ChinaRxiv

AI translation · View original & related papers at
chinarxiv.org/items/chinaxiv-201711.02116

Distribution of Heavy Metal Content and Factors Influencing Their Available Forms in Coastal Tidal Flat Soils: Postprint

Authors: Yao Rongjiang, Yang Jinsong, Xie Wenping, Chen Qiang, Wu Danhua, Bai Yanchao

Date: 2017-11-08T00:00:00+00:00

Abstract

To reveal the spatial distribution characteristics of soil heavy metal content in coastal areas and its associations with natural and anthropogenic factors, a tidal flat region in coastal Jiangsu with intensive reclamation development in recent years was selected as the study area. Using a combined approach of classical statistics and geostatistics, we investigated the status and spatial distribution of total and available contents of major heavy metals (Pb, Cr, Cd, As) in surface soil, analyzed the effects of land use patterns on heavy metal content in coastal tidal flat areas, and explored the correlations between available heavy metal content and soil physicochemical properties. The results indicated that: the current soil environmental quality of the study area is generally good; soil Pb, Cr, Cd, and As all exhibit accumulation trends but remain mostly below the Grade I standard values of soil environmental quality; land use patterns influence the total and available contents of Pb, Cr, and Cd to varying degrees, while the total and available contents of As are less affected by land use patterns; the total contents of soil Pb, Cr, and Cd and the available contents of Pb and Cr in the study area show significant trend effects, and the spatial distribution of both total and available heavy metal contents is jointly controlled by large-scale tidal action and small-scale anthropogenic factors; the available contents of soil Pb, Cr, and Cd are significantly negatively correlated with clay content, cation exchange capacity, and pH, and significantly positively correlated with organic matter, whereas the available content of soil As is only significantly positively correlated with soil pH. This study provides a scientific basis for source reduction, activity passivation, pollution mitigation, and risk prevention of soil heavy metals in coastal tidal flat areas.

Full Text

Content and Bioavailability Factors of Soil Heavy Metals in Mudflat Coastal Areas

YAO Rongjiang[1],[2], **YANG Jinsong**[1],[2], XIE Wenping[1], CHEN Qiang[3], WU Danhua[2], BAI Yanchao[4]

[1]State Key Laboratory of Soil and Sustainable Agriculture / Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China; [2]Dongtai Institute of Tidal Flat Research, Nanjing Branch of Chinese Academy of Sciences, Dongtai 224200, China; [3]Centre of Agricultural and Animal Husbandry Technology Extension of Hanggin Rear Banner of Inner Mongolia, Shaanba 015400, China; [4]School of Environmental Science and Engineering, Yangzhou University, Yangzhou 225000, China

Abstract: Coastal zones with tidal mudflats represent the most development potential for agriculture and industry in China. It is therefore vital to study the spatial patterns of soil heavy metals and identify the intrinsic relationships between these patterns and natural and human driving factors in coastal regions. Using classical statistical and geostatistical methods, this study investigated the effect of land use types on the contents of total and bioavailable heavy metals (Pb, Cr, Cd, and As) in surface soil, not only to delineate the spatial distribution of these heavy metal forms but also to determine the relationship between bioavailable heavy metal contents and basic soil physical and chemical properties. The study was conducted in a rapidly developing industrial and agricultural region in Jiangsu Province, China. Results indicated that soil environmental quality across the study area was generally good. The contents of soil Pb, Cr, Cd, and As were lower than the accepted environmental quality evaluation standard (first class), although there was an increasing accumulation trend for each heavy metal in recent years. Land use type affected total and bioavailable contents of Pb, Cr, and Cd to different degrees. Greenhouse facility soils and park green space soils had the highest contents of total and bioavailable Pb. Soil contents of total and bioavailable Cr were high in residential and industrial areas, whereas greenhouse facility soils had the lowest total and bioavailable Cd contents. Land use patterns had little impact on total and bioavailable contents of As. In addition to land use type, biological absorption was another important factor affecting soil heavy metal contents in the study area. Total soil Pb, Cr, and Cd and bioavailable Pb and Cr showed significant directional trends across the study area. The spatial pattern of total and bioavailable soil heavy metal contents was generally influenced by various factors at different scales. The overall spatial distribution of soil heavy metals showed a strip-like pattern due to large-scale tidal deposits, while patched local distributions were mostly controlled by small-range factors such as industrial emissions and human activity. Soil bioavailable Pb, Cr, and Cd exhibited significant negative correlation with soil clay particle content, cation exchange capacity, and pH. Due to the high fulvic acid content of soil, a positive correlation existed between bioavailable soil Pb, Cr, and Cd contents and soil organic matter content. Soil bioavailable As content was positively correlated with soil pH, but there was no significant correlation between soil bioavailable As and other soil physical and chemical properties. The correlation between bioavailability of soil heavy metals and soil basic physicochemical properties is critical for developing appropriate management practices that control heavy metal pollution in coastal mudflat regions. The findings of this research provide additional scientific basis for source reduction, ecological activity passivation, pollution abatement, and risk prevention of soil heavy metals in mudflat coastal areas.

Keywords: Coastal mudflat; Heavy metal; Spatial distribution; Land use type; Soil physical and chemical properties; Jiangsu Province

Introduction

Coastal mudflats are important transitional landscapes between land and sea, subject to combined natural and intensive human activities, and represent typical environmentally sensitive and fragile zones [1]. Jiangsu coastal areas possess abundant tidal flat resources, and numerous studies have shown that historical sediment transport and deposition from major rivers such as the Yangtze and Huai Rivers are important reasons for the exceptionally rich tidal flat resources along the Jiangsu coast [2-3]. With rapid socioeconomic development and accelerated urbanization in Jiangsu coastal areas in recent years, development and utilization have shown unconventional growth trends, and prominent potential environmental issues have emerged in local soils of certain tidal flat areas, port areas, wetlands, and cultivated lands [4-5]. Among various pollutants entering the sea or landing through various pathways, heavy metals have characteristics of latency, non-degradability, and enrichment, and easily enter soils through sewage discharge, wastewater irrigation, solid waste utilization, atmospheric deposition, and other pathways. They are the most threatening pollutants to the environment and human health and are therefore widely used in environmental assessments [6-7].

The land formation process of coastal mudflats is influenced by comprehensive factors such as hydrodynamic action, biogeochemical processes, and water physicochemical conditions, making mudflats not only an important sink for upstream heavy metal pollution but also a sink for heavy metal emissions during human development and utilization. In recent years, numerous domestic and foreign studies have been conducted on heavy metal pollution characteristics [8-9], source identification [10-11], migration processes [12-13], bioremediation [14-15], ecological risk assessment [16-17], spatial distribution patterns [18-19], and environmental geochemical processes [20] of heavy metals in coastal zone soils and sediments. Current research has mainly focused on the total content of heavy metals in tidal flat areas, with less research on the bioavailability of heavy metals in tidal flat soils. Recent research results have shown that heavy metals in soils have multiple occurrence forms, their forms are influenced by soil characteristics and human activities, and different forms of heavy metals exhibit different biological toxicity and migration characteristics. To a greater extent, judging the toxic response and ecological risk of soil heavy metals depends on their occurrence forms [21-22]. As one of the regions with the strongest development potential in eastern China, Jiangsu coastal areas have seen accelerated tidal flat reclamation, urbanization, industrialization, and agricultural modernization in recent years, as well as continuously rising total amounts of pollutants entering the sea through rivers, making the potential risk of heavy metal pollution in soils increasingly severe. However, there have been few reports on comprehensive studies considering the impacts of a series of human activities such as coastal mudflat reclamation, development, and utilization on soil heavy metal content and its influencing factors on bioavailability. Therefore, this study takes a typical tidal flat area in Gang Town, Dongtai City, Jiangsu Province, which has abundant reclaimed tidal flat resources and has developed rapidly in recent years, as an example to investigate the total and bioavailable contents of major heavy metals Pb, Cr, Cd, and As in surface soils of the area, analyze the impact of land use patterns on total and bioavailable heavy metal contents, and explore the correlation between bioavailable heavy metal contents and soil physicochemical properties, aiming to provide a basis for reasonable prevention and risk reduction of soil heavy metal pollution in coastal mudflat areas.

1.1 Study Area Description

The study area is located in the tidal flat area centered on the Dongtai Coastal Economic Zone in Jiangsu Province, with geographic coordinates between 120°49 36.7 -120°56 35.9 E, 32°43 31.4 -32°46 56.8 N (Fig. 1 [Figure 1: see original paper]), approximately 3.3 km east of the most recent reclamation seawall. This area belongs to the transition zone between subtropical and warm temperate zones, with four distinct seasons, an annual average temperature of 15.0°C, a frost-free period of 220 days, sunshine of 2,130.5 hours, and an average annual rainfall of 1,025 mm. Rainfall and heat occur in the same period, with uneven seasonal distribution of rainfall, where precipitation during the rainy season from June to September accounts for an average of 63.5% of the annual total. The soils in this area developed from Jianghuai alluvial-marine sediment parent material, approximately 150 km south of the Yangtze River estuary, with relatively high soil salinity. Soil properties are typical representatives of siltation-type plain coasts, with texture mainly sandy loam and silt loam, belonging to chloride-type salinized fluvo-aquic soils, with low organic matter content and poor water and fertilizer retention capacity. Land use types in the study area mainly include tidal flats, conventional fields, greenhouse facilities, park green spaces, industrial parks, and residential areas (Fig. 1). With the continuous increase in industrial and agricultural development and urban construction intensity in recent years, soil environmental quality and safety in this area have received increasing attention.

1.3 Sample Collection and Analysis

Based on field investigation and the functional layout characteristics of the study area, 48 effective soil samples were collected in mid-August 2014. Considering the rapid development of processing, facility agriculture, and urban construction in the coastal tidal flat area in recent years, 29 additional soil samples were collected in early December 2014. A total of 77 effective soil samples were collected, including 14 from tidal flat areas, 11 from conventional farmland, 23 from greenhouse facilities, 6 from park green spaces, 14 from industrial parks, and 9 from residential areas, covering the main land use types in the current study area and reflecting the soil environmental pollution status of the study area. Each sampling site was located using GPS, and its spatial location is shown in Fig. 1. For each sample site, six surface soil samples at a depth of 0-20 cm were collected using an "S" shaped multi-point sampling method within a 10 m × 10 m area. Before sampling, surface floating soil was scraped off at each sample site (<1 cm), and after on-site uniform mixing, 1 kg of soil sample was selected using the quartering method and placed in a self-sealing bag as a representative mixed sample for that point. The collected soil samples were brought back to the laboratory, air-dried, and debris, gravel, and plant materials were removed. The samples were then ground with a mortar and passed through 10-mesh, 20-mesh, and 100-mesh nylon sieves, and stored dry.

The heavy metal indicators measured in the collected soil samples included total and bioavailable contents of Pb, Cr, Cd, and As, and soil physicochemical properties included organic matter, cation exchange capacity, clay content (<0.002 mm), and pH. Aqua regia-H_2O_2 digestion and phosphoric acid as inhibitor were added to extract total Pb and Cd; HF-$HClO_4$-HNO_3 digestion was used to extract total Cr; HNO_3-H_2SO_4 digestion followed by $NaBH_4$ reaction was used to extract total As; DTPA-TEA extraction was used for bioavailable Pb, Cd, and Cr; and dilute hydrochloric acid extraction was used for bioavailable As [23]. Atomic absorption spectrometry with graphite furnace was used to determine Pb and Cd element contents, atomic absorption flame method was used to determine Cr element content, and atomic fluorescence photometry was used to determine As element content. Quality control for soil heavy metal analysis used national standard materials for spike recovery, with recovery rates for each heavy metal content being Pb (96.2%-108.6%), Cr (97.3%-114.1%), Cd (95.7%-116.8%), and As (96.1%-117.5%), meeting the U.S. EPA standard requirement range of 80%-120%. Soil organic matter and cation exchange capacity (soil samples passed through 100-mesh sieve) were determined using the potassium dichromate dilution-heat method and EDTA-ammonium acetate exchange method, respectively. Soil clay content (soil samples passed through 10-mesh sieve) was determined using the pipette method, and soil pH (soil samples passed through 20-mesh sieve) was determined using the potentiometric method.

1.4 Research Methods

The analytical methods used in this study included descriptive statistical analysis, Pearson correlation analysis, one-way ANOVA, and geostatistical analysis. To understand the heavy metal content status in the study area, reveal the impact characteristics of different land use patterns on total and bioavailable heavy metal contents, and clarify the correlation between bioavailable heavy metal contents and basic soil physicochemical properties, SPSS 15.0 software was used for descriptive statistical analysis, Pearson correlation analysis, and one-way ANOVA. To describe the spatial distribution of total and bioavailable heavy metal contents in the study area, universal kriging was used to predict the spatial distribution of total and bioavailable heavy metal contents. The specific principles, structure, and methods of universal kriging are referenced in the literature [24]. This study used ArcGIS 9.3 software for trend effect analysis, spatial prediction, and distribution mapping of soil heavy metal contents.

2.1 Soil Heavy Metal Content Status Analysis

The descriptive statistical characteristic values of total and bioavailable heavy metal contents in the study area soils are listed in Table 1 . It can be seen that, whether for total or bioavailable contents, there was considerable variation in heavy metal contents among different sites. The coefficient of variation for total heavy metal contents in the study area soils ranged from 11.50% to 61.48%, and for bioavailable contents ranged from 19.33% to 54.83%, both belonging to moderate variation intensity. Using the natural background values of environmental elements in Jiangsu coastal soils determined in the 1980s [25] as reference values for soil heavy metal elements in this area, one-sample t-test (two-tailed) showed that the mean values of total Pb and Cd in the study area soils were significantly higher than the background values ($P<0.01$), while the mean values of total Cr and As were significantly lower than the background values ($P<0.01$). Except for three sample points, the total Pb content of all other sample points was higher than the background value. Soils had 33, 58, and 27 sample points with total Cr, Cd, and As contents higher than the background values, respectively, and these sample points were mainly located near greenhouse facilities, residential areas, and industrial parks. From the perspective of bioavailable heavy metal contents, the mean values of bioavailable Pb, Cr, Cd, and As contents in all sample point soils were 1.14 $\mathrm{mg \cdot kg^{-1}}$, 0.397 $\mathrm{mg \cdot kg^{-1}}$, 0.0214 $\mathrm{mg \cdot kg^{-1}}$, and 0.0643 $\mathrm{mg \cdot kg^{-1}}$, respectively. According to the national GB15618-1995 soil environmental quality standard, the total Cr, Cd, and As contents of all sample point soils in the study area were below the first-class standard, while 30 sample points had total Pb contents above the first-class standard but below the second-class standard. Overall, the current soil environmental quality status in the study area is good. Except for some sample points where heavy metal contents exceed background values and the first-class soil environmental quality standard, there is no phenomenon of significant heavy metal contamination in soils.

2.2 Impact of Land Use Patterns on Heavy Metal Contents

One-way ANOVA results ($P<0.05$) for total and bioavailable contents of soil Pb, Cr, Cd, and As under different land use types showed (Fig. 2 [Figure 2: see original paper]): Greenhouse facilities and park green spaces had the highest total and bioavailable Pb contents, significantly higher than other land use types, and residential area soils had significantly higher total Pb contents than reclaimed tidal flats, while reclaimed tidal flats had significantly higher bioavailable Pb contents than industrial parks. Greenhouse facility soils had significantly lower total Cr contents than other land use types, park green space soils had significantly higher bioavailable Cr contents than reclaimed tidal flats, conventional fields, and greenhouse facility soils, while residential area soils had significantly higher bioavailable Cr contents than reclaimed tidal flats and conventional fields.

Greenhouse facilities and park green spaces had significantly lower total Cd contents than other land use types, but residential area soils had significantly higher bioavailable Cd contents than reclaimed tidal flats, greenhouse facilities, park green spaces, and industrial parks. Conventional fields and greenhouse facilities had significantly higher total As contents than reclaimed tidal flats, but showed no significant differences with park green spaces, residential areas, and industrial parks, while there were no significant differences in soil bioavailable As contents under different land use types.

Overall, greenhouse facilities and park green spaces showed significant accumulation of Pb in soils, which may be related to the continuous and large input of organic and phosphate fertilizers containing heavy metal Pb in greenhouse facilities, while Pb enrichment in park green spaces is related to their soils containing large amounts of construction waste and application of domestic sludge, which also resulted in significantly higher bioavailable Cr contents in park green spaces compared to other land use types. In addition, greenhouse facilities had the lowest total and bioavailable Cd contents. The greenhouse facilities in the study area have mainly been planting *Allium tuberosum*, *Capsicum annuum* var. *grossum*, and *Lycopersicon esculentum* in recent years, which may be closely related to the absorption effect of greenhouse vegetables. In summary, differences in heavy metal input, human disturbance, crop absorption, and soil properties caused by different land use patterns have had significant impacts on soil heavy metal content status in the study area.

2.3 Spatial Distribution Prediction of Soil Heavy Metal Contents

This study used kriging for spatial distribution analysis of soil heavy metal contents and bioavailable contents. Considering that the spatial distribution of soil heavy metal contents in coastal zones is influenced by the combined effects of multi-scale natural and human factors [26], it is necessary to conduct spatial trend effect analysis on soil heavy metal contents to eliminate its impact on kriging interpolation. Table 2 lists the correlation coefficients and multiple regression models of total and bioavailable heavy metal contents with longitude and latitude coordinates (where longitude and latitude were projected and converted to distance coordinates). It can be seen that the spatial trend effect of soil heavy metal contents cannot be ignored. Total Pb, Cr, and Cd contents and bioavailable Pb contents showed extremely significant trend effects in both east-west and north-south directions ($P<0.01$), and bioavailable Cr contents also showed significant trend effects in the east-west direction ($P<0.05$). The general approach to handling trend effects is to remove them during semivariogram/covariance function modeling and then add them back during kriging prediction. Therefore, this study used universal kriging for spatial interpolation of total Pb, Cr, and Cd contents and bioavailable Pb and Cr contents, while ordinary kriging was used for spatial interpolation of total As contents and bioavailable Cd and As contents.

The Kolmogorov-Smirnov (K-S) test was used to test the normal distribution of soil heavy metal contents ($P<0.05$, 2-tailed), and the results are listed in Table 3 . The total Pb, Cr, and Cd contents and bioavailable Pb and Cr contents were residuals after removing trend effects, while total As contents and bioavailable Cd and As contents were original values. From the results of kurtosis, skewness, and normality distribution significance tests, all soil heavy metals conformed to normal distribution, meeting the requirements for geostatistical analysis. Variogram analysis showed that the spherical model better fitted the semivariance of each heavy metal, with fitting parameters as shown in Table 3.

Using the semivariogram parameters in Table 3, spatial distribution of soil heavy metal contents can be estimated. Table 4 lists the cross-validation results of spatial estimation accuracy for total and bioavailable contents of soil Pb, Cr, Cd, and As in the study area. It can be seen that the mean error (ME), root mean square error (RMSE), and average standard error (ASE) for each heavy metal indicator were relatively small, and their root mean-square standardized error (RMSSE) was close to 1, indicating that the error in spatial estimation of soil heavy metal total and bioavailable contents by kriging was small. The correlation coefficient r between predicted and measured values for each heavy metal indicator ranged from 0.46 to 0.91, all showing extremely significant correlations ($P<0.01$), indicating that the soil heavy metal content distribution obtained by kriging has relatively high accuracy and credibility, basically reflecting the spatial distribution trends of total and bioavailable heavy metal contents in the study area.

2.4 Spatial Distribution Patterns of Total and Bioavailable Soil Heavy Metal Contents

The obtained spatial distributions of total and bioavailable contents of soil Pb, Cr, Cd, and As in the study area are shown in Fig. 3 [Figure 3: see original paper] and Fig. 4 [Figure 4: see original paper], respectively. It can be seen that both total and bioavailable Pb contents showed a strip-like distribution pattern gradually increasing from east to west, i.e., gradually increasing from the coast to inland, with the highest soil Pb contents located in greenhouse facilities in the southwestern part of the study area and park green spaces in the northwestern part. The spatial distribution of total Cr content showed an overall trend of gradually decreasing from the coast to inland, with higher contents in reclaimed tidal flats and conventional fields, especially in the northeastern corner of the study area. The reason for this phenomenon is that the tidal flat area in the northeastern part of the study area has developed large-scale solar photovoltaic power generation in recent years, and solar photovoltaic panels contain large amounts of heavy metals such as Cr and Cd. In fact, the distribution of total Cd content in soils shown in Fig. 3 has spatial similarity with total Cr content. Bioavailable Cr contents were higher in park green spaces and residential areas, while bioavailable Cd contents were higher in conventional fields and residential areas, which may be caused by the impact of human disturbance activities on soil properties and heavy metal bioactivity. The spatial distribution of total and bioavailable As contents showed a patchy distribution pattern, indicating that soil As is more susceptible to small-scale human disturbance activities.

2.5 Analysis of Factors Influencing Bioavailable Soil Heavy Metal Contents

The correlations between bioavailable heavy metal contents and clay content, organic matter (SOM), cation exchange capacity (CEC), and soil pH in the study area are shown in Table 5 . It can be seen that bioavailable Pb, Cr, and Cd contents were significantly negatively correlated with clay content, cation exchange capacity, and pH, i.e., the bioavailability of heavy metals Pb, Cr, and Cd decreased with increasing clay content. Soils with higher pH had lower heavy metal bioavailability, mainly because when pH decreases, the negative charges on soil clay mineral and organic matter surfaces decrease, leading to reduced adsorption capacity for heavy metals. Soil heavy metal bioavailability decreased with increasing CEC, because the increase in cation exchange capacity enhanced soil adsorption and fixation of heavy metal ions, reducing their bioavailability.

Bioavailable Pb, Cr, and Cd contents were significantly positively correlated with organic matter, which may be related to the relatively high fulvic acid content in soil organic matter in this region. Bioavailable As content was significantly positively correlated with soil pH, but showed no significant correlation with other physicochemical properties. The reason is that the hazard degree of soil As is greatly affected by pH and redox potential. High soil pH leads to reduced As adsorption (soil pH in this study area ranged from 7.7 to 9.6), causing As-containing anions to desorb into solution and increasing water-soluble As. In low pH soils, As-containing anions can be rapidly adsorbed by positively charged iron hydroxide adsorbents in soil, reducing their bioavailability, thus bioavailable As content increases with increasing pH [27].

This study analyzed the total and bioavailable contents of major heavy metals Pb, Cr, Cd, and As in surface soils of a typical tidal flat area in Jiangsu coast. Overall, the total Pb and Cd contents in the study area soils were significantly higher than background values, while total Cr and As contents were significantly lower than background values. All sample point soils had total Cr, Cd, and As contents below the first-class soil environmental quality standard, which is consistent with the research results of Wang et al. [28]. Comparison with existing reports [29] shows that soil Pb in the study area has significantly enriched in recent years. During the 2009 sampling period, the average value of total Pb content was 14.07 $\mathrm{mg \cdot kg^{-1}}$, with no sample points exceeding the background value. In this study during the 2014 sampling period, the average value of total Pb reached 28.0 $\mathrm{mg \cdot kg^{-1}}$, and except for three sample points, all other sample points had total Pb contents higher than the background value. Although current human activity interference and land development intensity have not yet caused significant heavy metal contamination in coastal mudflat soils, soil Pb shows an obvious accumulation trend. In addition, the bioavailable heavy metal contents in this study were significantly lower than the research results of many scholars [30-31], indicating that the current environmental risk and ecological toxicity of heavy metals in this area have not reached significant levels.

This study found that land use patterns are closely related to soil heavy metal total and bioavailable contents. Greenhouse facility soils had the highest total and bioavailable Pb contents and total As content, park green spaces had significantly higher bioavailable Pb and Cr contents than other land use types, and residential area soils had significantly higher bioavailable Cd contents than other land use types. In fact, soil heavy metal sources are influenced by various factors such as soil parent material, climate, and human activities, and different human activity impacts under different land use patterns cause different heavy metal accumulations. Many studies have shown that differences in human activities significantly affect soil heavy metal contents and bioactivity [32]. Jin et al. [33] found that in coastal zones, soil heavy metal Pb contents followed the order industrial area > port > roadside > farmland > residential area > wetland, while Cr contents followed industrial area > roadside > residential area > farmland > port > wetland, and land use patterns affected soil microbial populations and activities of soil acid phosphatase and urease to different degrees. Meanwhile, other studies have shown that land use patterns affect heavy metal element contents in soils at different depths differently. Wang et al. [34] showed that the fluctuation amplitude of heavy metal content profiles in agricultural cultivated soils was more obvious than in artificial forest land, and land use patterns had the greatest impact on heavy metal element contents in the 40–60 cm soil layer.

In addition, this study found that greenhouse facility soils had the lowest total and bioavailable Cd contents. The greenhouse facilities in this study area have mainly been planting leeks, green peppers, and tomatoes in recent years. Numerous studies have shown that heavy metal Cd has relatively high mobility in soils and is easily absorbed by vegetables [35], and the application of large amounts of organic fertilizers in greenhouse facilities promotes the transformation of exchangeable Cd to loosely bound organic forms and manganese oxide-bound forms, leading to strong enrichment of Cd by leafy and solanaceous vegetables [36]. This indicates that biological absorption may be an important factor affecting soil heavy metal contents in addition to land use patterns.

This study demonstrates that the spatial distribution of heavy metals in coastal mudflat soils is controlled by natural and human factors at different scales. Spatial analysis showed that total and bioavailable heavy metal contents in the study area had obvious trend effects, and their spatial distribution was influenced by the combined effects of multiple factors at different scales, presenting an overall strip-like pattern and local patchy distribution pattern. Cheng et al. [7] found that heavy metals such as Pb and Cr in surface soils of coastal areas showed a trend of first increasing and then decreasing from the coast to inland, which differs from the results of this study and may be related to industrial layout and local land use pattern differences in the study area. Kang et al. [9] found that the general distribution pattern of heavy metal contents in coastal mudflat soils was high tide flat > mid tide flat > low tide flat, mainly because tidal action caused large amounts of fine-grained sediments to deposit on high tide flats, and fine-grained sediments had higher organic matter and heavy metal contents. Wang et al. [37] showed that heavy metals such as Pb, Cr, and Cd in surface sediments of Yancheng coastal mudflats showed strip-like spatial distribution patterns in different sections, which was closely related to tidal action, sediment particles, and pollution from corrosion of long-term marine fishing residues. This is consistent with the results of this study, which found that the spatial distribution of total and bioavailable heavy metal contents was jointly controlled by large-scale tidal action and small-scale land use patterns, showing an overall strip-like pattern, while local patchy distributions were controlled by small-scale industrial and agricultural emissions and differences in land use patterns.

This study showed that bioavailable Pb, Cr, and Cd contents were significantly negatively correlated with clay content, cation exchange capacity, and pH, and significantly positively correlated with organic matter, which is consistent with most current research results [38-39]. Zhong et al. [40] believed that soil organic matter, pH, redox potential, and soil organisms are the main factors affecting heavy metal bioavailability, and the correlation of the same factor differs for different heavy metal types and forms. In this study, the significant positive correlation between bioavailable Pb, Cr, and Cd contents and organic matter is because soil organic matter is mainly composed of biomolecules and humus (mainly humic acid and fulvic acid), and its impact on heavy metal bioavailability is achieved through electrostatic adsorption, complexation, and chelation [41]. Fulvic acid is strongly acidic and highly mobile, can significantly promote the desorption of heavy metals from contaminated soils, and increase their bioavailability, while humic acid has higher absorption capacity and can significantly reduce the dissolution of heavy metals from contaminated soils [42]. Guan [43] showed that as soil buffer capacity decreases, the soil’ s buffering capacity for heavy metals increases, and heavy metals transform from bioavailable forms to bound forms, increasing soil fixation of heavy metals and reducing heavy metal bioavailability. In addition, Liu et al. [44] found that biochar can promote the transformation of acid-soluble heavy metals to reducible, oxidizable, and residual forms, significantly reducing bioavailable heavy metal contents in soils.

Currently, the overall soil environmental quality in the study area is good. However, with the gradual advancement of coastal development, future urbanization, increased industrial and agricultural development intensity, and the introduction of some transferred industries will inevitably cause continuous changes in soil environmental quality in this area. Therefore, continuous monitoring and comprehensive management and control of soil heavy metal pollution in this area are particularly important. The correlation between soil heavy metal bioavailability and basic physicochemical properties in this study can provide reference basis for health risk assessment, heavy metal activity passivation, and pollution reduction, effectively guiding soil management to prevent heavy metals from entering the soil-plant-(animal)-human chain. For example, for industrial parks and residential areas, long-term fixed monitoring points for soil pollution should be established to systematically understand the characteristics, migration, transformation, and fate of heavy metal pollution sources, strengthen source reduction, and promote centralized treatment of industrial and domestic waste pollution sources. For greenhouse facilities and conventional fields, reasonable deployment of farmland water management, in-situ passivation, and reform of cultivation systems and other agronomic measures can be implemented, or lime can be applied to reduce heavy metal bioavailability [45-46]. For park green spaces, measures such as reducing domestic sludge application or strictly controlling entry into the food chain can be taken to achieve heavy metal source reduction and ecological control. In addition, newly reclaimed tidal flats, as important sources of reserve land, should have their development scale and intensity controlled, entry of heavily polluting enterprises should be strictly prohibited, and planting hyperaccumulator plants is an inexpensive and practical ecological restoration method.

Soil heavy metals have characteristics of complex sources, diverse occurrence forms, and strong spatiotemporal variability. This study only analyzed the distribution and influencing factors of bioavailability of total and bioavailable heavy metals in surface soils of the study area. Further research work on source characteristics, migration and transformation, form fate, and spatiotemporal evolution of soil heavy metals in this area needs to be carried out through long-term in-situ monitoring.

Conclusions

The total Pb and Cd contents in the study area soils were significantly higher than background values ($P<0.01$). Bioavailable content analysis showed that the environmental risk and ecological toxicity of Pb, Cr, Cd, and As in the study area have not reached significant levels. Currently, the soil environmental quality status in the study area is good, with no phenomenon of significant heavy metal contamination, but soil Pb, Cr, Cd, and As have shown accumulation trends, especially for Pb element.

Land use patterns had varying degrees of impact on the total and bioavailable contents of different heavy metals. Greenhouse facilities and park green spaces had the highest total and bioavailable Pb contents, residential and industrial areas had relatively high total and bioavailable Cr contents, greenhouse facilities had the lowest total and bioavailable Cd contents, and land use patterns had little impact on total and bioavailable As contents.

The study area soils showed significant trend effects for total Pb, Cr, and Cd contents and bioavailable Pb and Cr contents. Spatial analysis revealed that the distribution of total and bioavailable heavy metal contents in the study area was controlled by multiple factors at different scales, showing an overall strip-like pattern, while local patchy distributions were controlled by small-scale industrial and agricultural emissions and differences in land use patterns.

Bioavailable Pb, Cr, and Cd contents were significantly negatively correlated with clay content, cation exchange capacity, and pH, and significantly positively correlated with organic matter. Bioavailable As content was significantly positively correlated with soil pH but showed no significant correlation with other physicochemical properties. The correlation between heavy metal bioavailability and physicochemical properties can provide a basis for heavy metal activity passivation and pollution reduction.

References

[8] Gao J H, Li J, Wang H V, et al. Distribution and their pollution assessment of heavy metals in the sediments of the Yalu River Estuary and its adjacent coastal waters[J]. Acta Oceanologica Sinica, 2009, 28(6): 12-23

[9] Kang Q S, Zhou J Z, Wu Y, et al. Distribution and research situation of heavy metals in tidal wetlands of Changjiang Estuary[J]. Marine Environmental Science, 2003, 22(3): 44-47

[10] Chang J N. Research of heavy metal pollution in intertidal flat of the Changjiang estuary and their source identification[D]. Shanghai: Eastern China Normal University, 2006

[11] Li Y, Zhang H B, Chen X B, et al. Distribution of heavy metals in soils of the Yellow River Delta: Concentrations in different soil horizons and source identification[J]. Journal of Soils and Sediments, 2014, 14(6): 1158-1168

[12] Zhao K L, Fu W J, Dai W, et al. Characteristics and quantitative model of heavy metal transfer in soil-rice systems in typical rice production areas of Zhejiang Province[J]. Chinese Journal of Eco-Agriculture, 2016, 24(2): 226-234

[13] Li J L, Jiang X, Wang S H, et al. Heavy metal in sediment of Danjiangkou Reservoir: Chemical speciation and mobility[J]. China Environmental Science, 2016, 36(4): 1207-1217

[14] He J, Chen X, Wang X Q, et al. The absorption and accumulation of heavy metals Cu, and Pb in tidal wetland sediments by plant *Suaeda heteroptera*

Kitag[J]. Journal of Dalian Fisheries University, 2012, 27(6): 539-545

[15] Griffiths B S, Hallett P D, Kuan H L, et al. Biological and physical resilience of soil amended with heavy metal-contaminated sewage sludge[J]. European Journal of Soil Science, 2005, 56(2): 197-206

[16] Zhang L H, Du Y F, Wang D D, et al. Distribution patterns of heavy metals in the *Spartina alterniflora* salt-marsh wetland of Rudong, Jiangsu Province[J]. Environmental Science, 2014, 35(6): 2401-2410

[17] Tang D H, Zou X Q, Liu X J, et al. Integrated ecosystem health assessment based on eco-exergy theory: A case study of the Jiangsu coastal area[J]. Ecological Indicators, 2015, 48: 142065

[18] Wang L, Coles N A, Wu C F, et al. Spatial variability of heavy metals in the coastal soils under long-term reclamation[J]. Estuarine, Coastal and Shelf Science, 2014, 151: 310-317

[19] Zhang H, Lu R, Shi W, et al. Application of RBF neural network in determining soil heavy metal spatial variability[J]. Chinese Journal of Eco-Agriculture, 2012, 20(4): 474-479

[20] Lü J S. The environmental geochemistry of heavy metals in soils and sediments in typical regions of Jiangsu coastal zone, Eastern China[D]. Nanjing: Nanjing University, 2015

[21] Yang Z F, Wang Y, Shen Z Y, et al. Distribution and speciation of heavy metals in sediments from the mainstream, tributaries, and lakes of the Yangtze river catchment of Wuhan, China[J]. Journal of Hazardous Materials, 2009, 166(2/3): 1186-1194

[22] Wang B, Huang B, Qi Y B, et al. Effect of air drying on speciation and plant availability of heavy metals in flooded rice paddies[J]. Transactions of the Chinese Society for Agricultural Machinery, 2013, 44(5): 89-95

[23] Davidson C M. Methods for the determination of heavy metals and metalloids in soils[J]. Environmental Pollution, 2013, 22: 97-140

[24] Tang F J, Zu Y Q. Research methods of spatial variability of heavy metals in soil[J]. Journal of Yunnan Agricultural University, 2008, 23(4): 558-561

[25] Chen B B, Hu R Q, Chen M D. The natural background values of environmental elements in the beach soils of Jiangsu Province[J]. Journal of Nanjing Agricultural University, 1985, 8(3): 54-60

[26] Hao L H, Zhang D M, Wu P F, et al. Spatial distribution of heavy metal content in the farmlands of Hainan Island[J]. Chinese Journal of Eco-Agriculture, 2009, 17(2): 230-234

[27] Yang J K, Barnett M O, Zhuang J, et al. Adsorption, oxidation, and bioaccessibility of As ( ) in soils[J]. Environmental Science & Technology, 2005, 39(18): 7102-7110

[28] Wang J J, Huang Y, Huang X, et al. Ecological risk assessment of heavy metals in surface sediments in Yancheng coastal mudflat[J]. Marine Science Bulletin, 2015, 34(3): 353-360

[29] Yao R J, Yang J S, Meng Q F, et al. Heavy metal content and pollution assessment of mudflat soils in the coastal area of northern Jiangsu Province[J]. Research of Environmental Sciences, 2012, 25(5): 512-518

[30] Yu W J, Zou X Q. The distributional characteristics of heavy metal in Jiangsu Province shoal sea[J]. Journal of Environmental and Public Health, 2013, 2013: 142065

[31] Fu J, Wang H, Billah S M R, et al. Heavy metals in seawater, sediments, and biota from the coastal area of Yancheng City, China[J]. Environmental Toxicology and Chemistry, 2014, 33(8): 1697-1704

[32] Wang J, Chen Z L, Wang C, et al. Heavy metal content and ecological risk warning assessment of vegetable soils in Chongming Island, Shanghai City[J]. Environmental Science, 2007, 28(3): 647-653

[33] Jin Z G, Shi W J, Gao Y, et al. Distribution of heavy metals and changes of soil biological activity under different land use patterns[J]. Journal of Soil and Water Conservation, 2009, 23(3): 74-77

[34] Wang L J, Pang J L, Ding M. Features and effects of heavy metals under different land use patterns[J]. Journal of Shaanxi Normal University: Natural Science Edition, 2010, 38(4): 88-93

[35] Fang H W. Cadmium uptake by different vegetable cultivars and their root morphological traits[D]. Wuhan: Huazhong Agricultural University, 2011

[36] Xue Y, Shen Z G, Zhou D M. Difference in heavy metal uptake between various vegetables and its mechanism[J]. Soils, 2005, 37(1): 32-36

[37] Wang J J, Zuo P, Huang Y, et al. Distribution characteristics and assessment of heavy metals in surface sediments along Xinyanggang estuary in Yancheng[J]. Environmental Protection Science, 2013, 39(5): 57-62

[38] Li Z Y, Zhang C L, Deng C B, et al. Analysis on spatial distribution of soil available heavy metals and its influential factors in a lead-zinc mining area of Guangxi, China[J]. Ecology and Environmental Sciences, 2009, 18(5): 1772-1776

[39] Walker D J, Clemente R, Bernal P M. Contrasting effects of manure and compost on soil pH, heavy metal availability and growth of *Chenopodium album* L. in a soil contaminated by pyritic mine waste[J]. Chemosphere, 2004, 57(3): 215-224

[40] Zhong X L, Zhou S L, Huang M L, et al. Chemical form distribution characteristic of soil heavy metals and its influencing factors[J]. Ecology and Environmental Sciences, 2009, 18(4): 1266-1273

[41] Dean J R. Heavy metal bioavailability and bioaccessibility in soil[J]. Methods in Molecular Biology, 2009, 599: 15-36

[42] Guo X F, Wei Z B, Penn C J, et al. Effect of soil washing and liming on bioavailability of heavy metals in acid contaminated soil[J]. Soil Science Society of America Journal, 2013, 77(2): 432-441

[43] Guan X. Effects of soil buffer capacity on heavy metal bioavailability in soil[D]. Shenyang: Shenyang University, 2014

[44] Liu J J, Yang X, Lu K P, et al. Effect of bamboo and rice straw biochars on the transformation and bioavailability of heavy metals in soil[J]. Acta Scientiae Circumstantiae, 2015, 35(11): 3679-3686

[45] Zhao Z, Tang Z J, Yang K, et al. Metal transportation and accumulation in sandy soil amended by fly ash and PAM[J]. Transactions of the Chinese Society for Agricultural Machinery, 2013, 44(7): 83-89

[46] Abd El-Azeem S A M, Ahmad M, Usman A R A, et al. Changes of biochemical properties and heavy metal bioavailability in soil treated with natural liming materials[J]. Environmental Earth Sciences, 2013, 70(7): 3411-3420

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.