Mobilisation of arsenic in the groundwater of the Blackfoot disease area in the Chia-Nan plain, Southwestern Taiwan

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Motivation

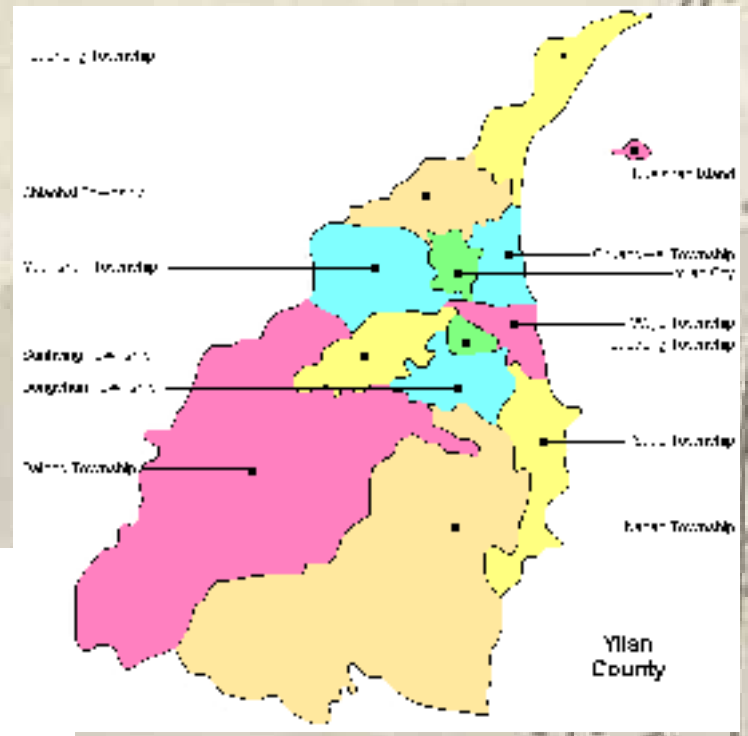
- The etiological agent of the BFD is rather complicated. Intriguingly, the symptoms for the patients that drank groundwater from the artesian well water in the southwestern coast of Taiwan (Chia-Nan plain) were significantly different from those in the northeastern coast of Taiwan (I-Lan plain). The chemistry of both groundwaters are mostly alike. The cause for BFD could be due to the differences in the constituents and biochemical structures of potential etiological agents, which remains a matter of debate. In this work we tried to emphasize on the mobility of arsenic in BFD groundwater.

Distribution of documented world problems with As in groundwater

Source: Smedley and Kinniburgh, Applied Geochemistry, 17, 259-284, 2002

Map of the study area

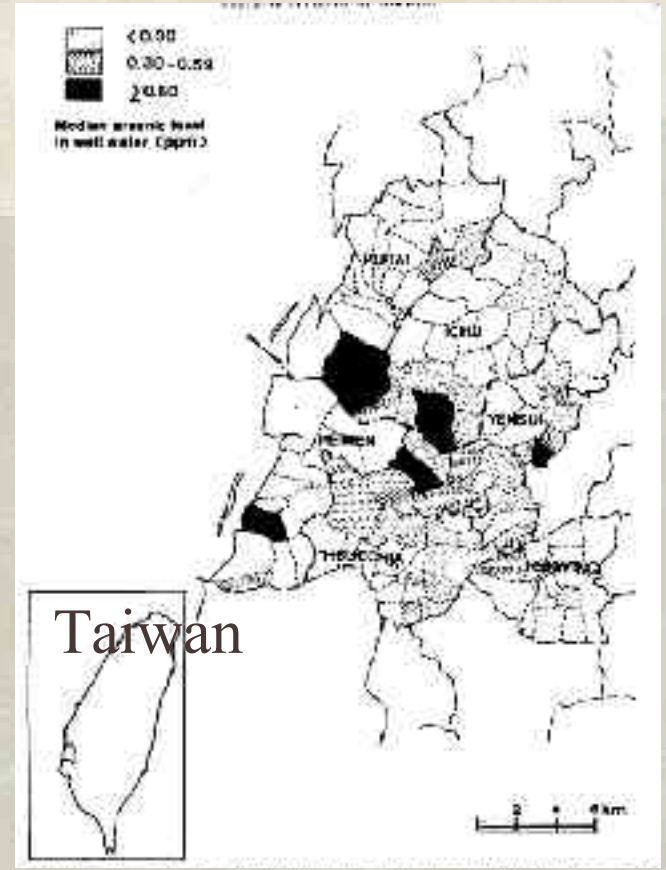
TAIWAN



I-Lan Plain (NE Taiwan)

Chia-Nan Plain
(SW Taiwan)

Chia-Nan Plain, SW Taiwan



- 42 rural villages of six townships (Putai, Ichu, Yenshui, Hsia-Inn, Hseuchia, Peimen) in coastal region of SW Taiwan were studied showing median arsenic level in well water (mg/L) (Wu et al., 1989)
- 14 villages were dependent upon artesian water wells.
- 28 villages have alternative water source (surface or shallow aquifer).

History of Blackfoot Disease (BFD)

- Sporadic cases of BFD occurred in the early 20th century and peak incidence was noted between 1956 and 1960, with prevalence rates ranged from 6.51 to 18.85 per 1000 population in different endemic villages of SW coast of Taiwan (Tseng, 2003).
- The incidence of BFD decreased dramatically after the implementation of tap water in these endemic villages over the past 2-3 decades (Tseng, 2003).
- Since 1990, almost no new BFD patients were found.

History of BFD (Cont'd)

- Arsenic in groundwater of I-Lan Plain does not have dose-response relationship to mortality rate, while fluorescent intensity has the dose-response relationship to mortality rate (Lin et al., 1986).
- The bladder and skin cancers mortality rates for males in the high As and high fluorescent intensity areas were higher than whole Taiwan areas, but not for females (Lin et al., 1986).
- In the low As and fluorescent intensity area, the skin cancer mortality rates for males and bladder cancer mortality rates for females were higher than in the high As and high fluorescent intensity area including whole Taiwan (Lin et al., 1986).
- Irrespective of sex and cancers, all standardized morality rates (SMR) in the low As and high fluorescent intensity areas were greater than or equal to high As and low fluorescent intensity areas (Lin et al., 1986).

Statistical data for the Blackfoot disease patients in Taiwan before 1975 (Wu et al., 1978)											
County/City	Bef. 1966	1967	1968	1969	1970	1971	1972	1973	1974	Unkn.	Total
Taipei County							1				1
Taoyuan County	2										2
Hsinchu County	1										1
Miaoli County	1						1		1		3
Taichung County	2						1		1		4
Changhua County	3					1		1			5
Nantou County	1							1	1		3
Yunlin County	7		2			1	1	3	2		16
Chiayi County	360	9	14	10	11	9	14	11	15	8	461
Tainan County	540	53	40	22	19	21	17	18	25	9	764
Kaohsiung County	12					1	1		2		16
Pingtung County	6			1			1		4		12
Taitung County	3					1					4
Hualien County							1				1
Penhu County											
Keelung City											
Taichung City	2						1				3
Tainan City	22	1		1		5	8		5		42
Kaohsiung City	19	1	1			4	5	6	3		39
Ilan County											
Total	981	64	57	34	30	43	52	40	59	17	1377
Source: Health Department of Administrative Yuan.											

Definition of BFD

- A BFD patient should be manifested by both arteriosclerosis obliterans and thromboangiitis obliterans.
- The BFD symptoms were manifested by limb numbness, cold sensation, pain, intermittent claudication and blackfoot (Lu, 1995; Tseng et al., 1961).
- Arsenic may cause arteriosclerosis obliterans but not thromboangiitis obliterans.
- Fluorescent humic substances may cause both arteriosclerosis obliterans and thromboangiitis obliterans.

Health Effects of Chronic Arsenic Exposure

BFD: SW Taiwan

Non-BFD: Bangladesh

Hyperkeratosis of the hands (Lamm and Kruse, 2004)

SW Taiwan Cases

Bangladesh case

Skin Cancers on hands, arm and chest (Lamm and Kruse, 2004)

BFD patients

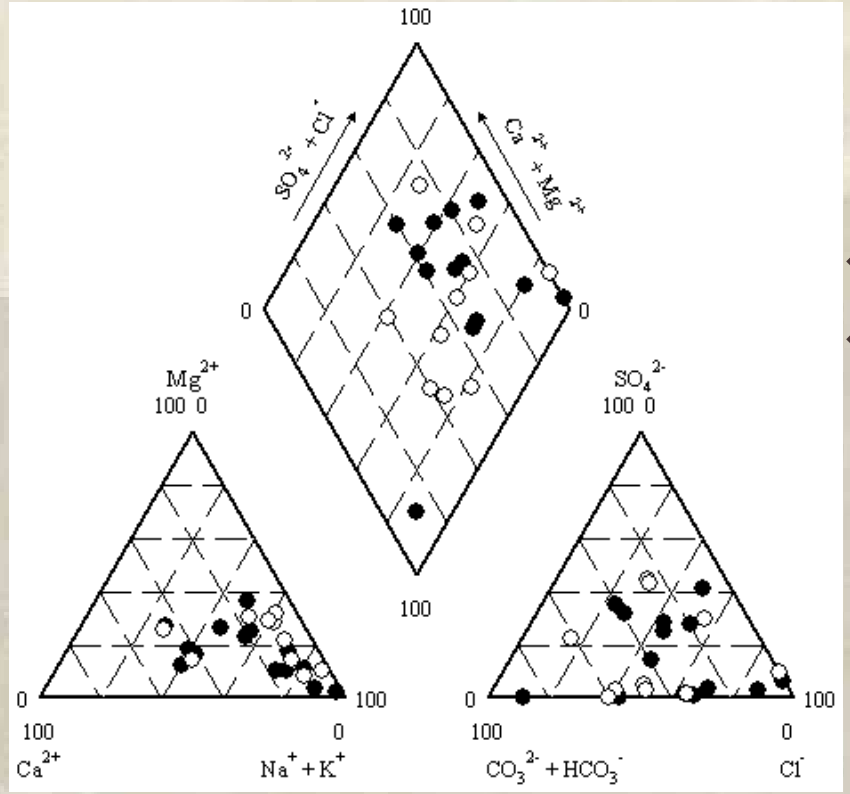
Interview with BFD patients

Name	Sex	Age	Township			Symptom	Age at Onset	Drinking GW before Onset	Remarks
W.-J. Guo	M	86 years	Yichu, Chiayi	TAO	ASO	Skin Disease	46	40 years	
K.-M. Hsu	M	72	Hseuchia, Tainan	-	ASO	-	67	10 years	
T.-J. Chen	M.	70	Hseuchia, Tainan	-	ASO	Hyperkeratosis pigmentation	68	20 years	
S.-M. Tsai	M	55	Butai, Chiayi	TAO	-	-	52	12 years	Cigarette, liquor
T.-J. Guo	F	82	Butai, Chiayi		ASO				
T.-H. Wang	F	82	Butai, Chiayi		ASO				
T.-T.-J. Wang	F	78	Anding, Tainan				74	29 years	
Y.-S. Tsai	F	76	Butai, Chiayi		ASO				
L.-Y.-L. Lai	F	73	Hseuchia, Tainan		ASO		68	25 years	
A.-S. Ju	F	72	Beimen, Tainan				40		

Health Effects due to Drinking Groundwater

Components	SW Taiwan	NE Taiwan	Bangladesh and West Bengal
Arsenic(mg/L)	max. 1.758 (Lu et al.,1985)	max. 1.5 (Lin et al.,1986)	max. 2.5~3.2 (BGS, 2001)
Fluor. Intensity	max. 315 (Lu et al.,1985)	max. 40 (Lin et al.,1986)	max. 125 (this study)
Symptoms	BFD; hyperkeratosis of the	Non-BFD; skin cancer,	Non-BFD; hyperkeratosis,
	hands; skin cancers on hands,	lung cancer, bladder	pigmentation, de-pigmentation,
	arm and chest; lung cancer,	cancer; cardiovascular and	skin cancer, liver cancer, and
	liver cancer and bladder cancer	brain vascular diseases	lung cancer

Chemical Characteristics of the BFD Groundwater

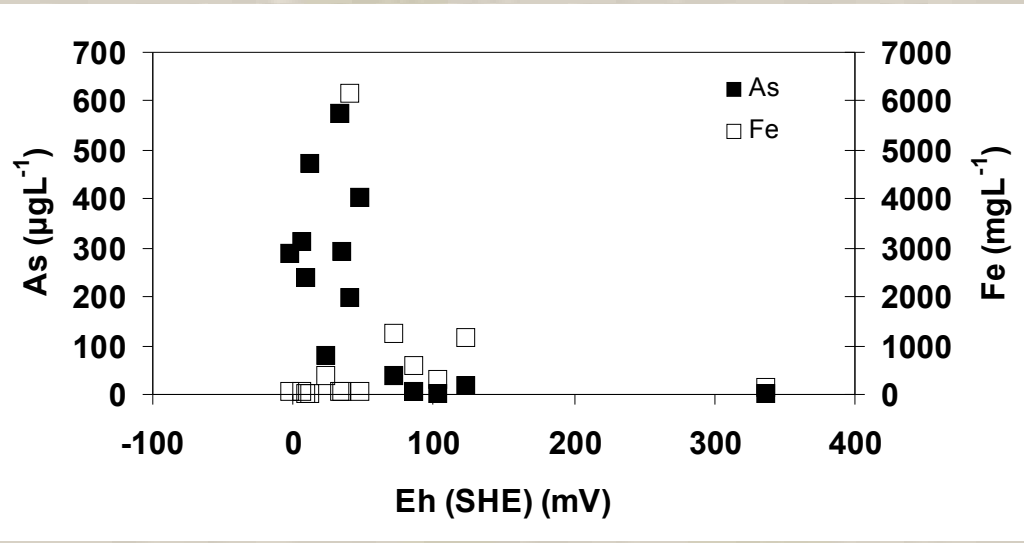


- Circumneutral groundwater
- In 2005, groundwater composition is the mixture of Na-Cl-SO_4-HCO_3, while in 2006; groundwater is the mixture of Na-Cl-SO_4.

Piper diagram illustrating the main hydrochemical features of the groundwaters from Chia-Nan plain. Open circle represents data from 2005 and closed circle for 2006.

Chemical Characteristics of the BFD Groundwater

Location	V (μg/L)	Cr (μg/L)	Mn (μg/L)	Co (μg/L)	Mo (μg/L)	Fe (μg/L)	As (μg/L)	Rb (μg/L)	Ba (μg/L)	Sr (μg/L)	Cu (μg/L)	Zn (μg/L)	Ni (μg/L)	Se (μg/L)
Beimen-2A	0.48	0.10	12	0.32	2.6	25	311	3.1	35	208	1.3	48	0.32	0.54
Beimen-2B	26	5.1	171	1.5	17	576	3.6	80	41	9254	214	30	260	0.46
Hsuechia-2	1.5	0.65	710	0.76	1.2	289	2.0	2.9	40	1056	1.6	156	1.9	0.09
Jiangjing-1B	0.42	0.23	16	0.59	0.72	34	575	3.3	50	236	0.87	36	0.18	0.23
Jiangjing-1C	2.5	0.34	20	0.59	15	27	291	3.7	18	111	1.3	25	0.85	0.17
Jiangjing-1D	1.4	0.25	21	0.42	0.61	39	288	3.7	57	252	0.93	22	0.53	0.12
Liujiao-2	0.20	0.34	40	0.15	0.83	381	78	1.4	5.0	131	0.47	188	0.34	0.04
Liujiao-2B	1.2	1.7	249	0.58	1.6	6151	196	2.2	20	583	1.7	376	1.8	0.13
Lucao-1A	0.62	0.48	51	0.37	1.4	1239	36	5.0	69	1094	1.6	150	0.95	0.04
Lucao-1B	1.2	2.7	83	0.61	2.3	1127	17	5.1	88	1055	1.6	280	2.9	0.07
Yenshui-1	0.17	0.09	15	0.13	13	11	237	4.9	3.8	184	0.31	3.0	0.16	0.42
Yenshui-2	0.14	0.07	11	0.09	8.2	20	470	4.7	2.5	244	0.60	13	0.20	0.15
Yenshui-3	0.12	0.09	9.2	0.12	2.2	26	402	2.0	5.4	352	0.39	21	0.08	0.13
Yichu-1A	0.56	0.40	95	0.23	0.11	139	1.3	0.52	5.2	130	0.64	71	0.56	0.38



- Elevated concentration of As, Fe and Sr

- High As and Fe contents observed under reducing condition, which is suggestive of reductive dissolution of As-bearing ferric (oxyhydr)oxides

Distributions of Arsenic species in Chia-Nan Plain

Sample no.	Well depth(m)	Total As (mg/L)	AsO_4^- (mg/L)	As(V) (mg/L)	As(III) (mg/L)	Reduction ratio (AsIII/total As)	Oxidation ratio As(V)/total As	As (III)/As(V)
Hsuechia#1	31	0.07	0.0196	0.0106	0.0594	84.86%	15.14%	5.6
Beimen#2A	277	0.282	0.2735	0.1477	0.1343	47.62%	52.38%	0.91
Jiangjing#1B	336	0.581	0.4569	0.2467	0.3343	57.54%	42.46%	1.36
Lucao#1B	10	0.015	Nd	Nd	Nd	Nd	Nd	Nd
Liujiao#1	13	0.037	0.0565	Nd	Nd	Nd	Nd	Nd
Liujiao#2	67	0.159	0.0298	0.0161	0.1429	89.87%	10.13%	8.88
Yenshui#1	23	0.27	0.0498	0.0269	0.2431	90.04%	9.96%	9.04
Yenshui#2	23	0.486	0.039	0.0211	0.4649	95.66%	4.34%	22.03
Yenshui#3	23	0.796	0.024	0.013	0.783	98.37%	1.63%	60.23
Yenshui#4	23	0.708	0.0181	0.0098	0.6982	98.62%	1.38%	71.24
Yenshui#5A	233	0.055	0.0044	0.0024	0.0526	95.64%	4.36%	21.92
Yichu#1A	20	0.036	0.006	0.0032	0.0328	91.11%	8.89%	10.25

Nd: Not detected

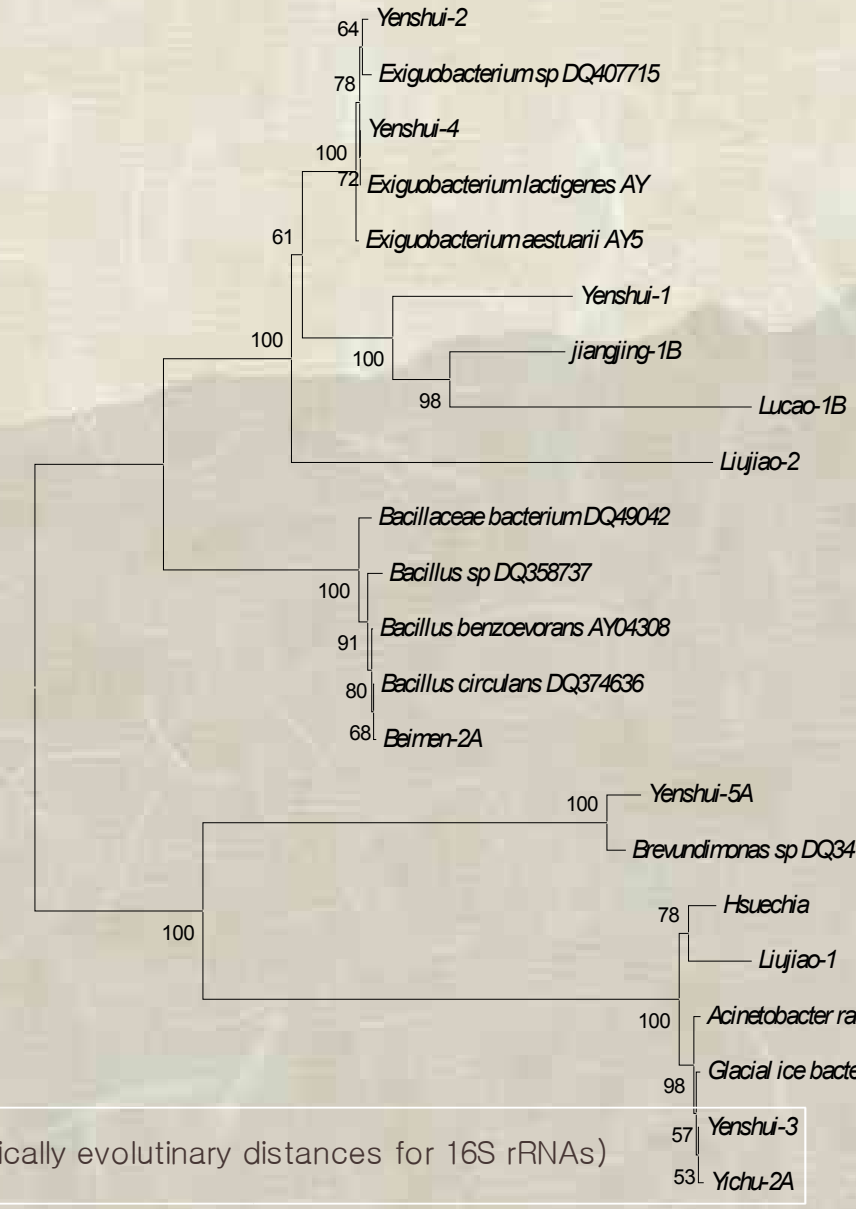
Values of the Saturation Indices computed by PHREEQC

Mineral phases	Beimen-2A	Hsuechia-2	Jiangjing-1B	Jiangjing-1C	Jiangjing-1D	Liujiao-2	Liujiao-2B	Lucao-1A	Lucao-1B	Yenshui-1	Yichu-1A
Aragonite	2.4	2.2	2.0	2.8	2.2	2.5	2.4	2.2	2.1	2.4	2.3
Arsenolite	-5.7	-9.8	-5.1	-5.9	-5.6	-6.9	-6.0	-7.5	-8.2	-5.9	-24
As_native	-3.8	-9.9	-3.4	-7.3	-3.1	-5.3	-5.2	-7.2	-10	-5.2	-30
Calcite	2.5	2.3	2.1	2.9	2.4	2.6	2.5	2.3	2.3	2.6	2.5
Claudetite	-5.7	-9.8	-5.1	-5.9	-5.6	-6.9	-6.1	-7.5	-8.2	-6.0	-24
Dolomite	4.7	5.0	4.0	5.5	4.9	5.2	4.8	4.2	4.1	5.4	4.3
Goethite	1.4	3.3	0.57	3.7	1.3	2.9	3.8	3.3	4.0	2.1	7.6
Halite	-3.4	-2.7	-3.6	-4.3	-2.4	-4.0	-4.4	-3.6	-3.9	-3.5	-4.3
Hematite	4.81	8.6	3.2	9.4	4.6	7.8	9.7	8.6	10	6.3	17
Maghemite	-5.9	-2.1	-7.6	-1.3	-6.1	-3.0	-1.0	-2.1	-0.6	-4.5	6.6
Magnesite	1.7	2.1	1.4	2.0	1.9	2.0	1.7	1.3	1.3	2.3	1.2
Magnetite	6.3	11	3.8	12	6.2	10	13	11	13	8	19
Manganite	-13	-10	-13	-10	-13	-12	-11	-12	-11	-12	-6.2
Pyrolusite	-24	-20	-25	-20	-24	-23	-22	-22	-20	-22	-12
Rhodochrosite	0.94	2.5	0.71	1.5	1.1	1.4	2.1	1.3	1.5	1.2	1.8
Scorodite	-15	-12	-15	-10	-15	-13	-12	-12	-10	-13	-6.3
Siderite	1.1	1.9	0.83	1.7	1.3	2.3	3.3	2.5	2.5	1.1	1.8

- Saturation indices computed using PHREEQC for groundwater from Chia-Nan plain, Southwestern Taiwan

- Positive values denotes precipitation, and negative values denotes dissolution of the special mineral

Phylogenetic tree



Firmicutes

α-proteobacteria

γ-proteobacteria

(Genetically evolutinary distances for 16S rRNAs)

Description of Bacterial Isolates

* Exiguobacterium sp.: gram-positive aerobic bacteria (Firmicutes)

* Bacillus sp.: gram-positive aerobic bacteria (Firmicutes)

* Brevundimonas sp.: gram-negative aerobic bacteria (α-proteobacteria)

* Acinetobacter sp.: gram-negative aerobic bacteria (γ-proteobacteria)

- The Batch Experiments on Adsorption/Desorption

Adsorption of Arsenic on $Fe(OH)_3$

5ppm initial As(V)

Time (Hour)	Concentration (ppm)		
	0.1	0.5	1
0	65.60%	73.00%	51.60%
4	37.60%	72.00%	17.20%
8	72.20%	72.00%	73.00%
12	72.80%	72.40%	71.80%
24	74.60%	74.20%	70.20%
36	26.40%	75.20%	76.00%
48	72.00%	46.60%	74.20%

The adsorption result of 5ppm initial As(V) solution with different concentration of $Fe(OH)_3$

Adsorption of Arsenic on $Fe(OH)_3$

10 ppm initial As(V)

Time (Hour)	Concentration (ppm)		
	0.1	0.5	1
0	36.90%	48.40%	46.40%
4	0.00%	48.30%	42.40%
8	48.90%	46.00%	48.00%
12	49.20%	43.20%	46.30%
24	47.00%	45.20%	28.80%
36	47.60%	0.00%	45.20%
48	9.70%	35.00%	42.50%

The adsorption result of 10ppm initial As(V) solution with different concentration of $Fe(OH)_3$

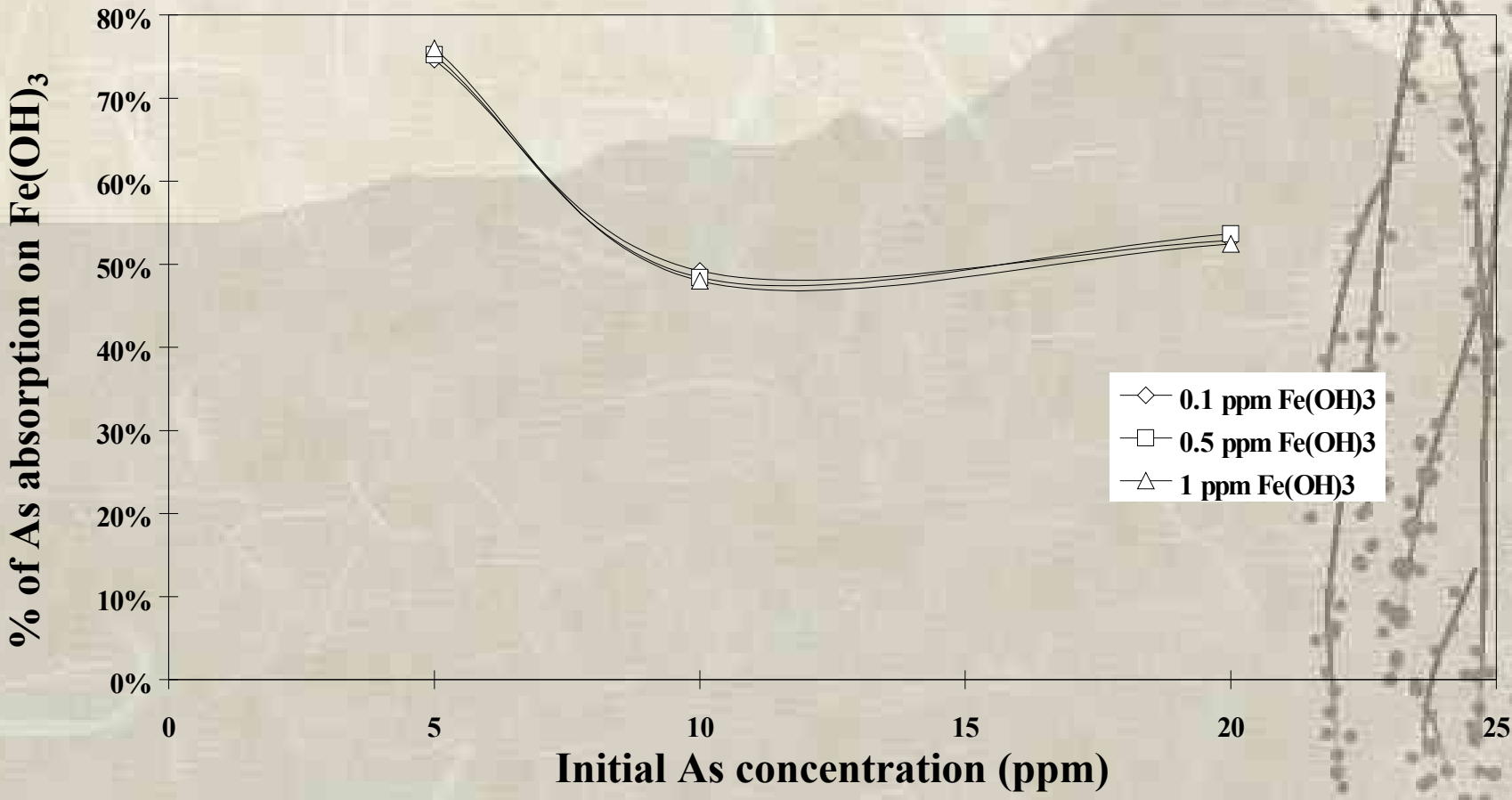
Adsorption of Arsenic on $Fe(OH)_3$

20 ppm initial As(V)

Time (Hour)	Concentration (ppm)		
	0.1	0.5	1
0	52.85%	52.15%	49.45%
4	50.00%	51.45%	52.45%
8	0.00%	53.65%	48.95%
12	52.60%	52.50%	51.00%
24	34.45%	52.75%	51.70%
36	50.00%	47.45%	52.10%
48	0.00%	48.30%	51.60%

The adsorption result of 20ppm initial As(V) solution with different concentration of $Fe(OH)_3$

Adsorption of Arsenic in $Fe(OH)_3$



Conclusion

- Groundwater contains considerable amount of arsenic, iron, manganese, and strontium with the abundance of reduced arsenic species (As-III), suggesting reductive nature of the BFD groundwater.
- Geochemical speciation calculation demonstrates that most of the Fe-bearing carbonates and few oxide phases are in supersaturated stage. This demonstrates that the above phase may act as a potential sink for arsenic at a local scale.
- The isolated bacterial strains includes *Acinetobacter radioresistens, Bacillus benzoevorans, Bacillus circulans, Brevundimonas sp., Exiguobacterium aestuarii, Glacial ice bacterium*, etc.
- The batch (adsorption/desorption) experiment revealed the importance of $Fe(OH)_3$ in adsorbing As(V) species.
- Our result is consistent with microbially mediated redox reactions and the release of arsenic into groundwater of the BFD area.

Future Research

- To identify BFD factors in SW Taiwan.
- Prospective studies in NE Taiwan, Bangladesh and West Bengal, India, where high arsenic exists without BFD.
- Compare the chemical components and biochemical structure of causative agents in NE and SW Taiwan.
- Understanding the different competing models for arsenic release including geomicrobiological study
- Fundamental chemistry and complexation behaviour of arsenic species interacting with humic substances and related organic compounds
- Investigation of the toxicological and pathological/carcinogenic effects, *in vivo* and *in vitro*, of organo-metallic compounds, arsenic and humic substances

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Thank you for your attention!!!