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Spatial analysis of human health risk associated with ingesting manganese in Huangxing Town, Middle China

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ABSTRACT

This paper spatially analyzed human health risk associated with ingesting manganese (Mn) contents in groundwater and vegetables irrigated with contaminated pond water in Huangxing Town, Middle China. The combination of monitoring data and sequential indicator simulation (SIS) was used to determine Mn exposure distributions in pond water and groundwater. Hazard quotient (*HQ*) associated with ingesting Mn was calculated to evaluate the risk to human health. Many *HQ*s determined from risks exceed 1 in the region, indicating that the use of groundwater and pond water poses potential risk to human health. Lower risk areas are located in the northwest and partly southeast of the region. The probabilistic risk assessment formulated suitable references for pollution remedy and control in Huangxing Town. Safe areas in 75th percentile of *HQ* map are suggested to be safe for use and, the manganese residues in the unsafe areas of the 25th percentile of *HQ* map is to be treated firstly.

1. Introduction

Manganese (Mn) is an essential nutrient which, in case of over-exposure via inhalation or ingestion, can turn into a potent neurotoxicant. Upon high exposure, Mn accumulates in the globus pallidus, but also in other basal ganglia including caudate and putamen (USEPA, 2008). Previous studies focused on the effect of Mn deficiency on human health. With the increasing attentions of environmental pollution associated with mining industry (Santos-Burgoa et al., 2001; Asante et al., 2007), industrial or municipal wastewater reuse for irrigation (Abbas et al., 2007; Arora et al., 2008) and so on (Agusa et al., 2006; Buschmann et al., 2008), a few researches have begun to study the effects of inhalation and ingestion excessive Mn on human health for its non-biodegradable nature, long biological half-lives and its potential to accumulate in different body parts (Pal et al., 1999; Bouchard et al., 2008).

Huangxing Town, a historic town for the production of manganese sulphate in China, has been heavily contaminated by the disorder emission of pollutants from manganese sulphate enterprises. Mn in wastewater from the original industrial waste residues has been leaking to groundwater and spreading to surface water, causing serious contamination and thus making it an ideal candidate for a case study to examine the effect of Mn exposure and hence risk. Cai et al. (2003) and Ge (2004) found the Mn concentrations ranged from 0.02 to 122.5 mg L^{-1} in groundwater and 0.002 to 2.48 mg L^{-1} in the pond water in this region, which is greatly exceeding manganese WHO guideline of 0.4 mg L^{-1}. In the region, contaminated groundwater has been used abundantly as drinking water, and pond water has been used for irrigation. Therefore, Mn in groundwater directly enters human bodies, and Mn in the ponds indirectly enters the food chain via vegetables and then bioaccumulates in human bodies.

To provide a reference of water use to local government and establish a set of cost-effective measurements for groundwater remedy and management, it is urgent to conduct human health risk assessment associated with ingesting Mn. Here, one of the key steps is to determine Mn concentrations in groundwater and surface water. Usually, monitoring data, a fate and transport model, or some combination of monitoring data and models are used to obtain environmental concentrations (Bennett et al., 1999; Zeng et al., 2001, 2003; Zhang et al., 2006; Su et al., 2007). The Mn concentrations in pond water can be determined using monitoring data. However, the spatial distribution of Mn concentrations in groundwater is commonly heterogeneous. Only a small proportion of in situ data can be analyzed in a field investigation owing to the time and cost constraints. And sparse measured data contain considerable uncertainty.

Geostatistics is widely used in modeling the spatial variability and distributions of field data with uncertainty. Sequential indicator

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simulation (SIS), which is an indicator-based non-parametric simulation method and makes no assumption on distributions of variables, is used to describe a joint realization of pollutants. It based on a sequential simulation approach. At each unsampled location, the estimated value incorporates all data available within a neighborhood, including the original data and all previous simulated values. The objective is to generate several equiprobable realizations in the studied region, which can effectively reflect the uncertainty resulting from heterogeneity. SIS has been frequently adopted to describe spatial patterns of contaminants distributions in groundwater and soil, and delineate their probabilistic risks to human health. For example, Jang et al. (2006) and Lee et al. (2008) used SIS to reproduce arsenic (As) exposure distributions in groundwater and spatially analyzed probabilistic potential carcinogenic risks associated with ingesting arsenic (As) contents bioaccumulated in fish in Tainwan. Jang (2008) also explored a safe utilization ratio (UR) of groundwater in fish ponds in terms of the regulation of arsenic (As) concentrations. Juang et al. (2004) adopted SIS to generate equiprobable spatial patterns of Cu concentrations in the soil and delineate contaminated areas. Gay and Korre (2006) used SIS to produce maps of soil contaminant levels and probabilistic human health risk.

However, the sequential simulation approach requires firstly modeling a prior distribution of the estimated value at each unsampled location, and then randomly draws a simulated value from this distribution as the estimated value. In SIS, the indicator simulation (IK) is used to build the prior conditional cumulative distribution function (*ccdf*) for the estimated locations. At an unsampled location, the estimated values by IK represent the probability of contaminant concentrations being lower than a given threshold (Hendricks Franssen et al., 1997; Meirvenne Van and Goovaerts, 2001; Liu et al., 2004; Amini et al., 2005; Hu et al., 2005; Lee et al., 2007; Tavares et al., 2008; Ungaro et al., 2008). Given several thresholds, the prior distribution can be built (Juang et al., 2004).

The objective of this work is to spatially analyze potential risks to human health associated with ingesting Mn contents in groundwater and vegetables in Huangxing Town, Hunan. Aimed at spatial variability and uncertainty of Mn concentration in groundwater, SIS was used to produce several equiprobable Mn exposure distributions. Then, the health risk assessment was conducted considering Mn distributions in groundwater and its content in pond water. Finally, the potential probabilistic risks to human health were calculated and mapped with GIS. The probabilistic risk assessment can be used to formulate suitable strategies under various remedial stages.

2. Materials and methods

2.1. Study area and hydrogeology

Huangxing Town (N28°08′, E113°06′) (Fig. 1) is located in Changsha County, 30 km far from Changsha City. The area is enclosed by Liuyang River to the west and south. Langli Town and Zhentou Town lie to the north and to the west, respectively. The region is divided into 22 villages with total population of over 40 000. The area of the town is approximately 80 km^2 with arable land of about 12 km^2.

In Huangxing Town, groundwater is the primary drinking water, and the pond water is used for irrigation. However, these water resources have been heavily contaminated by leakage of manganic residues discharged from manganese sulphate industries, which were begun in the 1980's and developed to 13 enterprises in 2002. Mn from the original industrial waste residues has been leaking to groundwater and spreading to surface water, causing seriously contamination.

There is an average annual precipitation of about 1570 mm and most of that is concentrated in the 5 months period from March to July. Hydrogeological study demonstrates that aquifer in the region is attributed to loose accumulated clay and pore water petrofabric formed in the Quaternary of Holocene Series. The pumping tests in boleholes and wells performed in 2000 showed that the aquifer had a depth of 2–6 m and thickness of 1–4 m, and the hydraulic discharge ranged from 0.1 to 0.5 L s^{-1}. The main source for groundwater recharge is the vertical infiltration of precipitation RCHGB (1976).

2.2. Data source

In 2002, Changsha Environmental Monitoring Central Station undertook groundwater and surface water quality survey in the region. Total 34 well samples and 22 pond water samples were collected, which characterized the whole studied region. The survey analyzed 17 water quality survey items in groundwater and 15 ponds water quality survey items in surface water, including the concentrations of Mn. An abnormal high Mn concentration was detected among these water quality items. Fig. 2 shows the cumulative distribution of the measured Mn concentrations. The average Mn concentrations were 18.08 and 39.12 mg L^{-1}, with a maximum value of 122.50 and 487.00 mg L^{-1}, in groundwater and surface water, respectively. Approximately, 38% of the sample wells had Mn concentrations greater than Chinese drinking water limit of 0.1 mg L^{-1}, 47% had concentrations greater than WHO acceptable limit of 0.4 mg L^{-1}. Meanwhile, 50% of the sampled ponds had Mn concentrations greater than WHO acceptable limit of 0.4 mg L^{-1}, and 38% had concentrations greater than irrigation standard limit in USA (there is no irrigation standard for Mn in China).

2.3. Mn exposure and bioaccumulation pathways

In Huangxing Town, groundwater is the primary drinking water, and the pond water is used for irrigation. Therefore, Mn contents in groundwater are the most primary Mn source bioaccumulated in human bodies, while Mn contents in pond water, which is also of high concentrations, can accumulate into the edible parts of leafy vegetables irrigated with Mn contaminated pond water.

2.4. Exposure media concentrations

The monitoring data for pond water is directly used to represent Mn exposure concentrations via irrigation. Because the heterogeneity of Mn concentration in groundwater, sequential indicator simulation (SIS), a most widely used indicator-based stochastic simulation method, is applied to simulate Mn exposure concentration via drinking. SIS includes all original data and part values that are simulated previously within a neighborhood. A sequential simulation approach requires the simulation of a prior distribution at each unsampled location. Therefore, in SIS, the IK estimator, a non-parametric geostatistical method for estimating the probability that the attribute value is no greater than a specific threshold, $z_{k,}$ at a given location x, is firstly used to model the prior *ccdf* at each unsampled location. Then the following procedures of SIS are employed:

(1) 0–1 Code transformations and variogram analysis

The sampled well concentration $Z(x)$ at location x is transformed into series indicator variables with a binary distribution, as follows:

$$I(x, z_k) = \begin{cases} 1, & \text{if } Z(x) \leqslant z_k \\ 0, & \text{otherwise} \end{cases} \tag{1}$$

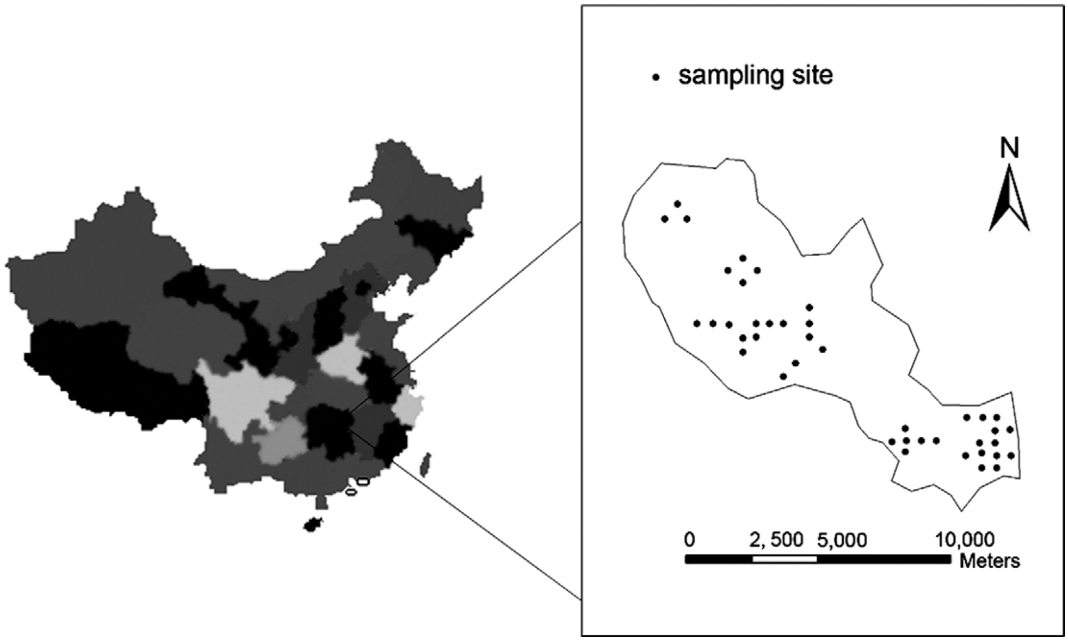

Fig. 1. The study site of Huangxing Town in Changsha. The closed circles mark the locations of the hydrogeological stations.

where z_k is a desired cutoff value of Mn concentration. For each of the cutoff values z_k, the experimental variogram of the indicator code is fitted by a theoretical model, $\gamma(h)$, which can be a spherical, exponential or Gaussian model, and three parameters of the fitted model – the nugget effect, the sill and the range – are determined.

(2) Prior distribution estimation

Define a random path to unsampled locations and visit each location to be simulated once only. At each unsampled location, the variogram is used in IK to estimate the probability of Mn concentrations being lower than a given threshold:

$$F(x, z_k|n) = \text{Prob}\{Z(x) \leqslant z_k|n\} = E[I(x, z_k|n)] \tag{2}$$

where $F(x, z_k|n)$ is the *ccdf* of $Z(x) \leqslant z_k$; $E[I(x, z_k|n)]$ is the expected value of $I(x, z_k)$, which is obtained with ordinary kriging:

$$I^*(x_0, z_k) = \sum_{j=1}^{n} \lambda_j(z_k) I(x_j, z_k) \tag{3}$$

where $I(x_j, z_k)$ represents the values of the indicator at the measured locations, x_j, $j = 1, 2, \ldots, n$, and λ_j is a weighting factor of $I(x_j, z_k)$ that is used in estimating $I^*(x_0, z_k)$. The prior distribution is then built with calculated probability of Mn concentrations being lower than several given thresholds.

(3) Sequential simulation

All original data and concentration values that are simulated previously within a neighborhood are included in the simulation. A linear interpolation yields a continuous ccdf within each class of threshold values $[z_{k-1}, z_k]$. The continuous ccdf at the lower tail and upper tail are extrapolated toward a zero using a negatively skewed power model with $\omega = 2.5$ and an infinite upper bound using a hyperbolic model with $\omega = 1.5$, respectively (Goovaerts, 1997; Deutsch and Journel, 1998).

Multiple realizations can be yielded. Each realization followed a random path which represents equiprobable spatial distribution of Mn concentrations in groundwater. Therefore, numerous realizations can be used to evaluate the variation and uncertainty of the Mn concentrations. This work used the *variofit* function of R software to perform the experimental variogram analysis (RCT, 2008), and used *ik* (indicator kriging) and *sisim* (sequential indicator simulation program) codes in GSLIB (Deutsch and Journel, 1998) to perform IK and SIS, respectively.

2.5. Human health risk assessment

After a comprehensive review of Mn toxicity data by U.S. EPA health scientists (USEPA, 2008), human health risk associated with ingesting Mn is assessed by hazard quotient (*HQ*) as follows (USEPA, 1989, 1992):

$$HQ = CDI/RfD \tag{4}$$

where *RfD* is reference dose of Mn suggested by EPA (mg kg^{-1} d^{-1}) (0.14 mg kg^{-1} d^{-1}) and *CDI* is chronic the daily intake of Mn, which is calculated by the following equation:

$$CDI = \frac{C \cdot IR \cdot EF \cdot ED}{BW \cdot AT} \tag{5}$$

where *C* is Mn concentrations in the environmental media (mg L^{-1}), *IR* is human ingestion rate (L d^{-1}), *EF* is exposure frequency (d yr^{-1}), *ED* is average exposure duration (year) (30 yr), *BW* is average body weight (kg), and *AT* is averaging time ($AT = 365 \times EDd$).

In this study, *EF* is supposed to be 365 d yr^{-1}, then the equations above can be rewritten considering the two pathways of exposure:

$$HQ = \frac{CDI_{VET} + CDI_{GW}}{RfD} = \frac{C_{PW} \times AF \times R_{factor} \times IR_{food\ intake} + C_{GW} \times IR_{water\ intake}}{BW \times RfD} \tag{6}$$

where C_{PW}, AF, R_{factor} and $IR_{food\ intake}$ represent the Mn concentrations in pond water (mg L^{-1}), Mn accumulate factor, conversion factor, and daily intake of vegetables, respectively. C_{GW} and $IR_{water\ intake}$ represent the Mn concentrations in groundwater and daily intake of water. The accumulate factor used to represent Mn accumulation in vegetables irrigated with contaminated pond water was 0.48. The conversion factor used to convert fresh green vegetable weight to dry weight was 0.085 (Rattan et al., 2006). The average adult and

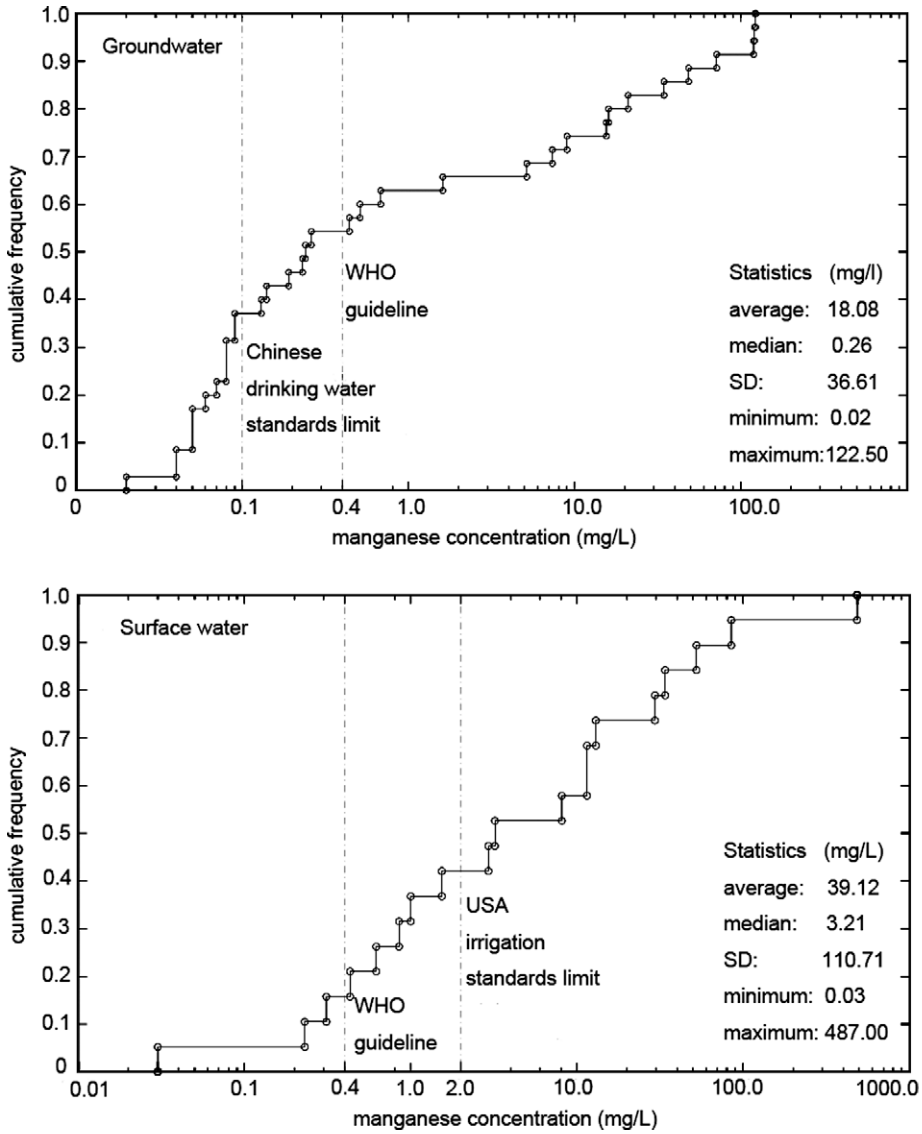

Fig. 2. Cumulative manganese distributions over wells and ponds.

child body weights were considered to be 55.9 and 32.7 kg, respectively. Average daily vegetable intakes for adults and children were considered to be 0.345 and 0.232 kg person^{-1} d^{-1}, respectively (Ge, 1992; Wang et al., 2005). Daily water intakes for adults and children were considered to be 2.2 and 1.8 L person^{-1} d^{-1}, respectively (Chen et al., 2008).

3. Results and discussion

3.1. Variogram analysis and realizations of Mn concentrations in groundwater

Four measured concentrations, 0.06 mg L^{-1} (20% percentile), 0.13 mg L^{-1} (40% percentile), 0.51 mg L^{-1} (60% percentile) and 16 mg L^{-1} (80% percentile), were used as thresholds, respectively. In the analysis of fitting experimental variogram, exponential variogram models were selected with the minimized mean square error (Table 1) to generate the best fitting variograms. Fig. 3 shows the four obtained experimental variograms and their parameters. The fitted parameter of nuggets, sills and ranges were 0.1014–0.2300 (mg L^{-1})^2, 0.0100–0.0628 (mg L^{-1})^2, and 0.1034–2.9990 km, respectively.

Table 1
Mean square errors of fitting variograms.

Threshold	Model type	MSE
1st	Spherical	0.0389
	Exponential	0.0356
	Gaussian	0.0452
2nd	Spherical	0.0184
	Exponential	0.0161
	Gaussian	0.0193
3rd	Spherical	0.0276
	Exponential	0.0247
	Gaussian	0.0350
4th	Spherical	0.2070
	Exponential	0.1950
	Gaussian	0.2360

Based on the parameters referred above, 1000 realizations of Mn exposures concentrations in groundwater were reproduced using SIS. The study region was discretized into a grid of 400 cells, with a spacing of 500 m (Jang et al., 2005; Li et al., 2007; Xiong et al., 2007).

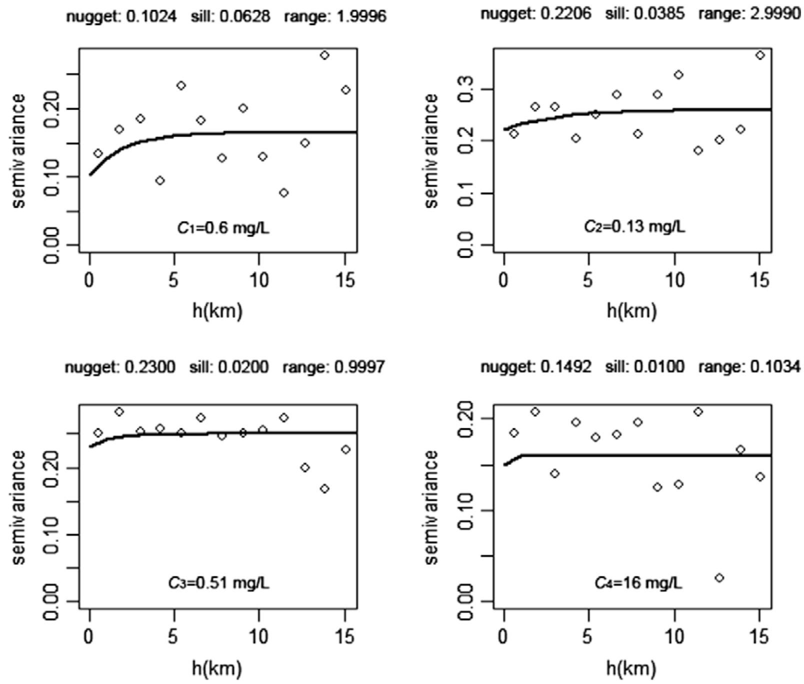

Fig. 3. Experimental variograms of indicator variables.

3.2. Human health risks associated with ingesting Mn

A series of human health risks with ingesting Mn were simulated integrating the aforementioned parameters as well as concentrations of Mn in groundwater and pond water using *HQ*. *HQ* is a ratio of determined dose of a pollutant to the dose level (a reference dose or *RfD*). If the ratio is less than 1, there will be no obvious risk. Conversely, an exposed population of concern will experience health risks if the dose is equal to or greater than the *RfD*. A higher level of *HQ* corresponds to a higher menace to human health and means a more strict control on groundwater and pond water use. Traditionally, the 5th, 25th, 50th, 75th, and 95th percentiles of risk were displayed to assess different likelihoods of exceeding risk levels. Fig. 4 shows cell-level geographic information system (GIS) maps of *HQ* for adults and children at the five percentiles. Two levels of *HQ*, <1 (safe) and >1 (unsafe), were displayed. At the 5th percentile of risk, 3.0% of *HQ* exceeded 1 for adults and 3.9% of *HQ* exceeded 1 for children. The proportion of *HQ* exceeding 1 at 25th, 50th, 75th, and 95th was 16.8%, 42.3%, 66.0%, and 83.9% for adults and 20.3%, 43.8%, 67.3% and 83.9% for children, respectively. The results also indicated that level of the human health risk with ingesting Mn in the study area for children was a little greater than that for adults.

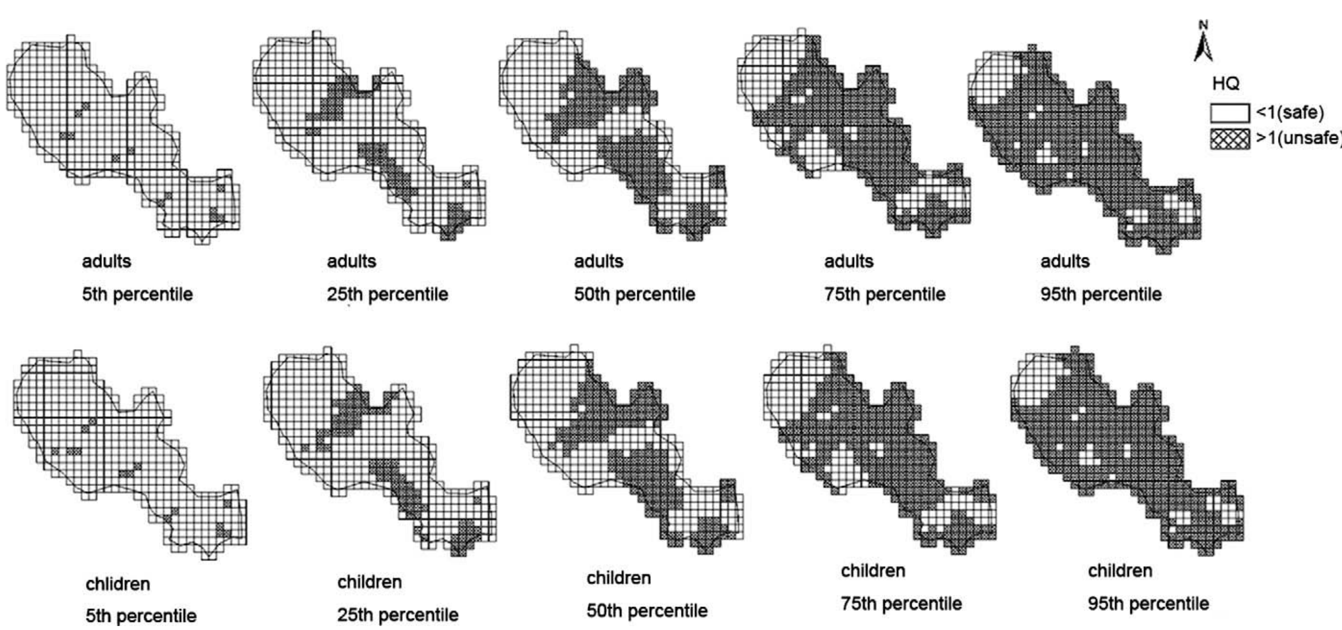

Fig. 4. Human health risks at given percentile.

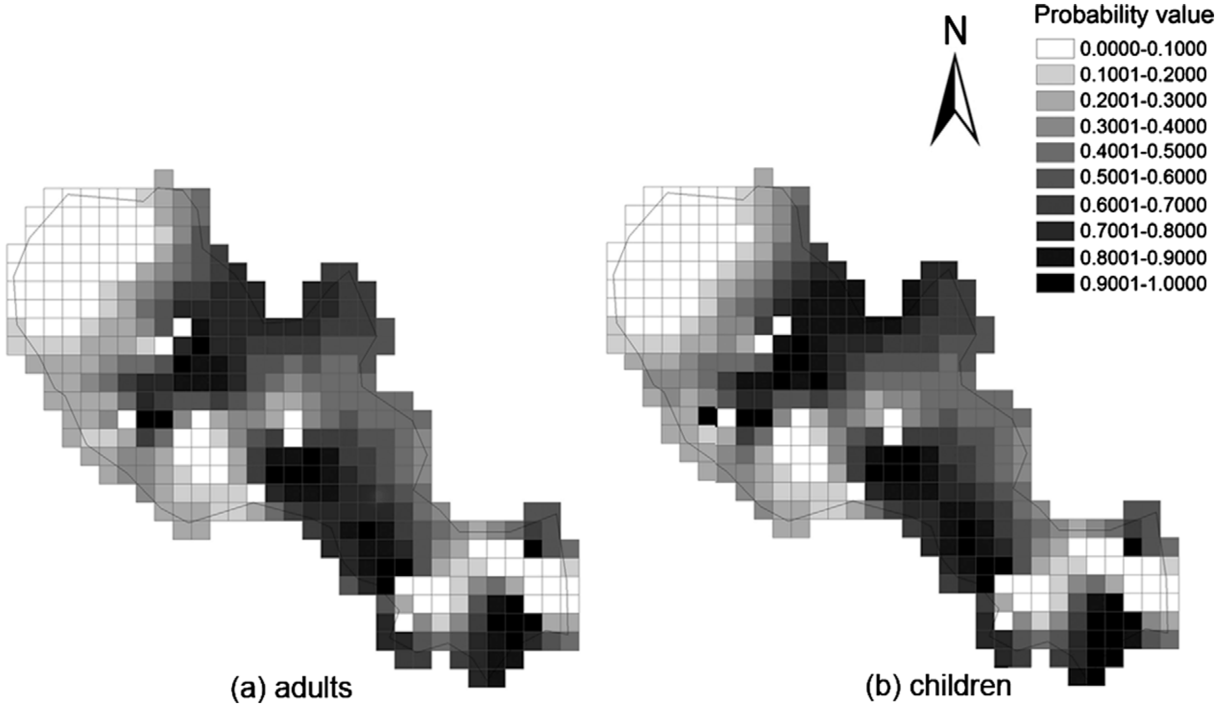

Fig. 5. Probability of human health risks associated with ingesting manganese.

The probability of risk is described in Fig. 5. Ten levels of risk probability averagely divided between 1 and 0 are displayed, which indicated that high risk regions were located in the northeast and southwest of the study area, and lower risk regions were located in the northwest and partly southeast of the study region.

Analyzed from Figs. 4 and 5, it was found that the 75th percentile of health risk covered the risk region with higher probability. Although the 95th percentile of risk was greater than any other percentile of risk, the 95th percentile was a strict standard and may not be easily implemented currently. Thus, this study suggested that 75th percentile of health risk for children be adopted to assess the risks of hazard associated with ingesting Mn contents in the contaminated groundwater and vegetables in performing the preliminary remedial framework. The spatial risk pattern also indicated that the groundwater and pond water in the northwest and partly southeast of the study region was safe for drinking and irrigation. In terms of treatment scheme, this study suggested that the manganese residues in unsafe region of the 25th percentile of health risk map be treated firstly for it covered the region with the highest probability in Fig. 5.

The conditional variance reflects the fluctuation of simulated *HQ* at any unsamples locations, which is adopted to represent the variability of spatial human health risk. Fig. 6 shows the conditional variance of *HQ*. The result indicated that the change of *HQ*

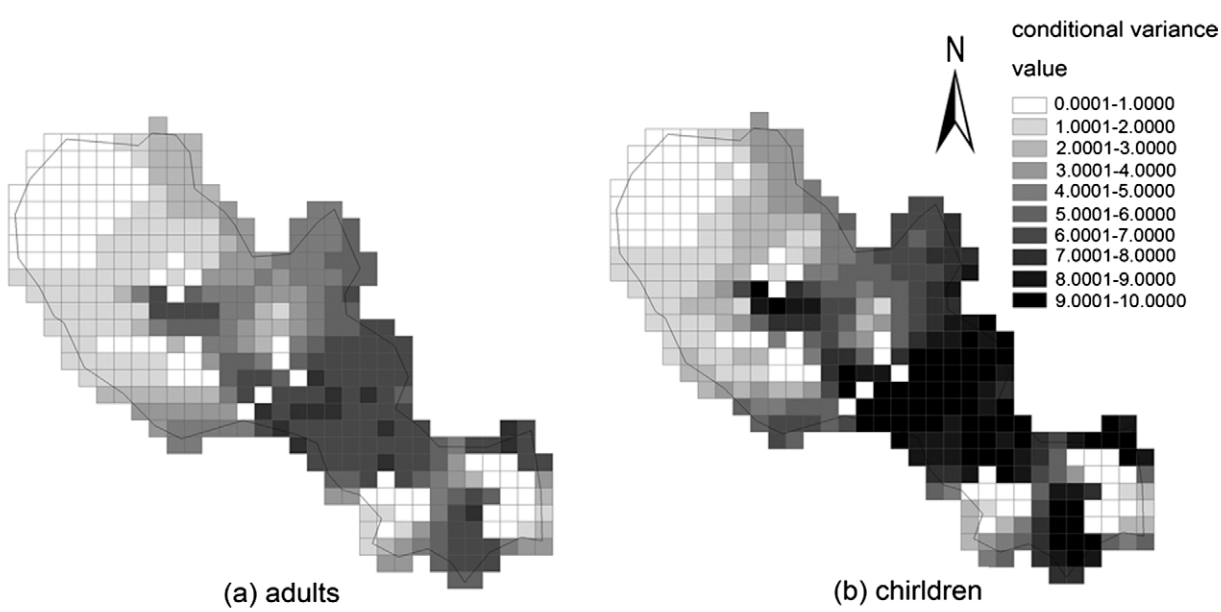

Fig. 6. Conditional variance of the generated realizations of human health risks.

was larger in the high-valued risk regions of the study areas where the groundwater concentrations fluctuated the most so that the largest variability was intuitively expected.

3.3. Other uncertainties in risk assessment

This work examined uncertainty as to the heterogeneity of Mn concentration in groundwater. The results offered probability-based information for risk management. However, there still lie other several uncertainties which affect the spatial pattern of the resulting human health risk. One uncertainty lies in the determined variogram, which is the base of geostatistical method. The accuracy in estimating from and their parameters of variogram depends on the representative and the absolute number of the existing samples (Yu et al., 2003). With more quantity and representation of sampled wells, less error of simulation will be attainted. Another uncertainty lies in the parameters associated with risk assessment, such as Mn accumulate factor *AF*, conversion factor R_{factor}, daily vegetables intake $IR_{food\ intake}$, daily water intake $IR_{water\ intake}$ and body weight *BW*. The obtained spatial risk pattern is based on the assumption that these parameters, which are of stochastic in nature, are certain in this work. A much greater uncertainty lies in the distribution of Mn concentration over time. The results of health assessment are based on the uncertain assumption that future concentrations will be the same as those at present. Actually, the Mn concentrations will not be constant over time as a consequence of hydrologic and geochemical processes as well as massive irrigation pumping.

4. Conclusions

In conclusions, this work spatially analyzed the probabilistic human health risk associated with ingesting Mn in Huangxing Town, where the groundwater and pond water were heavily contaminated by leakages from industrial waste residues. The combination of monitoring data and sequential indicator simulation (SIS), which properly accounted for the uncertainty of heterogeneity, was used to determine Mn exposure distributions in pond water and groundwater. One thousand equiprobable realizations showed that many *HQ*s determined from risks exceed 1 in the regions, indicating that the use of groundwater and pond water posed potential risk to human health for adults and children. Lower risk regions were located in the northwest and partly southeast of the region. The probabilistic outcomes provide a reference for safety of water use and pollution remedy and control.

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