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Original Research

All-Region Human Health Risk Assessment of Cr(VI) in a Coal Chemical Plant Based on Kriging

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Abstract

Human health risks of soil Cr(VI) in coal chemical plants have been seldom reported. In this study, we measured soil Cr(VI) concentrations of 153 sites in a coal chemical plant in China. Human health risks of Cr(VI) through three exposure pathways, including inhalation, skin contact and oral intake, were further assessed. A human health risk distribution map of Cr(VI) in the whole plant was obtained using Kriging. The integrated carcinogenic risk of soil Cr(VI) was 15~27 times of the acceptable standard (1.000E-06), while the hazard quotient was within the acceptable range (<1.000). Inhalation of soil particles was the main pathway of Cr(VI) exposure, contributing to 70.53% of the total carcinogenic risk, the recommended control threshold of which was the smallest (0.608 $mg \cdot kg^{-1}$) among that of the investigated exposure pathways and selected as Cr(VI) safety control threshold for this plant. Moreover, the sites under the highest carcinogenic risk and with the largest hazard quotient were the downwind areas of the slag pile sites of the power unit. This study may provide suggestions for reducing the human health risk of Cr(VI) in the coal chemical industry.

Keywords: coal chemical industry; soil; heavy metals; health risk assessment; kriging

Introduction

As China is short of oil and gas resources and rich in coal, it is beneficial for China to lay emphasis on the development of efficient and clean coal utilization and reduce external dependence of energy [1]. The advanced coal chemical industry moving towards a clean and efficient way to utilize coal has developed quickly in recent years. However, heavy metal and other harmful trace elements in coal may transfer to soil and other environmental media through a variety of ways, such as physical and chemical processes in coal chemical industry, threatening human health [2-4]. Research shows that 90% of human cancers are caused by chemical carcinogens such as heavy metals [5]. Cr(VI) exists in coal and has obvious toxic effects on the human body and it is listed as a metal element with carcinogenic effects in relevant laws, regulation documents and environmental standards by the United States Environment Protection Agency (USEPA) and the Ministry of Environmental Protection of China [6, 7].

Cr(VI) is a teratogen and mutagen with high toxicity that is 100 times as toxic as trivalent chromium and considered one of the 129 most important pollutants by the USEPA [7]. Cr(VI) can invade the human body in

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different ways. It may cause problems to the digestive tract, respiratory tract, skin, mucous membrane and so on. A large amount of chromium intake can lead to significant accumulation in organisms, thus causing Cr(VI) poisoning. The fatal dose of Cr(VI) for adults is 1.5~1.6 g [8]. Cr(VI) is a persistent potential toxic pollutant. There are different Cr(VI) exposure routes such as mouth intake of soil dust in the air, inhalation of soil particle and skin contact with soil, which seriously threaten human health [6].

Currently, human health risk in chromium-contaminated zones has raised more and more attention. Research that elucidates the characteristics and assesses the exposure risk of this pollutant in the soil of industrial areas has been reported. Zhang et al. [9] analyzed the source of chromium pollution in coal chemical area using the methods of Source Apportionment and showed that chromium in soil was mainly from cinder heap of the plant during the coal gasification process. Zhang et al. [10] carried out a study on chromium-contaminated sites in a chemical plant in Qinghai, China. 47 sampling points were set for analyses. The results showed that the central areas of the plant were under high levels of chromium pollution and Cr(VI) posed risks to human health through drinking groundwater and skin contact. All of the risk values exceeded the acceptable range. Eisa et al. [11] investigated the pollution characteristics of the Baghjar Chromite Mine (BCM) in Sabzevar Ophiolite Belt in northeastern Iran through analysis of 21 samples. It was shown that soil Cr(VI) in the plant could cause cancer risks to humans. Zhong et al. [12] conducted site risk assessment of a chromate chemical plant in Hebei Province of China, with 54 sampling points analyzed. The results showed that the major polluted areas were chromium yard, leaching workshop and conversion workshop. Borah et al. [13] analyzed 20 soil samples in order to evaluate the ecological risk of chromium in the soil near a paper mill in Assam, India. The results showed that the investigated area was widely polluted by chromium. However, the understanding of chromium pollution, especially its human health risk in soil environment in advanced coal chemical industry, is still limited. Moreover, most of the assessments on human health risks of the heavy metals in coal chemical industrial areas only took account of certain sites instead of the whole plant, which is quite one-sided. Kriging interpolation is a good method to obtain a map of the human health risks of soil Cr(VI) in the whole investigated area through simulation, which has been rarely used, however. In this study, human health risk assessment of soil Cr(VI) in an advanced coal chemical industrial area in northwestern China was conducted. Cr(VI) concentrations of 153 sites in this plant were measured. A distribution map of human health risks in the factory area was then concluded through simulation using the interpolation method of kriging. The results can be helpful for reducing human health risk of Cr(VI) in coal chemical plants.

Material and Methods

Overview of the Study Area and Sample Collection

The coal chemical plant investigated in this study is located in northwestern China with an area of 400,000 m^2 (500 m × 800 m) and is divided into 10 functional units. Details regarding the location, terrain, climate and the functional units of the plant were described in a previous study [14], which also included the methods of chessboard sampling and the geographic coordinates of those sampling points.

Determining Sample Content

Determining Total Chromium Content

Based on "general rules for analytical method of inductively coupled plasma mass spectrometry", after digestion pretreatment using a microwave digestion instrument (Milestone, Milano, Italy), total chromium contents in the soil samples were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) (X series II ICP-MS, Thermo Fisher Scientific, Waltham, MA, USA) [15]. The steps are as follows:

1) Take a proper amount of soil and dry it at 105ºC for 8 hours.
2) Sieve dried soil with a 200 mesh sieve after pulverizing it using a grinder and add 50 mg sifted soil to the digestion tank.
3) Add 5 ml hydrofluoric acid with a volume fraction of 40%, 2 ml nitrous acid solution with mass fraction of 65% and 1 ml hydrogen peroxide with a mass fraction of 30% to the digestion tank as digestive solution.
4) Digest for 175 minutes through temperature programmed route, including 6 steps.
   – Digest for 12 min under 60ºC and 100 bar with a microwave power of 1000 w.
   – Digest for 20 min under 125ºC and 100 bar with a microwave power of 1000 w.
   – Digest for 8 min under 160ºC and 130 bar with a microwave power of 1000 w.
   – Digest for 15 min under 240ºC and 160 bar with a microwave power of 1200 w.
   – Digest for 60 min under 240ºC and 160 bar with a microwave power of 1000 w.
   – Cool for 60 min.
5) 10 mL digestive solution was collected for total chromium content measurement by ICP-MS (II of X series). During this process, collision cell technology (CCT) was used to avoid interferences caused by polyatomic ions and eliminate test error of total chromium content.

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Determining Cr(VI) Content

Cr(VI) in soil samples was first separated using electromagnetic stirring with 0.4 mol/L KCl as the extracting agent. Then, Cr(VI) concentration of soil was measured using diphenylcarbazide spectrophotometry. The specific operational steps are as follows:

1) Take 5 g dry soil sample sifted by 2 ml sieve and put it in a beaker of 100 ml.
2) Add 50 mL potassium chloride solution whose concentration is 0.4 mol/L to the beaker and stir it with a magnetic stirrer for 5 minutes.
3) Transfer the soil suspension to a 50 ml centrifuge tube, and centrifuge for 3 min at 4000 r/min. Then transfer the supernatant into a 100 ml volumetric flask. Add 10 ml extraction agent into the residue and stir them for 2 min before centrifuge separation. Transfer the supernatant to a volumetric flask. Repeat 2~3 times and combine all the supernatants into one container for further analysis.
4) Analyze Cr(VI) concentration in soil using diphenylcarbazide spectrophotometry.

Human Health Risk Assessment Method

Taking both the features of the investigated coal chemical process and its pollution characteristics into consideration, this study determined the type of site, chose exposure routes for further experiments, calculated exposure levels, evaluated carcinogenic risk and hazard quotient of Cr(VI) and determined the corresponding threshold for Cr(VI) risk control referring to RBCA [16-19], Csoil [16,20], CLEA [17,21], HERA [22] and other typical models and methods for risk assessment of contaminated sites based on Technical Guidelines for Risk Assessment of Contaminated Sites (HJ 25.3-2014) [23]. On this basis, how carcinogenic risk of Cr(VI) was attributed to each exposure route was analyzed and environmental safety threshold of Cr(VI) in soil in the studied area was determined. The kriging interpolation method integrated with the existing human health risk assessment method was used to simulate the Cr(VI) risk distribution of the whole plant area based on the risk evaluation result of the sampling sites.

Exposure Situation

The investigated area is a coal chemical plant and the staff there are the main population who are affected. There are no specially protected residential areas, reservations and water sources or any other sensitive zones. Therefore, the analyzed land is under an insensitive exposure situation. When performing health risk assessment, the target population is mainly adults.

Selecting Exposure Routes and Calculating Exposure

Exposure routes of the pollutants are the ways in which they get into the human body and cause hazards, and there are nine major exposure methods [23]. In this study, the coal chemical industrial zone investigated is an in-sensitive industrial land. In addition, there are no surface water bodies near the plant, and underground water is not used as drinking water. Referring to

Table 1. Models for soil exposure dose calculation in three soil exposure pathways.

Number	Exposure routes	Explanation	Formula expression of exposure
1	Oral intake	Carcinogenic risk	$\mathrm{OISER_{ca}} = \frac{\mathrm{OSIR_a} \times \mathrm{ED_a} \times \mathrm{EF_a} \times \mathrm{ABS_0}}{\mathrm{BW_a} \times \mathrm{AT_{ca}}} \times 10^{-6}$
2		Non- carcinogenic risk	$\mathrm{OISER_{nc}} = \frac{\mathrm{OSIR_a} \times \mathrm{ED_a} \times \mathrm{EF_a} \times \mathrm{ABS_0}}{\mathrm{BW_a} \times \mathrm{AT_{nc}}} \times 10^{-6}$
3	Skin contact	Carcinogenic risk	$\mathrm{DCSER_{ca}} = \frac{\mathrm{SAE_a} \times \mathrm{SSAR_a} \times \mathrm{EF_a} \times \mathrm{ED_a} \times \mathrm{E_V} \times \mathrm{ABS_d}}{\mathrm{BW_a} \times \mathrm{AT_{ca}}} \times 10^{-6}$
4		Non- carcinogenic risk	$\mathrm{DCSER_{nc}} = \frac{\mathrm{SAE_a} \times \mathrm{SSAR_a} \times \mathrm{EF_a} \times \mathrm{ED_a} \times \mathrm{E_V} \times \mathrm{ABS_d}}{\mathrm{BW_a} \times \mathrm{AT_{nc}}} \times 10^{-6}$
5	Inhalation	Carcinogenic risk	$\mathrm{PISER_{ca}} = \frac{\mathrm{PM_{10}} \times \mathrm{DAIR_a} \times \mathrm{ED_a} \times \mathrm{PIAF} \times (\mathrm{fspo} \times \mathrm{EFO_a} + \mathrm{fspi} \times \mathrm{EFI_a})}{\mathrm{BW_a} \times \mathrm{AT_{ca}}} \times 10^{-6}$
6		Non- carcinogenic risk	$\mathrm{PISER_{nc}} = \frac{\mathrm{PM_{10}} \times \mathrm{DAIR_a} \times \mathrm{ED_a} \times \mathrm{PIAF} \times (\mathrm{fspo} \times \mathrm{EFO_a} + \mathrm{fspi} \times \mathrm{EFI_a})}{\mathrm{BW_a} \times \mathrm{AT_{nc}}} \times 10^{-6}$

Note: OISERca denotes the soil exposure dose in oral intake (carcinogenic) in $mg \cdot kg^{-1} \cdot d^{-1}$;
OISERnc denotes the soil exposure dose in oral intake (non-carcinogenic) in $mg \cdot kg^{-1} \cdot d^{-1}$;
DCSERca denotes the soil exposure dose in Skin contact (carcinogenic) in $mg \cdot kg^{-1} \cdot d^{-1}$;
DCSERnc denotes the soil exposure dose in Skin contact (non-carcinogenic) in $mg \cdot kg^{-1} \cdot d^{-1}$;
PISERca denotes the soil exposure dose in inhalation (carcinogenic) in $mg \cdot kg^{-1} \cdot d^{-1}$;
PISERnc denotes the soil exposure dose in inhalation (non-carcinogenic) in $mg \cdot kg^{-1} \cdot d^{-1}$.

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Table 2. Major parameters in the exposure dose calculation models.

Parameter	Definition	value	unit
$OSIR_a$	Daily soil intake for adults	100	$mg \cdot d^{-1}$
ED_a	Exposure period for adults	25	a
EF_a	Exposure frequency for adults	250	$d \cdot a^{-1}$
BW_a	Adult weight	56.800	kg
ABS_0	Efficiency factor of oral intake	1	/
AT_{ca}	Averaged time of carcinogenic impact	26280	d
AT_{nc}	Averaged time of non-carcinogenic impact	9125	d
SAE_a	Surface area of exposure for adults	2854.630	cm^2
$SSAR_a$	Sticking coefficient of soil on skin for adults	0.200	$mg \cdot cm^{-2}$
ABS_d	Absorption efficiency factor of skin	0.010	/
E_v	Daily frequency of skin contact	1	$times \cdot d^{-1}$
PM_{10}	Amount of inhalable suspended particles	0.150	$m^3 \cdot d^{-1}$
$DAIR_a$	Daily suction volume of air for adults	14.500	$m^3 \cdot d^{-1}$
PIAF	Retention rate of inhaled soil particles	0.750	/
Fspi	Ratio of soil particles to indoor aerosol particles	0.800	/
Fspo	Ratio of soil particles to outdoor aerosol particles	0.500	/
EFI_a	Indoor exposure frequency for adults	187.500	$d \cdot a^{-1}$
EFO_a	Outdoor exposure frequency for adults	62.500	$d \cdot a^{-1}$
C_{sur}	Pollutant content in topsoil	6.480~11.750	$mg \cdot kg^{-1}$
SF_0	Slope factor of carcinogenic impact of oral intake	0.500	$mg \cdot kg^{-1} \cdot d^{-1}$
SF_d	Slope factor of carcinogenic impact of skin contact	20	$mg \cdot kg^{-1} \cdot d^{-1}$
SF_i	Slope factor of carcinogenic impact of inhalation	329.050	$mg \cdot kg^{-1} \cdot d^{-1}$
SAF	Distribution coefficient of recommended exposure dose	0.200	/
RfD_0	Recommended dose through oral intake	3.000E-3	$mg \cdot kg^{-1} \cdot d^{-1}$
RfD_d	Recommend dose through skin contact	7.500E-5	$mg \cdot kg^{-1} \cdot d^{-1}$
RfD_i	Recommended dose through inhalation	2.550E-5	$mg \cdot kg^{-1} \cdot d^{-1}$

Note, ABS_0, ABS_d, Fspi, Fspo – Different heavy metal pollutants have different ABS_o, ABS_d Fspi and Fspo values in the standard (HJ25.3-2014).

previous research [23, 24], we selected three exposure pathways for analysis: oral intake of soil, skin contact with soil and inhalation of soil particles.

The reference models for soil Cr(VI) exposure level calculation of the three exposure routes in terms of carcinogenic effect and non-carcinogenic effect of single pollutant are shown in Table 1. The main parameters of these models are listed in Table 2 [23]. In terms of carcinogenic effect, the exposure doses of Cr(VI) through oral intake, skin contact and inhalation were 2.390E-08, 4.190E-07 and 4.950E-09 $mg \cdot kg^{-1} \cdot d^{-1}$, respectively. In terms of non-carcinogenic effect, the corresponding values were 6.880E-08, 1.210E-06 and 1.403E-08 $mg \cdot kg^{-1} \cdot d^{-1}$, respectively.

Risk Characterization and Contribution Rates

With the use of the models listed in Table 3, carcinogenic risk and hazard quotient of Cr(VI) in each sampling point via different exposure routes were obtained. Total carcinogenic risk and total hazard quotient of Cr(VI) through multi-exposure routes were obtained by summing up the values of every route [25]. The relative risk of the three different routes (mouth intake of soil, skin contact with soil and inhalation of soil particles) were respectively calculated with Formula (1).

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Table 3. Cancer risk and hazard quotient calculating formulas for three soil exposure routes.

Formula number	Exposure route	Formula description	Safety threshold calculating formulas
7	Oral intake	Carcinogenic risk	$\mathrm{CR_{ois}} = \mathrm{OISER_{ca}} \times \mathrm{C_{sur}} \times \mathrm{SF_o}$
8		Hazard quotient	$\mathrm{HQ_{ois}} = \frac{\mathrm{OISER_{nc}} \times \mathrm{C_{sur}}}{\mathrm{RfD_O} \times \mathrm{SAF}}$
9	Skin contact	Carcinogenic risk	$\mathrm{CR_{dcs}} = \mathrm{DCSER_{ca}} \times \mathrm{C_{sur}} \times \mathrm{SF_d}$
10		Hazard quotient	$\mathrm{HQ_{dcs}} = \frac{\mathrm{DCSER_{nc}} \times \mathrm{C_{sur}}}{\mathrm{RfD_d} \times \mathrm{SAF}}$
11	Inhalation	Carcinogenic risk	$\mathrm{CR_{pis}} = \mathrm{PISER_{ca}} \times \mathrm{C_{sur}} \times \mathrm{SF_i}$
12		Hazard quotient	$\mathrm{HQ_{pis}} = \frac{\mathrm{PISER_{nc}} \times \mathrm{C_{sur}}}{\mathrm{RfD_i} \times \mathrm{SAF}}$

Note: CRois – carcinogenic risk of mouth-intake-soil, and its dimension is 1;
CRdcs – carcinogenic risk of skin-contact-with-soil, and its dimension is 1;
CRpis – carcinogenic risk of inhalation of soil particle, and its dimension is 1;
HQois – non-carcinogenic risk of mouth-intake-soil, and its dimension is 1;
HQdcs – non-carcinogenic risk of skin-contact-with-soi, and its dimension is 1;
HQpis – non-carcinogenic risk of inhalation of soil particle, and its dimension is 1.

$$R_i = \frac{CR_i}{\sum CR_i} \times 100\% \tag{1}$$

where R_i is the proportion of carcinogenic risk or hazard quotient caused through a certain soil exposure route; CR_i is the carcinogenic risk or hazard quotient level for a certain soil exposure route, and the dimension is 1; and ΣCR_i represents total carcinogenic risk or total hazard quotient of soil through all the analyzed exposure routes.

Risk Control Thresholds

When the carcinogenic risk level or the hazard quotient of a pollutant through an exposure pathway exceeds the acceptable limits, a risk control threshold is determined with use of the equations listed in Table 4.

Kriging Interpolation Method

Kriging, based on the variogram theory and structural analysis, is a method to conduct best-unbiased

Table 4. Safety threshold calculating formulas for three soil exposure routes.

Number	Exposure route	Formula description	Safety threshold calculating formula
13	Oral intake	Carcinogenic risk	$\mathrm{RCVS_{ois}} = \frac{\mathrm{ACR}}{\mathrm{OISER_{ca}} \times \mathrm{SF_0}}$
14		Hazard quotient	$\mathrm{HCVS_{ois}} = \frac{\mathrm{RfD_0} \times \mathrm{SAF} \times \mathrm{AHQ}}{\mathrm{OISER_{nc}}}$
15	Skin contact	Carcinogenic risk	$\mathrm{RCVS_{dcs}} = \frac{\mathrm{ACR}}{\mathrm{DCSER_{ca}} \times \mathrm{SF_d}}$
16		Hazard quotient	$\mathrm{HCVS_{dcs}} = \frac{\mathrm{RfD_d} \times \mathrm{SAF} \times \mathrm{AHQ}}{\mathrm{DCSER_{nc}}}$
17	Inhalation	Carcinogenic risk	$\mathrm{RCVS_{pis}} = \frac{\mathrm{ACR}}{\mathrm{PISER_{ca}} \times \mathrm{SF_i}}$
18		Hazard quotient	$\mathrm{HCVS_{pis}} = \frac{\mathrm{RfD_i} \times \mathrm{SAF} \times \mathrm{AHQ}}{\mathrm{PISER_{nc}}}$

Note: RCVSois denotes the risk control threshold of Cr(VI) concentration for carcinogenic risk by oral intake in mg/kg;
RCVSdcs denotes the risk control threshold of Cr(VI) concentration for carcinogenic risk by skin contact in mg/kg;
RCVSpis denotes the risk control threshold of Cr(VI) concentration for carcinogenic risk by inhalation of soil particles in mg/kg;
ACR denotes the acceptable carcinogenic risk with a default value of 10^{-6} (dimensionless);
AHQ denotes the acceptable hazard quotient with a default value of 1 (dimensionless).

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estimations of local variables within a limited area. The formula is as follows,

$$Z\left(x_0\right)=\sum_{i=1}^{n}\lambda_i Z\left(x_i\right) \quad (2)$$

where *Z (Xo)* is the heavy metal concentration; *n* is the number of sampling sites; Z (*Xi*) is the heavy metal concentration at the i^{th} sampling site; and λ_i is the weight coefficient for the i^{th} sampling site. The determination of λ_i should ensure that Z (*Xo*) is an unbiased estimation with the smallest variance. To apply this method, the data should meet two assumptions. First, the data are in normal distribution. Second, the data are spatially auto-correlated.

Results and Discussion

Concentrations and Distributive Characteristics of Cr(VI) in the Coal Chemical Plant

Total chromium contents in the soil of the sampling sites were described in a previous study [14]. A description map of Cr(VI) concentrations in the sampled zone is displayed in Fig. 1, which were between 6.480~11.750 mg/kg with an average of 8.910 mg/kg. The concentrations were lower than the value of Grade-3 standard (30 mg/kg) in Environmental Quality Standard for Soil Cr(VI), but all of them exceeded China soil background value (6.100 mg/kg) and Ningxia soil background value (6.000 mg/kg). This indicates that Cr(VI) accumulated in the soil resulting from coal chemical production activities. Cr(VI) concentrations of the sampling sites showed a small extent of variation with a variation coefficient of 13.80%. This suggests little difference between the concentrations of Cr(VI) in different sites of the plant. The frequency of Cr(VI) concentrations in the sampled zone is displayed in Fig. 2. The sites with a Cr(VI) concentration of nearly 10.000 mg/kg accounted for the largest fraction (24.0%). Most of these sites were near power and gasification units.

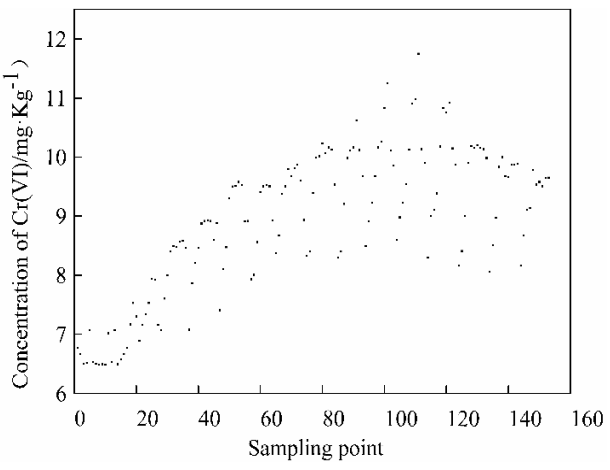

Fig. 1. Concentrations of soil Cr (VI) in 153 sampled sites in the coal chemical plant.

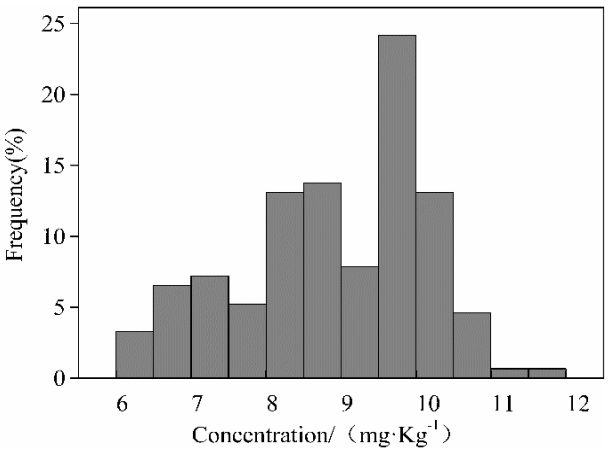

Fig. 2. Frequency of soil Cr (VI) concentrations in 153 sampled sites in the coal chemical plant.

Human Health Risk Assessment in Soil of the Coal Chemical Plant

Carcinogenic Risk

The carcinogenic risks posed by individual exposure pathway and the cumulative carcinogenic risks are summarized in Table 5. Total carcinogenic risk of soil Cr(VI) through the three pathways at each sampling site is shown in Fig. 3. Total Cr(VI) carcinogenic risk levels in the soil of the researched area were between (15.119~27.408)E-06 with an average of 20.800E-06, which was 20.8 times as much as the acceptable level for human health suggested by related standards. This indicates that soil Cr(VI) of all the sampled sites in the coal chemical area showed high carcinogenic risk to the human body.

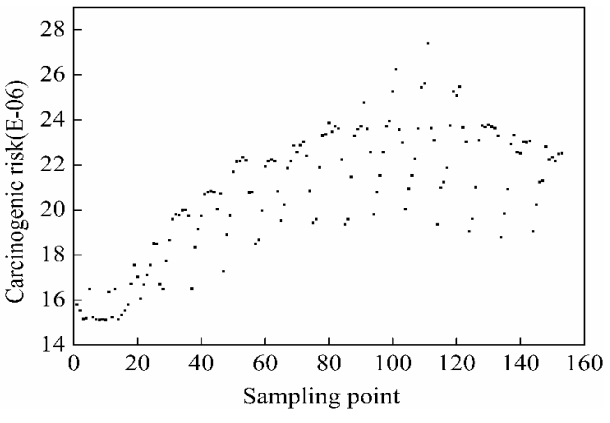

Fig. 3. Carcinogenic risk levels of Cr (VI) in the coalification area in 153 sampled sites in the coal chemical plant.

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Table 5. Results of carcinogenic risk levels and hazard quotient values of Cr(VI) in 153 sampled sites in the coal chemical plant.

Risk type	Data type	Exposure routes			Total carcinogenic risk
		Oral intake	Skin contact	Inhalation	
Carcinogenic risk	Minimum value	1.357E-06	3.098E-06	1.066E-05	1.512E-05
	Maximum value	2.460E-06	5.617E-06	1.933E-05	2.741E-05
	Mean	1.870E-06	4.260E-06	1.470E-05	2.080E-05
Hazard quotient	Minimum value	0.013	0.030	0.018	0.061
	Maximum value	0.024	0.054	0.033	0.093
	mean	0.018	0.041	0.025	0.084

Hazard Quotient

The hazard quotients of soil Cr(VI) through each individual exposure pathway and the commutative hazard quotient are summarized in Table 5. Total hazard quotient of soil Cr(VI) through the three pathways at each sampling site is shown in Fig. 4. Total hazard quotient of Cr(VI) in soil of the coal chemical plant was between 0.061~0.093, with an average of 0.084. Total hazard quotient of each sampling point was far less than the acceptable level (<1.000) as suggested by related standards [23].

Contribution Ratios of Human Health Risk for Different Exposure Routes

Based on Formula 1, the proportions of carcinogenic risk and hazard quotient of different exposure routes were calculated (Fig. 5). A comparison of carcinogenic risks caused by different exposure routes shows a rank of inhalation (70.53%) > skin contact (20.49%) > oral intake (8.98%). Inhalation of soil particles was the main way of posing carcinogenic risk of soil Cr(VI) in the coal chemical plant. The proportion of inhalation risk was 7.85 times as much as that of oral intake and 3.44 times as much as that of skin contact. Accordingly, while reducing the level of pollution risk in soil, the ways that can block or reduce soil pollutant inhalation such as wearing masks can be used to protect the staff. In terms of hazard quotient of Cr(VI), skin contact was the main exposure route that contributes to 48.88% of the total value.

Spatial Variation of Carcinogenic Risk and Hazard Quotient of Cr(VI) in Soil

Statistical analyses were done to discern the characteristics of carcinogenic risk and hazard quotient of Cr(VI) in soil (Table 6). Total carcinogenic risk and total hazard quotient of soil Cr(VI) in the sampled sites both followed normal distribution (P>0.05, 95% confidence level), as revealed by K-S analysis [26, 27]. Semi-variance analyses of total carcinogenic risk and total hazard quotient in the sampled sites were performed. The mean error and standard deviation of the former were -0.020 and 0.998, respectively, and the values of the latter were 0.017 and 0.863, respectively. The closer the mean error is to 0 and the closer the standard deviation is to 1, the more precise the data fitting analysis is. The results indicate that the model fit the data well.

The ratio of nugget value C to the sill value (C_0/Sill) smaller than 25% indicates strong spatial auto-correlation. C_0/Sill values of total carcinogenic risk

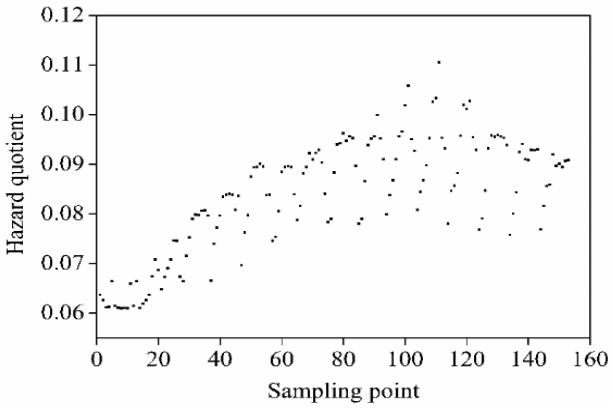

Fig. 4. Total hazard quotients of Cr (VI) in the coalification area in 153 sampled sites in the coal chemical plant.

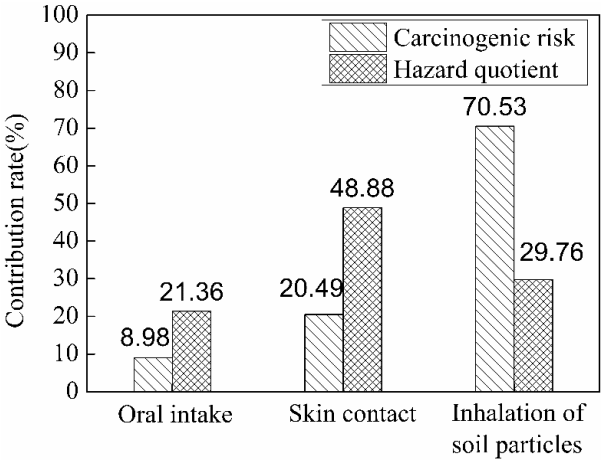

Fig. 5. Contribution ratios of carcinogenic risk and hazard quotient of the three exposure routes.

Table 6. Analysis on the statistic characteristics of carcinogenic risk levels and hazard quotient values of Cr(VI) in 153 sampled sites in the coal chemical plant.

Risk type	Model	Nugget Constant C_0	Sill value	$(C_0/Sill)$/%	K-S test P value	Mean Error	Standard Deviation
Total carcinogenesis	Gauss	0.001	0.007	14.29	0.082	-0.020	0.988
Total hazard quotient	Gauss	0.00004	0.00025	22.78	0.091	0.017	0.863

and total hazard quotient of all the sampling points were 14.29% and 22.78%, respectively, which are both less than 25%. Significant spatial autocorrelation was detected. The results indicate that the variations of total carcinogenic risk and total hazard quotient of Cr(VI) in soil caused by regional factors were significantly higher than those caused by non-regional factors (i.e., random factors) [28]. The R^2 of the cross-validation analysis of Cr(VI) risks was above 0.97 (Fig. 6). There were no outliers in the data, suggesting reliable predictive results of Cr(VI) risk distribution.

Spatial Distribution of Human Health Risk in the Coal Chemical Plant

Spatial Distribution of Carcinogenic Risk

Total carcinogenic risk map of Cr(VI) in the soil of all the functional units was simulated using kriging, as shown in Fig. 7. Total carcinogenic risk values of soil Cr(VI) in the chemical units were between (15.119~27.408)E-06 (the unit of the equivalent line is 1E-06), and were 15~27 times as much as the acceptable level for human health (1E-06). Risk values of soil Cr(VI) in all the plant area exceeded the standard. Gasification unit and power unit were central pollution areas and the pollution was descending to surrounding areas of the whole plant, which mainly resulted from the heavy pollution of the power unit and the effects of the leading wind direction in the studied area. This is similar to the results reported by Zhang et al. [9, 14]. On the contrary, the risk of gasification unit slag dump was relatively low because the ground had been hardened and Cr (VI) was less permeable.

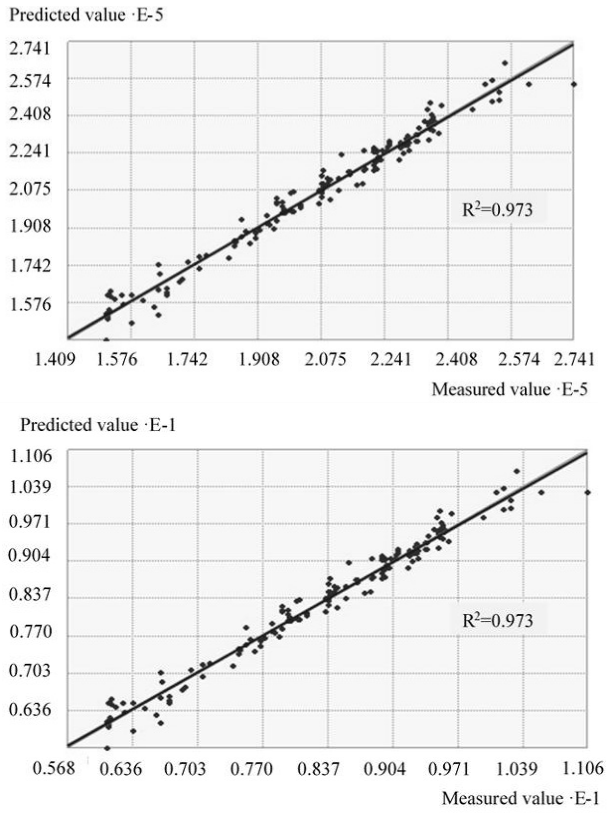

Fig. 6. Results of cross-validation analysis of carcinogenic risk of Cr(VI) (on the left side) and hazard quotient of Cr(VI) (on the right side).

Spatial Distribution of Hazard Quotient

Total hazard quotient risk map for Cr(VI) in the whole plant was obtained after stimulation using kriging (Fig. 8). As displayed in Fig. 8, total hazard quotient of Cr(VI) in the chemical units was between 0.061~0.111, which was far less than the acceptable level (1.000).

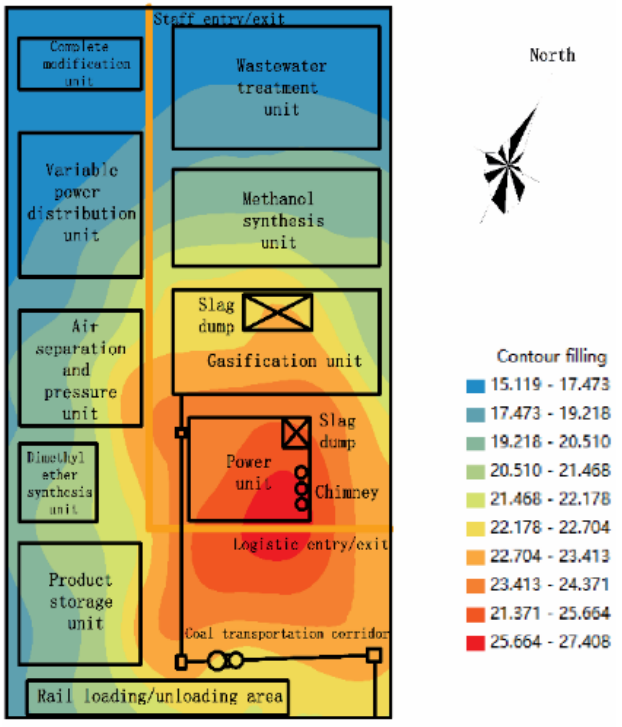

Fig. 7. Total carcinogenic risk map of Cr(VI) in the entire plant.

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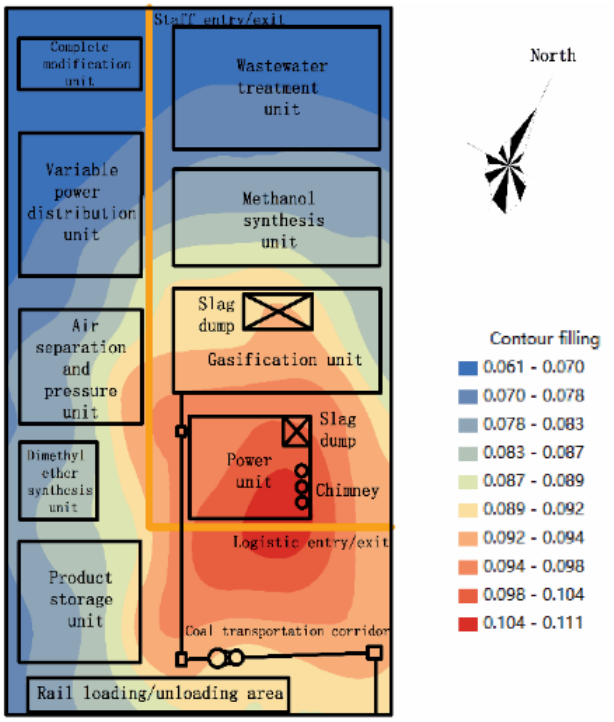

Fig. 8. Total hazard quotient risk map of Cr(VI) in the entire plant.

The values of hazard quotients nearly had the same trend with the carcinogenic risk values. The highest risk area was in the wind direction under the power unit slag field.

Overall, total hazard quotient of the three exposure routes for Cr(VI) in the soil of the main process unit of coal gasification was relatively low, which was far less than acceptable levels. However, with the operation of the industry, attention should be paid especially to the health of the workers in power unit and gasification unit, as long-term exposure to the pollutants may lead to a rise in hazard quotient of Cr(VI) in soil.

Safety Threshold of Cr(VI) in the Soil of the Coal Chemical Plant

According to human health risk assessment of Cr(VI) in soil of the coal chemical plant, carcinogenic risks of the sampled sites were all above the acceptable risk level. Therefore, risk control values of carcinogenic risk of the three exposure routes were calculated using the formulas in Table 4. Risk control values of hazard quotients were not calculated, as the hazard quotients of the investigated sites were all far less than the acceptable range.

According to the calculation results, in order to achieve a carcinogenic risk level less than 10^{-6}, when the exposure pathways is oral intake, skin contact and inhalation, respectively, the concentrations of Cr(VI) should be no more than 4.777, 2.092 and 0.608 mg·kg-1, respectively. Risk control value of Cr(VI) concentration for inhalation of soil particles was the lowest (0.608 mg/Kg), which therefore can be a strict standard of safety threshold of Cr(VI) concentration in soil for human health in this plant. On control of risk level, emphases and choices vary in different countries and regions. For example, the USEPA suggests safety thresholds of 10^{-6}~10^{-4}. The United Kingdom often takes 10^{-5} in practice, while it is 10^{-4} in the Netherlands [27], which is not that harsh. Considering industrial development strategy, control and restoration plan in long-term running of the coal chemical plant, safety threshold of soil Cr(VI) in coal chemical zones should be determined by combining Cr(VI) background values with geological conditions, bioavailability parameters, site soil characteristics, aquifer characteristics, regional characteristics of geographic climate, regional development plan and natural attenuation in the soil environment.

Conclusions

In this study, soil Cr(VI) concentrations of 153 sites in a coal chemical plant in China were measured. Human health risks of Cr(VI) through inhalation, skin contact and oral intake were evaluated. A human health risk distribution map of Cr(VI) in the whole plant was shown using kriging.

(1) Total carcinogenic risk values of Cr(VI) in the soil of main chemical units via three different exposure routes (oral intake, skin contact and inhalation of soil particles) were 15-27 times the acceptable levels for human health. The values exceeded the acceptable levels severely. Different production units showed different risk levels. The main polluted areas were the gasification and power units.

On the other hand, total hazard quotients of Cr(VI) were between 0.061~0.111, which were within the acceptable range. The distribution of hazard quotient values showed almost the same trend with that of carcinogenic risk. Although total hazard quotient of Cr(VI) in soil was relatively low, the areas near slag pile sites of power unit and gasification unit showed enriched Cr(VI) pollution. With the operation of the coal chemical plant, more attention should be paid because long-term input and accumulation of pollutants may lead to a rise in hazard quotient of Cr(VI) in soil.

(2) The carcinogenic risk of Cr(VI) through inhalation of soil particles accounted for 70.53% of the total risk. Inhalation of soil particles was the main route, causing carcinogenic risk of Cr(VI) in soil of the coal chemical plant. Accordingly, while reducing the level of pollution risk in soil, measures that can block or reduce inhalation exposure such as wearing masks are suggested to be taken to protect the staff.

(3) Minimum risk control value of soil Cr(VI) concentration was suggested for the exposure route of inhalation of soil particles (0.608 mg/Kg), which was selected as Cr(VI) safety control threshold for this plant. Safety threshold of Cr(VI) in soil of coal chemical areas

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should be comprehensively determined considering the differences in carcinogenic risk levels of countries and regions, Cr(VI) background levels of regional soil, regional geological environment, etc.

(4) From total carcinogenic risk map and total hazard quotient map of Cr(VI) in the whole plant obtained by using kriging, pollution was mainly concentrated near slag pile sites of power unit and gasification unit. Power units were centrally polluted areas with pollution descending to surrounding areas of the whole plant.

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Conflict of Interest

The authors declare no conflict of interest.

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