

Metal Distribution and Contamination Assessment in Drainage Ditch Water in the Main Rice/Vegetable Area of Sichuan Hilly Basin

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Abstract In order to assess the impact of four land use changes on metal concentrations in the hilly Sichuan Basin of China, 71 surface water samples were collected in July and November 2014. Samples from residential ditch water were found to have higher metal concentrations than those in other types of ditches, while the lowest occurred in barren land ditch water. However, the selected metals were below the Chinese surface water quality standards and WHO [\(2011](#page-5-0)). The pollution index of four determined land use types was also below the critical pollution index, suggesting there were low levels of pollution in Sichuan Basin. Arsenic was the most important pollutant of concern. Results indicate steps should be taken to control and reduce the risk of metals released from residential ditch water.

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Land use change and its effects on water quality continue to be highlighted across the globe. Accelerated water quality and capacity degradation of aquatic environments are among the greatest challenges facing water quality management (Sharpley et al. [1994](#page-5-0)). Anthropogenic activities and natural processes degrade surface waters and impair their use for drinking, industrial, agricultural, recreation or other purposes (Boesch [2002\)](#page-5-0).

Drainage ditches are integral parts of agricultural landscapes used to remove surface runoff and may act as major conduits for transporting pollutants from different types of land use to primary receiving surface waters (Moore et al. [2001](#page-5-0); Nguyen and Sukias [2002](#page-5-0)). Ditches, streams, wetlands, and rivers constitute the main inland water resources for domestic, industrial and irrigation purposes, and as such, it is imperative to prevent and control water pollution by having reliable information on water quality. Metals tend to be trapped in these water bodies and build up in sediment, which are potentially released to the water through sediment resuspension and reduction–oxidation reactions. These processes enhance the dissolved concentration of trace metals in water (Jones and Turki [1997](#page-5-0); Wright and Mason [1999\)](#page-5-0). Metals not only directly affect the physical and chemical properties of the water and its surrounding environment and hinder the supply of nutrients (Davis et al. [2003](#page-5-0)), but they also pose a threat to human health through absorption by the human body through food or air intake. Therefore, it is necessary to determine the sources of metal pollutants in water in order to provide a reference for environmental restoration and effective water management.

In intensively cultivated regions, hilly drainage ditches are severely affected by the input of pesticides and nutrients. These chemicals often enter ditches associated with soil particles as a result of erosion, caused by edge of field runoff from agricultural land. The hilly region has a moderate subtropical monsoon climate with favorable temperature and rainfall, making it an important production base for crops. Due to the fertile purple soils and favorable subtropical climate, the basin is one of the most densely populated agricultural regions in China, along with the largest distribution of drainage ditches. Hilly Sichuan drainage ditches flow into the Minjiang and Jialing rivers, which are the first–order tributaries of the Yangze River. Therefore, protection of ditch waters around the Minjiang and Jialing rivers is of great importance for safeguarding the water quality in the reservoir.

The present study aimed to evaluate the influence of different types of land use, i.e. rice field ditch (RFD), vegetable field ditch (VFD), barren land ditch 13 (BLD), and residential area ditch (RAD) on metal concentrations and to assess environmental risks. We hypothesized that ditch water could be affected by the types of land use, which would then lead to changes in the status of metal concentrations in water. This study will not only provide specific information on the effects of land use changes on metal distribution, but it will also give regionally—based relevant policy information on impacts of the Chinese national policy on land use change.

Materials and Methods

The location of the study area is the hilly area of the Sichuan Basin, where a dense net of drainage ditches exist. It covers an area of $105,000 \text{ km}^2$, with an altitude ranging between 250 and 850 m. It is the main farming area given its centralized population distribution. The hilly intensive farming area consists mostly of rice, vegetable, and wheat. There is no significant anthropogenic point source related to mining or industrial activities that could pollute the neighboring environment. Drainage ditches also receive domestic raw sewage and household waste from surrounding habitation and flow into the Minjiang and Jialing rivers. Sampling locations are shown in Fig. [1](#page-2-0). For this study, sampling locations were selected on the basis of different types of land use, including 42 from RFD, 11 from VFD, 10 from RAD and 8 from BLD. Samples were collected in June and November 2014 (Fig. [1](#page-2-0)).

Polythene bottles (500 mL), which had been cleaned by soaking in 10 % nitric acid overnight and rinsed with distilled water, were used as sample containers. At the sampling station, the containers were rinsed twice with

water to be sampled prior to collecting. Collected samples were then transported to the laboratory in an ice box and analyzed the next day. Water pH, electrical conductivity (EC), total dissolved solids (TDS), dissolved oxygen (DO), and temperature were recorded in situ using HACH electrodes. Water samples were filtered through a 0.45 µm Millipore membrane filter. Metal analyses were then carried out using inductively coupled plasma mass spectrometry (ICP-MS). National Standard Reference Material was used to check the precision and reliability of the analysis. Analytical precision was ± 5 % for all metals. Statistical analysis was performed using SPSS software (version 16.0 for Windows). Pearson's correlation analysis was used to identify the relationship among element pairs.

Heavy metal pollution index (HPI) (Mohan et al. [1996\)](#page-5-0), metal index (MI) (Tamasi and Cini [2004\)](#page-5-0), and degree of contamination (mCd) (Backman et al. [1997\)](#page-5-0) are useful and informative measures to evaluate drinking and agriculture water quality and have been extensively used for assessing individual and overall water quality with regard to metals. HPI, MI, and mCd were calculated using the following equation:

$$
HPI = \frac{\sum_{i=0}^{n} WiQi}{\sum_{i=0}^{n} Wi}
$$
 (1)

where Qi and Wi are the sub-index and unit weight of the ith parameter, respectively, and n is the number of parameters considered. The sub-index (Qi) is calculated by:

$$
Qi = \sum_{i=0}^{n} \frac{(Mi(-)Ii}{Si - Li} \times 100
$$
\n⁽²⁾

where M_i , I_i and S_i are the monitored metal, ideal, and standard values of the ith parameter, respectively. The sign (-) indicates numerical difference of the two values, ignoring the algebraic sign. Generally, pollution indices are estimated for any specific use of the water. The proposed index is intended for the purpose of water quality. The critical pollution index value of water quality is 100.

$$
MI = \sum_{i=1}^{n} \text{Ci}/\text{Hmac}
$$
 (3)

where Ci and H_{mac} are the monitored value and maximum admissible concentration (MAC) of the ith parameter, respectively.

$$
mCd = \sum_{i=1}^{n} Cf,
$$
\n⁽⁴⁾

$$
Cf = \frac{CAi}{CNi} - 1\tag{5}
$$

where; Cf, CAi, and CNi represent contamination factor, analytical value, and upper permissible concentration of

Fig. 1 The location of study area and distribution of sampling points in the hilly region of Sichuan, China

Table 1 Mean \pm SD metal concentrations (μ g L⁻¹) in ditch waters for four land use types

Cr	Cu	Zn	As	Cd	P _b
4.71 ± 0.49	1.71 ± 0.15	1.68 ± 0.02	5.59 ± 2.21	0.023 ± 0.01	0.15 ± 0.02
5.28 ± 0.58	1.95 ± 0.24	1.91 ± 0.16	7.23 ± 2.41	0.025 ± 0.01	0.18 ± 0.12
4.92 ± 1.07	1.72 ± 0.42	1.37 ± 0.26	3.51 ± 1.54	0.021 ± 0.01	0.13 ± 0.03
5.49 ± 0.56	2.71 ± 1.2	2.28 ± 0.5	18.54 ± 6.21	0.034 ± 0.11	0.19 ± 0.16

the I th component, respectively, and N denotes the 'normative value'. Here C_{Ni} is taken as MAC.

Results and Discussion

Mean concentration of metals in ditch waters for the four land uses are shown in Table 1. In general, As had the highest mean value, followed by Cr, Cu, Zn, Pb and Cd. The highest mean concentrations appeared in RAD and the lowest values of Zn, As, Cd and Pb were observed in BLD. With respect to Cr and Cu, the lowest values were found in RFD. Results indicate that land use change can have a strong impact on the distribution of these metals (Ribolzi et al. [2011\)](#page-5-0). Our results are consistent with other studies which have indicated residential land use is a main cause of substantial modification of chemical water properties (Bahar et al. [2008;](#page-5-0) Gasim et al. [2006](#page-5-0)). Mean concentrations Zn, Cr, Pb, Cu, As, and Cd in the vegetable field were higher than the rice field, which can be attributed to the high usage of fertilizers by Chinese farmers in vegetable production systems compared to grain systems. Long-term and excessive fertilization and organic manure use can easily run off into nearby ditch waters by rain, increasing the metal pollution of water bodies (Li et al. [2009\)](#page-5-0).

In the current study, mean values of six metals (As, Zn, Cu, Cr, Pb, and Cd) did not exceed the Chinese permissible limit of surface water quality standards [(GB 3838-2002) and WHO [\(2011](#page-5-0))] (Table 1 and 2). This analysis indicated the drainage ditch water of the hilly area of the Sichuan Basin contains permissible concentrations of metals which meet the urban living water standards (Table 2).

Correlation analysis was performed to establish the extent of relationships among metals in ditch waters (Table 3). Most elements in surface waters showed strong and significant positive correlations $(P < 0.01)$ among themselves, except Cr which did not correlate with any metal in ditch waters, suggesting perhaps different water sources from other elements. The significant relationship between all metals except Cr (and slightly As) indicates they have a common source of input, likely from natural sources. High correlations between metals may reflect similar levels of contamination and/or release from the

Table 2 Surface water quality standards of China (GB 3838-2002) and the Drinking Water Guidelines from World Health Organization (WHO [2011\)](#page-5-0) (μ g L⁻¹)

Metals	Chinese surface water (GB 3838-2002)					Drinking water	
		П	Ш	IV	V	China	WHO
$Cr \leq$	10	50	50	50	100	50	50
Cu<	10	1000	1000	1000	1000	1000	2000
Zn<	50	1000	1000	2000	2000	1000	
$As \leq$	50	50	50	100	100	50	10
Cd<	1	5	5	5	10	5	3
Pb<	10	10	50	50	100	10	10

Class I main source of water is the state nature reserve. Class II mainly suitable for centralized drinking surface water source protection areas, rare aquatic habitats, fish and shrimp spawn larvae of feeding grounds, etc. Class III mainly suitable for the second centralized drinking surface water source protection areas, fish and shrimp wintering grounds, migration channels, aquaculture, fishing waters and swimming areas, and other areas. Class IV is for general industrial water zone and indirect contact with non-human recreational water area. Class V is applied to agricultural water district and general landscape requirements

Table 3 Correlation coefficients of the concentrations of metals in the ditch surface water of the Sichuan Basin, China

	Cr	Cu	Zn	As	C _d	Pb
Cr						
Cu	0.161					
Zn	0.041	$0.476^{\rm a}$				
As	0.211	$0.531^{\rm a}$	0.221			
C _d	0.091	0.389^{a}	$0.404^{\rm a}$	0.187		
Pb	0.032	$0.513^{\rm a}$	$0.470^{\rm a}$	0.243^b	$0.457^{\rm a}$	

^a Correlation is significant at the 0.01 level (2-tailed)

 b Correlation is significant at the 0.05 level (2-tailed)</sup>

same sources of pollution, mutual dependence and identical behavior during their transport (Jiang et al. [2014\)](#page-5-0).

The HPI is an effective tool to characterize the composite influence of metals on the overall water quality (Sheykhi and Moore [2012](#page-5-0)). In general, HPI value for the basin ranged from 1.71 to 12.41 (mean 4.27), which is below the critical HPI value of 100. The HPI was also calculated in the four types of land use in order to compare the pollution load and evaluate

Fig. 2 Metal pollution index (HPI) (a) and metal index (MI) (a and b) in the four types of ditch water

the ditch water quality of the selected land use (Fig. 2a). HPI values in RAD were much higher than those in RFD, VFD, and BLD, whereas for metal index (MI) the order was $RAD > BLD > RFD > CD$ (Fig. 2ab). This is due to different water sources related to the various land uses. HPI consists of three classes: HPI < 15 (class 1, low degree of pollution), $15\lt HPI \lt 30$ (class 2, medium degree of pollution) and $HPI > 30$ (class 3, high degree of pollution). Thus, taking into account the categories of HPI, all the stations fall under the low class, indicating that ditch water in the basin is not critically polluted with respect to these metals. Metal index (MI) was also used as a tool to assess the pollution comprehensiveness in ditch waters. According to Bakan et al. ([2010\)](#page-5-0), MI value > 1 is a threshold of warning. MI values for the hilly Sichuan Basin ditch waters revealed a MI value below 1(Fig. 2ab). In order to estimate the extent of metal pollution, the degree of contamination (mCd) was applied. mCd is classified into three categories: low $(mCd < 1)$; medium $(mCd = 1–3)$, and high $(mCd > 3)$.The values mCd (data not shown) in all ditch water samples were observed to be negative for these metals, suggesting that the ditch water was not polluted by these metals.

Concentrations of Pb, Zn, and Cu generally had similar spatial distributions, with the highest concentrations appearing in the southern part of the study area. The zones with higher concentrations of Cr were confined to the northwestern and southeastern parts of the study area. The highest concentrations of As and Cd were in the northcentral and northwestern parts of the basin. Hilly areas in the Sichuan Basin play an important role in supplying food. Several studies have demonstrated that Cd and As are closely related to the intensive use of pesticides and chemical fertilizers and are usually considered as marker elements of agricultural activities (Rodríguez Martín et al. [2007\)](#page-5-0). In the Sichuan Basin, areas with agricultural land use are intensively distributed along the southwestern part of the study location. The hilly area in the Sichuan Basin is an important agricultural area in the southwest China, where the high usage of fertilizers, manures and other organic amendments exist. Consequently, Cd and As may mainly originate from agricultural sources.

A large number of studies have confirmed that rapid urbanization along with the increasing population, volume of domestic sewage, and cropping, lead to land use changes and result in water body degradation (Vander Laan et al. [2013](#page-5-0); Martinuzzi et al. [2014](#page-5-0)). In this study, metal loadings in ditch waters vary from one land use type to another. Significant accumulation of As was found in water of RAD. This result is consistent with earlier observations by Chatterjee and Banerjee [\(1999](#page-5-0)) who also observed that As was higher than other metals in residential areas. In this study, metals associated with vegetable land may arise from the use of animal manure, fertilizers and sewage sludge applications, mainly for cultivation of vegetables (Gupta and Charles [1999](#page-5-0); Antonious et al. [2008](#page-5-0)). Bigdeli and Seilsepour [\(2008](#page-5-0)) found that metals such as Cd, Cu, Pb, Cr, and As are important environmental pollutants, particularly in areas irrigated with wastewater. Studies have estimated that more than 20 million hectares in 50 countries are currently irrigated with irrigated by raw sewage, generally for cultivation of leafy vegetables (Arora et al. [2008](#page-5-0)). Concentrations of As in VFD are consistent with findings by Zhang et al. (2004) (2004) who detected 8.0 μ g As L^{-1} in ditch waters within vegetable farms in Florida. Occurrence of metals in RFD was probably related with soil metal accumulation in adjacent fields (Reddy et al. [2013](#page-5-0)). Phosphate fertilizers and other agrochemicals were the main sources of Cd and As in VFD. Franco-Uria et al. [\(2009](#page-5-0)) also reported Cd was found mainly in antropic wastes such as sewage sludge and phosphatic fertilizers. Yang et al. (2005) (2005) (2005) detected 0.009–2.58 mg kg⁻¹ of Cd in fertilizers. Considerable runoff loss of these metals from VFD can occur at high concentrations during wet conditions with significant rainfall, as the soil in this region is

sensitive to erosion (Zhang et al. 2004). Though the ditch water quality in the hilly region was not found to be critically contaminated with respect to metals, water was contaminated by As for some RAD stations. Therefore, careful measures should be taken in order to control and minimize the risk of metal release from RAD on surrounding natural resources.

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