshimura, H. Ohfui, H.M. Anwar, K. Akai, Mineralogical and geomicrobiological investigations on groundwater arsenic enrichment in Bangladesh, *Appl. Geochem.* 19 (2004) 215–230.

- [38] P. Bhattacharya, A.H. Welch, K.M. Ahmed, G. Jacks, R. Naidu, Arsenic in groundwater of sedimentary aquifers, *Appl. Geochem.* 19 (2004) 163–167.
- [39] J. Zobrist, P.R. Dowdle, J.A. Davis, R.S. Oremland, Mobilization of arsenite by dissimilatory reduction of adsorbed arsenate, *Environ. Sci. Technol.* 34 (2000) 4747–4753.
- [40] F.S. Islam, A.G. Gault, C. Boothman, D.A. Polya, J.M. Charnock, D. Chatterjee, J.R. Lloyd, Role of metal-reducing bacteria in arsenic release from Bengal delta sediments, *Nature* 430 (2004) 68–71.
- [41] H.C. Helgeson, T.H. Brown, R.H. Leeper, Mineral equilibria II: chemical potential diagrams, in: D.K. Nordstrom, J.L. Munoz (Eds.), *Geochemical Thermodynamics*, Blackwell, Cambridge, 1994, pp. 247–283.