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Spatial variations of Pb in the vertical zone of the soil-plant system in the Changbai Mountain National Nature Reserve

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Abstract: The characteristics of vertical and horizontal variations of lead element(Pb) in soil-plant system of vertical zone in Changbai Mountain National Nature Reserve(CNNR) were studied. The results showed that Pb concentrations in soils of vertical zone are all above 25 mg/kg, and the average Pb concentration of each soil zone negatively correlates its degree of variation, i.e. brown coniferous forest soil zone has the lowest average Pb concentration of four soil zones, and the highest horizontal variation; however, mountain soddy forest soil has the highest average Pb concentration, and the lowest horizontal variation; the average concentration of plant Pb of each plant zone is lower than the worldwide average level of Pb in plant(Clarke), respectively, and plant Pb content order is consistent with soil Pb content order, but their horizontal variations are different from those in soil zones, the variation of mountain *tundra* forest zone is highest, but *Betula ermanii* forest zone the lowest. Vertical variation of plant Pb is obviously higher than that in soils with variation coefficient of 89.76%; the enrichment capability of plant for Pb is depended on the plant types and the different organs of plant; parent material and parent rock, pH values, soil organic matter and soil particle fraction etc. are the main factors influencing variations of Pb content in soil-plant system of vertical zone in CNNR.

Keywords: Pb; variation characteristics; soil-plant system; vertical zone; Changbai Mountain National Nature Reserve

Introduction

Lead element (Pb) is one of the heavy metals which do harm to human beings, and it almost distributes throughout the world. Soil-plant system is the basic structural unit of biosphere. It is an critical component of the biogeochemical cycle of lead element and an effective "living filter", acting as the reservoir of lead dust and an environmental pathway or carrier of Pb from the sources (leaded gasoline, or lead emissions from industries and incinerators) to humans. And the variation characteristics of Pb both manifest the differences of sources and have close relation with Pb pollution. The nature reserve especially mountain nature reserve is among the areas which are less influenced by human activity and less polluted than other areas, so the nature reserve is the ideal place which is suited to such researches as the environmental background concentration and surface soil biogeochemistry. The landforms configuration is the external condition leading to regional redistribution of Pb, so the background concentration of Pb in mountain soil is obviously different from that in slope deposit and sediment, and it affects the transformation and transplant of elements in soils through impacting soil materials (Yin, 1999). The background level of Pb has been more studied at home and abroad(Yin, 1999). However, the study on variation of Pb content in the soil-plant system of mountain vertical zone is less. Therefore, this paper not only provide the base data and foundation to environmental monitoring and assessment in this region, but also provide comparative information to the studies on Pb concentration in soil-plant system in China.

1 Materials and methods

1.1 General ecological environment of Changbai Mountain National Nature Reserve(CNNR)

Changbai Mountain Nature Reserve(CNNR) is located between 41°58′ – 42°06′ N, 127°54′ – 128°08′E (Huang, 1996a), total area 196465 hm^2 (NCMBC, 1998), and its natural environment and ecosystem are better protected; moreover, it joined the network of nature reserve, "man and biosphere", in 1980. Owing to the direct influence of such factors as landform, climate, hydrology, parent material, soil and vegetation and so on, the vertical variation of mountain ecosystem is prominent in this region, and its vegetation and soil have typical vertical band spectrum. Plant zones from the below zone to the top one

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are mountain *tundra* zone, *Betula ermanii* forest zone, mountain dark coniferous forest zone and mountain coniferous and broad-leaf forest zone in turn, and the relevant soil zones are mountain *tundra* soil zone, mountain soddy forest soil, brown coniferous forest soil zone and dark brown forest soil zone, respectively. The climate in this region is continental monsoon climate(Huang, 1996b), mean annual temperature 4.9 to 7.3℃; mean annual precipitation 600 to 1340 mm, and precipitation mainly concentrates on the period from June to September, which almost accounts for 60 percent of annual precipitation; snow can last more than 6 months and its thickness can reach from 2m to 4m. The landforms are mainly volcano landform.

1.2 Samples and methods

Samples were collected from vertical zone on northern slope in CNNR, adding up to 40 soil samples and 40 typical plant(dominant plant) samples. The whole individual plants of the herbage, *Cladonia* sp. and *Aulacomnium* sp. were sampled, and the leaves and branches of shrubs were sampled respectively. All soil and plant samples were air-dried, ground to a fine power using muller and sieved.

Before determining Pb concentration, we should digest all soil and plant samples with sulfuric acid-perchloric acid, and wash the digested solution into 50 ml capacity bottles with 0.3 mol/L chlorhydric acid, respectively, finally determine Pb concentration using flame atomic absorption method, the apparatus is the atomic absorption spectrophotometer(GBC906) made in Australia, and the recovery rate can reach 95%. Soil organic matter is determined with dichromate titration, pH values of soil with potential method and soil grading with distribution of size instrument(RS-1000) made in Japan(Lu, 1999).

2 Results and discussion

2.1 Horizontal variations of Pb in soil-plant system of vertical zone in CNNR

The analyzed results(Table 1) showed that Pb concentrations in soils of vertical zone in CNNR are more than 25 mg/kg, two and a half times the worldwide average level(Clarke) in soil(Huang, 1996c). This may be because chemical weathering is relatively weaker in most regions and parent material is mainly weathered physically during the soil-forming process in CNNR, Pb concentration in soil keep the geochemical characteristics of parent material in great degree. Pb concentration in each soil zone approaches normal distribution, and the average concentration order of soil zones is successively mountain soddy forest soil > dark brown forest soil > mountain *tundra* soil > brown coniferous forest soil. However, the horizontal variation coefficients of soil zones have the opposite order: brown coniferous soil > mountain *tundra* soil > dark brown forest soil > mountain soddy forest soil. This manifests that the capability of enriching Pb of soil from mountain soddy forest soil zone is largest and its distribution is relatively even; brown coniferous soil zone has the weakest capability of enriching Pb, but variations of Pb contents in soils are most obviously significant.

Except *Betula ermanii* forest zone, the average concentration of Pb in plant of any other plant zones is lower than the worldwide average level(Clarke) in plant(Table 2; Huang, 1996), which is likely to be caused by the lower capability of absorption and enrichment of plants for Pb.

Table 1 Horizontal variation of soil Pb of vertical zone in CNNR

Soil zones	Altitude, m	Average, mg/kg	Standard deviation, mg/kg	Variation coefficient, %	Distribution type	Clarke value, mg/kg
Mountain *tundra* soil	2000—2740	29.1	6.79	23.33	Normal	10
Mountain soddy forest soil	1800—2000	32.9	5.42	16.47	Normal	10
Brown coniferous soil	1600—1800	26.75	6.60	24.67	Normal	10
Dark brown forest soil	600—1600	31.7	5.88	18.55	Normal	10

Pb concentrations in plants of *Betula ermanii* forest zone approach normal distribution, but those of the other three plant zones all approach logarithmic normal distribution. The order of the average Pb concentrations in plant zones is as follows: *Betula ermanii* forest zone > mountain *tundra* zone > mountain coniferous and broad-leaf forest zone > mountain dark coniferous forest zone, which is greatly consistent with that of Pb concentration of soil zones. This declares that Pb concentration in plant mainly depends on Pb concentration in soil in great degree. Plant Pb concentrations and soil Pb concentrations are analyzed by regression analysis, and the regression equation is $Y = 68.8299 + 3.5491X$($R = 0.8528$, $P = 0.01$, $n = 40$), in which Y denotes plant Pb concentration, and X denotes soil Pb concentration. However, the variant tendency of horizontal variation coefficients of plant zones is significantly different from those of soil zones, the variation coefficient order is not the same sequence as the inverted one of Pb concentrations in the order mountain *tundra* zone > mountain dark coniferous forest zone > mountain coniferous and broad-leaf forest zone > *Betula ermanii* forest zone. This testifies the capabilities of adsorption and enrichment of plants for Pb in *Betula ermanii* forest zone are close to each other, but in moutain *tundra* zone, the difference is very obviously significant(Huang, 1994).

Table 2 Horizontal variation of plant Pb of vertical zone in CNNR

Plant zones	Altitude, m	Average, mg/kg	Standard deviation, mg/kg	Variation coefficient, %	Distribution type	Clarke value, mg/kg
Mountain *tundra* zone	2000—2740	38.12	36.15	94.83	Logarithmic normal	50
Betula ermanii forest zone	1800—2000	53.09	11.68	22.00	Normal	50
Mountain dark coniferous forest zone	1600—1800	25.43	14.44	56.78	Logarithmic normal	50
Mountain coniferous and broad-leaf forest zone	600—1600	35.53	27.96	67.49	Logarithmic normal	50

2.2 Vertical variations of Pb in soil-plant system of vertical zone in CNNR

In soil-plant system of vertical zone in CNNR, the average concentration of Pb in soil is three times the worldwide average level(Clarke; Table 3), but that in plant is lower than the worldwide average level (Clarke). It also shows that the average concentration of Pb in parent material of vertical zone in CNNR is higher, and the capability of adsorption and enrichment of plants for Pb in this region is lower. Moreover, because the difference of the capability of adsorbing and enriching Pb of plants locating in different altitudes are prominent and soil is influenced by the higher Pb concentration in parent material, the vertical variation of Pb concentrations in plants is markedly higher than that in soil, with variation coefficient of 89.76%, about four times that of soil(TEMC, 1990; Liu, 1986).

Table 3 Vertical variations of Pb in soil-plant system of vertical zone in CNNR

Items	Range, mg/kg	Average, mg/kg	Standard deviation, mg/kg	Variation coefficient, %
Soil	19—50	29.87	6.82	22.83
Plant	5—100	39.67	35.61	89.76

3 Main factors influencing variations of Pb in soil-plant system of vertical zone in CNNR

3.1 Effects of soil-forming parent materials and parent rocks

The abundance value of Pb in the earth's crust is 10 mg/kg. And the amount of Pb entering the geological general circulation because of rock weathering is 5.6 t/a. However, Pb concentrations in various rocks are very different, i.e. peridotites of igneous rocks have the lowest Pb concentration, 0.2 mg/kg; and lead ores of sedimentary rocks have the highest Pb concentration, 100 mg/kg. Pb concentration order in various rocks of vertical zone in CNNR is zeolite > rhyolite > basalt > tuff and breccia > arenyte > volcanic(Table 4).

Table 4 The relationship between the concentration of Pb in soil and in parent rock

Types of rock	Items	The average concentration of Pb, mg/kg
Tuff and breccia	Parent rock	35.59
	Soil developed on it	30.7
Volcanic	Parent rock	31.2
	Soil developed on it	26.9
Zeolite	Parent rock	44.8
	Soil developed on it	34.6
Arenyte	Parent rock	33.6
	Soil developed on it	28.4
Rhyolite	Parent rock	42.3
	Soil developed on it	32.3
Basalt	Parent rock	41.25
	Soil developed on it	30.63

Geological action is the main interior condition for the redistribution of Pb element in soil, and soil-forming action is the exterior condition for that. Rocks are the main material sources of soil-forming materials of soil, and their Pb concentrations affect those in soil-forming materials which impact those in soils further. Because of influences of soil-forming materials and other soil-forming environment, the variation of Pb concentrations is obvious, and the average concentration of Pb is 15-25 mg/kg (Stahr, 1980). Pb concentrations in various soils developed on various parent rocks of vertical zone in CNNR varies greatly. And the order of Pb concentrations in soils is almost consistent with that in rocks, that is, soil developed on zeolite > soil developed on rhyolite > soil developed on tuff and breccia > soil developed on basalt > soil developed on arenyte > soil developed on volcanic (Table 4). The correlation analysis also declares Pb concentrations in parent materials and parent rocks have significantly positive correlation with those in soils in the probability level of 99%, with correlation coefficient of 0.993, which manifests Pb concentrations in soils of vertical zone in CNNR mainly depend on those in parent rocks. The regression equation can be gotten by the regression analysis: $Y = 12.68202 + 0.4693X$ ($R = 0.9329$, $P = 0.01$, $n = 40$), where Y denotes Pb concentration in soil, and X denotes Pb concentration in parent rock.

3.2 Influences of pH values, soil organic matter and soil granularity

The soil-plant system is an open system which is formed by the comprehensive influences of parent materials, organism, climate and landforms and so on, so the main factors affecting the variation characteristics of Pb include such factors as pH values, soil granularity, microorganismal activities, precipitation, temperature and plant species etc. The correlation analysis shows that in what degree the physico-chemical characteristics of soil influence Pb concentration in soil-plant system is different. Soil organic matter significantly positively correlates with Pb concentrations in soils in the probability level of 99%, and both mealy sand (0.01—0.005 mm) and clay (< 0.005mm) do in the probability level of 95%, but pH values have significantly negative correlation with Pb concentrations in soils. Thus declare soil organic matter, pH values and soil granularity are the another three key factors affecting Pb concentration in soil-plant system. The chelation of soil organic matter and the adsorption and enrichment of both mealy sand (0.01—0.005mm) and clay (< 0.005mm) influence the transplant and accumulation of Pb in soil. K. Stahr *et al*. (Stahr, 1980) still found the absorption of Pb is greatest on the organic material, but is still evident on the clay materials in the subsoils in ecosystems of the Bähalde watershed, and he also thought the greater adsorption in the topsoil in the Solling investigation may be due to higher pH values. The higher is soil organic matter content and the heavier is soil texture, the higher is Pb concentration. And the leaching loss and transplant pattern are diverse in soil with different textures, that is, the smaller is soil granule and the heavier is soil texture, the more difficulty does Pb element leach and the more easily does soil enrich Pb. Pb concentrations in plants mainly rely on those in soils, and effects of soil organic matter and soil texture on Pb concentrations in plants is realized by affecting Pb concentrations in soils. However, pH values influence Pb concentration in soil-plant system through affecting the microorganismal activities.

Table 5 Matrix of correlation coefficients between pH, soil organic matter, soil granularity and Pb concentration in soil-plant system in CNNR

Items	Soil Pb	Plant Pb	pH	Soil organic matter	Soil granularity 0.1 - 0.01 mm	0.01 - 0.005 mm	< 0.005 mm
Soil Pb	1						
Plant Pb	0.835**	1					
pH	-0.371*	-0.315*	1				
Soil organic matter	0.598**	0.456**	-0.265	1			
0.1 - 0.01 mm	-0.186	-0.019	0.114	-0.132	1		
0.01 - 0.005 mm	0.334*	0.326*	-0.283	0.338*	0.687**	1	
< 0.005 mm	0.313*	0.308*	0.171	-0.106	-0.436**	-0.445**	1

Note: (1) $n = 40$; (2) ** denotes extremely significant correlation, * denotes significant correlation

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