Application of reconstructed background in assessing heavy metal pollution of soils near Jilin Section of the Songhua River, China

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Abstract. The distinguishing and evaluation of natural and anthropogenic sources of heavy metals in soils have always been the important issues in the field of environmental science. In this research, natural sources of heavy metals in soils are calculated according to the relationships between major oxides and heavy metals. The individual sample has independent backgrounds of heavy metals, which is more reasonable. If the single environmental background is used as baseline, anomalies in regions with low background might be decreased or hided and those in regions with high background will be overstated. In this study, enrichment factor is defined as the ratio of measured concentration and reconstructed background of heavy metals, which is of specific significance in practical applications with no assumptions. The agricultural soils near Jilin section of the Songhua River are polluted by Hg seriously with more than half samples polluted greatly. And the soils are polluted by Cd moderately. A few samples are polluted by Zn moderately. The other heavy metals in soils are almost in the level of background with little human disturbance.

1. Introduction

Heavy metals in soils mainly originate from natural sources and anthropogenic sources. Soil parent materials and soil-forming processes may influence the concentrations of natural heavy metals. Industry, mining, agriculture and transportation, etc are the major anthropogenic sources. The two sources of heavy metals usually form two kinds of anomalies, natural anomaly and anthropogenic anomaly. In regions that disturbed by human, the anomalies often exist together. So it is very important to separate natural and anthropogenic anomalies when evaluating the environment pollution. In recent years, people began to attach importance to the separation and determination of natural and anthropogenic anomalies and put forward different methods. For example, some identify the background and anomalies with the method of robust geostatistics [1], discriminate anthropogenic anomalies on the basis of the environmental behaviour and geochemical characteristics of elements [2], [3] apply the accumulation index [4] to discriminate anthropogenic heavy metal pollutions. Nevertheless, most of the methods are relatively complicated in practical application. And some use sparse samples referring to single environmental background to determine the heavy metal pollution [5], actually pollutions evaluated by such a method contains the mixture of anthropogenic and natural sources, through which we cannot effectively distinguish and track the sources of pollutants.

Soil includes residual soil and transported soil [6]. Residual soil is formed from the materials accumulated in situ after rock weathering which inherits the properties of the underlying rocks, and the
transported soil is formed from the materials transported remotely by wind and water after rock weathering which inherits the properties of the rocks in the distance. Formed from different soil parent materials, soils may have different concentrations of rock-forming elements, therefore natural sources of heavy metals are correlated with major oxides. Based on this relationship, we put forward the method of quantifying the natural sources using reconstructed background regressed by soil major oxides. Through the ratios of measured and background concentrations of heavy metals, the degree of anthropogenic pollution can be obtained. The procedures could be applied to other similar environments.

2. Materials & method

2.1. Study Area
We conducted our research along the downstream of the Songhua River (figure 1). The Songhua River is located in Jilin, China. Regions along the river are important grain production bases in China. In 1960s-1970s, this river was seriously polluted by wasted water from petrochemical factories in Jilin City.

![Figure 1. Soil sample locations in the middle-down stream of the Songhua River.](image)

2.2. Sampling and analysis
We set four sections in the irrigation area across the Songhua River and took 10 soil samples every 250 meters in each section. A total of 300 surface soil samples (0-20cm) were collected for studying their contamination levels. Then two sections were set away from the river irrigation area, and a total of 63 samples were collected which are deemed as unpolluted samples. Each sample was composed of four sub-samples collecting randomly within each grid. Each sample weighed more than 1 kg. After natural drying and the removal of gravel and plant roots, samples were sieved using a 20-mesh screen and then sent to a laboratory to be further processed to 200 mesh.

All analyses were carried out in the Ministry of Land and Resources Supervision and Inspection Center, Changchun. The concentrations of As and Hg were analyzed by atomic fluorescence
spectrometry (AFS) and the detection limits were 0.9 mg kg\(^{-1}\) and 0.003 mg kg\(^{-1}\), respectively. Samples were prepared by mixing 0.5 g of soil with 5.0 ml of nitric and hydrochloric acid in a 25 ml colorimetric tube and shaken well. Samples were then dissolved in boiling water for 2 h, during which they were shaken every 15 min. Next, samples were cooled and then diluted to scale. Finally, the solution was filtered through dry filtration and the filtrate was used for the determination of As and Hg.

Concentrations of Cd were determined using graphite furnace atomic absorption spectrometry (GF-AAS) with a detection limit 0.02 mg kg\(^{-1}\). Samples were prepared by placing 0.3 g of soil into a 50 ml polytetrafluoroethylene crucible, wetting with water, and then adding 5 ml of hydrochloric acid. Samples were then decomposed on an electric heating plate under a fume hood on low heat. Following evaporation to ~2–3 ml, samples were removed and cooled, before 5 ml of nitric acid, 4 ml of hydrofluoric acid, and 2 ml of perchloric acid were added. Samples were then returned to the electric heating plate at high temperature for 1 h. After 1 h, the cover was opened and heating was continued in order to remove Si. According to the condition of digestion, 2 ml of nitric acid, 2 ml of hydrofluoric acid, and 1 ml of perchloric acid were added and the above process was repeated. The mixture was then dissolved in 1 ml of nitric acid and transferred to a 25 ml flask, where 3 ml of diammmonium phosphate solution was added. Finally, after diluting the solution with water, it was cooled and well shaken for analysis.

The contents of Cu and Pb were measured using X-ray fluorescence spectrometry (XRF) with a detection limit 1 mg kg\(^{-1}\) for both. After thorough mixing, soil samples were formed into pressed pellets for analysis. In order to guarantee the accuracy of the method, all analyses were tested against the national primary standard material (GBW).

2.3. Principles

Researches showed that concentrations of trace elements in different types of rocks differ greatly [7], [8]. SiO\(_2\) is of the highest contents in rocks which can reflect the basic property of rocks. There are always significant correlations between the concentrations of trace elements and SiO\(_2\) in magmatic rocks. Soil is the product of rock weathering, and thus inherits its chemical composition [9], [10]. And elements in soil migrate, disperse and enrich, etc in a certain degree during the pedogenesis. According to researches on natural soil, correlations between As, Cr, Cu, Mn, Ni, Pb, Zn and SiO\(_2\), Al\(_2\)O\(_3\), TFeO or MgO are significant and that of Cd and Hg are relatively weak. So only by eliminating the natural geochemical variability of heavy metals, can we better identify the natural and anthropogenic sources.

The following multivariate linear equation is used to describe the relationships of heavy metals and major oxides:

\[
C_{hi} = \alpha + \sum \beta_j C_{oj} + \varepsilon
\]  

Where \(C_{hi}\) is the concentration of heavy metal i and \(C_{oj}\) is the content of oxide j from unpolluted samples, \(\alpha\) and \(\beta_j\) are undetermined coefficients, \(\beta_j\) represents the concentrations of heavy metals which change with soil parent materials, \(\varepsilon\) is random error. Using a multivariate linear regression program, the undetermined coefficients can be calculated. Consequently, we think that the relation of trace elements and oxides of study samples is exactly that of unpolluted samples. And we can use the concentrations of oxides of study samples to calculate the backgrounds of heavy metals for individual sample. Measured concentrations that are higher than background are thought to be polluted by anthropogenic activities, and the ratios of the measured and background concentrations are defined as EFs. The measured concentrations subtract background then divided by measured concentrations can estimate the percentage of anthropogenic sources.

3. Results & discussion

3.1. Natural concentrations of heavy metals

Correlation analysis on basis data shows that there are significant correlations between all heavy metals and major oxides in different degrees (table 1). Therefore multiple regression analysis was
carried to obtain the regression equations and then the equations were applied to the data for study to reconstruct the backgrounds of heavy metals, namely the natural sources.

Table 1. Correlations of heavy metals and major oxides.

|       | As  | Cd  | Cr  | Cu  | Mn  | Ni  | Pb  | Zn  | Hg  |
|-------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| SiO₂  | Pearson | -.424 | -.098 | -.488 | -.681 | -.369 | -.726 | -.293 | -.594 | .005 |
|       | Significance | .000 | .122 | .000 | .000 | .000 | .000 | .000 | .940 |
| Al₂O₃ | Pearson | .353 | .115 | .730 | .641 | .205 | .567 | .370 | .556 | -.010 |
|       | Significance | .000 | .070 | .000 | .000 | .001 | .000 | .000 | .881 |
| MgO   | Pearson | .528 | .136 | .735 | .833 | .372 | .794 | .436 | .679 | -.022 |
|       | Significance | .000 | .031 | .000 | .000 | .000 | .000 | .000 | .735 |
| TFeO  | Pearson | .564 | .070 | .815 | .807 | .392 | .656 | .464 | .802 | .249 |
|       | Significance | .000 | .269 | .000 | .000 | .000 | .000 | .000 | .000 |

Graphs illustrating the measured and background concentrations of heavy metals are shown in figure 2. In general, measured concentrations of As are 4-12 mg kg⁻¹ which are close to the backgrounds of 2-14 mg kg⁻¹. If the single environmental background is used, most of the measured values are less than it showing that As is not disturbed by human. However, there are specific samples (arrow 1 and 2) with the measured concentrations higher than the single environmental background, but less than the reconstructed background. In fact, natural source of As is relatively high due to the influence of soil parent materials. So the measured values are higher than the single environmental background, but this is not anthropogenic pollution. Measured concentrations of some samples (arrow 3) are less than single environmental background, but are higher than the reconstructed concentrations, which suggests that the samples are disturbed by human activities. This suits for the other elements.

Figure 2. Measured concentrations and reconstructed backgrounds of heavy metals.
Measured concentrations of Cd are 0.05 to 0.37 mg kg\(^{-1}\), which range greatly in different sections. Reconstructed backgrounds of Cd range from 0.05 to 0.17 mg kg\(^{-1}\), which are higher than single environmental background suggesting that soil parent materials contribute much to the natural sources of Cd in study area. Measured concentrations of Cr, Cu, Mn, Ni are 40-110 mg kg\(^{-1}\), 10-25 mg kg\(^{-1}\), 300-1150 mg kg\(^{-1}\), 17-33 mg kg\(^{-1}\) and reconstructed backgrounds are 35-70 mg kg\(^{-1}\), 17-40 mg kg\(^{-1}\), 300-1100 mg kg\(^{-1}\) and 15-35 mg kg\(^{-1}\), respectively. Reconstructed backgrounds of the above heavy metals fluctuate near the single environmental background. Measured concentrations of Pb are 20-43 mg kg\(^{-1}\), and the reconstructed backgrounds are 23-27 mg kg\(^{-1}\), which are less than single environmental background showing that natural sources of Pb are relatively small. Measured concentrations of Zinc are 70-270 mg kg\(^{-1}\) and the reconstructed background are 60-125 mg kg\(^{-1}\). The reconstructed background are higher than single environmental background overall showing that the soil parent materials may contribute largely to the natural sources of Zn. Measured concentrations of Hg are 0.05 to 2.2 mg kg\(^{-1}\), and reconstructed background concentrations are about 0.05 mg kg\(^{-1}\), which are nearly equal to the single environmental background.

Thus it can be seen that the reconstructed backgrounds of most heavy metals differ from the single backgrounds greatly. Anomalies in regions with low backgrounds may be decreased or hided and that in regions with high background will be overstated if the single environmental background is used.

3.2. Enrichment levels of heavy metals

The enrichment factor is usually used to evaluate the enrichment degree of heavy metals [11], [12]. Enrichment factor is expressed as EF:

\[
EF = \frac{(C_x/C_n)_s}{(C_x/C_n)_b}
\]

Where \(C_x\) is the element under consideration, \(C_n\) is the chosen reference element and the subscript “s” or “b” indicates which medium the concentration refers to. Sutherland [13] classified the EF into five grades to judge the enrichment degree of heavy metals. When EF is approximately equal to 1, heavy metals are depleted or not polluted by human activities; 1 < EF < 2 is suggestive of minimal pollution; 2 < EF < 5, moderate enrichment, suggestive of moderate pollution; 5 < EF < 20, significant enrichment, suggestive of a significant pollution signal; 20 < EF < 40, very highly enriched, indicating a very strong pollution signal; EF > 40, extremely enriched, indicating an extreme pollution signal.

Reimann [14] pointed out that the normalizer must be one or more important constituents of carriers of heavy metals reflecting the change of granularity in sediments. Previous studies usually take Al, Ni, Ti, V, Y, Li or Rb as normalizers. Three assumptions fundamental to the EF concept are (1) the low variability in concentration for the reference elements relative to the elements of interest, (2) the similarity in regional distribution patterns for various reference elements, and (3) the conservation of crustal (regional) element ratios through various compartments of the ecosystem. Obviously, the above three assumptions in practical application are hard to meet. Many studies use the elements directly or indiscriminately as normalizers ignoring the inherent assumptions. Therefore, when the assumptions are not met, high EFs may not indicate human disturbance.

In the previous researches, average crustal abundance was usually chosen as reference baselines [15-18] proposed the regional geological background should be used as the reference baselines. However, as the above elaboration, for the heavy metals that influenced strongly by soil parent materials, single environmental background cannot be used as the baseline. Owing to the disadvantages of traditional EF method, the ratio of measured concentration and reconstructed background is defined as enrichmenfigurget factor of heavy metal. This method has no assumptions. As shown in figure 3, only one sample in section D is polluted by As weakly, and the other samples are not affected by human disturbance. Half of the samples are polluted by Cd moderately and four samples are polluted by Cd weakly. One sample in section A is polluted by Cr weakly, one sample in section B and two samples in section D are polluted by Cu weakly. Two samples in section D are polluted by Mn weakly. Ni in all samples are in the level of background with no human disturbance.
Individual samples in section B, C, D are polluted by Pb weakly. Individual samples in section B, C, D are polluted by Zinc weakly to moderately. One sample in section B is polluted by Hg extremely and some samples in section A, C and D are polluted by Hg moderately to significantly.

The agricultural soils near Jilin section of the Songhua River are polluted by Hg seriously with more than half samples of over moderate pollutions. The polluted heavy metal is Cd with half samples of moderate pollutions. And individual samples are polluted by Zn moderately. The other heavy metals are almost in the level of background with little human disturbance.

For the heavy metals that are polluted by human obviously, anthropogenic source of Hg accounts for 39-98%, and the percentage of anthropogenic Cd are 37-80% and that of Zn are 47-77%.

![Figure 3. EFs of heavy metals](image)

4. Conclusions

The soil geochemical background traditionally refers to concentration of trace element formed naturally. The influence of soil parent materials should be taken into account to determine the background of heavy metals. For heavy metals that have significant correlations with soil parent materials, natural sources may differ obviously. If the single environmental background is used the anomalies in regions with low background may be hided and that in regions with high background may be overstated and thus affecting the effect of environmental assessment.

In this study, EF is defined as the ratio of measured concentration and reconstructed background. This method has no assumptions and one sample with individual background. EF can represent the enrichment degree of anthropogenic sources relative to the natural sources, which is of significance in practical application relative to traditional method.

Our study shows that the soils near Jilin section of Songhua River are polluted by Hg and Cd, to a lesser extent, Zn. Plants and humans are facing great threat, therefore, more efforts should be made to prevent and control pollution.
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