Applied Organometallic Chemistry (1990) 4 197–203
0268-2605/90/030197-07$05.00

REVIEW

Arsenic in the natural environment. Part II: Arsenic concentrations in thermal waters from Japan

Takeshi Tanaka
Japan Consulting Engineers Association, No. 15, Mori Building, 8–10 Toranomon 2-chome, Minato-ku, Tokyo 105, Japan

Received 24 November 1989 Accepted 21 April 1990

Arsenic is ubiquitous in the atmosphere, hydrosphere, pedosphere, lithosphere, and biosphere of the earth. Hot springs in Japan have arsenic concentrations as high as 25 mg kg^{-1}. Generally, the hotter the water the higher are the arsenic concentrations. On average, acidic waters have higher arsenic concentrations than alkaline waters. The arsenic concentrations are positively correlated with the antimony and the lead concentrations. The daily discharge of arsenic from a geothermal well may reach a total of 220 kg. The arsenic concentrations, the temperatures, and the pH values for some Japanese thermal waters are tabulated.

Keywords: Arsenic, thermal waters, hot springs, geothermal plant

INTRODUCTION

Arsenic is ubiquitous in the atmosphere, the hydrosphere, the pedosphere, the lithosphere, and the biosphere of the earth.[1] Waters of elevated temperatures flowing from geothermal springs transport considerable amounts of arsenic from the lithosphere into the biosphere. The presence of arsenic in waters from hot springs has been known for a long time. The literature is replete with reports about concentrations of arsenic, other minor elements, and major elements in such waters. Recently, arsenic concentrations were determined in the thermal waters from the main geothermal fields in Japan that had been developed as geothermal energy sources.

This paper summarizes the arsenic concentrations in Japanese hot springs and presents relationships between arsenic concentrations and temperature, pH, concentrations of antimony, and concentrations of lead.

ARSENIC CONCENTRATIONS IN THERMAL WATERS

The presence of arsenic in thermal waters from hot springs in Japan has been reported by many authors. According to *Data for Thermal Springs in Japan* compiled by the National Hygiene Laboratory, 195 of the 1450 springs contain arsenic. The mean concentration of arsenic[2] from 16 acidic springs is 0.49 mg kg^{-1} and for 174 alkaline springs 0.28 mg kg^{-1}. The Geological Survey of Japan compiled data on the chemical composition of 2325 thermal water samples from the main geothermal fields in Japan, the locations of which are shown in Fig. 1. Arsenic is a constituent of 901 of these water samples.[3] Fields 1–5 are located in the Hokkaido District, fields 6–15 in the Tohoku District, fields 16–25 in the Kanto, Chubu and Kinki Districts, and fields 26–30 in the Kyushu District.

The average arsenic concentrations and their ranges in the thermal waters from the 30 geothermal fields are listed in Table 1. The arsenic concentrations, classified according to the temperature ranges of the waters, are presented in Table 2; and according to pH ranges in Table 3. In this compilation the geothermal fields 16–25 located in the Kanto, Chubu, and Kinki Districts are divided into two groups, the Kanto–Chubu group and the Chubu–Kinki group, with the Fossa Magna, the major fault crossing the central part of Honshu Island, serving as the dividing line. Several of the hot springs included in Table 1 have very high arsenic concentrations in the 10–25 mg kg^{-1} range. The data for these springs are summarized in Table 4. The temperatures of these springs vary widely between 31 and 99°C, as does the pH (1.20–8.29). The arsenic concentrations in Table 4 do not appear to be correlated with pH. However, the waters with temperatures

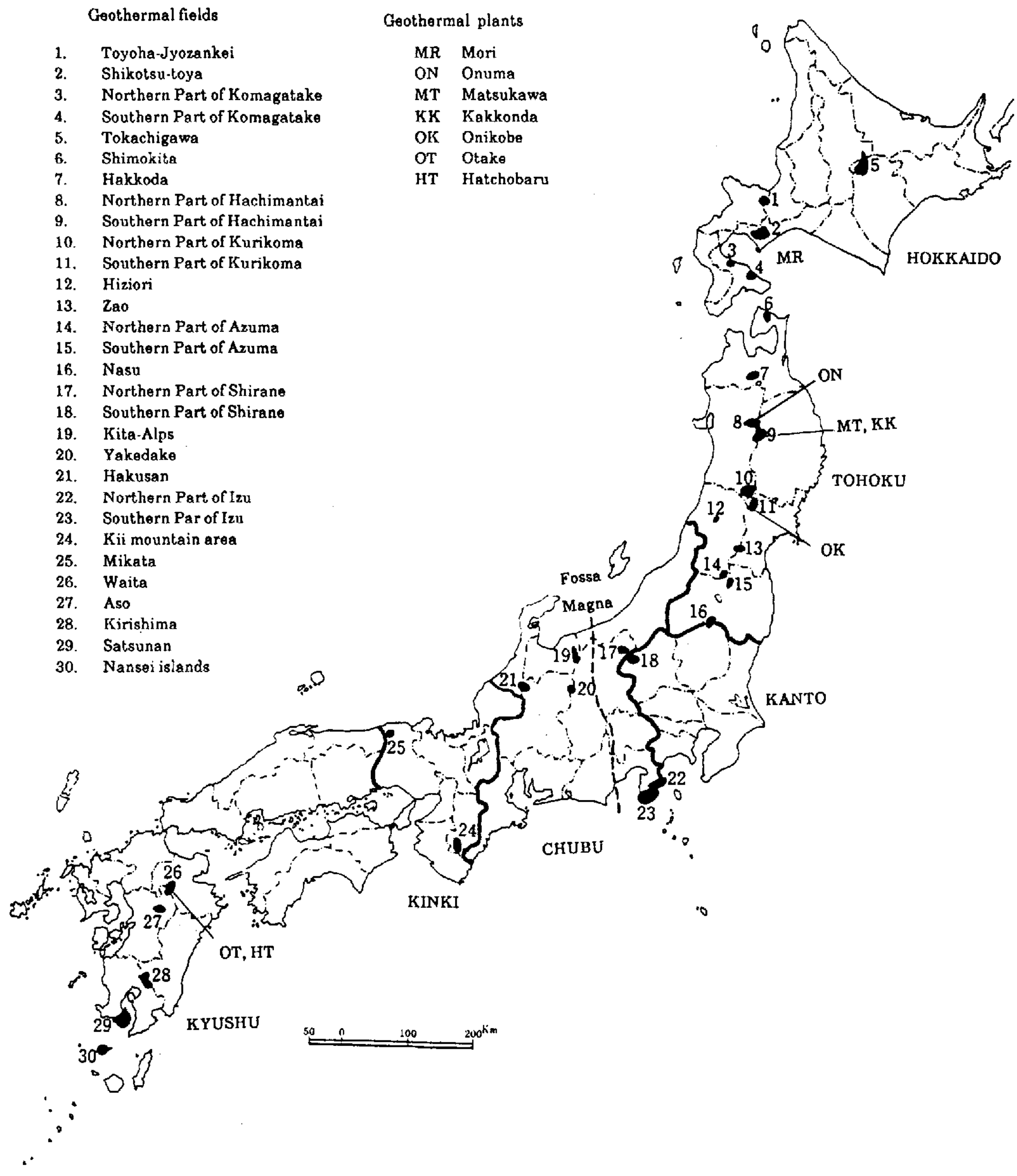

Figure 1 The location of geothermal fields and geothermal power plants in Japan.

above 95°C have lower arsenic concentrations than waters with temperatures between 43 and 53°C (Table 4). To check further on these correlations, all the data on arsenic concentrations, temperatures, and pH, with the exception of data listed in Table 4 and data for springs, for which temperature and/or pH are not available (20 samples), were plotted (Fig. 2). In contrast to the trend found for the high-arsenic springs (Table 4), the arsenic concentration generally increases with the temperature of the water. On average, acidic thermal waters (0.58 mg As kg^{-1}) have higher arsenic concentrations than alkaline waters (0.33 mg As kg^{-1}).

In addition to arsenic, the geothermal waters also contain antimony and lead. The antimony concentrations (one to two orders of magnitude smaller than the arsenic concentrations) are positively correlated to the arsenic concentrations (Fig. 3).[4] The ratio of arsenic to antimony in the

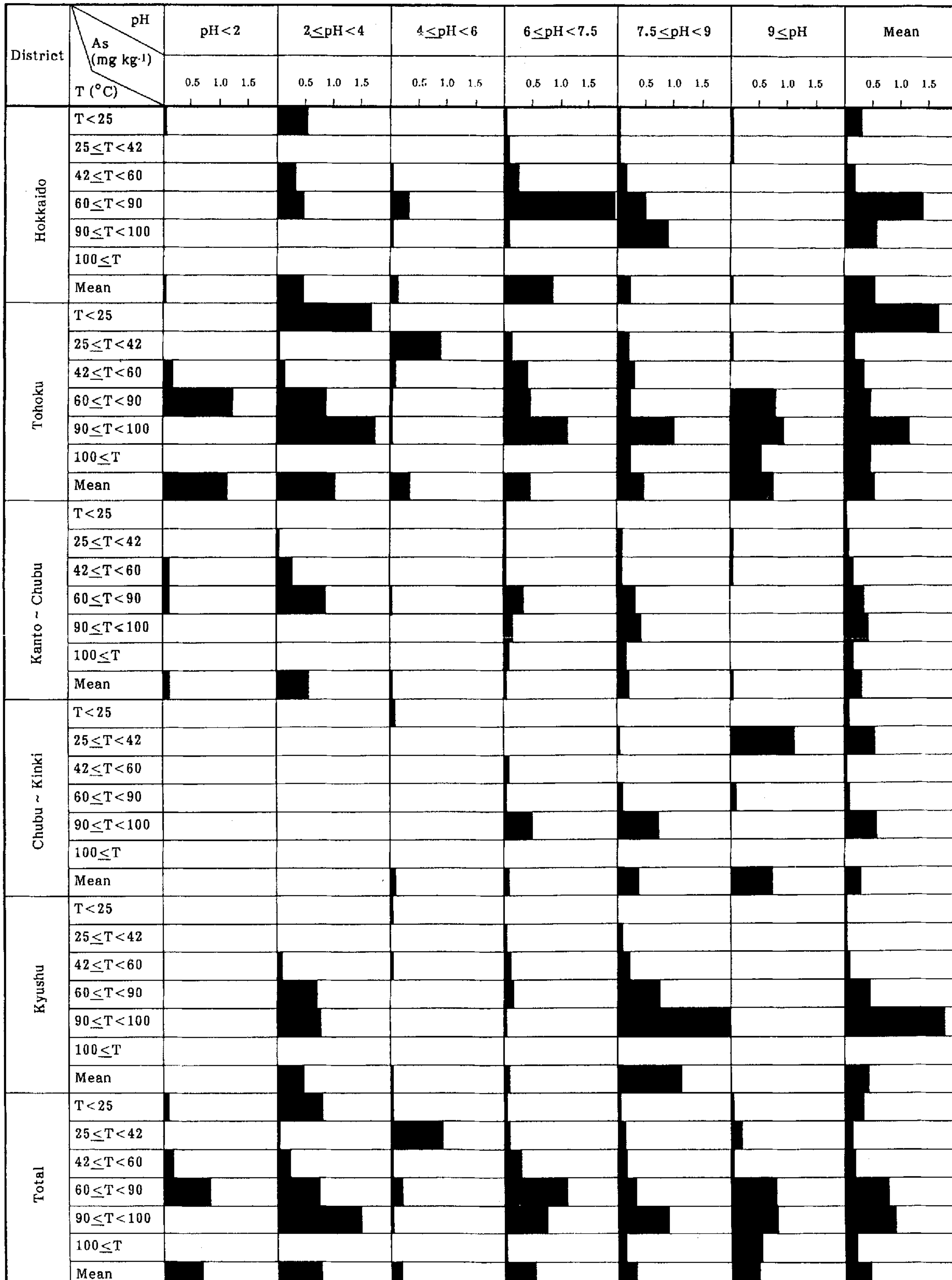

Figure 2 Arsenic concentrations (mg kg^{-1}) in geothermal waters arranged according to the temperatures and pH values of the waters.

Table 1 Arsenic concentrations (mg kg^{-1}) in thermal waters from 30 main geothermal fields

No.	Geothermal fields	Number of values	Range	Mean
1	Toyoha–Jyozankei	42	0.003–4.51	2.13
2	Shikotsu–Toya	151	0.002–2.48	0.29
3	Northern part of Komagatake	15	0.002–0.45	0.12
4	Southern part of Komagatake	13	0.003–0.22	0.044
5	Tokachigawa	29	0.001–1.62	0.24
6	Shimokita	12	0.010–2.27	0.43
7	Hakkoda	34	0.001–11.66	1.24
8	Northern part of Hachimantai	20	0.005–11.00	2.31
9	Southern part of Hachimantai	9	0.001–2.77	0.93
10	Northern part of Kurikoma	13	0.001–2.94	0.49
11	Southern part of Kurikoma	103	0.008–17.49	0.55
12	Hiziori	5	0.030–3.12	1.02
13	Zao	49	0.008–1.20	0.41
14	Northern part of Azuma	1	0.20	0.20
15	Southern part of Azuma	10	0.003–0.083	0.056
16	Nasu	8	0.008–0.81	0.25
17	Northern part of Shirane	8	0.008–3.11	1.20
18	Southern part of Shirane	17	0.004–25.51	1.93
19	Kita–Alps	3	0.006–0.38	0.17
20	Yakedake	17	0.003–1.22	0.32
21	Hakusan	1	0.1	0.12
22	Northern part of Izu	206	0.001–3.65	0.19
23	Southern part of Izu	40	0.001–0.89	0.078
24	Kii mountain area	0	—	—
25	Mikata	4	0.012–25.71	13.1
26	Waita	27	0.001–2.01	0.38
27	Aso	19	0.001–0.065	0.017
28	Kirishima	41	0.005–5.90	0.63
29	Satsunan	4	0.021–0.51	0.16
30	Nansei islands	0	—	—
	Total	901	0.001–25.71	0.57

earth's crust[5] is approximately 16. Thus, arsenic appears to be enriched in the thermal waters. The lead concentrations in the hot springs are similar in magnitude and positively correlated with the arsenic concentrations (Fig. 4).[6]

The amounts of arsenic discharged by the geothermal wells powering the main geothermal plants in Japan may reach 220 kg per day[7,8] (Table 5). The amounts of arsenic discharged by hot springs are lower (Table 6).

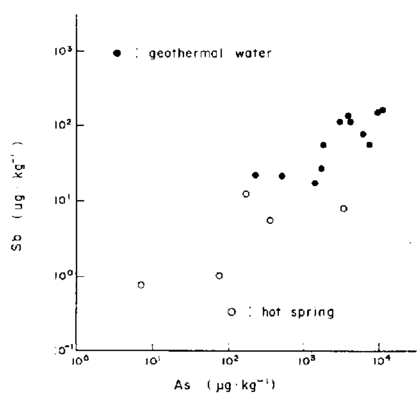

Figure 3 The correlation between concentrations of arsenic and antimony in geothermal waters and hot springs.

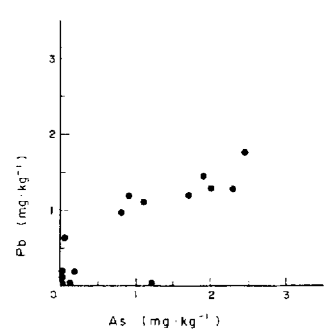

Figure 4 The correlation between concentrations of arsenic and lead in geothermal waters.

Table 2 Arsenic concentrations (mg kg^{-1}) in waters from the 30 main geothermal fields arranged according to the temperatures of the waters

District	No.	Geothermal fields	Temperature (°C) Unknown	$T<25$	$25\leq T<42$	$42\leq T<60$	$60\leq T<90$	$90\leq T<100$	$100\leq T$	Mean
Hokkaido	1	Toyoha–Jyozankei	2.65	0.012	0.049	1.94	2.52	—	—	2.13
	2	Shikotsu–Toya	0.16	0.49	0.11	0.19	0.68	0.39	—	0.29
	3	Northern part of Komagatake	—	—	0.009	0.037	0.18	0.45	—	0.12
	4	Southern part of Komagatake	—	—	0.068	0.040	0.008	0.011	—	0.044
	5	Tokachigawa	0.025	—	0.022	0.027	0.71	1.35	—	0.24
		Mean	1.08	0.33	0.075	0.20	1.41	0.59	—	0.57
Tohoku	6	Shimokita	—	—	1.72	0.38	0.046	—	—	0.43
	7	Hakkoda	—	—	0.011	0.64	1.88	—	—	1.24
	8	Northern part of Hachimantai	—	—	0.083	0.18	2.20	3.35	—	2.31
	9	Southern part of Hachimantai	—	—	0.013	0.003	0.001	1.68	—	0.93
	10	Northern part of Kurikoma	—	—	—	0.015	1.32	1.23	—	0.49
	11	Southern part of Kurikoma	—	1.68	0.046	0.33	0.23	1.16	0.51	0.55
	12	Hiziori	—	—	0.37	0.030	1.20	3.12	—	1.02
	13	Zao	—	—	0.24	0.41	0.59	—	—	0.41
	14	Northern part of Azuma	—	—	—	—	0.20	—	—	0.20
	15	Southern part of Azuma	0.077	—	0.045	0.008	0.003	—	—	0.056
		Mean	0.077	1.68	0.20	0.39	0.78	1.66	0.51	0.75
Kanto–Chubu	16	Nasu	—	—	—	0.19	0.27	—	—	0.25
	17	Northern part of Shirane	—	—	—	0.26	1.26	2.02	—	1.20
	18	Southern part of Shirane	0.99	—	0.012	3.83	0.57	—	—	1.93
	22	Northern part of Izu	0.23	0.006	0.11	0.13	0.24	0.43	0.19	0.19
	23	Southern part of Izu	—	—	0.11	0.066	0.13	0.051	0.011	0.078
		Mean	0.74	0.006	0.10	0.31	0.35	0.45	0.15	0.31
Chubu–Kinki	19	Kita–Alps	—	—	—	—	0.17	—	—	0.17
	20	Yakedake	—	0.060	—	0.023	0.015	0.58	—	0.32
	21	Hakusan	—	—	—	0.12	—	—	—	0.12
	24	Kii mountain area	—	—	—	—	—	—	—	—
	25	Mikata	—	—	8.97	25.7	—	—	—	13.1
		Mean	—	0.060	8.97	8.62	0.067	0.58	—	2.35
Kyushu	26	Waita	—	—	0.019	0.048	0.56	1.02	—	0.38
	27	Aso	—	0.001	0.014	0.024	—	—	—	0.017
	28	Kirishima	—	—	0.15	0.15	0.40	2.47	—	0.63
	29	Satsunan	—	—	—	0.053	0.044	0.51	—	0.16
	30	Nansei islands	—	—	—	—	—	—	—	—
		Mean	—	0.001	0.039	0.10	0.44	1.81	—	0.41
		Total	0.66	0.36	0.35	0.33	0.83	1.14	0.22	0.57

Table 3 Arsenic concentrations (mg kg^{-1}) for waters from 30 main geothermal fields arranged according to the pH values of the waters

District	No.	Geothermal fields	Unknown −pH	pH<2 (strong acid)	2≤pH<4 (acid)	4≤pH<6 (weak acid)	6≤pH<7.5 (neutral)	7.5≤pH<9 (weak alkaline)	9≤pH (alkaline)	Mean
Hokkaido	1	Toyoha–Jyozankei	—	—	0.017	—	2.29	1.73	0.010	2.13
	2	Shikotsu–Toya	0.001	0.056	0.53	0.12	0.38	0.23	—	0.29
	3	Northern part of Komagatake	—	—	—	—	0.065	0.263	—	0.12
	4	Southern part of Komagatake	—	—	—	—	0.059	0.032	—	0.044
	5	Tokachigawa	—	—	—	—	0.16	0.45	0.004	0.24
		Mean	0.001	0.056	0.49	0.12	0.86	0.29	0.007	0.57
Tohoku	6	Shimokita	—	—	—	1.72	0.42	0.043	—	0.43
	7	Hakkoda	—	5.15	0.019	—	0.46	0.27	—	1.24
	8	Northern part of Hachimantai	—	—	1.21	—	3.36	3.64	0.005	2.31
	9	Southern part of Hachimantai	—	—	1.00	0.005	0.001	1.24	2.77	0.93
	10	Northern part of Kurikoma	—	—	0.98	—	0.11	0.44	1.11	0.49
	11	Southern part of Kurikoma	0.20	—	0.86	0.08	0.36	0.79	0.61	0.55
	12	Hiziori	—	—	—	—	0.49	3.12	—	1.02
	13	Zao	—	0.13	—	—	0.54	0.39	0.008	0.41
	14	Northern part of Azuma	—	—	—	—	0.20	—	—	0.20
	15	Southern part of Azuma	—	—	0.03	0.003	0.054	0.20	—	0.056
		Mean	0.20	3.14	0.89	0.33	0.49	0.82	0.70	0.75
Kanto–Chubu	16	Nasu	—	—	0.49	0.008	0.008	—	—	0.25
	17	Northern part of Shirane	—	—	—	—	0.97	1.28	—	1.20
	18	Southern part of Shirane	—	0.43	3.02	—	0.021	—	—	1.93
	22	Northern part of Izu	—	—	—	—	0.091	0.20	—	0.19
	23	Southern part of Izu	0.015	—	—	—	0.058	0.088	0.023	0.078
		Mean	0.015	0.43	2.29	0.008	0.14	0.21	0.023	0.31
Chubu–Kinki	19	Kita–Alps	—	—	—	—	0.077	0.22	—	0.17
	20	Yakedake	—	—	—	0.060	0.11	0.47	0.095	0.32
	21	Hakusan	—	—	—	—	0.12	—	—	0.12
	24	Kii mountain area	—	—	—	—	—	—	—	—
	25	Mikata	—	—	—	—	25.7	12.9	1.17	13.1
		Mean	—	—	—	0.060	3.31	2.21	0.63	2.35
Kyushu	26	Waita	—	—	0.52	0.003	0.014	0.75	—	0.38
	27	Aso	—	—	—	0.001	0.015	0.043	—	0.017
	28	Kirishima	—	—	0.030	—	0.14	1.50	—	0.63
	29	Satsunan	—	—	—	—	0.047	0.51	—	0.16
	30	Nansei islands	—	—	—	—	—	—	—	—
		Mean	—	—	0.48	0.003	0.074	1.17	—	0.41
		Total	0.11	2.1	1.04	0.16	0.61	0.45	0.55	0.57

Table 4 Geothermal springs with high arsenic concentrations

Geothermal fields	Spring name	As ($mg\ kg^{-1}$)	T (°C)	pH
Hakkoda	Sukayu	11.66	89.0	1.20
Hakkoda	Sukayu	10.68	82.0	1.20
Northern part of Hachimantai	Toroko	11.00	99.0	8.60
Southern part of Kurikoma	Nakayama-daira	17.49	95.2	8.92
Southern part of Shirane	Hosho-no-yu	25.51	53.0	3.00
Mikata	Nanakama	25.71	31.0	7.50
Mikata	Futsukaichi	25.71	43.5	7.20

Table 5 Discharge of arsenic by geothermal power plants

Geothermal plants	District	pH	Arsenic concentration ($mg\ kg^{-1}$)	Total discharge of arsenic ($kg\ day^{-1}$)
Mori	Hokkaido	8.0–9.3	4.0–7.9	Unknown
Onuma	Tohoku	7.3–7.9	5.2–10.6	85
Matsukawa	Tohoku	Unknown	Unknown	0.5
Kakkonda	Tohoku	8.8–9.1	1.8–3.2	220
Onikobe	Tohoku	3.3–9.1	0.5–3.9	4
Otake	Kyushu	6.0–8.4	2.1	Unknown
Hatchobaru	Kyushu	4.7–6.5	2.4	55

Table 6 Discharge of arsenic by hot springs

Hot springs	District	Total discharge of arsenic ($kg\ day^{-1}$)
Jyozankei	Hokkaido	14–24
Tamagawa	Tohoku	10
Sakurajima (northern part)	Kyushu	1.3
Satsuma-Iōjima	Kyushu	6–60

REMOVAL OF ARSENIC FROM THERMAL WATERS

The arsenic concentrations in the geothermal waters exceed the evironmental limit of 0.5 $mg\ kg^{-1}$ (Table 5). For this reason, the waters after passing through the power plant cannot be discharged into surface waters, but must be re-injected into the underground formations. The reinjection disposal of thermal waters may pollute the groundwater and may cause micro-earthquakes. The problems associated with re-injection must be addressed soon.[9] A solution to these problems may be the chemical removal of arsenic from the thermal waters. The arsenite present in the waters can be oxidized to arsenate by sodium hypochlorite. The arsenate can then be coprecipitated with iron(III) hydroxide after addition of iron(III) chloride. In this manner the arsenic concentration can be reduced in the thermal waters to 0.5–0.05 $mg\ kg^{-1}$, concentrations below the environmental limit.[10]

REFERENCES

References marked by an asterisk are written in Japanese.

1. Tanaka, T *Appl. Organomet. Chem.*, 1988, 2: 283
2. Uzumasa, Y *Chemical Investigations of Hot Springs in Japan*, Tsukiji Shokan, Tokyo 1965: 101
3. Hirukawa, T, Ando, N and Sumi, K (eds) *Rep. Geol. Surv. Jpn*, 1977, 257: 1*
4. Kamata, M, Ozawa, T, Murakami, Y and Yoshida, M (eds) *Chinetsu-Ryutai-no-Kagaku*, Tokyo University Press, Tokyo, 1985, p 103*
5. Cox, P A *The Elements*, Oxford University Press, Oxford, 1989, pp 184, 185
6. Uzumasa, Y *Chemical Investigations of Hot Springs in Japan*, Tsukiji Shokan, Tokyo 1965: 102
7. Kamata, M, Ozawa, T, Muakami, Y and Yoshida, M (eds) *Chinetsu-Ryutai-no-Kagaku*, Tokyo University Press, Tokyo, 1985, p 170*
8. Ozawa, T *J. Jap. Geotherm. Energy Assoc. (Chinetsu)*, 1988, 24 (Ser. No. 100): 614*
9. Kaneko, M *J. Jap. Geotherm. Energy Assoc. (Chinetsu)*, 1983, 20 (Ser. No. 76): 3*
10. Yoshida, K *J. Jap. Geotherm. Energy Assoc. (Chinetsu)*, 1982, 19 (Ser. No. 74): 128*