Geochemical Baseline and Trace Metal Pollution of Soil in Panzhihua Mining Area^{*}

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Abstract: A total of 31 topsoil samples were systematically collected from the Panzhihua mining area including steel smelting, coal mining, urban and rural districts. A normalization procedure was adopted to establish the environmental geochemical baseline models for this area. By using the above baseline models, the regional geochemical baseline values of As, Cr, Cu, Ni, Pb and Zn were determined. On the basis of the baselines, the enrichment factors were used to analyze the mechanism of trace metal pollution in topsoil from anthropogenic sources, and the results showed that the serious trace metal pollution is caused by human activities in coal mine, iron mine, smelting factory, tailing dam and other industrial districts in the Panzhihua area.

Key words: geochemical baseline; trace metal pollution; enrichment factor; Panzhihua area, SW China

Introduction

The term "geochemical baseline" was officially introduced in 1993 in the context of IGCP 360 Project "Global Geochemical Baselines", and further discussion was made in the following five years in the IGCP 259 Project "International Geochemical Mapping" (Salminen and Tarvainen, 1997). A geochemical baseline for an element refers to its natural variations in concentration in the surficial environment (Salminen and Tarvainen, 1997). The difference between the geochemical baseline and the background is that: the geochemical background represents the natural element concentration of a substance, and the baseline represents the on-the-spot measured concentration of an element in some sites under human disturbance. It is usually not a geochemical background in the real sense. Because of wide human activities, it is hard to establish the geochemical background than the geochemical baseline. The geochemical baselines provide an approach to defining natural spatial variations in the Earth's surface materials, not only for guiding policy makers to make policies toward environmental issues, but also for educating those public groups who are interested in environmental issues and would influence the priorities of official policies (Darnley, 1997).

A baseline may be used as a reference standard to monitor environmental changes ispite of either natural or anthropogenic comparative standards or scales (Teng Yanguo et al., 2001). So

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the purpose of baseline study is to take the "geochemical snapshot" of an area, which will be used as the grounds to monitor future environmental changes in geochemical landscape (Eppinger et al., 2001). Events that could change the geochemical landscape environment include mining, flood, landslide, wildfire, or resource developing activities, though the changes would not be boundless.

Geochemical baselines are required to document the current state of Earth's surface environment and to provide a database to monitor environmental changes (Darnley, 1997). The Geochemical baselines of elements depend on geological background, sample collection, sample grain size and sample treatment (Salminen and Tarvainen, 1997; Salminen and Gregorauskiene, 2000; Miko et al., 1999; Selinus and Esbensen, 1995).

High degrees of urbanization and the concentration of industrial and mining sites have led to a strong risk of heavy-metal contamination in the environment. Environmental monitoring of industrial and mining areas has become an essential facet in the assessment of and control over anthropogenic impacts on urban ecosystems. Natural and anthropogenic anomalies coexist in environmentally geochemical environment, so it is important to distinguish anthropogenic anomaly from natural anomaly in environmental impact assessment (Chaffee et al., 1997; Chaffee and Carlson, 1998). Geochemical baselines and related indices can be used to distinguish anthropogenic influence from natural one. The objectives are: to establish baseline models by means of a normalization procedure; and to assess the contributions of trace elements from natural and anthropogenic sources.

Study Area

Panzhihua, an important industrial and mining base with abundant mineral resources, is located in the southwest of China (Fig. 1). The huge-sized Panzhihua V-Ti magnetite [Fe(V, Ti)₃O₄] deposit, located in the southern part of the NS-trending Panxi rift valley, along the Jinsha River(a tributary of the Yangtz River) in Southwest China, provides 20% of Fe, 64% of V and 53% of Ti supply for China. The mining camp includes 6 large-scale iron deposits hosted in basic-ultrabasic intrusions, numerous medium-sized coal, clay, dolomite and limestone deposits, and minor graphite, manganese and barite deposits. Production facilities include a large steel manufacturing mill and a steel rolling mill. Extensive mining and processing activities have caused serious environmental impacts (Ni Shijun et al., 2001; Teng Yanguo et al., 2000, 2001).

Mining activities have left huge uncovered slopes, large areas of gangue ground and extensive tailings dams. 11.50 million tons of Fe ore are mined per year, and more than 680 million tons of excavated ore and gangue, and 220 million m^3 of tailing reserves have been deposited near the Jinsha River. Thus there is severe threat of trace metal pollution both in the mining area and further down stream towards the Yangtze River (Ni Shijun et al., 2001; Teng Yanguo et al., 2000, 2001).

Mining and processing activities have increased the level of air pollution, with higher levels of soot, dust, smog and other deleterious gases. In the last 3 years, the total amount of pollutant gases is estimated at 84.8 billion m³. Measured abundances of SO₂, NO_x, TSP, and CO in the air have become higher regularly than what is permitted by government requirements (Ni Shijun et al., 2001; Teng Yanguo et al., 2000, 2001).



Fig. 1. Geographical position of the study area in China.

Material and Methods

Systematic sampling was conducted to collect topsoil weathered from the Xigeda Formation in July, 2000. Sampled topsoil has similar geochemical background, so it is convenient to analyze environmental impact on soil from mining activities. A total of 31 sites included in steel smelting, coal mining, iron mining, power plant, residential and agricultural areas were sampled (Fig. 2). With the use of Scanning Electronic Microscope and X-ray diffraction analysis, it is determined that soil from the Panzhihua area is composed mainly of silty loam and silty soil.

The soil samples were dried and sieved to acquire < 0.063 mm fractions. The soil samples were analyzed by ICP-MS for As, Cr, Cu, Ni, Pb, Zn and Sc at the Institute of Geochemistry, Chinese Academy of Sciences. The analytical results and relevant parameters are presented in Table 1.

Table 1. Analytical results and relevant parameters for trace metals in topsoil samples from the Panzhihua area (n = 31)

	As	Cr	Cu	Ni	Pb	Zn	Sc	Ti
Mean (mg/kg)	13.12	81.61	34.49	45.40	29.32	78.86	9.45	3720
Median (mg/kg)	12.32	81.04	34.68	44.67	28.46	72.09	9.00	3720
Max. (mg/kg)	48.26	108.40	49.96	66.40	43.61	166.20	13.09	4500
Min. (mg/kg)	5.41	50.12	20.92	30.24	20.20	48.27	6.93	3000
Stdev	7.50	14.79	8.47	9.52	5.75	23.79	1.60	360



Fig. 2. Sketch map showing sample localities in the Panzhihua area.

Geochemical Baseline

A geochemical baseline for an element refers to its natural variations in concentration in the surficial environment (Salminen and Tarvainen, 1997).

Since metal particulates from natural and anthropogenic sources are accumulated together (Loring, 1991), a distinction needs to be made between the two sources (Abraham, 1998). In order to establish baseline models, which can reflect natural element concentrations, a normalization procedure is used. Geochemical normalization of the trace metal data to a variety of 'conservative' elements is commonly employed (Sutherland, 2000). To compensate for grain-size and mineralogical effects on trace element concentrations and to assess if anomalous metal contributions are present, a common approach is to normalize the geochemical data using one element as a grain-size proxy (Covelli and Fontolan, 1997). The normalization element must be an important trace metal carrier of one or two major trace elements and can reflect their granular variability in the sediments or environmental samples (Loring, 1990), so the elements Al, Ti, Fe, Y, Eu, Ce, Sc, etc. are usually used as normalization elements (Windom et al., 1989; Din, 1992; Prokisch et al., 2000).

On the basis of the scatter plots of element concentrations against grain-size or a grain-size proxy as a means of normalizing geochemical data, the baseline models can be set up and natural and anthropogenic enrichments can be distinguished (Loring, 1990; Loring and Rantala, 1992). The correlations from the scatter plots between grain-size proxy factor and trace metal concentration are shown in Fig.3.

The linear relationships among Ti, mud, sand, clay and other trace metals are not obvious (Fig. 3) because of mining, processing and steeling of the ore $Fe(V, Ti)_3O_4$, so the element Ti is not suitable to be used as a normalization element in the study area. At the same time, the grainsize proxies of clay, mud, and sand are not suitable, either. However, the correlations between Sc and other trace metals are very good, and the correlation coefficients of Sc and As, Cr, Cu, Ni, Pb, Zn are: 0.194, 0.933, 0.840, 0.921, 0.668 and 0.556, respectively. In addition, the



Fig. 3. Scatter plot between grain-size proxy and As, Cr, Cu, Ni, Pb and Zn. The regression line and 95% confidence band are reported to have been computed by the STATIS-TICA soft package.

geochemical behavior of the element Sc is similar to that of Al. At the same time, the activity of Sc is weaker than that of Al in the supergene environment (Liu Yingjun et al., 1984), so Sc also can be used as a normalization element.

The linear relationships between trace elements and Sc have been established, as is described by the formula $C_m = aC_N + b$ (Table 2), where C_m is the predicted metal content (baseline value) and C_N is the normalizing element (here is Sc) concentration in the sample. The 95% confidence band was estimated by means of the STATISTICA soft package, thus defining a range of data variability around each significant (P < 0.05) regression line. Samples are considered to be metal-enriched when values exceed the upper 95% confidence limit (Windom et al., 1989; Loring, 1991) or the upper 95% prediction limits (Rule, 1986; Schropp et al., 1990). In order to establish baseline levels, samples believed to have been impacted by anthropogenic sources should be removed from the data set (Summer et al., 1996). The predicted equations, values and related parameters for topsoil samples from the Panzhihua area are listed in Table 2. On the basis of these equations, a predicted value for each element and each sample was computed from Sc.

Enrichment Factors of Trace Metals

For the assessment of anthropogenic inputs, it is recommended to use a non-dimensional en-

Table 2. Entear relationships between trace metals and Sc						
Equation	Correlation coefficient	Significance	Regional baseline value (mg/kg)			
As = 0.907 Sc + 4.550	0.194	0.05	11.521			
Cr = 8.621 Sc + 0.167	0.933	0.05	81.583			
Cu = 4.445 Sc - 7.520	0.840	0.05	35.496			
Ni = 5.482 Sc - 6.384	0.921	0.05	45.664			
Pb = 2.400 Sc + 6.644	0.668	0.05	28.533			
Zn = 8.272 Sc + 0.717	0.556	0.05	76.916			

Table 2. Linear relationships between trace metals and Sc

richment factor (EF) to calculate the degree of enrichment of an element by dividing its ratio to the normalizing element by the ratio found in the chosen baseline (Middleton and Grant, 1990; Covelli and Fontolan, 1997; Lee et al., 1994, 1997):

 $EF = (X/Y)_{\text{sample}}/(X/Y)_{\text{baseline}}$

where X is the concentration of the potentially enriched element and Y is the concentration of the proxy element (normalizing element). A value of unity denotes no enrichment or depletion relative to the baseline (Covelli and Fontolan, 1997).

When EF < 1, it means that the trace metal is leached out of soil; when EF > 1, it means that the trace metal becomes a polluting element in the soil (Xia Zenglu et al., 1987). The following descriptive classification is given for the EF by Sutherland (2000): <2 indicative of no or minimal pollution; 2 - 5, moderate pollution; 5 - 20, significant pollution; 20 - 40, very serious pollution; and >40, extreme pollution.

The calculated EF for each element are within the range of 0.5-2.5, indicative of 1- or 2level contamination, i. e., from no contamination to moderate pollution (Fig. 4). The EF of trace metals vary from high to low in order of Zn > Cu > Pb > Cr > Ni > As, which provides information about trace metal contamination in the Panzhihua area.

The distribution characteristics of enrichment factors of trace metals are shown in Fig. 5. Anthropogenic trace metal pollution of topsoil is commonly seen in coal mine and duns pile, iron mine, limestone mine, smelting factory, tailing dam, and power plant. But in the agricultural and residential areas, trace metal contamination is very weak. The most serious pollution is recognized in coal mine and power plant. These results show that mining and industrial activities may lead to the release of some trace metals into the environment.



Discussion and Conclusions

Fig. 4. Box- and whisker-plot of the enrichment factors of trace metals.

Natural and anthropogenic anomalies

coexist in the geochemical environment, so it is important to distinguish anthropogenic anomalies from natural ones. Environmentally geochemical baseline is the basis for distinguishing anthropogenic from natural influence. We applied a normalization procedure to establish geochemical



Fig. 5. Distribution characteristics of trace metal pollution in the Panzhihua area.

baseline models in the Panzhihua area. By using the above baseline models and selecting Sc as a normalization element, the regionally geochemical baselines of the study area have been established: As = 11.52 mg/kg, Cr = 81.583 mg/kg, Cu = 35.496 mg/kg, Ni = 45.664 mg/kg, Pb = 28.533 mg/kg, and Zn = 76.916 mg/kg.

The calculated EF of each element are within the range of 0.5-2.5, indicative of 1- or 2level contamination, i.e., from no to moderate pollution. The relevant information on trace metal pollution in the Panzhihua industrial and mining area indicates that the most serious anthropogenic contamination of topsoil is produced in coal mine, iron mine, smelting factory, tailing dam and power plant, demonstrating the above areas have been influenced by anthropogenic contamination sources.

References

- Abraham, J., 1998, Spatial distribution of major and trace elements in shallow reservoir sediments: An example from Lake Waco, Texas [J]: Environ. Geol., v. 36, p. 349 363.
- Chaffee, M.A. and R.R. Carlson, 1998, Environmental geochemistry in Yellowstone National Park [J]: Distinguishing natural and anthropogenic anomalies: Yellowstone Science, v.6, p.29.
- Chaffee, M.A., J.D. Hoffman, and R.R. Tidball, 1997, Discriminating between natural and anthropogenic anomalies in the surficial environment in Yellowstone National Park, Idaho, Montana, and Wyoming, in R.B. Wanty, S.P. Marsh, and L.P. Gough, eds., the Program with Abstracts, 4th International Symposium on Environmental Geochemistry [R]: U.S. Geological Survey Open-File Report 97 – 496; v.16, p.106.
- Covelli, S. and G. Fontolan, 1997, Application of a normalization procedure in determining regional geochemical baselines [J]: Environ. Geol., v. 30, p. 34-45.
- Darnley, A.G., 1997, A global geochemical reference network: the foundation for geochemical baselines [J]: J. Geochemical Exploration, v.60, p.1-5.
- Din, T.B., 1996, Use of aluminum to normalize heavy-metal data from estuarine and coastal sediments of Straits of Melake [J]: Mar. Poll. Bull., v.24, p.484-491.
- Eppinger, R.G., P.H. Briggs, Z.A. Brown et al., 2001, Baseline geochemical data for stream sediment and surface water samples from Panther Creek, the Middle Fork of the Salmon River, and the Main Salmon River from North Fork to Corn Creek, collected prior to the severe wildfires of 2000 in central Idaho [R]: U.S. Geological Survey Open-File Report 01 161, p. 1 20.
- Föstner, U. and G. Müller, 1981, Concentrations of trace metals and polycyclic aromatic hydrocarbons in river sediments: geo-

chemical background, man's influence and environmental impact [J]: Geojournal, v.5, p.417-432.

- Lee, D.S., J.A. Garland, and A.A. Fox, 1994, Atmospheric concentrations of trace metals in urban areas of the United Kingdom [J]: Atmos. Environ., v.28, p.2691-2713.
- Lee, P.K., J.C. Touray, and P. Baillif, 1997, Trace metal contamination of settling particles in a retention pond along the A-71 motorway in Sologne, France [J]: Sci. Total Environ., v.201, p.1-15.
- Liu Yingjun., Cao Liming, Li Zhaolin et al., 1984, Element geochemistry [M]: Beijing, Science Press, 281p. (in Chinese with English abstract)
- Loring, D. H. and R. T. T. Rantala, 1992, Manual for the geochemical analyses of marine sediments and suspended particulate matter [J]: Earth Sci. Rev., v. 32, p.235-283.
- Loring, D.H., 1990, Lithium—a new approach for the granulometric normalization of trace metal data [J]: Mar. Chem., v.29, p. 155 168.
- Loring, D.H., 1991, Normalization of heavy-metal data from estuarine and coastal sediments [J]: ICES, J. Mar. Sci., v.48, p. 101-115.
- Martin, C.W., 2000, Trace metal trends in floodplain sediments and valley fill, River Lahn, Germany [J]: Catena, v. 39, p. 53 68.
- Middleton, R. and A. Grant, 1990, Trace metals in the Humber estuary: Scrobicularia clay as a preindustrial datum [C]: Proc Yorkshire Geol Soc, v. 48, p. 75 - 80.
- Miko, S., G. Durn, and E. Prohie, 1999, Evaluation of terra rossa geochemical baselines from Croatian karst regions [J]: J. Geochemical Exploration, v. 66, p. 173 – 182.
- Müller, G., 1969, Index of geoaccumulation in sediments of the Rhine River [J]: Geojournal, v.2, p. 108-118.
- Ni Shijun, Zhang Chengjiang, Teng Yanguo et al., 2001, Environmental impacts of mining the giant Panzhihua V-Ti magnetite deposit, SW China [Z]; Eleventh Annual V.M. Goldschmidt Coference (2001), abstract No.3530.
- Prokisch, J., B.Kovacs, and A.J. Palencsav, 2000, Yttium normalization: a new tool for detection of chromium contamination in soil samples [J]: Environmental Geochemistry and Health, v. 22, p. 317-323.
- Schropp, S.J., F.G. Lewis, H.L. Windom et al., 1990, Interpretation of metal concentrations in estuarine sediments of Florida using aluminum as a reference element [J]: Estuaries, v.13, p.227-235.
- Salminen, R. and V. Gregorauskiene, 2000, Considerations regarding the definition of a geochemical baseline of elements in the surfical materials in areas differing in basic geology [J]: Applied Geochemistry, v. 15, p. 647-653.
- Salminen, R. and T. Tarvainen, 1997, The problem of defining geochemical baselines: A case study of selected elements and geological materials in Finland [J]: J. Geochemical Exploration, v. 60, p. 91-98.
- Selinus, O.S. and K. Esbensen, 1995, Separating anthropogenic from natural anomalies in environmental geochemistry [J]: J. Geochemical Exploration, v.55, p.55-66.
- Summers, J.K., T.L. Wade, V.D. Engle et al., 1996, Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico [J]: Estuaries, v. 19, p. 581 - 594.
- Sutherland, R.A., 2000, Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii [J]: Environ. Geol., v. 39, p. 611-627.
- Teng Yanguo, Ni Shijun, Zhang Chengjiang et al., 2001, Countermeasures to restore environment and rehabilitate ecology in the Panzhihua mining industry base [J]: Sichuan Environment, v. 20, p. 31-34 (in Chinese with English abstract).
- Teng Yanguo, Ni Shijun, Zhang Chengjiang et al., 2000, Countermeasures of reducing environmental impacts from mining activity in the Panzhihua iron and steel base [J]: China Mining Magazine, v.9, p.95-98 (in Chinese with English abstract).
- Teng Yanguo, Ni Shijun, and Zhang Chengjiang, 2001, Introduction to the study of environmental geochemical baseline [J]: Computing Techniques for Geophysical and Geochemical Exploration, v. 23, p. 135 - 139 (in Chinese with English abstract).
- Windom, H.L., S.J. Schropp, and F.D. Calder, 1989, Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States [J]: Environ. Sci. Technol., v.23, p.314-320.
- Xia Zenglu, Li Senzhao, Li Tingfang et al., 1987, Soil element background and study method [M]: Beijing, Meteorology Press, p. 92 - 94 (in Chinese with English abstract).