

## Spatial distribution and environmental risk of major elements in surface sediments associated Manwan Dam in Lancang River, China

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### Abstract

Bulk elements and grain sizes in sediments collected at upstream and downstream of Manwan Dam were studied to demonstrate the spatial distribution of heavy metals in the sediments and to assess their risk. Correlation analysis showed that the spatial distribution of Cd, Zn and Mg were significantly affected by dam construction. PCA analysis demonstrate that Cd and Zn were both controlled by Ca, As, Pb, organic matter and clay. Mg was controlled by silt, Al, P and K. The risk assessment demonstrated that the pollution of Cd, As, Zn were more serious than other heavy metals. Fine-grained sediments with higher risk level were found in the section near the upstream of dam, while coarse-grained ones with lower risk level were found in the section far away from the downstream of dam. The sections in tributary were lower in risk than those in the main stream. Heavy metal concentrations in the mainstream sediments were influenced by dam construction and those in tributary were influenced by both dam construction and human activities in locality. Unusual high concentrations of Cd, As, and Zn in both sections implied that more pollution prevention measures are needed in the Manwan Dam in order to prevent increased heavy metal pollutions in the Lancang-Mekong River.

**Keywords:** Manwan Dam, Elements, Spatial Distribution, Environmental Risk

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### Introduction

Dams have the abilities of producing electricity, improving shipping condition, enhancing the ability of defending flooding and being benefit to irrigation, which can support major conditions for the development of human beings (Fearnside, 2005). At the same time, dams have influences on the development of riverine ecosystem (Bai et al., 2009). After dams begin to run, the flow speed decreases and more sediments deposit in reservoir because of changes in the hydrological regime (Fu et al., 2008). Sediments in river system are sinks and the potential sources of pollutions such as heavy metals and nutrients (DelValls et al., 1998). The spatial distributions of elements in sediments caused by dam construction indicate different ecological risks (Klavinš et al., 2000). The concentrations of heavy metals are primary index to assess water quality and reflect the interference from humanity (Loska and Wiechuła, 2003). The necessary elements for organisms such as P, K, Mg, Ca, Na are also the symbols of potentially eutrophic risk (Arhonditsis et al., 2003). To identify the response of riverine ecosystem associated with dam construction, an effective assessment method is needed to understand the process of sediment element transportation and preservation.

In the dammed rivers, the contents of sediment elements are influenced by many factors such as sediments texture, background values, terrestrial soil and human activities. Fine fraction can absorb and perverse more

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matters through physical functions and process (Arndt et al., 2013). Because each area has its own environmental condition, the compositions of parent materials should be concerned in the assessment (Youssef and El-Said, 2011). Soils on the bank are broken by air-slake and transport into river by rainfall (Vukovic et al., 2014). The humanity in the drainage basin is a driving force for pollution inputs and enhances the preservation of elements (Liu et al., 2003).

Reservoir sedimentation, as an important hazard in hydroelectric construction in the Lancang-Mekong River basin, has been widely concerned by scholars in recent years. Fu et al. (2008) found that the Manwan Reservoir lost approximately 21.5-22.8% of its total storage capacity because of the sediment trap. Kumm and Varis (2007) reported that the flux of sediment from the upper Mekong River basin has been decreasing as a reason of sediment trapping by dams. Wang et al. (2012) found that heavy metals had accumulated in sediments of the Manwan Reservoir in the Lancang-Mekong River. Li et al. (2010) observed impacts of sediments in the Manwan Reservoir on the aquatic habitat and community. Li et al. (2013) stated that the sediments have changed the composition, biomass and biological integrity of phytoplankton assemblages. To date, few researchers have investigated the distribution of the elements in sediments in the upstream and downstream of dam construction. Therefore, we conducted this study to investigate the effects of dam construction on the dynamics of elements, select the major ones for assessing the environmental risks associated with dam construction.

## Material and Methods

### Study Area

The Lancang-Mekong River, an international river, is situated in the southeastern corner of the Eurasian continent and originates from Guyong-Pudigao creek at the foot of Mountain Jifu on the Qinghai-Tibet Plateau (Kumm and Varis, 2007). This trans-boundary river is generally divided into two parts, the upper and the lower basin. The upper basin includes the watersheds of China and Myanmar, and the lower basin includes the watersheds of Laos, Thailand, Vietnam and Cambodia. The territory of China includes 91% of the drop in elevation and produces abundant hydropower resources (He et al., 2005). Eight dams have been planned: four of them, i.e., Xiaowan, Manwan, Dachaoshan and Nuozhadu have already been completed. This study was conducted in the Manwan Reservoir (MR) in the upper reaches of the Lancang-Mekong River basin, below the Xiaowan dam and above the Manwan dam (Figure 1).

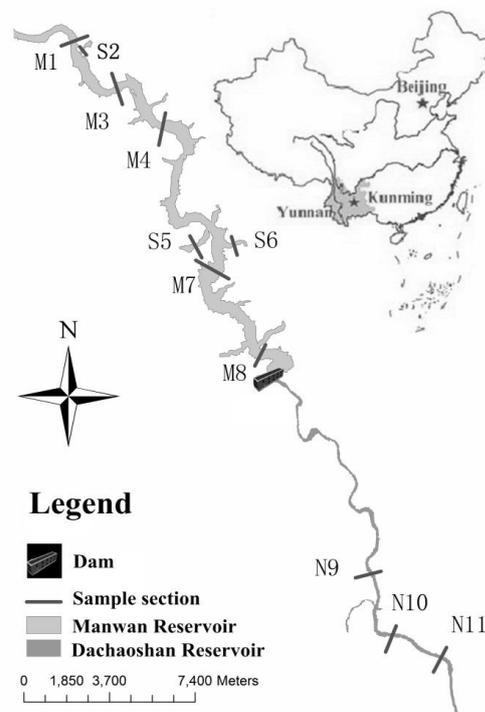


Figure 1. Locations of sampling sections around Manwan Dam

The watershed area of Manwan Reservoir is approximately 114500 km<sup>2</sup>. The Manwan Dam (MD) was the first dam, completed in 1995, along the Lancang-Mekong River for hydropower generation. The normal pool level is 994 m, and the annual mean sediment discharge is 40 million tons yearly. The average annual flow is 1230 m<sup>3</sup>/s, and the energy production is 7.8 billion kW·h per year. The dam site is located in the lower part of the bend of the "S" shape, and its maximum height is 132 m. There are eight sections located in the upstream of MD and three sections in the downstream (Figure 1). S2, S5 and S6 were located in the tributary, and other sections were located in the mainstream.

### Sample Collection

Surface (0-15 cm) sediments were sampled by using a bottom sampler. In each sampling section, one sample was collected in the middle, and two samples at each side close to the bank (2-3 m away from the bank). After the samples were lifted from the water, sediments were sealed in valve bags. All of the subsamples

were transported to the laboratory, stored in a freezer and then were freeze-dried to a constant weight. The samples from each section were mixed together in equal amounts before physical and chemical analysis.

## Sample Treatment and Measurement

### Physical and chemical analysis

The sediment grain-size composition was first treated by an ultrasonic disperser with sodium hexametaphosphate after being mixed with H<sub>2</sub>O<sub>2</sub> and HCl to avoid organic-matter and carbonate interference and was then examined with the laser particle analyser Microtrac Inc S3500. The total organic carbon was determined by TOC-V Total Organic Carbon analyzer (Shimadzu, Inc., Japan). Total nitrogen (TN) and total carbon (TC) were determined using a PerkinElmer 2400 CHN analyser. Heavy metals and K, P, Mg, Ca, Na were measured by ICP-AES (SPECTRO Analytical Instruments GmbH). All statistical analyses were performed with SPSS 18.0 and Canoco for Windows 4.5.

### Calculation

To indicate the enrichment factor (EF) of the sediments, heavy metals was considered to be the symbol of environmental risk (Zoller et al., 1974). The EF was calculated as follows:

$$EF = \frac{[C_x/C_{ref}]_{sample}}{[C_x/C_{ref}]_{background}} \quad (1)$$

where  $[C_x/C_{ref}]_{sample}$  is the measured value of element vs reference element, and  $[C_x/C_{ref}]_{background}$  is the background value of element vs reference element. Because the soils of Yunnan province are full of Al which is a stable element for resistance to weather and human disturbance. We chose Al as reference element to calculate EF value. The background values of metals are given in Table 1, and the pollution criterion based on the enrichment factor are given in Table 2.

Table 1. Background Value of Metal Elements in Yunnan Soil

| Heavy metals           | Al    | As   | Cd     | Cr   | Cu   | Mn  | Ni   | Pb | Zn   |
|------------------------|-------|------|--------|------|------|-----|------|----|------|
| Value/10 <sup>-6</sup> | 86500 | 10.8 | 0.1035 | 57.6 | 33.6 | 461 | 33.4 | 36 | 80.5 |

Table 2. Pollution criterion based on the enrichment factor

| Rank | EF    | Pollution level |
|------|-------|-----------------|
| I    | 0~2   | None or Mild    |
| II   | 2~5   | Middle          |
| III  | 5~20  | Significant     |
| IV   | 20~40 | Serious         |
| V    | >40   | Extreme         |

## Results and Discussion

### Variation of Grain Size, Heavy Metals and Non-heavy Metal

As shown in Figure 2, in the upstream of MD, the proportions of silt and clay in the mainstream increased with the decrease of distance to MD. As a result, the mean size decreased in that area. While in the tributary area, the proportions of fine fractions did not have significant changes and were higher than the sediments in the sections which have similar distance to MD. The mean sizes of sediments in tributary were also lower than the sections nearby. In the downstream of MD which belonged to Dachaoshan Reservoir, the macro-sand and micro-sand fraction became the major fraction in the sediments and the mean sizes were obviously higher than the upstream.

The spatial distributions of heavy metals were given in Table 3 and Figure 4. As the stable elements in earth, Al and Fe were not changed significantly in this study. Heavy metals all had C.V. values over 20%. The lowest values of As, Cd and Pb in sediments were found in S2 and the highest ones were found in M8. The highest values of Cr and Ni were found in S2 and the lowest values were found in M4. The highest values of Cu and Zn were found in M8 and the lowest values were found in M4 and N11, respectively. In general, most of heavy metals content were higher in M7 and M8 where more fine fraction were found in and became low in the downstream of MD except Cr and Ni. The contents of heavy metals of the sediments in mainstream were higher than that in tributary. The correlation analysis between distance (the distance is from sections to the

dam site belonging to the reservoir they locate in) and metal elements showed that only Cd and Zn had significantly negative relationship.

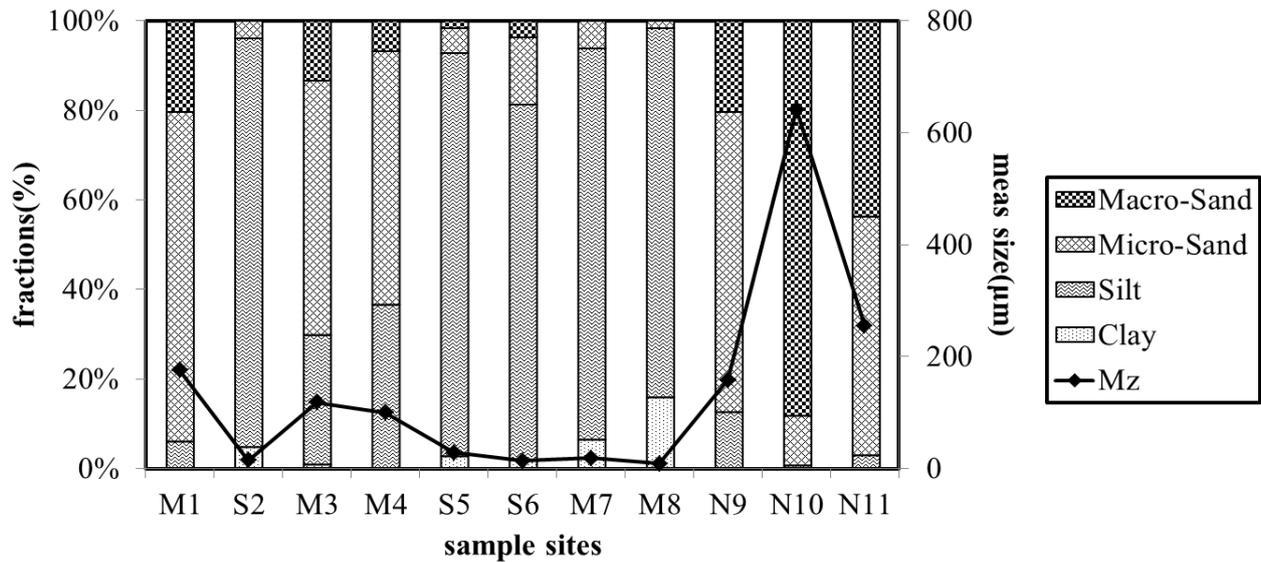


Figure 2. Variation of fractions and mean size in sediments

Table 3. Heavy metals contents in sediments

| Sample Sites | Al       | Fe       | As     | Cd     | Cr     | Cu     | Mn     | Ni     | Pb     | Zn     |
|--------------|----------|----------|--------|--------|--------|--------|--------|--------|--------|--------|
|              | µg/g     |          |        |        |        |        |        |        |        |        |
| Average      | 30299.57 | 31663.77 | 30.51  | 0.80   | 63.26  | 32.55  | 607.81 | 32.11  | 35.27  | 132.29 |
| STDEV        | 4021.48  | 4198.66  | 11.24  | 0.43   | 15.64  | 7.51   | 150.49 | 7.23   | 11.37  | 34.88  |
| C.V.         | 13.27%   | 13.26%   | 36.83% | 53.66% | 24.73% | 23.06% | 24.76% | 22.52% | 32.25% | 26.37% |
| Distance     | -0.53    | 0.30     | -0.26  | -0.67* | 0.41   | 0.10   | -0.50  | 0.05   | 0.01   | -0.62* |

Note: STDEV, standard deviation. C.V., variable coefficient. \*, significantly Correlation is significant at the 0.05 level (2-tailed)

As shown in Table 4, the non-metal elements including P, K, Na, Mg were not changed significantly in this area with C.V. values below 25%. The highest content of Ca were found in M3, and the lowest content were found in N11. The sediments collected in mainstream had a higher Ca value than that in tributary. TOC and TN had similar variation in this study. With the decrease of distance to dam site, the TOC and TN contents in the sediments collected in mainstream became higher. The samples collected in tributary had a higher TOC and TN contents than those in mainstream. The highest contents of TOC and TN were both found in S6 and the lowest ones were found in N10. The correlation analysis showed that only Mg had significantly negative relationship with distance.

Manwan Dam built in the Lancang-Mekong River changed the flow velocity and converted the river into a sedimentary environment because of the alteration of runoff (Fu et al., 2008). In this study, we further studied the effects of the dam on the physical and chemical profiles of the sediment and found that the dam may be associated with the spatial variations of Cd, Zn and Mg in the sediment profiles and the distribution of physical fractions. In the upstream, sediment may adsorb more organic matter and some elements with the help of fine fraction (Liu et al., 2013). In the downstream of MD, which is the upstream of Dachaoshan Reservoir, the high-velocity flow cannot lead a stable hydrogeological environment to preserve most elements (Vukovic et al., 2014). Comparing with the sediments in mainstream, samples collected in tributary are influenced more lightly and affected by its own upstream where villages and farmland locate in (He et al., 2004). Although the sediments of tributary are lower in heavy metals, as a strong organic matter input and a necessary sediment input, can enhance the preservation of elements especially the heavy metals have a positive relationship with organic carbon (Wen et al., 2012). The humanities on the band such as agricultural production and ordinary life enhance storage of non-metals in nearby sections (Coakley et al., 2002).

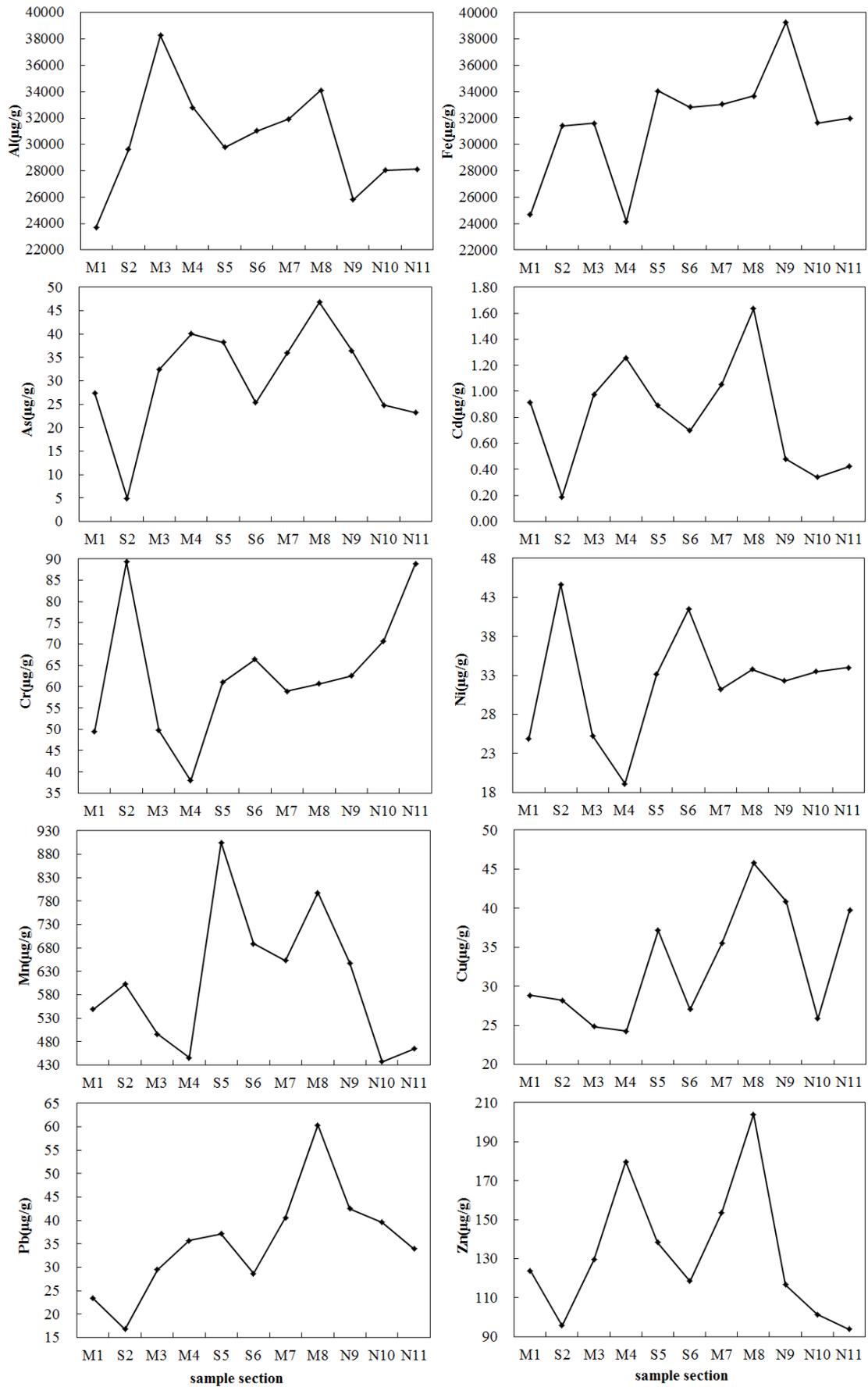


Figure 3. Spatial distribution of heavy metals in sediments

Table 4. Non-metals contents in sediments

| Sample Sites | P      | K        | Mg      | Ca       | Na       | TOC    | TN     |
|--------------|--------|----------|---------|----------|----------|--------|--------|
|              | μg/g   |          |         |          |          | g/kg   |        |
| M1           | 447.99 | 13617.29 | 3328.05 | 13251.85 | 7162.31  | 2.60   | 0.31   |
| S2           | 529.58 | 16052.63 | 5246.83 | 8486.23  | 4717.39  | 0.72   | 0.79   |
| M3           | 705.57 | 17265.97 | 5994.00 | 22063.22 | 10311.33 | 5.20   | 0.40   |
| M4           | 451.30 | 14965.30 | 5567.57 | 21615.22 | 8835.75  | 7.90   | 0.71   |
| S5           | 585.17 | 17469.06 | 4479.86 | 3758.77  | 8090.56  | 11.41  | 1.07   |
| S6           | 587.69 | 19842.16 | 5760.28 | 4905.39  | 7218.30  | 11.44  | 0.94   |
| M7           | 639.56 | 17702.34 | 5970.22 | 8670.54  | 9361.70  | 8.10   | 0.75   |
| M8           | 650.84 | 17700.67 | 5170.18 | 12015.84 | 8343.69  | 11.20  | 0.91   |
| N9           | 436.19 | 13750.79 | 2507.16 | 2650.77  | 6424.12  | 8.78   | 0.82   |
| N10          | 728.45 | 20489.41 | 4965.65 | 2162.42  | 8911.90  | 0.91   | 0.09   |
| N11          | 584.08 | 19157.44 | 3991.68 | 2132.81  | 6341.17  | 1.59   | 0.19   |
| Average      | 576.95 | 17092.10 | 4816.50 | 9246.64  | 7792.56  | 6.35   | 0.63   |
| STDEV        | 101.78 | 2304.94  | 1133.45 | 7315.25  | 1603.21  | 4.31   | 0.33   |
| C.V.         | 17.64% | 13.49%   | 23.53%  | 79.11%   | 20.57%   | 67.86% | 52.10% |
| Distance     | -0.07  | 0.04     | -0.616* | -0.51    | -0.29    | -0.52  | -0.59  |

Note: STDEV, standard deviation. C.V., variable coefficient. \*, significantly Correlation is significant at the 0.05 level (2-tailed)

### Environmental Effects on Spatial Distribution of Sediment Elements

To identify the interference factors of the spatial distribution of elements affected by dam, we use PCA method to analyse the relationship between key elements (Cd, Zn, Mg) and environmental factors (elements and structure indexes). As shown in Figure 4, Cd and Zn could be gather in one group which was affected by the same factors. Ca, As, TOC, TN, Na, Pb, As and clay fraction had positive correlation with Cd and Zn. Ni, Cr, mean size and macro-sand fraction had negative correlation with Cd and Zn. P, K and micro-sand fraction had no influence on Cd and Zn. Mg was controlled by other factors. Al, P, K and silt fraction had positive correlation with Mg, and Cu, micro-sand, Fe had negative correlation with it. Despite the influence of dam construction, organic matters including TOC, TN, Na, Al, Ca, silt and clay fraction also control the spatial distribution of Cd, Zn and Mg at the same time.

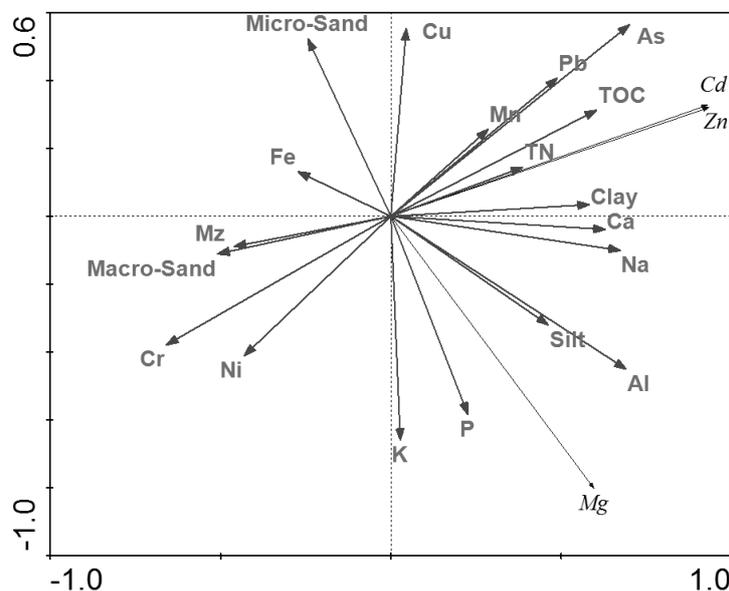


Figure 4. PCA analyses of elements and sediments structure indexes

According to correlation analysis and PCA, Cd and Zn as the elements affected by dam construction may both come from mining and electroplating in the upstream (Yanqun et al., 2005). They are adsorbed by anion and then form to stable complex and carbonate (N'Guessan et al., 2009). Due to the less industry in Manwan basin, most of heavy metals may exist in crystal lattice with residual form and transport by rainfall to riverine system (LeGalley et al., 2013). When organic matters and metals coexist and form to complex, the adsorption of silt and clay fraction can enhance (Pacifico et al., 2007). Mg is hurtless to riverine system and distribute independently due to less impact factor.

### EF Index for Heavy Metals

Because Cd and Zn were harmful elements to aquatic environment, we calculate the EF values of heavy metals to assess the environmental risk caused by dam construction. The results of enrichment factor were given in Table 5. As the pollution criterion shown in Table 2, all of the heavy metals were mild or over mild risk level. Cd was the most serious pollution factor with heavy pollution level except the sediment collected in S2. The sediments in M8 had the highest EF value (EF=40) which was significantly higher than that in downstream ( $10 \leq EF \leq 15$ ). As was also seriously pollution element with significantly pollution level except that in S2. Zn was a pollution factor with a mean EF value over 4. Due to the effect of dam construction, the sediment in M7 and M8 were polluted by Cd, Zn and As. The sediments in tributary had lower risk level than that collected in the nearby sections. With the accumulation of Cd, As and Zn in the front of dam, EF values of these elements are significantly higher than in other areas, indicating the environmental risk caused by dam construction. To decrease the environmental risk caused by heavy metals, hydropower station need enhance desilting.

Table 5. EF Index of Heavy Metals

| Sample sites | As | Cd | Cr | Cu | Mn | Ni | Pb | Zn |
|--------------|----|----|----|----|----|----|----|----|
| M1           | 14 | 32 | 3  | 3  | 4  | 3  | 3  | 6  |
| S2           | 1  | 5  | 5  | 2  | 4  | 4  | 1  | 3  |
| M3           | 7  | 21 | 2  | 2  | 2  | 2  | 2  | 4  |
| M4           | 10 | 32 | 2  | 2  | 3  | 1  | 3  | 6  |
| S5           | 10 | 25 | 3  | 3  | 6  | 3  | 3  | 5  |
| S6           | 6  | 19 | 3  | 2  | 4  | 3  | 2  | 4  |
| M7           | 9  | 27 | 3  | 3  | 4  | 3  | 3  | 5  |
| M8           | 11 | 40 | 3  | 3  | 4  | 3  | 4  | 6  |
| N9           | 11 | 15 | 4  | 4  | 5  | 3  | 4  | 5  |
| N10          | 7  | 10 | 4  | 2  | 3  | 3  | 3  | 4  |
| N11          | 7  | 12 | 5  | 4  | 3  | 3  | 3  | 4  |

### Conclusion

In this research, dam construction significantly affected the variation of sediment structure. With fine fraction deposit in the front of dam, Cd, Zn, Mg were found significantly higher than rest areas. The concentration of heavy metals in the sediment of mainstream was higher than that in tributary while more organic matters and fine fraction are found in there. Cd and Zn as one group were both controlled by many factor including TOC, TN As, Pb, Mn, Ca and clay fraction. Mg was controlled by Al, P, K and silt fraction. Due to the variation of EF index, Cd, As and Zn were seriously pollution factor and had the highest values in the front of dam site. Unusual high concentrations of Cd, As, and Zn in both sections implied that more pollution prevention measures are needed in the Manwan Dam in order to prevent increased heavy metal pollutions in the Lancang-Mekong River.

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