Environ Geol (2006) 49: 733–742
DOI 10.1007/s00254-005-0118-8

ORIGINAL ARTICLE

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Dissolved trace elements in river water: spatial distribution and the influencing factor, a study for the Pearl River Delta Economic Zone, China

Received: 31 May 2005
Accepted: 4 October 2005
Published online: 24 November 2005

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Abstract Twenty-nine water samples were collected from different river channels of the Pearl River Delta Economic Zone, China. An inductively coupled plasma-mass spectromonitor (ICP-MS) was used to measure concentrations of the trace elements in these samples. The results suggest that the average concentrations of rare earth elements in river water show an increasing trend from the West River, the North River, the rivers of the Pearl River Delta, and the Shenzhen River to the East River. Relatively high concentrations of heavy metals appear in the East River, the rivers of the Pearl River Delta and the Shenzhen River, while the West River and the North River have relatively low heavy metal concentrations. Trace element concentrations in samples collected near urban or industrial areas are much higher than those of samples collected from distant areas, away from urban and industrial areas. After natural conditions, human activities have significant influence on the trace element concentrations in river water. This trace element concentration's spatial distribution in the river water from the Pearl River Delta Economic Zone is actually an integrated effect of natural conditions and human activity.

Keywords Spatial distribution · Trace element · River water · The Pearl River Delta Economic Zone

Introduction

It is well known that trace elements in water, especially heavy metals, can impact human health. Water quality of the Pearl River water system has been evaluated in terms of some physicochemical parameters (Zhu et al. 1997; Lei and Xiao 1999; Luo 2002; Ouyang et al. 2005). Studies of major ions in the river water of the Pearl River water system have also been reported (Chen and He 1999; Zhang 2000). Few studies, however, have focused on trace elements in the river water from the Pearl River Delta (Wang et al. 1998). From an environmental management perspective, it is important to investigate the trace element concentrations in the river water of the Pearl River Delta Economic Zone (PRDEZ) and the effect of influencing factories. Numerous studies have already been published about trace elements or heavy metals in river water (Shiller 1997; Buykx et al. 1999; Iwashita and Shimamura 2003; Akpan et al. 2002; Rose 2002; Carvalho et al. 1999; Neal et al. 1996); this research focused on the trace element concentrations in the particular waters within the PRDEZ, China and the impact of human activities. Inductively coupled plasma-mass spectrometry (ICP-MS), used extensively by Paulsen and List (1997) and Ammann (2002) to yield high-quality data, was utilized for this study also.

Materials and methods

Study area

The study area, the Pearl River Delta Economic Zone, is one of the most developed economic areas in China and probably in the world. The PRDEZ is located from 112°00′E to 115°25′E and 22°30′N to 23°45′N. It is a region rich in small streams with several large drainage basins, the East River (ER), the West River (WR) and the North River (NR), which all converge into the Pearl River and then run through eight estuary gates and flow into the South China Sea (Fig. 1). Since the reforming and opening in late 1970s of China, economy of this area developed rapidly. However, this development mainly depends on industry and is still very extensive. In addition, some contaminative industries were introduced into this area only for economic purpose. As a result of this economic growth, lots of environmental problems emerged. Besides industry, some other human activities also impact the environment of the PRDEZ. According to the results of the fifth population census conducted in China, there are 39.68 million people living in the PRDEZ as of November 1, 2000 (Population Census Office of Guangdong Province 2002). The urbanization level of the PRDEZ was 71.4%. It is much higher than the average level of the country and Guangdong province (36.9 and 55.7%, respectively). Among these environmental problems, river water quality is the most important one in the PRDEZ. In this study, the spatial distribution and the influencing factor of dissolved trace element in river water were investigated using the analytical results of water samples collected from the WR, the NR, the ER and Rivers of the Pearl River Delta (RPRD) and the sample from the Shenzhen River (SR). The study area and the sampling sites are shown in Fig. 1.

As recorded by the Bureau of Geology and Mineral Resources of Guangdong Province (1982), the geological backgrounds for the five studied rivers are fairly similar within the PRDEZ. The river valleys of the WR, the NR and the RPRD are mainly developed in the Quaternary strata, as are the lower reaches of the ER. However, the upper reaches of the ER are developed in Lower Jurassic strata, and the SR drainage area is developed in Middle Jurassic. Granite can be found in many places along the valleys of the WR, the NR, the ER and the SR, while limestones are developed in the upper stream of the WR.

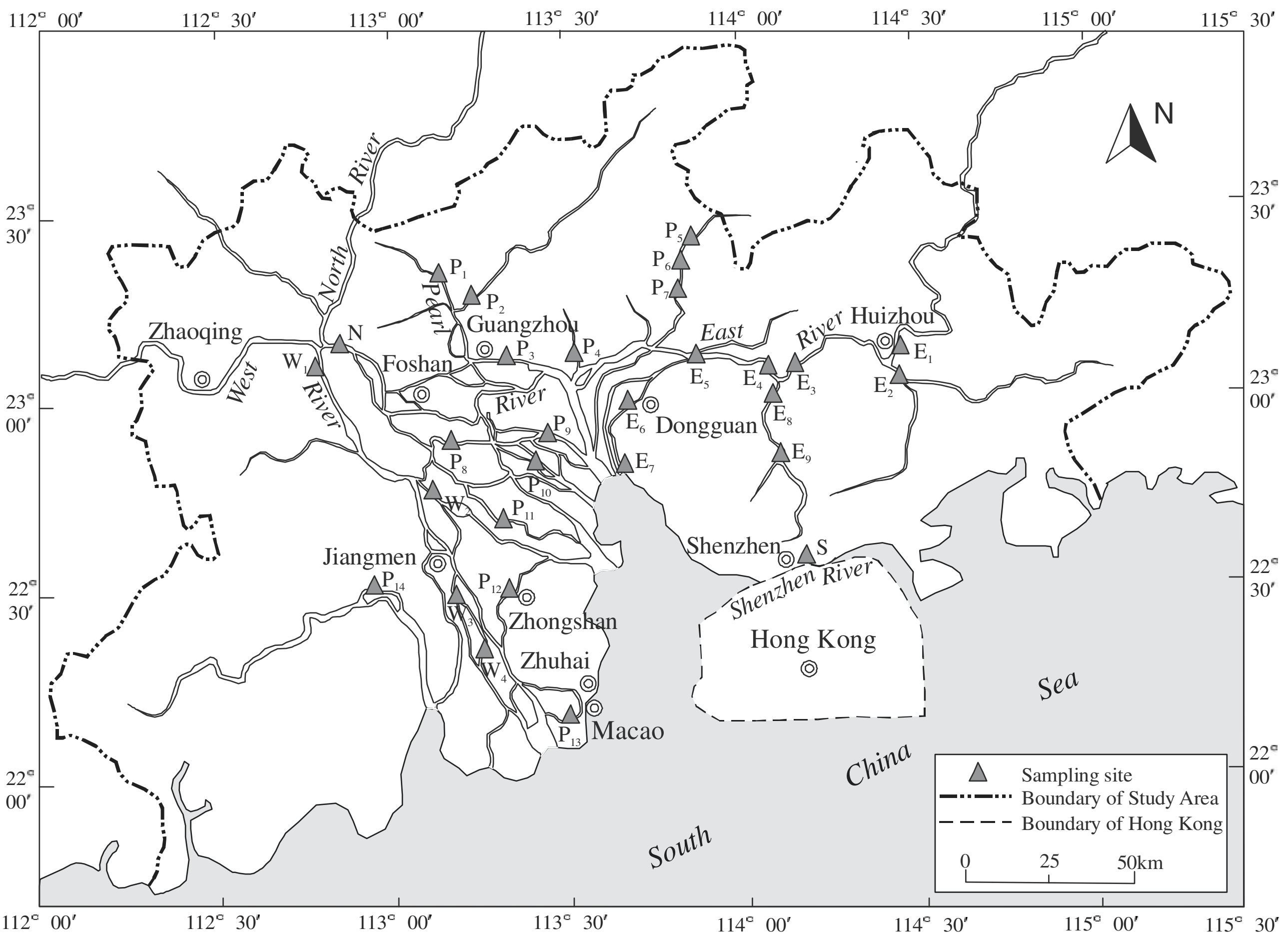

Fig. 1 Study area and the sampling sites

Table 1 Annual precipitation and runoff of the five studied rivers

River	Annual precipitation (mm)	Annual runoff ($\times10^8$ m^3)
WR	1,542.4	2,255
NR	1,803.1	490
ER	1,751.7	280
RPRD	1,865.0	313
SR	1,933.3	< 100

The whole Pearl River Delta watershed is composed of Quaternary interactive facies of marine and continental sediments. The WR drains a large area of red soil. The hydrological and climatic conditions of the five studied rivers are very different. The annual precipitation and runoff of the WR, the NR, the ER, the SR and the RPRD are listed in Table 1 (Water conservancy committee of the Pearl River of Ministry of Water Resources and Editorial committee of Annals of the Pearl River 1991).

Sampling sites and measurement

From different river sections of the PRDEZ, 29 water samples were collected during the low water period in the 2002 hydrological year, lasting from October to March. Sampling sites are illustrated in Fig. 1. All water samples were collected from 1 m below the water surface using 100 ml polythene bottles, which were soaked in dilute hydrochloric acid for 2 days and rinsed with distilled water before sampling. At sampling sites, the bottles were rinsed three times with the water to be sampled prior to filling. The upper part of the clean water in each bottle was taken out and then measured with ICP-MS for 43 trace elements. Precision was monitored as well. For most of the elements, average precisions of the 29 samples are much better than 10% RSD.

The 29 samples were classified into five groups according to the river segment where samples were collected. Four samples were collected from the WR. These sampling sites are labeled with characters beginning with "W" in Fig. 1. Nine samples were collected from the ER. These sampling sites are labeled with characters beginning with "E" in Fig. 1. From the RPRD, 14 samples were collected. These sampling sites are labeled with characters beginning with "P" in Fig. 1. For the NR and the SR only one sample each was collected. These two sampling sites are labeled "N" and "S", respectively, in Fig. 1.

Background and threshold values

Based on the sampling location, ten samples collected a significant distance from city, town, and industrial areas can be regarded as samples that were not influenced by human activity. These ten samples were selected for the calculation of background and threshold values for all measured elements in the study area. Here, the background means the natural mean value without human influence. The threshold is the upper boundary of geochemical anomaly with consideration of geological and geochemical factors. The monitoring trace element concentrations should range between background and threshold values without considering human activity. Concentrations higher than threshold values are probably results of human activities. The method used is drawn from the monograph *Exploration Geochemistry* (Liu and Qiu 1987), and the following formulae were used for the calculation:

$$T = \bar{C}_b + 1.96 S_b, \tag{1}$$

$$\bar{C}_b = \frac{1}{N}\sum_{i=1}^{N} C_i, \tag{2}$$

$$S_b = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(C_i - \bar{C}_b)^2}, \tag{3}$$

where T represents the threshold; $\bar{C}_b$ the background value; S_b the standard deviation; C_i the concentration of sample i; and N the number of samples used for calculation. The results of the background ($\bar{C}_b$) and the threshold (T) values are listed in the last two rows of Table. 2 and 3 for all elements.

Results and discussion

Based on the location of sampling sites, samples are divided into two groups. The samples located near or within urban or industrial areas are considered as one group, urban samples. This classification includes samples E_1, E_2, E_5, E_6, E_8, P_2, P_3, P_4, P_6, P_8, P_9, P_{10}, P_{12}, P_{13}, P_{14}, W_1, W_4, and S. The samples collected far away from urban and industrial areas but close to rural areas are considered together as rural samples. This group includes samples E_3, E_4, E_7, E_9, P_1, P_5, P_7, P_{11}, W_2, W_3, and N. Analytical results were compared with background and threshold values and discussed among the different rivers and different sites within the same river systems. The analytical results, with background and threshold values, are listed in Table. 2 and 3 for rare earth elements and heavy metals, respectively.

Rare earth element

The average concentrations of the 15 rare earth elements are illustrated in Fig. 2. The light rare earth element concentrations in river water show an increasing trend

Table 2 Rare earth element concentrations, $\bar{C}_b$, and *T* in river water (unit: ppb)

	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
P_1	0.037	0.033	0.103	0.008	0.023	0.007	0.001	0.008	0.001	0.006	0.002	0.005	0.001	0.007	0.002
P_2	0.029	0.022	0.045	0.004	0.018	0.004	0.001	0.006	0.001	0.004	0.001	0.004	0.001	0.008	0.001
P_3	0.026	0.011	0.020	0.003	0.009	0.003	0.001	0.003	0.001	0.006	0.002	0.006	0.001	0.009	0.002
P_4	1.356	2.372	1.112	0.470	1.659	0.262	0.031	0.280	0.036	0.174	0.035	0.097	0.012	0.069	0.010
P_5	0.072	0.072	0.186	0.020	0.081	0.019	0.002	0.013	0.002	0.012	0.003	0.008	0.001	0.009	0.001
P_6	0.110	0.166	0.199	0.022	0.082	0.014	0.002	0.015	0.002	0.011	0.002	0.007	0.001	0.007	0.001
P_7	0.160	0.208	0.394	0.045	0.205	0.041	0.008	0.031	0.006	0.035	0.008	0.021	0.003	0.017	0.002
P_8	0.071	0.085	0.203	0.023	0.075	0.022	0.003	0.012	0.002	0.014	0.003	0.007	0.001	0.008	0.001
P_9	0.026	0.009	0.019	0.003	0.011	0.002	0	0.004	0	0.002	0.001	0.002	0	0.002	0
P_{10}	0.014	0.006	0.006	0.001	0.004	0.001	0	0.003	0	0.001	0	0.001	0	0.001	0
P_{11}	0.015	0.008	0.017	0.002	0.008	0.002	0	0.003	0	0.002	0	0.001	0	0.001	0
P_{12}	0.016	0.009	0.014	0.001	0.009	0.002	0	0.004	0	0.002	0	0.002	0	0.002	0
P_{13}	0.017	0.009	0.017	0.002	0.007	0.002	0.001	0.004	0	0.002	0	0.001	0	0.002	0
P_{14}	0.079	0.063	0.155	0.013	0.053	0.011	0.001	0.013	0.002	0.009	0.002	0.006	0.001	0.006	0.001
E_1	0.096	0.141	0.235	0.038	0.136	0.027	0.004	0.026	0.003	0.017	0.004	0.012	0.002	0.009	0.001
E_2	0.258	0.289	0.600	0.079	0.251	0.054	0.006	0.053	0.007	0.042	0.008	0.025	0.004	0.028	0.005
E_3	0.213	0.307	0.647	0.082	0.361	0.061	0.010	0.036	0.007	0.038	0.008	0.025	0.003	0.020	0.003
E_4	0.226	0.364	3.029	0.098	0.320	0.067	0.011	0.062	0.007	0.041	0.009	0.025	0.003	0.024	0.004
E_5	0.395	1.715	1.338	0.157	0.567	0.119	0.021	0.076	0.015	0.075	0.016	0.041	0.007	0.040	0.006
E_6	0.043	0.018	0.034	0.004	0.016	0.004	0	0.005	0	0.003	0.001	0.003	0	0.003	0.001
E_7	0.043	0.007	0.004	0.002	0.002	0.001	0.001	0.001	0	0.001	0.001	0.001	0	0.002	0
E_8	0.076	1.136	3.872	0.040	0.115	0.015	0.002	0.013	0.002	0.011	0.002	0.014	0.003	0.022	0.004
E_9	0.080	0.030	0.049	0.008	0.029	0.004	0	0.005	0.001	0.004	0.001	0.003	0.001	0.003	0.001
W_1	0.043	0.044	0.079	0.009	0.035	0.009	0.002	0.009	0.001	0.008	0.002	0.005	0.001	0.006	0.001
W_2	0.024	0.012	0.016	0.003	0.017	0.002	0.001	0.006	0	0.002	0.001	0.002	0	0.001	0
W_3	0.020	0.012	0.017	0.004	0.013	0.003	0.001	0.003	0	0.002	0	0.002	0	0.001	0
W_4	0.016	0.009	0.019	0.002	0.007	0.002	0	0.002	0	0.001	0	0.001	0	0.001	0
N	0.062	0.107	0.196	0.023	0.079	0.017	0.002	0.013	0.002	0.010	0.002	0.006	0.001	0.007	0.001
S	0.219	0.190	0.220	0.046	0.177	0.034	0.006	0.045	0.006	0.032	0.007	0.021	0.003	0.019	0.004
$\bar{C}_b$	0.068	0.083	0.170	0.020	0.084	0.017	0.003	0.013	0.002	0.012	0.003	0.008	0.001	0.008	0.001
T	0.198	0.278	0.571	0.070	0.308	0.055	0.009	0.035	0.007	0.038	0.008	0.024	0.003	0.020	0.003

Y yttrium, *La* lanthanum, *Ce* cerium, *Pr* praseodymium, *Nd* neodymium, *Sm* samarium, *Eu* europium, *Gd* gadolinium, *Tb* terbium, *Dy* dysprosium, *Ho* holmium, *Er* erbium, *Tm* thulium, *Yb* ytterbium, *Lu* lutetium

from the WR, the NR, the RPRD, and the SR to the ER. For heavy rare earth elements, however, the order of increase is from the WR, the NR, the RPRD, and the ER to the SR. This spatial distribution characteristic may be mainly due to natural geological and hydrometeorological factors. The difference in trend between light and heavy rare earth elements probably resulted from different geological backgrounds between the ER and the SR. As shown in Table 1, the WR and the NR have the most abundant annual runoff, which serves to dilute trace element concentrations. The ER and the SR are developed in relatively older strata. The annual runoff of the ER and the SR is lowest within this watershed, further increasing elemental concentration. Relatively low concentrations of trace elements occur in the WR and the NR, and relatively high rare earth element concentrations appear in the ER and the SR. Though the water quantity of the RPRD as a whole is relatively affluent, the water quantity of each water channel of the RPRD is rather small. The spatial variations of rare earth element concentrations of different rivers for the urban samples and the rural samples also follow the above pattern. Natural hydrogeological and geochemical backgrounds are important influencing factors for rare earth element concentrations.

Results for the five studied rivers can be compared with background and threshold values, as well as between urban samples and rural samples. In the WR, all the rare earth concentrations were below background for every sample, probably due to the large runoff of the WR. However, the average concentrations of samples W_1 and W_4, urban samples, are much higher than those of rural samples W_2 and W_3, for all the 15 rare earth elements. Human activity and urban life add to rare earth element concentrations in the WR. In the NR, the concentrations of several rare earth elements were slightly above background but still below threshold and therefore considered normal. Since the NR sample belongs to the rural group, these results might be due to natural circumstance.

In the RPRD, though the concentrations of some rare earth elements exceed background levels at sampling station P_5, they are usually within normal values. However, concentrations for all 15 rare earth elements exceeded threshold values at the P_4 sampling station. The natural background of P_4 is almost the same as

Table 3 Heavy metal concentrations, $\bar{C}_b$, and T in river water (unit: ppb)

	Ni	Cu	Zn	Li	Al	Sc	Ti	Cr	Fe	Mn	Ba	Rb	Sr	Tl	Co	Cd	Pb	Bi	V	Ga	Ge	As	Se	Zr	Mo	Cs	U	Th
P_1	29.78	6.85	12.23	4.27	63.00	1.67	2.05	13.85	76.00	196.72	28.38	22.58	103.02	0.01	0.34	0.04	0.14	0.004	0.86	0.28	0.13	0.29	0.02	0.090	3.25	0.39	0.58	0.017
P_2	19.57	25.65	24.49	3.22	37.00	1.70	1.58	13.78	47.00	191.23	29.48	20.35	87.14	0.02	0.29	0.07	0.10	0.032	1.28	0.28	0.10	0.25	0.01	0.014	2.60	0.39	0.24	0.011
P_3	32.28	2.63	23.92	11.61	25.00	2.17	2.21	17.61	44.00	157.12	25.85	24.26	141.19	0.01	0.35	0.02	0.14	0.005	1.92	0.25	0.15	0.40	0.02	0.021	8.13	0.46	0.25	0.007
P_4	178.89	95.41	706.25	28.01	111.70	3.25	10.74	56.03	701.75	512.29	119.93	51.44	202.01	0.07	2.23	0.09	2.26	0.032	4.24	1.15	0.14	0.11	0.26	0.459	6.04	0.32	0.34	0.078
P_5	0.35	4.56	2.38	2.20	136.00	2.39	3.37	5.41	100.00	5.44	11.86	8.89	24.92	0.03	0.04	0.01	0.22	0.007	0.38	0.13	0.03	0.10	0.01	0.028	0.40	0.15	0.10	0.051
P_6	0.98	21.96	226.79	10.13	61.00	2.24	1.46	3.61	43.00	77.64	17.61	9.81	29.31	0.30	1.19	1.34	0.61	0.015	0.31	0.17	0.04	0.06	0.01	0.002	0.34	0.17	0.01	0.003
P_7	0.81	3.78	14.21	2.41	322.00	2.49	4.81	4.91	175.00	27.80	16.70	9.46	27.31	0.07	0.11	0.09	1.81	0.021	0.62	0.19	0.03	0.16	0.01	0.087	0.48	0.15	0.18	0.12
P_8	4.95	3.58	3.71	2.57	245.00	1.76	5.43	13.43	139.00	11.91	25.81	6.46	90.30	0.03	0.15	0.07	0.42	0.017	1.22	0.27	0.05	0.26	0.01	0.173	2.32	0.08	0.28	0.059
P_9	3.29	4.89	5.71	2.64	17.19	1.56	1.64	14.64	22.14	1.56	23.92	5.99	78.27	0.14	0.08	0.03	0.24	0.003	1.65	0.25	0.06	0.10	0.04	0.080	1.33	0.03	0.23	0.005
P_{10}	4.48	3.13	6.18	1.16	12.12	1.12	0.91	14.58	15.81	0.33	30.24	3.29	103.70	0.11	0.09	0.03	0.18	0.001	1.34	0.30	0.04	0.09	0.03	0.056	1.12	0.02	0.20	0.002
P_{11}	1.85	1.84	4.93	0.96	21.34	1.06	1.13	14.66	21.49	0.36	31.93	2.59	107.10	0.11	0.09	0.03	0.22	0.001	1.30	0.32	0.05	0.09	0.03	0.062	0.99	0.01	0.17	0.002
P_{12}	18.05	13.35	4.99	3.23	13.82	1.45	2.60	15.51	23.63	5.18	37.97	12.22	145.80	0.03	0.25	0.01	0.19	0.002	1.97	0.36	0.07	0.19	0.06	0.137	4.18	0.13	0.34	0.003
P_{13}	2.75	3.61	4.45	1.36	15.35	1.12	1.87	15.74	17.15	0.64	30.04	4.36	116.10	0.08	0.11	0.02	0.15	0.001	2.27	0.31	0.05	0.10	0.04	0.092	1.20	0.02	0.22	0.002
P_{14}	2.78	3.54	4.68	3.10	168.70	1.48	4.17	7.25	73.58	1.27	23.64	10.59	105.80	0.22	0.10	0.02	0.31	0.007	1.28	0.24	0.06	0.05	0.06	0.342	1.23	0.06	0.09	0.053
E_1	1.68	1.20	1.92	2.04	131.00	1.99	3.10	5.03	106.00	4.78	15.03	6.84	24.37	0.02	0.05	0.01	0.24	0.005	0.53	0.15	0.03	0.06	0.01	0.112	0.46	0.04	0.05	0.045
E_2	142.93	28.27	16.09	2.78	359.00	2.31	6.44	13.35	425.00	163.01	19.21	14.44	41.04	0.02	0.41	0.05	0.57	0.010	0.61	0.20	0.05	0.22	0.01	2.601	1.53	0.30	0.09	0.136
E_3	12.14	4.42	3.36	2.28	414.00	2.18	7.07	7.03	205.00	9.33	14.30	7.78	24.86	0.02	0.10	0.02	0.54	0.012	0.80	0.17	0.04	0.09	0.01	0.181	0.55	0.12	0.07	0.145
E_4	13.56	4.22	3.90	2.41	502.00	2.37	7.82	7.33	331.00	12.21	16.57	8.32	27.52	0.02	0.12	0.02	0.69	0.017	0.98	0.20	0.04	0.11	0.01	0.241	0.61	0.14	0.09	0.191
E_5	20.20	4.08	7.56	2.32	999.00	2.57	13.37	9.65	358.00	31.18	18.73	8.65	28.73	0.03	0.15	0.34	1.03	0.024	1.47	0.26	0.06	0.12	0.01	0.441	0.68	0.19	0.16	0.366
E_6	24.28	26.15	24.68	2.84	26.31	2.02	5.29	10.04	68.48	2.47	16.60	20.76	57.89	0.04	0.38	0.02	0.23	0.003	1.69	0.16	0.07	0.09	0.05	0.416	1.40	0.48	0.03	0.009
E_7	5.35	21.65	4.80	29.61	2.55	1.14	2.29	7.79	41.76	0.48	28.36	16.27	790.60	0.08	0.22	0.05	0.16	0.001	2.84	0.22	0.08	0.23	0.82	0.067	2.07	0.15	0.28	0.001
E_8	12.93	4.48	13.57	5.64	57.00	2.00	4.12	16.99	127.00	16.72	59.13	19.08	106.97	0.01	0.38	0.03	2.64	0.004	1.45	0.51	0.17	0.25	0.01	0.064	3.51	0.43	0.19	0.028
E_9	3.33	2.26	6.34	2.66	19.52	1.35	1.70	6.89	26.45	0.34	16.18	7.73	22.29	0.10	0.04	0.01	0.14	0.003	0.60	0.15	0.04	0.03	0.02	0.106	0.32	0.07	0.02	0.012
W_1	1.73	1.79	1.74	1.63	122.00	1.34	3.01	12.89	78.00	5.32	26.12	3.76	121.07	0.03	0.16	0.08	0.15	0.003	1.24	0.26	0.05	0.20	0.01	0.067	1.54	0.03	0.23	0.024
W_2	0.65	1.28	3.97	1.20	33.02	1.07	1.41	13.56	24.09	1.47	31.66	2.43	105.20	0.10	0.10	0.03	0.21	0.002	1.71	0.33	0.04	0.08	0.03	0.118	0.89	0.01	0.23	0.005
W_3	1.27	1.48	4.18	1.10	33.37	1.05	1.33	13.32	24.96	0.43	31.60	2.63	107.10	0.13	0.10	0.02	0.21	0.002	1.53	0.33	0.04	0.08	0.03	0.102	0.97	0.01	0.20	0.004
W_4	1.00	1.28	3.01	1.00	39.12	1.06	1.26	13.99	24.09	1.49	30.67	2.61	103.20	0.12	0.10	0.02	0.16	0.002	1.59	0.31	0.04	0.09	0.03	0.080	0.98	0.01	0.18	0.005
N	8.09	6.60	5.79	3.34	160.00	1.73	3.27	15.07	97.00	9.22	18.37	6.83	58.36	0.03	0.08	0.13	0.38	0.018	0.60	0.19	0.06	0.25	0.01	0.147	1.91	0.10	0.24	0.051
S	41.55	6.32	33.50	6.94	53.60	3.03	16.41	32.97	600.70	346.30	20.51	42.40	147.80	0.02	1.05	0.03	0.76	0.039	1.27	0.21	0.08	0.12	0.10	0.249	4.70	0.74	0.15	0.018
$\bar{C}_b$	7.62	5.82	7.73	2.26	134.17	1.67	2.90	11.45	84.85	44.73	24.04	8.73	76.61	0.05	0.14	0.05	0.40	0.01	1.03	0.25	0.06	0.16	0.02	0.09	1.36	0.14	0.22	0.04
T	27.34	20.05	21.82	4.40	397.16	2.73	6.58	19.27	208.46	199.70	39.49	22.91	152.73	0.14	0.33	0.13	1.40	0.03	1.89	0.39	0.12	0.32	0.04	0.19	3.24	0.42	0.49	0.14

Ni nickel, *Cu* copper, *Zn* zinc, *Li* lithium, *Al* aluminum, *Sc* scandium, *Ti* titanium, *Cr* chromium, *Fe* iron, *Mn* manganese, *Ba* barium, *Rb* rubidium, *Sr* strontium, *Tl* thallium, *Co* cobalt, *Cd* cadmium, *Pb* lead, *Bi* bismuth, *V* vanadium, *Ga* gallium, *Ge* germanium, *As* arsenic, *Se* selenium, *Zr* zirconium, *Mo* molybdenum, *Cs* cesium, *U* uranium, *Th* thorium

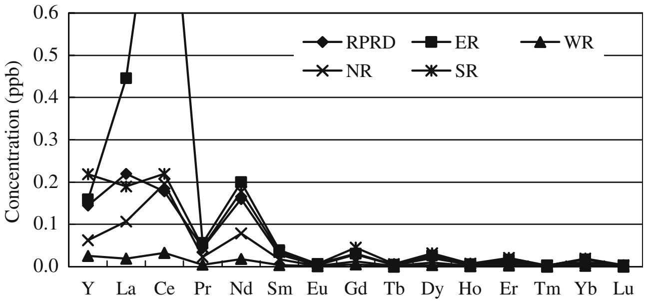

Fig. 2 Average concentrations of rare earth elements for the five rivers

other samples from the PRPD, but the site is located downstream of a bleach and dye factory near Guangzhou City. Concentrations of all rare earth elements are still within normal range for the other sampling stations within the RPRD. This specific factory must have a significant impact on rare earth element concentrations in the river water.

With the ER and the SR, normal concentrations occur at sampling stations E_1, E_6, E_7, and E_9, while abnormalities occur at stations E_2, E_3, E_4, E_5, and E_8. At E_2, E_3, E_4, and E_5 particularly, concentrations of almost all the rare earth elements exceed threshold values. In the SR, concentrations of yttrium, gadolinium, and lutetium exceed the threshold, but values for other rare earth elements are normal. This may be partially due to the older strata of the ER and the SR river valleys. All average concentrations of rare earth elements in urban samples are higher than rural samples in the ER. Comparisons were performed between rural samples of the ER and urban samples of the WR and the RPRD, respectively. The average concentrations of urban samples from the WR are much lower than those of rural samples from the ER. Surprisingly, average concentrations of urban samples from the RPRD are much higher than those of rural samples from the ER. Within the RPRD, human activities and urban life have already influenced rare earth concentrations.

Heavy metal element

The spatial distribution of the 28 heavy metals is not so regular as that of the rare earth elements (Table 3). In general, the ER, the RPRD, and the SR waters have relatively higher concentrations of heavy metals, while the WR and the NR waters have relatively lower heavy metal concentrations. The highest concentrations of all 28 heavy metals occurred in the ER, the RPRD, and the SR, while none appeared in the WR and the NR. As previously discussed, concentrations above background but below threshold and concentrations below background are defined as ‘‘normal’’. Concentrations above threshold are considered as ‘‘abnormal’’. The stations with abnormal heavy metal concentrations are listed in Table 4.

No abnormal heavy metal concentrations appeared in the WR, and only cadmium exceeded the threshold in the NR (Table 4). Other abnormalities appeared in the ER, the RPRD, and the SR, perhaps due to natural conditions of the five rivers or human activities. Most of the manufacturing factories within the PRDEZ discharge to the lower reaches of the ER, the RPRD, and the SR. Again, sample P_4 should be emphasized; concentrations of 21 of the 28 heavy metals exceeded thresholds at this station. Natural conditions here are not significantly different from those of the other samples from the RPRD, except for the bleach and dye factory upstream.

There are 107 abnormal values at different sites for the 28 heavy metals listed in Table 4. Among these 107 abnormalities, more than 80% are at urban sampling points. Urban development seems to have a significant impact on the heavy metal concentrations. Results are very different for urban and rural samples. Descriptive

Table 4 Stations with abnormal concentration of heavy metals

Element	Station	Element	Station	Element	Station
As	P_3	Tl	P_6, P_9, P_{14}	Ni	P_1, P_3, P_4, E_2, S
U	P_1	Cd	P_6, E_5, N	Ti	P_4, E_3, E_4, E_5, S
Sc	P_4, S	Pb	P_4, P_7, E_8	Fe	P_4, E_2, E_4, E_5, S
Cr	P_4, S	Bi	P_2, P_4, S	V	P_3, P_4, P_{12}, P_{13}, E_7
Mn	P_4, S	Al	E_3, E_4, E_5	Mo	P_1, P_3, P_4, P_{12}, E_8, S
Ga	P_4, E_8	Rb	P_3, P_4, S	Zn	P_2, P_3, P_4, P_6, E_6, S
Sr	P_4, E_7	Th	E_3, E_4, E_5	Li	P_3, P_4, P_6, E_7, E_8, S
Ba	P_4, E_8	Cs	P_3, E_6, E_8, S	Cu	P_2, P_4, P_6, P_{12}, E_2, E_6, E_7
		Ge	P_1, P_3, P_4, E_8	Zr	P_4, P_{14}, E_2, E_4, E_5, E_6, S
		Se	P_4, P_{12}, P_{14}, E_7	Co	P_1, P_3, P_4, P_6, E_2, E_6, E_8, S

Ni nickel, *Cu* copper, *Zn* zinc, *Li* lithium, *Al* aluminum, *Sc* scandium, *Ti* titanium, *Cr* chromium, *Fe* iron, *Mn* manganese, *Ba* barium, *Rb* rubidium, *Sr* strontium, *Tl* thallium, *Co* cobalt, *Cd* cadmium, *Pb* lead, *Bi* bismuth, *V* vanadium, *Ga* gallium, *Ge* germanium, *As* arsenic, *Se* selenium, *Zr* zirconium, *Mo* molybdenum, *Cs* cesium, *U* uranium, *Th* thorium

Table 5 Summary of descriptive statistical analysis of heavy metal concentrations (unit: ppb)

Element	Urban samples Mean	Urban samples Minimum	Urban samples Maximum	Rural samples Mean	Rural samples Minimum	Rural samples Maximum
Ni (nickel)	28.573	0.980	178.890	7.016	0.350	29.780
Cu (copper)	13.962	1.200	95.410	5.358	1.280	21.650
Zn (zinc)	61.847	1.740	706.250	6.008	2.380	14.210
Li (lithium)	5.123	1.000	28.010	4.767	0.960	29.610
Al (aluminum)	138.551	12.120	999.000	155.164	2.550	502.000
Sc (scandium)	1.898	1.060	3.250	1.682	1.050	2.490
Ti titanium)	4.756	0.910	16.410	3.295	1.130	7.820
Cr (chromium)	15.949	3.610	56.030	9.984	4.910	15.070
Fe (iron)	161.907	15.810	701.750	102.068	21.490	331.000
Mn (manganese)	85.024	0.330	512.290	23.982	0.340	196.720
Ba (barium)	31.694	15.030	119.930	22.355	11.860	31.930
Rb (rubidium)	14.851	2.610	51.440	8.683	2.430	22.580
Sr (strontium)	96.149	24.370	202.010	127.116	22.290	790.600
Tl (thallium)	0.072	0.010	0.300	0.064	0.010	0.130
Co (cobalt)	0.418	0.050	2.230	0.122	0.040	0.340
Cd (cadmium)	0.127	0.010	1.340	0.041	0.010	0.130
Pb (lead)	0.577	0.100	2.640	0.429	0.140	1.810
Bi (bismuth)	0.011	0.001	0.039	0.008	0.001	0.021
V (vanadium)	1.518	0.310	4.240	1.111	0.380	2.840
Ga (gallium)	0.313	0.150	1.150	0.228	0.130	0.330
Ge (germanium)	0.073	0.030	0.170	0.053	0.030	0.130
As (arsenic)	0.153	0.050	0.400	0.137	0.030	0.290
Se (selenium)	0.043	0.010	0.260	0.091	0.010	0.820
Zr (zirconium)	0.300	0.002	2.601	0.112	0.028	0.241
Mo (molybdenum)	2.405	0.340	8.130	1.131	0.320	3.250
Cs (cesium)	0.217	0.010	0.740	0.118	0.010	0.390
U (uranium)	0.182	0.010	0.340	0.196	0.020	0.580
Th (thorium)	0.047	0.002	0.366	0.054	0.001	0.191

statistical analysis was performed for urban samples and rural samples for the 28 heavy metals using SPSS software. The results are summarized in Table 5.

Average and maximum concentrations of almost all heavy metals from urban samples are much higher than those from rural samples, with the exception of the element aluminum for mean value and the elements strontium, selenium, and uranium for maximum concentration (Table 5). Aluminum, strontium, selenium, and uranium are mainly affected by specific industrial activities in the upper reaches. The minimum concentrations of urban samples are similar to those of rural samples. This indicates that wastewater discharge has impacted heavy metal concentrations. For the eight heavy metals: copper, zinc, lead, cadmium, chromium, nickel, arsenic, and mercury, frequently considered in environmental management, the concentration of mercury exceeds the measuring limit of ICP-MS and is not listed here. The mean concentrations of the other seven from urban samples are several times higher than those from rural samples (Table 5).

When the ranges of the trace element concentrations are reviewed, 25 of the 28 maximum heavy metal concentrations occurred in urban samples from the RPRD. This value for the ER and the WR was 22 and 21, respectively. In addition, most of the minimum heavy metal concentrations were acquired from the rural samples from each river, another indication of human influence. The kinds and number of factories that discharge to the river are also important influencing factors to the trace element concentration. The main kinds and numbers of investigated factories that discharge to different rivers provided by the Bureau of Environmental Protection, Guangdong Province (2003) are listed in Table 6. The wastes discharged from these factories should be another influence to the heavy metal concentrations. Compared to the environmental quality standards for surface water, concentrations of both iron and manganese in the SR exceed boundary values of class III as specified in the national standard GB3838-88. The definitions and their usage of different classes are listed in Table 7. However, geological formations rich in iron and manganese do not occur in the SR basin (Bureau of Geology and Mineral Resources of Guangdong Province 1982). Sources for these iron and manganese concentrations must be mainly from industrial or domestic discharge. Wastewater is the main pollution source for river water and may include many trace elements. The high heavy metal concentrations in this study are mainly ascribed to industrial activities and urban daily life.

It may be useful to describe this contribution with the concept "wastewater discharge load". The value of the wastewater discharge load is the ratio of the quantity of discharged wastewater divided by urban land area. The

Table 6 Main kinds and numbers of investigated factories discharge to different rivers

Kind of industry	Number of factories				Percentage of total investigated factories			
	RPRD	ER	SR	WR	RPRD	ER	SR	WR
Textile industry	504	532	40	28	17.06	40.74	5.68	15.30
Metal products	432	326	201	24	14.62	24.96	28.55	13.11
Non-metal mineral products	437	75	14	24	14.79	5.74	1.99	13.11
Raw chemical materials and chemical products	132	9	16	20	4.47	0.69	2.27	10.93
Electric equipment and machinery	128	8	18	5	4.33	0.61	2.56	2.73
Food processing	107	28	16	11	3.62	2.14	2.27	6.01
Food manufacturing	100	5	17	9	3.39	0.38	2.41	4.92
Papermaking and paper products	124	81	10	4	4.20	6.20	1.42	2.19
Leather, furs, down, and related products	91	47	29	10	3.08	3.60	4.12	5.46
Electric and telecommunications equipment	103	122	130	5	3.49	9.34	18.47	2.73
Garments and other fiber products	68	10	23		2.30	0.77	3.27	0.00
Electric power, steam, and hot water production and supply	62	18	13		2.10	1.38	1.85	0.00
Plastic products	90	10	14		3.05	0.77	1.99	0.00
Instruments, meters, cultural and office machinery	6	2	23	4	0.20	0.15	3.27	2.19
Cultural, educational, and sports goods	7	1	13		0.24	0.08	1.85	0.00
Total investigated factories	2,954	1,306	704	183	100	100	100	100

quantity of discharged wastewater is from the environmental statistical data provided by the Bureau of Environmental Protection of Guangdong Province (2001). Urban land area data are obtained from the report about ‘‘Integrative Remote Sensing Survey on the Urbanization in the Pearl River Delta Economic Zone’’ (Zhu et al. 2002). The values of wastewater discharge load of each river for the year 2000 are listed in Table 8.

The value of total and domestic wastewater discharge load increases in the following order: the WR, the ER, the RPRD, and the SR (Table 8). This increasing order is identical with heavy metal concentrations. The order is almost identical for industrial wastewater discharge except for the SR. Shenzhen is a relatively new city that has newer technical industries around with less reliance on typical manufacturing industries that consume large amounts of water and discharge more serious pollutants (Table 6). Values of industrial wastewater discharge load for the SR are relatively low. The high wastewater discharge load and large number of factories discharge to the SR and the RPRD (Table. 6, 8), together with the weak capability of self-purification in the SR and the RPRD, combine to result in high heavy metal concentrations in these rivers. For each city and river, the domestic wastewater discharge load is much larger than the industrial wastewater discharge load (Table 8). With the increase of treatment coefficient for industrial wastewater, urban life has more influence than industry as related to trace element concentrations in river water. According to the Chinese Census (Population Census Office of Guangdong Province 1992, 2002), increasing rate of urban population was more than 90% during the decade of 1990–2000 in the study area. The population continues to grow in the whole PRDEZ, but land area is limited. As a result, increased discharge of domestic wastewater is inevitable unless some measures are taken to control the waste discharge. The high heavy metal concentrations in river water will eventually influence human healthy in response to the increasing pollution. Else, we must look to better and more efficient wastewater treatment technologies.

Table 7 Definitions and usage of different classes in the national standard GB3838-88

Class	Definition
I	Used for headwaters and national natural protection area
II	Used for first protection area of drinking sources, rare fish, and spawn field for fish and shrimp
III	Used for second protection area of drinking sources, ordinary fish, and swimming field
IV	Used for industrial water and non-touched entertainment waters
V	Used for agriculture and ordinary sightseeing waters

Table 8 Wastewater discharge load of each river for the year 2000

River	Total wastewater discharge load (10^4 tons/km^2)	Domestic wastewater discharge load (10^4 tons/km^2)	Industrial wastewater discharge load (10^4 tons/km^2)
RPRD	84.735	56.994	27.741
ER	64.819	47.373	17.447
SR	102.379	93.452	8.928
WR	40.531	27.675	12.856

Conclusions

In the study area, the average concentrations of rare earth elements in river water exhibit an increasing order in samples from the WR, the NR, the RPRD, the SR to the ER. For heavy metals, relatively higher concentrations occur in the ER, the RPRD, and the SR, while relatively lower heavy metal concentrations appear in the WR and the NR. In terms of the concentrations of all trace elements, urban samples are much higher than rural samples.

Distribution characteristics of trace element concentrations in the study area is the result of combined influence of natural conditions and human activity. Except for geological and hydrometeorological backgrounds, human activities exert the greatest influence on distribution of trace element concentrations and river water quality. The high trace element concentrations can be mainly ascribed to industrial activities and urban daily life. Distribution of rare earth elements in the study area is mainly controlled by geological background, precipitation, and runoff. Distribution of heavy metals in the study area is the result of an integrated effect of natural conditions and human activities. Human activities, in particular urban daily life, seem to be the major factor influencing heavy metal concentrations.

Though human activities have not yet caused serious degradation of river water quality from trace elements, some heavy metal concentrations have already exceeded the related national standards. Attention must be paid to pollution from trace elements in the waters of the PRDEZ.

Acknowledgments This work was partially supported by the National Basic Research Program of China (no. 2004CB720204), the "Group program of NSF of Guangdong Province (grant no. 04201163)", and the program of "Integrative Remote Sensing Survey on the Urbanization in the Pearl River Delta Economic Zone (grant no. 20001500012041-08)". Prof. Xianglin Tu is thanked for his help in the concentration measurement with ICP-MS and Mr. Jinsong Zhao and Mr. Ganlin Wang for providing assistance in collecting water samples. Thanks are also due to Dr. Chunyun Wang for his help in the preparation of this manuscript.

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