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Distribution and speciation of metals (Cu, Zn, Cd, and Pb) in agricultural and non-agricultural soils near a stream upriver from the Pearl River, China

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ABSTRACT

The distribution and chemical speciation of typical metals (Cu, Zn, Cd and Pb) in agricultural and non-agricultural soils were investigated in the area of Nanpan River, upstream of the Pearl River. The investigated four metals showed higher concentrations in agricultural soils than in non-agricultural soils, and the site located in factory district contained metals much higher than the other sampling sites. These observations suggested that human activities, such as water irrigation, fertilizer and pesticide applications might have a major impact on the distribution of metals. Metal speciation analysis presented that Cu, Zn and Cd were dominated by the residual fraction, while Pb was dominated by the reducible fraction. Because of the low mobility of the metals in the investigated area, no remarkable difference could be observed between upstream and downstream separated by the factory site.

1. Introduction

The presence of metals in agricultural soils is of increasing concern due to their health risks to human and animal as well as their adverse effects to soil ecosystems (Mireles et al., 2004). However, the bioavailability and environmental behavior of metals in soil are not only related to their total concentrations, but to a large extent, determined by their chemical speciations (Fernández et al., 2000; Impellitteri et al., 2003; Sastre et al., 2004). Therefore, the total concentrations of metals in soil could not accurately reflect their toxicity and the trend to be absorbed and accumulated by organisms (Morel, 1997). Metals in soils could be recognized as several chemical forms: weak acid soluble fraction, oxidizable fraction, reducible fraction and residual fraction (Ure et al., 1993). The residual fraction of metals could not be taken up by organisms, while weak acid soluble fraction is fully bioavailable. The activity of reducible fraction and oxidizable fraction decrease successively. The metal fractions could directly influence their transfer and bioavailability in soils. The fraction distribution is related to metal properties, soil compositions and properties (Abollino et al., 2002; Qiao et al., 2003; Ying et al., 2003; Chen et al., 2008).

Pearl River is the third largest river in China, and Nanpan River is its upstream in Yunnan. Nanpan River derives from southern Maxiong Mountain in Qujin, Yunnan with the elevation of 2433 m. It is 677 km long with the catchment of 58,000 km^2, covering 15.2% of Yunnan province. Agricultural crops such as wheat, rice and vegetables are mainly grown in this area. Because of the importance of this catchment to the local area as well as to the downstream, the environmental assessment and pollutant behavior are of great concern for both scientific research and soil management. However, no research has been conducted on the status of metal speciation and behavior in this area. In addition, the comparison of metal species between agricultural and non-agricultural soils provides valuable information regarding tillage management and food safety issues. This line of study is lacking, specifically in Nanpan River region.

In this paper, the sequential extraction procedure (Ure et al., 1993; Rauret et al., 1999) modified by Bureau Communautaire de Référence (BCR) was applied to study the total concentration and speciation distribution of typical metals (Cu, Zn, Cd and Pb) in agricultural and non-agricultural soils in the upstream of Pearl River. The pollution of these four heavy metals in Yunnan province has attracted lots of research and public attention. The impact of agricultural activity on metal behavior will be the center of discussion. This study provides fundamental information for land management and environmental protection in Nanpan River area.

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2. Materials and methods

2.1. Soil collection and preparation

The sampling area is located at Nanpan River (25°24′∼25°46′N, 103°51′∼103°55′E), the upstream of Pearl River. Twelve sites were set along Nanpan River (A1–A12) as indicated in Fig. 1. All the sampling sites were located at agricultural area, except for A8 at a factory district. For each sample, surface soil of 3 random points with 50 m away from each other were collected and mixed as one sample. The soils were collected only with depth of 0–10 cm and about 1 kg soil particles were collected for each sample from November 12 to 13 in 2011. Non-agricultural soil particles were collected nearby agricultural soil after inquiring the local farmers. The collected soil samples were put into clean polyethylene sample bags, labeled and then stored in the lab. A small portion of the moist soil samples were separated for microbial biomass carbon (MBC) determination. The soils were dried at room temperature, grilled into pieces with a wood stick, and then filtered with a 2-mm nylon sieve. The gravels and plant residues were manually picked out. The soils were further grounded and filtered with a 0.149-mm nylon sieve for the analysis of soil pH, total organic carbon (TOC), metal total concentrations and their chemical fractions.

2.2. Sample analysis

2.2.1. Soil pH

Soil pH was measured in a 1:2.5 (w/v) ratio of soil to water by a pH meter (Leici, ZD-2). Soil samples (5 g) were introduced a beaker (25 mL), and DI water (12.5 mL) were added to the beaker, and stirred the suspension several times over a 30 min interval. Let the soil suspension allow most of the clay to settle out from the suspension. Immerse the combination electrode just below the suspension, read and record the pH.

2.2.2. Soil TOC and MBC

TOC was measured using an elemental analyzer (MicroCube, Elementar, Germany). MBC was measured with chloroform fumigation (Inubushi et al., 1991). Briefly, moist soil were ground and filtered through a 2 mm filter. Plant residues were manually excluded. Twenty grams of the soils were fumigated under dark vacuum at 25 °C for 24 h, and extracted using 0.5 mol L^{-1} K_2SO_4 with the ratio of 1:4 (soil:solution) for 30 min. The mixture was filtered (0.45 μm filter membrane) after centrifugation at 3000 r/min for 5 min. Dissolved organic carbon (DOC) in the filtered water was measured with a TOC Analyzer (Apollo 9000), and MBC was calculated according to the difference between the samples with and without fumigation.

2.2.3. Soil metals

Total Cu, Zn, Cd and Pb concentrations in soils were determined with HCl–HNO_3–$HClO_4$ digestion followed by ICP-OES (VISFA-MPX). Soil samples (0.5 g) were introduced in a Teflon crucible (50 mL) containing 15 mL of aqua regia. The solutions were heated on a hot plate at 140–160 °C for about 10 min. After that, 5 mL of $HClO_4$ were added to the crucible, and heated until complete evaporation of the solution. The residues were dissolved in 10 mL 5% HNO_3. The solutions were then transferred to volumetric polypropylene tubes (50 mL) and diluted to 50 mL. Quantification of metal concentrations in these solutions stands for total metal concentrations.

The metals in all the soil samples were also fractionated (weak acid soluble, oxidizable, reducible and residual fractions) according to BCR sequential extraction (Ure et al., 1993; Rauret et al., 1999) as briefly described below.

Step one: **Weak acid soluble fraction**. Soil samples (1 g) were introduced in a 50 mL polypropylene centrifuge tubes containing 40 mL of HOAc (0.11 mol L^{-1}) and then shaken for 16 h at room temperature. The solution and solid phase were separated by centrifugation at 3000 rpm for 20 min. Subsequently, the suspension was filtered through a 0.45 μm membrane filter. The supernatant

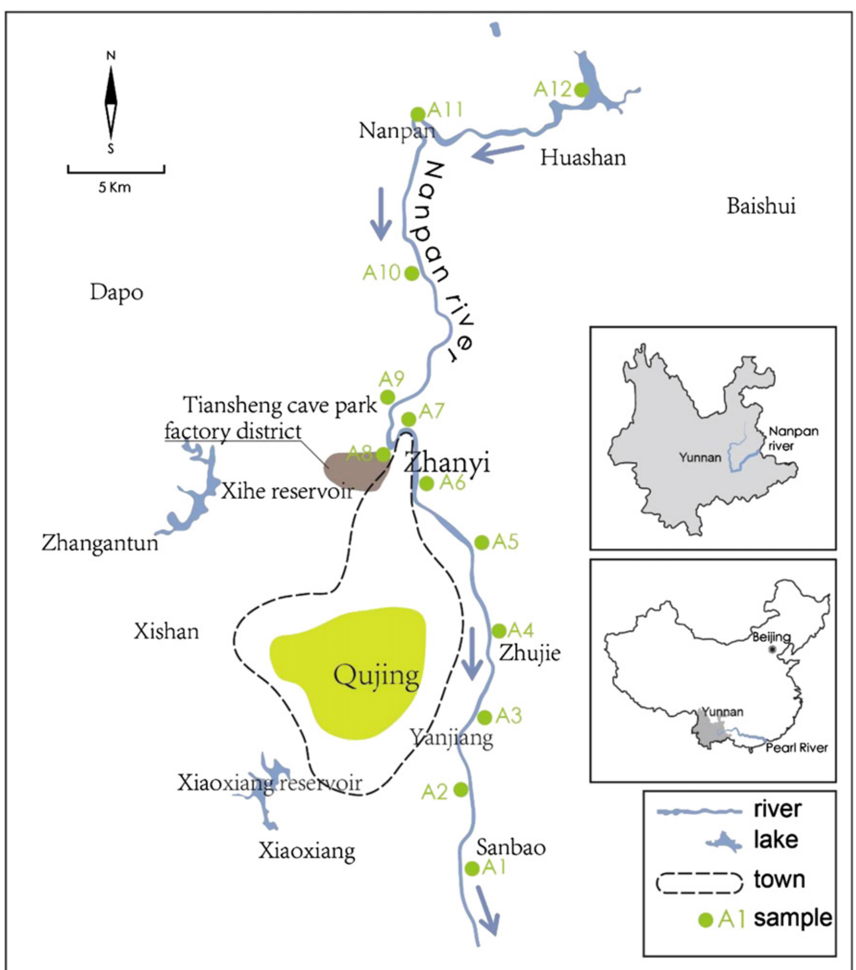

Fig. 1. Sampling area and site locations.