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Effect of long-term fertilization on element contamination (Pb, Cd, Cu, Zn, Ni and Cr) and environment risk assessment in the Meadow Black Soil in China

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Abstract. To identify the effect of fertilization on the heavy metal concentration and assess the soil environmental quality, Meadow Black Soil (MBS) samples were collected from Long-term location fertilization base located in the Changchun City, Jilin Province of China. Subsequently, MBS samples were analyzed to determine the total concentrations of specific elements (Pb, Cd, Cu, Zn, Ni and Cr), for which data were available for 1984, 1989 and 2012. Under long-term location fertilization conditions, this investigation revealed that the mean concentrations of Pb, Cd, Cu, Zn, Ni and Cr exceeded their corresponding background values and the accumulations of Pb and Cd were readily apparent in the MBS and were beyond of the second grade of China soil standards. Pb and Cd were accounted for mainly by chemical fertilizers. In addition, the accumulations of Cu, Zn, Ni and Cr did not appear to reach pollution levels, and no obvious pollution was observed in the MBS. Significant correlations were observed between Pb and Cd, Cu and Ni, Cu and Cr, Ni and Cr, suggesting that they might originate from a common source. However, Pb and Ni, Cu and Zn showed negative correlations, suggesting a different source. The quality of the soil environment and the heavy metal pollution were evaluated by the Single-Pollution Index and Nemerow-Pollution Index method. Each treatment soil sample had a low or slight pollution index (*PI*) of Cu, Zn, Ni and Cr， whereas the *PI* values of Pb and Cd were high, and samples were classified as being moderately or heavily contaminated by Pb and Cd. Although practically uncontaminated by Cu, Zn, Ni and Cr, a potential danger may emerge in the future depending on the agricultural activities in this region. The results of heavy metal assessment in the MBS will be helpful for the formulation of strategic sustainable agriculture in Jilin Province and improvement of corn quality and safety.

Introduction

In China, heavy metal pollution in agricultural soils has become serious with the rapid industrialization, urbanization and increases in the release of agrochemicals into the environment during the last two decades[1,2]. Soils in many regions have been polluted by various pollutants in different levels. Soil pollution could be harmful for human health. For example, it could cause toxicity, cancer, and gene mutation. Specifically, the soil heavy metal pollution is one of the most important issues because of the innate traits of heavy metals. Some researchers have indicated the need for a better understanding of suburban agricultural soil pollution[3,4], and, indeed, increasing researches have focused on heavy metals in suburban farmland soils. Jilin Province is one of China's most important agricultural regions and also is an important corn production base. In 2014, the grain yield reached 70.656 billion tons, accounting for 5.82 % of the total yield in China, which continued to be in the fourth in China. However, continuous corn planting for many years has caused the decline of soil fertility. So, some chemical fertilizers have to been applied into the soils to improve the corn yield every year. Chemical fertilizers and organic manure were important measures to improve soil productivity and ensure high grain yield[5]. This fact has increased the fertilizer consumption in each crop year. During the 1960s, approximately 46 million tons of fertilizers were used, and in 2030 it was estimated that 157.3 million tons of them will be necessary for crops throughout the world[6,7].

The mineral and chemical raw materials used in production of chemical fertilizers contain a variety of heavy metals, radioactive elements and other harmful ingredients. These matters that crops do not need will accumulate in the soils and may cause the soil contaminated. The high-content heavy metals in fertilizers will cause soil quality degradation[8]. This common operational pattern has caused some concerns about potential contamination of heavy metals in soils[9,10]. Reportedly, one major cause to heavy metal pollution [11] was overuse of chemical fertilizers in farmlands, which exceeded the nutrition levels demanded by crops[12,13]. Commercial nitrogen fertilizers such as urea, ammonium bicarbonate and ammonium nitrate are synthesized directly by chemical companies and have very low contents of heavy metals. Phosphorus fertilizer was one of the important sources for heavy metals in agro-soils.

In addition to inorganic fertilizer applications, organic fertilizers also were applied in the soil in order to improve the water and fertilizer holding capacity of the soil. In the production, corn straws often were returned back to the soil by covering the soil or plowing into the soil in Jilin Province. Straw incorporation has been considered an effective means of increasing the efficiency of nutrient cycling, and thereby reducing the extent of fertilizer application[14]. After returning the soils, the corn straws would be decomposed gradually through the microbial processes and further formed soil humus[15,16]. Humus could complex with the heavy metals in the soil solution and affected the heavy metal speciation by changing the chemical property of the soil solution, such as pH, Eh, etc [17]. A number of studies have demonstrated that long-term application of inorganic and organic fertilizer significantly increased the heavy metal contents in the soil surface[18]. The farmland soils in some areas have even been polluted by heavy metal accumulation[2]. Lead, cadmium and zinc represent a subset of the most frequently reported metal contaminants in soils. These metals, many of which co-occurred at the same site, had the deleterious effects to food supply and human health [19]. In view of these facts, it becomes necessary to assess the impact of the long-term fertilization on the contamination rate and distribution of heavy metals such as Pb, Cd, Cu, Zn, Ni and Cr.

Meadow Black Soil (MBS) is a major soil type for corn production and the studied region is representative of the MBS in Jilin province. To date, little research on the accumulative properties of heavy metals in the MBS after long-term fertilization has been conducted. Soils were sampled from the long location experimental base with different fertilization treatments. In the present manuscript, the effects of long-term fertilization on heavy metal contamination in the meadow black soil in China were investigated by measuring the heavy metal concentrations in the soil samples in two different years after long-term use of chemical fertilizers ($CO(NH_2)_2$, $Ca(H_2PO_4)_2$ and K_2SO_4). The risks posed by these heavy metals were evaluated by the single-pollution index and Nemerow-pollution index. This will provide knowledge of the distribution of these metals in soils and then evaluate the environmental impact caused by long-term fertilizer application. The results obtained in this work provide a scientific basis estimates for soil environmental quality and reasonable fertilization techniques for high yield and high quality corn production.

Materials and methods

Study area and experiment design

The long-term location experiment began in 1984 in the Agricultural Science Experimental Base in the Jilin Agricultural University (123°29′352″E and 42°04′001″N; average altitude 211 m). The area belongs to temperate zone sub-humid climate with a mean annual temperature, precipitation and evaporation of about 5 ℃, 600mm and 1300mm, respectively. The Experimental Base covers an area of 300 m^2. A randomized block experimental design was used in uniform grids 2m^2, and each grid center was a sampling point with three replications. The long-term fertilization experiments were designed by four different inorganic fertilizer doses (CK, N 150 kg/hm^2 , P_2O_5 75 kg/hm^2 , K_2O 75 kg/hm^2) and three different corn doses (0 kg/m^2 , 0.25 kg/m^2 , 0.5 kg/m^2) for a total of 12 treatments and 36 experimental plots. N, P, K were added as $CO(NH_2)_2$(N 46%), $Ca(H_2PO_4)_2$(P_2O_5 46%) and K_2SO_4(K_2O 50%)**,** respectively. All of P, K and 1/3 N fertilizers were applied into soil before sowing as base fertilizers and 2/3 N fertilizers were applied during Corn Big Trumpet Period. The average concentrations of the heavy metals in the three fertilizers were measured and listed as Table 1.

Table1 The concentration of heavy metal in the fertilizer[mg/kg]

Fertilizers	Pb	Cd	Cu	Zn	Ni	Cr
$CO(NH_2)_2$	0.25	0.03	0.28	2.34	0.25	*23.98*
$Ca(H_2PO_4)_2$	15.8	0.63	8.32	45.27	1.37	40.62
K_2SO_4	0.83	0.05	1.30	4.47	0.38	27.53

Note: each fertilizer had 6 samlpes.

Sampling and analysis

Topsoil samples (0-20 cm) were collected from 36 different grids in 1984, 1989 and 2012, respectively. At each point, soil sample was 1kg in weight, which was combined five sub-samples and then reduced to about 1 kg with sample quartering in the field. All soil samples were air-dried at room temperature, and then ground, sieved through a 2 mm nylon sieve to remove coarse materials and other debris. Then a portion of each sample was further ground until all particles passed through a 0.15 mm nylon sieve.

For the analysis of total heavy metal concentrations, one gram of each dry soil sample was digested by using acid digestion method according to the standard, GB15618[20]. The concentrations of heavy metals in the extractants were measured using flame atomic adsorption method or graphite furnace atomic adsorption method (AAS 700 equipped with GFAAS, PerkinElmer, USA).

The background values of soil environmental quality

Up to 1984, the studied experimental area had been little interfered by anthropogenic activities and could basically represent the original characteristics of the MBS. Compared to Jilin soil background (Table 2), it could be found that the contents of all elements in 1984 were similar to or lower than the background value. The contents of Pb, Cu and Ni were slightly more than the background value of soil. In order to make the background value more representative, the measured values in 1984 were selected as region background value of soil environment quality.

Table 2 Background values and detected concentration In 1984 of MBS [mg/kg]

	Pb	Cd	Cu	Zn	Ni	Cr
Detected concentration In 1984	38.7	0.104	21.9	67.7	28.5	42.7
background values	28.8	0.099	17.1	80.4	21.4	41.4

Assessing long-term accumulation of heavy metals using model approach

To assess the soil environment quality, Single-Pollution Index (PI)[21] of each metal and an Integrated-Pollution Index (IPI) (also called Nemerow Pollution Index)[22, 23]of the six metals were used. The PI was defined as the ratio of the heavy metal concentration in the study to the background concentration (BC). They were computed using the following equations:

$$\text{Single-Pollution Index} \quad PI = C_i / S_i \qquad (1)$$

Where PI——is the pollution index of a given heavy metal in the meadow black soil, C_i——is the measured concentration of the given heavy metal in meadow black soil, S_i——is the background concentration.

PI$\leq$1 indicates that the soil is uncontaminated; PI > 1 indicated that the soil has been contaminated. In detail, the PI of each metal is calculated and classified as either low (PI < 1), middle (1 < PI < 3) or high (PI > 3). The greater PI indicates the heavier heavy metal pollution.

First of all, the pollution of each heavy metal was analyzed using the Single- Pollution Index. Then, the integrated pollution levels of heavy metals were divided by the integrated pollution index.

$$\text{Integrated-Pollution Index} \quad IPI=[P_{ave}^{2}+P_{max}^{2}/2]^{1/2} \qquad (2)$$

Where IPI──is the Integrated-Pollution Index for MBS, P_{ave}── is the average value of all the P_i P_{max}──is the maximum among all the PIs.

IPI can not only show the integrated effect of all Single-Pollution Index on the soil quality but also highlight the effect of the worst index on the soil quality. The greater IPI indicates the more severe integrated pollution in this area. The integrated pollution degree of the soil by the heavy metals could be concluded by the following Table 3 .

Table 3 Classification standard of Integrated-pollution Index (*IPI*) for the soil quality

Classification	IPI	Scale of pollution
I	IPI ≤ 0.7	Practically uncontaminated
II	0.7 < IPI ≤ 1	Uncontaminated to moderately contaminated
III	1 < IPI ≤ 2	Moderately contaminated
IV	2 < IPI ≤ 3	Moderately to heavily contaminated
V	IPI > 3	Heavily contaminated

All of the above statistical calculations were carried out with SPSS 13.0 and Origin 6.0 software.

Results and Discussion

Physico–chemical properties of the Meadow Black Soil

The effects of long-term fertilization on some basic soil physic-chemical properties were listed in Table 4. Apparently, pH decreased to different degrees from initial values, where pH was reduced by 0.87 after N treatment without corn straw addition. Organic carbon contents after treatments ranked in the order of $S_{0.5}$ > $S_{0.25}$ >CK, which suggested that straw rotation could increased the organic matters in the MBS. Total N, P and K were all increased by adding N fertilizer, P fertilizer and K fertilizer, respectively. Available N, P and K contents changed in the same way as total N, P and K.

Table 4 Physico–chemical properties of the Meadow Black Soils in 1984 and after 28 years fertilizer application

Treatments	Organic carbon[g/kg]	pH	Total N[g/kg]	Available N[g/kg]	Total P[g/kg]	Available P [g/kg]	Total K[g/kg]	Available K [g/kg]
Initial value	22.80	7.12	1.39	125.0	0.53	13.6	23.10	218.0
CK	21.47	6.93	1.20	115.9	0.37	9.7	21.93	159.4
N	21.98	6.25	1.41	138.2	0.37	10.5	21.60	139.3
P	21.69	6.59	1.33	96.5	0.68	24.8	22.99	119.5
K	22.00	6.61	1.25	112.8	0.36	11.2	24.02	249.4
$S_{0.25}$	30.47	7.11	1.34	111.7	0.61	15.2	22.35	219.5
$N+S_{0.25}$	31.08	6.43	1.45	141.5	0.59	18.7	22.23	202.5
$P+S_{0.25}$	30.67	6.67	1.28	115.6	0.69	22.3	22.17	209.6
$K+S_{0.25}$	30.81	6.73	1.35	118.4	0.63	15.2	24.49	259.5
$S_{0.5}$	31.82	7.16	1.31	116.7	0.65	12.8	23.10	239.4
$N+S_{0.5}$	33.12	6.61	1.41	140.5	0.72	15.3	23.09	179.4
$P+S_{0.5}$	31.45	6.75	1.27	126.4	0.81	21.2	23.10	229.5
$K+S_{0.5}$	31.89	6.71	1.25	123.4	0.75	17.4	24.35	279.7

Effect of long-term fertilization on heavy metal accumulation in the MBS

Total contents of Pb, Cd, Cu, Zn, Ni and Cr in the MBS after different fertilizations were showed from Fig.1 to Fig.6. Considering the convenient comparison, soil quality second grade standard guidelines (Table 5) for the heavy metals were also shown in the figures.

The Pb and Cd contents for most of treatments were greater than the second grade of China soil standards (GB 15618-1995). In 1989, the contents of Pb and Cd in the MBS were about twice of the soil background level in Jilin Province. After 23 years long-term continuous fertilizations, the total Pb and Cd contents for each treatment were significantly different, which were increased from 37% to 205%, 9%-146%, respectively. And this increase followed the order as P > K > N > CK. The raw material for phosphate fertilizers was phosphate rock, which contained a certain amount of Pb and Cd [24]. Concentrations of heavy metals including Pb and Cd in potassium and nitrogen fertilizers were rather low[25] and were not regarded as significant contributors to their accumulation in cropland soils. In China, phosphate rocks contained 0.7-4.0 mg/kg Cd on average, of which 70-80% will finally be transmitted to phosphate fertilizers After application of phosphate fertilizers, total Cd and available Cd in soil would be increased[26]. The environmental capacity of Cd was very low compared with Pb, Cu and Zn. So, a slight increase of total Cd in soil would improve the total Cd content in crops and thus potentially harm human health. Therefore, attention should be given to the potential pollution caused by Cd containing fertilizers.

Table 5 The soil environmental quality standards [mg/kg]

Grade	Natural background in Jilin province	First grade Natural background	Second grade	Third grade
Pb ≤	28.8	35	80	500
Cd ≤	0.1	0.20	0.45	1.00
Cu ≤	17.1	35	100	400
Zn ≤	80.4	100	250	500
Ni ≤	21.4	40	90	200
Cr ≤	41.4	90	200	300

When the amounts of Pb exceeded purification ability of plant and soil, Pb would accumulate in soil [27,28]. From Fig.1, it can be found that corn straw mineralization after decomposing was beneficial to the Pb accumulation. After several decades' rotation to the soil, Pb at the μg/g level in straw also could increase its contents in soil[29]. So, with the amount of straw application increased, Pb contents in the MBS increased slightly. The content of Pb and Cd in CK treatment (kg/m^2 corn doses) was greater in 2012 than that of 1989, which indicated that environmental factors had contributed to Pb and Cd accumulation. Heavy metals in the agriculture soil are derived from different anthropogenic sources, such as automobile exhaust emission, chemical fertilizer pollution, and atmospheric deposition. Coal power plants and motor vehicle exhaust fumes were the main emission sources[30]. The extensive use of coal as a source of energy and motor vehicle fuel containing Pb in Changchun City of Jilin Province were widespread, from which Pb and Cd could reach soil through the deposition of dust particles, resulting in greatly enhanced levels.

Cu and Zn are the trace elements needed by plants for maintenance of normal living activities, and are the components of catalysts of various enzymes. Cu and Zn are widely involved in various living activities, but Cu and Zn over a certain level will cause negative effects on plants, such as disorders of metabolic processes, blocking of growth and development, and even death. As can be seen from Fig. 3, the initial Cu content in MBS was similar, for each treatment within 20-26 mg/kg. The content of Cu reached to 21-29 mg/kg after the 23 years fertilizations, which increased by 1.15-18.46 %. Corn straw rotation had a few effect on the Cu accumulation in the MBS. The Cu contents were equal to or even lower than the natural background value (35mg/kg), which showed that the existing fertilizer methods would not cause the Cu accumulation in the MBS.

Figure 4 showed that the differences of Zn contents for CK treatments were not significant in the last 23 years period with different corn straw doses, which indicated no positive effects of these treatments on Zn accumulation. For all the treatments, Zn contents in the MBS had not exceeded the background value of soil environment. For the treatments with N and K application, a decreasing effect (9.25%-11.13%, 1.73%-11.87%) on Zn accumulation was observed. The Zn contents after P fertilizer application remained constant, only the Zn content was decreased by 8.2% without corn straw addition. Zinc was the necessary trace element for corn growth and corn was considered susceptible to Zn deficiency[31]. Large amounts of Zn had been removed from the soil through plant harvesting. Although there was more zinc in P fertilizer than that of N and K fertilizers, zinc would format phosphate precipitation and was not available to corn[32].

The natural background values of Ni and Cr from the soil environment quality standard were 40 mg/kg and 90 mg/kg, respectively. The chemical fertilization and straw rotation in the MBS improved the Ni and Cr contents by 30.52%-33.39 %, and 4.88%-40.08 %, respectively. These cumulative effects were slow, so the content of Ni and Cr were not beyond the natural background value of soil after 23 years continuous fertilization.

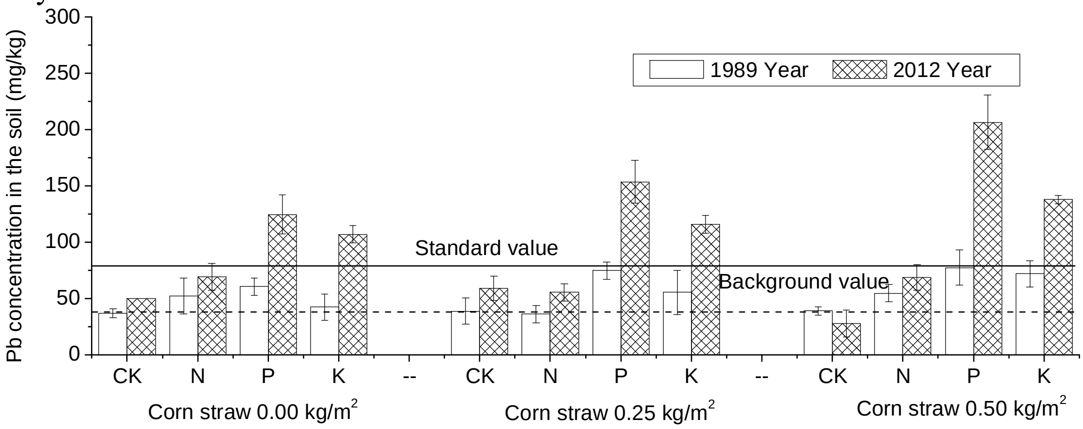

Fig.1 Effects of different fertilizer treatments on Pb concentration of MBS

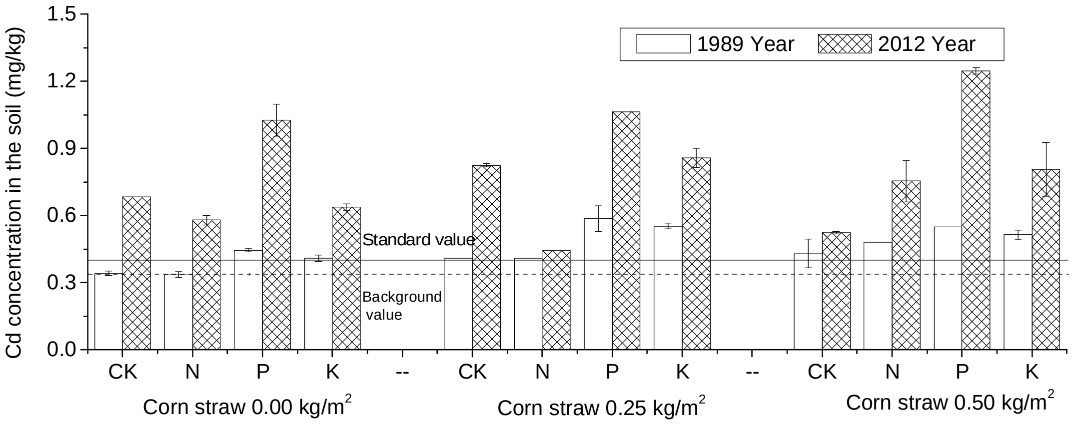

Fig.2 Effects of different fertilizer treatments on Cd concentration of MBS

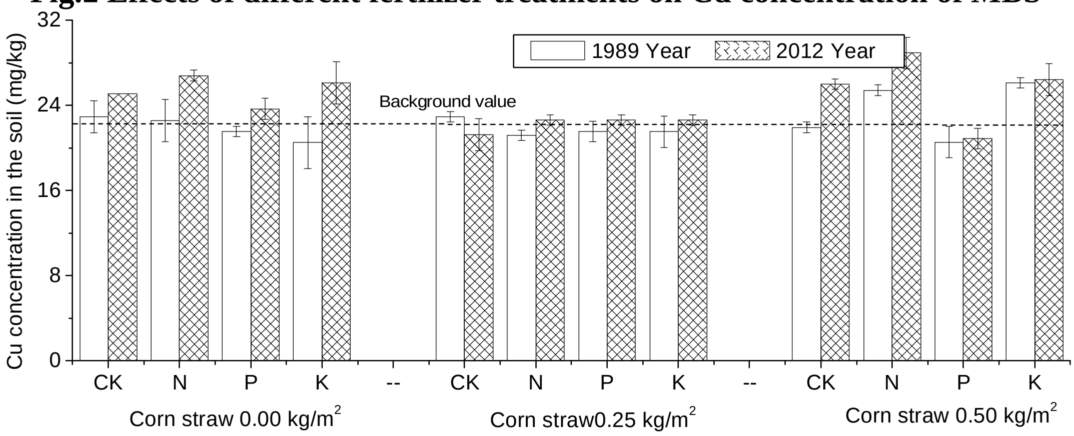

Fig.3 Effects of different fertilizer treatments on Cu concentration of MBS

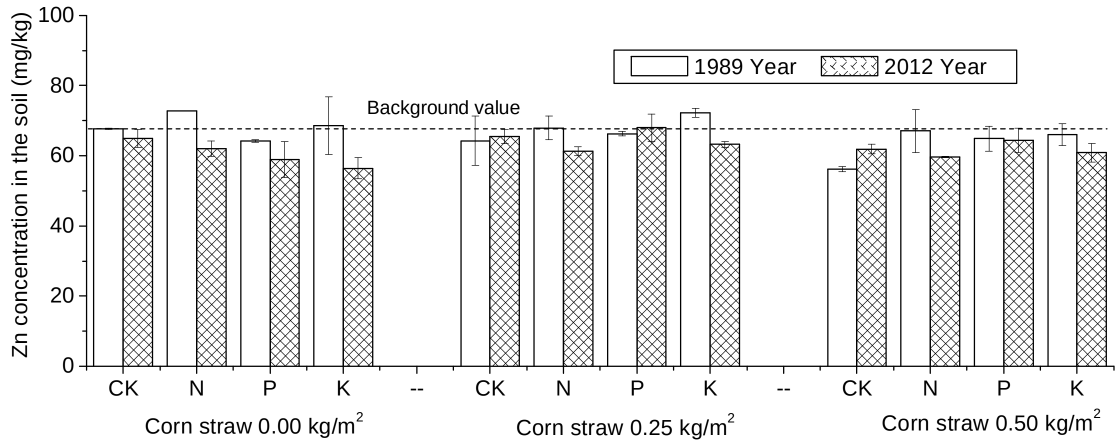

Fig.4 Effects of different fertilizer treatments on Zn concentration of MBS

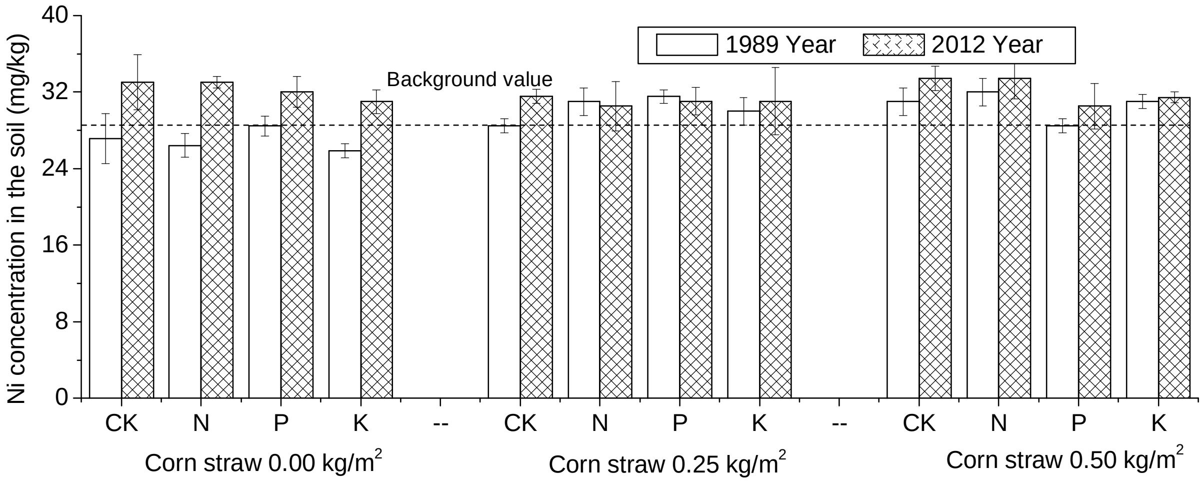

Fig.5 Effects of different fertilizer treatments on Ni concentration of MBS

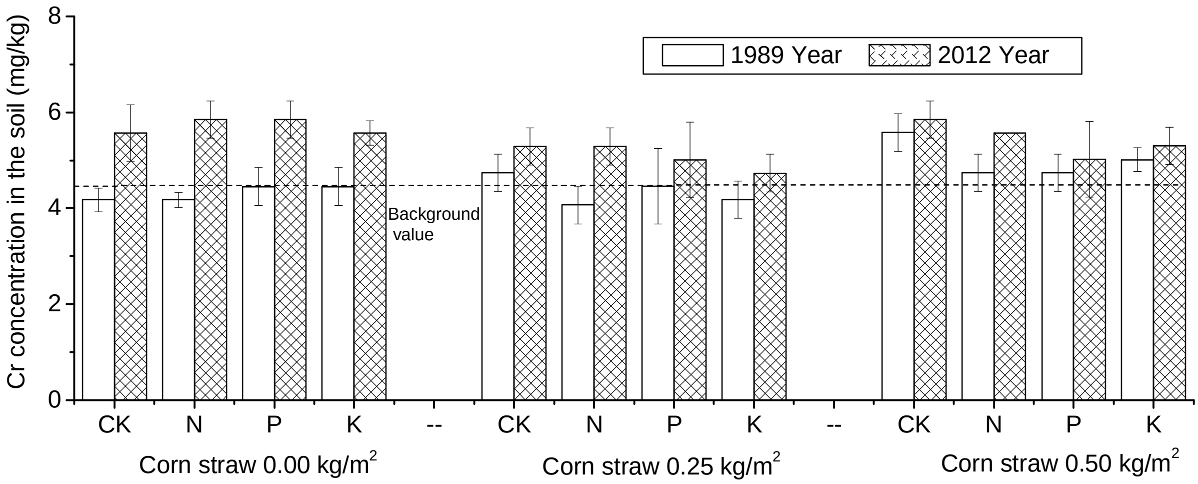

Fig.6 Effects of different fertilizer treatments on Cr concentration of MBS

To assess the effects of long-term fertilization on soil environmental quality

The PIs, calculated according to the BC of heavy metals, varied greatly across the different heavy metals (Table 6). Zn and Cr exhibited lower values, ranging from 0.83 to 1.00 and from 0.83 to 1.03, respectively. For Zn and Cr, the mean PIs were 0.92, 0.95 and all of the samples had low or mid-level PIs, indicating that the concentration of Zn and Cr in the long-term fertilization application soil samples were comparable with the BC of the MBS of Jilin Province. The mean PIs for Cu and Ni were 1.11 and 1.12, respectively and slightly more than 1. But the PIs for most of samples were close to or slightly greater than 1 with the max value 1.32 and 1.17, min value 0.95 and 1.07, respectively. The PI value of

Cd ranged from 1.31 to 3.66 were classified as being moderately or heavily contaminated. Pb also exhibited higher PI values, ranging from 0.71 to 5.33 moderately or heavily contaminated.

The IPIs of all the treatments varied from 1.50 to 4.34 with an average of 2.47. There was no IPI less than 1, suggesting no clean soil in the location experimental base after long-term fertilization. The IPIs of CK, N, N+$S_{0.25}$ and $S_{0.5}$ treatments were between 1 and 2. The IPIs of P, K, $S_{0.25}$, K + $S_{0.25}$ and N+$S_{0.5}$ treatments were between 2 and 3. The IPIs of P+$S_{0.25}$, P+$S_{0.5}$ and K+$S_{0.5}$ treatments were greater than 3, indicating the presence of heavily heavy metal pollution. Thus the soil quality of long-term location fertilizer application has clearly been impacted, particularly P fertilizer application.

Table 6 Parameters of the Single-Pollution Index and Integrated-Pollution Index for the heavy metals 2012

Straw does [kg/m^2]	Treatments	P_{Pb}	P_{Cd}	P_{Cu}	P_{Zn}	P_{Ni}	P_{Cr}	*IPI*
0.00	CK	1.29	2.01	1.14	0.96	1.16	0.98	1.90
	N	1.79	1.71	1.22	0.92	1.16	1.03	1.82
	P	3.21	3.02	1.08	0.87	1.12	1.03	2.85
	K	2.76	1.88	1.19	0.83	1.09	0.98	2.43
0.25	CK	1.52	2.42	0.97	0.97	1.11	0.93	2.16
	N	1.43	1.31	1.03	0.91	1.07	0.93	1.50
	P	3.96	3.13	1.03	1.00	1.09	0.88	3.36
	K	2.99	2.52	1.03	0.93	1.09	0.83	2.63
0.50	CK	0.71	1.54	1.18	0.91	1.17	1.03	1.54
	N	1.77	2.22	1.32	0.88	1.17	0.98	2.10
	P	5.33	3.66	0.95	0.95	1.07	0.88	4.34
	K	3.56	2.37	1.20	0.90	1.10	0.93	3.02
Max		5.33	3.66	1.32	1.00	1.17	1.03	4.34
Min		0.71	1.31	0.95	0.83	1.07	0.83	1.50
Mean		2.53	2.32	1.11	0.92	1.12	0.95	2.47

Correlation analysis of the six heavy metals

The correlations between heavy metals can represent the pollution or source similarity of heavy metals[33,34]. The correlations between the six kinds of heavy metals of the soils in 2012 were analyzed and the result indicated that the relative coefficients (n=12, $p < 0.05$) for Pb and Cd, Cu and Ni, Cu and Cr, Ni and Cr were 0.855, 0.710, 0.616 and 0.722, respectively, suggesting that these heavy metals might originate from a common source, such as agricultural activities. Pb and Ni, Cu and Zn had the negative correlations with the relative coefficients -0.632 and -0.569, suggesting that they had a different source. There were no correlations among the other elements. This result showed that the source of Pb and Cd in the Meadow Black Soil was consistent. Considering the heavy metal content analysis above, the contents of Pb and Cd increased dramatically after long-term fertilization, which indicated that fertilizer application was the dominant source of Pb and Cd. It could be concluded from the correlation analysis that the pollution or source of Cu, Ni and Cr was similar. But the long-term fertilizer application has a little bit effect on the content increase of Cu, Ni and Cr. Because the contents of Cu, Zn, Ni and Cr were close to the background value, the source for these heavy metals was likely the parent soil materials.

Conclusions

This investigation revealed that long-term fertilization improved the total contents of heavy metals in the Meadow Black Soil from long-term location experimental case in Jilin Province. After fertilization, the contents of Pb and Cd had an obvious increase. For the other four heavy metals, the mean concentrations of Cu, Zn, Ni and Cr exceeded their corresponding background values, but did not result in a significant increase. Significant correlations were observed between Pb and Cd, Cu and Ni, Cu and Cr, Ni and Cr, suggesting that they might originate from a common source. However, Pb and Ni, Cu and Zn showed negative correlations, suggesting a different source. Based on the Single-Pollution Index and Integrated-Pollution Index, all treatments of the MBS had low or slight PIs of Cu, Zn, Ni, Cr. However, Pb and Cd exhibited high PI values, and the soils were classified as being moderately or heavily contaminated with Pb and Cd. Although practically uncontaminated by Cu, Zn, Ni and Cr, a potential danger might emerge in the future depending on the agricultural activities in this region. Therefore, the soil quality in most of the long-term location base has deteriorated, further highlighting the importance of conducting more studies related to the application of mineral fertilizers for accumulation of heavy metals. These findings indicate that more attention should be paid to reducing the accumulation of heavy metals in soils by more rational use of fertilizers for long-term continuous crop production.

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