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Trace Element Hydrochemistry Indicating Water Contamination in and Around the Yangbajing Geothermal Field, Tibet, China

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Abstract Thirty-eight water samples were collected at Yangbajing to investigate the water contamination resulting from natural geothermal water discharge and anthropogenic geothermal wastewater drainage. The results indicate that snow or snow melting waters, Yangbajing River waters and cold groundwaters are free from geothermal water-related contamination, whereas Zangbo river waters are contaminated by geothermal wastewaters. Moreover, there may exist geothermal springs under the riverbed of a tributary stream of Zangbo River as shown by its Cd, Li, Mo and Pb concentrations. The efforts made in this study show trace element hydrochemistry can well indicate water quality degradation related to geothermal water exploitation.

Keywords Geothermal water · Trace element · Water contamination · Yangbajing

Water supply and quality are fundamental issues for mankind, and water pollution has become a major challenge for sustainable management of water resource in recent decades. Water quality deterioration can be induced in many different ways. Since geothermal water (especially high-temperature geothermal water) commonly contains some constituents hazardous to environment and human health, its natural discharge or anthropogenic drainage may result in severe water contamination.

The Yangbajing geothermal field, located to the northwest of Lhasa City, the capital of Tibet, has the highest reservoir temperature among all Chinese hydrothermal systems and is the only field where high temperature geothermal fluids have been used for electricity generation. There are two reservoirs at Yangbajing: one is the shallow reservoir at a depth of 180–280 m and the other the deep reservoir at 950–1850 m (Duo 2003). Besides the geothermal waters, shallow cold groundwaters with burial depth of 10–20 m occur within the field as well. The surface water bodies include the Yangbajing River, the Zangbo River, and several smaller streams receiving snowmelt of the Nyenchen Tonglha Mountains. At present, the geothermal wastewaters generated by the first and second Yangbajing power plants (Fig. 1) are drained directly into the Zangbo River and its two tributary streams.

Our earlier work in 2006 (Guo et al. 2007a) detected B, As, and F contamination of the Zangbo River waters. However, there are only five Zangbo River water samples collected in 2006, which is not enough to effectively delineate the water quality variation along the river. Furthermore, trace elements in water samples were not measured in 2006. As useful tracers, trace elements have been applied in environmental monitoring within geothermal areas (Bargagli et al. 1997; Loppi et al. 1999; Loppi 2001). However, there are few systematic studies on water contamination induced by geothermal water drainage using trace elements as indicators. In this study, more water samples were collected from the aquatic environment of the Zangbo River and trace elements were analyzed to identify the water contamination in and around the Yangbajing field.

Materials and Methods

In this study, 6 geothermal water samples, 4 geothermal wastewater samples (two of them were mixed with stream

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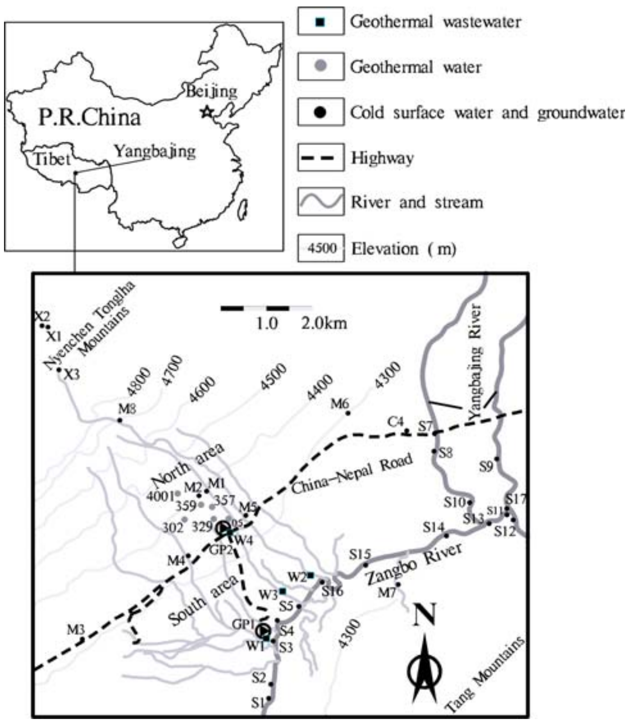

Fig. 1 Simplified map of the study area and sampling locations. GP1 and GP2 represent the first and the second Yangbajing geothermal power plants, respectively

waters), 2 cold groundwater samples, 3 snow or snow melting water samples, 10 Zangbo River water samples, 6 Yangbajing River water samples, and 7 stream water samples were collected in and around the Yangbajing geothermal field in August and September of 2007. The sampling locations are shown in Fig. 1. Five of all geothermal water samples were collected from the geothermal production wells drilled into the shallow reservoir, and one of them from the only well related to the deep reservoir. Two geothermal wastewater samples were collected from the wastewater draining exits of the first and second geothermal power plants, and the other two from two streams with runoff <0.1 m^3/s where the geothermal wastewaters from the second power plant were drained (the sampling sites are near the conjunctions between these two streams and the Zangbo River). Cold groundwaters were sampled from a cold spring located in the north area of the field and a production well for pumping drinking waters that lies to the east of the field. Two snow samples were collected from the ridge of the Nyenchen Tonglha Mountains at the elevations of 5450 and 5469 m (above mean sea level), respectively. The snow melting water sample was collected in front of the Nyenchen Tonglha Mountains (below the local snow line). Zangbo River waters and Yangbajing River waters were sampled along their flow directions. Stream water samples were collected from several streams receiving snow melting waters from the Nyenchen Tonglha Mountains. The sampling temperature and elevation as well as the type of all water samples are listed in Table 1.

When sampling, all water samples were filtered through 0.45 μm filter on site. Samples were stored in new 350 mL polyethylene bottles. The bottles had been rinsed with deionized water twice before sampling. For trace element analysis, reagent-quality HNO_3 with molar concentration up to 14 M was added to these polyethylene bottles until pH of the samples reached 1. Unstable hydrochemical parameters including pH, EC and DO were measured in situ using portable pH meter, electric conductivity meter, and dissolved oxygen meter. The concentrations of trace elements in all samples were measured using Inductively Coupled Plasma (ICP) technique within 2 weeks after sampling. The average concentrations of these trace elements of snow or snow melting water (Type A), stream water (Type B), Zangbo River water (Type C), Yangbajing River water (Type D), cold groundwater (Type E), geothermal water (Type F), and geothermal wastewater (Type G) are given in Table 2.

Results and Discussion

The average EC values of 6 geothermal water samples, 4 geothermal wastewater samples, 26 surface water samples and 2 cold groundwater samples were compared and shown in Fig. 2, the results indicating that geothermal waters and wastewaters have much higher EC values than cold surface waters and groundwaters. Other average chemical characteristics of these four groups of water samples, including DO, pH, and concentrations of Al, Li, Ba, Mn, Mo, Pb, Cd, Co, P, and Zn were illustrated in Fig. 3. It can be clearly seen from Fig. 3 that the Li, Cd, Mo, and Pb concentrations of geothermal waters and wastewaters are much higher than those of cold waters, whereas DO and the Al, Mn, Co, P and Zn concentrations of geothermal water and wastewater samples lower than those of cold surface water samples. Further analysis using *T*-test between geothermal water samples (including wastewater samples) and cold water samples indicates that there are significant differences in statistics between these two groups of samples in all their chemical constituents given in Table 3 except for Ba and Zn. Moreover, very significant statistical differences in Li, Cd, Mo, and Pb concentrations with p-level < 0.00005 were distinguished (these constituents are also specially enriched in geothermal waters), which means that these four elements can be regarded as the characteristic constituents of geothermal waters and used as the indicators of water contamination in and around the field induced by geothermal water discharge and/or wastewater drainage. In fact, Li with very high concentration in high-temperature geothermal water with magma as its heat

Table 1 Type, elevation (m), and water temperature (°C) of all water samples

No	Type	*E*	*T*	No	Type	*E*	*T*	No	Type	*E*	*T*	No	Type	*E*	*T*
X1	A	5450	–	S1	C	4279	12.1	S7	D	4277	10.2	302	F	4362	86
X2	A	5469	–	S2	C	4278	12.9	S8	D	4275	10.1	329	F	4332	86
X3	A	5027	9.2	S3	C	4277	19.4	S9	D	4277	11.3	357	F	4348	86
M1	B	4364	18.4	S4	C	4276	15.3	S10	D	4268	13.3	359	F	4359	86
M3	B	4321	14.7	S5	C	4274	15	S12	D	4260	12.3	4001	F	4373	86
M4	B	4325	18.8	S11	C	4264	12.1	S17	D	4269	12.9	W1	G	4288	86
M5	B	4324	18.3	S13	C	4265	12.4	C4	E	4310	11.1	W2	G	4276	25
M6	B	4336	13.6	S14	C	4269	20.3	M2	E	4365	11.5	W3	G	4286	17.8
M7	B	4282	18.1	S15	C	4272	20.9	05	F	4330	86	W4	G	4315	60.4
M8	B	4681	12.2	S16	C	4273	13.1								

E and T in the headline of the table mean elevation (above mean sea level) and temperature, respectively. Type A: Snow or snow melting water; Type B: Stream water; Type C: Zangbo River water; Type D: Yangbajing River water; Type E: Cold groundwater; Type F: Geothermal water; Type G: Geothermal wastewater or mixing water of geothermal wastewater with stream water

Table 2 Average hydrochemical properties and trace element concentrations of water samples of type A, B, C, D, E, F and G (in mg/L except Electrical Conductivity (EC) in μS/cm and pH)

Type	pH	EC	DO	Al	Ba	Cd	Co	Li	Mn	Mo	P	Pb	Zn
A (3)	8.40	17	0.34	0.029	0.002	–	0.0003	–	0.007	0.002	–	0.003	–
B (7)	8.30	171	5.10	1.084	0.014	0.0008	0.0007	0.233	0.027	0.005	0.011	0.019	0.006
C (10)	7.94	146	5.48	1.871	0.041	0.0002	0.0011	0.046	0.098	0.006	0.037	0.013	0.014
D (6)	7.80	90	5.61	2.454	0.043	–	0.0016	0.013	0.100	0.005	0.048	0.015	0.021
E (2)	8.56	94	4.61	0.208	0.005	–	0.0001	0.002	0.027	0.004	–	0.005	0.002
F (6)	6.51	2358	0.51	0.321	0.041	0.0145	–	6.940	0.014	0.033	–	0.034	0.003
G (4)	8.70	1403	3.79	0.735	0.032	0.0093	0.0002	3.680	0.035	0.026	0.009	0.022	0.007

Figure in parentheses is the total number of water samples. The meanings of sample types A, B, C, D, E, F and G are the same as in Table 1. "–" means that the concentrations of water samples are below detectable limit

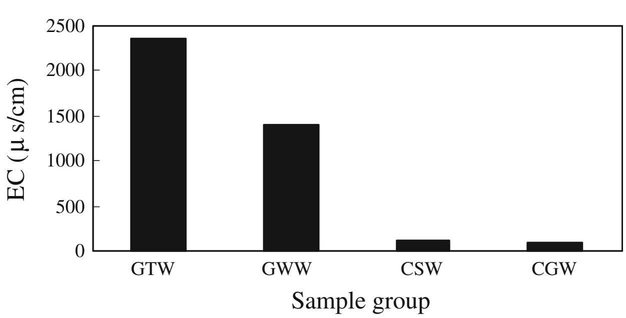

Fig. 2 Average EC values of 6 geothermal water samples (GTW), 4 geothermal wastewater samples (GWW), 26 surface water samples (CSW) and 2 cold groundwater samples (CGW)

source is usually expected to originate from degassing magma (Tong and Zhang 1981). For the Yangbajing hydrothermal system, the abundances of Li element in reservoir hostrocks (granite) and recharge waters (snow melting waters) are very low, so it should be unlikely that the enrichment of Li in the geothermal waters results from the recharge of snow melting water or the water-rock interaction during the geothermal water ascent. Furthermore, since the existence of magma heat source at Yangbajing has been verified by the geophysical and geochemical studies (Nelson et al. 1996; Brown et al. 1996; Makovsky et al. 1996; Kind et al. 1996; Chen et al. 1996; Guo et al. 2007b), Li in the geothermal waters at Yangbajing appears to have a magma degassing origin and can therefore serve as a characteristic constituent of geothermal waters. Similarly, Cd, Mo, and Pb were also employed to indicate water contamination due to natural (as hot springs) or man-made (wastewaters from the two power plants) discharge of geothermal waters in this study.

The Box and whisker plots (Fig. 4) of the concentrations of Cd, Li, Mo and Pb in snow (or snow melting waters), stream waters, Zangbo River waters, Yangbajing River waters and cold groundwaters were made to indicate if these waters were affected by the drainage of geothermal waters. It can be seen from Fig. 4 that snow (or snow melting water) samples, Yangbajing River water samples and cold groundwater samples have very low Cd and Li concentrations and relatively low Mo and Pb

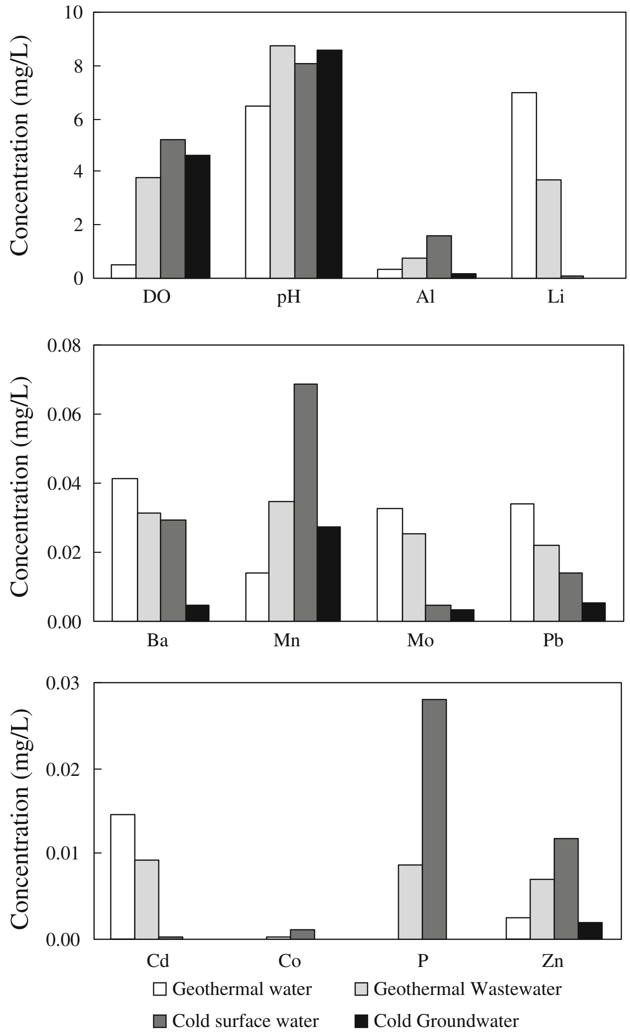

Fig. 3 Average DO and pH values and concentrations of Al, Li, Ba, Mn, Mo, Pb, Cd, Co, P, and Zn of 6 geothermal water samples, 4 geothermal wastewater samples, 26 surface water samples and 2 cold groundwater samples

concentrations, indicating that these waters have little relation to geothermal waters. However, stream waters and Zangbo River waters have comparatively higher Cd, Li,

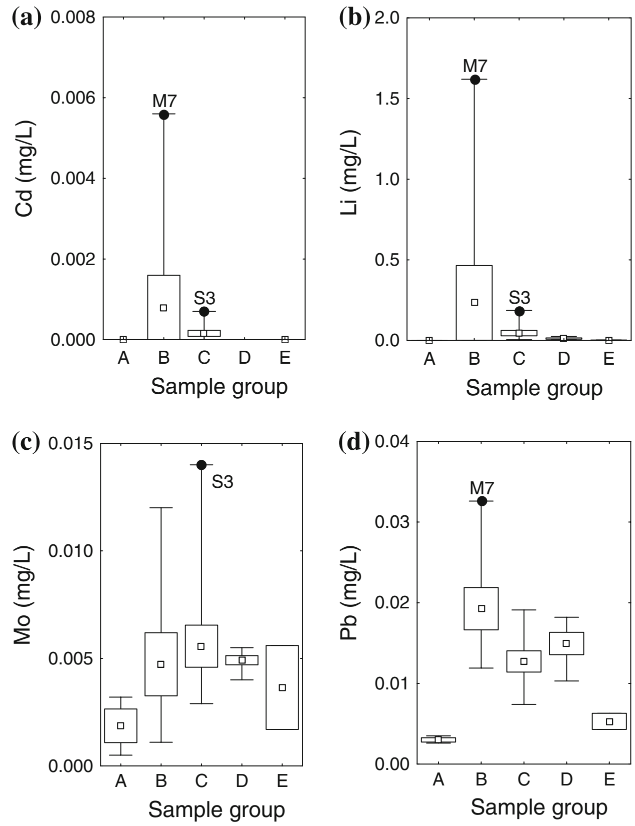

Fig. 4 *Box* and *whisker plots* of the concentrations of (**a**) Cd, (**b**) Li, (**c**) Mo, and (**d**) Pb in water samples of type A, B, C, D and E. The meanings of type A, B, C, D, and E are the same as in Table 1. The *boxes* show the mean value minus *standard error*, the mean value, and the mean value plus *standard error*. The smallest and largest values are indicated by the smackall *horizontal bars* at the end of the *whiskers*. ● represents outlier values

Mo and Pb concentrations, which means that the geothermal waters may be responsible for the elevated concentrations of the above constituents in these surface waters. In particular, it is worth noting that the Cd, Li, Mo and Pb concentrations of two water samples were identified as outlier values in Fig. 4: one is the stream water sample M7, and the other the Zangbo River water sample S3. Since the

Table 3 *T*-test results between DO, pH, and concentrations of Al, Li, Ba, Mn, Mo, Pb, Cd, Co, P, and Zn of geothermal water and wastewater samples and those of cold water samples

Index	Average-G	Average-C	*t*-value	*p*-level	Index	Average-G	Average-C	*t*-value	*p*-level
DO	1.82	4.78	−3.2	<0.005	Mo	0.03	0.005	8.58	<0.000001
pH	7.39	8.09	−2.19	<0.05	Pb	0.029	0.013	4.6	<0.00005
Al	0.487	1.483	−2.32	<0.05	Cd	0.0124	0.0003	8.37	<0.000001
Li	5.636	0.078	6.46	<0.000001	Co	0.0001	0.0009	−3.07	<0.005
Ba	0.037	0.028	1.45	>0.05	P	0.003	0.026	−2.43	<0.05
Mn	0.022	0.066	−2.72	<0.01	Zn	0.004	0.011	−1.91	>0.05

Average-G in the headline of the table means the average values of geothermal water and wastewater samples (mg/L except for pH), and Average-C means the average values of cold water samples (mg/L except for pH)

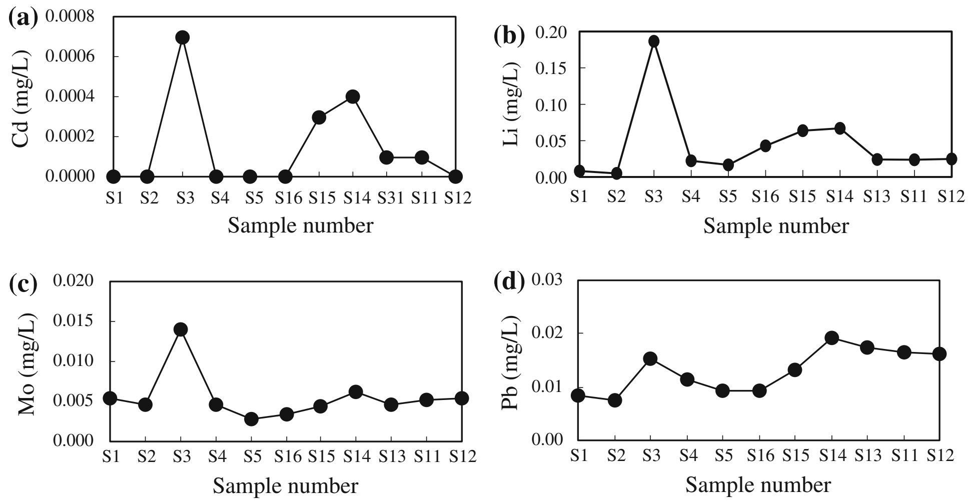

Fig. 5 Variations of (**a**) Cd, (**b**) Li, (**c**) Mo, and (**d**) Pb concentrations in Zangbo River waters along the flow direction (cf. Fig. 1)

sample S3 is just located in the nearest downstream of the wastewater draining exit (namely the sampling location of W1) of the first geothermal power plant (Fig. 1), its very high Cd, Li, Mo and Pb concentrations should indicate the effect of geothermal wastewater drainage. The water sample M7 was collected from one stream flowing into the Zangbo River from south. This sample has EC value and trace element chemistry similar to those of the geothermal water samples, and therefore it can be speculated that this stream may be recharged by some geothermal springs under the streambed. Moreover, the Cd, Li, Mo and Pb concentrations of M7 are 0.0056, 1.620, 0.012, and 0.033 mg/L, respectively, much higher than the corresponding average values of the other stream water samples (0, 0, 0.004, and 0.017 mg/L, respectively), which may also indicate the impact of geothermal water discharge.

Among all the surface water bodies at Yangbajing, the water quality of Zangbo River should have been most seriously affected by the geothermal wastewater drainage. According to our field investigation in 2007, there are three geothermal wastewater draining exits along the Zangbo River. The geothermal wastewaters from the first power plant are immediately drained into the river, and those from the second power plant into two streams that flow into the river from north. Three corresponding wastewater samples, namely W1, W2, and W3, were collected in these three draining exits. To illustrate the impact of the geothermal wastewater drainage on the water quality of the Zangbo River, the variations of Cd, Li, Mo and Pb concentrations of the river water samples along the flow direction were shown in Fig. 5.

From Fig. 5, it can be noticed that the samples S1 and S2 located upstream of the wastewater draining exit of the first power plant have very low Cd, Li, Mo and Pb concentrations, indicating that these samples are free from contamination induced by the power plant wastewaters. By contrast, the Cd, Li, Mo and Pb concentrations of the sample S3 collected at the nearest downstream of the wastewater draining exit are markedly higher than those of the samples S1 and S2, showing the evident contamination of the river waters by geothermal wastewaters. From S3 to S4 to S5, the concentrations of these elements sharply decline, due to self-purification of the Zangbo River, as a result of dilution of river waters and adsorption onto riverbed sediments. However, from S5 to S16 to S15, the Cd, Li, Mo and Pb concentrations increase gradually, under the mixing effect of the two streams where the geothermal wastewaters from the second power plant are drained. Besides S3, the location of the sample S14 on Fig. 5 is another peak point. It should be the result of the inflow of the stream with geothermal origin where the sample M7 was collected. From S14 to S13 to S11 to S12, the concentrations of Cd, Li, Mo and Pb generally decrease again. The inflow of the Yangbajing River has no significant influence on the trace element chemistry of the Zangbo River water.

To conclude, trace elements including Cd, Li, Mo and Pb were used as effective tracers to identify the water quality deterioration related to geothermal water discharge and geothermal wastewater drainage at Yangbajing. The water quality investigation performed in this study confirms that trace elements can serve as a very useful tool for delineating water pollution.

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