

## BACKGROUND VALUES AND TREND DISTRIBUTION OF Cu, Zn AND Ni IN SOILS IN CHINA

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**ABSTRACT:** The background values of Cu, Zn and Ni are discussed based on the analytical data of 21 main soil types collected from various regions in China. According to statistics of many samples, the background value of Cu is  $23.4 \pm 10.2$  mg / kg (482 samples), Zn  $77.9 \pm 2.39$  mg / kg (474 samples), Ni  $30.0 \pm 12.8$  mg / kg (482 samples).

**KEY WORDS:** Soil, Background values of Cu Zn and Ni, trend distribution

### I. BACKGROUND VALUES OF Cu, Zn, Ni IN DIFFERENT SOILS

Since the conditions of physical geography are varied and soil parent material is complicated, the background values of Cu, Zn and Ni in main soil types in China are greatly different. (see Table 1)<sup>[1]</sup>

In a sense, background values of chemical elements reflect their characteristics of accumulation and leaching in the soil profile. From Table 1, we can see that the background values of red soil in south China are low. For example, the background value of Cu is 12.3 mg / kg, Ni is 17.5 mg / kg and Zn is 57.6 mg / kg. The reason is tropical and subtropical acid environment and leaching<sup>[2]</sup>. In general, ash content in tropical plants is not high (3%—5%), average value of Cu in plant body is 6.32 mg / kg (average of 77 tropical plants) Zn 28.9 mg / kg and Ni 4.49 mg / kg.<sup>[3]</sup> All these material will finally return to soil after plants died. Meanwhile, the decomposition of soil organic matter is much quicker in the acid environment than in the other climatic zones of China, and humid climate condition also has intensive leaching, all of these make the movement of Cu, Zn, and Ni in the soil profile speed up, and make tropical soil background values drop. Life activity of plant organisms leads to biological circulation of minerals, which plays an important role in the formation of chemical element in the soil profile.

**Table 1 Background values of Cu, Zn, and Ni in main soil types in China**

Soil types	Sampling site	Elements	Number of samples	Range	Average value	Standard deviation	Average of surface
Paddy soil	Zhujiang Delta Changjiang R. valley Qiantang R. valley	Cu	43	6.2-55.6	21.0	14.5	29.3
		Zn	43	5.6-111.6	65.7	32.3	65.5
		Ni	43	3.1-56.5	26.1	13.4	24.6
Latosol	Hainan Island Leizhou Peninsula	Cu	16	6.0-69.0	32.1	22.7	29.1
		Zn	16	12.2-126.0	72.3	51.4	61.1
		Ni	16	12.7-175.7	91.7	62.4	85.7
Lateritic rde soil	Guangdong Hainan Island	Cu	59	0.8-86.4	10.1	13.8	7.60
		Zn	59	15.5-246.0	51.9	37.1	46.7
		Ni	59	3.0-73.2	13.9	13.3	12.4
Red soil	Guangdong	Cu	12	2.0-34.4	12.3	12.4	10.7
		Zn	12	34.0-93.0	57.6	17.7	56.5
		Ni	12	4.5-40.4	17.5	10.9	15.1
Dry red soil	Hainan Island	Cu	9	1.6-14.8	4.98	3.97	3.0
		Zn	9	17.2-47.5	29.9	10.5	24.4
		Ni	9	7.5-26.8	14.7	7.23	10.0
Yellow soil	Guangdong Hainan Island	Cu	23	1.6-26.0	9.04	7.23	7.35
		Zn	23	6.0-126.0	39.5	30.4	36.1
		Ni	23	5.0-30.5	16.7	7.46	15.7
Yellow brown soil	Nanjing	Cu	40	5.5-59.5	27.3	12.7	25.2
		Zn	40	36.5-360.6	97.4	65.1	85.8
		Ni	40	7.5-87.5	32.7	14.0	29.2
Mountain brown soil	Mountainous areas in Beijing and Wutai Mountain	Cu	13	18.9-43.1	25.1	10.1	20.4
		Zn	13	48.5-118.0	79.9	28.0	83.2
		Ni	13	28.1-46.0	42.0	4.48	40.5
Drab soil	Beijing, North China mountains	Cu	52	16.3-66.2	30.2	9.60	27.3
		Zn	52	32.1-170.0	76.3	22.4	75.8
		Ni	52	16.0-72.1	43.9	13.8	41.1
Chao soil	Nanjing, Tianjin and North China Plain	Cu	70	9.7-59.4	32.2	10.5	32.7
		Zn	70	63.5-294.2	174.9	53.9	140.0
		Ni	70	18.0-117.2	43.9	17.1	43.1

to be continued

Soil types	Sampling site	Elements	Number of samples	Range	Average value	Standard deviation	Average of surface
Chernozem	Heilongjiang	Cu	11	16.3-25.5	22.5	2.69	21.1
		Zn	11	50.0-68.0	60.2	4.46	56.4
		Ni	11	13.0-44.0	33.7	8.30	27.9
Meadow soil	Xizang (Tibet) Xinjiang and North China mountains	Cu	13	10.0-32.8	20.6	7.38	21.3
		Zn	13	38.5-140.0	70.9	26.2	67.1
		Ni	13	20.0-48.8	38.2	8.33	38.6
Solonchak	Tianjin Guangdong, north Jiangsu and North China Plain	Cu	30	2.8-48.2	28.4	11.3	25.2
		Zn	30	13.0-269.0	175.9	71.9	124.5
		Ni	30	12.7-82.2	41.5	14.7	37.6
Limestone red soil	G u a n g d o n g Hainan Island	Cu	10	19.0-80.0	34.3	20.9	26.9
		Zn	10	120.5-462.0	250.0	127.1	232.0
		Ni	10	54.3-151.1	107.1	37.4	98.8
Purple soil	Guangdong Sichuan	Cu	19	4.2-28.0	10.2	6.21	7.52
		Zn	19	9.5-90.5	50.1	20.7	44.5
		Ni	19	12.5-40.5	24.4	7.87	22.3
Chestnut soil	Inner Mongolia North Shanxi	Cu	41	10.1-42.2	23.4	8.81	22.4
		Zn	41	35.0-180.0	85.7	41.7	77.1
		Ni	41	8.0-58.5	25.3	12.4	27.9
Brown soil	Xinjiang	Cu	14	20.0-59.3	37.9	19.0	35.8
		Zn	14	55.0-118.8	96.2	24.2	94.3
		Ni	14	21.0-48.8	36.9	7.37	34.8
Gray desert soil	Xinjiang	Cu	9	9.5-25.6	20.7	4.92	17.9
		Zn	9 <sup>a</sup>	26.0-137.0	72.9	35.1	60.6
		Ni	9	16.8-31.5	26.0	6.88	18.6
Dark brown soil	Heilongjiang	Cu	9	7.1-35.6	19.8	8.34	15.5
		Zn	9	48.5-173.0	90.5	48.0	64.7
		Ni	9	19.6-50.5	27.9	11.0	20.3
Lou soil	Shaanxi Shanxi	Cu	14	17.0-27.0	23.2	2.75	23.2
		Zn	14	50.0-71.0	63.7	6.51	63.7
		Ni	14	18.9-47.0	40.9	4.85	39.5

The distribution of Cu, Zn, Ni in chernozem, carbonate drab soil, brown desert soil and laterite are shown in Fig.1.

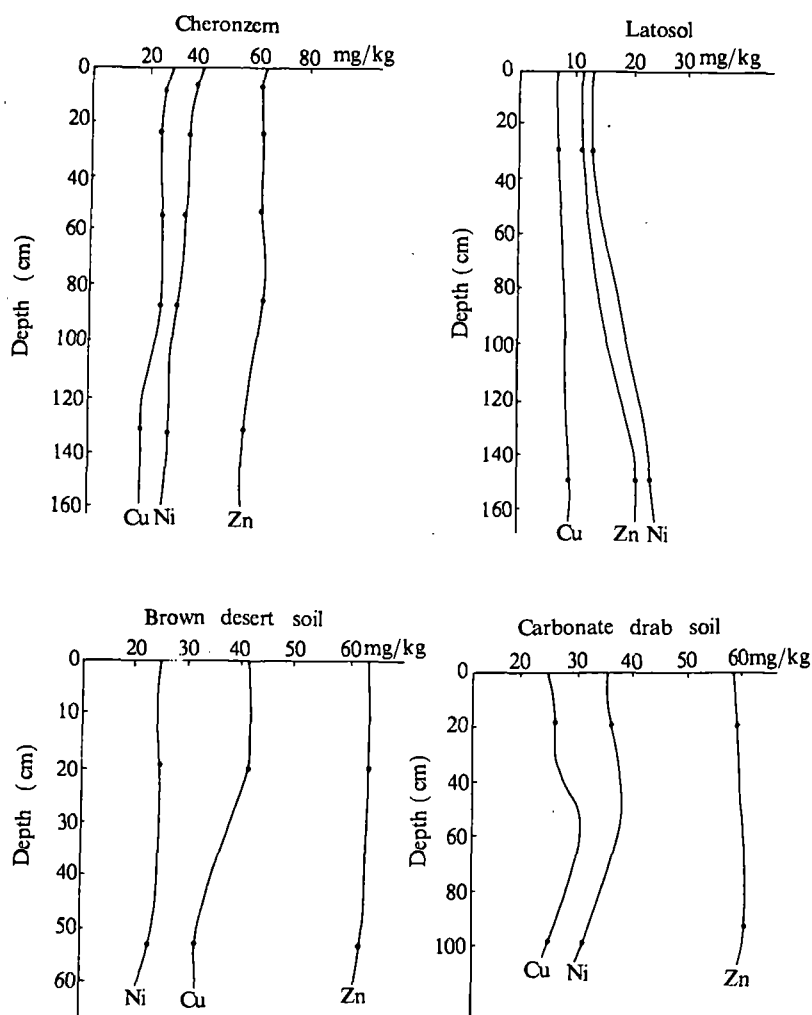


Fig.1 Vertical differentiation of Cu, Zn and Ni in four soil profiles

The distribution of Cu, Zn, Ni in chernozem clearly show that the background value in the surface is much higher than that in the subsurface layer. Chernozem was formed in herbaceous plants, and summer climate condition make herbaceous plants grow density. On the other hand, due to the longer cold season, frozen soil horizon can keep for almost half year, which restrain organic matter decomposition and make organic matter accumulate as humus. The content of organic matter in chernozem is generally 5%–10%, this type of soil has better absorbing power so contain a great deal of both trace elements and nutrient elements. In northeast China, Cu content is 25–30 mg / kg, Zn 60–70 mg / kg, Ni 25–40

mg / kg in chernozem humus horizon which can reach 70–100 cm. With the decrease of humus content, the contents of Cu, Zn and Ni reduce.

By statistics of seven brown desert soils in Turpan Basin, the contents of Cu, Zn and Ni in surface horizon are not low. For example, Cu is 41.9 mg / kg in surface and 32.5 mg / kg in subsurface layer. The elemental content of the soil is related to the weathering of parent material. Dry and hot climatic condition made weathering, leaching and biological process to be weak. The distribution difference of Cu in the soil is not obvious. But Cu contents in the subsurface layer of the residual solonchak and saline meadow soil are higher than that in the surface layer. Because the residual solonchak is distributed widely in the central part of the basin and the middle–lower part of the dry delta where surface water and ground water have caused salt accumulation. Part of ground water comes back up to the surface and evaporates away leaving a salt residue to accumulate in the soil profile. However, a large amount of Cu and other salts had been carried to the soil profile previously, and has not leached away due to the dry climate. Cu in the two types of soil is mainly from groundwater, Cu and other salts were accumulated in the soil profile, they didn't move later owing to no leaching.

Organic matter in carbonate drab soil is very low (1–3%). Leaching and accumulation of carbonate of lime attended a certain degree in drab forming, surface carbonate drab loss obviously but not completely. There are remarkable carbon accumulation horizon in the layer of 50–100 cm and from surface to subsurface layer the values of Cu, Zn, and Ni trend high, for example, in carbonate drab soil distributed in front of Taihang Mountain, Cu is 40 mg / kg, Zn is 75.6 mg / kg, Ni is 55.3 mg / kg. With the long history of cultivation, organic matter reduce, the more elements can not accumulate in surface.

## II. PROBABILITY DISTRIBUTION OF Cu, Zn AND Ni IN THE SOILS

According to analysis of 482 soil surface samples of 21 soil types, and statistics of Cu, Zn and Ni background values, we studied the probability distribution of Cu, Zn and Ni in the soils in order to give the correct background values. During soil-forming process, elemental geochemical value must show a statistic character and correspond to some probability distribution in theory.

### 1. Frequency of Cu in Soils in China

The background values of Cu ranges from 1.2 to 62.1 mg / kg (surface horizon). All measured data were divided into nine groups to make a frequency table (Table 2). We can see that the distribution of Cu exhibited a normal distribution on paper of probability. In order to examine the reliability of normal distribution, we count all data by  $X^2$  method. The formula is:

$$X^2 = \sum_{j=1}^n \frac{(Q_i - E_i)^2}{E_i}, \quad D_f = n - k$$

where  $Q_i$  is observing frequency

$E_i$  is theory frequency

$n$  is number of sample groups

$k$  is number of statistic by estimate parameter

**Table 2 Frequency of Cu in 482 soil samples in China**

Group	Frequency of samples	Relative frequency	Accumulative frequency	Percent of accumulated frequency
0-5	20	4.2	20	4.2
5-10	33	6.9	53	11.1
10-15	46	9.5	99	20.6
15-20	75	15.6	174	36.2
20-25	101	20.9	275	57.1
25-30	81	16.8	356	73.9
30-35	58	12.0	414	85.9
35-40	37	7.7	451	93.6
40-45	31	6.4	482	100.0
	482	100.0		

Usually, when probability  $p > 0.5$ ,  $X^2 < X^2_{0.05}$ , the hypothesis is right. Now we can get  $X^2$  value of Cu. When  $D_f = 6$ , from  $X^2$  table,  $X^2_{0.05} = 12.59$ ,  $X^2$  of Cu = 5.9764, and  $X^2 < X^2_{0.05}$ . So the hypothesis is right and the degree of confidence  $p > 0.05$ .

Cu can appear normal distribution under complicated soil-forming condition, which indicates that it distributes in various soil types (surface horizon) with an equal percentage in China, and its content changes in a regular range. It does not appear some excessive high or low values.

## 2. Frequency of Zn in Soils in China

When we study the frequency of Zn in soils in the same way, we get the other result, namely the content of Zn by paper of logarithmic probability is a straight line. So we can consider that the concentration distribution of Zn in soil is logarithmic normal distribution.

The side of lower than average value in the concentration distribution have high sample number and become much higher with the content.

In the other side, the distribution curve is smooth. So the whole picture grow a long tail toward the side of high content. The reason is that soil surface which grow from calcified parent material and in North China Plain have high content of Zn.

### 3. Frequency of Ni in Soil in China

According to frequency of Ni concentration in soil surface, using the same way as Cu and Zn, we studied the distribution character of Ni and got the conclusion that its distribution is neither normal nor logarithmic normal, it is a deviation normal distribution and its fiducial limit is  $1 > P > 0.05$ . The range of Ni in soil is from 3.0 to 162.0 mg / kg, which appear three peaks between 10–40 mg / kg, the relative frequency is about 77.8 per cent.

## III. BACKGROUND VALUES OF Cu, Zn AND Ni IN SOIL AND THEIR COMPARISON

### 1. Background values of Cu, Zn and Ni

Based on the statistics of 482 soil surface samples, we use arithmetic mean and standard, geometric mean and standard to indicate the background values, the results are shown in Table 3. The background values of Cu, Zn and Ni in soil surface in China are all in the range of world average values.

Table 3 Background values of Cu, Zn and Ni in soil (surface layer) in China

Elements	Number of samples	Range (mg / kg)	Arithmetic mean value (mg / kg)		Geometric mean value (mg / kg)	
			Average value	Standard deviation	Average value	Standard deviation
Cu	482	1.2– 62.1	23.4	10.2	25.4	1.46
Zn	474	12.2–174	72.8	25.2	77.9	2.39
Ni	482	3.0–162	30.0	12.8	35.1	1.55

### 2. Comparison of Background Values of Cu, Zn and Ni in Some Areas in China

Now the background values of Cu, Zn and Ni in 18 regions in China have been gotten. As to these background values, there are some difference in getting methods of samples, sample numbers, analytical methods and statistical methods, we have to use these materials to study these background values. However, if the background values of Cu, Zn and Ni are

credible and include 21 main types of soil in China, the background values of Cu is 23.4 mg / kg, Zn is 77.9 mg / kg, Ni is 30.0 mg / kg. But the background values of Cu, Zn and Ni in arid region of China are much higher than the standard given in this paper, for example, the background values of Cu, Zn and Ni in Turpan Basin of Xinjiang are beyond the standard, those of Urumqi and the Loess Plateau except Zn are all beyond too. On the contrary, in south China the background values in many areas do not exceed the standard, the background values of Cu, Zn and Ni in Guangzhou and Zhenjiang region are all within the standard. Climate condition and weathering are the factors to cause the difference in the background values.

#### IV. DISTRIBUTION TREND OF Cu BACKGROUND VALUE IN SOILS

##### 1. Divided Background Values into Four Areas

High background value areas, low background value areas and the region related to parent material must be pointed out when studying soil background values in China. In order to resolve these problems, when we studied the distribution of Cu in China's soils, we used trend analysis method, that is, using mathematical simulation method to approach the physical geographical trend. All real data determined are divided into two parts, trend part and residual part. The soil background values of China's soils can be divided into four physical areas:

1) North of the Huanghe (Yellow) River, east of Hetao, including the North China Plain and the Sanjiang Plain in northeast of China. This area is in humid and semihumid areas of warm temperate and temperate zones.

2) South of the Huanghe River, east of Yunnan-Guizhou Plateau, including middle and lower reaches of the Changjiang (Yangtze) River, the Huaihe River and Zhujiang River valleys. This area is in subtropical and tropical zones.

3) West of the Loess Plateau, including Gansu, Qinghai and Xinjing. This area is a northwest arid area to the west of the Loess Plateau, including Gansu, Qinghai and Xinjiang.

4) The Qinghai-Xizang Plateau

First we give cord ( $X_i$ ) in each area as their points in geographical network, then, indicate all data on the map and count their arithmetic mean, finally, use these values to finish trend computation. The simulated formula is:

$$Y_i(X_i) = A + BX_i + CX_i^2$$

where  $Y_i$ —trend value in geographical network

$X_i$ —geographical network cord

A, B, C—coefficient

## 2. Characteristics of Distribution of Soil Background Values

After counting the soil distribution trend, the map of Cu distribution trend in four physical background areas are given in Fig.2. The characteristics of Cu distribution trend are as follows:

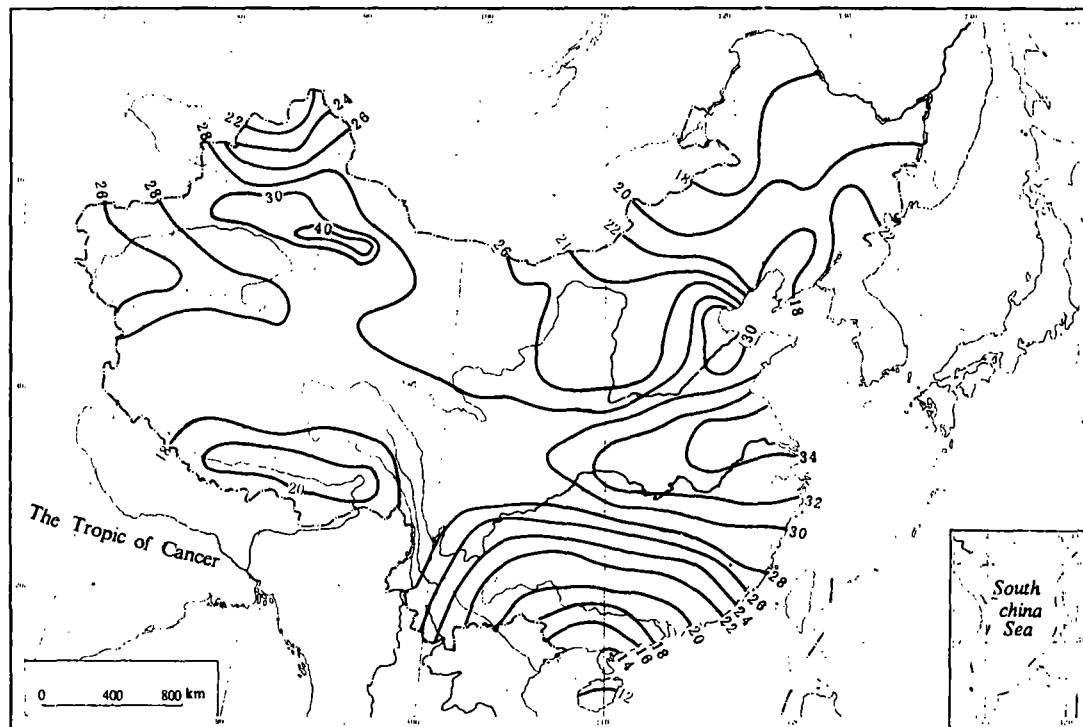


Fig.2 Trend distribution of Cu in soils in China

1) The North China Plain and the middle and lower reaches of the Changjiang River are high background value areas. The rivers bring a lot of materials from upper reaches and make good condition for element deposition. The Huanghe River, the Changjiang River and the Haihe River carry a lot of silt with their flow, the silt is accumulated constantly in coastland. Such heavy metal elements as Cu and Ni are adsorbed by suspended matter, which made a high Cu background value area be formed in east coastland.

2) Arid area in northwest China are high background value area. Weathering made chemical elements into soil-forming process, and under the weak leaching condition, the elements can hardly move away from soil. In northwest arid area, plaster stone and salt deposition horizon and alkalization phenomenon could be seen everywhere. Like other elements Cu can easily accumulate in soil surface and also in inland basin. For example, in

Turpan Basin the highest Cu content is 106.2 mg / kg, and the average of 44 samples is 37.7 mg / kg, too.

3) Tropical and subtropical zone in south China are low background value areas. The climate there is advantageous to weathering and leaching, and the acid character of soils is also favorable for Cu leaching. In the meanwhile, granite covers a large area in Guangdong, Fujian and Hunan provinces,<sup>[6]</sup> Cu content in granite is only 12–28 mg / kg.<sup>[7]</sup> Cu content in parent material is low, so Cu content in soils is low. For example, the Cu background value in Hainan Island is only 15.8 mg / kg. So we get the conclusion that the chemical composition of soils can change the distribution trend of Cu in soils in China, this is one of the characteristic of the distribution of soil background values.

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