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Spatial Structures and Relations of Heavy Metal Content in Wastewater Irrigated Agricultural Soil of Beijing's Eastern Farming Regions

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As one of the most significant sources of soil pollution, wastewater from industrial and domestic sources introduces a huge amount of inorganic and organic contaminants, including heavy metals, into agricultural land through the practice of wastewater irrigation. This is a particularly acute problem in areas used for agricultural purposes adjoining large urban areas, especially in northern China where scarcity of water necessitates wastewater reuse for a variety of different purposes, most importantly crop agriculture (Zhang et al. 1988).

A number of studies demonstrate that with their long history of wastewater irrigation (more than 30 years), part of the agricultural soils adjacent to Beijing have been subject to a marked increase in the contents of heavy metals (Xu and Yang 1982; Xia et al. 1983). Such basic information is not enough to develop a clear picture of heavy metals in wastewater irrigated soils. Our study assesses the spatial distribution pattern and relations of heavy metals (Co, Cr, Cu, Mn, Fe, Ni, Pb and Zn) in agricultural soil irrigated with wastewater in the eastern outlying farming areas of Beijing.

MATERIALS AND METHODS

A great deal of the eastern agricultural regions associated with Beijing have been irrigated with wastewater for more than three decades. A large, fairly comprehensive study of soil, water and crop contamination in these regions was taken *in* 1980's (*Study Group for Pollution Investigation and Control of Suburb of Beijing, unpub. report*). The sampled site for our study in the eastern regions is shown in Figure 1 and was selected because of its nearness to major wastewater outlets, which other studies (Feng et al. 1992) have shown to be locations of high heavy metals concentrations. Approximately three-fourths of our study site is paddy field, with the rest being used as vegetable gardens. Farmers at such sites use untreated wastewater from domestic and industrial sources contaminated by heavy metals, nutrients and organic compounds (Dong and Chen 1982) for their irrigation and fertilization (increased organic matter) purposes. The wastewater outlets are constructed along the northern edge of the site and have been relocated recently to the middle of the site due to road construction. The wastewater disperses evenly over the site after leaving the outlets, with no obvious physical hindrances being observed.

Within the survey site, 190 surface soil samples (0-10cm in depth) were collected in the summer of 1995, using a grid of 19 samples across the E-W length of the

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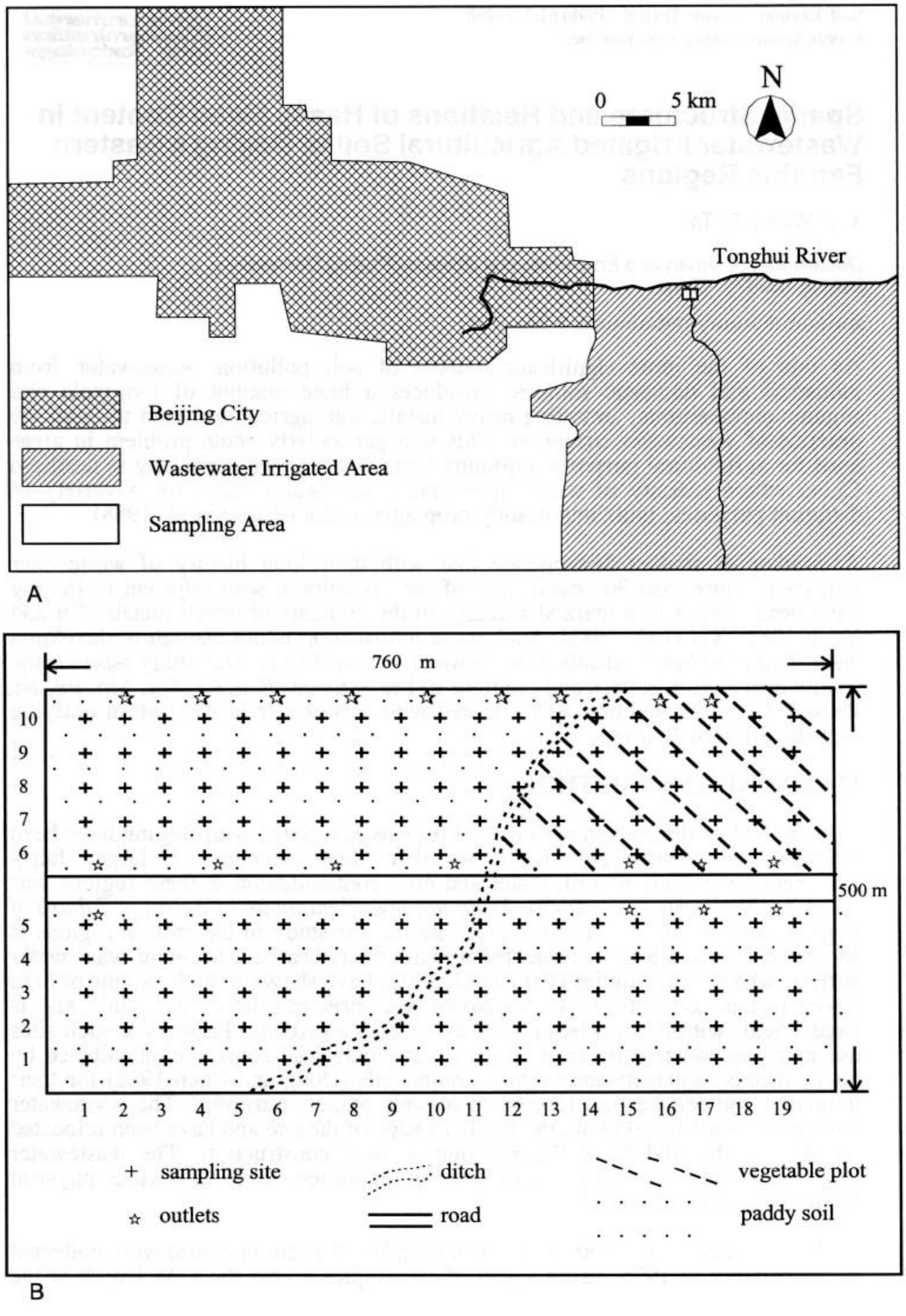

Figure. 1 A. Map of Beijing indicating the location of sampling area; B. Sampling locations

site and 10 samples down the N-S width of the site at intervals of 40m and 50m respectively. Soil samples were air-dried and passed through 1mm sieve before the measurements of grain size (< 0.01mm) and organic matter content. With respect to the content analysis of the heavy metals, the samples were further ground in an agate mortar to pass a 100-mesh sieve. The contents of eight metals (Co, Cr, Cu, Mn, Fe, Ni, Pb and Zn) in the samples were measured by flame atomic absorption spectrometry after dilution with nitric-perchloric-hydrofluoric acids, using the standard procedure (including quality control) developed by the National Environmental Monitoring Center of China (1990). In order to limit outside contamination, all glassware was soaked in 10% (v/v) nitric acid over night, with analytical grade reagents used throughout.

While classical statistical procedures only measure various features associated random variables without necessarily considering their locations, the geostatistical approach is much better able to treat explicitly the variables of interest as regionalized variables and demonstrate their actual spatial distribution pattern (Webster and Oliver 1990; Tao 1995a). In related fashion, multivariate relationships have been traditionally assessed through techniques such as principal component analysis based on linear combinations of the variables. Such techniques do not explicitly and adequately consider the spatial relationships among the variables (Grunsky and Agterberg 1992). Grunsky and Agterberg (1988) have demonstrated that the application of spatial factor analysis, produces linear combinations of variables that have maximum correlations based on auto-/cross-correlation estimates at specific lag intervals are useful for exploring the relationships of regionalized variables over various spatial domains with specific orientations and lag intervals. Thus, we have also relied on spatial factor analysis in the following exercise.

In our study, the conventional statistical analysis and variogram analysis were conducted using SAS (SAS Institute Inc. 1989) and GEO-EAS (Englund and Sparks 1991). The spatial correlation analysis and spatial factor analysis were conducted using FUNCORR (Grunsky and Agterberg 1991a) and SPFAC (Grunsky and Agterberg 1991b). The outliers in the raw data set were identified using Grubb's Test at a significant level of 0.05 prior to all statistical analysis, and only a few outliers were eliminated from further analysis.

RESULTS AND DISCUSSION

The averages, ranges and other related statistics for heavy metals and organic matter content, with information on clay particles, are provided in Table 1.

Table 1. Statistics for heavy metal contents and soil properties ($mgkg^{-1}$)

Variable	Mean	Range	Outlier	Standard deviation	Coefficient of variance	Skewness	Kurtosis
Co	10.97	0.78-19.18	0.78, 0.98	4.05	0.37	-0.75	3.02
Cr	62.42	12.4-125.9		26.1	0.42	0.418	2.45
Cu	41.59	17.7-84.5		14.1	0.34	1.30	4.79
Fe(%)	2.48	1.97-2.96		0.23	0.09	-4.39	44.06
Mn	484.0	307.7-679.2		63.2	0.13	0.31	2.98
Ni	29.9	18.9-41.2		4.53	0.15	-0.075	2.49
Pb	31.7	14.9-55.9		11.7	0.37	3.77	29.0
Zn	124.2	49.7-200.5		52.3	0.42	3.64	22.2
P[a]	43.9	27.7-64.1		7.38	0.17	0.39	3.04
OM[b]	2.15	0.82-4.19		0.66	0.31	1.04	5.63

The averages of the eight heavy metals investigated are higher than those for the same background heavy metals found in alluvial agricultural soils around Beijing, as reported by Deng et al. (1986). The mean study site values are 41.6, 124.2 and 31.7 $mgkg^{-1}$ for Cu, Zn and Pb compared to 13.1, 50.6 and 15.9 $mgkg^{-1}$ for the baseline Deng et al. figures for the same heavy metals. The substantial difference between the two heavy metal contents is caused by wastewater irrigation, as no other confounding input was recorded in the study site. Study shows that the average contents of Cu, Pb, Zn and Cr in Tonghui River (a wastewater channel near our sampling site; the waters of the river were used for irrigation; see Figure 1) sediment were 410.7, 136.2, 1131.5 and 270.5 $mgkg^{-1}$, respectively (*Study Group for Pollution Investigation and Control of Suburb of Beijing, unpub. report*).

Similar to the rising contents of the heavy metals, the coefficient of variation (CV) for each of the study site heavy metals were also found to be higher than those from other baseline studies (Deng et al. 1986). Heavy metals in a small area of long term cultivated agricultural soil are usually evenly distributed without much variation (Li et al. 1986). For wastewater irrigated soil, however, heavy metals often accumulate in a localized fashion near the irrigation outlets (Feng et al. 1992), thereby rendering the incidence and dispersion of the heavy metals more variable over the site concerned. This localized accumulation is also confirmed through the results of variogram analysis.

Experimental variograms of all eight heavy metals, the organic matter content and clay particles were calculated, both omnidirectionally and in the four standard directions (east-west, southeast-northwest, south-north, and northeast-southwest), with tolerance of 22.5 degrees around the axis. A spherical model was used to fit all experimental variograms. The parameters of the theoretical variograms (the nugget, sill and range) are given in Table 2, while Figure 2 illustrates the variation in ranges of the models in the four directions for all variables.

Table 2. Parameters of the theoretical variograms

Variable	Nugget	Sill	Range (m)
Co	7.5	13	300
Cr	270	430	370
Cu	10	200	380
Fe	0.01	0.021	390
Mn	900	3000	320
Ni	9.0	13.0	310
Pb	15	50	380
Zn	420	800	400
P[a]	35	20	350
OM[b]	0.09	0.30	420

P[a] = clay particles, <0.01mm particle (percent)
OM[b] = organic matter (percent)

In Table 2, the close similarity in ranges (300-420m) for all heavy metals indicates that the spatial variation for each is similar to the others, especially for Cr, Cu, Pb, and Zn which are known as the major contaminants of the wastewater (*Study Group for Pollution Investigation and Control of Suburb of Beijing, unpub. report*).

Positive nuggets were observed for all heavy metals and soil properties taken from our survey site. In contrast, Tao's geochemical survey (1 sample per square

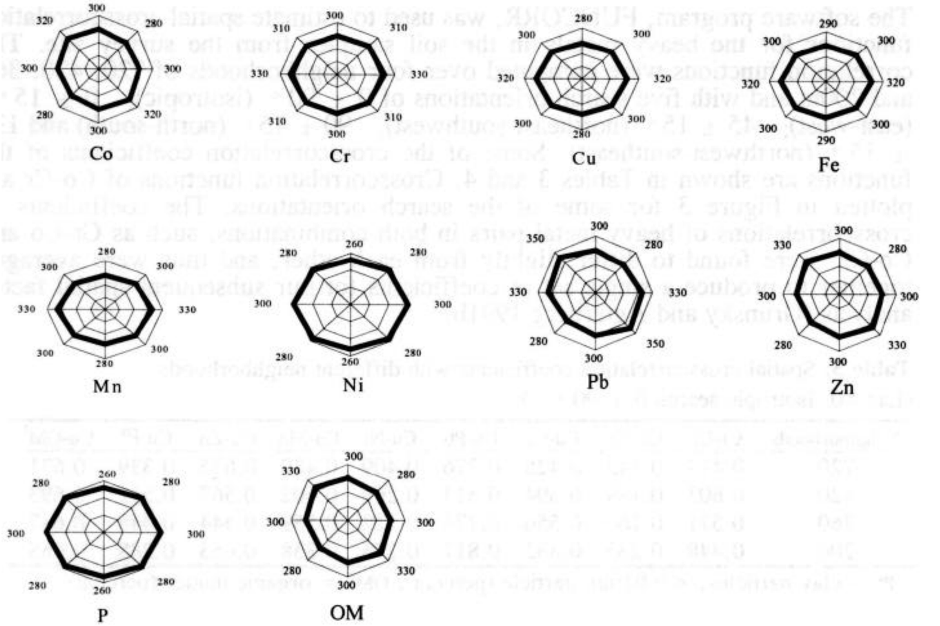

Figure. 2 Ranges of the theoretical variograms

kilometer) in Shenzhen Area of China showed zero nuggets for copper, lead and mercury (Tao 1995b). The existence of nuggets in the study site compared to surveys such as Tao's is explained by the localized accumulation of the heavy metals near irrigation outlets, as well as the relatively big distance between sampling locations.

The variograms of all heavy metals and soil properties in Figure 2 show some anisotropy, with anisotropic ratios falling between 1.10 and 1.25, with the mean value of 1.16. The relatively low ratios for Cr, Fe and Pb, over the whole site, indicate incidence of these heavy metals along any one direction is similar to that found along the other directions. The major axis of variograms for Co, Pb, Zn and organic matter are along the NW-SE direction, while those for Cu, Cr, Fe, Mn, Ni and clay particles are in the E-W direction.

The layout of the irrigation outlets, which generally round east-west along the north edge and along both sides of the road running across the survey site is the most important factor accounting for the variable spatial distribution of the heavy metals. Relatively high variation in the north-south directions is explained by this generally east-west layout of outlets shown in Figure 1. The spatial distribution has, however, been affected by heavy metals associated with a vegetable garden in the northeast corner of the survey site, where contaminated sludge has been periodically applied as fertilizer.

Correlations among heavy metals, organic matter content, and clay particles have been found in many studies due to the high affinities of heavy metals to such organic matter and clay minerals (Adriano 1986; Wang and Chen 1994). Similarly high spatial crosscorrelations were found in our study, which are accounted for by high concentrations of all heavy metals near irrigation outlets.

The software program, FUNCORR, was used to estimate spatial crosscorrelation functions for the heavy metals in the soil samples from the survey site. The correlation functions were computed over four neighborhoods of 720, 420, 360 and 200m and with five search orientations of 0 ± 90 °(isotropic); 0 ± 15 ° (east-west); 45 ± 15° (northeast-southwest); 90 ± 15 °(north-south) and 135 ± 15 °(northwest-southeast). Some of the crosscorrelation coefficients of the functions are shown in Tables 3 and 4. Crosscorrelation functions of Co-Cr are plotted in Figure 3 for some of the search orientations. The coefficients of crosscorrelations of heavy metal pairs in both combinations, such as Cr-Co and Co-Cr, were found to differ slightly from each other, and thus were averaged together to produce a single set of coefficients for our subsequent spatial factor analysis (Grunsky and Agterberg 1991b).

Table 3. Spatial crosscorrelation coefficients with different neighborhoods (Lag=0. Isotropic search 0 ± 90 °)

Neighborhoods	Cr-Cu	Cu-Co	Cu-Cr	Cu-Pb	Cu-Ni	Cu-Mn	Cu-Zn	Cu-P[a]	Cu-OM[b]
720	0.413	0.143	0.425	0.776	0.409	0.489	0.635	0.339	0.671
420	0.603	0.189	0.594	0.813	0.269	0.602	0.567	0.512	0.693
360	0.571	0.160	0.556	0.774	0.222	0.559	0.544	0.448	0.647
200	0.448	0.233	0.432	0.817	0.275	0.338	0.653	0.288	0.668

P[a] = clay particles, <0.01mm particle (percent); OM[b] = organic matter (percent)

Table 4. Spatial crosscorrelation coefficients with different directions (Lag=0. Neighborhood=360m)

Direction	Cr-Cu	Cu-Co	Cu-Cr	Cu-Pb	Cu-Ni	Cu-Mn	Cu-Zn	Cu-P[a]	Cu-OM[b]
0 ± 15 °	0.462	0.156	0.457	0.728	0.119	0.466	0.519	0.386	0.642
45 ± 15 °	0.748	0.279	0.703	0.713	0.192	0.527	0.479	0.662	0.616
90 ± 15 °	0.648	0.027	0.632	0.957	0.453	0.670	0.767	0.331	0.744
135 ± 15 °	0.482	0.407	0.469	0.675	0.205	0.523	0.430	0.566	0.618

P[a] = clay particles, <0.01mm particle (percent); OM[b] = organic matter (percent)

Table 3 and 4 and Figure 3 and other results of the spatial correlation analysis show that the combined coefficients of crosscorrelations for most heavy metal pairs varied significantly. For each variable pair, the coefficients also differ with the neighborhood and orientation of the area around the sampling location. The crosscorrelations were more significant between Cu, Cr, Pb and Zn, which have been determined as major pollutants in the wastewater of the eastern agricultural regions in which our study site is located (*Study Group for Pollution Investigation and Control of Suburb of Beijing, unpub. report*), Co and Ni show weak crosscorrelations with Cu and Cr.

The crosscorrelation coefficients for heavy metal combinations, particularly for those found in large concentrations in the wastewater used for irrigation (i.e., Cu, Cr, Pb and Zn), differ by direction due largely to the uneven distribution of irrigation outlets. Clay particles and organic matter content also showed strong crosscorrelations with Cu and other major pollutants, confirming the affinity of such heavy metals to organic matter and clay minerals. Organic matter was found in high concentrations in wastewater (*Research Group for Pollution Investigation and Control of Suburb of Beijing, unpub. Report*).

Nine variables (Co, Cr, Cu, Mn, Ni, Pb, Zn, clay particles and organic matter) were selected for our factor analysis and spatial factor analysis. Non-spatial R-mode factor analysis with varimax rotation was first conducted. The variance

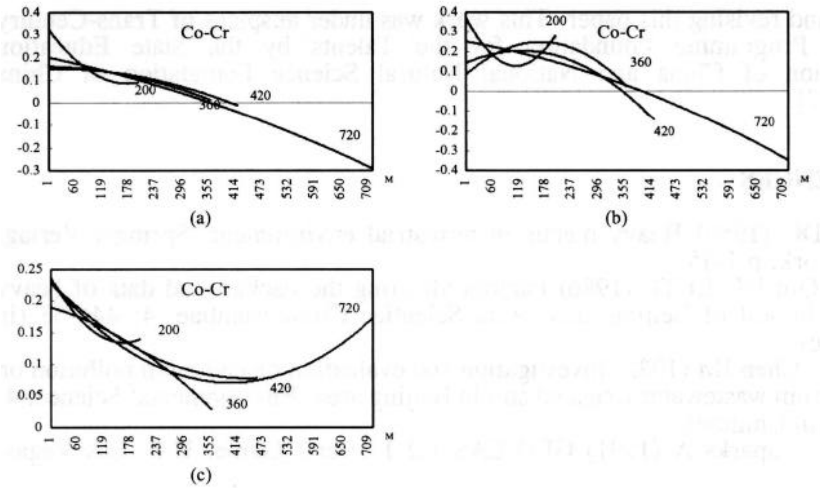

Figure. 3 Spatial crosscorrelation function of Co-Cr
(a: search orientation of 0 ± 90°; b: 0 ± 15° ; c: 90 ± 15°)

contributions of Factors 1, 2 and 3 are 67.1% , 15.6 % and 8.5 % respectively. It is quite clear that Factor 1 is the major factor accounting for the relation of the variables to one another, as it contributes over two third of the total variance. The associations making up each factor are as follows:

Factor 1 (Cu, Pb, Zn, Cr, organic matter)
Factor 2 (Ni, Zn, Mn, Cu, Pb)
Factor 3 (Co, Cr, clay particles)

Factor 1 has high positive loadings for Cu, Pb, Zn, Cr and organic matter, and demonstrates the effects of wastewater irrigation, i.e., Cu, Pb, Zn and Cr are major pollutants in wastewater, and the contents of organic matter in the wastewater is also quite high. In contrary, the explained variance of Factor 2 and 3 is too slight to provide a clear explanation of these factors.

Spatial factor analysis was undertaken for these data at the different neighborhoods and orientations based on the spatial crosscorrelation analysis. As an example, the results with neighborhood of 360m and north-south direction are discussed here. In this example, the eigenvalue and predication ability are for: Factor 1, 1.12 and 0.071; .Factor 2, 0.86 and 0.025; and Factor 3, 0.66 and 0.034, respectively. The total predication ability and noise are 0.174 and 13.2%. The associations making up each factor are as follows:

Factor 1 (-Cr, -Cu, -Pb, -Zn, -clay particles, -organic matter)
Factor 2 (Mn, Co, -Pb, -organic matter, -Cu, -clay particles)
Factor 3 (Co, -Cr, -organic matter)

These associations are quite similar to the result of non-spatial factor analysis, and demonstrate the impact of wastewater irrigation on the spatial combination and mutual association of specific heavy metals in this area.

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