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Heavy metal contamination and source in arid agricultural soil in central Gansu Province, China

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Abstract

Concentrations of copper (Cu), lead (Pb), chromium (Cr), mercury (Hg), and arsenic (As) were measured in arid agricultural and irrigated agricultural soils collected in Daba Village, Shajiawuan Village, Gangou Village and Sifangwu Village, located in central Gansu Province, China. Concentrations except Hg and Pb were lower than the background values in grey calcareous soil in the selected arid agricultural soils. Pb concentration exceeded the threshold of arid agricultural soils in China by 72.46%. These results showed that there was indeed serious pollution with Pb, a slight pollution problem for other selected metals in the irrigated agricultural soils in Daba Village. Principal component analysis (PCA) was used to assess the soil data, applying varimax rotation with Kaiser Normalization. The result showed that the irrigated factor, agricultural factor and anthropogenic factor all contributed to the relations between selected chemical properties. The main factor of accumulation of Cu, Pb, Cr, Hg and As was lithological factor in arid agricultural areas. There is a striking dissimilarity of origin of Cu, Pb, Cr, Hg and As in agricultural soil between the irrigate agriculture and arid agriculture.

Key words: arid agricultural area; irrigate agriculture; principal component analysis (PCA)

Introduction

Modern high-intensity agriculture is a high cost industry and leads to the contamination of groundwater, release of greenhouse gases, loss of crop genetic diversity and eutrophication of rivers, streams, lakes and coastal marine ecosystems. It is also associated with the loss of soil fertility, the erosion of soil, the increased incidence of crop and livestock diseases, and the high energy and chemical inputs. The contamination of the ecosystem can pose long-term environmental and health implications (Needleman, 1980; Mueller, 1994; Mclaughlin *et al*., 1999). Coupled with the lack of pollution controls, human activities associated with these developments have caused significant impacts on the local environment (Chen, 1996; Florig, 1997; Hills *et al*., 1998; Ji *et al*., 2000; Li *et al*., 1997). An increase in contaminant emission may have a substantial implication on local agriculture, as heavy metal and other chemical material may enter and even accumulate in agricultural soils through agricultural activities and atmospheric deposition, which could enhance the risk of chemical contamination of the food chains in agricultural ecosystem (Tripathi *et al*., 1997; Chen *et al*., 1999). Hence, it is important to assess the environmental quality in the farming area. Marijia and Davor (2003) indicated that when the estimation of the heavy metal content in soils indicates the degree of contamination, the origin and difference between natural and anthropogenic contribution should be considered. The principle components analysis (PCA) has been widely used in geochemical applications to identify the origin of heavy metals (Thurston and Spengler, 1985; Marijia and Davor, 2003; Stanimirova *et al*., 1999; Latinka *et al*., 2004; Tahri *et al*., 2005).

The central Gansu Province is situated in the Loess Plateau in northwestern China. It has a total area of 34,600 km^2 with a population over 6.28 million. Owing to rapid economic development, heavy metal contamination of agricultural soils has also become increasingly serious in China (Siamwalla, 1996; Chen *et al*., 1999). In central Gansu Province, the average application of chemical fertilizers increased from 178 kg/hm^2 in 1988 to 444 kg/hm^2 in 2002, annually increase of 10% (Wei *et al*., 2004). Some of counties and cities, such as Jingyuan County and Huining County are generally called as the arid agricultural area for the majority of its agricultural lands are dry land in the area. And it is one of the poorest regions in China. However, we found less input of agrochemicals in arid agricultural activities than that of high-intensity agriculture in developed area, and the industrial pollution is much

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slight in this region.

The objectives of this study were to: (1) determine the concentration of heavy metal and As in the soils; (2) identify natural or anthropic factors that have influenced behavior of heavy metal and arsenic (As) using PCA; and (3) analyse the characters of the heavy metal and As in agricultural soil in the four study area.

1 Materials and methods

1.1 Site description

To analyses the difference of the source of the heavy metal and contamination levels of heavy metal between arid agricultural soil and irrigated agricultural soil, four study areas were selected in the loess Plateau of the central Gansu Province, in northwestern China (Fig.1).

Soil samples were taken from the arid agricultural soil at the four areas in 2004 (Fig.1). The four areas include Shajiawuan Village (SJW), Daba Village (DB), Gangou Village (GG) and Sifangwu Village (SFW). The DB is located in Jingyuan County; SJW, GG and SFW are located in Huining County. Huining County has a semiarid continental climate with an average annual temperature of 8.8°C. Monthly mean temperatures range from 18°C in July to −6.8°C in January. The average annual precipitation is 312 mm and the average evaporating capacity is 1,559.3 mm. Height above sea level is about 2,000 m. Because of the semiarid geographical location and absence of water for irrigation, arid agriculture is the dominant farm land use in this region. The annual rainfall is 170–350 mm in Jingyuan County, and the average annual temperature is 8.0°C. In Daba Village irrigated agriculture is the dominant farm land use. Soils of these study area are classified as gray calcareous soil.

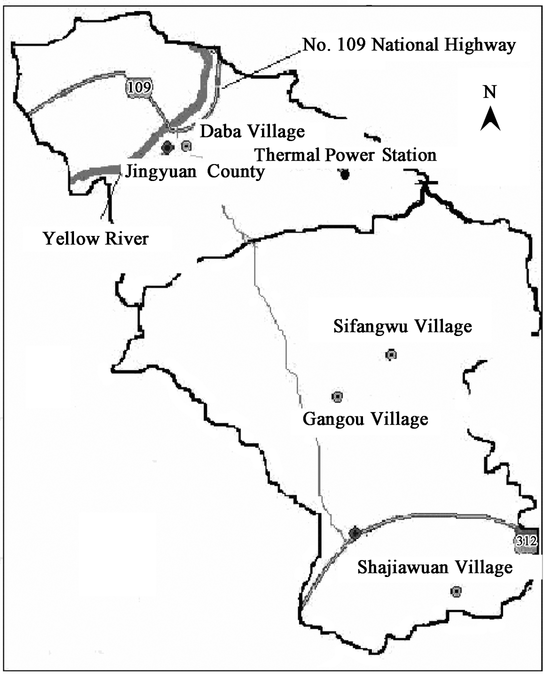

Fig. 1 Location of four study areas and Pingchuan thermal power station.

1.2 Soil sample collection

In all study areas the same method was used to collect soil sample. Fifteen sample plots were selected in each study area. These sample plots were all located on an east-west transect line. Each plot is at least 200 m apart from the next. If the sample plot was located on uncultivated land, or the distance between the sample plot and boundary ridge of the field was less than 5 m, the sample plot was discarded. Five subplots (25 cm × 25 cm) for soil sampling were selected in principle at the centre and on the diagonal lines of each sample plot. Subsamples were collected from 0–20 cm depth using a hand-auger. Then five subsamples were mixed and homogenized to form one soil sample (about 2 kg). All soil samples were immediately transported to the laboratory and stored in polyethylene bags at 4°C before analysis. A total of 60 soil samples were collected. All plastic instruments used for sample collection were cleaned sequentially with a phosphate-free detergent, rinsed with distilled water, then with 10% nitric acid, and finally with distilled water. The auger was rinsed with tap water, cleaned with a detergent, and then rinsed with distilled water.

1.3 Analytical methods

Concentrations of copper (Cu), lead (Pb), chromium (Cr), and As were analyzed by an Agilent 7500 inductively coupled plasma mass spectrometer (ICP-MS) at the Instrument Analysis Research Center, Lanzhou University. Complete digestion method was based on the procedure described by Hernandez *et al*. (2003) with minor modification.

For determining concentration of mercury (Hg), 0.5 g air-dried soil was treated with concentrated HNO_3 (10 ml) and H_2SO_4 (20 ml) for 1 h at 70°C (Loring and Rantala, 1992). When being cool, the volume of the digest was kept to 100 ml with deionised water. An aliquot of the solution was added with 1 ml $K_2Cr_2O_7$ solution and analyzed by cold vapor atomic fluorescence spectroscopy (960 CRT, Shanghai Precision and Scientific Inc., China) after reducing Hg with a stannous chloride solution.

All vessels used in these analyses were soaked in 10% nitric acid overnight and rinsed thoroughly with deionized water before use. The quality control of analytical accuracy was by duplicate samples (10% of total), reagent blanks and reference China Standard GSS-1.The analytical precision measured as relative standard deviation was routinely between 5% and 6%, and not higher than 10%.

1.4 Statistical analysis

PCA was used as a factorial analysis which makes it possible to reduce the size of the space of the variables (Massart and Kaufman, 1983). In the PCA, varimax with Kaiser Normalization was used as the rotation method in the analysis. With using the PCA, a great number of correlated parameters are replaced by a small number of independent factors (principal components). All the statistical analyses were conducted using SPSS 10.0.

2 Results and discussion

2.1 Heavy metal and As concentrations in agricultural soils

Concentrations of heavy metal and As in agricultural soils in arid agricultural area of central Gansu Province were listed in Table 1. Median values were given for the sites where more samples were analyzed. Hg, Pb, Cr, Cu and As concentrations in arid agricultural soils exhibited generally low levels, closed to those reported for unpolluted soils in northwest China (NEPA, 1990). Moreover, these metals and As displayed quite homogeneous distributions across the arid agricultural area and therefore lower standard deviations. These suggested a major natural source. However, heavy metal and As concentrations in agricultural irrigation soils showed high levels. High concentrations coupled with high standard deviation values suggested anthropogenic sources for these elements in agricultural irrigation soil.

2.2 Enrichment factors (EFs)

Heavy metal and As EFs for the soil samples were calculated by assuming the background value in gray calcareous soils in China reported in Table 1. Thus, EF is equal to element concentration in agricultural soil/element concentration in average natural loess. The results are represented in Fig.2. EFs were generally less than 1 for Hg, Pb, Cr, Cu and As, which suggested a natural source for these elements in arid agricultural soil. However, all heavy metals concentrations mostly enriched in agricultural irrigation soils (Fig.2). This strongly suggested that the agricultural irrigation soils received a higher input of anthropogenic heavy metal, possibly related to the usage of agrochemicals and other soil amendments for the high annual crop production.

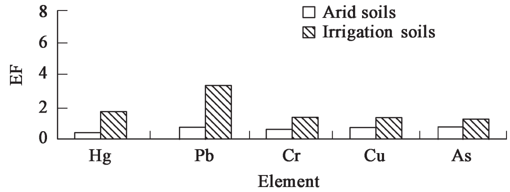

Fig. 2 Enrichment factors (EFs) for heavy metal and As. Data used in calculating EFs are those in Table 1.

2.3 Principal component analysis

By PCA, complex linear correlations between concentrations of heavy metal and As in soil were calculated, which enabled the interpretation of correlation of selected chemical properties in the study areas. Table 2 shows the factor loadings of principal components after varimax orthogonal rotation obtained by PCA statistical analysis using the concentrations of the heavy metal and As in agricultural soil in the four study areas. Graphical representations of these results are shown in Fig.3. According to the Kaiser criterion (Kaiser, 1960), the number of significant principal components with eigenvalue higher than 1 was selected. Thus, there are only the first three principal components (PCs) in DB, the first two PCs in SJW, the first three PCs in GG and the first three PCs in SFW were retained, because subsequent eigenvalues were all less than 1. Hence reduced dimensionality of the descriptor space are three in DB, GG and SFW, and two in SJW.

Table 1 Heavy metals and arsenic concentrations in arid agricultural soils and agricultural irrigation soils (unit: mg/kg)

Subgroup		Hg	Pb	Cr	Cu	As
Arid agricultural soils (n=45)	Mean	0.03	23.30	40.10	17.10	8.80
	Median	0.02	31.40	12.80	16.40	11.50
	SD[a]	0.02	11.80	36.80	11.80	4.50
Agricultural irrigation soils (n=15)	Mean	0.15	21.44	38.82	27.20	11.17
	Median	0.14	25.13	38.04	17.59	11.05
	SD	0.03	8.41	1.05	23.80	23.94
Background value in China[b]		0.0074	18.20	61.80	20.30	12.00
Threshold of arid agricultural soils in China (NEPA, 1995)		⩽ 0.35	⩽ 50	⩽ 120	⩽ 60	⩽ 20

[a] Standard deviation. [b] The values indicate that in gray calcareous soils in China.

Table 2 Factor loadings for principal components (PCs)

Sampling site	PCs	Hg	Pb	As	Cr	Cu
DB	PC 1 (irrigated factor)	0.932*	–0.057	0.938*	0.606	–0.012
	PC 2 (agricultural factor)	0.276	–0.002	–0.191	0.603	0.973*
	PC 3 (anthropogenic factor)	0.094	0.988*	–0.181	–0.386	0.050
GG	PC 1 (lithological factor)	0.993*	0.115	0.007	–0.598	0.754*
	PC 2 (agricultural factor)	–0.024	0.985*	0.020	0.605	0.559
	PC 3 (atmospheric factor)	0.010	0.081	0.997*	0.096	0.291
SWF	PC 1 (lithological factor)	0.545	0.198	–0.076	0.948*	0.816*
	PC 2 (agricultural factor)	0.080	0.761*	0.234	0.071	0.223
	PC 3 (atmospheric factor)	0.772*	0.247	0.943*	–0.087	0.362
SJW	PC 1 (lithological factor)	–0.667	0.037	0.830*	0.877*	0.854*
	PC 2 (agricultural factor)	0.222	0.967*	0.194	–0.007	0.129

Rotation method: varimax with Kaiser Normalization. * Values are statistically significant. DB: Daba Village; SJW: Shajiawuan Village; GG: Gangou Village; SFW: Sifangwu Village.

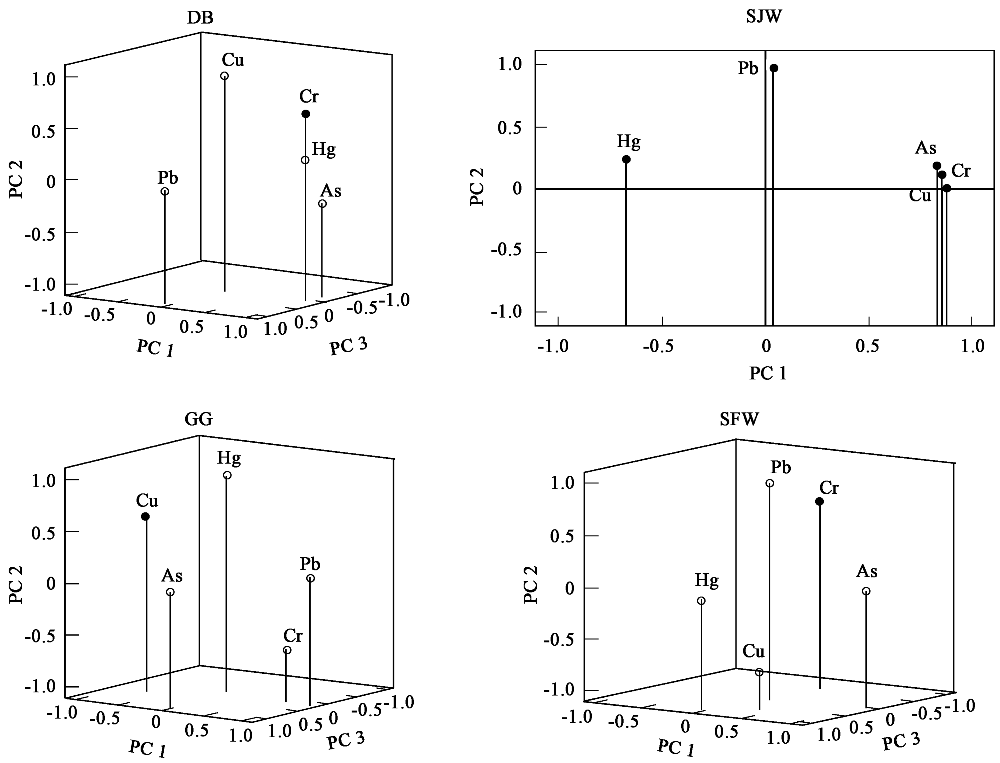

Fig. 3 Factor loadings for PCs (principal components) for agricultural soil of the four study areas.

In DB, the agricultural irrigation area, the first component comprises Hg and As with high loadings (Table 2 and Fig.3) explains 48.929% of total variance (Table 3). Heavy metal contamination in soil is influenced by a number of factors, including: agriculture (Kabata-pendias, 1995); sewage irrigation, parent materials (Oliver, 1997). In this county, the field was irrigated with yellow river. Furthermore there is a lot of sewage into the yellow river in the area. This factor, dominantly loaded by Hg and As, is attributed to the irrigated influence. This is why this latent factor (PC 1) is named as "irrigated factor". It is well known that the resource of Cu in agricultural soil is pesticide and herbicide applications on the agricultural field (Emine *et al*., 2004). In DB, for there is abundance of water to irrigate, it is rested with the using of fertilization and pesticide for obtaining the prospective yield. Therefore Cu in irrigated soil in this area may be from sewege and the PC 2 is named "agricultural factor".

Table 3 Eigenvalues of principal component (PCs) for agricultural soil of the four study areas

	PCs	Initial eigenvalues		
		Total	Variance (%)	Cumulative (%)
DB	PC 1	2.446	48.929	48.929
	PC 2	1.227	24.545	73.474
	PC 3	1.038	20.754	94.228
SJW	PC 1	2.650	52.997	52.997
	PC 2	1.025	20.498	73.49
GG	PC 1	2.660	53.190	53.190
	PC 2	1.153	23.062	76.252
	PC 3	1.009	20.171	96.423
SFW	PC 1	3.152	45.026	45.026
	PC 2	1.318	18.832	63.858
	PC 3	1.087	15.524	79.383

The aerial deposition was considered as the main source of lead emmission. The Jingyuan County is intersected by a busy ring road. The No. 109 National Highway runs across the county. The distance between the highway and the study area at Daba Village is about 5 km. Lead petrol is still not fully replaced by unleaded petrol in China. Pb has the highest loading in PC 3 and its concentration could be almost completely ascribed to the anthropogenic influence and the PC 3 is named "anthropogenic factor".

PCA results show that the irrigated factor, the agricultural factor and anthropogenic factor all contribute to the relations between heavy metal in DB. Considering the different contribution of these components (48.929% for PC 1, 24.545% for PC 2, and 20.754% for PC 3), the first component named irrigated factor plays a more important role (Table 3). Therefore accumulation of the heavy metal and As in agricultural soil in this area is mainly attributed to the anthropogenic factor which explains 48.929% of the total variance.

In the other three areas, because of the semi-arid geographical location and absence of water for irrigation, arid agriculture is the dominant farm land use in this region. These farmers apply only a little pesticide and herbicide to the agricultural field in the three counties. The PC 1 consists of Cr and Cu with loadings higher than the threshold of 0.7 in SFW. In SJW, the first component comprises As, Cr and Cu. The first component comprises Hg and Cu in GG. Cu has the all highest loading in PC 1 in the three areas. In SJW, the mean concentrations of Cr and As are lower than the natural background in gray calcareous soils in China, so are the mean concentration of Hg and Cr in the soils in GG. Therefore, these factors, dominantly loaded by Cu and other elements, are attributed to the geochemical influence. This is why this factor (PC 1) is named “lithological factor” in the three areas.

The second PC only consists of Pb with loadings higher than the threshold of 0.7 in the three areas, where are all far from busy ring roads. A possible explanation is that a lot of farm plastic membrane was used in these areas in recent years. The heat-stable inhibitor used in producing farm plastic membrane comprises Pb. The heat-stable inhibitor is degraded, then Pb will be released and enter into soil. To sum up, the Pb in soil in the three areas arise from agricultural practice and PC2 is named “agricultural factor”.

The third PC group is As (Table 2 and Fig.3) in GG and SFW. There is a thermal power station in Pingchuan Borough, Jingyuan County with installed capacity 1,800 MW. And the annual coal consumption is about 4×10^6 t. The distance between the Pingchuan Thermal Power Station and SFW and GG are about 70 and 75 km (Fig.1). Coal smoke, mill dust and floating dust contain Hg, Zn and As. If coal is burnt adequately, the As releasing from coal will be increased observably (Liu *et al*., 1999). Therefore As in arid agricultural soil in this study area may be from aerial deposition and the PC3 is named “atmospheric factor”.

Cu has positive loadings in all PCs in the three areas, which indicates that Cu in soil has agricultural and atmospheric sources except lithological source, thus it is understandable that Cu concentration is higher than background value.

Pb and Cu are main pollutants in the three areas, with significant agricultural and lithological sources, respectively. But the first factors are all lithological factors in the three areas. The first factor explains 52.997%, 53.190% and 45.026% of the total variance in SJW, GG and SFW, respectively (Table 3). There is a striking dissimilarity of origin of heavy metals in agricultural soil between the irrigate agriculture and arid agriculture. Accumulation of the heavy metal and As in arid agriculture is mainly attributed to the lithological factor and in irrigated agriculture is mainly attributed to the irrigated factor.

3 Conclusions

In central Gansu Province, the mean concentrations of the heavy metals and As except Hg and Pb are lower than background values in the selected arid agricultural soils, and the mean concentrations of heavy metals and As are higher than the background values. Pb concentration exceeds the threshold of arid agricultural soils in China by 72.46%. There is indeed serious pollution with Pb, a slight pollution problem for other selected heavy metals in the irrigated agricultural soils in DB.

According to calculation of the EFs, the heavy metal and As concentrations most enriched in agricultural irrigation soils. It strongly suggested that the agricultural irrigation soils received a higher input of anthropogenic heavy metal, possibly related to the use of agrochemicals and other soil amendments for the high annual crop production.

In irrigated agricultural soils by PCA, it is clear that the irrigated, agricultural, and anthropogenic factors contribute to the chemical properties of irrigated soils. The first component, irrigated factor plays a more important role. Therefore accumulation of the heavy metal and As in agricultural soil in the area is mainly attributed to the anthropogenic factor which explains 48.929% of the total variance. The main factor of accumulation of the heavy metal and As is lithological factor in three arid agricultural areas. There is a striking dissimilarity of origin of heavy metal and As in agricultural soil between the irrigate agriculture and arid agriculture.

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