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Spatial Distribution and Corresponding Factors of Heavy Metals Concentrations in the Dongjiang River Basin, Southeast China

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Abstract: The Dongjiang River Basin (Southeast China) is the world's most populous and highly economic development region over the last few decades. The present study is the first systematic analysis of heavy metals of the aquatic environment in this area. Eighty seven samples were taken from the tributaries of the river network to investigate the characteristics of heavy metal pollutants within the catchment, which suggests a generally good water quality in terms of heavy metals, i.e., the mean metal concentrations of the tributaries are generally well below those recommended for drinking purposes and lower than metal concentrations in other regions and in world average background concentrations. Different multivariate statistical techniques are combined to analyze the spatial pattern and the origin of, and the land-use effects on heavy metal pollutants. Principal Component Analysis (PCA) and Redundant Analysis (RDA) are applied to group the different heavy metals according to their variability at different sites. Relatively high levels of Hg originated from various sources and cannot be quickly scavenged in the Dongjiang River system. An improved understanding of the sources and their binding behaviors of heavy metals have implied the trend of elevated toxic potential from certain metal groups in this aquatic ecosystem, which suggests the analysis of contaminates should probably be combined with biological evaluations of toxicity at specific sites in future work.

Key words: Anthropogenic sources, contamination transport, PCA, pearl river delta, RDA, surface water

INTRODUCTION

Since the launch of China's reform programme in 1979, the Pearl River Delta Economic Zone (PRDEZ) has become one of the leading economic regions and a major manufacturing centre of China and the world. The region's GDP grew from just over US$8 billion in 1980 to more than US$89 billion in 2000 and nearly US$221.2 billion in 2005 (PRWRC, 2006). The Dongjiang River is the eastern tributary of Pearl River Delta (PRD) and generally commissioned with the important responsibility of providing drinking water for nearly about 40,000,000 people in the area. This significant water demand and withdraw restrains the ability of the river resource to continue to meet the needs of ecological development and aquatic environment. The Dongjiang River and its tributaries also receive large amount of contaminants released from industrial, domestic/sewage and agricultural effluents. About 60% of industrial and domestic wastewaters are not treated effectively prior to discharge (PRWRC, 2006). Moreover, the policy of early period has long suffered an inferior status in relation to economic development and inadequate understanding from the relevant ministries of the government. Consequently, the Dongjiang River Basin faces threats of severe resource shortages and environmental degradation (Chen *et al*., 2008; Gong *et al*., 2009).

Contamination of surface waters with heavy metal pollutants has raised water health concerns in the Dongjiang River Basin. However, the levels of heavy metals of rivers are highly heterogeneous at different spatial scales. Land management of the catchment for agriculture, forestry, horticulture, conservation, industry and urban areas influences the pollutant discharge including heavy metal contamination that enters the aquatic system in different manner (Johnes and Heathwaite, 1997). It is becoming increasingly aggravated due to the need for economic development and long-term irrational utilization by humans. Understanding the spatial distribution of heavy metals in the basin is indispensable for determining their orginating sources and transport processes of the contamination.

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A national key water project has been conducted, in order to quantify the impact of economic development on catchment water resources and to recommend water resource management actions. As part of this project, detailed hydrological investigations of 8 metals (Mn, Cd, Cr, Cu, Pb, Zn, Hg, As) at 87 sites have been conducted, in order to (1) assemble baseline heavy metal data for Dongjiang River basin (2) to determine the use of such chemical data for investigating the sources and potential interactions between different pollutants with factor analysis at specific sites. Different multivariate statistical techniques, such as Principal Component Analysis (PCA) and Redundancy Analysis (RDA), are applied to assist the interpretation of complex data matrices to better understand the water quality and ecological status of the studied systems. These methods allow the identification of possible factors that influence water environment systems and offer a valuable tool for reliable management of water resources (Caccia *et al*., 2003; Simeonov *et al*., 2003; Shrestha and Kazama, 2007; Reid and Spencer, 2009; Vega *et al*., 1998). With these methods, we determined the spatial variations and corresponding controlling factors of heavy metal concentrations in the Dongjiang River and correlated them with environmental parameters. The cause and effect relationship between the various stresses imposed on the aquatic ecosystem is vital to help make informed decisions concerning the future management strategies of the natural resources and ensuring conservation of biological diversity in the high-speed capacity developing economic area.

MATERIALS AND METHODS

Study area: The Dongjiang River basin (between 113º30' E and 115º45' E, 22º45'N and 25º20'N) covers an area of about 35,340 km^2, with topographic relief of 50~500 m. The climate is subtropical monsoonal with average annual rainfall of 1,750 mm and pan evaporation of 1,297 mm (PRWRC, 2006). The mainstream flows from northeast to southwest and discharges into the Pearl River estuary. It is about 562 km long with an average slope of about 0.39‰ (Liu *et al*., 2010). The freshwater and sediment discharges from land are 33.1×10^9m^3/a and 24.7×10^3t/a (Boluo Station, Fig. 1), respectively (PRWRC, 2006). During 1958-1974 a number of dams and reservoirs were built in the Dongjiang River basin for multiple purposes, and major dams and reservoirs are the Fengshuba and Xinfengjiang in the middle- and up-stream. The waterways were generally from catchments with large proportions of native vegetation such as Xunwu, Longchuan, Heyuan, parts of Shilong County and the rural section of Shenzhen. Forest covers headwater areas and the average forest cover of the whole basin is about 53.9%. The intensive cultivation dominates other parts of hills and plains lower in the basin, in addition to urban development and surface water. The region is influenced by complex natural processes and intensified human activities.

SAMPLING AND ANALYTICAL METHODOLOGY

Water samples were taken at a total of 87 sampling points during a measurement campaign in July of 2010 covering most tributaries of the Dongjiang River Basin (Fig. 1). Samples were collected in polyethylene bottles (washed three times with detergent, de-ionized water, and surface water). Three replicates from each site were taken and the final average of laboratory analytical results in each three samples from the same site was used for further analysis and discussion. A sample of 500 mL of water was taken by totally immersing the bottles and lifting up, and was acidified to pH = 2 with 10% HNO_3 (with two pipette drops of concentrated HNO_3) and placed in ice bath and brought to the lab. This procedure prevents microbial growth, flocculation and reduces any adsorption on container surfaces. At each site, additional samples of water were taken for analysis of electrical conductivity, pH, salinity and turbidity and major ions. Major anions (Cl^-, SO_4^{2-} NO_3^- N, Na^+,K^+,Ca^{2+},Mg^{2+}) were analyzed by inductively coupled plasma optical emission spectrometry facility (ICP, DX-600, USA) at Beijing Normal University. The temperature and $HCO_3^-$of the water was also determined during sampling. Storage, preservation and chemical analyses followed the standard methods recommended by the American Public Health Association (APHA, 1998). All the water samples were firstly filtered through a 0.45 µm micro porous membrane filter and stored in the laboratory at 4ºC before analysis. Finally, analysis was done at the Analytical and Testing Centre, Beijing Normal University, using ICP-SPECTRO (SPECTRO ARCOS EOP, USA). All results presented in this paper are the means of triplicate analysis.

Buffer analysis of landscape: Buffer analysis was used to extract landscape data for a region 1 km on each site of the river. The percentage of land cover for each site was divided into the following categories: tillage, orchard, forest, urban and watershed. Catchment land-cover data were derived from a digital version of the Vegetative Cover of the Dongjiang Basin (2009) using ArcView GIS software. Catchments of interest were digitized using 1:250,000 topographic data (primarily contour maps). Once all layers had been checked for accuracy, it was

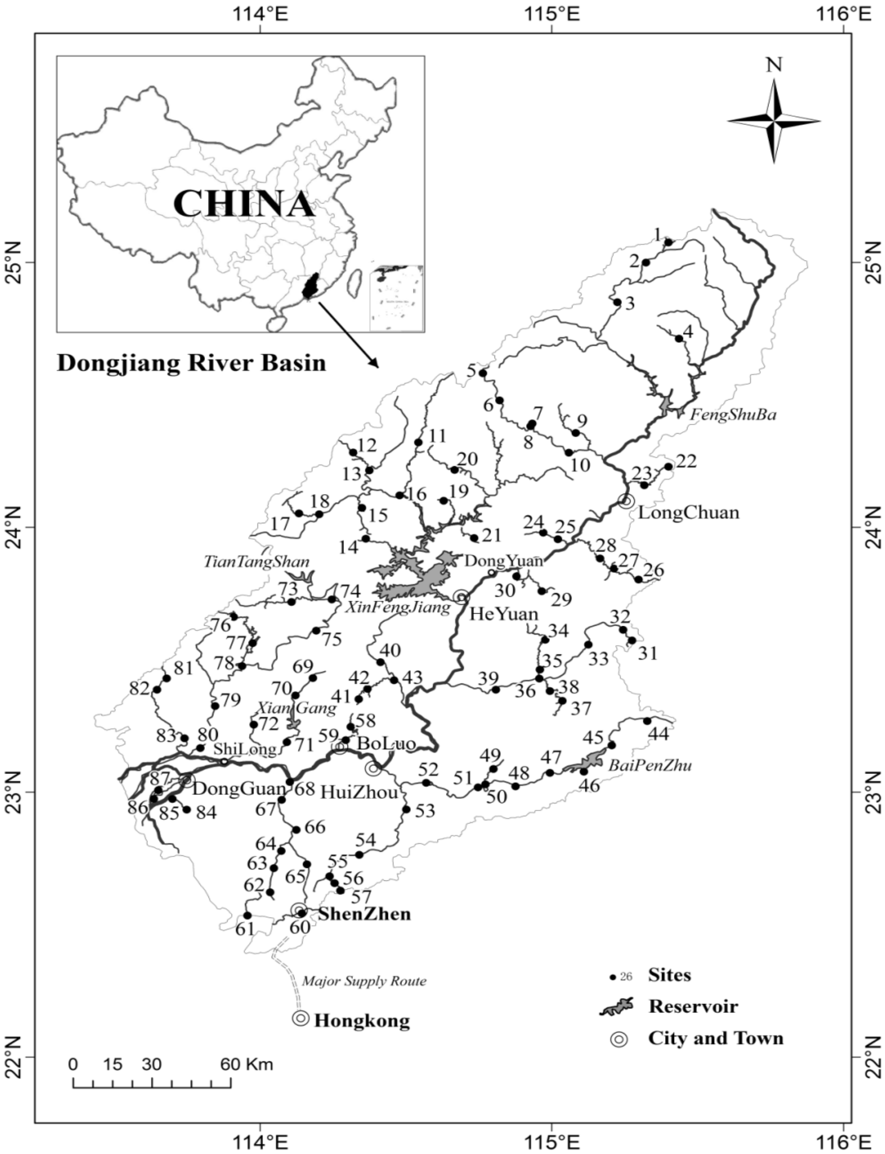

Fig. 1: Map showing the location of the study area and the sampling sites (87 sites) in Dongjiang River Basin

used to calculate the percentage of land cover in the catchment. Identical analysis was performed on both the buffer and whole catchment data to determine interrelationships between landscaped and heavy metal concentrations (Johnson *et al*., 1997). The buffer zone is defined to be 1 km, because it exceeds the minimum mapping unit of the land use data.

Statistical analysis: Principal Component Analysis (PCA) and Redundancy Analysis (RDA) were performed to determine the variation in the species data within a narrow range, which could be attributed to linear coupling (Amano *et al*., 2011). PCA was conducted to transform the original heavy metal variables into new, uncorrelated variables known as Principle Components (PCs) in this study. These PCs provided information regarding the most meaningful parameters that could be used to describe the entire dataset, thereby enabling a reduction in data with a minimal loss of original information (Helena *et al*., 2000). Equation (1) gives the basic concept of PCA expressed in the controlling factors:

$$Z_{ij} = a_{i1}x_{1j}+a_{i2}x_{2j}+a_{i3}x_{3j}+....+a_{im}+x_{mj} \qquad (1)$$

where *a* is the component loading, *z* the component score, *x* the measured value of *a* variable, *i* the component number, *j* the sample number and *m* the total number of variables.

Kaiser-Meyer-Olkin (KMO) was applied to examine the suitability of the data for PCA. Meanwhile, eigenvalues indicate the significance of each PC, with higher values indicating greater significance, and usually only components with eigenvalue larger than 1.0 are considered as principal components. RDA is a multivariate technique that reduces the number of variables to a more manageable and informative scale. Specifically, a matrix of predictor variables (e.g., basic aquatic data or landscape data) is used to quantify variation in a matric of response variables (e.g., heavy metals concentrations). We used PCA and RDA to determine the relative influences of aquatic and landscape variables on heavy metals that were carried out using SPSS Statistics 19 and CANOCO (v. 4.5) software. In the RDA computations, the correlation matrix option was selected, and scaling was conducted on a correlation biplot. The significance of each environmental variable was tested using Monte Carlo permutation tests (499 permutations, $\alpha = 0.05$) (Ter Braak and Smilauer, 1998).

RESULTS AND DISCUSSION

Characteristics and distribution pattern of the heavy metals: Table 1 summarizes the statistical results of the heavy metals concentration of 87 water samples in the tributaries of Dongjiang River, while comparing with water quality standards currently effective in China SEPA, 2002), other Environmental Guidelines (WHO, 2006; USEPA, 1989) and study results that were obtained from the literature (Liu *et al*., 2002; Quan *et al*., 2010; (Yuan *et al*., 2008). In China the environmental quality standards for surface water divide surface water quality into five classes. Class I refers to the natural cleanest water from key water sources and national natural reserve; Class II refers to clean water that can be applicable for the abstraction for human consumption in first class protection area, for recreational purposes or for irrigation. Class III refers to fairly clean water that can be used for the abstraction for human consumption in second class protection area, for recreational purposes or for fishing, farming, etc. Class IV includes polluted water, which can only be used as industrial water after treatment. Class V refers to heavily polluted water that should not be used at all. If the measured concentration of a metal in the stream is lower than the standards given for Class III, the Dongjiang River is accepted as unpolluted and safety in respect to this element. In general, the mean concentrations of Chromium (Cr), Manganese (Mn), Nickel (Ni), Copper (Cu), Zinc (Zn), Arsenic (As), Cadmium (Cd) and Lead (Pb) are well below the permissible limit of the national water quality standards of Class II, except Mercury (Hg). However, up to 25% of samples exceeded the standard for Mn (22 sites), while the Ni content exceeded the standard in 9% of samples (8 sites). Most sample concentrations falling below the SEPA. None of the water samples exceeded Class III for Cr, Cu, Zn, As, Cd and Pb. However, there is significant potential risk of heavy metal pollutants to the aquatic ecosystem, especially in some particular sites for different elements. The data also reveal that all samples exceeded the standard of Class III for Hg. The higher concentration

Table 1: Summary of the heavy metals concentrations of the mainstream in the Dongjiang River comparing with other guidelines and studies results (µg/L)

N = 87	Cr	Mn	Ni	Cu	Zn	As	Cd	Hg	Pb
This study[a]									
Max	6.26	754	132.73	25.47	74.71	13.25	0.27	3.23	16.89
Min	0.42	1.07	0.04	0.18	1.24	0.13	0.00	0.21	0.07
AM	1.01	92.96	7.20	4.09	17.39	2.39	0.04	1.29	2.70
SD	0.83	119.2	18.38	5.52	17.75	2.20	0.03	0.48	2.60
China(2002)[b]									
Class I	10	-	-	10	50	50	1	0.05	10
Class II	50	100	20	1000	1000	50	5	0.05	10
Class III	50	100	20	1000	1000	50	5	0.1	50
Class IV	50			1000	2000	100	5	1	50
Class V	100			1000	2000	100	10	1	100
(WHO, 2006) [c]	50	500	20	2000	3000	10	3	1	10
USEPA (CCC) (1989) [d]	11	50	52	9	120	36	2.2	-	2.5
European Union (Standards)[c]	50	50	20	2000	-	10	5	1	10
Japan (Standards)[c]	50	50	-	1000	1000	10	10	0.5	10
Shoreline, Hong Kong[e]	-	-	-	69	92	-	45	-	660
Pearl River Estuary[f]	56.4	-	-	39.0	110.9	5.24	0.34	1.40	59.4
Yangtze River[g]	-	-	-	21.54	31.65	-	0.81	-	16.78
Yellow River[h]	51.3	-		21.8	75.7	12.9	0.31	0.20	21.4
Gaoping River, Taiwan[i]	1.80	-	5.59	2.49	15.5	2.13	0.16	<0.33	1.77
Buriganga River, Bangladesh[j]	587.2	-	8.80	163.1	-	-	9.34	-	65.5
Dipsiz stream, Turkey[k]	0.09	-	-	0.37	1.05	-	0.17	-	0.41

a: Number of examined samples 87; Min/max: Minimum/maximum levels; AM: Arithmetic mean; SD: Standard deviation;-: Not determined;
b: Environmental quality standards for surface water of China (SEPA, 2002);
c: Guidelines for Drinking Water Quality (WHO, 2006);
d: National Recommended Water Quality Criteria-Correction (USEPA, 1989);
e: Hong Kong, shoreline (Demirak *et al*., 2006);
f: Pearl River Estuary (Liu *et al*., 2002);
g: Yangtze River (Quan *et al*., 2010);
h: Yellow River (Yuan *et al*., 2008);
i: Gaoping River, Taiwan (Doong *et al*., 2008);
j: Buriganga River, Bangladesh (Ochieng *et al*., 2007);
k: Dipsiz stream, Turkey (Mogollón *et al*., 1996)

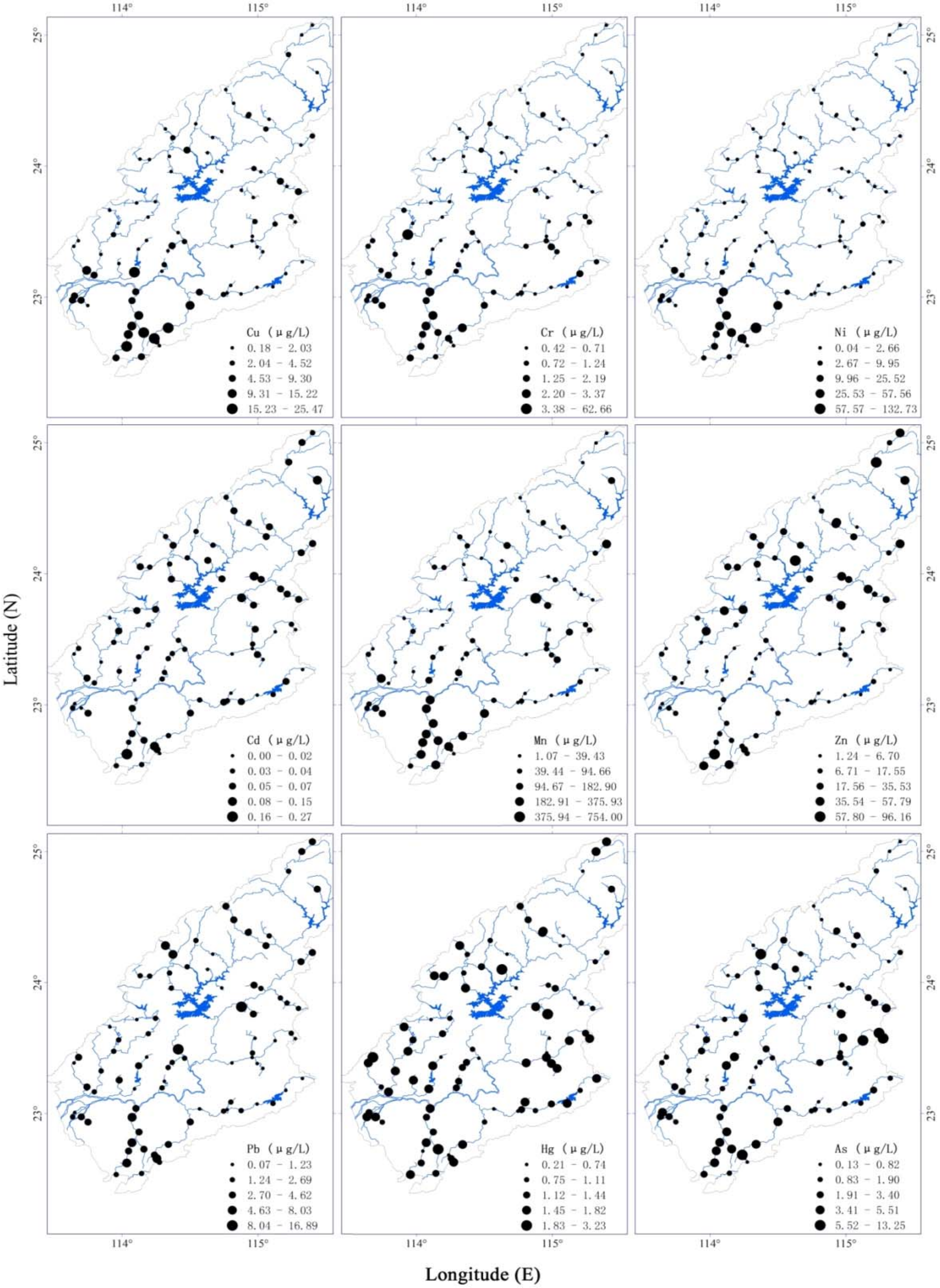

Fig. 2: Spatial distribution of heavy metal contents in the Dongjiang Rivers

Table 2: Pearson correlation matrix for the heavy metal concentrations

	Cr	Mn	Ni	Cu	Zn	As	Cd	Hg	Pb
Cr	1								
Mn	0.35**	1							
Ni	0.57**	0.53**	1						
Cu	0.51**	0.54**	0.74**	1					
Zn	-0.20	0.07	-0.14	0.01	1				
As	0.23*	0.21*	0.30**	0.40**	-0.03	1			
Cd	0.00	0.37**	0.11	0.37**	0.51**	0.13	1		
Hg	0.17	0.05	0.10	0.00	-0.03	-0.12	-0.21	1	
Pb	0.09	0.60	0.17	0.21	0.20	0.07	0.43**	0.07	1

*: Correlation is significant at the 0.05 level (two-tailed); **: Correlation is significant at the 0.01 level (two-tailed)

Table 3: Loadings of 22 variables on five significant principal components for all water samples

Components	PC1	PC2	PC3	PC4	PC5
Cr	0.58	-0.37	0.18	0.17	0.17
Mn	0.69	0.25	0.43	0.09	-0.09
Ni	0.76	-0.27	0.18	0.08	0.07
Cu	0.84	-0.07	0.15	-0.09	-0.11
Zn	0.02	0.69	-0.19	0.14	-0.32
As	0.42	0.06	0.13	-0.50	0.50
Cd	0.33	0.73	0.10	-0.07	-0.27
Hg	0.00	-0.23	0.32	0.72	0.07
Pb	0.41	0.57	0.20	0.36	0.12
Cl	0.92	-0.12	-0.06	0.02	-0.08
NO3	0.48	-0.06	-0.26	-0.16	-0.26
SO4	0.94	-0.06	0.06	-0.01	-0.02
HCO3	0.83	0.17	-0.28	-0.03	0.13
Na	0.92	-0.06	-0.08	0.01	-0.10
K	0.93	0.00	0.00	-0.02	-0.10
Mg	0.77	0.10	-0.38	-0.06	0.19
Ca	0.91	0.01	-0.21	-0.07	0.13
temp	0.63	-0.12	-0.08	0.22	0.13
DO	-0.83	0.09	-0.14	0.11	0.11
pH	-0.36	0.40	-0.42	0.27	0.53
TSS	0.05	0.46	0.62	-0.24	0.31
TOC	0.72	0.11	-0.21	0.29	0.08
Eigenvalue	10.1	2.14	1.45	1.27	1.07
% Variance explained	45.7%	9.72%	6.58%	5.76%	4.84%
% Cumulative variance	45.7%	55.5%	62.0%	67.8%	72.6%

of Hg above the water quality guidelines values has implied the occurrence of deleterious ecological effects in the Dongjiang River.

In general, the order of mean metal concentrations in the water samples was Mn>Zn>Ni>Cu>Pb>As>Hg>Cr>Cd. The spatial distribution of these heavy metal concentrations is shown in Fig. 2. In order to establish inter-element relationships in water samples, correlation coefficients for those metals were calculated (Table 2). Firstly, the significant positive correlation between Cr, Cu, Mn and Ni indicates a common source for these metals. The spatial distributions of their contents are remarkably similar over large areas which are especially elevated in urban areas in the south of the study area. Associations among these metals can be indicative of sources related to human activities or geogenic and pedogenic characteristics. However, measurements of Zn, Cd and Pb do not show an increasing trend from upstream to downstream; high concentrations are mostly recorded at upstream and downstream ends of the study area. A significant positive correlation (0.51) was found between Zn and Cd. The concentration of As corresponds well to the extent of urban areas and the curve fluctuates for different areas. Hg is also distributed irregularly. Since Hg is not well correlated to other metals, which suggests a different source from others. The overall concentrations of most heavy metal (except Hg) are generally well diluted to a low concentration level, however the data still indicates some potential threat posed on the aquatic water health of the tributaries. It could have dramatically affected by both point sources and areal sources associated with the intensified agriculture, industry and urbanization.

Spatial variation and trends of the heavy metals in PCA:

PCA factors: PCA was conducted to transform the 22 original variables describing the water quality of the Dongjiang tributaries into new, uncorrelated variables known as principle components (PCs). Five PCs were extracted with values that cumulatively explained 72.6% of the variance in the original dataset. Variable loadings and the amount of variance explained are shown in Table 3. All PCs were classified as strong and moderate (>0.5) based on the standards that are shown in bold. PC1 accounted for 45.7% of the total variance and was highly and positively influenced by Cr, Mn, Ni and Cu, all the major ion elements (Ca, Mg, Na, K, Cl, SO_4, HCO_3), and temperature, DO and TOC. This suggests that PC1 might probably act as a factor of general natural influence, which strongly conducts the natural contents changes of the major ion elements (Ca, Mg, Na, K, Cl, SO_4, HCO_3), and temperature, DO and TOC. As easy self-clearing metal elements, Cr, Mn, Ni and Cu could be moved up in a similar pattern and quickly scavenged with sediments load of quick runoff.

PC2, which explained 9.72% of the total variance, has high loadings of Zn, Cd and Pb. These items are primarily related to the application of fertilizer and pesticides originating from soils with lots of agriculture activity. They are mainly associated with soil inorganic fraction and are released when weakly acidic conditions are established. The presence of PC3, captured 6.58% of variance, had high loading values for TSS. Generally, elevated TSS in the Dongjiang River is closely associated with external causes such as runoff from drainage basin, re-suspension of sediments due to the dredging, rainfall, or boating activity, etc. PC4 explained 5.76% of the variance and had a strong and positive load of Hg. Hg concentrations are greater than its background level and no correlations with other parameters. It seems that the elevated concentrations of Hg in rivers with pollutants possibly carried from non-point sources, direct dumping of wastes, mineral exploitation, etc. PC5, accounted for 4.84% of the variance with higher loadings of pH and As. It could be caused by sources different from iron mining and agricultural chemical input.

Spatial trends of the Dongjiang River: Plots of the five PCs of each sample were constructed to evaluate the spatial patterns (Fig. 3). The values on the x-axis are arranged in order of the sites. Considering the larger PC values indicate a higher contribution to the total dataset, we conclude that:

- PC1 (highly related to Cr, Mn, Ni, Cu) was generally stable and slightly below zero, with some sharp positive peaks being observed in samples collected from Site 53~55 and 60~68. This indicates that the corresponding monitoring sites have been highly polluted by Cr, Mn, Ni, Cu elements from Boluo to Shenzhen. The higher value sites of the downstream appear to reflect proximity to metal sources or indicative of heterogeneous sources from urban effluents, generally located close to the major cities of Dongguan, Boluo, Huizhou and Shenzhen.
- PC2 score (highly related to Zn, Cd and Pb) was higher in samples collected from first 30 sites with the highest of Site 62 and 30 and lower in the rest sites with the most negative peak value in sample 54, 78. PC2 mainly indicated a distinctly increasing trend of Zn, Cd and Pb from upstream to downstream. In the Dongjiang River, the soils of the

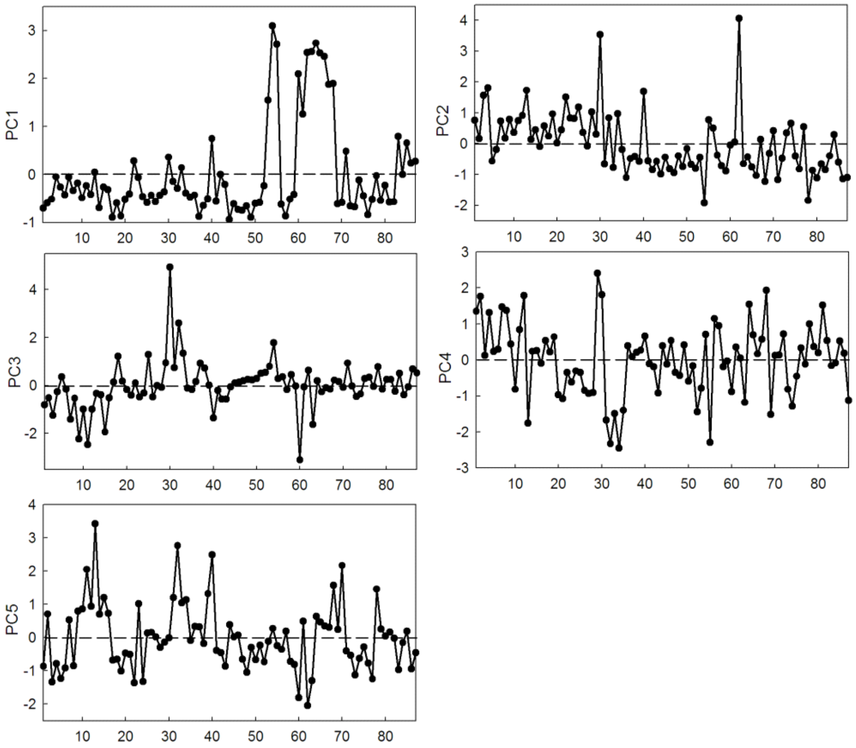

Fig. 3: Spatial patterns of principal components of 87 samples in Dongjiang Rivers

upstream could be contaminated by a number of pollutants from industrial, agricultural and transportation activities. Mining and ore dressing of such sites dominates upstream, light industry and chemical engineering dominates mid-stream. It is apparent that heavy metal of Zn, Cd and Pb solubility and mobility must be correlated to the soils erosion and industries that is influenced by human activities.

- PC3 (highly related to TSS) was lowest in sample 60 and positive peak value in sample 30. It indicates that the upstream of Heyuan has higher levels of sediment transport than the downstream regions of Shenzhen.
- PC4 (highly related to Hg) fluctuated more regularly and showed many small peaks around zero, with several negative peaks being observed in Site 29, 30 and several positive peaks being observed in sites Site 13, 34, 55. It has been suggested that Hg exists in the parent materials (widespread non-ferrous mineral deposits in this region) and stronger weathering effects under the subtropical climate in southern China (Chen *et al*., 2000; Ho *et al*., 2003). Nevertheless, the anthropogenic enrichment of metals in flood-plain soils and surface sediments is the most important reason to be concerned with. The high Hg concentration in Dongjiang River implies the possible hazard to human health.
- PC5 showed many small peaks around zero, with several negative peaks being observed in downstream region and several positive peaks being observed in upstream region.

Above all, it has demonstrated that water quality became more and more polluted as it flowed downstream in the Dongjiang River. The spatial trends of five PCs suggests that low-pollution sites were located mainly in the main river channel and large tributaries, whereas moderate-and high-pollution sites were in small tributaries. These results showed that the concentrations of heavy metals could probably be closely related to the sampling sites and historically influenced by anthropogenic sources, such as land use/land cover and urbanization, etc.

Relationship between the heavy metals and the land use/cover: The influence of environmental variables (physico-chemical variables and landuse data) on measures of heavy metal variables were investigated using Redundancy Analysis (RDA). It is to assess the statistical significance of independent variables. The covariance matrix of the nine analyzed variables was calculated from data normalized to standards and coincides with the correlation matrix. Firstly, ordination analysis of the heavy metal species (DCA) showed the gradient length of axis 1 is 1.24, so the heavy metal species distribution and measurements were related by means of a RDA. Figure 4 shows the results of the RDA analysis where the first axis accounted to the 84.6% of the species-environment relation while the second axis accumulated the 89.8% of the relation. This triplot showed the potential relationships between the heavy metal concentration and the physico-chemical environmental factors, as well as land-use types at a large scale. Both physico-chemical and land-use types variables are presented by red arrows, which could be interpreted similarly PCs as the metal species closed. Arrow pointing in the same direction reflects high positive correlation whereas arrows pointing in opposite directions indicate a high negative correlation. Variables with long arrows have the greatest variance in the data set. Table 4 summarizes the results of the RDA. Of the measured variables, heavy metals was strongly correlated with all the selected environmental variables (r = 0.98, p<0.01).

When present land-use data are combined with the heavy metal variables that is possible to see how land use affects heavy metals. Significant land-use characteristics, as indicated by long arrows (Fig. 4), are urban land-use types (industry, urban dense and urban sparse) and forest percentage. Urban land is closely positive (λ = 0.75) correlated with RDA1 whereas Forestland is negative correlated (λ = -0.52) with it. In this data set, tillage and orchard percentage had little significance in influencing the sediment geochemical composition, as indicated by short arrows (Fig. 4). The landscape of the Dongjiang River Basin is characterized by hills and plains, comprising 78.1 and 14.4% of the basin area, respectively (Chen *et al*., 2010). As most of the forest covers

Table 4: Summary of the results from the RDA (Fig. 4) performed on data of the Dongjiang Rivers

Axes	RDA1	RDA2	RDA3	RDA4	Total inertia
Eigenvalues	0.48	0.03	0.02	0.01	1.000
Species-environment correlations	0.98	0.57	0.56	0.48	
Cumulative percentage variance					
Of species data	47.6	50.6	52.4	53.7	
Of species-environment relation	84.6	89.8	93.0	95.3	
Sum of all eigenvalues					1.000
um of all canonical eigenvalues					0.563
Inter-set correlations of environmental variables with axes					
Tillage	−0.18	−0.03	−0.09	0.15	
Orchard	−0.14	−0.15	0.01	−0.37	
Forest	−0.52	0.17	0.03	−0.08	
Urban	0.75	−0.16	−0.04	0.13	
Watershed	−0.06	−0.31	−0.19	0.08	

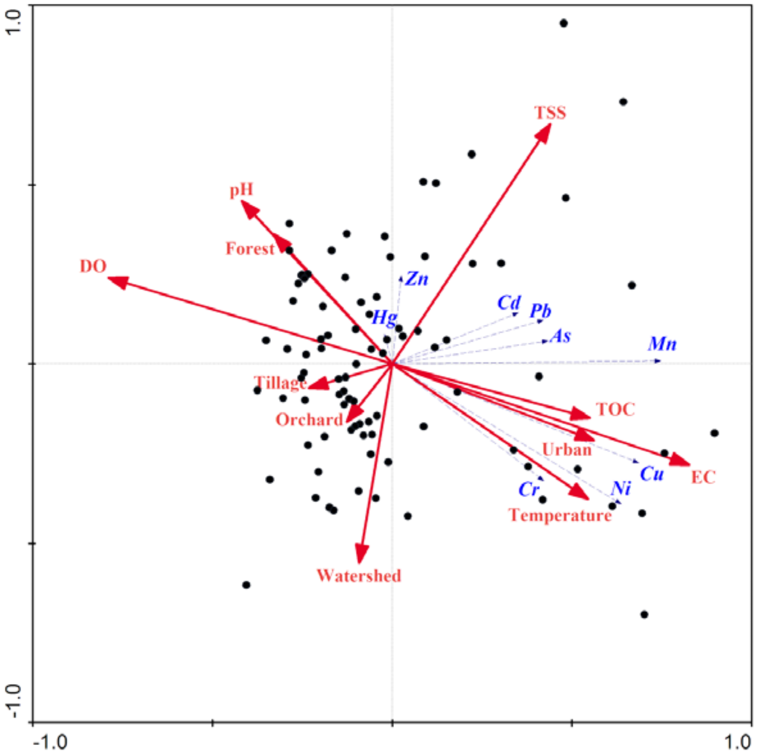

Fig. 4: RDA ordination diagram with heavy metal species (blue arrowheads), sites (circles), and variables (red arrows) of 87 samplings sites. First axis is horizontal; second axis is vertical

headwater areas, the lower of Dongjiang Basin has been experiencing rapid economic growth and urbanization over the past two decades. As a result there has been an increasing pollution potential and competition for water. The highest percentages of urban land-use types (industry, urban dense and urban sparse) are at downstream end of the basin. The heavy metal indicators that characterize this land-use type are Ni, Cr and most importantly Cu concentrations.

Therefore, land use correlations imply that increased urban development (both residential and commercial) and greater impervious surface coverage carry increased concentrations of heavy metals, suspended solid (TSS), organic and fecal coliform bacteria (TOC) and surfactants to surface waters. All of these compounds can be attributed largely to anthropogenic sources and hence their correlation with landscape characteristics confirms their utility as indicators of urban metals pollution.

Urban disturbance of the heavy metal levels in the Dongjiang River Basin: Heavy metals covering the whole measured sites of the Dongjiang River Basin come from both Point-Sources (PS) and Non-Point-Sources (NPS) pollution, such as domestic wastewater, effluent from wastewater treatment plants and agricultural runoff. Generally, most heavy metal pollution is considered to be PS pollution from industries in the Dongjiang River Basin. Meanwhile, the lack of organized collection of solid waste in urban areas often leads to indiscriminate dumping of refuse. A shortage of sewage disposal and solid waste disposal systems is threatening water resources.

The pollution industries of economic mainstays (paper mills, chemical plants, food processing, textiles, mining, electric power, etc) occupies a large proportion. Most representative metal species of PCA and RDA is primarily explained as discharged from smelting and heavy industrial enterprises. However, waste disposal can create serious pollution of surface water resources, especially where there is no control of waste disposal in or near bodies of water. The total domestic water consumption in urban areas of Dongjiang river amounted to 2.5×10^9 t/y. The majority of this water was consumed in Dongguan city, amounting to 1.1×10^9 t/y (44% of the total). Moreover, some other cities of Longchuan, Heyuan, Huizhou and Shenzhen are also responsible for the highest water consumption and wastewater drainage per capita, amounting to 99.7×10^6 and 802.7×10^6 t/y, respectively. The levels of heavy metals generated by domestic sewage of the major cities are considerably higher (Table 5). An outlets in PS, soil erosion of the land use changed areas, and the atmospheric emissions of the heavy metals are likely to be the main NPS of increasing concentrations for the heavy metals observed, especially in the higher levels of the moderate and lower Dongjiang River reaches. However, most sewage with pollutant

Table 5: Summary of the water levels, runoff discharge, wastewater of 2007 and their relationship with our heavy metals of the corresponding sites in the Dongjiang River

	Water sources area[a]	Heyuan	Huizhou	Dongguan	Shenzhen
Precipitation (mm)	1578	1799	1910	1637	1318
Discharge (×10^9 m^3)	64.3	58.9	85.3	80.6	0.4
Water level (m)	66.9	30.9	9.7	3.85	-
Total wastewater (×10^6 t)	115.5	99.7	269.7	1133.5	802.7
Industrial wastewater (×10^6 t)	48.3	31	87.3	651.7	92
GDP (×10^9 yuan)	7.13	39.4	129	370	780.7
Industrial production (×10^9 yuan)	1.88	19.8	217	722.2	1628.4
Population (×10^6 people)	0.88	3.46	3.93	6.95	8.77
Rate of urbanization (%)	16	40.5	61.3	86.4	100
Cr (µg/L)	0.49	0.91	1.82	1.65	1.24
Mn (µg/L)	73.80	754.0	310.6	105.2	220.2
Ni (µg/L)	0.12	1.80	53.18	4.13	3.97
Cu (µg/L)	0.84	1.89	15.22	6.13	5.52
Zn (µg/L)	10.70	28.75	7.69	14.31	46.13
As (µg/L)	0.82	0.39	5.04	2.41	1.90
Cd (µg/L)	0.05	0.10	0.06	0.02	0.03
Hg (µg/L)	0.86	1.65	1.03	1.64	1.12
Pb (µg/L)	3.56	16.89	4.09	2.86	1.82

a: Data collected from Longchuan and adjacent area

levels above those permitted by national standards is allowed to drain into natural bodies of water without any treatment, thereby polluting most rivers in and near cities. Fortunately, the enormous loads of anthropogenic pollutants disposed to the river are diluted by the large water discharge of the Dongjiang River even during the low flow parts, resulting in relatively low concentration levels of heavy metals observed (Ho and Hui, 2001; Ho *et al*., 2003). With the self-purification capacity of water conservancy projects and reservoirs of the Dongjiang rivers, heavy metals may accumulate in sediments to lower pollutant dispersal efficiency. In particular, Xinfengjiang Reservoir and Fengshuba Dam have been made notable progress on the main stream of the catchment over the last two decades. The water leaving the reservoir is very clear, and this could affect the river downstream of the dam. The water flow rate in the main river was quite slow and the downstream reaches are subjected to tidal flushing, which provides a certain degree of “cleansing” on the sediments in the downstream. There are an increased likelihood of adverse effects within the estuary of Dongjiang River, and a self-clearing and sedimentary process of heavy metals from upper reaches in the reservoir.

Sources and factor analysis of heavy metal contaminants should be better estimated with biological evaluations of toxicity at specific sites. Little is known about the bioavailability of heavy metals and associated contaminants to organisms in the Dongjiang River. In addition, it is becoming increasingly important to understand metal accumulation within food chains, because, once these heavy metals reach human, they may produce chronic and acute ailments (EI Nabawi *et al*., 1987). Human activities affecting the local aquatic ecosystems are more likely to disrupt natural patterns and processes with large concentrations of toxic elements and serve species may not have the ability to adapt to the rapid changes to their environment that can occur. As the results above, higher levels of Hg would most probably responsible for the serious potential risk of aquatic environment in the Dongjiang River. If high contents of heavy metals resulted in large degradation of bioavailability over the whole basin, the water resource and ecosystems could not retain their utility, the community may assess these changes as being unacceptable.

Therefore, the corresponding sewage and industrial waste treatment facilities are needed to keep pace with the growth in population and industry in the area. It is generally acceptable that the management of aquatic environments requires an understanding of the important linkages between ecosystem properties and human activities. The evaluations of human-induced hydrologic changes can serve to advance research on the biotic implications of hydrologic alteration and to support ecosystem management and restoration plans.

CONCLUSION

The heavy metal signature of aquatic ecosystems of Dongjiang River is obviously reflected in water under highly anthropogenic development and the major rearrangement of water resources. The heavy metal concentrations in the present study generally indicate good level of the aquatic environment in most parts of the Dongjiang tributaries. The order of mean metal concentrations in the water samples was Mn>Zn>Ni>Cu>Pb>As>Hg>Cr>Cd and are generally lower than concentrations in other regions in China and the world average background concentrations. The spatial distributions of Cr, Cu, Mn and Ni contents are remarkably similar over large areas, and are especially elevated in urban areas of the south area. However, measurements of Zn, Cd and Pb showed that high concentrations are mostly recorded at upstream area and the ends of the alluvion. The concentration of As corresponds well to the extent of urban areas and the curve fluctuates for different areas, however, Hg is distributed irregularly through the basin.

In this case study, different multivariate statistical techniques were used to evaluate spatial variations in heavy metals of Dongjiang River and tributaries. The spatial trends of five PCs probably indicated that low-pollution occurs in the main river channel and the large tributaries, whereas moderate- and high-pollution occur in small tributaries. Redundancy analysis (RDA) examined land use correlations, suggesting that increased urban development (both residential and commercial) and greater impervious surface coverage relate to increased concentrations of heavy metals, suspended solid (TSS), organic and fecal coliform bacteria (TOC), and surfactants to surface waters. Land use changes, soil weathering, runoff and self-clearing, municipal and industrial wastewater, and waste disposal site leaching were among the major sources responsible for heavy metals in rivers. Practices and valuable suggestions to address the current status and future trends of heavy metals control in the Dongjiang River were provided. These results and suggestions should help local authorities control and manage pollution of the Dongjiang River. It is recommended that the propagation and evolution of the heavy metal pollutants in the catchment and river be investigated by applying a hydrodynamic water quality model to the basin.

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