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Original Research Paper

Analysis of Existing Speciation and Evaluation of Heavy Metals Pollution of Soil in a Shooting Range

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ABSTRACT

In this paper, we have made an investigation and analysis of the concentrations of Pb and Cu in the surface soil samples from a small arms shooting range in Guangxi Province of China by using the U.S.EPA3050B (HNO_3-H_2O_2) method, and evaluated the pollution in the sampling area through the single factor index method and the composite pollution index Nemrow method. The results of our investigation and analysis showed that the soil of the small arms shooting range is heavily polluted by heavy metals, and the main pollution elements are Pb and Cu. The composite pollution index reached 59.18, and the single-factor pollution indexes of Pb and Cu have been the highest in the area of dropping bombs, which reached 72.90 and 10.12 respectively, indicating that the pollution has been to a serious level. The sources of heavy metal pollution comprise residual bullets and cartridge cases. We have also done analysis of the concurrent speciation of Pb and Cu in the soil with the sequential extraction method of Tessier, and discovered that the chemical speciation distribution order stands as follows: Resid–Pb > FeMnO–Pb > Org–Pb > Carb–Pb > Exch–Pb. As to the distribution characteristics of Cu, the order can also be listed as follows: Resid–Cu > Org–Cu > FeMnO–Cu > Carb–Cu > Exch–Cu. It can be seen that heavy metal Pb do much more serious to the ecological environmental contamination risk. Once the environmental conditions change, Pb and Cu can be easily transformed into bioavailability speciation. Because the pollution of heavy metal Pb and Cu in shooting range is serious, it is unfeasible to turn the shooting range soil into agricultural soil.

INTRODUCTION

Soil pollution by heavy metals is one of the major environmental problems and has the characteristics of strong concealment, extensive pollution area, long-term damage and difficult governance (Chen et al. 2011). With the development of human society, heavy metal pollution sources become increasingly diversified. Apart from strengthening prevention and control efforts towards smelting, printing, transportation and other traditional pollution sources, soil heavy metal pollution caused by shooting bullets has gradually become the focus of this field (Rantalainen et al. 2006, Li et al. 2009). According to the research, heavy metals in soil exist in various forms and their existing forms and proportions are the key factors that affect the ecological environment around (Liu et al. 2009), and they have a direct impact on migration and transformation of heavy metals, ecological effect as well as the harm to crops (Dermatas et al. 2006).

This research selects the soil of the small arms shooting range in Guangxi as the object. Based on the monitoring analysis of six common heavy metals (Pb, Cu, Zn, Co, Ni, As) in the soil, the research evaluates heavy metal pollution degree of the soil of the shooting range, analyses effective forms of Pb and Cu (their content in the soil is much higher than the background value) and their proportions of the total heavy metal content in the soil of the bomb-beaten area and discusses the effect of effective forms of heavy metals in the soil. The research is of vital significance to have an understanding of migration characteristics of heavy metals and their harm to the surrounding crops, and the feasibility of turning into a farming land of the research area.

MATERIALS AND METHODS

Soil sample collection: Soil samples were collected in the small arms shooting range of a military academy in Guangxi, and the shooting range covers an area of about 4.38×10^4 m^2 and has been put into use for more than 20 years. The whole area can be divided into bomb-beaten area, non-bomb dropping area and barrack area. Non-bomb dropping area consists of submachine gun shooting area, pistol shooting area and gully weeds area (Fig. 1). Bomb-beaten area, pistol shooting area and submachine gun shooting area use grid arrangement method and gully weeds area adopts serpentine arrangement method (NEPA HJ/T166-2004). Every grid of pistol shooting area and submachine gun shooting area is about 10 m × 10 m with total sampling of 80, and every grid of the bomb-beaten area is about 8m × 8m with total sampling of 24. Adhering to the diagonal (4 vertices and a centre)

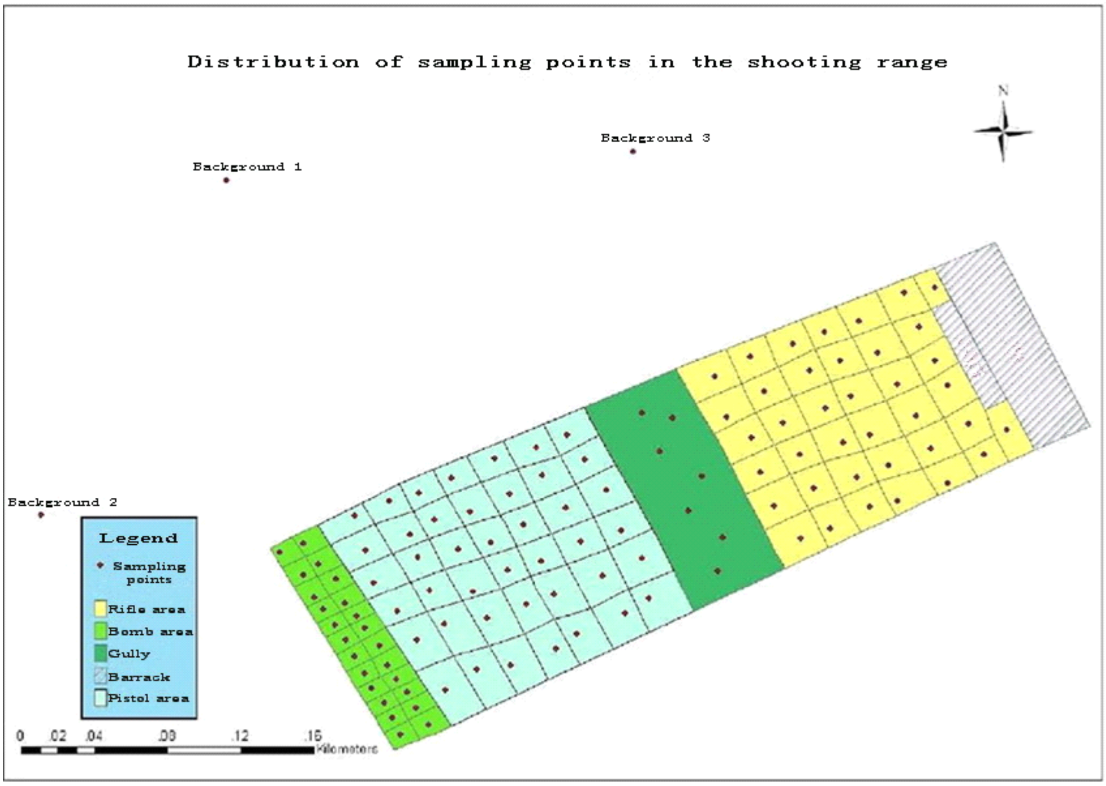

Fig. 1: Distribution of sampling points in the shooting range.

principle, about 0~20 cm surface soil of 0.5 kg is collected in each grid, and according to quartering, about 1 kg soil is selected as the standard soil sample after they are mixed evenly. Deep vegetation makes sampling very difficult in the gully weeds area, therefore, serpentine arrangement method is adopted and soil of the two points within 3 meters away is collected and mixed into a standard soil sample with total soil sampling of 7. Moreover, areas that are 200 meters away from the shooting range and are less influenced by shooting training are selected for soil sampling with 3 background soil samples and 114 samples in total. The soil samples are taken to a laboratory, and after air drying, their plant residues and rock particles are picked out, finely ground (through 100 mesh) and are bagged for later use (Bao 2000).

Soil sample analysis: Sampled soil type belongs to red earth and average pH value of the soil is 6.64.

Total quantity of heavy metals in the soil has been determined by adopting U.S.EPA3050B method recommended by Environmental Protection Agency of the United States and plasma emission spectrometer–ICP-OES (Optima-7000). National standard soil reference materials (GSS-2 and GSS-4) were used for analytical quality control so as to make sure that the results can meet the quality control requirements.

Tessier sequential extraction method is used for speciation analysis of heavy metals in the soil. Heavy metal speciation in the soil is defined as five categories: exchangeable state (water-soluble and ion-exchangeable states), carbonate combination state, iron and manganese oxidation state, organic combination state, and residual state (Tessier et al. 1979).

RESULTS AND DISCUSSION

Monitoring Results of Total Amount

The authors have made an analysis of 24 surface soil samples of the bomb-beaten area, 87 surface soil samples of the non-bomb dropping area as well as 3 background soil samples in the experiment with monitoring of six heavy metals, Pb, Cu, Zn, Co, Ni and As. The result is that Cu and Pb contents are much higher than the background value, which is shown in Table 1.

Pb content peaks at 2763 mg/kg, its standard deviation value is larger and variation coefficient is smaller in the bomb-beaten area, which is contrary to the results of Pb in non-bomb dropping area due to the fact that Pb content

Table 1: Analysis of monitoring results of surface soil samples in the shooting range.

Area Division	Element Name	Number of Samples	Minimum mg/kg	Maximum mg/kg	Mean Value mg/kg	Standard Deviation	Coefficient of Variation
Bomb-beaten area	Cu	24	104.00	306.90	214.62	53.10	0.247
	Pb	24	414.40	2763.00	1375.35	546.54	0.397
Non-bomb Dropping area	Cu	87	17.04	226.20	41.95	30.40	0.725
	Pb	87	22.58	153.70	55.21	24.79	0.449

Table 2: Analysis of monitoring results of background of Pb and Cu in the shooting range.

Element Name	Background 1 mg/kg	Background 2 mg/kg	Background 3 mg/kg	Mean Value mg/kg	Standard Deviation	Coefficient of Variation	Evaluation Criterion (Si)mg/kg
Cu	22.37	25.76	27.42	25.18	2.57	0.102	30.33
Pb	33.93	36.63	34.36	34.97	1.45	0.042	37.87

Table 3: Single-factor index evaluation results of surface soil samples in the shooting range.

Area Division	Element	Pollution Index of Single Factor						
		Maximum	Minimum	Mean Value	Unpolluted Area	Mildly Polluted Area	Moderately Polluted Area	Seriously Polluted Area
Bomb-beaten	Cu	10.12	3.43	7.08	0	0	0	24
Area	Pb	72.95	10.94	36.31	0	0	0	24
Non-bomb	Cu	7.46	0.56	1.38	28	50	4	5
Dropping Area	Pb	4.06	0.60	1.46	23	49	13	2

varies greatly between the bomb-beaten area and the non-bomb dropping area. Cu content peaks at 306.90 mg/kg in the bomb-beaten area and Cu content difference between the bomb-beaten area and the non-bomb dropping area is smaller than that of Pb. According to the research, Pb content of bullets, the main pollution source in the bomb-beaten area, is far higher than that of Cu, which leads to larger Pb content difference between the bomb-beaten area and the non-bomb dropping area. And there are more cartridge cases that have higher Cu content in several areas of the non-bomb dropping area, which reduces Cu content difference between the bomb-beaten area and the non-bomb dropping area to some extent.

Pollution Index of Single Factor

Evaluation index calculation and evaluation standard: Single factor index method is the most frequently used method for evaluating pollution degree of a heavy metal element and its calculation formula is as follows.

$$Pi = Ci/Si$$

Where, *Pi* refers to single factor index of the pollution element, *Ci* refers to measured concentration (mg/kg) and *Si* refers to soil environmental evaluation standard (mg/kg).

Soil Environmental Quality Standard (NEPA GB 15618-1995) or background value method is taken as the standard for evaluating heavy metal pollution in China. In order to further highlight the effect of shooting training on the soil environment of the sampled areas, this research adopts background value method and sets the monitored background values that are added with two times of standard deviations (NEPA GB HJ/T166-2004) as the evaluation standard for soil environment. Pollution grading: If $Pi \leq 1.0$, the soil is unpolluted; if $1.0 < Pi \leq 2.0$, the soil is mildly polluted; if $2.0 < Pi \leq 3.0$, the soil is moderately polluted; and if $Pi > 3.0$, the soil is seriously polluted. The larger the *Pi* value is, the more seriously the soil is polluted (NEPA GB15618-1995).

Background values of Pb and Cu and soil evaluation standard in three background sampled points of the shooting range are given in Table 2.

Evaluation results: Single factor pollution indexes and pollution degree of Cu and Pb in the shooting range are given in Table 3. Single factor pollution index of Cu ranges from 0.56 to 10.12, and there are 29 seriously Cu-polluted areas with 24 in the bomb-beaten area and 5 in the non-bomb dropping area. And single factor pollution index of Pb ranges from 0.60 to 72.59, and there are 26 seriously Pb-polluted areas with 24 in the bomb-beaten area and 2 in the non-bomb dropping area. The results show that Pb and Cu pollution is serious in the bomb-beaten area. According to the analysis, more residual bullets in the soil of the bomb-beaten area are the main sources of Pb and Cu with the result that seriously polluted areas are mainly in the bomb-beaten area. As there are fewer bullets in the soil of the non-bomb dropping area, cartridge cases of several areas cause relatively lighter pollution. However, under the action of acid and alkali corrosion, natural dust, rain washing, direct surface runoff and biological migration, Pb and Cu in the bomb-beaten area gradually spread to the non-bomb dropping area, as a result, the non-bomb dropping area is also seriously polluted.

Nemrow Composite Pollution Index

Evaluation index calculation and evaluation criterion: Nemrow index has strong applicability and is generally acknowledged as one of the effective methods for evaluating composite soil pollution by heavy metals. Its calculation formula is:

$$P_N = \sqrt{\frac{P_{ave}^2 + P_{max}^2}{2}}$$

In the formula, P_N refers to Nemrow composite pollution index, P_{ave} refers to arithmetic average value of each pollutant index and P_{max} refers to maximum value of each pollutant index.

Based on the analysis of single factor index evaluation, Nemrow composite pollution index takes the initial value of soil pollution in the shooting range (average value of soil environmental background plus two times of standard deviation) as the evaluation standard, consults the previous research findings and grades soil environmental quality into four levels. If $P_N < 1.0$, the soil is unpolluted; if $1.0 < P_N \leq 2.5$, the soil is mildly polluted; if $2.5 < P_N \leq 7.0$, the soil is moderately polluted; if $P_N > 7.0$, the soil is seriously polluted (Chen 2005).

Evaluation results: Table 4 describes Nemrow composite pollution index evaluation results of Pb and Cu in the soil of the shooting range. It shows that P_N ranges from 9.25 to 59.18 in the soil of the bomb-beaten area and from 0.70 to 6.18 in the soil of the non-bomb dropping area. The mean value of P_N in the bomb-beaten area is 18.8 times as much as that of non-bomb dropping area, and 24 areas in the bomb-beaten area are all seriously polluted while the non-bomb dropping area has only 8 moderately polluted areas and has no seriously polluted area. These also prove that main pollution sources of Pb and Cu are bullets and cartridge cases in the soil of the shooting range.

Effective Form

Bioavailability of heavy metals refers to the character that heavy metals can be absorbed by plants or generate toxicity towards plants and can be evaluated by indirect toxicity data or organism concentration data. According to speciation and bioavailability of heavy metals, heavy metals can be divided into available state, potentially available state and unavailable state (Vleek et al. 2011). Available state, also known as effective form, includes water-soluble state and ion exchange state that are collectively called exchangeable state F1 in Tessier sequential extraction method and are immediate providers for heavy metals in available state to organisms. Potentially available state mainly includes carbonate combination state F2, iron and manganese oxides combination state F3, and organic combination state F4. Heavy metals in this speciation can release themselves to become available state and have a certain relationship with heavy metal bioavailability under the appropriate environmental conditions. Residual state F5, commonly referred to as ineffective or unavailable state, cannot be utilized by organisms and almost has no effect on heavy metal bioavailability (Pueyo et al. 2004, Huang et al. 2007).

The research uses Tessier sequential extraction method to determine speciation distribution characteristics of Pb and Cu in 24 surface soil samples of the bomb-beaten area (Table 5). In addition, percentage figure of 5 states of Pb and Cu is drawn according to the monitoring data of 24 samples in the shooting range (Fig. 2).

1. Pb and Cu in the soil of the bomb-beaten area of the shooting range exist mainly in the residual state, ranging from 27.17% to 72.01% and from 28.23% to 67.10% respectively. Both Pb and Cu content in exchangeable state are lower, and the average value of Pb content in exchangeable state is 45.73 mg/kg, accounting for 2.29% of the total. Pb proportion in every speciation in descending order is: Resid–Pb > FeMnO–Pb > Org–Pb > Carb–Pb > Exch–Pb. The average value of Cu content in exchangeable state is 1.57 mg/kg, accounting for 0.61% of the total, and Cu proportion in every speciation in descending order is: Resid–Cu > Org–Cu > FeMnO–Cu > Carb–Cu > Exch–Cu. Moreover, the average value of proportion Pb content in exchangeable state of the total is higher than that of Cu.
2. The average proportions of Pb and Cu in exchangeable state in the 24 soil samples of the shooting range are 2.29% (between 0.16% and 15.74%) and 0.61% (between 0.11% and 1.58%) respectively and their variation coefficients are 1.529 and 0.714 respectively. Proportions of

Table 4: Composite contamination evaluation results of surface soil in the shooting range.

Area Division	Nemrow Composite Pollution Index			Unpolluted Area	Mildly Polluted Area	Moderately Polluted Area	Seriously Polluted Area
	Maximum	Minimum	Mean Value				
Bomb-beaten area	59.18	9.25	29.92	0	0	0	24
Non-bomb-dropping area	6.18	0.70	1.59	17	62	8	0

Table 5: Speciation characteristics of heavy metals in surface soils in the shooting range.

Element	(mg/kg)	Element Speciation	Mean Value (mg/kg)	Maximum (mg/kg)	Minimum (mg/kg)	Standard Deviation	Coefficient of Variation
Pb	1993.99	F1	45.73	313.90	3.17	69.92	1.529
		F2	202.77	445.10	79.46	94.04	0.464
		F3	382.38	898.05	136.28	200.10	0.523
		F4	371.24	828.46	83.22	186.02	0.501
		F5	991.87	2037.81	189.17	490.61	0.495
Cu	257.08	F1	1.57	4.06	0.27	1.12	0.714
		F2	26.48	52.48	7.43	13.26	0.501
		F3	40.59	115.94	9.54	24.46	0.603
		F4	48.37	115.72	24.07	19.23	0.398
		F5	140.07	328.57	46.19	59.39	0.424

F1: exchangeable state (Exch-), F2: carbonate combination state (Carb-), F3: iron and manganese oxides combination state (FeMnO-), F4: organic combination state (Org-), F5: residual state (Resid-).

Pb and Cu in exchangeable state fluctuate greatly, and especially Pb, for Pb is higher in several samples and its proportion of the total is also higher than that of Cu. Furthermore, toxicity of Pb after entering the organism is higher than that of Cu. Therefore, Pb contributes more to bioavailability and biotoxicity of heavy metals than Cu.

3. Cu and Pb in carbonate combination state in the soil of the shooting range from 2.95% to 24.76% and from 2.81% to 30.17% respectively. Proportion of Pb in carbonate combination state is higher than that of Cu and carbonate has a huge effect on potential bioavailability, so potential bioavailability of Pb is higher. Pb and Cu in iron and manganese oxides combination state in the soil of the shooting range are also higher with Pb ranging from 8.03% to 31.78% and Cu ranging from 4.68% to 41.35%, and Pb and Cu in organic combination state vary from 6.86% to 39.51% and from 11.44% to 29.32% respectively.

Based on the above analysis, lower proportions of Pb and Cu content of the total in exchangeable state in the shooting range mean lower proportions of the effective states. Compared with Cu, Pb has higher bioavailability and biotoxicity and higher environmental pollution risk. What is more, some soil samples have higher Pb and Cu in potentially available state, and if soil conditions alter, potentially available state is very likely to change into available state, namely effective state, which will aggravate soil pollution by heavy metals in the shooting range.

Influence Factor

Heavy metals in effective form from soil solution can be absorbed and utilized by plants directly, which will do much harm to human beings and the environment while heavy metals that are closely mixed with soil particles generally can not be utilized by plants and will do little harm. Influenced by various factors, forms of heavy metals in the soil are in dynamic equilibrium and it is the dynamic equilibrium that determines bioavailability of heavy metals in soil.

Soil type and physicochemical properties: Soil of the shooting range belongs to red earth. Different soil types differ in speciation proportions of heavy metals, which relates to composition of soil particles. According to Sanderson's research on an Australian shooting range, heavy and clay soil contains lower heavy metals in exchangeable state and higher heavy metals in residual state, so its bioavailability is lower. But higher viscosity of red earth is conductive to reducing effective forms of heavy metals, which plays a positive role in reducing bioavailability of heavy metals in the soil of the shooting range (Sanderson et al. 2012). Soil organic matter content has a great effect on bioavailability of heavy metals in that different organic matter functions differently to state transformation of heavy metals. Research of Ashworth et al. (2004) shows that migration of Cu, Zn and Ni can have different effects, which may have some relationship with complex function between soil organic matter and various forms of heavy metals. Hu-

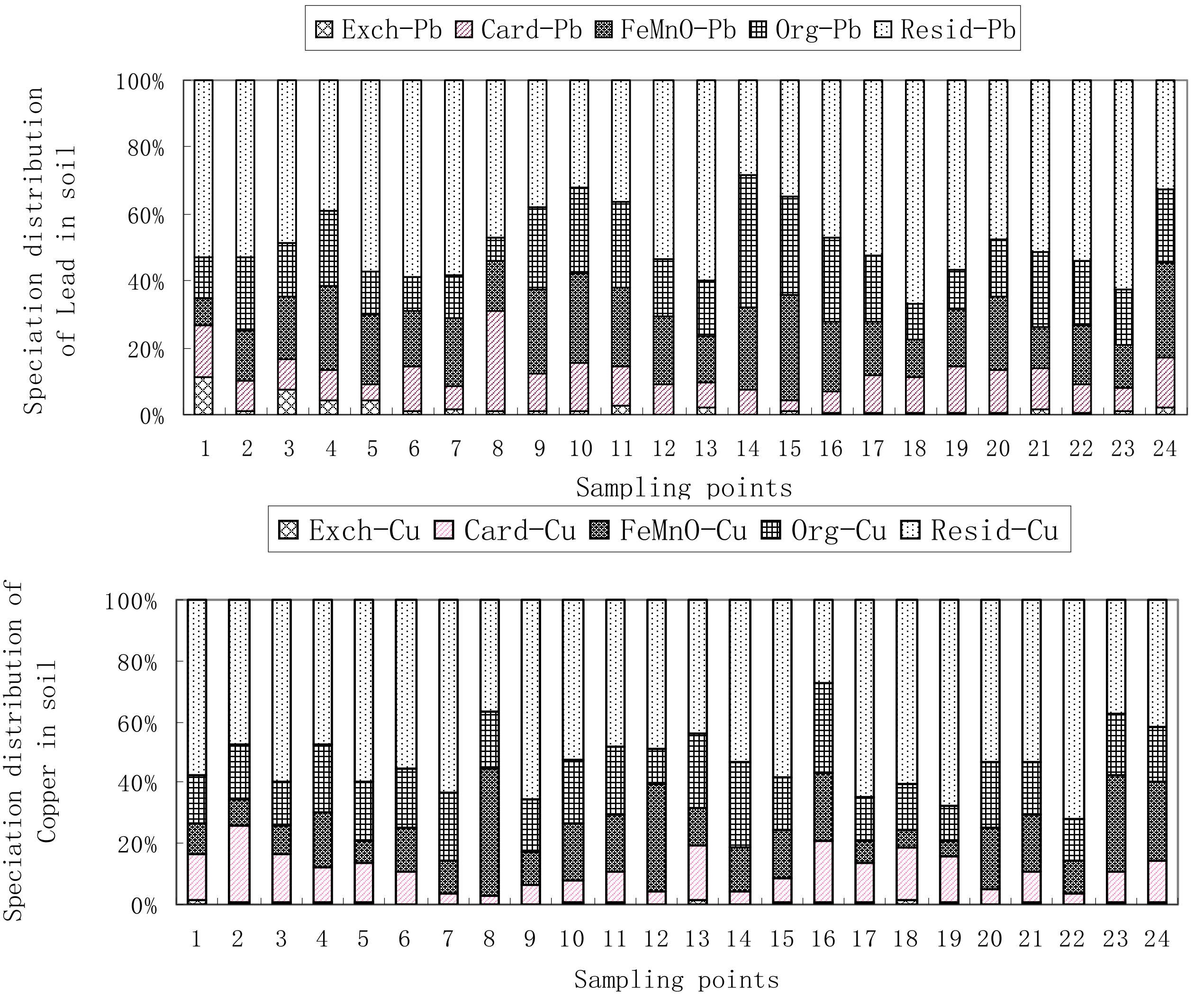

Fig. 2: Speciation analysis results of heavy metals Pb and Cu in the shooting range.

mic acid and fulvic acid, and other humus in organic matter have a huge influence on forms of heavy metals. According to Steely et al. (2007) research, mole mass fraction of humic acid of soil has a great effect on concurrent speciation of Sb. As the shooting range stands in south China where humus content in soil is higher, it will necessarily have certain effects on speciation transformation of Pb and Cu in the soil. Bioavailability of heavy metals is closely related with pH of soil, which increases with the decrease of pH in most cases, for instance, Chrysochoou et al. (2007) have found that when pH is greater than 6, it will significantly reduce dissolution and migration of Pb in soil, a conclusion reached when they studied solidification effect of phosphate on Pb in soil. pH of soil in the shooting range is relatively smaller and it will help to improve bioavailability of Pb and Cu.

Combined pollution of heavy metals: When combined pollution of heavy metals happens in the soil, interaction among various heavy metals can also affect the bioavailability. There may be additive, antagonistic or synergistic interactions among heavy metals. It is generally believed that antagonism is prone to occur among congeners and elements of similar physicochemical properties that will compete against each other for binding sites, which is similar to chemical properties of periodic elements. Some researches have shown that competition between Cd and Zn absorbed onto soil colloid for the adsorption site leads to the release of Zn to soil solution, which increases content of Zn in effective form and reduces the biotoxicity of Cd; and in the interaction between Cd and Pb, presence of Pb can promote absorption of Cd by rice while Cd can inhibit the absorption of Pb by rice (Wang et al. 2001). The pollution in the shooting range also belongs to combined pollution of heavy metals, therefore, Pb and Cu compete with each other for adsorption site in the soil colloid and heavy metal Cu is likely to promote dissolution of Pb to soil solution and increases the bioavailability of Pb under complicated soil environment.

Plant species and root environment: Bioavailability of heavy metals in soil is associated with surface growing plant species, and is greatly affected by root environment of plants. Owning to the influence of plant root exudates, chemical forms of heavy metals differ in content and distribution in rhizosphere and non-rhizosphere environment as rhizosphere activity can activate heavy metals in the rhizosphere environment and promote their bioavailability. According to Debela et al. (2010), citric acid, malic acid, oxalic acid and other small molecular organic acids that are frequently seen in plant root environment will promote the release of Pb to soil solution. Plants in the shooting range mainly include *Hemerocallis fulva*, *Bauhinia championi* and *Iresine herbsii*, all common plant species in the local area. Different varieties of plants will produce corresponding root exudates and form the root environment of their own, but some organic acids in their root exudates may have some positive effects on effective forms of Pb and Cu in the soil.

CONCLUSIONS

The research draws the following conclusions through sampling and analysis of the soil in the shooting range. The evaluation results through single factor index and Nemrow composite pollution index show that the soil of the shooting range is polluted by Pb and Cu and the bomb-beaten area has reached the serious pollution level, in general, with Nemrow pollution index arriving at 59.18. And residual bullets and cartridge cases are the main reasons.

The speciation distribution order of Pb in the bomb-beaten area is Resid–Pb > FeMnO–Pb > Org–Pb > Carb–Pb > Exch–Pb and speciation distribution order of Cu is Resid–Cu > Org–Cu > FeMnO–Cu > Carb–Cu > Exch–Cu. The heavy metals Pb and Cu are mainly exist in residual speciation ranging from 27.17% to 72.01% and from 28.23% to 67.10% respectively and proportions of effective speciation of Pb and Cu are lower, varying from 0.16% to 15.74% and from 0.11% to 1.58% respectively. Pb contributes more to bioavailability and biotoxicity of heavy metals in soil than Cu.

The dominant causes that affect the proportions of Pb and Cu in effective speciation in the soil of the shooting range are soil type, physicochemical property, combined pollution by heavy metals, plant species and root environment. So seriously polluted by Pb and Cu that plant growing is of higher risk, and the shooting range can hardly be transformed into an agricultural land.

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