Characteristics of Baseline and Analysis of Pollution on the Heavy Metals in Surficial Soil of Guiyang

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1. Introduction

The term “Environmental Geochemical Baseline (EGB)” first appeared in the International Geochemical Mapping Program (IGCP259) and the International Geochemical Baseline Program (IGCP360) of International Geo-graph Contrast Program. The definition of EGB refers to natural changes in the concentrations of chemical materials (chemical elements) in the Earth’s surface material (Salminen & Tarvainen, 1997). But the definition is becoming clearer with deepening research on EGB. The geochemical baseline reflects the natural concentration of one element in a particular material (e.g. soil, sediment, and rock). At the same time, it can be described as the unitary limit to distinguish the geochemistry backgrounds and anomalies (Salminen & Gregorauskiene, 2000).

As for the EGB, it is required to establish the archives of the current Earth’s surface environment and provide the database to monitor environmental variation. The aim of EGB is to reveal natural changes in mineral and chemical elements so as to make comparisons with anthropogenic influences. The EGB provides the definition of geochemical variation in natural space. It can not only guide policy-makers to make policies toward environmental problems, but also can educate the public who are interested in environmental problems (Darnley, 1997).

All countries attach great importance to the study of EGB, e.g. Mapping of EGB in Europe (Darnley, 1997). For coping with the world EGB studies, China kicked off the program of “Chinese Environment Geochemistry Supervision and Control Network, and the National Dynamic Mapping of Geochemistry Items” in 1992 (Chen Hangxin et al., 1998). Use of the EGB to study the environment impact of mining and smelting activities was carried out in the region of Panzhihua, Sichuan Province, Southwest China (Teng Yanguo et al., 2002, 2003).

In this chapter there has been established the surficial soil EGB of heavy metals (Hg, Cd, As, Pb, Cr, Cu, Ni and Zn) in Guiyang City (covering an area of 8046 km²), Guizhou Province. With soil environmental geochemistry research as the main line the spatial distribution of the heavy metals in surficial soil is combined with research on environmentally geochemical mechanism. An appropriate guideline is chosen to distinguish the influence of natural processes from that of anthropogenic processes on soil environment.

2. Materials and methods

2.1 Study area

Guiyang City was selected as the study area which is the capital of Guizhou Province in South-west China. Guiyang City, situated between east longitude $106^{\circ}07'$ to $107^{\circ}17'$, north latitude $26^{\circ}11'$ to $27^{\circ}22'$, lies in the middle of Guizhou Province and on the eastern slope of Yunnan-Guizhou Plateau (Fig.1). Guiyang, with abundant natural resources, ample energy resources and good natural environment, has a mild-moist subtropical climate because of diversity in geographical and topomorph features, high elevation and low latitude. The total area of Guiyang was 8046 km², including farmland (35.91%), woodland (33.09%), grassland (3.59%), water area (1.89%), construction land (e.g. residential area, industry, mining, transportation, et al.) (6.00%), garden area (0.70%) and no-use land (18.82%)(e.g. wilderness, ribbing, lake-beach, et al.) according to the land use. Soils in the study area mainly include yellow soil (3.335×10^5 hm², 41.53%), umber soil (1.49%), limestone soil (2.021×10^5 hm², 25.17%), rocky soil (2.17%), coarse-bone soil (12.64%), purple soil (1.93%), marsh soil (0.11%), paddy soil (1.156×10^5 hm², 14.39%), and mountainous meadow soil (0.5%) (Fig.2).

Fig. 1. Map showing the study site in Guizhou.

Fig. 2. The distribution of surficial soil of Guiyang, Guizhou.

2.2 Sampling

The snake-form distribution sampling method was adopted because of the bigger sampling area, relief topography and un-uniform soil. The topsoil layer (5~15 cm) was sampled after cover rock and remained roots were removed(HJ/T 166-2004). Guiyang has 1286 villages 83 towns and the sample of Hg, Cd, Pb, Cr and As localities were distributed in 487villages and 75 towns of Guiyang. So the samples account for 37.87% and 90.36%, respectively. The sample of Cu, Ni and Zn localities were distributed in 332 villages and 50 towns, and the samples account for 25.82% and 60.24%. Hg, Cd, Pb, Cr and As localities are shown in Fig. 3. Cu, Ni and Zn localities are shown in Fig. 4.

The soil samples were collected 67 at January19 to March 4, and 420 at July 11 to October 11.

Fig. 3. The distribution on of Cd, Hg, Cr, Pb, As sites in Guiyang, Guizhou.

Fig. 4. The distribution on of Cu, Zn, Ni sites in Guiyang, Guizhou.

2.3 Analytical techniques

The content of As was digested with a mixture acids: $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-HClO}_4$ (H_2SO_4 / HNO_3 / HClO_4 , 1:1:3) and using diethyl disulfide generation amino acid silver spectrophotometric

method to determine the contents of As in the samples(GB/T17134-1997). The limits of determination were 0.5 mg/kg (As) according to 0.5g sample which was dispelled in 50ml. The content of Pb and Cd were digested with mixture acids: HCl-HNO₃- HF- HClO₄, and using graphite furnace atomic absorption spectrometry to determine the contents of Pb and Cd, the limits of determination were 0.1mg/kg (Pb), 0.01mg/kg (Cd) according to 0.5g samples which were dispelled in 50ml(GB/T17141—1997). The total content of Cr were determined by diethyl carbon phenol by two spectrophotometric method after the samples were digested with a mixture acids: HCl-HNO₃-HF, and the limits of determination was 1.0mg/kg(Cr) according to 0.5g samples which was dispelled in 50ml (GB/T17137—1997). Using flame-atomic absorption spectrophotometry to determine the contents of Cu, Zn and Ni in the samples(Cu and Zn: GB/T17138—1997; Ni: GB/T17139—1997). The limits of determination were 1.0 mg/kg (Cu), 5.0 mg/kg (Ni), 0.5 mg/kg (Zn) according to 0.5g sample which was dispelled in 50ml. The samples of Cu, Ni and Zn were digested with HCl-HNO₃- HF- HClO₄. The total content of Hg was digested with a mixture of ultrapure acids: H₂SO₄-HNO₃-KMnO₄(H₂SO₄/HNO₃,1:1) and analyzed by cold atomic absorbent spectrophotometry, the limits of determination was 0.005mg/kg(Hg) according to 2g samples which was dispelled in 50ml(GB/T17136—1997). The concentrations of Hg, Pb, Cd, Cr, Cu, As, Ni and Zn in the solution were measured under the optimum condition. For quality assurance and quality control, reagent blanks, 20% duplicated samples and sol standard reference materials GSS-1, GSS-3, GSS-4 obtained from Center of National Standard Reference Material of China were prepared and analyzed with the same procedure and reagents.

The table 1 showed that the accuracy and precision of testing of the above.

The available data sets were analyzed using the SPSS 16.0, ArcGIS, and ArcView.

Elements	SU	SS	GV(mg/kg)	ORM(mg/kg)	IRSD (%)	RSDBR(%)	RE(%)
As	14	GSS-1	10.7±0.8	10.7	2.0	5.6	0.0
	15	GSS-3	15.9±1.3	17.1	1.3	4.3	7.5
	12	GSS-4	11.4±0.7	11.4	3.8	4.8	0.0
Cd	25	GSS-1	0.083±0.011	0.080	3.6	6.2	-3.6
	28	GSS-3	0.044±0.014	0.045	4.1	8.4	2.3
Cr	16	GSS-1	57.2±4.2	56.1	2.0	9.8	-1.9
	18	GSS-3	98.0±7.1	93.2	2.3	8.3	-4.9
	35	GSS-1	20.9±0.8	20.7	2.3	6.8	-0.96
Cu	34	GSS-3	29.4±1.6	29.2	2.0	4.8	-0.68
	30	GSS-4	26.3±1.7	25.6	2.3	3.9	-2.7
	25	GSS-1	0.016±0.003	0.016	6.2	32.5	0.0
Hg	26	GSS-3	0.112±0.012	0.100	3.4	20.0	-10.7
	24	GSS-4	0.021±0.004	0.019	8.4	20.5	-9.5
	29	GSS-1	29.6±1.8	29.1	2.5	8.4	-1.7
Ni	32	GSS-3	33.7±2.1	34.0	2.6	6.0	0.89
	33	GSS-4	32.8±1.7	34.1	2.9	9.1	4.0
Pb	19	GSS-1	23.6±1.2	23.7	4.2	7.3	0.42
	21	GSS-3	33.3±1.3	33.7	3.9	8.6	1.2
Zn	32	GSS-1	55.2±3.4	56.2	2.8	7.3	1.8
	31	GSS-3	89.3±4.0	88.4	1.6	5.0	1.0
	31	GSS-4	69.1±3.5	68.1	3.2	4.1	-1.4

SU: sample numbers; SS: standard samples; GV: guaranteed value; ORM: overall mean

IRSD: indoor relative standard deviation; RSDBR: relative standard between room; RE: relative error

Table 1. The accuracy and precision of contents of heavy metals in soil.

3. Experimental results

Table2 indicated that the statistical analysis results of soil heavy metals concentrations in Guiyang city. The mean value, standard deviation and maximum of As separately are 18.09 mg/kg, 11.57 mg/kg and 79.30 mg/kg in the surficial soil in Guiyang. The content of As in 95.9 per cent sample are smaller than 40 mg/kg., of Cd separately are 0.302mg/kg, 0.363mg/kg, 2.620mg/kg and 95.7 percent smaller than 1.000mg/kg., of Cr 75.3 mg/kg, 37.3 mg/kg, 271.0 mg/kg and 95.9 percent smaller than 150.0 mg/kg, of Cu separately are 43.1mg/kg, 30.3mg/kg, 213.0mg/kg and 94.6 percent smaller than 100.0mg/kg, of Pb are 43.2mg/kg, 31.3mg/kg, 318.9mg/kg and 95.5 per cent smaller than 100.0mg/kg, of Hg are 0.222mg/kg, 0.531mg/kg, 7.030mg/kg and 98.2 smaller than 1.000mg/kg, of Ni are 38.3mg/kg, 14.9mg/kg, 102.5mg/kg and 95.8 percent smaller than 70.0mg/kg, of Zn are 84.7mg/kg, 49.8mg/kg, 385.0mg/kg and 94.3 percent smaller than 150.0mg/kg.

Elements	SN	Min(10 ⁻⁶)	Max(10 ⁻⁶)	Mean(10 ⁻⁶)	SD	CV
As	486	2.70	79.00	18.09	11.57	0.64
Cd	487	0.001	2.620	0.302	0.363	1.20
Cr	487	6.9	271.0	75.3	37.3	0.50
Cu	333	2.1	213.0	43.1	30.3	0.70
Pb	487	0.9	318.9	43.2	31.3	0.7
Hg	487	0.010	7.030	0.222	0.531	2.39
Ni	333	9.2	102.5	38.3	14.9	0.39
Zn	333	0.1	385.0	84.7	49.8	0.59

SN: sample numbers; SD: standard deviation; CV: coefficient of variation

Table 2. The statistical analysis results of heavy metals concentration in soil, Guiyang city.

4. Analysis and discussions

4.1 Results analysis

4.1.1 Establishment of the baselines of heavy metals in surficial soil

4.1.1.1 Establishment of the baselines of As in surficial soil

4.1.1.1.1 Relatively accumulative total amount analysis

Assuming the concentrations of chemical elements in natural surficial soil are of logarithmic normal distribution, the inflexion in the figure of relatively accumulative density to the concentration of chemical element represents the boundary line between the background value and the abnormal value. The range of baseline values of chemical elements is the average value plus double standard deviation of less than the boundary value (Lepeltier, 1969).

The double logarithmic figure of relatively accumulative density (RAD) to the concentration of the chemical element As in topsoil of Guiyang was shown in Fig.5. The inflexion (black points in the figure) is 17.2 mg/kg. So the range of baseline values of As in topsoil of Guiyang is 7.75~15.15 mg/kg, i.e., the average value of 11.45mg/kg plus a double standard deviation of 3.70 mg/kg less than 17.2 mg/kg.

Fig. 5. The logarithm of the concentrations on As and the logarithmic curve of relatively accumulative density in surficial soil.

4.1.1.1.2 Relatively accumulative frequency

The normal decimal coordinates are adopted. There are two inflexions in the figures of relatively accumulative frequency to the concentration of chemical element. The lower one may represent the upper limit of the baseline of chemical elements and the upper one may represent the lower limit of abnormality, i.e., the influence of human activity on the two inflexions. The average or median that is less than the lower inflexion can be regarded as the baseline of chemical elements. The metrical values between the two inflexions may have something with the influence of human activities, or have nothing to do. If the distribution curve looks like a straight line, the measured values may represent the baseline range (Bauer & Bor, 1993, 1995; Bauer et al. 1992; Matschullat et al., 2000)

The figure of relatively accumulative frequency to the concentration of As in topsoil of Guiyang is shown in Fig. 6. There are two inflexions: one is 13.0 mg/kg and the other is 29.0 mg/kg. So the first inflexion (13.0 mg/kg) represents the upper limit of baseline values of As in topsoil of Guiyang. The average of 9.20 mg/kg or the median of 9.04 mg/kg less than the first inflexion can be regarded as the baseline of As in topsoil of Guiyang. The second inflexion (29.0 mg/kg) may represent abnormality, i.e., the influence of human activity.

Fig. 6. The probability functions of As in surficial soil.

Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 9.04mg/kg as the baseline values of As in topsoil of Guiyang.

4.1.1.2 Establishment of the baselines of Cd in surficial soil

4.1.1.2.1 Relatively accumulative total amount analysis

The double logarithmic figure of RAD to the concentration of the chemical element Cd in topsoil of Guiyang was shown in Fig.7. The inflexion (black points in the figure) is 0.189 mg/kg. So the range of baseline values of Cd in topsoil of Guiyang is 0.029~0.123 mg/kg, i.e. the average value of 0.076mg/kg plus double standard deviation of 0.047 mg/kg less than 0.189mg/kg.

Fig. 7. The logarithm of the concentration on Cd and the logarithmic curve of relatively accumulative density in surficial soil.

4.1.1.2.2 Relatively accumulative frequency

The figure of relatively accumulative frequency to the concentration of Cd is shown in Fig.8. One inflexion is 0.149 mg/kg and the other is 1.010 mg/kg. So the first inflexion (0.149 mg/kg) represents the upper limit of baseline values of Cd in topsoil of Guiyang. The average of 0.068 mg/kg or the median of 0.068 mg/kg less-than the first inflexion can be regarded as the baseline of Cd in topsoil of Guiyang. The second inflexion (1.010mg/kg) may regard as represent abnormality, i.e., the influence of human activities.

Fig. 8. The probability functions of Cd in surficial soil of Guiyang.

Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 0.068 mg/kg as the baseline values of Cd in topsoil of Guiyang.

4.1.1.3 Establishment of the baselines of Cu in surficial soil

4.1.1.3.1 Relatively accumulative total amount analysis

The double logarithmic figure of RAD to the concentration of the chemical element Cu in topsoil of Guiyang is shown in Fig.9. The inflexion (black points in the figure) is 32.6 mg/kg. So the range of baseline values of Cu in topsoil of Guiyang is 14.2~28.4 mg/kg, i.e., the average value of 21.3mg/kg plus a double standard deviation of 7.1 mg/kg less than 32.6 mg/kg.

Fig. 9. The logarithm of the concentrations on Cu and the logarithmic curve of relatively accumulative density in surficial soil.

4.1.1.3.2 Relatively accumulative frequency

The figure of relatively accumulative frequency to the concentration of Cu in topsoil of Guiyang is shown in Fig.10. There are two inflexions: one is 28.1 mg/kg and the other is 68.4 mg/kg. So the first inflexion (28.1 mg/kg) represents the upper limit of baseline values of Cu in topsoil of Guiyang. The average of 18.8 mg/kg or the median of 21.9 mg/kg less than the first-inflexion can be regarded as the baseline of Cu in topsoil of Guiyang. The second inflexion (68.4 mg/kg) may represent abnormality, i.e., the influence of human activity.

Fig. 10. The probability functions of Cu in surficial soil.

Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 18.8 mg/kg as the baseline values of Cu in topsoil of Guiyang.

4.1.1.4 Establishment of the baselines of Zn in surficial soil

4.1.1.4.1 Relatively accumulative total amount analysis

The double logarithmic figure of RAD to the concentration of the chemical element Zn in topsoil of Guiyang is shown in Fig.11. The inflexion is 114.0 mg/kg. So the range of baseline values of Zn in topsoil of Guiyang is 46.5~91.3 mg/kg, i.e., the average value of 68.9mg/kg pluses double standard deviation of 22.4 mg/kg less than 114.0mg/kg.

Fig. 11. The logarithm of the concentrations on Zn and the logarithmic curve of relatively accumulative density in surficial soil.

4.1.1.4.2 Relatively accumulative frequency

The figure of relatively accumulative frequency to the concentration of Zn in topsoil of Guiyang is shown in Fig.12. There are two inflexions. One inflexion is 56.5 mg/kg and the other is 112.0 mg/kg. So the first inflexion (56.5 mg/kg) represents the upper limit of baseline values of Zn in topsoil of Guiyang. The average of 41.6 mg/kg or the median of 46.3 mg/kg less-than the first inflexion can be regarded as the baseline of Zn in topsoil of Guiyang. The second inflexion (112.0 mg/kg) may regard as represent abnormality, i.e., the influence of human activities.

Fig. 12. The probability functions of Zn in surficial soil.

Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 46.3 mg/kg as the baseline values of Zn in topsoil of Guiyang.

4.1.1.5 Establishment of the baselines of Pb in surficial soil

4.1.1.5.1 Relatively accumulative total amount analysis

The double logarithmic figure of RAD to the concentration of the chemical element Pb in topsoil of Guiyang is shown in Fig.13. The inflexion (black points in the figure) is 26.8 mg/kg. So the range of baseline values of Pb in topsoil of Guiyang is 14.0~25.4 mg/kg, i.e., the average value of 19.7mg/kg plus a double standard deviation of 5.7 mg/kg less than 26.8 mg/kg.

Fig. 13. The logarithm of the concentrations on Pb and the logarithmic curve of relatively accumulative density in surficial soil.

4.1.1.5.2 Relatively accumulative frequency

The figure of relatively accumulative frequency to the concentration of Pb in topsoil of Guiyang is shown in Fig.14. There are two inflexions: one is 20.4 mg/kg and the other is 70.1mg/kg. So the first inflexion (20.4 mg/kg) represents the upper limit of baseline values of Pb in topsoil of Guiyang. The average of 16.0 mg/kg or the median of 14.8 mg/kg less than the first-inflexion can be regarded as the baseline of Pb in topsoil of Guiyang. The second inflexion (70.1mg/kg) may represent abnormality, i.e., the influence of human activity.

Fig. 14. The probability functions of Pb in surficial soil of Guiyang.

Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 14.8 mg/kg as the baseline values of Pb in topsoil of Guiyang.

4.1.1.6 Establishment of the baselines of Hg in surficial soil

4.1.1.6.1 Relatively accumulative total amount analysis

The double logarithmic figure of RAD to the concentration of the chemical element Hg in topsoil of Guiyang is shown in Fig.15. The inflexion (black points in the figure) is 0.082 mg/kg. So the range of baseline values of Hg in topsoil of Guiyang is 0.031~0.075 mg/kg, i.e., the average value of 0.053mg/kg plus double standard deviation of 0.022 mg/kg less than 0.082mg/kg.

Fig. 15. The logarithm of the concentrations on Hg and the logarithmic curve of relatively accumulative density in surficial soil.

4.1.1.6.2 Relatively accumulative frequency

The figure of relatively accumulative frequency to the concentration of Hg in topsoil of Guiyang is shown in Fig.16. There are two inflexions. One inflexion is 0.072 mg/kg and the other is 0.530 mg/kg. So the first inflexion (0.072mg/kg) represents the upper limit of baseline values of Hg in topsoil of Guiyang. The average of 0.050 mg/kg or the median of 0.045 mg/kg less-than the first inflexion can be regarded as the baseline of Hg in topsoil of Guiyang. The second inflexion (0.530 mg/kg) may regard as represent abnormality, i.e., the influence of human activities.

Fig. 16. The probability functions of Hg in surficial soil.

Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 0.045 mg/kg as the baseline values Hg in topsoil of Guiyang.

4.1.1.7 Establishment of the baselines of Cr in surficial soil

4.1.1.7.1 Relatively accumulative total amount analysis

The double logarithmic figure of RAD to the concentration of the chemical element Cr in topsoil of Guiyang is shown in Fig.17. The inflexion (black points in the figure) is 67.8 mg/kg. So the range of baseline values of Cr in topsoil of Guiyang is 31.0~59.8mg/kg, i.e., the average value of 45.4mg/kg plus a double standard deviation of 14.4 mg/kg less than 67.8 mg/kg.

Fig. 17. The logarithm of the concentrations on Cr and the logarithmic curve of relatively accumulative density in surficial soil.

4.1.1.7.2 Relatively accumulative frequency

The figure of relatively accumulative frequency to the concentration of Cr in topsoil of Guiyang is shown in Fig.18. There are two inflexions: one is 63.8 mg/kg and the other is 100.2 mg/kg. So the first inflexion (63.8 mg/kg) represents the upper limit of baseline values of Cr in topsoil of Guiyang. The average of 45.7 mg/kg or the median of 44.0 mg/kg less than the first-inflexion can be regarded as the baseline of Cr in topsoil of Guiyang. The second inflexion (100.2 mg/kg) may represent abnormality, i.e., the influence of human activity.

Fig. 18. The probability functions of Cr in surficial soil.

Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 44.0 mg/kg as the baseline values of Cr in topsoil of Guiyang.

4.1.1.8 Establishment of the baselines of Ni in surficial soil

4.1.1.8.1 Relatively accumulative total amount analysis

The double logarithmic figure of RAD to the concentration of the chemical element Ni in topsoil of Guiyang is shown in Fig.19. The inflexion is 27.6 mg/kg. So the range of baseline values of Ni in topsoil of Guiyang is 18.1~26.7 mg/kg, i.e., the average value of 22.4 mg/kg pluses double standard deviation of 4.3 mg/kg less than 27.6mg/kg.

Fig. 19. The logarithm of the concentrations on Ni and the logarithmic curve of relatively accumulative density in surficial soil.

4.1.1.8.2 Relatively accumulative frequency

The figure of relatively accumulative frequency to the concentration of Ni in topsoil of Guiyang is shown in Fig.20. There are two inflexions. One inflexion is 27.8 mg/kg and the other is 57.0 mg/kg. So the first inflexion (27.8 mg/kg) represents the upper limit of baseline values of Ni in topsoil of Guiyang. The average of 19.5 mg/kg or the median of 17.0 mg/kg less-than the first inflexion can be regarded as the baseline of Ni in topsoil of Guiyang. The second inflexion (57.0 mg/kg) may regarded as represent abnormality, i.e., the influence of human activities.

Fig. 20. The probability functions of Ni in surficial soil.

Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 17.0 mg/kg as the baseline values of Ni in topsoil of Guiyang.

4.2 Discussions

4.2.1 Geo-accumulation analysis of heavy metals in surficial soil

Geo-accumulation Index was commonly called Muller Index (Muller, 1969; Forstner & Muller, 1981), was widely used in studying quantitative index for heavy metals pollution in sediments (Forstner et al., 1990; Chen Cuihua et al., 2008; Yi xiu et al., 2010; Hu Mianhao, 2010), and the expression as this.

$$I_{\text{geo}} = \log_2 \left[\frac{C_n}{1.5 \bullet BE_n} \right] \quad (1)$$

C_n represents the concentration of element n in sample. BE_n means the baseline concentration, 1.5 was modified index for characterizing sedimentary characteristics, rocky and other effects.

Geo-accumulation Index can be divided into several levels, e.g. it was divided into seven levels by Forstner (referred to hereafter as F classification), and five levels by Anon (referred to hereafter as A classification). It indicated pollution degrees of heavy metals by different classes of I_{geo} .

F classification			A classification		
I_{geo}	levels	Pollution degrees	I_{geo}	levels	Pollution degrees
<0	1	W.P.	<0	1	W.P. or slight pollution
0~1	2	W.P. to M.P.	0~1	2	M.P.
1~2	3	M.P.	1~3	3	M.P. or S.P.
2~3	4	M.P. to S.P.	3~5	4	S.P.
3~4	5	S.P.	>5	5	S.S.P.
4~5	6	S.P. to S.S.P.			
>5	7	S.S.P.			

W.P.: without pollution; M.P.: mid-pollution; S.P.: strong pollution; S.S.P.: super strong pollution

Table 3. Degrees of pollution by heavy metals indicated by different classes of I_{geo} .

The means of Geo-accumulation indexes of heavy metals in surficial soil of Guiyang city were analyzed (Fig.21 to Fig.28). By the results, we get the surficial soil in 41 per cent of the Guiyang did not suffer the arsenic contaminative, 43 per cent is between without pollution to mid-pollution, 14 per cent mid-pollution, only 2 per cent is between mid-pollution to strong pollution. In 40 per cent did not suffer the cadmium contaminative, 19 per cent between without pollution to mid-pollution, 14 per cent mid-pollution, 19 per cent between mid-pollution to strong pollution, 7 per cent strong pollution, 1 per cent between strong pollution to supper strong pollution. In 46 per cent did not suffer the chromium contaminative, 47 per cent between without pollution to mid-pollution, 6.8 per cent mid-pollution, only 0.2 per cent between mid-pollution to strong pollution. In 38 per cent did not suffer the copper contaminative, 38 per cent between without pollution to mid-pollution, 22 per cent mid-pollution, only 2 per cent between mid-pollution to strong pollution. In 18 per

cent did not suffer the lead contaminative, 47 per cent between without pollution to mid-pollution, 28 per cent mid-pollution, only 3 per cent between mid-pollution to strong pollution. In 12 per cent did not suffer the mercury contaminative, 37 per cent between without pollution to mid-pollution, 36 per cent mid-pollution, 11 per cent between mid-pollution to strong pollution, 2 per cent strong pollution, 1 per cent supper between strong pollution to supper strong pollution, 1 per cent supper strong pollution. In 19.2 per cent did not suffer the nickel contaminative, 63.7 per cent between without pollution to mid-pollution, 16.8 per cent mid-pollution, only 0.3 per cent between mid-pollution to strong pollution. In 41 per cent did not suffer the zinc contamination, 50per cent between without pollution to mid-pollution, 7 per cent mid-pollution, only 2 per cent between mid-pollution to strong pollution.

Fig. 21. Distribution of I_{geo} for As in surficial soil.

Fig. 22. Distribution of I_{geo} for Cd in surficial soil.

Fig. 23. Distribution of I_{geo} for Cr in surficial soil.

Fig. 24. Distribution of I_{geo} for Cu in surficial soil.

Fig. 25. Distribution of I_{geo} for Pb in surficial soil.

Fig. 26. Distribution of I_{geo} for Hg in surficial soil.

Fig. 27. Distribution of I_{geo} for Ni in surficial soil.

Fig. 28. Distribution of I_{geo} for Zn in surficial soil.

4.2.2 Contamination degree analysis of heavy metals in surficial soil

Contamination Degree (CD) was the most intuitive and commonly used one of the parameters for evaluating heavy metals pollution. The parameter represented the content of heavy metals in soil was over the national standard, and it was expressed as shown.

$$CD = \frac{c_i}{c_A} - 1 \quad (2)$$

C_i represents the analysis value in i sample of an element (the concentration of an element in sample). C_A means the maximum limit of the element concentration in environment, which was commonly the Quality Standard of Soil Environment. The primary standard of national quality standard in soil environment (GB15618-1995) was used to calculate the heavy metals pollution degree for C_A .

The contamination degrees of heavy metals in surficial soil of Guiyang city were analyzed (Table 4 to Table 11). The results indicated that the maximum of arsenic contaminative degree of surficial soil in Guiyang is 4.27. 50.2 per cent surficial soil did not suffer the pollution. The contaminative degree in 97 per cent surficial soil in Guiyang is smaller than 2 and the total contaminative degree is slightly over zero. So the surficial soil of Guiyang suffers the slight pollution. Of cadmium are 12.1. 57.9 per cent surficial soil did not suffer the pollution. 96 per cent is smaller than 4 and the total is over zero. So suffers pollution of Cd. Of chromium are 2.01. 69 per cent did not suffer the pollution, 30.6 per cent slight pollution. The total is less than zero. So not suffer pollution of Cr. Of copper are 5.09. 53.2 per cent did not suffer the pollution. The total is slightly over zero. So suffers slight pollution of Cu. Of lead are 8.11. 49.9 per cent did not suffer the pollution. The total is slightly over zero. So suffers slight pollution of Pb. Of mercury are 45.87. 56.1 per cent did not suffer the pollution. The total is over zero. So suffers pollution of Hg. Of nickel is 1.56. 64 per cent did not suffer the pollution. The total is less than zero. So not suffer pollution of Ni. Of zinc are 2.85. 77.8 per cent did not suffer the pollution. The total is less than zero. So not suffer pollution of Zn. Consideration the pollution to join with 8 kinds of heavy metals, 40.2 per cent have no contamination of heavy metal, 15 per cent from no pollution to slight pollution, 36.1 per cent slightly pollution, 7.2 per cent mid-pollution, 1.4 per cent serious pollution in the surficial soil of Guiyang.

CD_{As}	$x \leq 0$	$0 < x \leq 1$	$1 < x \leq 2$
Number	244	187	42
Ratio	50.2%	38.5%	8.6%
CD_{As}	$2 < x \leq 3$	$3 < x \leq 4$	$x > 4$
Number	6	4	3
Ratio	1.2%	0.8%	0.6%
Note: Average: 0.206; Min:-0.81; Max: 4.27			

Table 4. The contamination degree on As in surficial soil of Guiyang city.

CD _{Cd}	$x \leq 0$	$0 < x \leq 1$	$1 < x \leq 2$	$2 < x \leq 3$
Number	282	72	48	42
Ratio	57.9%	14.8%	9.9%	8.6%
CD _{Cd}	$3 < x \leq 4$	$4 < x \leq 5$	$5 < x \leq 6$	$x > 6$
Number	22	7	5	9
Ratio	4.5%	1.4%	1.0%	1.9%
Note: Average:0.51; Min:-0.995; Max:12.1				

Table 5. The contamination degree on Cd in surficial soil of Guiyang city.

CD _{Cr}	≤ 0	$0 < x \leq 0.5$	$0.5 < x \leq 1$
Number	337	118	24
Ratio	69.2%	24.3%	4.9%
CD _{Cr}	$1 < x \leq 1.5$	$x > 1.5$	
Number	7	1	
Ratio	1.4%	0.2%	
Note: Average:-0.16; Min:-0.92; Max:2.01			

Table 6. The contamination degree on Cr in surficial soil of Guiyang city.

CD _{Cu}	≤ 0	$0 < x \leq 1$	$1 < x \leq 2$
Number	177	99	43
Ratio	53.2%	29.7%	12.9%
CD _{Cu}	$2 < x \leq 3$	$x > 3$	
Number	11	3	
Ratio	3.3%	0.9%	
Note: Average:0.23; Min:-0.94; Max:5.09			

Table 7. The contamination degree on Cu in surficial soil of Guiyang city.

CD _{Pb}	≤ 0	$0 < x \leq 1$	$1 < x \leq 2$
Number	243	189	37
Ratio	49.90%	38.80%	7.60%
CD _{Pb}	$2 < x \leq 3$	$3 < x \leq 4$	$x > 4$
Number	7	8	3
Ratio	1.50%	1.60%	0.60%
Note: Average:0.23; Min:-0.98; Max:8.11			

Table 8. The contamination degree on Pb in surficial soil of Guiyang city.

CD _{Hg}	≤0	0< x≤1	1< x≤2	2<x≤3
Number	273	155	33	10
Ratio	56.1%	31.8%	6.8%	2.1%
CD _{Hg}	3< x≤4	4< x≤5	x>5	
Number	6	1	9	
Ratio	1.2%	0.2%	1.8%	
Note: Average:0.48; Min:-0.93; Max:45.87				

Table 9. The contamination degree on Hg in surficial soil of Guiyang city.

CD _{Ni}	≤0	0< x≤0.5	0.5< x≤1
Number	213	88	27
Ratio	64.0%	26.4%	8.1%
CD _{Ni}	1<x≤1.5		x>1.5
Number	4		1
Ratio	1.2%		0.3%
Note: Average :-0.04; Min:-0.77; Max:1.56			

Table 10. The contamination degree on Ni in surficial soil of Guiyang city.

CD _{Zn}	≤0	0< x≤0.5	0.5< x≤1	1<x≤1.5
Number	259	52	11	5
Ratio	77.8%	15.6%	3.3%	1.5%
CD _{Zn}	1.5<x≤2	2<x≤2.5	x>2.5	
Number	2	2	2	
Ratio	0.6%	0.6%	0.6%	
Note: Average:-0.15; Min:-1.00; Max:2.85				

Table 11. The contamination degree on Zn in surficial soil of Guiyang city.

4.2.3 The correlation of heavy metal elements in surficial soil

The correlation of heavy metals were analyzed and twin-elements that correlation coefficient reached extremely significant level ($P < 0.01$) were As–Pb, Cd–Cr, Ni–Cd, Cu–Cr, Cr–Ni, Cr–Zn, Cu–Ni, Cu–Pb, Cu–Zn, Ni–Zn, Pb–Zn, the twin-elements which correlation was $P < 0.05$ were As–Zn, Cd–Hg, Cd–Zn, Pb–Ni by using SPSS16.0 with CA (Table 12). The correlation between heavy metals mainly because of heavy metal elements between parent rocks associated. For example, the correlation of metalloid element As and Pb reached extremely significant level, of As and Zn reached significant level, for As ore often associated in the sulfide mineral of Pb and Zn, and were produced together with other minerals such as pyrite and sphalerite. The content of As was less than 5-10000 mg/kg in the galena, abnormal area were formed when As were released in the ore mining and smelting

(Liao Z J, 1992). Pb-Zn deposits were mainly distributed in the northeast area, northwest area, south-central area and southwest area (Xu H N and Xu J L, 1996). As and its compound were often accompanied in the non-ferrous metal and precious metal ore, arsenide was distributed in the kinds of intermediate product (Li Q and Mo D L, 1997). The correlation of Cd and Zn reached significant, because there was no separate Cd ore, Cd was often accompanied with Zn ore, Cd was generally existed in the Zn ore as the forms of CdS and CdCO₃, and the concentration of Cd was between 0.01% and 0.5%.

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
As	1						** (+)	* (+)
Cd		1	** (-)		* (+)	** (+)		* (-)
Cr			1	** (+)		** (+)		** (+)
Cu				1		** (+)	** (-)	** (+)
Hg					1			
Ni						1	* (-)	** (+)
Pb							1	** (+)
Zn								1

*: significant level(P<0.05); **: extremely significant level(P<0.01);
(+): positive correlation; (-): negative correlation

Table 12. The relativities between contaminating elements in surficial soil of Guiyang.

4.2.4 The influences of soil types in heavy metals pollution

On the basis of measured values in the different characteristics of soil types on heavy metals in surficial soils, the space isoline map and soil type distribution map of Guiyang City were overlaid by using the software ArcView 3.2. The different level concentrations of heavy metals were statistical analyzed according to the different soil types. Meanwhile, to facilitate analysis, , soil types within the study area were divided into three types by human impact: man-influenced soil type, soil type by human impact in general and soil type with less human impact.

4.2.4.1 Soils types with stronger human impact: Yellow earths, limestone soils, paddy soils

Yellow soil lands an area of 3.335×10^5 ha for the area of Guiyang City it totally lands 41.5% land area of Guiyang City. Yellow was born in hot and humid environmental conditions, rock weathering and fast weathering by strong leaching, base captions and silicon ions have leached, clay and the formation of secondary minerals constantly, ferric oxide relative aggregation, in which iron oxide by strong hydration, the formation of high water content of goethite ($\text{Fe}_2\text{O} \cdot \text{H}_2\text{O}$), limonite ($\text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$), more water, iron oxide ($\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), the

yellow hue of the minerals is the main hue(Sun,2002). Lime area 2.021×10^5 ha, accounting for land area of Guiyang City, 25.2%. Guiyang Karst landforms, carbonate rocks are widely distributed, accounting for 80.63% area of Guiyang City, the corrosion - erosion, the erosion severe cases, the carbonate rocks exposed, weathering and limestone soil. Corrosion of carbonate karst weathering process is the release of Ca leaching, the residual calcium carbonate and clay minerals into the soil formed by the lime soil, shallow soil, and more with rock debris, soil properties affected by lithology great, are rock soil. Limestone soil, with the abundant calcium and substitution of base level is high, the leaching process, due to constantly add calcium carbonate to the soil base to be preserved, weathering alteration of other minerals are also weak, delayed Al-rich off the role of silicon occur so long in a juvenile state. Distribution of lime in the soil and the soil zone boundaries clearly.

Paddy area is 1.156×10^5 ha, accounting for the total land area of Guiyang City, 14.40%. In dam and hills in the valley bottom of the groove, light and heat conditions are good, as the irrigation and drainage conditions are good, the piece of the paddy field in the long-term hydroponics are the formation of the hydromorphic paddy soils that was the advanced stage of development of the paddy soil. As the periodic irrigation and drying, the soil, reduction and oxidation in alternating, the soil of iron, manganese and substances to restore migration, oxidative deposition, mind patterns of soil to form a brown rust, rust, and prism-like structure, which is a typical paddy soil types, is the main farming soil in Guiyang. The development at the initial stage of paddy rice soil infiltration education, are located in higher ground water table is low, almost no groundwater impact position. In the artificial irrigation, the irrigation of the soil affected by seasonal, alternating reduction and oxidation process, iron, manganese and base material was transported, deposited, in the former home territory, based on the formation of more than 20cm percologenic layer, initially with the characteristics of paddy soil. At the same time as soil pollution is not serious.

It shows that the levels of heavy metals were distributed at different levels, but mostly the first level and second level from Table 13 to Table 15. These three categories of soil type are the major soil types in Guiyang. By densely constraints, these three main soil types are local residents using the soil type. Yellow soil that the layer of soil and humus are thicker and soil acidity as well is the top soil for building timber forest and tea orchard. And its natural environment in which conditions is good, so it was open to most of the yellow land. Lime soil with high organic matter content, neutral to slightly alkaline, but the soil is thin, easy to dry; paddy soil water and heat conditions are better in the land after long-term aging and the formation of farming. In the long-term cultivation in the maturation process, human activities on soil heavy metal content of more. Therefore, the heavy metals content in different levels will have the distribution, while not a serious problem due to soil contamination, so in the first level and second level of the majority.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	73.2	20.2	74.2	96.7	37.2	63.7	68.4
2 th level	21.1	61.1	18.9	1.5	45.4	29.0	23.4
3 th level	3.7	16.5	4.1	0.5	12.3	4.8	4.6
4 th level	1.4	1.9	1.8	0.3	4.0	1.7	1.7
5 th level	0.4	0.3	0.5	0.2	0.8	0.5	1.9
6 th level	0.2	0.0	0.5	0.8	0.3	0.3	0

Table 13. The percentage (%) of different concentration levels of heavy metals in Yellow earths of Guiyang.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	61.2	30.4	70.3	97	38.4	69.2	73.8
2 th level	31.9	51.1	20.8	2.0	37.7	26.6	20.4
3 th level	4.8	13.4	5.8	0.4	13.3	2.9	5.1
4 th level	1.1	4.6	2.7	0.3	6.9	1	0.5
5 th level	0.5	0.4	0.4	0.2	3.3	0.1	0.2
6 th level	0.5	0.1	0	0.1	0.4	0.2	0

Table 14. The percentage (%) of different concentration levels of heavy metals in Limestone soils of Guiyang.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	69.6	22.6	74.2	96.8	40	68.3	72.6
2 th level	21.7	58.2	17.4	2.3	39.9	28.1	18.1
3 th level	6.3	16.7	4.9	0.4	13.7	2.6	6.5
4 th level	1.6	2	1.5	0.4	4.7	0.8	1.5
5 th level	0.3	0.5	1.5	0.1	1	0.1	1.3
6 th level	0.5	0	0.5	0	0.7	0.1	0

Table 15. The percentage (%) of different concentration levels of heavy metals in Paddy soils of Guiyang.

4.2.4.2 Soils types with common human impact: Skeleton soils, purplish soils, litho soils, yellow-brown earths

Thick bone was 1.015×10^5 ha of 12.64% total land area in Guiyang city. Thick bone parent rocks were the weathering slope and residual consisting of shale and sand-shale. The soil body of soil type was instability, developed badly, thin soil and serious soil erosion. Phosphorus, potassium content is low. Purple soil area 104 ha, Guiyang 1.20 land area of 1.9%. Purple soil are mainly Jurassic purple red sandstone and mudstone tertiary surface soil after a. Purple rock type soft and crunchy, physical weathering speed, soil erosion is fast. And constantly weathering has added to make purple soil in the early stage of long-term. Purple clay mineral grains by weathering, silicon, carbonate etc iron compounds to form complex was stable in surface film, delaying the chemical weathering, keep the minerals of iron ore, the properties of soil siderite, thus presents. The rock soil due to constantly weathering of supplement, natural fertility soil of natural vegetation, also grew thick.

It can be seen in the heavy metals element content level mainly focus on four levels from Table 16 to Table 19. These four types of soil or natural conditions, using value is not high, Either the area is small, but the natural conditions, so the natural vegetation, soil for use, so not easily by the four types of human influence, but also affect the three types of great influence. Therefore, the four kinds of soil heavy metal content mainly concentrated in the top four.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	71.2	28.3	67.0	96	44.5	68	72.2
2 th level	24.6	43.8	21.2	3.7	34.3	31.8	21.2
3 th level	3.8	25.3	6.0	0.1	12.3	0.2	6.6
4 th level	0.4	2.6	3.9	0.1	8.1	0	0
5 th level	0	0	1.7	0	0.8	0	0
6 th level	0	0	0.2	0.1	0	0	0

Table 16. The percentage (%) of different concentration levels of heavy metals in Skeletal soils.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	68.3	21.1	87.5	91.4	41.8	78.1	68.6
2 th level	22.3	67.1	10.1	6.6	42.2	15.8	26.2
3 th level	7.5	9.9	1.1	0.7	8.2	4.7	4.8
4 th level	1.9	1.9	1.3	0.7	2.5	1.4	0.4
5 th level	0	0	0	0.6	4.3	0	0
6 th level	0	0	0	0	1.0	0	0

Table 17. The percentage (%) of different concentration levels of heavy metals in Purplish soils.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	51.3	37.7	51.4	98.9	21.4	78.5	66.0
2 th level	39.3	38.0	33.1	1.1	42.7	18.5	30.6
3 th level	7.8	11.4	11.1	0	16.9	1.4	3.2
4 th level	1.5	7.0	4.4	0	6.2	1.6	0.2
5 th level	0.1	5.6	0	0	5.1	0	0
6 th level	0	0.3	0	0	7.7	0	0

Table 18. The percentage (%) of different concentration levels of heavy metals in Litho soils.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	52.3	28.5	90.0	79.3	45.2	41.7	78.6
2 th level	42.8	71.1	10.0	13.8	41.5	21.0	16.7
3 th level	4.9	0.4	0	3.1	7.3	25.1	0.7
4 th level	0	0	0	2.2	2.7	10.3	1.4
5 th level	0	0	0	1.3	3.3	0.4	2.6
6 th level	0	0	0	0.3	0	1.5	0

Table 19. The percentage (%) of different concentration levels of heavy metals in Yellow-brown earths.

4.2.4.3 Soils types with less human impact: Mountain meadow soils and bog soils

In Guiyang City, The area of the Bog soils is 902ha, accounting for 0.11% of the total. On the surface of the local ground of the plateau, peal coal was formed by the accumulation of wet plants in the ancient swamp. Crustal movement in the later, ground up-list, swamp marsh

broke off marsh gradually, black peat accumulated, the lower layers was white washing, which is the current peat.

Mountain meadow soil 379ha, accounting only 0.05% of land area of Guiyang. Mountain meadow soil is within the forest line, the gentle mountain top hi wet meadow and meadow shrub coppice Semis formed a class of soil. Such thin layers of soil, and generally contain gravel, grass surface layer with.

As shown in Table 20 to Table 21,the content of heavy metals in these two soil types are mainly concentrated in a Single interval, this phenomenon may be related to less human impact (such as fertilizer), heavy metals content in these soil types are mainly concentrated in the range corresponding their baseline values.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	0	16.8	100	0	100	0	100
2 th level	100	83.2	0	100	0	0	0
3 th level	0	0	0	0	0	17.4	0
4 th level	0	0	0	0	0	82.6	0
5 th level	0	0	0	0	0	0	0
6 th level	0	0	0	0	0	0	0

Table 20. The percentage (%) of different concentration levels of heavy metals in Bog soils.

	Cd	Cr	Cu	Hg	Ni	Pb	Zn
1 th level	100	65.8	98.2	100	0	0	100
2 th level	0	34.2	1.8	0	100	100	0
3 th level	0	0	0	0	0	0	0
4 th level	0	0	0	0	0	0	0
5 th level	0	0	0	0	0	0	0
6 th level	0	0	0	0	0	0	0

Table 21. The percentage (%) of different concentration levels of heavy metals in Meadow solonchaks.

5. Conclusions

1. The mean value, standard deviation and maximum of As separately are 18.09 mg/kg, 11.57 mg/kg and 79.30 mg/kg in the surficial soil in Guiyang, of Cd separately are 0.302mg/kg, 0.363mg/kg, 2.620mg/kg and 95.7 percent smaller than 1.000mg/kg., of Cu separately are 43.1mg/kg, 30.3mg/kg, 213.0mg/kg and 94.6 percent smaller than 100.0mg/kg, of Pb are 43.2mg/kg, 31.3mg/kg, 318.9mg/kg and 95.5 per cent smaller than 100.0mg/kg, of Hg are 0.222mg/kg, 0.531mg/kg, 7.030mg/kg and 98.2 smaller

- than 1.000mg/kg, of Ni are 38.3mg/kg, 14.9mg/kg, 102.5mg/kg and 95.8 percent smaller than 70.0mg/kg, of Zn are 84.7mg/kg, 49.8mg/kg, 385.0mg/kg and 94.3 percent smaller than 150.0mg/kg.
2. Comprehensively considering the results of calculation using the two kinds of methods, we respectively take 9.04mg/kg, 0.068 mg/kg, 18.8 mg/kg, 46.3 mg/kg, 14.8 mg/kg, 0.045 mg/kg, 44.0 mg/kg, 17.0 mg/kg as the baseline values of As, Cd, Cu, Zn, Pb, Hg, Cr and Ni in topsoil of Guiyang.
 3. By the results of Geo-accumulation analysis of heavy metals in surficial soil, we get the surficial soil in 41 per cent of the Guiyang did not suffer the arsenic contaminative, In 40 per cent did not suffer the cadmium contaminative, In 46 per cent did not suffer the chromium contaminative, In 38 per cent did not suffer the copper contaminative, In 18 per cent did not suffer the lead contaminative, In 12 per cent did not suffer the mercury contaminative, In 19.2 per cent did not suffer the nickel contaminative.
 4. By the results of contamination degree analysis, the maximum of arsenic contaminative degree of surficial soil in Guiyang is 4.27. Of cadmium are 12.1. Of chromium are 2.01. Of copper are 5.09. Of lead are 8.11. Of mercury are 45.87. Of nickel is 1.56. Of zinc are 2.85.
 5. The soil types in this area were divided into three types of soil by the human impact degree. The three soil types of yellow soil, limestone soil and paddy soil that were the main soil types in Guiyang city were greatly influenced by human. The four soil types of skeleton soil, purple soil, stone soil and yellow brown soil that were not easily used were certainly influenced by human, the concentration of heavy metals in boggy soil and mountain meadow soil were concentrated on an interval, and tow types of soil (boggy soil and mountain meadow soil) were less influenced by human.

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