China Geochemical Baselines: A new contribution to Global-scale Geochemistry

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Introduction

"The primary purpose of geochemistry is to determine quantitatively the composition of the earth and its parts, and to discover the laws which control the distribution of the individual elements" (Goldschmidt,1954). Geochemical mapping is an unique technique to illustrate spatial distribution of elements on the earth. Little is known, however, of their spatial distribution in the Earth's surface. Global-scale geochemical mapping has been carried out with the proposal of the IGCP Project 259 'International Geochemical Mapping' (1988-1992) and the IGCP Project 360 'Global Geochemical Baselines' (1993-1997) (Darnley, 1995). Since then, slow but significant progress has been or is being made with approximately 22% of the world's land surface covered by the global/continental-scale geochemical projects (Plant et al., 1996; Xie and Cheng, 1997; Salminen, 2005; Prieto, 2009; Govil et al., 2009; Caritat and Cooper., 2011; Smith, 2012, 2013; Reimann et al., 2014a, 2014b; Wang and the CGB Team, 2015).

However, critical problems of sampling and laboratory analysis still exist in globally harmonious geochemical data. Firstly, optimal sampling methodologies need to be updated or developed for the world's diverse landscape terrains; secondly, some key elements of recommended 71 elements by the blue book (Darnley et al. , 1995) for environmental studies and mineral resource investigations have not been determined, and high-quality reference standards are not used by continental-scale projects to control between-laboratory variations.

A new project named China Geochemical Baselines Project (CGB Project) was launched in 2008 and completed in 2014 (Wang, 2012; Wang and CGB Team, 2015). The project is intended to provide high-resolution and high-quality geochemical baseline data by developing improved sampling and laboratory analysis methodology. The China Geochemical Baselines Atlas with 81 parameters produced is a new contribution to Global-scale Geochemistry.

Methodology

Sampling

In China floodplain sediments were verified its suitability as sampling medium in hilly and alluvial plain terrains for global geochemical mapping in the Environmental Geochemical Monitoring Network Project (EGMON) in 1994-1996 by Prof. Xie Xuejing (Xie and Cheng, 1997). However, floodplain sediment samples are not available in other terrains, such as in desert (including the Gobi desert) and grassland in northern and north-western China. Thus, the sampling methodology for the China Geochemical Baselines (CGB) was updated or developed for China's diverse landscape terrains of mountains, hills, plains, desert, grassland, loess and karst in order to obtain nationwide representative baseline data. Floodplain sediment or alluvial soil was used as the sample medium in plain and hilly landscape terrains of exorheic river systems in eastern China. Overbank sediment was adopted as the sampling medium in mountainous terrains of exorheic river systems in south-western China. Methods of collecting catchment basin and lake sediments were developed in desert and semi-desert terrains, respectively, in endorheic drainage systems in northern and north-western China.

Two sampling sites were allocated to each CGB grid cell of 1° (long.) $\times 40'$ (lat.), approximately equal to 80×80 km in size. At each site, two samples were taken; one from a depth of 0-25 cm and a second, deeper sample from a depth greater than 100 cm or the deepest part of horizon C as possible as we can take . A total of 6617 samples from 3382 sites have been collected at 1500 CGB grid cells across the whole of China (9.6 million km^2), corresponding to a density of approximately one sample site per 3000 km^2. In addition, 11,943 rock samples have also been collected to aid in the interpretation of geogenic sources of elements.

Laboratory analysis

Before chemical analysis, the soil and sediment samples were sieved to <10 mesh (2.0 mm) and ground to <200 mesh (74 μm), rock samples were pulverised to <200 mesh (74 μm). Seventy-six chemical elements (Ag, As, Au, B, Ba, Be, Bi, Br, Cd, Cl, Co, Cr, Cs, Cu, F, Ga, Ge, Hf, Hg, I, In, Ir, Li, Mn, Mo, N, Nb, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Zn, Zr, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, SiO_2, Al_2O_3, Total Fe_2O_3, MgO, CaO, Na_2O, K_2O) plus 5 additional chemical parameters of Fe^{2+}, Organic C, CO_2, H_2O^+ and pH were determined under strict laboratory analytical quality control (Zhang et al., 2012).

Map plotting and data management

The primary objective of the CGB project is to establish nation-wide geochemical baselines against which future human-induced or natural chemical changes may be recognized and quantified. It is important to display baseline maps. The spatial distribution map were produced from gridded data by the in-house software Geoexpl2009® (http://www.drc.cgs.gov.cn/GeoExplGeoMDIS/). Raw analytical data were interpolated to generate a regular output grid of 80×80 km, using an exponentially weighted moving average model. The 18-grade colour mapped classes are based on the following percentiles of raw data: 2.5, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 75, 80, 85, 90, 95, 97.5.

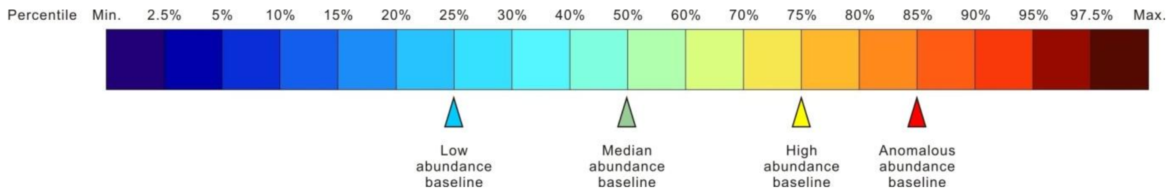

Fig. 1. 18-grade colour scale and 4 baselines used for China Geochemical Baseline Maps based on percentiles

The percentiles at 2.5 (dark blue), 25 (blue), 50 (green), 75 (yellow), and 85 (red) were selected to present the geochemical baseline maps (Fig. 1). The range of abundances with values less than the 25th percentile represents low abundance areas indicated by the dark blue shades on the maps; with values between the 25th and 50th percentile represents low background areas indicated by the light blue shades on the maps; with values between the 50th and 75th percentile represents high background areas indicated by the green-yellow shades on the maps; with values between the 75th and 85th percentile represents high abundance areas indicated by the orange shades on the maps; with values more than the 85th represents anomalies abundance areas indicated by the red shades on the maps (Fig. 1). All the baseline levels are meaningful for recognizing the natural or human-induced chemical changes or for evaluation of environmental and health problems, for example, the low abundance areas (< the 25th percentile) could be applied to assessing the deficiency of nutrition elements, and the anomalous areas (>the 85th percentile) could be used for the evaluation of environmental risks. Fig.2 shows Hg baseline map for the deep soil samples.

An Internet-based software named Digital Geochemical Earth was developed for managing the database and maps. The software provides a virtual globe of geochemical information allowing people to access vast amounts of geochemical data and maps through internet-based software to better understand the chemical characteristics.

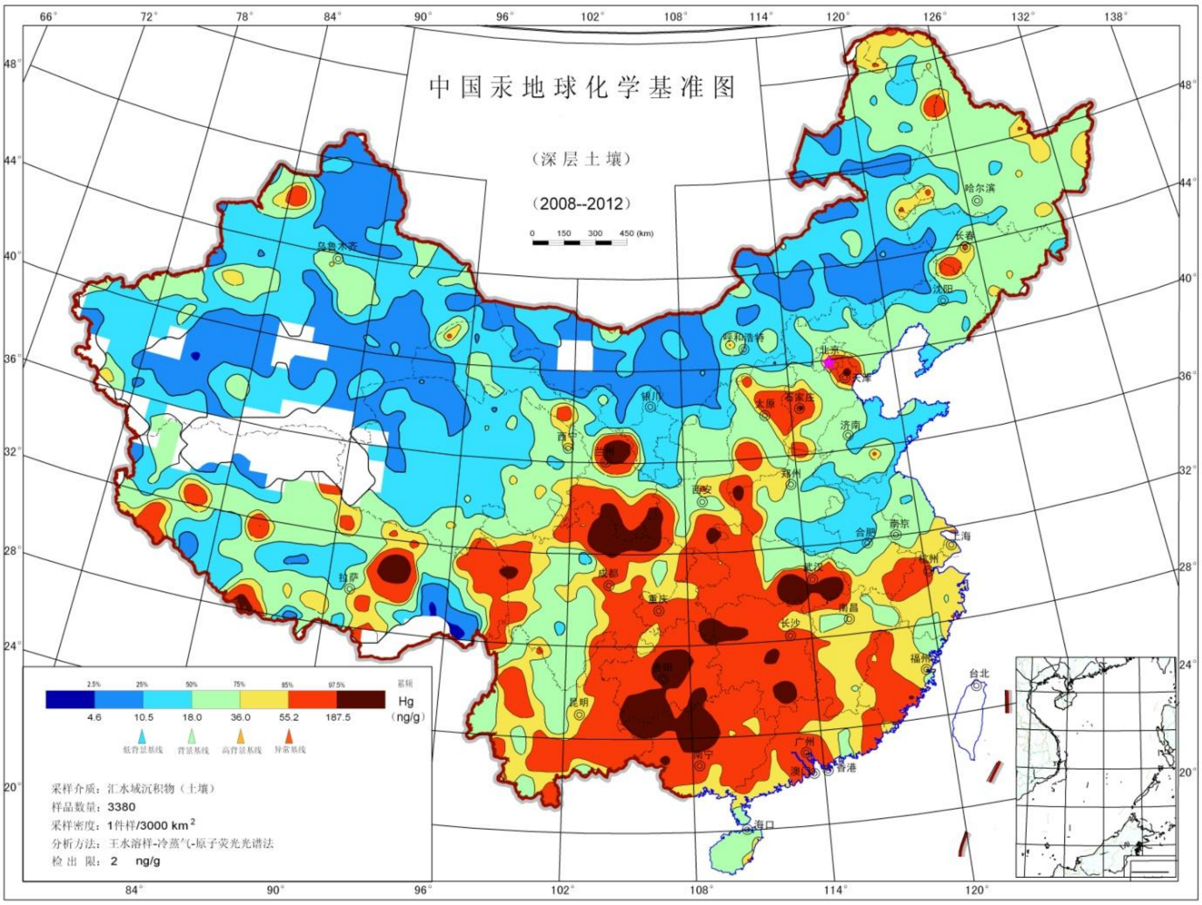

Figure 2. Hg geochemical baseline map for the deep soil samples in China

Results

General results

Initial results show excellent correlations of element distribution with lithology, mineral resources, mining activities, industry and urban activities, agriculture, and climate. Elements of Ti, V, Co, Ni, Cr, Fe, Mn and PGEs are correlated with lithology and mineral resources, particularly related to mafic or ultramafic rocks such as basalts. Elements of W, Sn, Au, Ag, Cu, and REE are correlated with metallogenic provinces. The concentration of many potentially toxic elements, such as Cd, Hg, As, Pb, P and the halogens, in surface soil are influenced by human activities. Some major elements, such Ca, show the influence of climate and acid rain.

Quantifying the changes

The database and accompanying element distribution maps represent a geochemical baseline against which can be quantified future human-induced or natural changes to the chemistry of the Earth. Can we recognize or quantify the changes using "China Geochemical Baselines"? The authors take CaO, which is sensitive to acid rains, and Cd, which is easily polluted by human activities, for example to quantify the environmental changes in an about 15-year interval by the EGMON project in 1994-1996 (Xie and Cheng, 1997) and by the CGB project in

2008-2012 (Wang, 2015). The similar sample media, and the same analytical method and quality control used by the two projects may provide us an un-bias opportunity to quantify the changes. Alluvial soils (floodplain sediments) from 846 catchments at an approximately density of 1 sample/15000 km^2 by the EGMON project, alluvial soils (floodplain/overbank/catchment basin sediments) from 3390 catchments at an average density of 1 sample/3200 km^2 by the CGB project. Calcium was analyzed by powder-pressed pellet X-ray fluorescence spectrometer and Cd was analyzed by 4-acid digestion ICP-MS in the two projects (Zhang et al., 2012).

Calcium is chemically reactive and its concentrations in soils are highly sensitive to supergene environment. Studying on the relationship of CaO geochemical changes with natural changes in the surface Earth is possible.

In the CaO geochemical baseline maps, CaO concentrations are generally decreasing from northwest to southeast of China (Fig. 3). This national-scale patterns are mainly related to annual average rainfall and acid rain distribution in China. High CaO baselines in the northwest are relevant to evaporated calcium minerals developed in caliche horizon of soils due to dry with the average annual rainfall of less than 200 mm, even less than 50 mm in extreme arid regions. Low CaO concentration areas in the southeast of China are corresponding to the exposure to acid rain where pH of rain is lower than 5.6 (Fig. 4).

When comparing the statistical results, it is found that average CaO concentration decreases from 0.53% to 0.41% in acid rain regions from 1994-1996 to 2008-2012. Dramatic changes of CaO distribution dimension area of concentrations <1% CaO extends from 872 000km^2 (1994-1996) to 1073 000km^2 (2008-2012) increasing 23% compared to that in 1994-1996. The changes is due to leaching of $CaCO_3$ by acid rains influenced by human activities in southern China. Increase of acid rain precipitation are mainly due to coal, oil and gas burning, because the duration of the past 15 years is the fastest increase phase of industrialization and urbanization in the history.

Cadmium in top soils is significantly anthropogenic impacted by human activities. Table 1 shows statistical parameters of Cd concentrations in top and deep samples for EGMON and CGB project. For EGMON project, the median Cd in top samples is 0.12μg/g and in deep samples 0.12%, with a range varying from 0.02μg/g to 3.06μg/g in top samples and 0.02μg/g to 0.44μg/g in deep sample. For CGB project, the median Cd in top samples is 0.14μg/g and in deep samples 0.11μg/g, with a range varying from 0.02μg/g to 45.98μg/g in top samples and 0.02μg/g to 21.2% in deep sample. The results shows that there is no difference for low abundance (P25) and median abundance between the two projects, but significant difference for mean concentrations in top samples from 0.15μg/g in the EGMON to 0.26μg/g in the CGB.

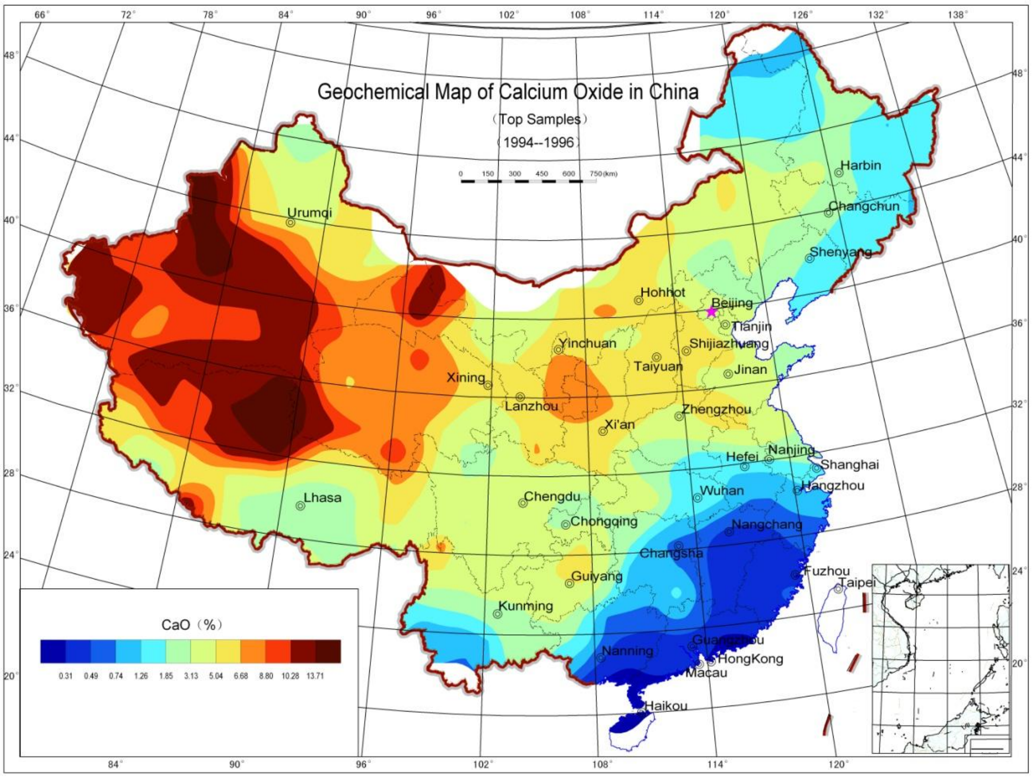

Figure 3. CaO distribution map of top soil samples from EGMON project in China

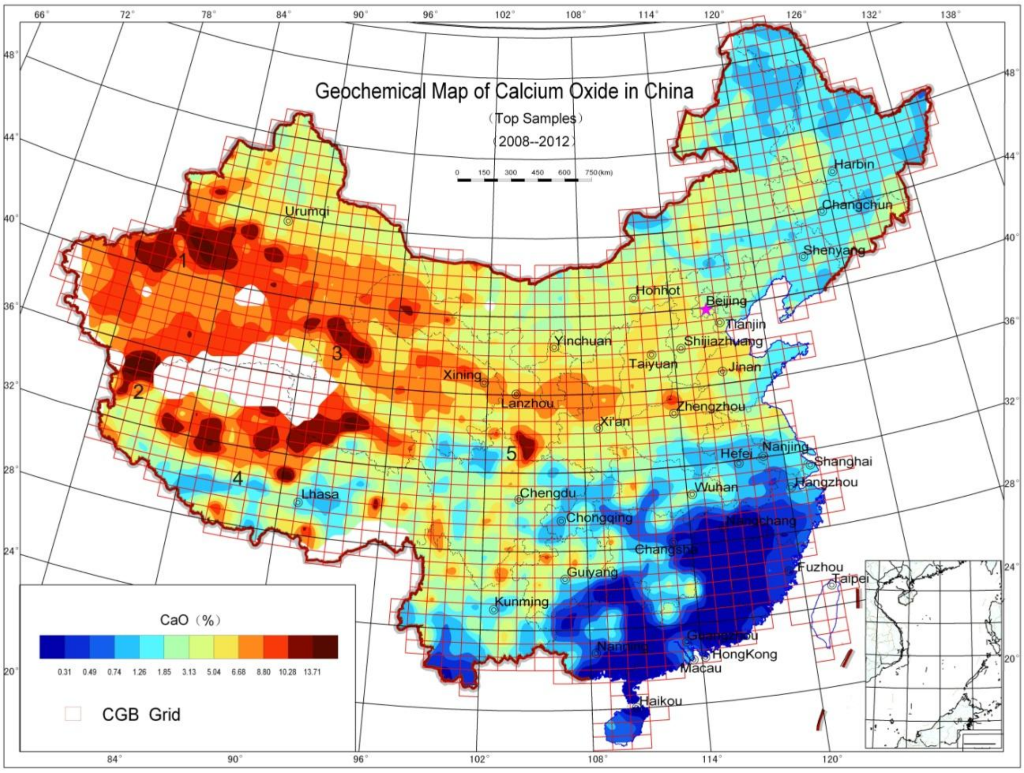

Figure 4. CaO distribution map of top soil samples from CGB project in China

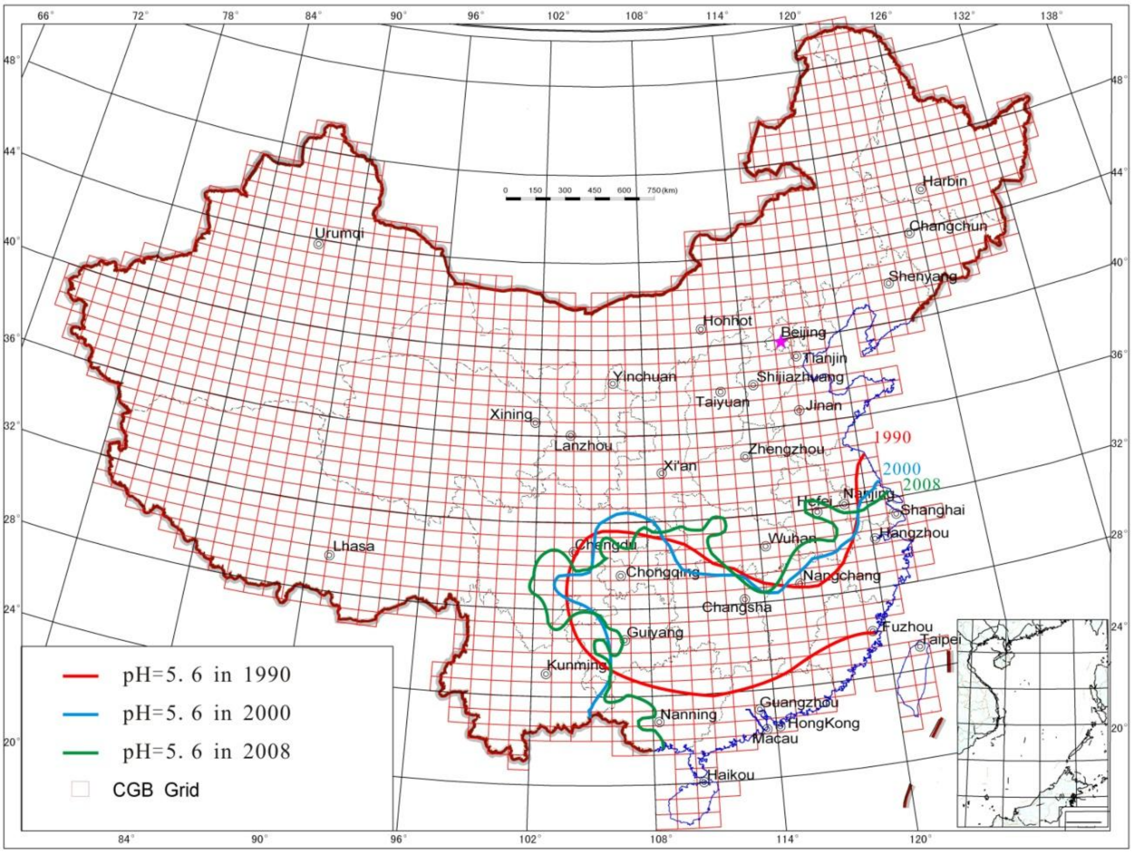

Figure 5. Distribution map of acid rains in China

Figure 6 presents the Cd statistical distribution of top and deep samples in the form of boxplots. The boxplots indicate the presence of a limited number of lower outliers, while there is a considerable number of upper outliers. This aforementioned statistical information shows that there is no, or only a small, difference between top and deep samples at low abundance concentrations, and there are large difference at high abundance concentration and systematic enrichment in top samples.

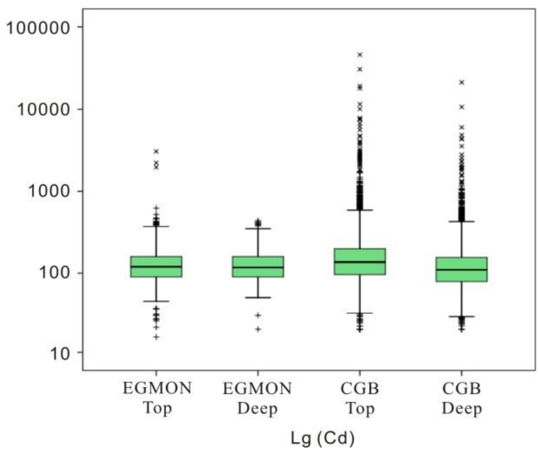

Figure 6. Cd statistical distribution results in the form of boxplots

When comparing the statistical parameters of CGB and EGMON top soil samples, it is found that Cd contents and distribution area significantly increase from 1994-1996 to 2008-2012. Table 2 lists the proportion of sample sites relative to total sampling locations that exceed the limit values of 0.2-0.3 µg/g for slight pollution, 0.3-1.0µg/g for moderate pollution, and >1.0µg/g for heavy pollution set by the National Environmental Standards for Heavy Metals of the People's Republic of China (GB 15618-1995). Therefore, the proportion of top soil samples exceeding the limit of 0.2 µg/g Cd increase from 12.2% to 24.9%, 4.3% to 12.3%, 0.4% to 2.1% of total sample sites, respectively.

Table 1 Statistical parameters for CaO from EGMON and CGB project

Project	Soil horizon	Analytical Method	Detection limit	Min	Mean	median 50%	25%	75%	Max
EGMON 1994-1996	Top	4 Acid-ICP-MS	0.02µg/g	0.02	0.15	0.12	0.09	0.16	3.06
	Deep	4 Acid-ICP-MS	0.02µg/g	0.03	0.13	0.12	0.09	0.16	0.44
CGB 2008-2012	Top	4 Acid-ICP-MS	0.01µg/g	0.02	0.26	0.14	0.1	0.2	45.98
	Deep	4 Acid-ICP-MS	0.01µg/g	0.02	0.17	0.11	0.08	0.16	21.2

Table 2 Proportion of sample sites relative to total sampling locations that exceed the limit values

Years	Samples	total	Clean <0.2 µg/g		Slight pollution 0.2-0.3µg/g		Moderate pollution 0.3-1.0µg/g		Heavy pollution >1.0 µg/g	
EGMON 1994-1996	Top	845	742	87.8%	103	12.2%	36	4.3%	3	0.4%
	Deep	468	405	86.5%	63	13.5%	15	3.2%	0	0.0%
CGB 2008-2012	Top	3284	2468	75.2%	816	24.9%	405	12.3%	69	2.1%
	Deep	2943	2499	84.9%	444	15.1%	210	7.1%	30	1.0%

Discussion

Sampling and laboratory analysis is the key points for obtaining globally harmonious geochemical data. In the past there was little research on global-scale sampling for endorheic drainage systems in arid and semi-arid inland terrains without river systems, which stream/overbank/floodplain sediments are not available. Since desert terrains take up approximately one third of the Earth's land surface, it is necessary to develop specific sampling methodology. The sampling methodology for the China Geochemical Baselines (CGB) was updated for China's diverse landscape terrains particularly for desert and semi-arid grassland in order to obtain homogeneity and representativeness of geochemical baseline data.

Calcium and Cadmium shows that sampling layout based on catchments is more likely to recognize or quantify the human- or nature-induced chemical changes, because in exorheic or endorheic drainage system where water constantly flows out to the catchments basins alluvial materials by man-made or natural process are deposited in the catchment basin or outlet plain region.

Calcium is chemically reactive and its concentrations in soils are highly sensitive to supergene environment. Studying on the relationship of CaO geochemical changes with natural changes in the surface Earth is assumed possible. Calcium ions (Ca^{2+}), as the major base cation in soils, is readily leached by water. Thus the rainfall is a crucial factor that strongly influence CaO concentrations in soils. Low precipitation and high evaporation lead to the formation of evaporate minerals, such as calcites, gypsum, anhydrite and glauberite in northwestern China. Nevertheless, in the southeast China, soil solution with low pH has a greater capacity to dissolve carbonate minerals. The insoluble carbonates change into soluble bicarbonates, and migrate with water into the depth or surface stream. Thus CaO contents of samples in the southeast of China, where karst landscapes are widely distributed, are quite low.

Cadmium in top soils is significantly anthropogenic impacted by human activities, particularly by Pb-Zn mining and smelting, and phosphate fertilizer which is produced from phosphorite containing high content of Cd in regions with a high-degree of mining and phosphate fertilizer use in the duration of the past 15 years, which is the fastest increase phase of industrialization and agriculture increase in the history.

The catchment sediment/soil sampling has advantage for recognizing changes of chemical elements. The geochemical data and maps generated by the CGB will go beyond the traditional customers of the mineral exploration community and environmental management. Such data will also be useful for global-scale monitoring of the state of freshwater and the oceans by providing broad-scale data on the chemical loads from main rivers into the oceans and by linking the data of freshwater systems to river catchments.

Conclusions

Floodplain sediment or alluvial soil was used as the sample medium in plain and hilly landscape terrains of exorheic river systems in eastern China. Overbank sediment was adopted as the sampling medium in mountainous terrains of exorheic river systems in south-western China. Methods of collecting catchment basin and seasonal lake sediments were developed in desert and semi-desert terrains, respectively, in endorheic drainage systems in northern and north-western China.

Seventy-six elements and five parameters, including packages for mineralization, environment, health, REE, rare elements, and halogen elements, were analyzed by the CGB Project. For some elements it provides maps, where never before has something comparable been produced for such a large area. The CGB project, which provided an insight into geochemical baselines for 76 elements throughout China covering 9.6 million km^2, will make great contribution to a global harmonious geochemical database.

Geochemical baselines by using comparison data (values) and distribution maps (area of anomalies) can be applied to quantifying the environmental changes induced by human activities and natural factors.

During the last few years results from a number of continental-scale geochemical mapping projects have become available: Australia, Europe, the United States of America. This new geochemical atlas of China leads our geochemical community again one step closer to an old dream: a geochemical overview of the whole world.

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