Watershed-scale assessment of arsenic and metal contamination in the surface soils surrounding Miyun Reservoir, Beijing, China

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ABSTRACT

Concentrations of As and selected metals were determined in surface soils of the Miyun Reservoir watershed of Beijing, China. The degree to which concentrations of As and metals exceeded the corresponding background concentration of soils was: $Cr > Cu > Zn > As > Ni$ with no apparent anthropogenic contamination with Cd and Pb. Based on the results of a combination of multivariate statistics and geostatistical analysis, greater concentrations of Cr and Ni in soils were determined to be primarily from iron ore mining near where the Chaohe River enters the northeast portion of the reservoir. Agricultural activities were responsible for the observed elevated concentrations of Cu and Zn in soils. Relatively great concentrations of As were found in soils near the upstream regions of the Baihe River in Chicheng County where small gold mining activities have taken place. The greatest potential for adverse effects of Cr and Cu occurred along the eastern shore of Miyun Reservoir.

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1. Introduction

Miyun Reservoir is the main source of drinking water for Beijing, China. Miyun Reservoir has been influenced over the past 30 years, particularly during the 1980s, by agricultural and industrial development in the northern portions of the Beijing region. In particular runoff from non-point sources, direct dumping of wastes, mineral exploitation, and pollutants carried by rivers have resulted in elevated concentrations of As and metals in soils and surface waters.

Soils can be contaminated by a number of pollutants from industrial, agricultural, and transportation activities. The increasing amounts of As and metals in soils can reach surface and ground waters through runoff and leaching. Therefore, accumulation of As and metals in soils can affect the quality of water which can potentially affect terrestrial and aquatic communities and can directly and indirectly affect the quality and quantity of drinking water (Bonten et al., 2006; Schipper et al., 2008). Contaminated

soils can affect human health through the water supply and aquatic and terrestrial food chains (Zhang et al., 2007).

Evaluation of the status and trends in concentrations, distribution, and sources of As and metals measured in soils is challenging but necessary to provide information required for comprehensive environmental risk assessments. Multivariate statistical techniques such as principal component analysis (PCA) and cluster analysis (CA) and geostatistical analysis have been widely used as to identify probable sources of As and metals and attribute sources natural or human-caused contributions, and to describe spatial distribution of pollutants (Tao, 1995; Facchinelli et al., 2001; Li et al., 2004; Luo et al., 2007; Rodríguez Lado et al., 2008). Combining statistical and spatial analysis tools has been shown to be particularly useful in risk assessment (Carlton et al., 2001).

Earlier work has examined As and metals in soils upstream of Miyun Reservoir. It has been reported that some soils have been contaminated by As and metals including Cr, Cu, Ni, and Hg. Concentrations of As and metals in soils have been attributed primarily to mining activities, including iron, chromite and gold, upstream of Miyun Reservoir (Gao and Liao, 2007). In recent years, concentrations of As and metals in water upstream of the reservoir have increased gradually (Liu et al., 2005). Some elements such as Cu, Cr, Ni, Cd, As, Pb and Hg have been detected in drinking water

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and the sediment of Miyun Reservoir (Ge et al., 2003; Liu et al., 2005; Zhuang et al., 2005). As and metals in water and sediment of the reservoir present potential risks for the aquatic ecosystem and human health (Ge et al., 2003). Historically, metal contamination, sources and risk in soils around Miyun Reservoir and its watershed had not been systematically assessed. Thus, it has been difficult to identify potential sources of As and metals or determine the risk posed to water ecosystems at the watershed scale or to formulate effective management plans and policies to reduce metal inputs to soil and sources of water for drinking.

The aims of the study were to: (1) determine average concentrations of As and selected metals (Cr, Cu, Cd, Pb, Zn and Ni) in soils near sources of drinking water for Beijing; (2) define their natural or anthropogenic sources using multivariate statistical and geo-statistical analysis; (3) use spatial analysis method in GIS to produce geochemical maps of As and metals and identify possible hot-spots of elevated concentrations of As and metals; and (4) assess the risks from As and metals in soils around drinking water source sites.

2. Materials and methods

2.1. Site description

Miyun Reservoir, situated in the mountainous area of Miyun County of the Beijing District, is the largest reservoir in north China, with a surface area of 188 km² and watershed area of 15,788 km². Constructed in 1960, it is now the only drinking water source for Beijing City. More than ten million people inhabiting the city of Beijing depend on Miyun Reservoir for drinking water. The upper basin of the reservoir, covering an area of 1,535,400 ha, includes two counties in Beijing and six counties in Hebei Province. The main sources of water to Miyun Reservoir are the Chaohe and Baihe Rivers (Fig. 1). The average annual runoff of the Baihe River (7.22×10^9 m³) is greater than that of the Chaohe River (4.05×10^9 m³) (Wang et al., 2003). The main land uses are forestry and farming which represent 50% and 15% of the total land area, respectively. The vicinity to the north of Miyun Reservoir is mountains and forests with a sparse population. To the east of Miyun Reservoir are lower hills with dense populations. Therefore, human activities are focused to the east of the reservoir. The soil types around Miyun Reservoir are mainly argosols, cambosols and aridosols, namely, luvisols, alisols, cambisols, calcisols and gypsisols respectively, based on World Reference Base for Soil Resources (Gong et al., 2002). Upstream of Miyun Reservoir has thin soil and little vegetation cover, which results in great soil erosion (Liu et al., 2005). Therefore, the Miyun Reservoir watershed was considered a priority area for soil conservation. To protect drinking water, agricultural and industrial activities in this area are strictly limited and regulated. However, contamination from the watershed of Miyun Reservoir is still severe. The contamination mainly comes from non-point sources such as fertilizer (especially manure), pesticides and some point sources, such as mining exploration, especially in the delta of the Chaohe River (Gao and Liao, 2007).

2.2. Soil sampling

A total of 95 sampling blocks (100 m × 100 m) were identified from an area of approximately 250 × 200 km² on an irregular grid fitted to the local conditions (including soil types, land use, terrain and landscape), based on a nested sampling design. To evaluate concentrations of As and metals in soils and the potential for adverse effects to the reservoir, sample locations were most densely collected near the reservoir and its tributaries where the most human-impacted areas were also located. Samples were spaced farther apart with increasing distance from Miyun Reservoir and its tributaries where

there was less human activity and lesser variability in concentrations of As and metals and the presence of mountains and narrow valleys (Fig. 1). Throughout the survey a global positioning system (GPS) was used to determine sampling positions. At each sampling block, 5 sub-samples (0–20 cm depth) were taken from the 4 vertexes and the center of a square block and mixed thoroughly to select 1 kg soil as the representative sample of the block. This procedure resulted in 95 composite soil samples from a total of 475 individual soil sub-samples. The soil sampling was performed, based on The Technical Specification for Soil Environmental Monitoring (State Environmental Protection Administration of China, 2004).

2.3. Chemical analysis

Soil samples were air-dried, crushed in an agate mortar, passed through a nylon sieve of 100 mesh, and digested with HNO₃ and H₂O₂ using Method 3050B (USEPA, 1996). All materials used during analytical determinations were kept in Teflon or other metal-free containers. Total concentrations of Cd, Cr, Zn, As, Cu, Ni and Pb were measured by inductively coupled plasma mass spectrometry (ICP-MS). To check the quality of preparation and analysis, replicate determinations were performed on approximately 25% of samples. The method detection limit (MDL), which is defined as the minimum concentration of substance that can be measured and reported with 99% confidence, was determined using EPA 40CFR Part 136, Appendix B. Standard reference materials, GSS-1 soils, obtained from the Center of National Standard Reference Material of China were analyzed as part of the quality assurance and quality control (QA/QC) procedures. Satisfactory recoveries were obtained for Cu (91–97%), Ni (99–105%), Pb (95–104%), Cd (96–101%), As (98–103%) and Zn (92–104%).

2.4. Statistical analysis and risk assessment

Distributions and associations of concentrations of As and metals were investigated by a combination of univariate and multivariate parametric statistics. In multivariate statistics and linear geostatistics, a normal distribution for the variables under study is desirable (Webster and Oliver, 2001). Concentrations of As and metals were log₁₀-transformed to make the data less skewed and more closely approximate a normal distribution. Normality of the log₁₀-transformed concentrations was assessed using the Kolmogorov–Smirnov (K–S) test. Correlation analysis and principal component analysis (PCA) were used to evaluate concentrations of As and metals. Correlations were evaluated using the bivariate method, with two-tailed significance and Pearson correlation coefficients. In the PCA, Varimax with Kaiser normalization was used as the rotation method in the analysis (García et al., 2004). As suggested by the Kaiser criterion (Kaiser, 1960) all principal factors with eigenvalues >1.0 extracted from the variables were retained. Statistical analysis were performed using SPSS 13.0[®] statistical software.

Geostatistical methods were used to calculate the semivariogram (Eq. (1)):

$$r(h) = \left(\frac{1}{2N(h)} \right) \sum_{i=1}^{N(h)} [Z(x_i) - Z(x_i + h)]^2 \quad (1)$$

where: $Z(x_i)$ represents the measured value for concentrations of As and metals in soil at locations of x_i , and $r(h)$ is the semivariogram for a lag distance h between observations $Z(x_i)$ and $Z(x_i + h)$, and $N(h)$ is the number of data pairs separated by h . Semivariograms $r(h)$ for the concentrations of As and metals in soils were calculated and

Fig. 1. Map of soil sampling sites around Miyun Reservoir.

the scatter plot of $r(h)$ vs. h was generated. Then different theoretical semivariance models (e.g., spherical, exponential, Gaussian, linear, and linear to sill) were used to fit the experimental semi-variogram. The appropriate theory model and the parameters for kriging interpolation (e.g., range, nugget (C_0) and sill ($C+C_0$)) were obtained. In this study, ordinary kriging was used to interpolate concentration values and create the spatial distribution maps of As and metals. For the assessment of contamination risks, the disjunctive kriging technique was used to estimate the probability that the true values of concentrations of As and metals at unsampled points exceed the specified thresholds. The disjunctive kriging is based on the assumption that our data are a realization of a process with a second-order stationary bivariate distribution. This method was described in more detail by Rivoirard (1994) and Matheron (1962). This method can be used to estimate the original soil variable, and the conditional probability for specified thresholds. The experimental semi-variogram functions were computed and modeled by using the software package GS+ (Gamma Design, 1994), while kriging estimation and spatial distribution maps of As and metals were obtained by using the geostatistical analyst extension of ArcGIS 9.2® for Windows.

3. Results and discussion

3.1. Descriptive statistics of concentrations of As and metals in soils around Miyun Reservoir

Summary descriptive statistics of the concentrations of Cr, Ni, Cu, Zn, Cd, As and Pb are provided (Table 1). The application of the

K–S test confirmed that the concentrations of As and metals in the soils were not normally distributed but the $\log_{10}$ -transformation resulted in a distribution that approximated a normal distribution ($K-S\ p > 0.05$). Therefore, the geometric means (geomean) of As and metals were compared with background concentrations in soils of Beijing (Chen et al., 2004). The geomean of Cr ($37\text{ mg kg}^{-1}\text{ dw}$) was significantly greater than the background concentration ($31\text{ mg kg}^{-1}\text{ dw}$) (one-sample test, $P < 0.05$). The geomeans of As and the other metals were generally similar to or less than Beijing background concentrations. The number of samples exceeding the corresponding background concentration for Cr, Cu, Zn, As and Ni was 56, 40, 37, 10 and 6, respectively. Multiplying the ratios of the geomeans to the corresponding background concentrations by the number of values exceeding the respective background concentration provides a combined estimate of both the magnitude and the extent of contamination around the reservoir. This weighted result suggests that the magnitude of exceeding the background concentrations of As and metals in soils around Miyun Reservoir is in the descending order of $\text{Cr} > \text{Cu} > \text{Zn} > \text{As} > \text{Ni}$. All the concentrations of Cd and Pb were less than their respective background concentrations, indicating no apparent anthropogenic contamination with Cd and Pb. The variations in concentrations of Cr, Cu and Zn were indicative of heterogeneous sources and likely due to human activities. It has been reported that mining activities (such as iron, chromite and gold mines) have existed in Miyun County where the iron ore deposit is very rich (about 9×10^9 tons, accounting for 98% of its total deposit in Beijing) (Gao and Liao, 2007). The main component of iron mine tailings in this area was ferrous chromite (FeCr_2O_4)

Table 1

Summary statistics of arsenic and metal concentrations in surface soil (from measurements in mg kg⁻¹ dw).

	Cr	Ni	Cu	Zn	Cd	As	Pb
Sample number	95	95	95	95	95	95	95
Arithmetic mean	40	18	23	64	0.05	6.5	11
Geometric mean	37	17	19	55	0.049	5.5	9.9
Median	33	16	18	55	0.050	6.7	10
Standard deviation	20	8.3	20	18	0.022	2.1	0.6
Minimum	15	4.9	5.5	12	0.023	3.5	5.0
Maximum	1.3 × 10 ²	58	68	1.0 × 10 ²	0.055	11	24
Skewness	1.9	2.3	2.0	0.39	-4.9	0.60	1.6
Kurtosis	5.0	9	5.9	1.3	35	2.7	4.2
K-S p	0.040	0.13	0.035	0.75	0	0.25	0.21
Beijing background concentration	31 ^a	28 ^a	20 ^a	60 ^a	0.15 ^a	7.8 ^a	25 ^a
Number exceeding background concentration of Beijing	56	6	40	37	0	10	0
Log-transformation							
Skewness	0.87	-0.12	0.20	-1.5	-6.5	-0.61	0.20
Kurtosis	0.99	2.0	0.10	7.9	49	2.4	0.9
K-S p	0.14	0.21	0.68	0.79	0	0.22	0.52

^a Chen et al. (2004).

(Westbrook, 1983; Gao and Liao, 2007). On the other hand, anthropogenic inputs of Cr in fertilizers, limestone and manure are, generally, less than concentrations already present in soils (Facchinelli et al., 2001). Consequently, long-term mining of iron ores is the most likely cause of elevated Cr contamination in soils (Marmolejo-Rodríguez et al., 2007). In fact greater concentrations of Cr were observed in the vicinities of the iron ore mine (Marmolejo-Rodríguez et al., 2007). Fertilizer and pesticides are considered as important sources of Zn and Cu in the environment (Xue et al., 2000; Nicholson et al., 2003). Thus, it can be hypothesized that the source for Zn and Cu in the soils are from application of fertilizer and pesticides in agriculture. The small and fairly consistent concentrations of Cd and Pb are consistent with minor anthropogenic input of these metals to soils of this region. It was reported that concentrations of these metals near iron ore mines were small (Marmolejo-Rodríguez et al., 2007).

3.2. Statistical analysis

In order to establish inter-element relationships in soil samples, correlation coefficients for As and metals were calculated (Table 2). The significant positive correlation between Cd, Cu, Zn and Ni is consistent with a common source for these metals. Associations among these metals can be indicative of sources due to human activities or geogenic and pedogenic characteristics (Facchinelli et al., 2001; Rodríguez Martín et al., 2008). As and Pb were significantly negative correlated to Cd, Cu, Zn and Ni. Therefore, As and Pb have different sources from those of Cd, Cu, Zn and Ni. Significant positive correlation (0.68) was found between Cr and Ni and thus, it seems likely that they are from the same source. Since As was not correlated to Pb, As had no the same source with Pb.

Principal component analysis was conducted to ascertain possible contributing factors towards the concentrations of As and metals and thereby determine which elements have a common origin. By extracting the eigenvalues and eigenvectors from the correlation matrix, the number of significant factors, the proportion of variance explained by each of them and rotated component matrix are given (Table 3). Only three eigenvalues were found to be >1 and explained approximately 90% of the variance. The first three eigenvalues were therefore selected for further analysis, while

Table 2

Pearson correlation matrix for arsenic and metal concentrations.

	Cr	Ni	Cu	Zn	Cd	As	Pb
Cr	1						
Ni	0.68**	1					
Cu	0.2	0.76**	1				
Zn	-0.17	0.53**	0.86**	1			
Cd	-0.27*	0.41**	0.68**	0.88**	1		
As	-0.02	-0.32**	-0.47**	-0.53**	-0.4**	1	
Pb	-0.11	-0.32**	-0.27*	-0.26*	-0.41**	-0.16	1

*correlation is significant at the 0.05 level (two-tailed); **Correlation is significant at the 0.01 level (two-tailed).

other small but non-zero eigenvalues were discarded for the purpose of establishing a probable number of contributing source factors. The initial eigenvalues extracted were “cleaned up” by means of Varimax rotation. It is evident from the rotated component matrix that As and metals are explained by three factors. The first factor spanning the greater amount of variance (50.33%) includes Cu, Zn, Cd and Ni. This factor (source) is likely due to both human activities and natural influences. Apparently, anthropogenic influences to these metals include application of fertilizer and pesticides in agriculture. Soil parent materials are the natural factors that account for lesser concentrations of these metals than their background concentrations. Both Cr and Ni appear in the second factor, which is likely due to anthropogenic influences. The significant human activities that affect concentrations of elements in soils are primarily iron ore mining activities (Xue et al., 2000; Wang and Wang, 2005) which are responsible for greater concentrations of Cr and Ni than their background concentrations around Miyun Reservoir. Pb concentrations are less than the background concentrations, which represent the source of parent rocks. It seems that arsenic is included in neither the second factor nor the first or the third factor. Furthermore, considering 10 samples having As concentrations greater than its background level and the correlations between As and metals, it could be deduced that greater concentrations of As than its background level could be caused by sources different from iron mining and agricultural chemical input.

3.3. Spatial analysis

3.3.1. Geostatistical analysis

Geostatistics provides an advanced methodology which facilitates quantification of the spatial features of soil parameters and enables spatial interpolation (Zhang and Selinus, 1998; Hengl et al., 2009; Carlon et al., 2001). It has become a useful tool for the study of spatial uncertainty and hazard assessment (Goovaerts, 2001). Semivariogram models and best-fit model parameters are given (Table 3), while diagrams are plotted (Fig. 2). These models were chosen based on regression coefficient of determination (R^2) and residual sums of squares (RSS) provided by GS+ software. Spherical, exponential and Gaussian models were chosen as appropriate for all direct semivariograms after visual inspection of sample semivariograms and a cross-validation check. In all cases the models were assumed to be isotropic. Therefore, kriging was performed assuming a circular search radius, with a range equal to the semivariogram range, and a maximum number of 10 neighbors. The optimal theoretical models of Cu and Zn were spherical models. Cr was best fit to an exponential model. Cd, Ni, Pb and As were best fit to gaussian models. The existence of a positive nugget effect in some of the variables studied can be explained by sampling error, short-range variability, and unexplained and inherent variability (McGrath et al., 2004). It is shown (Table 4) that all semivariograms

Table 3Total variance explained and component matrices.^a

Total variance explained									
Component	Initial Eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.52	50.33	50.33	3.52	50.33	50.33	3.29	47.01	47.01
2	1.63	23.25	73.58	1.63	23.25	73.58	1.82	25.96	72.97
3	1.17	16.68	90.26	1.17	16.68	90.26	1.21	17.29	90.26
4	0.43	6.09	96.35						
5	0.17	2.37	98.72						
6	0.05	0.67	99.40						
7	0.04	0.60	100.00						
Component matrices									
Element	Component matrix			Rotated component matrix					
	PC1	PC2	PC3	PC1	PC2	PC3			
Cr	0.15	0.96	0.15	−0.18	0.97	0.02			
Ni	0.77	0.60	0.05	0.52	0.82	0.13			
Cu	0.93	0.07	0.08	0.85	0.39	0.05			
Zn	0.92	−0.32	0.01	0.97	0.00	0.05			
Cd	0.84	−0.41	−0.22	0.91	−0.14	0.25			
As	−0.57	0.19	−0.64	−0.64	−0.12	0.59			
Pb	−0.40	−0.17	0.82	−0.26	−0.14	−0.88			

^a Extraction method: principal component analysis. rotated method: varimax with Kaiser normalization.

are generally well structured with small nugget effect, showing that the sampling density is adequate to reveal the spatial structures.

The range is considered as the distance beyond which observations are not spatially dependent (Gallardo, 2003). Comparing the range of As and metals, it was found that Cd and Pb have longer effective ranges than As and the other metals, which indicates that Cd and Pb have better spatial structure and less variation caused by extrinsic factors. Human activities have effects on only short and medium-range scales of variation (Rodríguez Martín et al., 2008). In this study, semivariograms of Cr, Cu and Zn are dominated by short-range structure, and the semivariogram of As and Ni are of medium-range variation. This result suggests that human activities affect the spatial distribution of Cr, Cu and Zn while the spatial distribution of the As and Ni are equally controlled by both geological process and human activities.

3.3.2. Spatial distribution and risk assessment

The variogram models were used as input for ordinary kriging and the resulting contour maps are shown (Fig. 3). The general trend was that concentrations of Cr were greater around the reservoir in Miyun County and in most of Xinglong County. The greater concentrations of Cr in these areas are presumably of anthropogenic origin on a local scale. It has been reported that most iron ores are found to the east of the reservoir, especially in the delta of the Chaohe River. Contamination of soils by Cu was only observed in patches located to the east of the reservoir where ore mining activities and large-scale animal feeding has taken place (Gao and Liao, 2007). Coincidentally, orchard land in which Cu fungicides were repeatedly used (Loland and Singh, 2004) are mainly distributed to the east of the reservoir. Thus, applications of metal-containing fungicides in orchards can result in increased Cu content in soils. Greater Zn contamination was observed in the east of Xinglong County and the south of Chengde County. These places are remote from Miyun Reservoir. However, there is still a patch in which the concentrations of Zn can be greater than its background concentration (60 mg kg^{−1} dw). This area is close to and in the northwest of the reservoir where three rivers (namely Tanghe, Heihe and Baihe Rivers) converge and enter the reservoir. Animal feeding and fertilizer application are focused in this area, causing high levels of Zn in the soils. The maximum concentrations of Ni

were distributed in the east of Miyun Reservoir in Miyun County where the mining activities occurred. A good correlation between concentrations of Ni and Cr (Table 2) was consistent with mining activities being the source of enrichment of Ni in the study area. The greater concentrations of As were found upstream in the Baihe River in Chicheng County where small-scale gold mining activities existed. It has been reported that As was a concomitant in gold ore (Liu et al., 2005). This might be the reason for the greater concentrations of As at upstream regions of the Baihe River. Although the area of greater concentrations of As was remote from the west of Miyun Reservoir, its potential impact on water in Miyun Reservoir is still possible.

Mean and maximum concentrations of Cd and Pb (Table 1) were considered small relative to corresponding background concentrations (Chen et al., 2004). Thus, these two metals are unlikely to constitute a risk for environmental pollution or threat to human health. Compared with background concentrations (Table 1) the probabilities of Cr, Cu, Zn, As and Ni were estimated. The risk patches resulted from disjunctive kriging were given (Fig. 4). The probability of concentrations of Cr in soils to the east of Miyun Reservoir including Xinglong, part of Miyun and Chengde Counties exceeding the background concentration was 0.75–0.97 (Fig. 4). For soil Cu, the probability of Cu exceeding 20 mg kg^{−1} exhibited a small patch of greater contamination risk with estimated probability (0.69–0.83) to the east of the reservoir in Miyun County. The probability of Zn exceeding 60 mg kg^{−1} was estimated to be 0.5–0.75 at the areas far from the reservoir. However, the probability of As exceeding 7.8 mg kg^{−1} was estimated to be 0.29–0.33 in the upstream region of the Baihe River. For soil Ni, the probability of exceeding 28 mg kg^{−1} indicated a small patch of contamination risk with estimated probability (0.29–0.39) to the east of the reservoir in Miyun County.

If the water quality of the Miyun Reservoir is to be protected, concentrations of Cr, Zn, Cu, As and Ni which already exceed background concentrations or where the probabilities of their exceeding those values are substantial should not be allowed to increase further. Control will be needed to reduce risk from these metals in the soils. Maps of As and metal concentration and conditional probability provide the information for that purpose. The data also provided a scientific basis for best-management practices for Miyun Reservoir watershed.

Fig. 2. Experimental semivariograms of arsenic and metals in soils with fitted models.

Table 4
Best-fitted semivariogram models of arsenic and metals and their parameters.

Metals	Transformed	Model	C_0	$C + C_0$	Range (km)	R^2	RSS
Cr	Log	Exponential	0.0048	0.11	5.4	0.81	2.4×10^{-4}
Ni	Log	Gaussian	0.050	0.10	29.5	0.65	1.3×10^{-3}
Cu	Log	Spherical	0.0002	0.17	11.4	0.74	1.6×10^{-3}
Zn	Log	Spherical	0.0001	0.042	12.7	0.61	1.6×10^{-4}
Cd	Log	Gaussian	0	2×10^{-6}	46	0.75	1.9×10^{-12}
As	Log	Gaussian	1×10^{-3}	0.46	24	0.78	0.045
Pb	Log	Gaussian	0.05	0.079	52	0.66	1.1×10^{-3}

C_0 , nugget variance; $C + C_0$, sill variance; R^2 , regression coefficient of determination; RSS, residual sums of squares.

Fig. 3. Contour maps for arsenic and metal concentrations in the soils around Miyun Reservoir.

Fig. 4. The estimated probability maps of Cr, Cu, Zn, As and Ni being greater than the background values.

4. Conclusions

Mining activities (especially iron ore) in the northeast areas of the Miyun Reservoir have caused serious Cr contamination and the elevated concentrations of Ni in the soils. Cd, Cu, Zn and Ni are inter-correlated, originating from natural processes and human influences. Using fertilizers, pesticides and fungicides related to agricultural practices in the study area has increased the concentrations of Zn and Cu in the soils. The greater concentrations of As occurred at upstream portions of the Baihe River in Chicheng County. To reduce its risk, some measures should be taken to reduce the release of As from small scale gold mining activities in Chicheng County. Currently concentrations of Pb and Cd in soils do not present a risk.

Transport of As and metals from mining activities is representative of a class of water quality problems. Unmanaged metals such as Cr, Cu, Zn, As and Ni released from upland sources, their transport across the land surface, and delivery to watershed systems can have adverse water quality and ecological impacts upon the reservoir to a considerable extent. Thus, the Beijing government should forbid any mining activities (especially iron and gold ore mining) and limit the agricultural chemical input to the Miyun Reservoir watershed.

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