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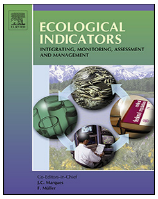

Original Articles

Revealing the correlations between heavy metals and water quality, with insight into the potential factors and variations through canonical correlation analysis in an upstream tributary

Huaibin Wei[a], Huibin Yu[b,*], Guangcai Zhang[b,c], Hongwei Pan[a,b], Chunjian Lv[b], Fansheng Meng[b,*]

[a] North China University of Water Resources and Electric Power, Zhengzhou, Henan 450011, PR China
[b] State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Science, Beijing 100012, PR China
[c] School of Geography and Environment, Shandong Normal University, Jinan 250014, PR China

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ABSTRACT

Water pollution is a worldwide problem that requires urgent attention and prevention. Multivariable analyses have been applied to water quality data for insight into potential factors, identification of pollution sources and determination of a dynamic set of physico-chemical interactions and equilibrium. Canonical correlation analysis (CCA) and hierarchical cluster analysis (HCA) were employed simultaneously to water quality data sets with 14 parameters measured at 9 sampling sites in an upstream tributary in March, June, September and December. The sampling sites were grouped into three clusters using case HCA with the rescaled squared Euclidean distance (SED) < 5, proving that the decreasing order of the water quality level was approximately reservoirs > mainstem > tributaries. The potential factors of the water quality were sought using variable HCA with SED < 0.5, which included As, *E. coli*, F^-, Zn, TP, COD_{Cr}, pH and Cd. According to correlation analysis, the heavy metals not only showed correlations with each other but stronger correlations with F^-. The CCA of the sampling sites determined that *E. coli*, TEMP, COD_{Cr}, DO and pH were the potential factors differentiating the sites, revealing that natural processes deeply influenced the reservoirs, while anthropogenic activities deeply influenced the tributaries and mainstem. The CCA of the months indicated that the seasonal factors included *E. coli*, TEMP, COD_{Cr}, DO, pH and BOD_5, demonstrating that June and September were considerably impacted by no-point source and natural pollution, while March and December by point source and natural pollution. The CCA of the heavy metals showed that F^-, TP, *E. coli* and COD_{Cr} were potential factors, which could be associated with industrial activities and household wastewater.

1. Introduction

Water is an indispensable renewable resource for sustaining life on Earth (Wolf, 2007; Fthenakis and Kim, 2010). For high-speed economic and urban development, a variety of contaminants have been produced and loaded into rivers through anthropogenic activities (industry, agriculture, domesticity and urbanization) and natural processes (weather and erosion) (Zaimes et al., 2008; Van Landeghemet al., 2012; Zhao et al., 2016). This has deteriorated water quality, disturbed the natural equilibrium and led to serious environmental problems (Singh et al., 2004; Hambright et al., 2010; He et al., 2016). Hence, water pollution is a worldwide problem that requires urgent attention and prevention (Kowalkowski et al., 2006; Schwarzenbach et al., 2010; Kasel et al., 2013).

Water quality is not only indicative of water's suitability for maintaining various industrial applications and processes but is also potential factor in supporting biological health (Xinget al., 2014; Khan et al., 2015; Duan et al., 2016). Water quality may be generally expressed as the concentration of inorganic and organic material in the water, which includes physical, chemical and biological parameters (Duan et al., 2013; Wang et al., 2014; Jiang et al., 2015). The main reasons for monitoring water quality have been the need to assess water quality status against existing standards and to verify whether the observed water quality is suitable for prospective applications. Combined with multivariate analyses, water quality research has not only evolved to investigate trends in the aquatic environment but also to seek its potential factors and to identify pollution sources (Pinto and Maheshwari, 2011; Eisenberg et al., 2013). This has been utilized as a useful tool in the efficient management of water resources and as a valuable solution for water pollutions (Kazi et al. 2009; Noori et al.,

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* Corresponding authors at: Chinese Research Academy of Environmental Sciences, Beijing 100012, PR China.
E-mail addresses: yhbybx@163.com (H. Yu), mengfs@craes.org.cn (F. Meng).

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2012).

During recent years, heavy metal pollution in river systems has become a widespread focus in the scientific community (Varol, 2011; Diop et al., 2015). Compared to nitrogen and phosphorus nutrients and organic pollutants, heavy metals can not be removed by natural degradation processes (Huertadiaz and Morse, 1990; Varol and Şen, 2012). Heavy metals can be loaded into aquatic systems, by weathering and erosion of heavy metal-rich soil and rock, and through anthropogenic activities involved in mining, smelting and using heavy metal materials and/or substances containing heavy metals (Rai, 2008; Hartmann et al., 2013). Investigating spatio-temporal variations of heavy metals can reveal a dynamic set of physico-chemical interactions and equilibrium.

Hence, multivariate analyses were applied to the data sets of water quality and heavy metals in the Chonglingjiang River, an upstream tributary of the Xiangjiang River, for investigating the variations, seeking potential factors, and determining interactions and equilibrium. First, the water quality and heavy metal parameters were discriminated selectively for their variations with spatio-temporal matrices. Second, hierarchical cluster analysis (HCA) was used to explore differences and similarities at the sampling sites. Finally, canonical correlation analysis (CCA) was applied to reveal correlations between the quality water and heavy metals to investigate potential factors of the heavy metals.

2. Materials and methods

2.1. Study area

The upstream tributary is located in the south of Hunan Province, China, between latitudes 25°35′ N and 26°28′ N and longitudes 112°06′ E and 112°54′ E (Fig. 1a). The river originates in the Renxingshan Mountains in Lansan County, traverses Jiahe County, Linwu County and Guiyang County, and enters the Xiangjiang River in Changning County (Fig. 1b). The river extends 223 km from south to north, and its catchment covers 6623 km^2. For approximately ten years, the average runoff volume has been approximately 72.651 $m^3\ s^{-1}$. The river catchment has a typical, subtropical, humid, monsoon climate with a mean annual precipitation of 1325 nm and an annual average temperature of 17 °C over approximately the past five decades. The water quality in the entire catchment is much higher than Grade III (SEPA, 2002). Mineral resources are rich in the catchment, where metallic and non-metallic minerals are extensively present. Mining and various industrial activities could potentially produce heavy metal pollution, which could lead to water quality deterioration and ecological degradation (Bridge, 2004; Diop et al., 2015).

2.2. Samples collection

Based on the types of water body, sampling sites were selected in the tributaries, mainstem and reservoirs. Sampling sites #1 and #2 were located in the tributaries, in which metallic and non-metallic minerals were present. Sampling sites #3 to #6 were located in the mainstem, positioned behind the inlets to the main tributaries. Sampling sites #7 to #9 were located in reservoirs, where drinking water sources originated. Water samples were collected in March, June, September and December, which generally represent the spring, summer, autumn and winter seasons.

The water samples were collected at mid-depths of the tributaries and mainstem using a 10 L Van Dorn water sampler. The water samples were collected in the center of the reservoirs, except for at sampling site #9, where the water samples were collected at the reservoir head. The water samples were stored in the containers with dilute HCl, and shipped to the lab in a cooled container. In situ measurements for the temperature (TEMP), pH and dissolved oxygen (DO) of each water sample were performed with an YSI 600 multi-probe.

2.3. Laboratory analyses

Measurements of the water samples in the laboratory were conducted generally based on national standards (SEPA, 2002). Ammonia nitrogen (NH_3-N) and fluoride (F^-) are measured using filtered water samples (0.45 μm membrane), while chemical oxygen demand (COD_{Cr}), 5-day biochemical oxygen demand (BOD_5), total phosphorus (TP), total nitrogen (TN) and *Escherichia coli* (*E. coli*) are measured using unfiltered samples (Specchiulli et al., 2008). The NH_3-N is determined by the Nessler's reagent method, the TP by ammonium molybdate method, and the TN by the alkaline persulfate digestion method (Kazi et al., 2009). The COD_{Cr} is estimated with the dichromate reflux method, and

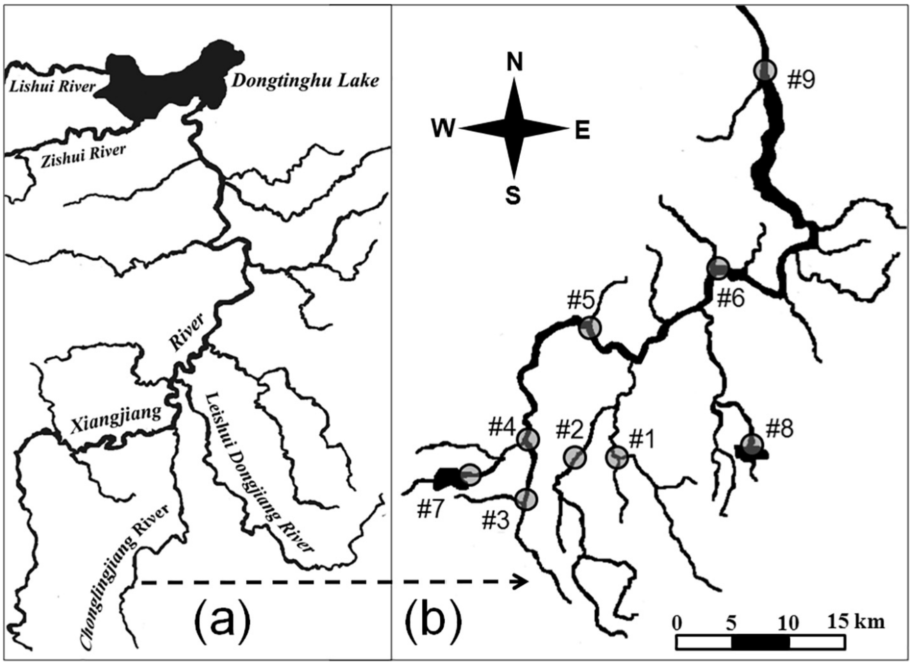

Fig. 1. Water sheds of the Xiangjiang River (a) and the Chonglingjiang River (b) and location of the sampling sites.