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Variation of Zn content in soils under different land-use types in the Hetao oasis, Inner Mongolia of China

ZHU Yangchun*, ZHAO Xueyong, LIAN Jie, CHEN Min

Naiman Desertification Research Station/Urat Desert-grassland Research Station, Cold and Arid Regions Environmental and Engineering Research Institute, Chinese Academy of Sciences, Lanzhou 730000, China

Abstract: Understanding the status and distribution of the micronutrient Zn in soils is important for managing plant growth and preventing soil pollution for agricultural irrigation systems in arid and semi-arid regions. In this study, a total of 195 soil samples from five soil layers (0–20, 20–40, 40–60, 60–80 and 80–100 cm) in the three land-use types (wasteland, forestland and cropland) after long-term agricultural fertilization and irrigation with Yellow River water were collected in the middle of the Hetao oasis, i.e. the Yongji irrigation sub-oasis. We analyzed the vertical and spatial distributions of Zn content and its relationship with soil properties to determine whether differences of Zn content existed in the soil profiles. The results revealed that the mean content of Zn was 107 mg/kg, 1.9 times higher than the background value (55.7 mg/kg) of the Hetao oasis and much lower than the secondary standard value (300 mg/kg) of the Chinese Environmental Quality Standard for Soils when pH>7.5. Soil Zn contents were not significantly different and the coefficients of variation of Zn contents were less than 50% in the five soil layers. Soil Zn content was similar from southern to northern parts but increased from western to eastern parts in the sub-oasis. Soil Zn contents did not differ significantly among the three land-use types, but soil total nitrogen (TN) contents were significantly higher in the agriculturally managed forestland and cropland than in the wasteland ($P<0.05$). Zn was significantly and positively correlated with TN ($F=36.6$, $P<0.001$). The use of fertilizers may increase the content of Zn in soils, but flooding irrigation may minimize the differences in the spatial distribution of soil Zn content in the whole sub-oasis. This research is of important value for soil pollution control and sustainable land use management in arid and semi-arid regions.

Keywords: fertilizer; land-use type; spatial distribution; soil profile; soil property

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Zinc (Zn) is a widespread traceable metal in agricultural soil systems and an essential nutrient for plant growth (Struckhoff et al., 2013). As a nutrient element in soils, if Zn content exceeds its optimum value, the elevated Zn may affect soil microbial activity, resulting in long-term risks on soil systems (Jacquat et al., 2009), and thus threatening human health through the water supply and food chain (Qu et al., 2013). However, some soils are regarded as potentially Zn deficiency all over the world, generally in soils with high pH calcareous or low organic matter (Behera et al., 2011), particularly in arid and semi-arid regions. Growing plants in Zn-deficient soils causes

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*Corresponding author: ZHU Yangchun (E-mail: zhuyangchun1008@sina.com)

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severe depression in shoot growth and results in the occurrence of necrotic spots on the younger leaves (Köleli et al., 2004). Zn deficiency in animal and human bodies results in parakeratosis, diarrhea and weight loss, and retards the skeletal growth (Lallès et al., 2007; Kwun et al., 2010). Therefore, the level of Zn in agricultural soils is directly associated with agricultural production and health risks.

Generally, land-use types and soil physical-chemical properties are the dominant factors affecting the residue levels of Zn in soils (Xu et al., 2013). Soil organic matter, pH and temperature are important parameters affecting the solubility and mobility of Zn in soils (Antoniadis et al., 2008; Fernández-Calviño et al., 2012; White et al., 2012). Zn adsorption onto soil constituents depends on soil pH change, and Zn uptake by crop is enchanced by reduced soil pH (Antoniadis et al., 2008). In the soil profile, Zn is assumed to move from the top layer to the deeper layer, attaching to fine grain clay or organic matter particles (Wijnhoven et al., 2006).

The Hetao irrigation oasis (40°19′–41°18′N, 106°20′–109°19′E) is located in the west part of Inner Mongolia. It is bounded by the Yellow River to the south, by the Yinshan Mountains to the north and by the Ulan Buh Desert to the west. The oasis has been irrigated by the Yellow River through artificial irrigation systems for more than 2,000 years, which is considered as one of the three largest and important agricultural production bases of commodity grains and oil in China. Due to long-term irrigation, low precipitation and high evaporation in this arid and semi-arid region, soil salinization has become a great concern and seriously threatens crop production in the oasis (Yu et al., 2010; Guo et al., 2013; He et al., 2013). The oasis is a representative area affected by endemic diseases of fluoride (F) and arsenic (As) (He et al., 2013). Some previous studies have also demonstrated the impacts, distribution and sources of F and As in groundwater and soils in this area (Neidhardt et al., 2012; Shan et al., 2013). Furthermore, frequent irrigation and agricultural activities increase the metal contents in soils, such as the hazardous metals (Cd (cadmium), As (arsenic) and Pb (lead)) and micronutrient elements (Zn and Cu (copper)), and lead to significant differences of metals in the soil profiles (Klay et al., 2010; Parelho et al., 2014; Zhao et al., 2014). However, few studies were conducted on the nutritional trace metals in the agricultural soils in the Hetao irrigation oasis from the aspect of Zn changes. The purpose of this study was to determine the content of Zn in soils and analyze the distribution of Zn content in relation to other soil factors under different land-use types after long-term management in this oasis.

1 Study area and methods

1.1 Study area

The Yongji irrigation sub-oasis (40º36′–41º13′N, 107º13′–107º42′E) lies in the center part and is the typical one of the five sub-oases (Yigan, Jiefangzha, Yongji, Yichang and Wulate irrigation sub-oases) in the Hetao irrigation oasis, Inner Mongolia, China. It has one main sub-canal (the Yongji Canal) and two main sub-drainages (the Fourth Drainage and the Fifth Drainage) in its eastern and western sides (Fig. 1). The sub-oasis is irrigated by the Yellow River through the sub-canal from the Main Canal and drains into the two sub-drainages to the Main Drainage at last. The area is characterized by a cold and arid desert climate with low annual precipitation of 100–270 mm, high annual evaporation of 1,300–2,400 mm, and an annual average air temperature of 3.9°C–7.6°C. Soil type in this area is anthropogenic-alluvial soil, comprising silty sand, fine sand and muddy clay. Wasteland, forestland and cropland are the major land-use types, and forestland and cropland are agriculturally managed in the sub-oasis. Cropland is mainly cultivated with wheat, maize and sunflower for centuries, and forestland belongs to the economic forestland and is usually planted with *Populus bolleana* and *Salix* sp. for 1–10 years. Wasteland is the abandoned saline-alkali land, normally abandoned for heavy salinization and poor drainage for more than 10 years. The main fertilizers in the forestland and cropland are nitrogen (N) fertilizer and animal manure, while no fertilizer is applied to the wasteland. According to the field survey, the annual consumption of chemical fertilizers for cropland and forestland was 1,500–3,000 kg/hm^2, and the total consumption of chemical fertilizers was 5.06×10^7 kg in 2013 in the sub-oasis (Inner Mongolia Bureau of Statistics, 2014). Soils in the investigated area (including wasteland) are irrigated with water from the Yellow River using the flooding irrigation method, and the irrigation period includes spring, summer and autumn.

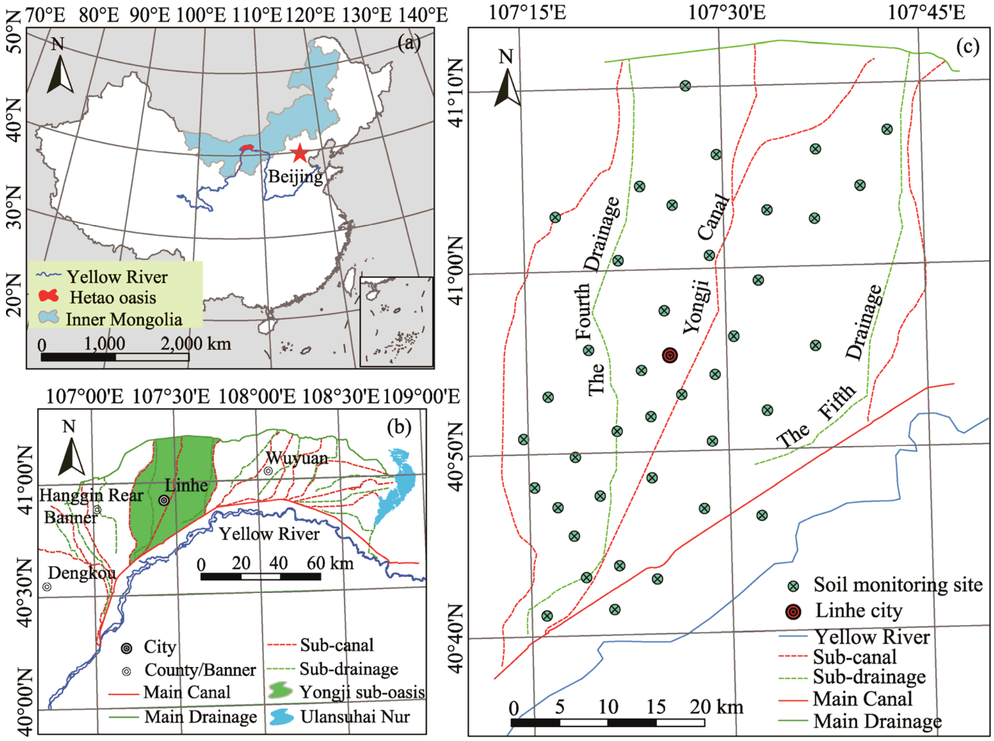

Fig. 1 Map of the Hetao irrigation oasis (a, b) and soil sampling sites in the Yongji irrigation sub-oasis (c)

1.2 Soil sampling and chemical analysis

Soil samples were collected from 39 different sampling sites (0.3–0.5 hm^2 for each site), with three replicates from each layer of 0–20, 20–40, 40–60, 60–80 and 80–100 cm. Soil samples were collected after harvesting for maize and sunflower lands and at seeding for wheat land. The three replicates from each layer were mixed into one sample. Thus, a total of 195 uniformly distributed samples were collected using a wood spade and stainless steel auger from the five soil layers of the three different land-use types in early May 2013 (Fig. 1). During the sampling period, the related information, such as land-use history, vegetation and soil types were recorded in detail for each sampling site. Soil samples were stored separately in polyethylene bags to avoid contamination and transported to the laboratory immediately. Soil moisture of the fresh soil samples was directly measured with the oven-drying method at 105°C–110°C for 10 h. Other samples were air-dried at room temperature, passed through 2- and 0.149-mm sieves, and stored at ambient temperature before analysis.

Soil pH was measured in H_2O and 0.1 M KCl with a combined glass electrode using a 1:5 soil:water suspension. Total Zn was measured with a flame atomic absorption spectrometer (AAS) and digested with $HCl\text{-}HF\text{-}HNO_3\text{-}HClO_4$, and the limit of detection was 0.5 mg/kg. Soil total nitrogen (TN) was measured using the micro-Kjeldahl method, and total organic carbon (TOC) was analyzed using a Vario Macro Cube (Elementar Analysensysteme GmbH, Hanau, Germany).

1.3 Statistical analyses

First, we tested the data of soil Zn, pH, moisture, TOC and TN with the Kolmogorov-Smirnov normality test (K-S test) to analyze whether the data followed a normal distribution. We also applied the frequency tables and the ordinary Kriging method to analyze the distribution of Zn content in soils, and the least-significant difference (LSD) to determine whether differences in Zn contents existed among the five soil layers. Then, we analyzed the differences in the indicators of soil Zn, pH, moisture, TOC and TN among the three land-use types. Correlation and regression analyses were applied to identify the relationship between soil Zn and soil properties. The K-S test, frequency tables, LSD, correlation and regression analyses were performed with the SPSS 19.0 software for Windows, and the ordinary Kriging method was performed with ArcGIS 9.3.

2 Results

2.1 Soil Zn content

After the outliers were eliminated, Zn contents of all soil samples did not pass the K-S test; however, it followed a lognormal distribution after data transformation. Soil Zn content ranged from 58.4 to 270 mg/kg and the mean value was 107 mg/kg (Fig. 2). In the Yongji sub-oasis, Zn content was in the range of 75–115 mg/kg in most soil samples (approximately 65% of the total), while it was above 120 mg/kg in 23.6% of the total soil samples (Fig. 2).

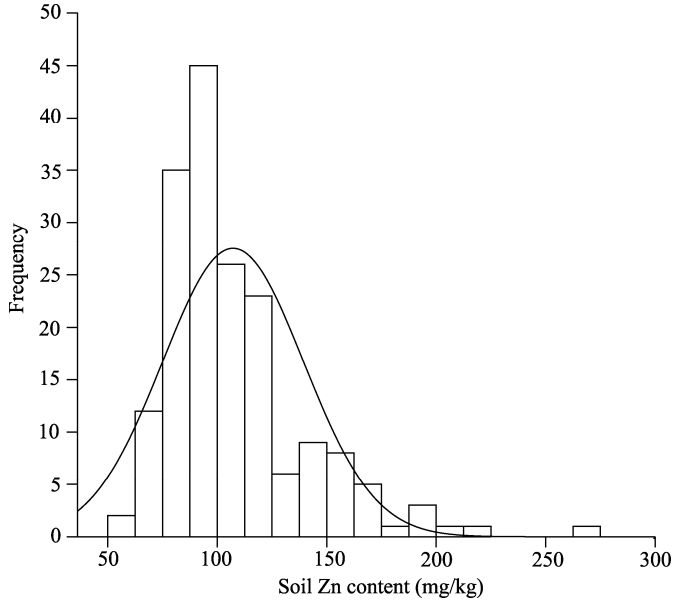

Fig. 2 Frequency distribution of Zn content for 178 soil samples

2.2 Vertical distribution of Zn content in soil profiles

There was no significant difference in Zn contents among the five soil layers (F=1.54, P>0.05). The mean value of Zn in the five soil layers varied from 105 to 112 mg/kg (P>0.05; Table 1). In this study, the CVs (coefficients of variation; %) of Zn contents were less than 50% for all five soil layers, suggesting that the fluctuation of Zn was moderate in the soil profiles. The CVs of Zn content in the soil profile of 0–100 cm depths decreased in the order of 20–40, 60–80, 80–100, 40–60 and 0–20 cm.

2.3 Spatial distribution of soil Zn content in the irrigation sub-oasis

The spatial distribution of Zn content in the topsoil layer (0–20 cm) in the Yongji irrigation sub-oasis is shown in Fig. 3. Higher contents of soil Zn (above 120 mg/kg) were only found in several sampling sites near the Main Canal. In addition, the sites with lower Zn content (below 100 mg/kg) were generally found around the Fourth Drainage. Soil Zn content from southern to northern sections of the sub-oasis exhibited the same distribution along the Yongji Canal while it showed an increasing trend from western to eastern sections along the Main Canal.

2.4 Characteristics of soil Zn content in different land-use types

The mean levels of Zn in soils of wasteland, forestland and cropland were 106, 109 and 107 mg/kg, respectively (Table 2). Soil Zn contents did not differ significantly among the three land-use types (F=1.13, P>0.05).

Table 1 Zn content in the five soil layers

Soil layer (cm)	*n*	Zn content (mg/kg)			SD	CV (%)
		Mean	Maximum	Minimum		
0–20	36	107^{a}	199	72.2	25.6	23.8
20–40	36	112^{a}	270	68.3	42.5	37.8
40–60	35	105^{a}	174	59.8	27.3	26.1
60–80	36	107^{a}	213	62.9	33.1	31.1
80–100	35	105^{a}	198	58.4	31.1	29.6

Note: SD, standard deviation; CV, coefficient of variation. The same lowercase letters indicate the differences of Zn content between soil layers are not significantly different at the P<0.05 level. *n* is the number of soil samples.

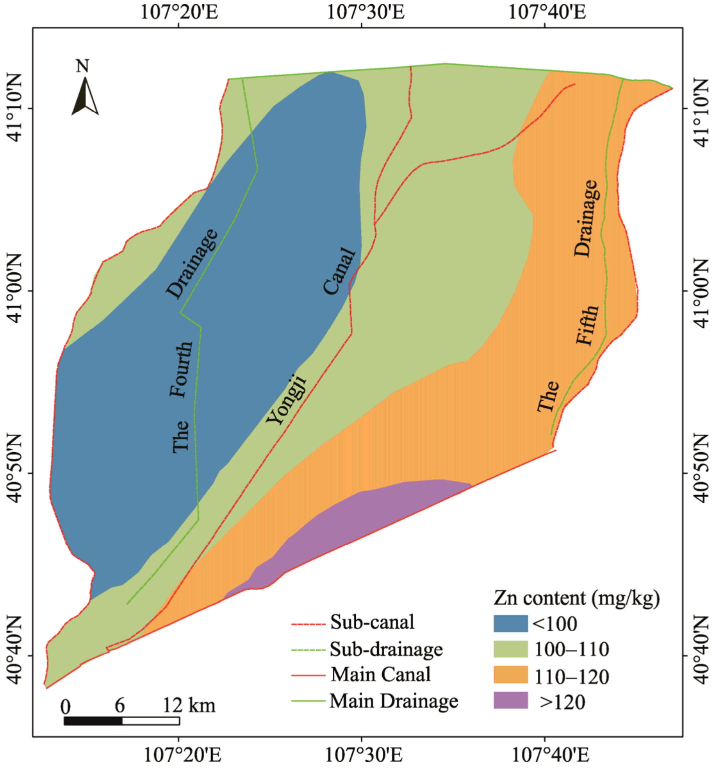

Fig. 3 Spatial distribution of Zn content in the surface soil layer (0–20 cm) in the Yongji irrigation sub-oasis

Table 2 Soil Zn, pH, moisture, TOC and TN in the three land-use types

Land-use type	*n*	Zn (mg/kg)	pH	Moisture (%)	TOC (%)	TN (g/kg)
Wasteland	50	106^{a}	9.38^{a}	19.6^{a}	0.52^{a}	0.367^{a}
Forestland	45	109^{a}	8.95^{b}	16.9^{b}	0.74^{b}	0.566^{b}
Cropland	83	107^{a}	9.08^{c}	17.0^{b}	0.69^{b}	0.523^{b}

Note: TOC, total organic carbon; TN, total nitrogen. The same lowercase letters indicate that the differences between parameters are not significantly different at the P<0.05 level among the three land-use types. *n* is the number of soil samples.

Soil pH, moisture, TN and TOC in all soil samples passed the K-S test (P<0.05) and were significantly different among the three land-use types (F_{pH}=15.1, P<0.001; $F_{\text{soil moisture}}$=3.62,

$P<0.05$; $F_{TOC}=10.7$, $P<0.001$; $F_{TN}=13.9$, $P<0.001$; Table 2). The value of soil pH in the wasteland (9.38) was higher than those in the forestland (8.95) and cropland (9.08; $P<0.05$).

Soil TOC content varied from 0.17% to 1.28%, with the mean value of 0.66%. Soil moisture was highest in the forestland with the value of 0.74%, statistically higher than that in the wasteland (0.52%; $P<0.05$). The average soil TN content was 0.490 g/kg in the whole study area, and the values for wasteland, forestland and cropland were 0.367, 0.566 and 0.523 g/kg, respectively. Soil TOC and TN contents in the wasteland were both significantly lower than those in the forestland and cropland, and there was no significant difference in soil moisture, TOC and TN between forestland and cropland ($P>0.05$).

2.5 Correlation between soil Zn and soil properties

The correlation coefficients (Spearman) among soil Zn, pH, moisture, TOC and TN are shown in Table 3. Soil Zn only showed a significant positive relationship with TN ($r=0.390$, $P<0.001$) and the regression relationship between them is shown in Fig. 4. Soil pH was significantly negatively correlated with TN ($r=-0.238$, $P<0.01$) and significantly positively correlated with soil moisture ($r=0.270$, $P<0.001$). Moreover, the correlation between soil TN and moisture was significantly negative ($r=-0.231$, $P<0.01$), and the relationships between soil TOC and other soil parameters were weak ($P>0.05$).

Table 3 Pearson's correlation coefficients for Zn, pH, TOC, TN and moisture in soils

	Zn	pH	TOC	TN	Moisture
Zn	1.000				
pH	0.062	1.000			
TOC	–0.038	0.076	1.000		
TN	0.390^{***}	-0.238^{**}	–0.130	1.000	
Moisture	–0.106	0.270^{***}	0.066	-0.231^{**}	1.000

Note: ** and *** indicate significant difference at the $P<0.01$ and $P<0.001$ levels, respectively.

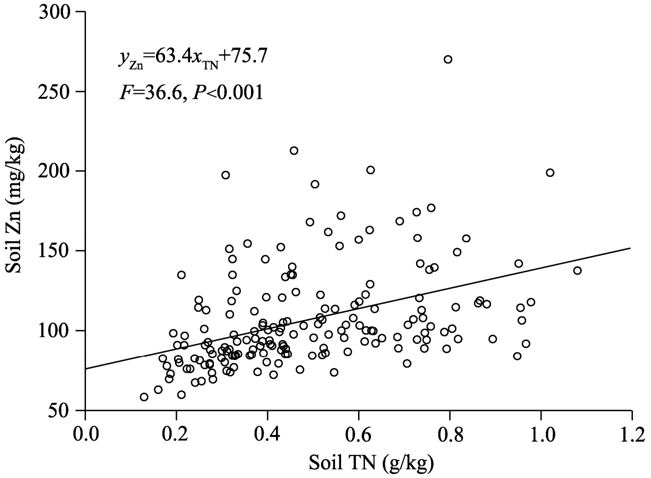

Fig. 4 Regression relationship of soil Zn and TN (total nitrogen)

3 Discussion

3.1 Vertical and spatial distributions of soil Zn content in the sub-oasis

Fernández-Calviño et al. (2012) suggested that the total Zn content in natural soils in average ranges from 40 to 120 mg/kg and it mainly depends on the lithological characteristics. In this study, Zn content exceeded 120 mg/kg in approximately 23.6% of the total soil samples, while it ranged from 75 to 115 mg/kg in most soil samples (65%). Zn contents of all soil samples in our study area were higher than the background value in the Hetao oasis (Wang et al., 2007), and the mean value of soil Zn was 1.9 times the background value, suggesting an anthropogenic source compared with the background value. Moreover, the mean value was much lower than the secondary standard value (300 mg/kg) of the Chinese Environmental Quality Standard for Soils (GB 15618-1995) when $pH>7.5$ (State Environmental Protection Administration of China, 1995). Observing the distribution of Zn content in the soil profiles, both the peak value of Zn content and the highest CV value appeared in the 20–40 cm soil layer, indicating that human activity is the main factor influencing Zn accumulation in this soil layer. Generally speaking, human inputs (the addition of commercial fertilizers, liming materials, manures and so on) into the agricultural systems resulting in the accumulation of Zn are normally found in the topsoil layer of 0–20 cm (Bourennane et al., 2010; Fernández-Calviño et al., 2012). Researchers have found that temperature changes can significantly influence the Zn content in soil profiles, for example, the freezing-thawing process could result in the redistribution of elements in the soil profile, which includes the movement of water and heat, phase change and salt accumulation (White et al., 2012). The soil in the Hetao irrigation oasis belongs to the typical of seasonal frozen soil for approximately six months (Yu et al., 2010). The frozen soil depth in the oasis is approximately 80–130 cm, freezing beginning in the middle of November and thawing steadily in the middle of March next year (Li et al., 2012). The stored soil water is from the last autumn irrigation period at the time of soil freezing, and it affects the transfer of heat and the redistribution of water in the soil profiles during the freezing/thawing period in the Hetao irrigation oasis (Li et al., 2013). This water and heat changes may influence the redistribution of Zn along the soil profiles and cause the accumulation of Zn under surface soils. More research is needed on the impact of alternating freezing and thawing on soil Zn.

The spatial distribution of Zn content in the surface soils demonstrated that the higher contents (above 120 mg/kg) were found near the Main Canal, while the lower contents (below 100 mg/kg) were generally found around the drainage area. Along the Yongji Canal, Zn content in the topsoil layer from southern to northern parts of the sub-oasis was similar but it increased from western to eastern parts along the Main Canal. The mechanism for such a distribution pattern was probably driven by the irrigation with water from the Yellow River through the Main Canal via the Yongji Canal into the drainages. The high content of heavy metal in the water was delivered into the mainstream of the Yellow River by the highly polluted tributaries from the increased discharge of agricultural and industrial waste and sewage and the erosion of the Loess Plateau into its upper reaches (Bi et al., 2014). Zn content in the water was approximately 81.07 mg/m^3 in the upper reaches of the Yellow River in the Inner-Mongolia section (Zhang et al., 2014). Furthermore, the Yellow River is famous for its high sediment load, and 99% heavy metals are absorbed by fine-grained suspensions in the sediments (Fan et al., 2013; Bi et al., 2014). The annual suspended sediment content in the Inner-Mongolia section of the Yellow River was reported to be 4.33×10^6 mg/m^3 during the period of 1950–2009 (Fan et al., 2013). Therefore, irrigation with water from the Yellow River caused the Zn accumulation, and it might be the dominant driving factor affecting the spatial distribution of Zn in soils along the irrigation canal in the sub-oasis.

3.2 Correlation between soil Zn and soil properties

Long-term land-use changes alter the soil physical-chemical properties (soil organic matter content, nitrogen content, pH and clay content) and the biochemistry of element cycling (Citeau et al., 2003), affecting the availability of Zn in several ways (Singh et al., 2006; Behera et al., 2011). In our study, after long-term land-use changes, soil pH significantly differed among the three land-use types ($F_{pH}=15.1$, $P<0.001$; Table 2). The highest pH value was measured in the wasteland, and the lowest was in the forestland ($P<0.05$). There may be two possible reasons. On the one hand, in the wasteland, the vegetation cover is lower (less than 5%), soil microbial activity is weaker and evaporation is stronger, leading to salt accumulation in the surface soil layer. On the other hand, in the forestland, leaf litter decomposition released some organic acid into the soils and reduced the soil pH (Dai et al., 2009). Meanwhile, *Populus bolleana* absorbed much more alkali and alkaline earth metals (e.g. Ca^{2+}, Mg^{2+} and K^+), which reduced the pH values of forestland (Brady and Weil, 2002). Moreover, the acidifying effect on soils is caused by the addition of fertilizers on the cropland and forestland. As a consequence of fertilizer application on soils, soil pH was significantly decreased because of H^+ release during root uptake and nitrification to NO_3^--N (Johnson et al., 2013). The significant negative correlation between soil pH and TN ($r = -0.238$, $P<0.01$) in our study also indicated that the lower soil pH values ($P<0.05$) in the fertilized soils (forestland and cropland) might be due to N addition. Soil pH is considered as the most significant factor controlling the absorption and transformation of heavy metals in soils, and it has strong effects on solubility and speciation of heavy metals and then influences the contents of total metals in soils (Huang et al., 2014). However, the correlation between soil Zn and pH was weak ($P>0.05$) in this study, thus soil pH may indirectly influence on soil Zn through TN.

In this study, soil TN was significantly higher in the agriculturally managed soils (forestland and cropland) than that in the non-agriculturally managed soils (wasteland) ($P<0.05$), implying that the application of fertilizers and cultivation effectively increased the content of TN in soils. The local farmers apply chemical fertilizers and animal manure for cropland and forestland with flooding irrigation. Wang et al. (2014) proposed that soil TN content was significantly increased after the application of fertilizers and was distinctly enhanced when applications comprised half compost and half fertilizers (Bedada et al., 2014). This implied that fertilizer inputs combined with agricultural activities (cultivation, cropping and irrigation) are the major source of soil TN in the irrigation sub-oasis. In our study, soil Zn content only had a significant positive correlation with soil TN content ($P<0.001$). Zn and its compounds are widely used in fertilizers (Cai et al., 2012), and Zn content in agricultural soils is usually higher than that in non-agriculturally managed soils due to the addition of commercial fertilizers and animal manure (Fernández-Calviño et al., 2012). Fertilizers, particularly phosphate fertilizers, are mainly from phosphate rock containing various amounts of heavy metals. For example, the content of Zn in phosphate fertilizers varies from 50 to 600 mg/kg (Kassir et al., 2012). In addition, animal manure has been reported to contribute to the Zn accumulation in soils due to the use of Zn-enriched feed additives (Kelepertzis, 2014). Historically, flooding irrigation is a common irrigation method in the study region, and most of the fertilizers could be stored in soils through soil leakage. Therefore, the significant positive relationship between soil Zn and TN might be explained by the massive use of fertilizers combined with flooding irrigation.

On the contrary, there was no significant difference in Zn contents between the managed (forestland and cropland) and non-managed soils (wasteland) in our study (Table 2). In other words, the differences in fertilization, cropping, tillage and other farming practices did not contribute to any significant difference in soil Zn content. According to the field survey, the wasteland is normally located at the lower elevations and it receives surface and/or subsurface flows from nearby irrigated cropland and forestland with the flooding irrigation method. As in other studies reported, irrigation can improve a more reliable water supply for better application of complementary agricultural inputs to crop growing (Domènech, 2015) and change the forms and contents of elements in flooded soils (Haque et al., 2015). Hence, flooding irrigation could cause the redistribution of Zn content in soils and reduce the differences of Zn content in soils under different land-use types.

4 Conclusions

Human activity has profound impacts on the biological and chemical-physical process of Zn in the irrigation oasis. The mean value of soil Zn in the Yongji irrigation sub-oasis was higher than the corresponding background value in Hetao oasis. This suggested that human activities had already influenced Zn accumulation in soils. There was no significant difference in Zn content among the five soil layers. Freezing-thawing cycling may influence the vertical redistribution of Zn content in the region.

Irrigation with water from the Yellow River was the main driving factor influencing the difference in the spatial distribution of soil Zn content in the sub-oasis. Along the irrigation direction around the Yongji Canal, Zn content in the topsoil layer was similar from southern to northern parts but increased from western to eastern parts along the Main Canal.

Soil Zn contents in the forestland and cropland were higher than that in the wasteland. However, the differences in land-use types did not make any significant differences in soil Zn content. Soil TN content was significantly higher in the agriculturally managed soils than in the non-managed soils. Soil Zn was significantly and positively correlated with TN. This indicated that the application of fertilizers increased the Zn content in soils, by contrast, flooding irrigation diluted the differences in Zn contents in the three land-use types of the sub-oasis.

The addition of fertilizers and quality of irrigation water with flooding irrigation method may lead to the accumulation of Zn and affect the spatial distribution of Zn content in the sub-oasis. Therefore, the government should increase the intensity of supervision in the quality of water and sediments of the Yellow River; and local farmers should pay more attention to the application of fertilizers and change the method of irrigation in the future.

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