The long-term agricultural reclamation since 1950s has resulted in significant land use change from natural landscape to cultivated land in the Sanjiang Plain of Northeast China, which has had important consequences for many soil physical, chemical and biological processes. However, it is not very clear how the drastic land-use conversions impact the geochemical behavior of heavy metals in soil. In this study, we examined the geochemical variability of Pb, Cd, Cu, Zn, Cr and Ni in soil after the land use conversions from natural wetland to paddy land and from natural forestland to dry farmland. In addition, the influencing factors of heavy metal variations in the different land use conversions were identified. Overall, these findings can help to improve the sustainability and safety of intensive agricultural activities in Northeast China as well as other similar areas.

Geochemical variability of heavy metals in soil after land use conversions in Northeast China and its environmental applications

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The long-term agricultural reclamation since 1950s has resulted in significant land use change from natural landscape to cultivated land in the Sanjiang Plain of Northeast China, which has had important consequences for many soil physical, chemical and biological processes. To understand the impact of land use conversions on heavy metal geochemistry, soil samples were collected from natural wetland, natural forestland, paddy land and dry farmland in a case study area and they were analyzed for total concentrations and chemical fractions of Pb, Cd, Cu, Zn, Cr and Ni, as well as pH, soil organic matter (SOM) and particle size distribution. Results showed that the natural wetland reclamation for paddy land has caused obvious losses of Cd, Cu and Zn from the soils. In addition, a significant decrease in the Zn concentration was found after the land conversion from natural forestland to dry farmland. Because all the analyzed heavy metals predominated in the stable residual fraction regardless of land use type, the response of metal mobility to the land use conversions was generally weak. Consequently, soil erosion was identified as the major factor that enhances heavy metals losses in the cultivated lands, especially in the paddy land. The close link between heavy metal loss and the reduction of clay and organic matter contents after land reclamation suggested that the diffuse heavy metal pollution occurred mainly in the small erosion events. Considering the continuous paddy land expansion, special attention should be paid to the bioaccumulation of Pb in the paddy rice. Overall, these findings can help to improve the sustainability and safety of intensive agricultural activities in Northeast China as well as other similar areas.

Introduction

Soil is of central significance in the environment because it acts like a pivot for material and energy exchanges among atmosphere, hydrosphere, biosphere and lithosphere. Once pollutants are introduced into the soil, they can be transferred to other environmental components and eventually affect human health through water supply and food chain.[1] Among numerous soil pollutants, heavy metals are especially dangerous due to their toxicity, persistence and non-degradability.[2,3] Many human activities such as industrialization, urbanization, and agricultural intensification can contribute to heavy metal accumulation in soils. However, there is usually a poor relationship between the total metal concentration and its biological effect.[4] To a large degree, the mobility, bioavailability and related eco-toxicity of heavy metals in soil are determined by their geochemical fractions of occurrence.[5]

In general, soils in agricultural areas tend to receive lower metal inputs from anthropogenic sources than do soils in industrial or urban areas.[6,7] Nevertheless, they may also cause a high human health risk via food production when considering the fact that ingestion is the dominant exposure pathway for heavy metals.[8] As a result, a large number of studies have been conducted on the heavy metal accumulation in agricultural soils.[9,10] Such studies indicated heavy metal contents usually exhibit significant differences among land use types. Overall, the reason for those variances is rooted in the fact that different agricultural lands have special cultivation practices that alter the geochemical behaviour of heavy metals in soil. There are diverse factors affecting the heavy metal geochemistry and therefore, soil property is the basic and important factor.[11] With increasing food demands, the reclamation of natural land into farmland in rural areas has become popular worldwide. Consequently, an increased heavy metal contents would generally be expected in the reclaimed soils due to the continuous application of agrochemicals, which contain a variety of heavy metals as impurities.[12] However, is this true of all cases? In fact, any change in land use has important consequences for many soil physical, chemical and biological processes, which can affect the heavy metal geochemistry indirectly and needs deeper analysis under specific conditions.

The Sanjiang Plain is a typical agricultural reclamation area located in Northeast China. This plain was covered with extensive natural wetland and forestland before the 1950s, since then it has been affected by widespread land reclamation. Up to now, the large-scale agricultural development has converted approximately 3,800,000 ha of natural wetlands and 1,200,000 ha of natural forestlands into cultivated lands.[13] Therefore, much attention has been given to agricultural reclamation problems of Sanjiang Plain in recent years. However, previous researches were focused mainly on soil nutrient changes[14,15], and there have been very limited efforts relating the heavy metal variations after the drastic land use conversions.

In this paper, soil samples were collected from four representative land uses in the Sanjiang Plain (i.e., natural wetland, natural forestland, paddy land and dry farmland) and analyzed for total concentrations and chemical fractions of heavy metals. The primary objectives of this study were: (1) to examine the geochemical variability of Pb, Cd, Cu, Zn, Cr and Ni in the soils after the land use conversions from natural wetland to paddy land and from natural forestland to dry farmland; (2) to identify the controlling factors of heavy metal variations in the different land use conversions; and furthermore, (3) to assess the environmental implications of heavy metal geochemistry under the long-term agricultural development.

Materials and methods

Study area description

A case study area was selected from the northeast corner of Sanjiang Plain (133°50′–134°33′E, 47°18′–47°50′N), which has a typical rural landscape and where natural and socio-economic conditions are representative of the reclaimed floodplain. The climate in this area is cold-temperate monsoon, with an average annual temperature of 2.94 °C and an annual precipitation of 600 mm.[14] This area was historically dominated by natural wetland and forestland, however, has been experiencing an intensive agricultural reclamation since the 1956. At present, the land use percentages are 57% cropland, 26% wetland, 12% forestland, 1.8% construction land, 1.7% water area and 1.5% grassland.[16] According to the local land use policy, more virgin lands, such as wetland and forestland, would be reclaimed into paddy land and dry farmland. Rice and maize are the two main types of crops being cultivated. There is no important anthropogenic point source related to mining or industrial activities in this area and all the irrigation water comes from natural rainfall, groundwater and the Wusuli River (boundary river of China and Russia). Although agriculture may not be the greatest source of heavy metal contamination, the long-term cultivation practice and land use conversion has changed many soil physicochemical properties in the Sanjiang Plain[17,18], which may therefore affect the geochemical behavior of heavy metals in soil.

Sample collection

As heavy metals introduced by anthropogenic activities mainly accumulate in the topsoil, 36 soil samples of the arable layer (0-20 cm in depth) including 8 samples from natural wetland, 8 samples from natural forestland, 10 samples from paddy land and 10 samples from dry farmland were collected in the study area in June 2012. Sampling sites were selected at random, with special consideration for the land use conversion type to ensure that all paddy lands sampled were reclaimed from natural wetland and all dry farmlands were reclaimed from natural forestland. According to the World Reference Base for Soil Resources, the soil in the wetland is classified as Histosols with albic property, while the soil in the forestland is classified as Luvisols.[19] The coordinates of sampling sites were recorded using a global positioning system receiver (60CSX, Garmin, USA) (Fig. 1). At each site, 5 sub-samples were collected using an s-shaped sampling distribution method on an area of approximately 500 m^2, and they were fully mixed to obtain a composite sample.

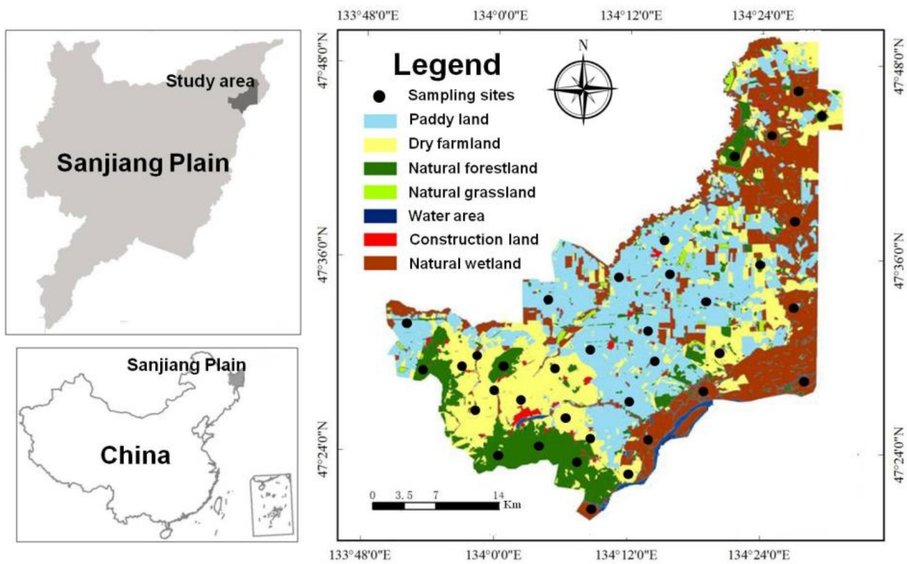

Fig. 1 Location of the study area and distribution of sampling site

Sample preparation and analysis

All soil samples were placed in polyethylene bags and brought to the laboratory immediately, where they were air dried at room temperature and sieved through a 2-mm nylon sieve to remove coarse debris. Portions of all samples were ground further until they passed a 0.149-mm nylon sieve. The soil pH was analyzed using a pH meter (Orion 310P-01N, Thermo Fisher Scientific, USA) in a 1:2.5 (w/v) soil to water suspension. Soil organic matter (SOM) content was measured by weight loss on ignition to 400 °C.[20] Soil particle size distribution was determined using a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd, UK).

For analysis of the total Pb, Cd, Cu, Zn, Cr and Ni concentrations, soil samples were digested with HNO_3–HF–$HClO_4$ mixture (5:2:3, v/v/v) in Teflon tubes at 160 °C for 6 h. The solution of the digested samples was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; SPECTRO ARCOS EOP, SPECTRO Analytical Instruments GmbH, Germany). Quality assurance and control were assessed using reagent blanks, triplicates and standard reference materials (GBW-07402, Chinese Academy of Measurement Sciences), which were included with each batch of samples (1 blank and 1 standard for every 10 samples). The analytical results showed no signs of contamination and the analytical precision was < 10%. The obtained recovery rates for the heavy metals in the standard reference material were between 96.12 and 104.76%.

A sequential extraction scheme developed by the Community Bureau of Reference, BCR (now the Standards, Measurements and Testing Program) was used to analyze the chemical fractions of heavy metals in the soils. This BCR method is described in detail elsewhere.[21] It separates a heavy metal into four fractions operationally defined as acid-soluble (exchangeable and carbonate-bound metals), reducible (Fe/Mn oxide-bound metals), oxidizable (organic matter/sulfide-bound metals), and residual fraction (silicate-bound metals). After each successive extraction, separation was done by centrifugation at 4,000 x g for 15 min. The supernatant was analyzed for Pb, Cd, Cu, Zn, Cr and Ni by ICP-AES. Quality controls were similar to those used for total metal analysis. The overall recovery rates, calculated by comparing the total metal concentrations with the sum of the four sequential chemical extractions, ranged from 90.75 to 104.12%.

Statistical analysis

The soil physicochemical properties, total metal concentrations and their chemical fractions from different land uses (i.e., natural wetland, natural forestland, paddy land and dry farmland) were compared using one-way analysis of variance (ANOVA) followed by post-hoc Least Significant Difference (LSD) test. Before running ANOVAs, all the data sets were checked for the normality and the homoscedasticity. The Spearman correlation coefficient was used to identify the relationships between selected heavy metals and soil physicochemical properties in different land use conversions (i.e., natural wetland reclamation for paddy land and natural forestland reclamation for dry farmland). All the statistical tests presented in this study were carried out using SPSS 16.0 for Windows (SPSS Inc, Chicago, USA).

Results

Soil property variation among different land uses

The selected soil physicochemical properties of natural wetland, natural forestland, paddy land and dry farmland are summarized in Table 1. In general, these parameters were significantly different among the land uses. The pH values varied from 4.35 to 5.09, with the highest value observed in paddy land and the lowest value in natural wetland. The SOM content in natural wetland was 13.67%, which was much higher than in natural forestland, dry farmland and paddy land. Similar land use impact was also found for the clay content, i.e. natural wetland showed a significantly higher level than other three land uses. The natural forestland was found to exhibit the highest silt content (47.38%), followed by dry farmland (45.58%), paddy land (43.12%), and natural wetland (40.11%). However, the sand content arranged in the following order: paddy land (31.31%) > dry farmland (24.60%) > natural forestland (19.49%) > natural wetland (15.43%).

Table 1 Selected soil properties in the different land uses of Sanjiang Plain

	pH	SOM (%)	Clay (%)	Silt (%)	Sand (%)
Natural wetland	4.35 ± 0.22^{a}	13.67 ± 1.93^{a}	44.41 ± 1.77^{a}	40.11 ± 2.00^{a}	15.43 ± 1.37^{a}
Natural forestland	4.61 ± 0.26^{ab}	4.62 ± 0.38^{b}	33.49 ± 2.11^{b}	47.38 ± 3.11^{b}	19.49 ± 1.68^{b}
Paddy land	5.09 ± 0.48^{c}	3.44 ± 0.43^{c}	25.57 ± 1.90^{c}	43.12 ± 2.43^{c}	31.31 ± 2.79^{c}
Dry farmland	4.85 ± 0.28^{bc}	3.94 ± 0.68^{d}	30.27 ± 2.41^{d}	45.58 ± 3.41^{bc}	24.60 ± 2.42^{d}

Means in a column followed by the same letter were not significantly different

Heavy metal variation among different land uses

The total concentrations of Pb, Cd, Cu, Zn, Cr and Ni in the four land uses are presented in Table 2. When compared with the soil background values of Sanjiang Plain, the Pb, Cu and Cr concentrations in these land uses were all elevated. In addition, higher concentrations were observed for Zn from natural wetland and forestland. However, they did not exceed the upper safe limits for agricultural production and human health according to the Chinese Environmental Quality Standard for Soils. Among the four land uses, natural wetland was found to exhibit the highest heavy metal concentrations; this was especially true for Cd, Cu and Zn, of which the mean concentrations in natural wetland were 2.22-, 1.57-, 1.68-fold the lowest value in other land uses. Although the mean Pb concentration in natural wetland was much higher than in paddy land or natural forestland, it did not significantly differ from that observed in dry farmland.

Fig. 2 illustrates the partitioning of Pb, Cu, Zn, Cr and Ni between acid-soluble, reducible, oxidizable and residual fractions in the four land uses. The chemical fractions of Cd were not reported because they fell below the detection limit of the techniques utilized. In general, there were no obvious differences in the heavy metal fractionation among the land uses. The residual fraction was the predominant chemical fraction in the five heavy metals that were analyzed (68.74-89.10%); this was true regardless of the land use type from which the samples were taken. In all cases the percentages of the other three chemical fractions were substantially lower. Paddy land was found to exhibit the highest partitioning levels of heavy metals in the acid-soluble fraction. For most heavy metals, the reducible fraction was greater in natural wetland than in other land uses—an observation that holds for the oxidizable fraction as well. The higher partitioning levels of heavy metals in the residual fraction were always observed in natural forestland, but they showed no significant differences among the four land uses.

Table 2 Total metal concentrations in the different land uses of Sanjiang Plain

Land use types	Heavy metals (mg kg^{-1})					
	Pb	Cd	Cu	Zn	Cr	Ni
Natural wetland	23.66±1.77^{a}	0.16±0.034^{a}	39.14±5.96^{a}	105.66±8.35^{a}	60.63±4.69^{a}	26.63±1.82^{a}
Natural forestland	21.16±1.96^{b}	0.073±0.041^{b}	26.43±5.24^{b}	77.18±6.61^{b}	58.07±4.84^{a}	26.25±5.87^{a}
Paddy land	21.86±0.95^{bc}	0.072±0.032^{b}	26.19±4.35^{b}	66.86±6.22^{c}	58.80±7.58^{a}	25.77±3.50^{a}
Dry farmland	23.43±2.33^{ac}	0.077±0.017^{b}	24.88±3.84^{b}	62.75±4.96^{c}	56.79±6.23^{a}	25.15±2.52^{a}
Background value①	17.79	–	22.60	70.30	28.20	27.10
Guideline value②	250	0.3	50	200	150	40

Means in a column followed by the same letter were not significantly different

① Soil background values of Sangjiang Plain

② Chinese Environmental Quality Standard for Soils[22]

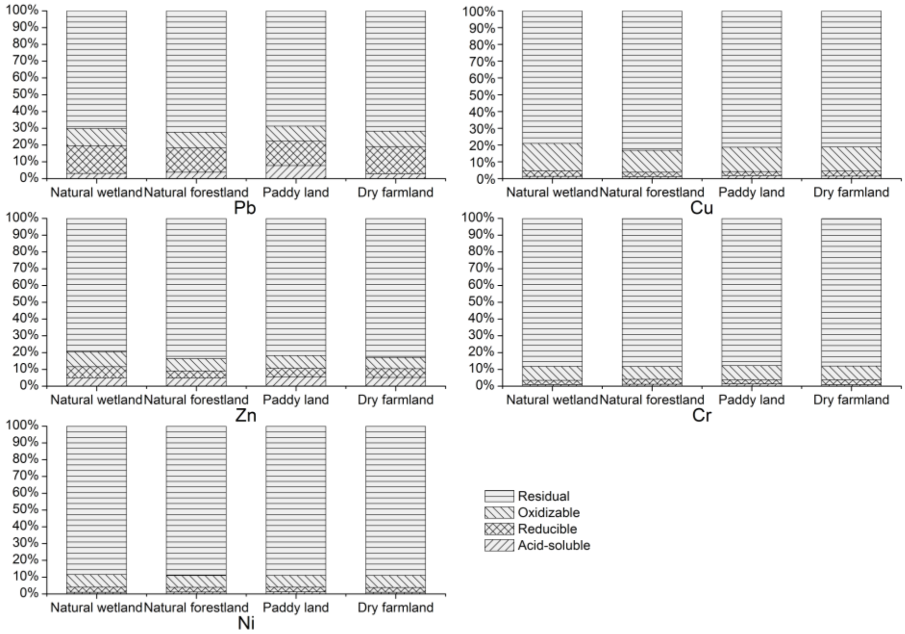

Fig. 2 Chemical partitioning of heavy metals in the different land uses of Sanjiang Plain

Heavy metal response in different land use conversions

As all paddy lands sampled were reclaimed from natural wetland and all dry farmlands were reclaimed from natural forestland, the heavy metal variability in the two land use conversions was further analyzed through grouping these land uses by couples. As shown in Fig.3, the long-term wetland reclamation for paddy land has generally decreased heavy metal concentrations in surface soils. The average decreases were 7.61%, 55.00%, 33.09%, 36.72%, 3.02% and 3.23% for Pb, Cd, Cu, Zn, Cr and Ni, respectively, when comparing concentrations in paddy land with concentrations in natural wetland. Similarly, the natural forestland reclamation for dry farmland has led to the 5.86%, 18.70%, 2.21% and 4.19% decreases in the Cu, Zn, Cr and Ni concentrations. However, an inverse change was observed for Pb and Cd. After forestland reclamation, the dry farmland exhibited higher concentrations of Pb and Cd in surface soils, which was considerably different from other heavy metals.

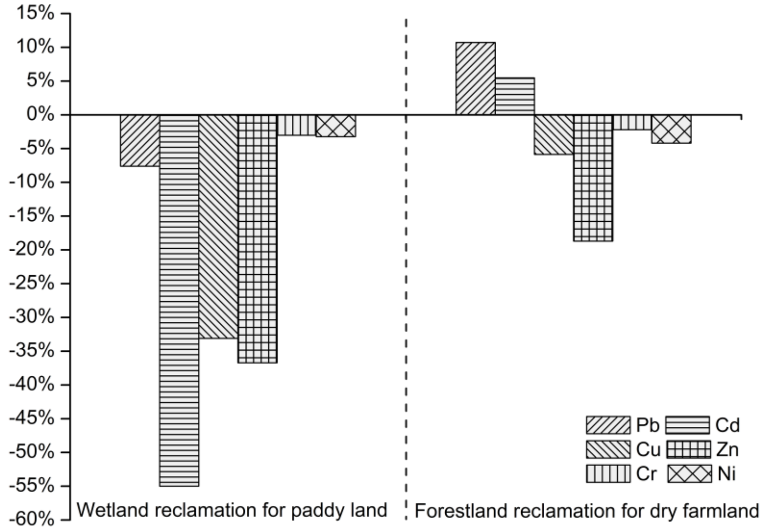

Fig. 3 Heavy metal variability in the different land use conversions

Relationships between heavy metals and soil properties in different land use conversions

To identify the influencing factors of heavy metal variations in the different land use conversions, the relationships between total metal concentrations and selected soil properties were evaluated using Spearman correlation. As significantly lower concentrations occurred only for Cd, Cu and Zn when wetland was reclaimed into paddy land, the interactions of soil properties with these three heavy metals were displayed in Fig.4. It was found that the interaction varied greatly among soil parameters in the land conversion from natural wetland to paddy land. In general, the SOM and clay contents exhibited significant positive relationships with these metals, which meant the heavy metal loss was closely related to the reduction of SOM and clay contents in paddy land. However, the soil pH and sand content had the reverse impact. For the same reason, Fig.5 illustrates the interactions of soil properties with Pb and Zn in the land conversion from natural forestland to dry farmland. Compared to wetland reclamation, the soil property impact on heavy metal variation was generally weak in the forestland reclamation. However, the SOM and clay contents were still identified as the major factors affecting Zn loss in dry farmland. Contrary to Zn loss, the forestland reclamation and subsequent cultivation practices has generally elevated Pb concentration in surface soils, which weaken the soil property impact and eventually led to the fact that element Pb was not sensitive to the reduction of SOM and clay contents.

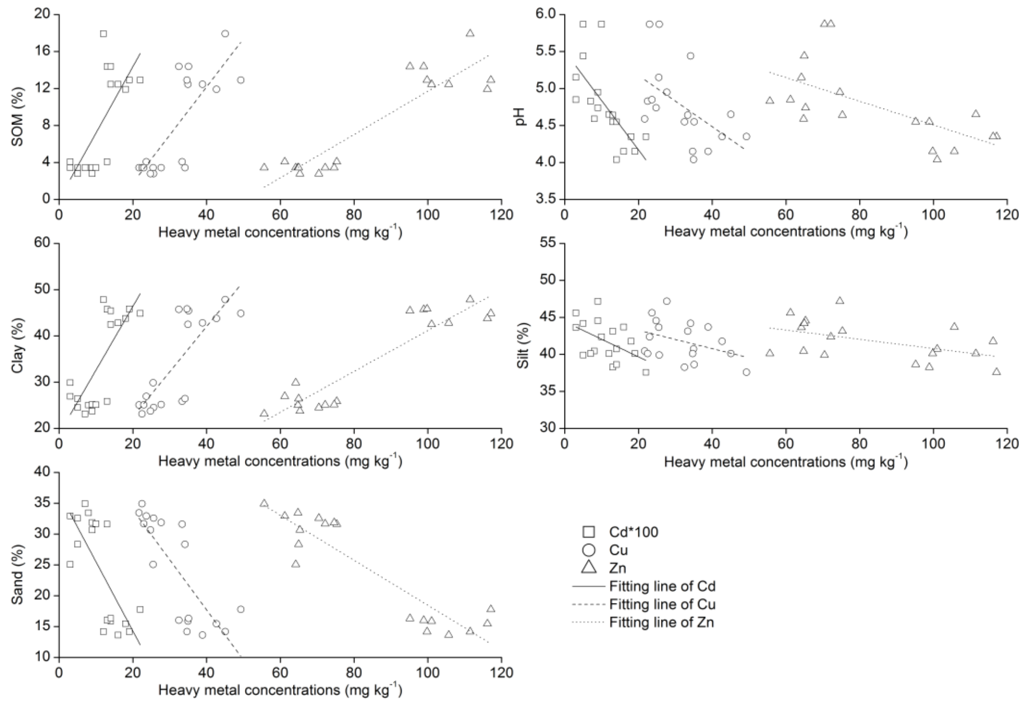

Fig. 4 Relationships between heavy metals and soil properties in the land conversion from natural wetland to paddy land

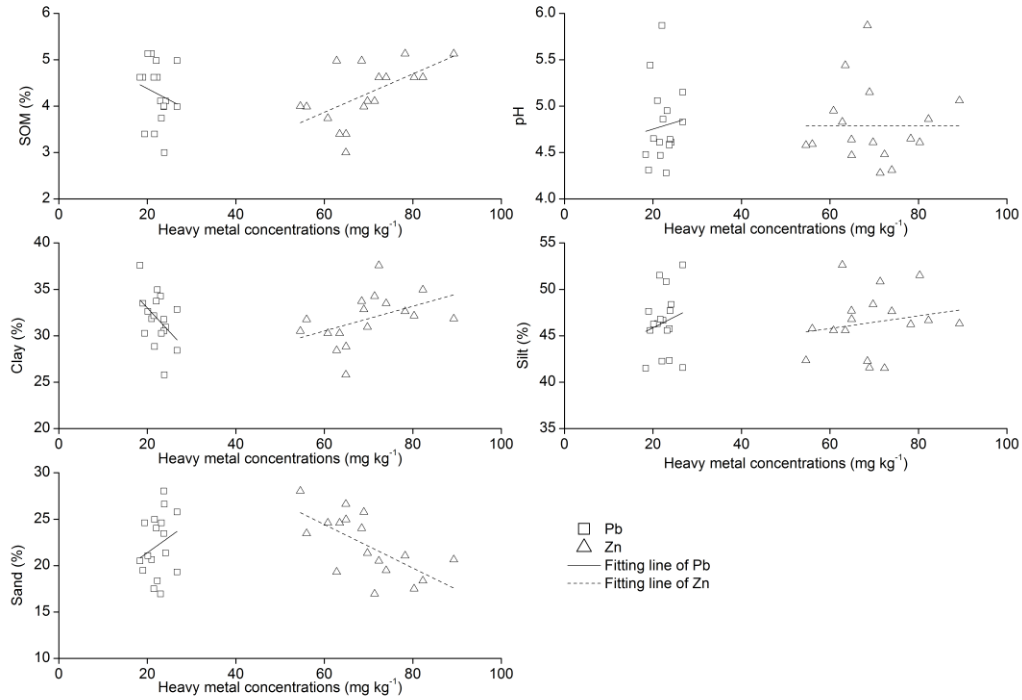

Fig. 5 Relationships between heavy metals and soil properties in the land conversion from natural forestland to dry farmland

Discussion

Land use impact on the heavy metals in soil

With the rapid development of agricultural intensification, elevated heavy metal concentrations in cultivated lands have been found in many agricultural areas around the world.[23,24] However, this is not the case in the study area. After long-term wetland reclamation, the paddy land showed significantly lower concentrations of Cd, Cu and Zn in surface soils, which suggested that natural wetland reclamation for paddy land has caused obvious losses of these heavy metals from the soils. In addition, a significant decrease in the Zn concentration was found after the land conversion from natural forestland to dry farmland. Previous studies have reported that the continuous agricultural tillage may induce some significant changes in soil properties affecting metal mobility, thus promoting the release of heavy metals from combination patterns in soil aggregates to water bodies and organisms.[25] In this study, higher partitioning levels of heavy metals associated with more strongly bound fractions (reducible, oxidizable and residual fractions) were always observed in natural wetland or forestland, which reflected the land use impact on metal mobility to some extent. However, this impact may be much weaker when considering the fact that all the analyzed heavy metals predominated in the stable residual fraction regardless of land use type. Obviously, besides the metal binding pattern, there were other factors causing heavy metal losses in the cultivated lands.

In the long winter of cold areas, the suppressed microbial activities in the frozen soil result in accumulated SOM content in deep humus horizon, but the soil is vulnerable to erosion because of cycle's freezing and thawing.[26] Soil erosion is often implicated in the transportation of many contaminants that bound strongly to soil colloids and organic matter; this is especially true for cultivated lands where the frequent tillage can greatly disrupt soil structure, causing more erosion and associated materials loss than under natural conditions. Based on 6 years of field monitoring data, Quinton and Catt[27] demonstrated that water erosion on agricultural soil can act as an important vector for the movement of heavy metals. Therefore, soil erosion may be the major factor that induces heavy metal losses in the cultivated lands. By comparison, the heavy metal loss was more serious in paddy land than in dry farmland. A possible reason for this is that the aquatic condition in paddy land accelerates the erosion process. After forestland reclamation, however, the dry farmland exhibited elevated concentrations of Pb and Cd in surface soils. This was most likely attributed to the high rate of fertilizer application in the dry farmland. In addition, more heavy machines have been used for sowing, fertilizing and harvesting since 1980s, which brought with the possibility of atmospheric Pb and Cd deposition. Overall, these findings indicate that heavy metal accumulation in cultivated lands depends not only on the input from different sources, but also on the losses by soil erosion, leaching and plant removal.[28] However, Bai *et al.*[29] presented that cultivation history is also an important factor related to the accumulation of heavy metals in soil, particularly of Pb, Cu and Zn in cultivated wetlands.

Soil conservation in the agricultural reclamation area

In agricultural reclamation areas, the land conversion and subsequent cultivation can negatively alter many characteristics of soil quality, thus directly or indirectly affecting the geochemical behavior of heavy metals in soil. The soil pH is known to play an important role in controlling the metal solubility and mobility.[30] In this study area the acid soil generally favors the migration of heavy metals, although a significant increase in soil pH was found after the wetland reclamation for paddy land. As waterlogging may cause the pH of acid soil to increase, the soil pH in the paddy land should be ultimately close to neutral. On the other hand, the continuous urea application can also consume hydrion in soil solution.[31] However, the effect of soil pH change on heavy metal accumulation maybe very weak when considering the great heavy metal loss caused by erosion. The significant negative relationship between soil pH and Cd, Cu or Zn in the land conversion from natural wetland to paddy land confirmed this hypothesis. The SOM content is one of the most important indexes for the soil quality assessment in agricultural management. In general, the content of SOM in this area had a high background level, but large SOM loss occurred when natural land was reclaimed into farmland. The dry farmland was found to exhibit higher SOM content than paddy land, which did not coincide with many previous studies.[32] More frequent manure applications and crop residuals such as maize straw may be accountable for the high SOM content in the dry farmland. With the correlation analysis, we concluded that the reduction of heavy metal contents in farmlands was closely associated with the SOM loss. In addition to soil erosion impact, the decrease in SOM content might be related to the accelerated oxidation process after land conversion from natural wetland and forestland. Wetland reclamation always starts with the construction of drainage ditches to reduce excess water, and frequent tillage can increase the fluxes of O_2 into and CO_2 out of the soil. Under these conditions the SOM in farmlands can be gradually degraded, thus leading to a release of soluble metals.[33] This conclusion was supported by many researchers[34]and suggested that SOM can act as a major sink for heavy metals due to its strong complexing capacity for metallic contaminants.

The particle size distribution of soil particles can also deeply affect the soil property and behavior. From the particle-size fractions (clay, silt and sand), the finer soil particles usually display higher metal concentrations because of increased surface areas, higher clay minerals and organic matter content, and the presence of Fe-Mn oxides and sulphides.[35] After long-term agricultural reclamation, the paddy land and dry farmland all displayed a significant decrease in the clay content. This was most likely attributed to the intense soil erosion in farmlands, which can affect the evolution of soil texture. Previous studies have presented that vegetation coverage has a major impact on both preventing soil erosion and decreasing loss ratio of fine particles.[36] Therefore, if we want to effectively improve the soil quality of farmlands, great attention should be paid to the loss of fine particles, especially in rainy seasons after the crops are harvested. Soil erosion can be a highly selective process, often preferentially detaching and transporting clay and silt.[37] However, the impact of silt fraction on heavy metal contents was not as strong as expected due to the low correlation among them. Consequently, clay may be the major soil fraction responsible for the heavy metal loss during erosion episodes. Although there was a significant increase in the sand content after land reclamation, heavy metals in this fraction are mainly of natural origin that contributes to background.

Implications for environment and food safety

In such a purely agricultural area, the continuous agrochemical application can be identified as the major anthropogenic source of heavy metals in the soils. Wastewater irrigation is usually an important source of heavy metal contamination in water-limited areas of China[38], but it cannot be a main source in this area because all the irrigation water came from natural rainfall, groundwater and the Wusuli River. As a result, the heavy metals in the soils generally indicated low levels of contamination. However, the soil erosion induced by cultivation was especially serious in this area, which posed a great threat to the local water environment. Generally speaking, more intense erosion events can mobilize a wide range of particle sizes, whereas lower intensity events mobilize and transport only the finer but more metal-rich materials. In this study, the close link between heavy metal loss and the reduction of clay and organic matter contents after land reclamation suggested that the diffuse heavy metal pollution occurred mainly in the small erosion events. This is quite important because lower intensity events are more frequent. Therefore, any mitigation strategy for decreasing the heavy metal transport by erosion should address large low-frequency erosion events as well as the smaller high-frequency events.

As one of the major commodity grain production bases in China, the Sanjiang Plain plays an important role in meeting the national food demand. In the last two decades, more and more dry farmlands have been changed into paddy land for achieving higher grain output. However, this type of land use change may increase the potential food safety risk from heavy metals. Rice cultivation in paddy fields generally requires moderate flooding. Under these conditions, the heavy metals in soil can be easily transformed from stronger bound fractions to weaker bound carbonate and exchangeable fractions, thereby promoting their transfer to crops.[39] According to a RAC code[40], the acid-soluble Pb in some paddy soils has been close to the medium risk level of 10%. This was mostly related to the reduction of Fe-Mn oxides, which can serve as important scavengers of Pb in soil.[41] Lead is considered as very toxic element, its entry into food chain may result in an increased susceptibility and exposure to Pb poisoning for human beings (especially for children), causing hematological, gastrointestinal and neurological dysfunctions.[42] Therefore, from a food safety perspective, special attention should be paid to the bioaccumulation of Pb in the paddy rice in the future.

Conclusions

Results obtained in this study showed that the heavy metal concentrations in natural wetland were much higher than those in natural forestland, paddy land and dry farm land. However, they did not exceed the upper safe limits for agricultural production and human health according to the Chinese Environmental Quality Standard for Soils. The residual fraction was the predominant chemical fraction in the Pb, Cu, Zn, Cr and Ni; this was true regardless of the land use type from which the samples were taken. By grouping these land uses by couples, the heavy metal variability in different land use conversions was further analyzed. After long-term wetland reclamation, the paddy land showed significantly lower concentrations of Cd, Cu and Zn in surface soils, which suggested that natural wetland reclamation for paddy land has caused obvious losses of these heavy metals from the soils. In addition, a significant decrease in the Zn concentration was found after the land conversion from natural forestland to dry farmland. With the analysis of relationships between these heavy metals and soil properties, it was found that the heavy metal loss after wetland reclamation was closely related to the reduction of SOM and clay contents. Similar impact was also observed for SOM in the land reclamation from forestland to dry farmland.

Because all the analyzed heavy metals predominated in the stable residual fraction regardless of land use type, the response of metal mobility to the land use conversions was generally weak. Consequently, soil erosion was identified as the major factor that enhances heavy metals losses in the cultivated lands, especially in the paddy land. In addition, the close link between heavy metal loss and the reduction of clay and organic matter contents after land reclamation suggested that the diffuse heavy metal pollution occurred mainly in the small erosion events. Therefore, any mitigation strategy for decreasing the heavy metal transport by erosion should address large low-frequency erosion events as well as the smaller high-frequency events. According to a RAC code, the acid-soluble Pb in some paddy soils has been close to the medium risk level of 10%, which posed a potential threat to the food safety. Considering the fact that processes following agricultural reclamation are complex in such a freeze-thaw area and different soil conditions prevailing in other sites can result in different geochemical behaviours of heavy metals, more field research is needed to get a better insight into the heavy metal variability involved.

Acknowledgements

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Unlike most other areas in the world, the long-term agricultural reclamation in Northeast China has significantly decreased some metal concentrations in soil.