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National multi-purpose regional geochemical survey in China



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ABSTRACT

Since 1999, a new geochemical mapping project, the National Multi-Purpose Regional Geochemical Survey (NMPRGS), has been carried out in the agriculturally and industrially developed regions of China, covering mainly the plains of the eastern and central parts of the country. The primary purpose of this project is to generate systematic multi-medium geochemical data that can be used by subject-matter experts to support the development of policies for protecting the surface environment, improving the efficiency of agriculture and supporting land use planning. Surface (0-20 cm) soils were collected at a density of 1 sample/km² and deep soils (150-180 cm) were taken at a density of 1 sample/4 km². Samples from 4 km² for surface soils, 16 km² for deep soils, were composited for chemical analysis. Additionally, lake sediments and near-shore sediments were collected at a lower density. Each sample was analyzed for total content of 52 components (Ag, As, Au, B, Ba, Be, Bi, Br, Cd, Ce, Cl, Co, Cr, Cu, F, Ga, Ge, Hg, I, La, Li, Mn, Mo, N, Nb, Ni, P, Pb, Rb, S, Sb, carbon and pH. As of the end of 2012, sampling of 1.7 million km² has been completed and samples from 1.5 million km² have been analyzed. Preliminary achievements have been made in the studies of geochemical variations, the establishment of the natural background and eco-geochemical assessment. An encouraging progress has been made in the application of geochemical knowledge to protecting the surface environment, improving the efficiency of agriculture and promoting sustainable land use.

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1. Introduction

In China, the first national geochemical mapping project, Regional Geochemistry-National Reconnaissance Program (RGNR), was initiated in 1978 with a strong focus on mineral resource exploration (Xie et al., 1989, 1997, 2008, 2009). Standardized sampling protocol, cost-effective and low detection limit analytical scheme, and rigorous analytical quality control have led to the discovery of thousands of mineral deposits during the thirty-five years since its inception. The RGNR project has been seen as one of the most successful geochemical mapping projects in the world (Darnley, 1995). Since the early 1990s, a range of projects have been launched to make their efforts to global geochemical mapping. The Environmental Geochemical Monitoring Network (EGMON)

Program, which commenced in 1992, involved extremely low density geochemical mapping using floodplain samples. This project was a pilot study for using floodplain sediment as a sampling medium for global geochemical mapping (Cheng et al., 2008a; Xie and Cheng, 1997). The Seventy-six Geochemical Elements Mapping Project in S.W China and S. China has also made a great contribution to mineral exploration, especially for rare elements (Cheng et al., 2012a; Xie et al., 2008). Since 2008, the China Geochemical Baselines Project (CGB) has been carried out to sample rocks, soils and overbank/floodplain sediments for the establishment of China nationwide geochemical baselines (Wang, 2012).

With the great success of geochemical mapping in mineral exploration, the significance of geochemical knowledge, soil geochemistry specifically, to support environmental and agricultural studies has gradually been recognized (Garrett et al., 2008). Preliminary studies were conducted in the 1980s and 1990s to understand the environmental and health effects of potential toxic elements in soils and stream sediments in China (Xie and Ren, 1993). The relationship between soil elemental concentrations and crop yields has also been investigated (Gu et al., 1998). Pilot geochemical surveys have been carried out in

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alluvial plains and urban areas (Zhang et al., 1993; Zhu et al., 1996). China has also conducted two national-scale soil surveys in the meantime. The first was the Second National Soil Survey, which sampled soils in 1979–1984 at an average density of 1.5–3 samples/km². Two million soil samples of tillage layer were collected across about 2800 counties of the whole country and analyzed for nutrient concentrations (National Soil Survey Office, 1998). The second was the National Soil Background Survey in the late 1980s, which collected soils from A, B and C horizons of 4095 soil profiles and analyzed for concentrations of 13 elements (As, Cd, Co, Cr, Cu, F, Hg, Mn, Ni, Pb, Se, V and Zn), pH and organic matter. Surface soils from 860 typical profiles were also analyzed for another 48 elements, resulting in the national soil background values of 61 elements (Chen et al., 1991; China Environmental Monitoring Center, 1990; Wei et al., 1991). The data sets generated by the two surveys above have been the most-often-cited reference for all soil-related studies in China.

With the rapid industrial development and urbanization occurring in China since the 1980s, soil geochemical patterns have likely been modified due to human activities such as disposing of wastes from agricultural and industrial processes onto the soil. The current available soil geochemical data have become totally inadequate to meet the increasing demands from land-use management departments, environmental regulatory agencies, and the public health sector.

In this context, a new geochemical mapping project, named the National Multi-Purpose Regional Geochemical Survey (NMPRGS) Project, was initiated in 1999 by the China Geological Survey (CGS) (Xi, 2005). The primary purpose of this project is to provide newer, higher density, more sensitive, more systematic and multi-medium geochemical data for supporting science-based decisions related to assessing land resources, protecting the surface environment, and improving the efficiency of agriculture. Thanks to the valuable experiences from the RGNR project, the standardized sampling and analytical methodology to be used in this new project were well developed after only three years of pilot surveys in Zhejiang, Guangdong and Sichuan (1999-2001). From 2002, this project, jointly supported by CGS and nearly all the provincial governments, has been carried out in the agriculturally and industrially developed regions, mainly in the plains of eastern and central China. The provincial geological survey or institute in each province was responsible for the work in its province. This paper will provide an overview of the methodology, the progress and major achievements of the NMPRGS project through 2012.

2. Methodology

2.1. Sample collection and preparation

Systematic sampling using a regular grid was applied in this project to ensure an even distribution of selected sites (CGS, 2005a). Generally, surface soils at 0–20 cm depth were collected at a density of 1 sample/km², increasing to 2 samples/km² in urban areas. In order to help study any anthropogenic influences on the surface layers, deep soils at 150–180 cm depth, or soils from C horizon if soil depth is less than 150 cm, were taken at a density of 1 sample/4 km². Samples from 4 km² for surface soils, 16 km² for deep soils, were composited, in order to reduce the analytical cost. Among them, about 2%–3% of the sampling sites were re-sampled to assess sampling variation.

In agricultural areas, the sampling site was selected from the most representative land-use type within the most common soil type in the sampling cell. Surface soils were composited from 3 to 5 subsamples collected within 50 m of the sampling site. No sample was collected within 100 m from a major road or a railway, no sample was collected from obviously contaminated areas, and no sample was collected at the time of fertilizing. In urban areas, soils were taken in age-old gardens, schools and residential areas, avoiding newly piled soils.

To understand the distribution of organic compounds in soils, surface samples were taken separately, generally at a lower density

such as 1 sample/64 km². Normally, the sampling sites were evenly allocated and avoided roadside and intensive industrial areas. Due to high cost of analyses, soil organic pollution survey was only performed in the most developed areas such as Guangdong, Fujian and Zhejiang provinces. The results will not be included in this paper.

Sediments in big lakes, and near-shore sediments in coastal areas at seawater depth of less than 10 m, were also collected. The sampling density was 1 sample/4 $\rm km^2$ for surface sediments, and 1 sample/16 $\rm km^2$ for deep samples. The sampling sites were normally allocated in the center of the sampling cell.

Each single sample weighed no less than 1000 g. All the sampling positions were pinpointed by means of Global Positioning System (GPS).

Visible plant detritus and any rock fragments were removed from the soil samples. After air-dried, the samples were crumbled by a wooden hammer, sieved with 20 mesh screen (<0.84 mm) and further processed with $-200 \ \rm mesh$ (<0.074 mm) for analysis. Sample material remaining after chemical analysis was stored in the sample archive in each province for future research. Those samples collected for future determination of organic compounds were stored in glass jars in a freezer at $-18\ ^{\circ}\text{C}$.

Surface water and shallow groundwater were collected at a density of 1 sample/ 16 km^2 to 1 sample/ 64 km^2 . The water sampling was optional and it was not implemented in all the provinces. The details of sampling and analytical procedures will not be discussed in this paper.

2.2. Chemical analysis

The total content of 52 components (Ag, As, Au, B, Ba, Be, Bi, Br, Cd, Ce, Cl, Co, Cr, Cu, F, Ga, Ge, Hg, I, La, Li, Mn, Mo, N, Nb, Ni, P, Pb, Rb, S, Sb, Sc, Se, Sn, Sr, Th, Ti, Tl, U, V, W, Y, Zn, Zr, SiO₂, Al₂O₃, TFe₂O₃, MgO, CaO, Na₂O, K₂O and total carbon), organic carbon and pH was determined for each soil and sediment sample. Chemical analyses were conducted in some 20 laboratories throughout China.

Requirements for the multi-element analytical protocols used in this project included the following:

- (1) The detection limits should not be higher than those listed in Table 1, which are obviously lower than the crustal abundance for each element.
- (2) At least 90% of the reportable concentrations for each element should be above the detection limit.
- (3) 12 primary soil reference materials (SRMs) should be analyzed twelve times for each specific analytical method. Table 2 presents the acceptable limit of accuracy and precision of the analysis for each analytical method used in this project.
- (4) The analysis should be efficient and of reasonable cost.

After numerous experiments and full discussion, seven analytical schemes mainly using X-ray fluorescence spectrometry (XRF), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES) and instrumental neutron activation analysis (INAA) as backbone methods were developed and recommended to reach lower detection limits and higher precision and accuracy than required in the RGNR project. One recommended analytical scheme employed in Anhui Province is shown in Table 1 (CGS, 2011a).

For those elements determined by ICP-MS and ICP-OES, the sample was decomposed using a mixture of HF, HNO₃, HClO₄ and aqua regia. If As, Sb, Bi and were determined by atomic fluorescence spectroscopy (AFS), the sample was dissolved in aqua regia. Fluorine was determined by ion selective electrode (ISE) after fusion of the sample NaOH. The detailed analytical procedures are introduced by Zheng et al. (2005).

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