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# Temporal dynamics of urbanization-driven environmental changes explored by metal contamination in surface sediments in a restoring urban wetland park



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#### HIGHLIGHTS

- Urban-rural distribution pattern of metals in sediment faded out with urbanization.
- Urban emissions were identified as sources of metal elevation in surface sediment.
- Metal level homogenization with urbanization posed a moderate risk to the public.

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## ABSTRACT

Spatial patterns of metal distribution along urban-rural or multi-city gradients indicate that the urbanization process directly lead to metal enrichment and contamination in the environments. However, it has not yet looked at homogenization dynamics of an urban-rural gradient pattern over time with urbanization process in an area. This study monitored anthropogenic metals (Cr, Cu, Pb, and Zn) in surface sediments from channels of a newly-opened National Wetland Park to elucidate the urbanization-driven dissolution of urban-rural gradient pattern between 2008 and 2011. Sixty-eight surface sediment samples were taken from these channels in July of both 2008 and 2011. Results showed that a spatial distribution pattern of total metal contents along the gradient of urbanization influence, evident in 2008, was homogenized in 2011 with the area development. The lead stable isotope ratio analysis identified anthropogenic Pb origins from vehicular exhausts, cements, and coal flying ashes, which elevated metal contents in the inner channels via atmospheric deposition. Specific hazard quotients of the metal contamination in surface sediment were also assessed and enhanced over time in the study wetland park. These findings suggest that emissions from traffic, construction, and energy generation contribute metal loadings in the urbanizing environment.

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## 1. Introduction

Urbanization has been one of crucial anthropogenic activities that drive global changes [1]. The Future Earth Committee launched a core project titled "Urbanization and Global Environmental Changes" in 2014. Urbanization-driven environmental changes have been widely studied across the world because urbanization makes consumptions of resources (e.g. food and energy) in a

highly concentrated way. However, the extent of the environmental impacts by urbanization is mostly determined by how the urban population behaves (consumption and living patterns), not just by how large its size is [2].

Metal contamination in the urban environment is typically more severe than in the rural or natural environments. Anthropogenic metals in the urban environment have been identified by a number of studies in urban areas globally. Lead (Pb), zinc (Zn), copper (Cu), chromium (Cr), cadmium (Cd), and other metals were widely considered as toxic anthropogenic metals based on environmental hazard and health risk assessments [3–5]. Numerous urban-rural gradient studies have demonstrated that metal enrichment in the urban environment originates at least from traffic exhaust (muffler

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emission and wear/tear of automotive parts), construction emission (cement dust), energy generation (coal combustion and flying ash), and industrial activities [6-11]. Within a multi-city urbanization gradient along the Grand Canal in China, however, higher metal loadings in surface water were general found in towns and small-sized cities than in mid- and large-sized cities [12]. This is in agreement with Torrey [2], i.e. the environmental impacts of urbanization are determined by urban population behaviors, not by the urban size. Nevertheless, these studies revealed that the spatial patterns of metal loads in the environment are driven by urbanization. In a few of them, using the space-for-time substitution approach revealed dynamics of urbanization-driven changes [12]. The real story of temporal dynamics of urbanization-driven environmental changes needs a long-term study. We hypothesize that when a rural or suburban area turns to be urbanized, anthropogenic metals will be elevated in the environmental matrices and the existing urban-rural/suburban pattern of metal spatial distribution will be diffused.

China has been rapidly urbanizing since 1980s and has become a living laboratory for studying urbanization-driven environmental changes [13]. Nowadays, China is facing a critical period for development transformation. A "new-style" of urbanization policy has been implemented since 2012 that focuses on improving the wellbeing of urban residents and overcoming the environmental problems associated with the "old-style" urbanization (such as over 19% of sampling points in arable lands were contaminated nationwide according the first soil pollution survey in 2014). Given the urbanizing China with diverse and dynamical urbanization practices, we have opportunities to explore the dynamics of urbanization-driven environmental changes over time. In this study, we monitored a National Wetland Park since its opening to the public in the suburban area of Hangzhou, China in 2008 restored from thousands of fishponds and aquatic agricultural lands. By 2011, the area surrounding the park was rapidly developed with a dense road network and commercial communities. From 2008 to 2011, anthropogenic metal loadings (Cr, Cu, Pb, and Zn) in water and surface sediment were monitored in channels of the park in an attempt to test our above-mentioned hypothesis. This study tried to understand the temporal dynamics of urbanization-driven environmental changes, in confirmation with the nonlinear spatial changes discovered in the multi-city urbanization gradient using the space-for-time substitution approach [12]. Findings from this study might be of significance for urban environment management by identifying metal emission origins and strategizing energy structure and policy.

# 2. Materials and methods

# 2.1. Site description

The Xixi National Wetland Park was open to the public in 2008, restored from thousands of fishponds and aquatic agricultural lands. The park occupies 11.5 km² and entered the list of the Ramsar Site of International Importance in 2009. In 2014, the park received over 600,000 visits. The region surrounding the Park has rapidly urbanized since its opening. The park core wetland, approximately 4 km², was investigated in 2008 and 2011, surrounded by the Yanshanhe Channel (adjacent to urbanized area), Xinkaihe Channel (adjacent to urbanizing area), and two inner touring channels (Wuchanggang and Jiangcungang Channels) (Fig. 1). All these channels are connected and the water table remains relatively stable adjusted by water shutters. These channels in combination with the channels within the core wetland not for touring (thereafter, inner channels) consist of a gradient of urbanization influence. Sediments in the Yanshanhe channel were dredged once in 2009–2010

and the channel has been flushed for water quality improvement by a diversion work from the Qiantang River starting in late 2009 according to the park administration office. Changes of the Xixi Wetland Park and surrounding areas between 2008 and 2011 are shown in Fig. 2, cropped from the Google Earth®.

### 2.2. Sampling design

In total, 68 points were sampled for surface sediment using a sediment core sampler in July 2008 and July 2011 along the gradient of urbanization influence. Eleven points were set along the Yanshanhe Channel, ten points along the Xinkaihe Channel, eleven points along the Jiangcungang Channel, nine points along the Wuchanggang Channel, and twenty-seven points in the inner channels (Fig. 1). At each sampling point, surface sediment (0–20 cm) was collected into a polyethylene bag and transported back the laboratory in an ice cooler. The collected surface sediments were frozen and stored in a freezer over 7 days at  $-18\,^{\circ}$ C in the laboratory before freeze-drying using a lyophilizer. The dried surface sediment samples were ground to pass through nylon sieves (Mesh 10 for analyses of pH and electrical conductivity (EC) and Mesh 100 for analyses of metals) prior to chemical analyses.

### 2.3. Chemical analysis

pH and EC were measured in a sludge suspending sediment into deionized water at a ratio of 1:2.5 using a pH and EC meter (Accumet® Excel XL60, Fisher Scientific Inc, USA). Pseudo-total contents (thereafter shorten as total content) of Cr, Cu, Pb, and Zn in surface sediments were measured using an inductively coupled plasma-mass spectrometer (ICP-MS, 7500CX, Agilent, USA) after an acid (concentrated HNO<sub>3</sub>-HClO<sub>4</sub>) digestion [14]. Every digestion batch (50 heating positions) had 3 reagent blanks (with all reagents without sediment samples) and 3 tubes for quality assurance and quality control (with a standard reference material (GBW07317 stream sediment, certified by the National Research Center for Certified Reference Materials of China)). Recovery rates of metals in the standard reference material were 88%, 111%, 87%, and 104% for Cr, Cu, Pb, and Zn, respectively. Stable lead isotope ratios in the surface sediments were measured exactly following the procedure of Li et al. [14] using the NIST 981 (Common Pb Isotope) as the standard reference material (National Institute of Standards and Technology, Gaithersburg, MD, USA).

# 2.4. Specific hazard quotient (HQ)

The HQ of metal contamination was calculated by ratios of metal content in surface sediment to sediment quality guidelines (SQGs), such as the United States National Oceanic and Atmospheric Administration (NOAA)—Effects Range Low (ERL) and the Marine Sediment Quality Guidelines of China (GB 18668-2002)—Class I used in this study, multiplying with risk weights (W) (1.0 for Cr, Cu, and Zn; and 1.1 for Pb) according to Piva et al. [15]. The equation is provided as follows:

$$HQ = \frac{\sum_{i=1}^{N} \left(\frac{C_i}{SQC_i} \times W_i\right) \le 1}{N} + \sum_{j=1}^{M} \left(\frac{C_j}{SQC_j} \times W_j\right) > 1$$

where N and M are the number of metals with weighted ratios of  $\left(\frac{C}{SQG} \times W\right)$  respectively  $\leq 1$  or > 1, while i and j are indices from 1 to N and M, respectively. This equation only cumulatively counts the weighted ratios above 1 (contaminated) and the average of the weighted ratios less than 1 (not contaminated) for metals. The hazard risk classification according to the expert judgment by Piva et al. [15] is absent with HQ<0.7, negligible with HQ

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