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Geochemical assessment of agricultural soil: A case study in Songnen-Plain (Northeastern China)

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ABSTRACT

Agricultural soil pollution is a serious problem that can endanger ecology, food safety, and human health. The study evaluated the accumulation and distribution of major and trace elements in the agricultural soil of the Gannan area in the northwest Songnen-Plain, a very important base of grain production in northeastern China. To identify the concentrations and sources of pollutants and also to assess the soil environmental quality, a total of 2400 topsoil (0–20 cm) samples and 10 subsoil (180–200 cm) samples were collected. Then 6 major elements (CaO, Fe_2O_3, K_2O, MgO, Na_2O, SiO_2), 18 trace elements (As, B, Cd, Co, Cr, Cu, F, Hg, I, Mo, Mn, N, Ni, P, Pb, Se, S, and Zn), pH, and C_{org} (organic carbon) were analyzed. The accumulation of Cd, Cu, Pb, Zn, Hg, and F was apparent in the agricultural soils. Correlation coefficient analysis showed that most major and trace elements, as well as pH and C_{org}, were significantly positive correlated in agricultural soil. Principal component analysis (PCA) indicated two main anthropogenic sources for trace elements in agricultural topsoil. The first component including B, Cr, Cu, Mg, Ni, and Zn, represented a mixture of atmospheric deposition and livestock manures; whereas the second component, relating to Ca, F, Cd, Hg, Se, and P, suggested the inorganic fertilizers and lime, as well as agrochemicals. Spatial distribution patterns using GIS contour maps and an integrated soil pollution index were established for the selected metal concentrations. In general, the range of *RI* (the potential ecological risk index) was from 43.6 to 556, with a mean value of 106, indicating low ecological risk in this study area. This study indicated that more attention should be paid to metal pollution of agricultural soil in the rural area to safeguard both soil and food safety.

1. Introduction

Contaminants in agricultural soil may bioaccumulate in crops and possibly interfere with crop growth, while exposure to contaminants may impair human health (Luo et al., 2009; Sun et al., 2010). In China, rapid industrialization and urbanization and increasing reliance on agro-chemicals have increased agricultural soil pollution, which threatens food security (Liu et al., 2006; Luo et al., 2009). The contamination of the soil has long-term environmental and human health implications (Su and Zhu, 2008). Therefore, reduction of toxic trace element inputs in soil has been a focus in agriculture policies in China (State Council of PRC, 2005).

The largest pollution inputs into agricultural soils are mainly from atmospheric deposition, sewage sludge and livestock manures, whereas other sources, such as inorganic fertilizers and lime, agrochemicals, irrigation water, industrial by-product 'wastes' and composts are responsible for a relatively small contribution (Luo et al., 2009; Nicholson et al., 2003). Understanding the sources of pollutants is critical for environmental management and decision-making.

Songnen-Plain is an important part of the northern Songliao-Plain, one of the world's 10 greatest plain. Songnen-Plain is surrounded by Da Hinggan Mountains, Xiao Hinggan Mountains, Changbai Mountains and Songliao watershed. The plain space spans more than 103,000 km^2. The soil of the plain is fertile and thick, and consequently it has been a traditional grain production area of China. Grain yields account for 6.4%, more or less, in China (ECCAY, 2011). Songnen-Plain is a very important zone from both agricultural and socio-economic viewpoints.

The selected area is relatively complex, with a great diversity of soils and crops, and both villages and small towns were included. Accordingly, selection on typical land quality geochemical assessment has been carried out in the multi-target geochemical survey in Gannan County in Songnen-Plain.

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The anthropogenic activity could have strong negative impacts not only on the soil, but also on the quality of agricultural products. Despite of its regional importance, few researchers have investigated potential pollution sources in this area.

2. Materials and methods

2.1. The study area

The research area (47°40′–48°00′, 123°15′–124°00′, see Fig. 1) is located in Gannan County of Heilongjiang province, northeastern China. Gannan County is situated in the northwest region of Songnen-Plain. The study area includes Yinhe Town and Shuanghe Farm (SHF), with a total area of roughly about 600 km^2. The climate is semi-arid, with an average annual temperature of 3.5 °C, including a long and cold winter and short summer. Monthly mean temperature varies from 22.4 °C in July to −18.4 °C in January. The average annual precipitation is 462 mm and most rains occur in the summer season. Semi-arid agriculture is the dominant farm land usage in this region, with two staple crops, including rice and corn.

2.2. Sample collection and analysis

Between March 2009 and March 2010, totally 2410 samples were collected from the Gannan agricultural area, including 2400 samples from topsoil (0–20 cm) and 10 samples from subsoil (180–200 cm). Sampling was based on the specifications of the National Multipurpose Regional Geochemical Survey carried out by China Geological Survey (CGS) in 2005. For topsoil, about 1 kg was collected from a 0.5 × 0.5 km grid (plowing layer, 0–20 cm) and each sample consisted of about 3–5 subsamples obtained in a 2 m × 2 m grid from the sample plot using a stainless steel hand auger. For subsoil, about 500 g were also collected at depth (180–200 cm) in order to understand the soil parent material geochemical characteristics. The locations chosen were based on soil types and the sample was numbered according to the order of collection. The coordinates of the sample locations were recorded with a portable GPS, and the sampling sites were shown in Fig. 1.

All samples were air-dried at room temperature (20–25 °C) and then sieved to 2 mm to remove large plant roots and gravel-sized materials before analysis. Soil chemical properties were analyzed following standard procedures given in Page et al. (1982). The pH values were determined in water with a soil to solution ratio of 1:2.5 (w:w). Percentage of organic carbon (C_{org}) in soil was measured by the oxidation using $K_2Cr_2O_7$. Cation exchange capacity (CEC) was determined by using a standard extracting solution method (US-EPA, 1986). Elemental contents in soil were extracted by digestion (HF, HNO_3 and $HClO_4$) in a microwave (Xia et al., 2011) in accordance with the ISO 11466 procedure (International Organization for Standardization, 1995). The total concentrations of Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn were determined by inductively coupled plasma mass spectrometry (ICP-MS, GV Instruments), whereas As, Se, and Hg were measured by atomic fluorescence spectrometry (AFS, AFS-230E). The elements (Al_2O_3, B, CaO, Fe_2O_3, I, K_2O, MgO, Na_2O, and P) in soil samples were analyzed by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES, Therrmo Fisher Scientific). F concentration was determined by ion selective electrode (Boyle, 1981). Sulfur and nitrogen were determined by dry combustion (at 1350 °C), with a LECO CNS-2000 Nitrogen and Sulfur analyzer. SiO_2 was determined by X-ray fluorescence analysis (Indresand and Dillner, 2012).

The precision and quality accuracy of all the methods were determined by the analysis of duplicate samples, blanks and reference materials (about 20% of the total number of samples was used for this purpose). Standard reference materials for soil (GBW-07401, GBW(E) 070043) were obtained from the China National Center for Standard Reference. To verify the accuracy and precision of digestion and subsequent analysis procedure, blanks and reference materials were included in every batch of microwave acid digest along with the samples. For these procedures, analytical quality control showed good precision throughout. The recovery rates in the standard reference materials ranged from 91% to 110% for trace and major elements. Standard

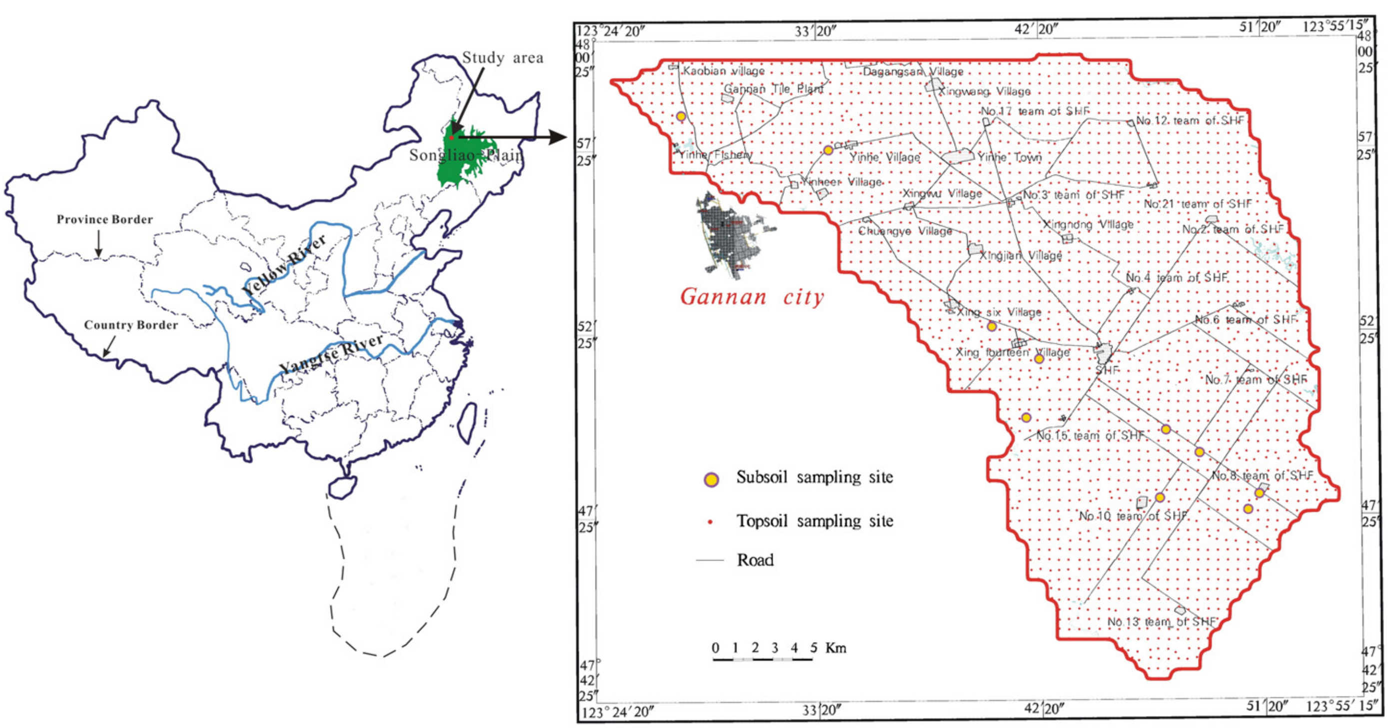

Fig. 1. Sampling locations of topsoil and subsoil in Gannan area.

deviation was lower than 5%, and blank samples were also performed throughout all the experiments.

2.3. Statistical analysis and spatial analysis based on GIS

Principal component analysis (PCA) has been widely used in geochemical studies to identify the relationship and the origin of trace elements (Lu et al., 2010) and also to reduce the data dimension sets to lower dimensions by identifying independent factors and associations among groups of observed variables (Davis et al., 2009).

The analytical results and field data were analyzed using SPSS (version 15.0). The methods included one-way analysis of variance (ANOVA), the Mann–Whitney test, and principal component analysis (PCA). Statistical significance was determined at alpha = 0.05. Non-parametric tests were conducted to determine the differences.

A geochemical map was developed using GIS (MapGis 6.7, ZONDY CYBER). GIS-based data have been used in environment research for managing, manipulating, analyzing, and presenting geographically related information. In particular, the geochemical mapping produced by GIS provides a reliable means of monitoring environmental conditions (Facchinelli et al., 2001; Li et al., 2004).

A soil pollution index (SPI) was calculated at each location and then interpolated to better visualize pollution sources (Lee et al., 2006).

$$\mathrm{SPI}_i = \frac{\sum_j \frac{\mathrm{MC}_i}{\mathrm{TC}_j}}{N}.$$

where, i = sampling locations; j = the heavy metals that are enriched; MCi = the metal concentrations at i_{th} sampling location; TC_j = the target concentrations of j_{th} heavy metal that are highly enriched, and N = the number of heavy metals that are enriched. We selected the average concentrations obtained from the subsoil samples as the target concentrations.

2.4. Potential ecological risk assessment

The method of potential ecological risk assessment was first introduced by Håkanson (1980) and has been widely applied to the pollution assessment of sediment and soil (Li et al., 2011). Håkanson's method is based on the hypothesis that an ecological risk index for toxic substances should account for the following requirements: (1) the potential ecological risk index (*RI*) grows with the metal(loid) pollution increase in the substrate; (2) the ecological harm of different metal(loid)s in the substrate has synergistic effects, and the potential risk of the resultant synergistic damage should be more serious; and (3) the toxicity response of each element varies, and those metal(loid)s exerting greater toxicity should play a larger role in the *RI*. Hence, the process integrates the concentration and ecological toxicity of different pollutants, and then gives a potential ecological risk index for the study area, as shown in

$$RI = \sum_{i=1}^{n} E_i = \sum_{i=1}^{n} T_i \times C_i$$

where, *RI* is the potential ecological risk index for the study area; E_i is the potential ecological risk factor for a given pollutant (i); T_i is the "toxic-response" factor for a given pollutant as calculated by Håkanson (1980) and Xu et al. (2008), i.e., Hg = 40, Cd = 30, As = 10, Pb = Cu = Ni = Co = 5, Cr = 2, Zn = Mn = 1; C_i is the ratio of metal(loid) concentration in the soil to the corresponding background in Songnen-Plain. The *RI* index is divided into four levels according to Håkanson's (1980) method, namely, $RI < 150$, low ecological risk for the study area; $150 \leqq RI < 300$, moderate ecological risk for the study area; $300 \leqq RI < 600$, considerable ecological risk for the study area; $RI > 600$, very high ecological risk for the study area.

3. Results and discussion

3.1. Chemical properties of topsoil samples

Fig. 2 shows the chemical characteristics of the agricultural topsoil in the Gannan area. C_{org} ranged from 0.22 to 8.26%, with 37.3% of the sample values greater than the background level of Chinese soils (3.1%) (CNEMC, 1990). The soil pH ranged from 3.37 to 9.96, suggesting acid to sub-alkaline conditions for all topsoil samples. The mean value of pH was close to the background level of Chinese soils (6.7) but slightly lower than the background value of Songnen-Plain (8.06) (HLJIGS, 2009). In general, the values of the cation exchange capacity (CEC) were variable (9.47–35.24 $\mathrm{cmol \cdot kg^{-1}}$), with a mean value of 21.17 $\mathrm{cmol \cdot kg^{-1}}$. The C/N ratio of soil spanned from 2.54 to 17.7 (mean 11.9), which was comparable to the Songnen-Plain average value of 12.3 (Zhang et al., 2011).

3.2. Concentrations of major elements

Major elements (Ca, Fe, K, Mg, Na, and Si) shown in their oxide formats (CaO, Fe_2O_3, K_2O, MgO, Na_2O, and SiO_2) were listed in

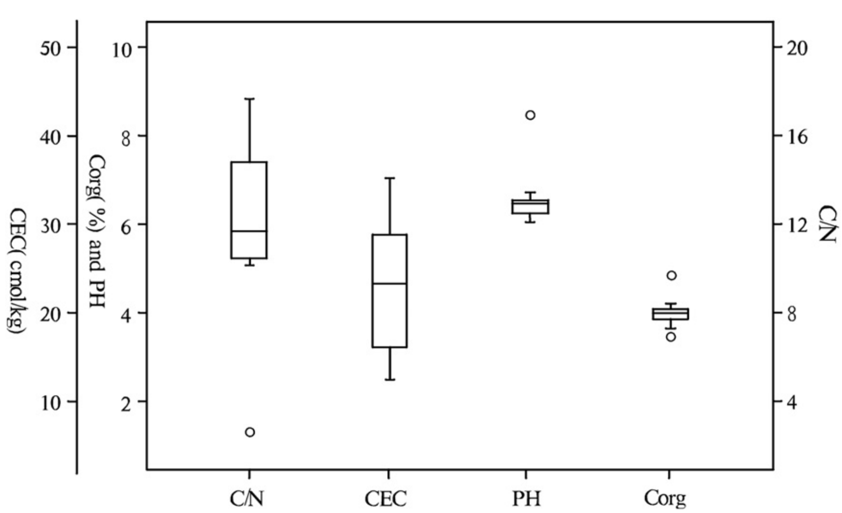

Fig. 2. Chemical characteristics of topsoil in Gannan area.

Table 1
Trace element (mg kg^{-1}) and major element (%) concentrations of topsoil and subsoil in Gannan area.

	N[a]	Minimum	Maximum	Mean of topsoil	Mean of subsoil	China BK[b]	Songnen–Plain BK[c]	Standard deviation	Variation coefficient	Skewness	Kurtosis	Threshold of the first grate[d]
As (mg k g^{-1})	2400	1.6	39.8	7.16	8.84	9.2	8.6	3.64	0.51	1.96	5.71	15
Hg (mg kg^{-1})	2400	0.01	0.24	0.02	0.01	0.04	0.02	0.01	0.5	6.59	91.08	0.15
Cr (mg kg^{-1})	2400	18.6	142.3	50.86	41.39	53.9	53.6	13.97	0.27	0.38	0.25	90
Cd (mg kg^{-1})	2400	0.01	1.5	0.08	0.06	0.07	0.09	0.05	0.68	12.74	274.82	0.2
Cu (mg kg^{-1})	2400	5.6	39.2	16.52	13.93	20	18.6	5.67	0.34	0.32	−0.59	35
Pb (mg kg^{-1})	2400	16.3	55.7	24.7	24.99	23.6	21.7	4.67	0.19	2.46	7.92	35
Zn (mg kg^{-1})	2400	24.3	131.5	51.52	51.05	67.7	55.9	13.29	0.26	0.69	0.26	100
Ni (mg kg^{-1})	2400	2.7	92.1	21.99	19.36	27	23.3	8.45	0.38	0.92	2.33	40
Co (mg kg^{-1})	2400	2.6	57.6	10.19	12.08	12.7	10.7	5.97	0.59	2.66	9.91	–
Se (mg kg^{-1})	2400	0.07	0.85	0.2	0.11	0.29	0.2	0.08	0.39	1.82	6.42	–
F (mg kg^{-1})	2400	200	5000	523.75	397.6	480	444	231.27	0.44	5.59	74.17	–
B (mg kg^{-1})	2400	5.2	52.5	21.56	16.47	48	27.7	6.53	0.3	0.62	0.62	–
I (mg kg^{-1})	2400	0.2	5.7	1.08	1.54	3.8	2.9	0.78	0.72	2.26	5.39	–
S (mg kg^{-1})	2400	124	424	287.2	98.1	266	–	130.4	0.45	−0.25	−2.1	–
N (mg kg^{-1})	10	907	2635	1779.5	354.7	1553	–	664.69	0.37	−0.3	−1.73	–
Mn (mg kg^{-1})	2400	137	3562	439.15	817.8	585	617	409.34	0.93	3.28	12.67	–
P (mg kg^{-1})	2400	161	5831	597.4	370.3	–	595	217.7	0.36	9.53	180.2	–
Mo (mg kg^{-1})	2400	0.24	6.29	0.97	1.39	2	0.55	0.54	0.56	2.56	11.54	–
SiO_2 (%)	2400	46.26	76.03	66.13	68.85	65	61.98	4.62	0.07	−0.68	0.89	–
Fe_2O_3 (%)	2400	1.66	9.57	4.09	3.41	4.25	4.05	1.22	0.3	0.7	0.07	–
K_2O (%)	2400	1.72	3.63	2.73	3.14	2.26	2.57	0.36	0.13	0.18	−0.74	–
Na_2O (%)	2400	0.69	3.17	1.85	2.41	1.5	1.86	0.47	0.25	−0.29	−0.51	–
CaO (%)	2400	0.7	16.12	1.68	1.04	1.3	3.46	1.69	1.01	4.48	22.59	–
MgO (%)	2400	0.35	2.4	0.92	0.89	1.23	1.42	0.27	0.3	0.71	0.48	–

[a] Number of the topsoil samples.
[b] Background values of Chinese soils(CNEMC), A layer(0–20 cm), more than 4000 samples.
[c] Background values of Chinese soils (Multi-objective regional geochemical survey report of Songnen-Plain).
[d] Class I value of the Environmental Quality Standard for Soils in China (GB15618-1995).

Table 1. The mean values of these major elements except for CaO were similar to the background values of the Songnen-Plain. Compared with the contents of subsoil, CaO, MgO, and Fe_2O_3 were enriched whereas K_2O, Na_2O, and SiO_2 were lower, probably due to the dilution effect of agricultural fertilizer (Jiang, 2006). There was no significant difference between the concentrations of elements in the topsoil and these in the subsoil.

3.3. Concentrations of trace elements

Results for As, B, Cd, Co, Cr, Cu, F, Hg, I, Mn, N, Ni, P, Pb, S, Se, and Zn were summarized in Table 1. The Kolmogorov–Smirnov test ($p < 0.05$) showed that all elements' concentrations fit in a normal distribution. A comparison between topsoil and subsoil indicated a potential migration of elements in different depths (Motuzova and Van, 1999; Teng et al., 2010). The background values in topsoil were important for the assessment of soil fertility, contamination status, and the application of sewage sludge to agricultural land (Bak et al., 1997; Li et al., 2008; Teng et al., 2010). We found the mean concentrations of all elements, except for F and Mn, were comparable to the background concentrations observed in the Songnen-Plain (HLJIGS, 2009). F and Mn, however, were 18% higher and 29% lower than the background, respectively.

Two independent sample tests (Mann–Whitney U) were conducted to determine whether element values differed between different media (topsoil, and subsoil) (Chen et al., 2010). Compared with subsoil samples, the mean concentrations of As, Co, Pb, and Zn in topsoil samples were similar or slightly lower, whereas the mean concentrations of Cd, Cr, Cu, F, Hg, Ni, and Se were significantly higher ($p < 0.05$). For Mn, the topsoil contained almost the half the subsoil did. Based on the Standards for Soil Environmental Quality of China (SEPAC, 1995), the average concentrations of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were all below the first grade of the standard (GB15618-1995), indicating the overall clean conditions of these elements.

The mean concentrations of B, I, N, P, and S were 1779.5, 597.4, 21.56, 1.08, and 287.2 mg kg^{-1}, respectively. These were comparable to the background levels of Chinese soil or Songnen-Plain, except for B and I (HLJIGS, 2009). The mean values of B and I in the analyzed soils in the Gannan area were 44.3 and 71.5% lower than the background values of Chinese soils, respectively; however, the large coefficient of variation (CV) of iodine (I), which was 72.4%, implied a heterogeneous nature of the dataset.

The soil types included aridisol, which is used to grow corn or soybeans, or paddy fields for rice-growing cultivation. The As and Co levels were slightly higher whereas the Cr, Cu, Mn, Ni, Zn levels were slightly lower in aridisol compared to these in the paddy fields, respectively. The differences of metals' concentrations between these two soil types were not statistically significant ($p > 0.05$).

3.4. Source identification

From the descriptive statistical analysis, the elevated concentrations of B, CaO, Cd, Cr, Cu, F, Hg, N, Ni, P, S, Se, and Zn in topsoil indicated anthropogenic sources of these elements. However, the Fe_2O_3, MgO, Ni, and Zn concentrations were slightly higher than or approximately equal to the subsoil values with the other elements lower in topsoil than in subsoil, suggesting less influence from anthropogenic activities. The relatively high skewness and kurtosis values suggest that CaO, Cd, F, Hg, and P were different from the other elements.

PCA was applied to extract quantitative information for the identification of the sources of pollutants (Lu et al., 2010). Table 2 displayed the factor loadings using Varimax Normalized rotation as well as the eigenvalues for the topsoil samples of the Gannan area, respectively. The 4 factors together explained 78% of the variance in the data set. As, B, Co, Cr, Cu, Fe, I, Mg, Mn, Na, Ni, Pb, and Zn obtained high scores on PC1; Ca, F, K, pH, and Si on PC2; Cd, C_{org}, Hg, and P on PC3; and Mo and Se on PC4.

From the PCA results, two main anthropogenic sources may be identified (1) B, Cr, Cu, Mg, Ni, and Zn have mixed sources of atmospheric deposition and live-stock manures; (2) Ca, F, Cd, Hg, Se, and P represent inorganic fertilizers and lime sources, as well as agrochemicals, especially for Hg. Se may be from two sources due to similar loadings in PC1, PC2, and PC3.

One group of elements (B, Cr, Cu, Mg, and Zn) was positively correlated in PCA. For Zn and Cu, approximately 78%–88% of the total annual inputs to agricultural land were derived from atmospheric and livestock manures (Nicholson et al., 2003). The heavy metals contributing to atmospheric pollution included energy production, mining, metal smelting and refining, manufacturing processes, transport, and waste incineration (Nicholson et al., 2003; Nriagu, 1990). In addition, in the study area, the average trace element flux values were 1.09 (As), 0.15 (Cd), 7.29 (Cr), 3.52 (Cu), 0.13 (Hg), 3.20 (Ni), 7.86 (Pb), 36.4 (Zn), and 77.9 (Mn) $mg \cdot m^{-2} \cdot yr^{-1}$, respectively (Deng et al., 2012). Large-scale agricultural machinery has become a major source of pollution. At the same time, car ownership has also increased in China's rural areas (Cai and Tang, 2011). Cu–Pb–Zn may reflect vehicle emissions. Pb pollution is linked to traffic activities due to the use of Pb-based gasoline for some time (Lee et al., 2006; Wang et al., 2003; Yang et al., 2008). Additionally, Zn may be derived from corrosion of galvanized automobile parts and the wear and tear of vehicle tires (Al-khashman, 2007a; Jiries et al., 2001; Lu et al., 2010). Also, Cu is often used in vehicle lubricants (Al-khashman, 2007b). For all livestock, Zn and Cu are added to growing animal diets as a cost-effective method of enhancing performance and for the control of post-weaning sours (Holm, 1990; Rosen and Roberts, 1996), and thus will be present in manure that is subsequently applied to land (Nicholson et al., 2003). The major sources of Cr to agricultural land include phosphate fertilizers, sewage sludge, and atmospheric deposition (Nicholson et al., 2003). On the other hand, relatively lower loading factors of Cr, with significant loadings from B, Cu, Zn, and Mg in PC1 suggested that they originated from a single source. Therefore, we suggest that the source of B, Cr, and Mg may be atmospheric deposition, similar to Cu, Zn, and Cr.

A second group, in which elements was strongly correlated among each other, consisted of Ca, F, Cd, Hg, P, and Se. Cadmium is present in all phosphate fertilizer materials (Nicholson et al., 2003). Fluorine combines with Ca to form a stable compound. Calcium fertilizer, including lime and phosphate fertilizer mostly, is widely used in agriculture to increase the content of F (Liao, 1992). Mercury is correlated with Cd and P (they entered PC3), but not with As. Hg- and As-containing pesticides are no longer permitted, suggesting a source other than agrochemicals. Se has similarity loading factors in PC1 (0.432), PC3 (0.425), and PC4 (0.598) indicating a mixed source. In addition, the higher concentrations of P, N, and S are mainly associated with inorganic fertilizers used in agriculture soil of the Gannan area. Overall, PC2, PC3 and PC4 are associated with agricultural chemical fertilizer.

Table 2
Rotated factor loading (varimax normalized) of selected elements in topsoil (n = 2400).

Component	Topsoil samples (2400)			
	Factor 1	Factor2	Factor3	Factor 4
As	0.877	0.14	−0.047	−0.181
B	0.753	0.017	0.109	0.295
Ca	−0.053	0.874	0.141	−0.167
Cd	0.124	0.046	0.718	−0.193
Co	0.935	0.156	0.061	−0.006
Corg	0.041	0.401	0.643	0.367
Cr	0.765	0.335	0.183	0.388
Cu	0.735	0.379	0.293	0.406
F	0.247	0.749	0.102	0.069
Fe	0.883	0.284	0.126	0.257
Hg	0.004	0.2	0.499	0.165
I	0.817	−0.048	0.043	−0.287
K	−0.449	−0.668	−0.285	−0.436
Mg	0.773	0.523	0.134	0.115
Mn	0.905	−0.002	−0.038	−0.273
Mo	0.038	−0.192	−0.033	0.685
Na	−0.764	−0.463	−0.279	−0.261
Ni	0.824	0.363	0.191	0.241
P	0.135	0.131	0.766	0.032
Pb	0.927	−0.014	0.01	0.068
pH	0.133	0.773	0.215	−0.102
Se	0.106	0.432	0.425	0.598
Si	−0.534	−0.75	−0.277	−0.148
Zn	0.834	0.237	0.223	0.257
Eigenvalue	9.63	4.43	2.52	2.15
Total variance (%)	40.13	18.47	10.5	8.96
Cumulative eigenvalue	9.63	14.07	16.59	18.74
Cumulative percentage	40.13	58.61	69.1	78.06

3.5. Spatial distributions and risk assessment

The spatial distribution of trace elements and pH, C_{org} in topsoil was analyzed using GIS (Lee et al., 2006; Li et al., 2004). The contour maps of the selected elements, including As, Cd, Cr, Cu, F, Hg, Mn, Ni, P, Pb, and Zn, were illustrated in Fig. 3.

Three spatial patterns were obtained from the geochemical maps in this study area. The spatial distribution maps for As, Cu, Pb, Zn, and Mn showed similar geographical trends, with high concentrations in northwest area and the north of Gannan urban district. Moreover, the spatial distributions of Hg, Cd, P, and F were distinctly different from the trace elements discussed above and high concentrations of these elements were mainly found in the southwest. Furthermore the spatial distributions of Cr and Ni revealed lower values in the central Gannan area.

The study area was highly enriched with some elements, including As, Cd, Cr, Cu, F, Hg, Mn, Ni, P, Pb, and Zn. The soil pollution index (SPI) was used to represent the overall degree of element enrichment in soil (Fig. 3). In general, the range of SPI spanned from 3.78 to 23.2, with a mean value of 8.67. The relatively high enrichment areas were located nearby an urban district in the northwest region of the study area. This may be related to rapid population growth and urban development in recent years, which may impact the agricultural soil (Liu et al., 2006; Zhang, 2006).

The ecological impact of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn pollution to the soil was overwhelmingly “low”, with 91.8% samples feathered with low ecological risk, 7.8% moderate ecological risk and 0.4% considerable ecological risk, respectively. In general, the *RI* for the study area spanned from 43.6 to 556, with a mean value of 106 (low ecological risk).

4. Conclusions

In this work, we evaluated the accumulation and distribution of major and trace elements in agricultural soil in the Gannan area of the northwest Songnen-Plain. The concentrations of major elements reflected the geochemical characteristics of this area. Agricultural soil in the Gannan area was found to have elevated concentrations of a number of metals, including Cd, Cr, Cu, F, Hg, Ni, and Se. The mean values of metals were higher than the values of subsoil in this region.

Results from PCA indicated two anthropogenic sources of trace elements, including atmospheric deposition and agricultural sources such as manure, inorganic fertilizer, and lime sources.

The geochemical maps of selected elements of agricultural surface soils were produced using GIS method and several hot-spot areas were identified. The relatively high enrichment areas were located in the northwestern region, according to the map of the soil pollution index.

These findings indicate that more attention should be paid to agricultural soil in rural areas in order to protect food security. During the process of urbanization, a primary task should be the protection of agricultural soil. More stringent laws and rules may be needed at the national level to control and reduce toxic element inputs. We recommend that a multiple approach strategy be implemented for

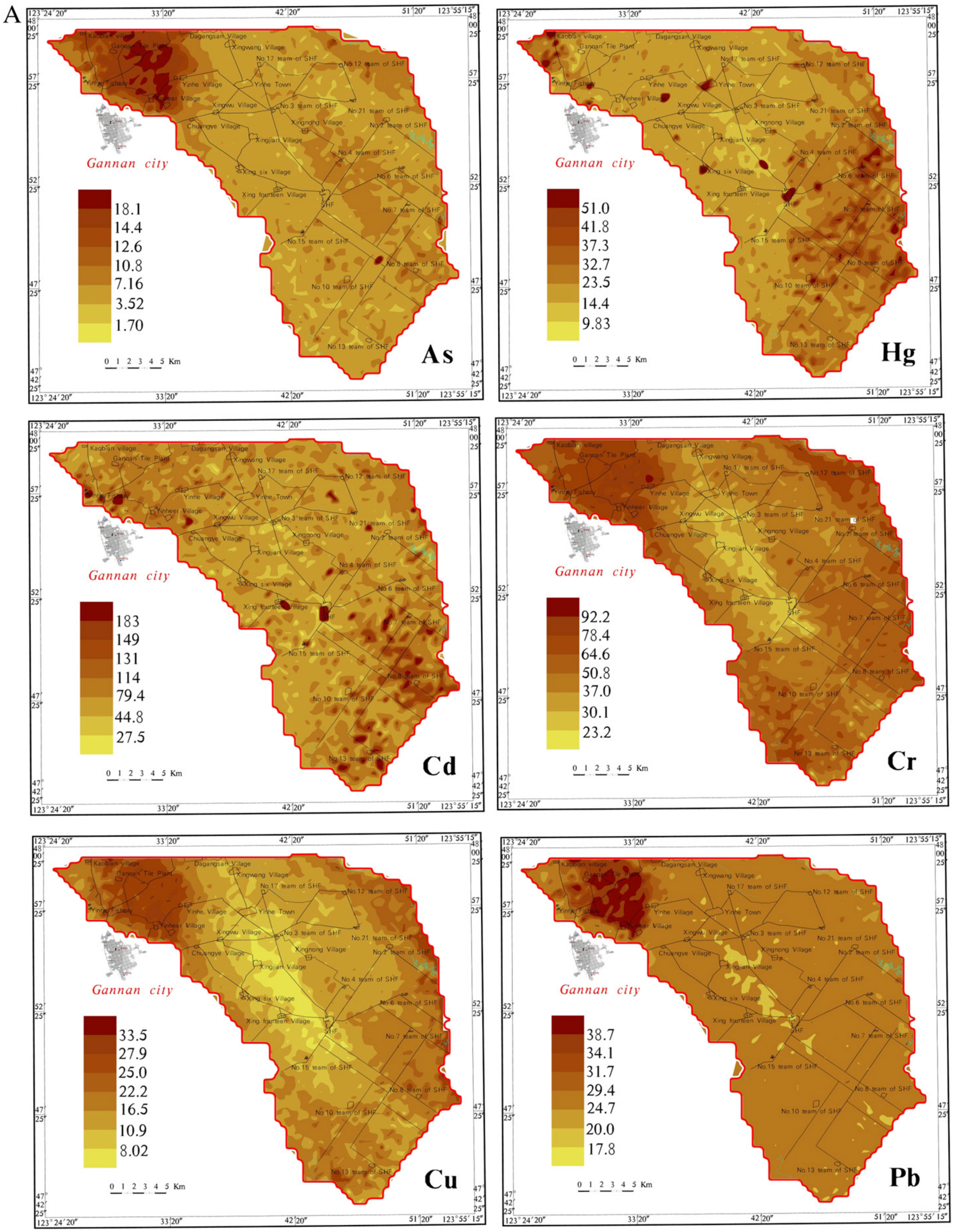

Fig. 3. Spatial distribution of As, Cd, Cr, Cu, Pb, Zn, Ni, F, P, Mn, Hg and SPI in agricultural topsoil.

B

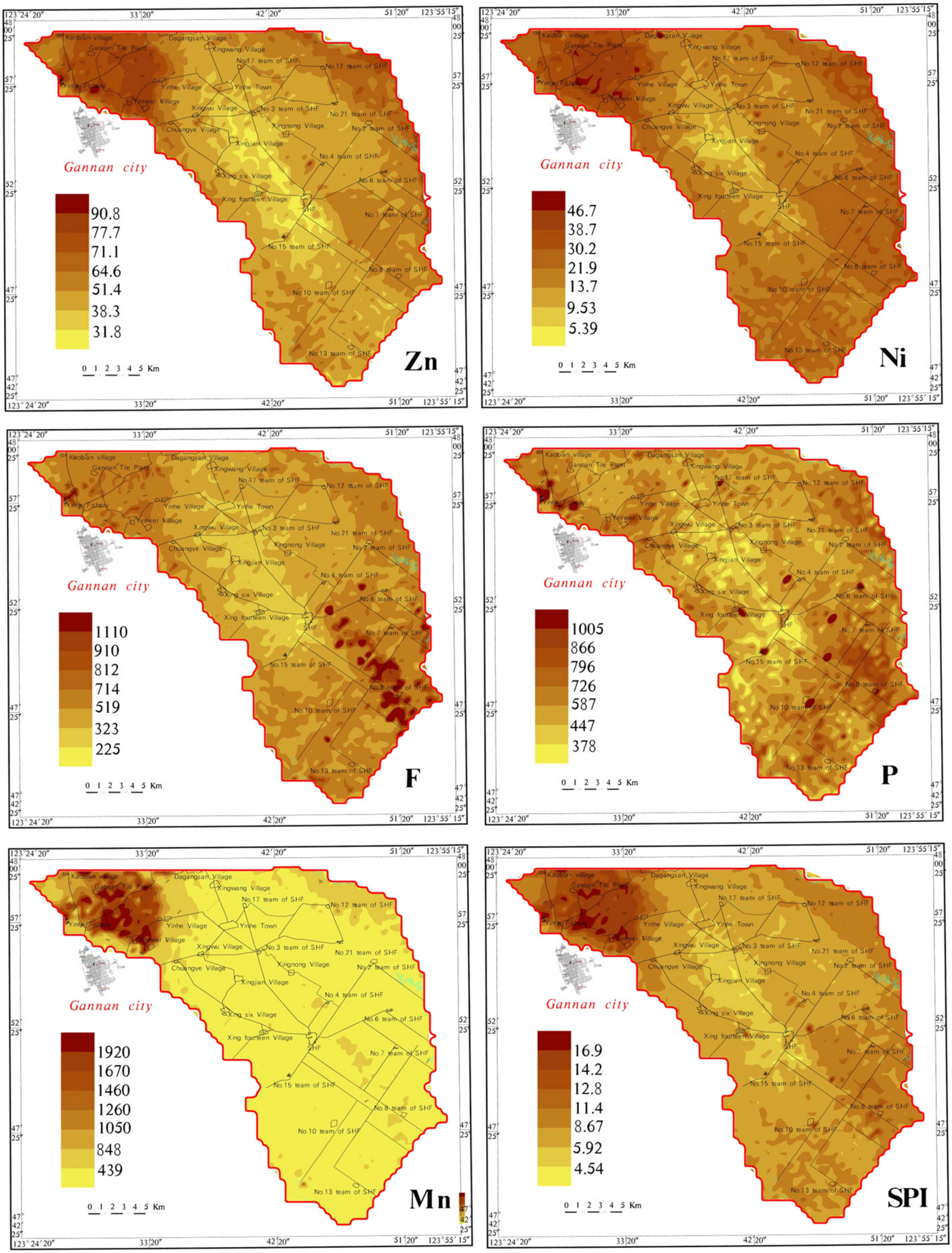

Fig. 3 (*continued*).

agricultural soil management of enforcing effective restrictions for the deposition through commercial fertilizer, agricultural chemicals and lime, also the atmospheric deposition, and encouraging the use of clean energy for agricultural machinery.

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