

HEAVY METALS IN THE WATER AND SEDIMENTS OF GUAN-TING RESERVOIR

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ABSTRACT The distribution and behavior of heavy metals (Cu, Pb, Zn, Cd) in the water and sediments of Guan-Ting reservoir, which is a water supply of Beijing city, were studied. The results for the water column show that the mean percentage of metals in the solute phase is 4.2%, and that most are associated with suspended sediment. The content of metals in bed materials is from 5000 to 10 000 times higher than dissolved in the water. The exchangeable metals in the bed materials represents only 0.6% of the total. This indicates that metals in sediments are not greatly affected by surface adsorption. The spatial distribution of metals within the reservoir reflects pollution from various sources. The spatial variation in metal concentrations provides information on temporal changes in water quality and pollution. The trends for metals in water show that pollution increased in from 1973 to 1985, but it decreased since 1985.

DESCRIPTION OF GUAN-TING RESERVOIR

The Guan-Ting Reservoir is located on the upstream reach of the Yongding River on the western edge of Beijing city. It was constructed in 1953 to control floods and to supply drinking water to that city. The Yongding River with its tributaries Yang and Sanggan, drains a basin of 43 000 km² and delivers an average annual runoff of 1.07×10^9 m³ and an annual sediment load of 50×10^6 t.

The reservoir has a surface area of 225 km² and a total storage of 2.27×10^9 m³. The reservoir consists of two arms joining at Station 1010 (Fig. 1), which is about 5 km upstream of the dam. The left arm, viewed from upstream, is on the Guishui River and contains 60% of the total storage. The remaining storage is in the right arm on the Yongding River which has two tributaries, the Yang River and the Sanggan River, which join at Station 1042 about 25 km upstream of the dam.

Water supply operations require that only clear water be released from the reservoir. Storage of floods and release of clear water over the years have resulted in large amounts of sediment deposition in the reservoir. Up to the present, the total amount of sediment deposited in Guan-Ting reservoir is 622×10^6 m³ and occupies 27.4% of the available storage. The sediment load of the Yongding is so large that the depositional delta in the right arm of the reservoir is extending rapidly towards the dam. As a result, a bar has already developed at the mouth of Guishui River. The position of the Yongding River inflow into the reservoir has changed over the years because of the sediment deposition in the delta and in the backwater regions of the Yongding arm of the reservoir.

The discharge and sediment loads of the Yongding River and Guishui River differ markedly. The minimum discharge of the Yongding River is 2.27×10^9 m³ year⁻¹, but that of the Guishui is 0.098×10^9 m³ year⁻¹. At least 95.9% of the discharge comes from the

Yongding River. The suspended sediment concentration in the Yongding and Guishui Rivers also differs ($14\,650\text{ mg l}^{-1}$ in the Yongding River and 6 mg l^{-1} in the Guishui River). The sediment load from Yongding Basin provides 99.998% of the total sediment input into the reservoir. Any investigation of the sediment transport by the Yongding River, therefore, is likely to be representative of the sediment input to the reservoir.

METHODS

Field

Samples for investigating the spatial distribution and temporal variation of metal levels were collected from 16 stations selected from the existing network. The historic water quality data were from 22 existing stations (see Fig. 1). The existing stations generally had monthly water quality records for 1973-1989. Thirty constituents, including DO, temperature, and pH were measured at each station. The synoptic samples of sediment and bed material were collected from selected stations (2, 3, 6, 9, 17, and 21) during two seasons and frozen in polyethylene bottles until they were analyzed.

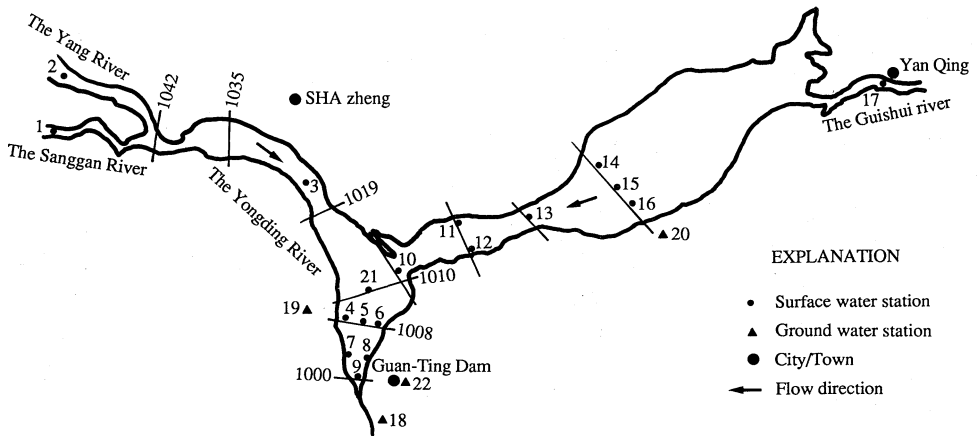


FIG.1 Location of the sample collection sites in the Guan-Ting Reservoir.

Laboratory

The solute samples were analyzed for heavy metals by graphite furnace atomic absorption (GFAA) and polarographic analyzer (PA). The suspended sediment samples were prepared by filtering an appropriate volume of sample through a $0.45\ \mu\text{m}$ organic membrane. They were then dried, weighed and extracted with 50 ml 1N nitric acid. After extraction, they were filtered and analyzed by GFAA and PA. At the same time, the concentration of suspended sediment in the water sample was measured.

The bed material samples were prepared in different ways. (a) Metals adsorbed on sediment were extracted by 1N ammonium acetate (NH_4OAC). Approximately 24 g of dry sediment were extracted in 200 ml 1N ammonium acetate (pH 7) by shaking for 6 h.

(b) Metals incorporated in bed materials were extracted with 1N nitric acid. Approximately 60 g of oven-dried bed material were obtained from the frozen cores and 200 ml 1N nitric acid was added to each flask containing bed material. The flasks were shaken for 6 h. (c) Metals in the bed material were digested. The bed material samples were digested with hydrochloric and nitric acid (3:1) and perchloric acid for analyses of total metal contents. Approximately 15 g of dried sediment were digested with 50 ml nitric-hydrochloric acid and 30 ml perchloric acid, filtered (if necessary), and diluted to 200 ml. The extracts for each preparation were analyzed by GFAA for Cu, Pb, and Zn, and by PA for Cd.

Replicate frozen bed material cores were analyzed for particle size distribution and organic matter content. The samples were passed through a No. 300 polyethylene sieve with 0.05 mm mesh. The dry weight of each particle size was recorded. Oven-dried bed material from the cores was ignited at 500°C for 12 h to obtain loss on ignition.

TABLE 1 Concentrations of Cu, Pb, Zn, Cd in the water column and in bed materials (complete digestion).

Site	metal	total		water column dissolved		suspended sediment		bed material	
		mg l ⁻¹	%	mg l ⁻¹	%	mg l ⁻¹	%	mg kg ⁻¹	
3	Cu	.087	100	.004	4.6	.083	95.4	27.29	41.5
	Pb	.151	100	.001	0.7	.15	99.3	49.33	186.0
	Zn	.20	100	.01	5.0	.19	95.0	62.48	156.0
	Cd	.005	100	.0001	1.9	.005	98.1	1.71	4.4
21	Cu	.09	100	.005	5.5	.086	94.5	20.93	37.5
	Pb	.18	100	.001	.6	.18	99.4	43.31	164.9
	Zn	.30	100	.016	5.4	.28	94.6	68.86	100.0
	Cd	.005	100	.0002	4.8	.005	95.2	1.29	2.6
6	Cu	.004							48.3
	Pb	.016	100	.001	6.5	.015	93.5	13.20	39.2
	Zn	.06	100	.004	6.7	.056	93.3	51.44	97.1
	Cd	.0004							.4
mean for all stations and metals					4.2		95.0		

RESULTS AND DISCUSSION

Distribution of metals in water, suspended sediment, and bed material

Metals in the water column are almost exclusively associated with suspended sediment (Table 1). The mean metal content in solution is only 4.2%, and in bed materials is about 500-1000 times higher than in water column.

The metals adsorbed on bed material is only 0.6% of the total in the sediment and the exchangeable metals content generally is less than 1.5% (Table 2). Also, the metals associated with carbonates, hydrous Fe and Mn oxides, organic matter, and sulfides, generally,

is 32% of the total metal content. These results indicate that metals in sediments are not generally associated with surface adsorption, even where samples were composed of smaller particle sizes and contain considerable organic matter. For example, for station No. 6 the loss on ignition and fine particle content is high. The loss on ignition is 9.09% and percentage of particle size <0.05 mm is 99.2%, but the exchangeable Cu, Pb, Zn and Cd is 0.1%, 0.1%, 0.01%, and 0.02%, respectively. Exchangeable metals, therefore, do not directly cause pollution of the aquatic environment under natural pH conditions.

TABLE 2 Distributions of different species of Cu, Pb, Zn, and Cd in bed material.

Site	Metal	Adsorption		Species digested by		complete digestion	
		NH ₄ OAC	(%)	HNO ₃	(%)	(mg kg ⁻¹)	(%)
3	Cu	0.6	1.4	12.3	29.6	41.5	100
	Pb	4.9	2.6	137.1	73.7	186.0	100
	Zn	0.1	0.06	25.3	16.2	156.6	100
	Cd	0.0	0.0	0.9	22.1	4.4	100
21	Cu	0.0	0.0	1.1	2.9	37.5	100
	Pb	1.2	0.7	114.6	69.5	164.9	100
	Zn	0.0	0.0	18.8	18.8	100.0	100
	Cd	0.07	2.6	1.2	45.8	2.6	100
6	Cu	0.05	0.1	16.0	40.8	48.3	100
	Pb	0.05	0.1	5.8	14.7	39.2	100
	Zn	0.01	0.01	10.0	10.3	97.1	100
	Cd	0.01	0.02			0.4	100
9	Cu	0.0	0.0	1.0	2.4	40.6	100
	Pb	0.06	0.2	6.1	16.4	37.3	100
	Zn	0.01	0.01	4.2	4.0	104.9	100
	Cd	0.0	0.0	1.0	30.1	3.2	100
2	Cu	0.1	0.5	7.2	38.3	18.8	100
	Pb	0.05	0.2	18.0	83.3	21.6	100
	An	0.8	1.5	8.3	15.6	53.1	100
	Cd	0.0	0.0	0.3	15.7	1.9	100
17	Cu	0.2	1.1	5.5	31.7	17.3	100
	Pb	0.1	0.4	10.2	46.8	21.8	100
	Zn	0.1	0.2	9.3	16.8	55.3	100
	Cd	0.03	3.1	0.9	91.8	0.98	100
mean		0.6		32.0			

The proportions of different metals in solution and associated with suspended sediment differs and is probably dependent on the solubility of the metal under given pH conditions. In Guan-Ting reservoir, pH generally ranges from 8.0 to 8.5, and the solution phase of metals therefore is very small and in the order of $Zn > Cu > Cd > Pb$. For example, at station No. 3 the percentage of Zn in solution is 5.0%; Cu is 4.6%; Cd is 1.9%; and Pb is only 0.7%. The dissolved concentrations of Cu, Pb, Zn, and Cd do not affect water use. In contrast, the metal concentrations of the suspended sediment and bed material is more important, because they clearly indicate the presence and historical record of metal pollution in the reservoir.

TABLE 3 Soil background values of Cu, Pb, Zn, and Cd for the Beijing district and Guan-Ting reservoir area; concentrations in $mg\ kg^{-1}$ are for the complete digestion.

Metal	Mean	95% confidence limits	Area
Cu	18.05	16.22-20.08	Beijing district
Pb	19.75	17.79-21.53	
Zn	117.9	104-131	
Cd	0.065	0.044-0.085	
Cd	0.039 (for 1973)		Guan-Ting reservoir
Cd	0.094 (for 1974)		

TABLE 4 Concentration trends for Cu, Pb, Zn, and Cd in the water of Guan-Ting Reservoir, 1973-1979. M = mean; P = Statistical probability; and S = slope.

Metal	Trends	Station number							
		1	2	3	6	9	14	18	20
Cu	M					0.004			0.004
	P					0.09			0.02
	S					0.0002			-0.0003
Pb	M		0.006	0.007					
	P		0.05	0.009					
	S		0.0006	0.0008					
Zn	M	0.016	0.014	0.017	0.013	0.015	0.013	0.015	0.02
	P	0.009	0.005	0.019	0.026	0.0005	0.026	0.003	0.006
	S	0.004	0.003	0.002	0.0014	0.003	0.001	0.002	0.002
Cd	M		0.0004	0.0003		0.0003	0.0004		
	P		0.04	0.07		0.07	0.07		
	S		-0.0002	-0.0001		-0.0001	-0.0001		

To assess the extent of pollution in Guan-Ting reservoir, we compared the metal content of bed material from several stations in the reservoir with background soil data from Beijing and the reservoir catchment (Tables 2 and 3). Metal pollution of Cu, Pb, and Zn has not occurred yet at stations 2 and 17. This suggests that the metal pollution is not associated with the Guishui River (station 17) or Yang River (station 2). In contrast, stations 3, 21, 6, and 9 exhibit metal pollution of Cu, Pb, Zn, and Cd. For example, Cu concentrations for stations 3, 21, 6, and 9 are 41.5, 37.5, 48.3, and 40.6 mg kg⁻¹, respectively, and these concentrations are greater than the background soil (Table 3).

Spatial and temporal variation of heavy metals in bed materials.

Figure 1 and Table 2 provide information on the spatial and temporal variation of Cu, Pb, Zn, and Cd concentrations in bed material. In 1989, the flow direction in the reservoir was from station 2 through 3 to 21, but several years ago in 1980, the flow direction was from station 2 through 3 to 6 and 9. The spatial distribution of the metal pollution was affected by pollution flux and decreased along the water course. Current metal concentrations along the water course increase from background between stations 2 and 3, and then decrease to station 21. For example, Pb concentrations in bed material increase from 21.6 mg kg⁻¹ at station 2 to 186 mg kg⁻¹ at station 3 and decrease to 164.9 mg kg⁻¹ at station 21. The metal pollution apparently occurs between station 2 and 3, and may be caused by inputs from Sha Zheng city. The concentration decrease between stations 3 and 21 may have occurred by exchange between water and suspended sediment and deposition of sediment between the stations.

TABLE 5 Concentration trends for Cu and Zn in the water of Guan-Ting Reservoir, 1980-1984. M = mean; P = Statistical probability; and S = slope.

Metal	Trends	Station number				
		2	14	18	19	20
Cu	M	0.03				
	P	0.000002				
	S	0.005				
Zn	M	0.02	0.02	0.01	0.02	0.01
	P	0.05	0.009			
	S	0.0006	0.0008			

Because the direction of flow in the reservoir has changed during the period of record, the spatial distribution of metal concentrations in bed material provides a historical record. For example, the bed material at station 6 and 9 had high metal concentrations in 1980-81 and station 2 and 21 had similarly high concentrations in 1988-89. Comparing data for stations 6 and 3, and 9 and 21, and the change in metal concentrations in the bed material between the two sampling periods indicates that metal pollution increased rapidly from 1980

to 1989. For example, Pb concentration at station 6 and 9 is 39.2 and 37.3 mg kg⁻¹, respectively, but at station 3 and 21, it is 186 and 164.9 mg kg⁻¹. Results for Cu, Zn, and Cd are similar, indicating that the spatial distribution of metals provides pollution history.

TABLE 6 Concentration trends for Pb and Zn in the water of Guan-Ting Reservoir, 1985-1989. M = mean; P = Statistical probability; and S = slope.

Metal	Trends	Station number							
		1	2	3	4	6	9	13	14
Pb	M		0.03		0.005		0.003		0.003
	P		0.01		0.001		0.02		0.01
	S		-0.006		-0.001		-0.0005		-0.0005
Zn	M	0.02	0.03	0.03	0.02	0.02	0.02	0.01	
	P	<0.0001	<0.0001	0.004	0.007	0.001	0.0003	0.001	
	S	-0.005	-0.01	-0.004	-0.004	-0.004	-0.004	-0.004	

TABLE 7 Trend of suspended sediment concentration (SSC, in mg l⁻¹) and mean monthly discharge (Q, in m³ s⁻¹) into Guan-Ting reservoir.

Period	Trend of SSC			Trend of Q		
	Mean	Prob.	Slope	Mean	Prob.	Slope
1980-1984	11600	0.94	0.015	22.54	0.0001	-2.3
1985-1989	14650	<0.0001	-1.68	10.81	0.0042	-1.3

Trends of Heavy Metals in Water

To examine trends associated with Cu, Pb, Zn, and Cd levels in water, the seasonal Kendall test was used (Hirsch *et al.*, 1982). It is a non-parametric method, and is suitable for water quality data. When the seasonal Kendall test is used with water quality data, problems of seasonality, skewness, censoring (less than detected limit), serial dependence, missing values and non-normal distributions do not effect the accuracy of test. Trend analysis was performed on the historical data for 1973-1989 by analyzing 3 separate periods. The trends of Cu, Pb, Zn, and Cd at 22 stations during the 3 periods were evaluated. The results are summarized in Tables 4, 5, and 6.

Concentration are increasing for Cu, Pb, and Zn in water during the period 1973-1979, whereas Cd concentrations are decreasing (Table 4). The trends are highly significant (P<0.01) for Zn at stations 1, 2, 9, 18, and 20 and only slightly less significant (P<0.05) at the other three stations. For Pb, the trend is highly significant (P<0.01) only for station 3.

Significant level trends for Cu and Cd may exist for several stations, but the probability level ($P < 0.10$) is less than that for Zn or Pb. It is necessary to consider why the trends differ for Cu, Pb, Zn and Cd. Because Cd trends are not associated with major industrial or agricultural sources, including municipal point sources, atmospheric deposition is probably the most important source of Cd. The trends of Cu, Pb, and Zn, however, are associated with the discharge of wastewater and nearby atmospheric sources. Zn and Pb concentrations decreased at several stations from 1985 to 1989 (Table 6); the probability levels indicate that these trends are very significant. Zn concentrations increased at several stations from 1980 to 1984 (Table 5), but Cu concentrations only increased at station 2 during this period.

Trend results compared by time periods (Tables 4, 5, and 6) indicate that the trend direction of some metals changed from period to period over the length of record, 1973-1989. Zn concentrations at station 3 increased during 1973-1979, showed no trend in 1980-1984, and declined during 1985-1989. At station 2, the change is from an increase in 1973-1984 to a decline in 1985-1989. If the trends for Zn in water and in bed material are compared, it can be seen that they are in the same direction during 1973-1984, but not in 1985-1989. The Zn concentrations of bed material increase from 1980 to 1989, but those of water increase only from 1980 to 1984, after which they decrease. To explain these differences, the trends of suspended sediment concentration and discharge into the reservoir also were evaluated (Table 7).

Discharge decreased from 1980 to 1989 (Table 7). Suspended sediment concentration showed no statistically significant trend from 1980 to 1984, but concentration decreased from 1985 to 1989. In addition, the sediment loads decreased significantly from 1985 to 1989. A plausible explanation of why Zn concentrations of the water also decreased is that Zn in the water exchanged with the bed material by reaction at the interface.

CONCLUSION

Analysis of distribution, trends and relations for heavy metals in water, suspended sediment and bed material show:

- (a) The dissolved fraction of metals in the water column is very small in the Guan-Ting reservoir. Most metals are associated with suspended sediments.
- (b) Results indicate that exchangeable fraction of the metal on the sediment (extract by NH_4OAC) is too small to be important, in general, to water quality, i.e. most of the metal is strongly bonded to the sediment. Also, metal in the water can be removed by adsorption with and deposition by the sediment.
- (c) The pollution history can be established by investigating the distribution of metals in bed material during different periods.
- (d) Trends for metals in the water column and bed materials are highly correlated. However, the trend for metals in water is more complex than in bed material. The trend reflects not only the concentration of metals in suspended sediment, but the suspended sediment load as well.

REFERENCE

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