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Evaluation and Spatial Diffusion of Health Risk of Persistent Organic Pollutants (POPs) in Soils Surrounding Chemical Industrial Parks in China

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ABSTRACT

A case study of the cancer risk to humans posed by persistent organic pollutants (POPs) in an industrial area of China, which has a long history of contamination from many sources, is presented. Relatively great concentrations of POPs around the chemical industrial parks have the potential to be chronically carcinogenic to local people. Sixteen individual PAHs listed for priory control by the U.S. Environmental Protection Agency (USEPA), metabolites of DDTs, and isomers of HCHs were measured in soils and a human health risk assessment was conducted by use of USEPA exposure models for children and adults, respectively. Geostatistical methods were used to simulate the spatial diffusion of potential carcinogenic risk, and non-parametric Mann-Whitney U and Kruskal-Wallis tests were employed to analyze the impact of point sources on the surrounding area. The mean value of the sum of Excess Lifetime Cancer Risk ($\sum$ELCR) exceeded the generally acceptable risk level of 1.0E-06 recommended by the USEPA for carcinogenic chemicals. The maximum $\sum$ELCR was 2.9E-04 for children, which was observed inside the chemical industrial parks. Contamination at the chemical industrial parks caused significant spatial diffusion of ELCR values caused by PAHs, DDT, and HCH.

Key Words: persistent toxic substances, carcinogenic risk, soil exposure, spatial distribution.

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INTRODUCTION

Due to their bioaccumulation potential, persistence, toxicity, and long-range environmental transport, Persistent Organic Pollutants (POPs) are of concern to both the public and government managers (China 2007; Dewailly *et al*. 2006). Some of the POPs are considered to be possible or probable human carcinogens, and hence attention has been paid to their distribution in the environment and potential exposure to humans (Tao *et al*. 2006). Soil is often a significant repository and potential source of contaminants that can result in exposures of humans through ingestion, either deliberate or involuntary, inhalation, and dermal absorption and affect their health (Oliver 1997; Shifrin *et al*. 1996).

In China, organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) have been the most frequently studied POPs in soil, and more than 600 soil samples collected from different cities and regions have been analyzed for the occurrence of PAHs and OCPs (Cai *et al*. 2008). Concentrations of PAHs in soil have been increasing for 100–150 years, especially in urban areas (Jones *et al*. 1989). Concentrations of OCPs have been measured in more than 30 studies (Cai *et al*. 2008). However, relatively few studies have investigated the potential for these residues to affect the health of humans. There are a number of locations in China where OCPs were manufactured, stored, or disposed. Even though production at these sites has ceased, the residues may present hazards to humans, especially when these sites are converted to other uses (Swartz *et al*. 2003). Few assessments of the potential health effects of these sites on human health have been conducted in China.

The probabilistic risk assessment method involves characterization of variability (natural variation) and uncertainty (lack of knowledge) for risk management decisions (Oberg and Bergback 2005). Variability and uncertainty in the input parameters (variables or constants) are described by probability distributions, and the output (risk or exposure) is likewise presented as probability distributions (USEPA 1991b). Probabilistic risk assessment methods were introduced in the nuclear industry 30 years ago (USNRC 1975). Other environmental applications came later, a substantial number of probabilistic risk assessments have been conducted at contaminated sites in North America, Europe, and Asia. Examples of contaminants involved are lead (Mari *et al*. 2009), manganese (Zeng *et al*. 2009) and PAHs (Chen and Liao 2006).

With China's rapid industrialization and economic development, historical chemical industrial parks have become an issue. Three of these areas in the Tianjin Binhai New Area (BHNA) were investigated for their potential effects on humans. The three sites include the Hangu Chemical Industrial Park, Dagu Chemical Industrial Park, and Dagang Oil-refinery Region, located in Hangu, Tanggu, and Dagang districts, respectively. There has been a long history of pollution and complex sources of contamination at the BHNA. The Tianjin Chemical Company and the Dagu Chemical Company, located in the Hangu and Dagu Chemical Parks, separately, were once among the largest producers of OCPs in China. Large amounts of lindane, dicofol, and technical-grade hexachlorocyclohexane (HCH) as well as most of the hexachlorobezene (HCB) and technical DDT in China were produced there (Tao *et al*. 2006).

The Tianjin Soda Plant, established in 1917, was well known as the cradle of the Chinese soda industry and the base of the modern chemical industry in China. The Tianjin Chemical Plant was a large-scale alkali-chlorine enterprise founded in 1938. In addition, some other manufacturers in the BHNA have produced dicofol since 1990 (Hu *et al*. 2005). Furthermore, in the national development plan for oil refinery and ethylene development, Tianjin has been identified as the national petrochemical industry base, with two or three projects planned that will have a capacity of one million tons of ethylene production, and 10 million tons of oil refinery. At the same time, many older factories in these regions rely on coal for energy, and thus these facilities were also sources of PAHs. These sites are characterized by contaminated areas where OCPs were stored or waste products dumped. In particular, the sites are contaminated with technical mixtures of DDT and HCB.

Due to the persistence and bioaccumulative potential of some of these OCPs and PAHs, the potential chronic carcinogenic effects on humans living around these industrial parks were investigated. The specific purposes of the study were to: (1) quantify POPs in surface soil of the BHNA; (2) evaluate the potential cancer risk to humans posed by POPs in the BHNA; (3) determine the spatial distribution of human cancer risk of POPs in the BHNA on a relatively large scale and to develop a map of the sum of Excess Lifetime Cancer Risk ($\sum$ELCR); (4) identify the factors that influence the risk distribution of POPs in the BHNA. Two representative types of persistent pollutants were examined in this study: PAHs and OCPs. These were both used as POPs soil contamination indicators at the BHNA (Blanchard *et al*. 2007; Motelay-Massei *et al*. 2004).

MATERIAL AND METHODS

Study Area and Soil Sampling

The BHNA (38°40′–39°00′ N and 117°20′–118°00′ E) is located in northern China at the intersection of the Beijing-Tianjin-Hebei Economic Zone and the center of the Bohai Bay Rim city belt, approximately 100 km northeast to Beijing. The total area of the BHNA is approximately 2270 km^2, in three administrative districts, Hangu, Tanggu, and Dagang from north to south (Figure 1). The Tanggu District is the most developed of the three sites and is where the oldest Chemical Industry Park, Dagu, is located. There were multiple large-scale chemical enterprises in this area and coal was burnt as the primary fuel. With a relatively long history, the technology applied and the equipment used were relatively old and pollution reduction measures were either absent or not effective. The newest of the areas is the Hangu Chemical Industry Park, which was established in 1996 and is located in Hangu District. Since this facility is newer, a series of environmental measures, such as sewage treatment, garbage disposal and exhaust discharge treatment have been implemented. The Dagang Oil-refinery Region is located in the Dagang District, where the predominant industrial activity is oil exploitation and the petrochemical industry. The facility is adjacent to a wetland.

Sampling locations were evenly distributed across the area and some series of soil samples surrounding the chemical industrial parks were collected for the study.

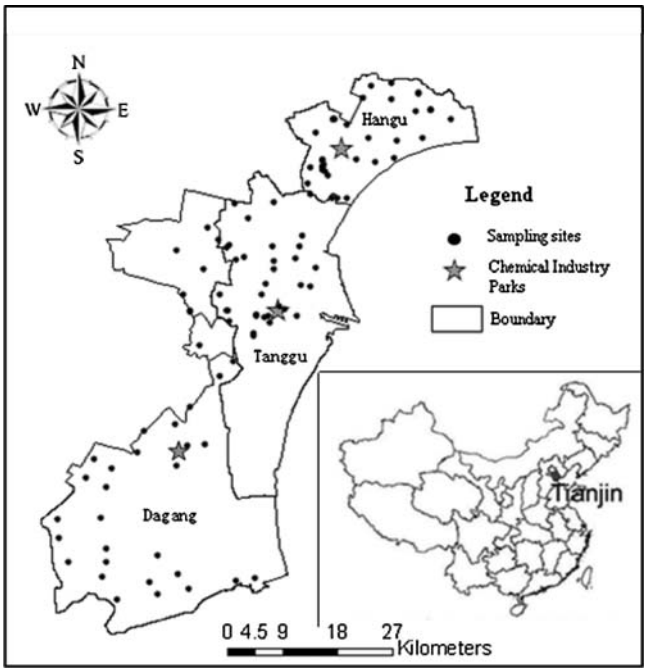

Figure 1. Map of sampling sites within the BHNA.

A total of 105 composite samples of surface soils were collected. Each sample represented a composite of five sub-samples collected from five locations in an area of about 100 × 100 m^2 (at the four corners and the center). All soil samples were collected at a depth of 0–20 cm using a stainless steel shovel. Grass and other extraneous materials were removed from the surface of each location before the sample was collected. Site descriptions including land use type and major environmental features were recorded at the time of sampling.

Analytical Methods

The methods used for sample extraction, and identification and quantification of compounds of interest have been described in detail elsewhere (Jiao *et al*. 2009; Li *et al*. 2008). Briefly, soils were air-dried at room temperature (Nadal *et al*. 2004), sieved through a 100-mesh sieve, and stored at 4∞C. PAHs were extracted by Soxhlet apparatus, and concentrations of the 16 PAHs listed for priory control by the USEPA were quantified by use of an Agilent 6890 GC equipped with a 5973 mass selective detector (MSD) operated in selected ion monitoring mode (SIM). The OCPs were extracted twice with 35 mL hexane/dichloromethane (1:1, v/v) by ultrasonication for 60 min, and DDT and HCH were analyzed by GC-μECD operated in splitless injection mode.

Exposure Scenario

Potential exposure to POPs through soil was assessed by use of the USEPA residential scenario (USEPA 2002). Under residential land use, the risk of exposure to

contaminants in surface soils is assumed to be due to direct ingestion, inhalation of particulate from the soil, and dermal absorption. Taking into account the natural differences between children and adults, including daily soil ingestion rates, physiological characteristics, activity frequencies, and so on, the risk values were calculated for two exposure groups. The first group was children 1 to 6 years of age while the second was adults aged 7 to 31 years old (USEPA 1991a). After the assessments were conducted, the conclusions were based on the group predicted to be more exposed.

Statistical Analysis and Geostatistical Methods

Frequency distributions of concentrations of POPs were investigated by calculating skewness and kurtosis coefficients. Since the data were not-normally distributed (even after log-transformation), non-parametric Mann-Whitney U and Kruskal-Wallis tests were used to identify differences in POPs exposure risk for people who were living in chemical parks and those who were not. Geostatistics can be useful in characterizing spatial variability and mapping residues in soil. Kriging was employed to analyze the horizontal distribution of exposure risk of POPs (Isaaks and Srivastava 1989) and spatial maps were generated by use of GIS software version 9.0 for Windows (Esri China (Beijing) Limited).

Uncertainty Analysis

A Monte Carlo technique based on probability distributions for each parameter was used to calculate the uncertainty around estimated risk values (Matlab 7.1; The MathWorks, China). This uncertainty analysis allowed potential biases to be described and evaluated so that overestimation could be avoided Crystal Ball 7.2 software (Decisioneering Inc. USA) was employed to do sensitivity analysis to rank the input parameters on the basis of their contribution to variance in the output.

RESULTS AND DISCUSSION

Preliminary Data Description of POPs in the BHNA

OCPs were detected in 99% of surface soil samples from the BHNA (Table 1), and total concentrations of DDTs varied from less than the limit of quantification (ND) to 2417 ng/g, dw (with a mean value of 73.9ng/g, dw), while HCHs residues were detected in 97.1% of soil samples, and the total concentrations varied from ND to 51,299 ng/g, dw (with a mean value of 653.6ng/g, dw). These concentrations are significantly greater than those reported previously, which has indicated that the soils at the BHNA are heavily contaminated by HCHs (Gong *et al*. 2004; Li *et al*. 2006; Manz *et al*. 2001; Zhang *et al*. 2006b).

PAHs were detected in 100% of the surface soil samples at the BHNA, with total concentrations of ranging from 68.7 to 43,930 ng/g, dw (with a mean value of 1225 ng/g, dw). These values were greater than those reported for other developed regions in China (Hao *et al*. 2004; Liao and Chiang 2006). According to the benchmark classifications proposed by Maliszewska-Kordybach (1996), only 7.6% of the soil samples were classified as unpolluted (< 200 ng/g, dw), while 45.7% were classified as slightly polluted (200–600 ng/g, dw), 22.9% were considered moderately

Table 1. Concentrations (ng/g, dw) and compositions of PAHs and OCPs in soil samples from the BHNA.

Pollutants	50th centile measured concentration in soil (ng/g, dw)	95th centile measured concentration in soil (ng/g, dw)	Frequency of detection (%)
α-HCH	0.00	19.60	32.4
β-HCH	2.75	27.94	76.2
γ-HCH	27.88	1035.52	97.1
δ-HCH	0.00	3.51	13.3
p,p′-DDE	1.90	91.76	59
p,p′-DDD	0.00	162.33	44.8
o,p′-DDT	0.00	15.28	17.1
o,p′-DDT	0.00	68.72	48.6
Naphthalene	127.34	445.28	89.4
Acenaphthylene	0.00	0.00	0.0
Acenaphthene	0.00	23.07	9.6
Fluorene	16.75	64.19	89.4
Phenanthrene	49.05	205.57	95.2
Anthracene	21.54	161.62	80.8
Fluoranthene	41.21	271.46	99
Pyrene	30.34	207.26	100
Benz[a]anthracene[a]	9.48	295.97	77.9
Chrysene[a]	32.49	230.80	100
Benzo[b]fluoranthene[a]	33.84	256.36	91.3
Benzo[k]fluoranthene[a]	15.60	193.63	97.1
Benzo[a]pyrene[a]	20.95	172.70	97.1
Indeno[1,2,3-cd]pyrene[a]	25.12	161.55	95.2
Dibenz[a,h]anthracene[a]	0.70	123.81	95.2
Benzo[g,h,i]perylene	21.68	175.72	95.2

[a]Carcinogenic compounds.

polluted (600–1000 ng/g, dw), and 23.8% were classified as severely polluted by PAHs (>1000 ng/g, dw).

Exposure Quantification

An emphasis was placed in this study on assessment of OCPs and PAHs that can result in chronic effects or carcinogenic risk. The Chronic Daily Intakes (CDI) and chemical-specific Excess Lifetime Cancer Risk (ELCR) were used to evaluate risk. The pathway-specific ELCR is an estimate of the increased cancer incidence to a receptor suffering from an exposure to a single chemical via a single exposure route, including ingestion, inhalation, or dermal, and was calculated by multiplying the CDI and the corresponding cancer slope factor (SF) of the specific exposure route (USEPA 2002). The chemical-specific ELCR is an estimate of the increased cancer incidence to a receptor from an exposure to a single chemical within three exposure routes (including ingestion, inhalation and dermal). The ELCR values for humans were determined for all environmental media exposure routes (USEPA

1989), and the resulting ELCRs was compared to acceptable guideline values. The USEPA has defined the target risk levels for contaminants in soils to be between a one-in-ten-thousand (1×10^{-4}) and a one-in-a-million (1×10^{-6}) excess lifetime cancer risk for carcinogens (USEPA 1992).

The slope factor is used to estimate an upper-bound probability of an individual developing cancer as a result of a lifetime of exposure to a particular level of a potential carcinogen. Cancer slope factors for oral exposure to OCPs were obtained from the USEPA's Integrated Risk Information System (IRIS 2008) (Table 2). Quantitative toxicity estimates for dermal exposures have not been developed by the USEPA. An extrapolation method is commonly used when there is no toxicity data about a particular exposure route. An inhalation cancer slope factor (SF_i) can be calculated by Eq. (1) (USEPA 2009; USEPA 1999).

$$SF_i = (IUR(\mu g/m^3)^{-1}) * 70(kg) * 1000(\mu g/mg)/(20 m^3/d) \quad (1)$$

where: IUR = inhalation unit risk factor $(ug/m^3)^{-1}$; 70 kg = default adult human body weight; 1000 $\mu g/mg$ = unit transfer factor; 20 m^3/d = average adult human daily rate of inhalation.

Except for special organic pollutants like benzo(a)pyrene (BaP), the cancer slope factor for dermal exposure and the cancer slope factor for dermal exposure can be regarded as interchangeable if there are only one of them existed (Siriwong *et al*. 2009; USEPA 2002; USEPA 2004). The dermal cancer slope factor of BaP (25 $(mg/kg\ d)^{-1}$) was obtained from IRIS (2008).

At present, due to the lack of basic data on health assessment of PAHs, BaP is the only PAH for which cancer slope factor data is sufficient (Peters *et al*. 1999; Villeneuve *et al*. 2002). BaP's slope factor (SF) and toxic equivalency factors (TEFcarc) were used to quantify the carcinogenicity of other PAHs relative to BaP and to estimate BaP-equivalent carcinogenic risk (Nadal *et al*. 2004).

The ELCR calculated for direct exposure to POPs was estimated by applying the existing methods to make probabilistic estimates of risk of excess cancer due to intake of chemicals through ingestion (Eq. 2) (USEPA 1991a) (Table 3), inhalation

Table 2. Toxicological data of interest chemicals.

Chemical	Oral $SF_o((mg/kg\ d)^{-1})$	IUR $((ug/m^3)^{-1})$
BaP[b]	7.3[a]	0.0011 (USEPA 1999)
α-HCH[b]	6.3[a]	1.8E-03 (USEPA 2002)
β-HCH[c]	1.8[a]	5.3E-04 (USEPA 2002)
p,p'-DDD[b]	0.24[a]	
p,p'-DDE[b]	0.34[a]	
p,p'-DDT[b]	0.34[a]	9.7E-05 (USEPA 2002)

[a]SF available from Integrated Risk Information System (IRIS 2008).
[b]Weight-of-Evidence classified as B_2 class; probable human carcinogen.
[c]Weight-of-Evidence classified as C class; possible human carcinogen.

Table 3. Parameters for POPs used in exposure and risk calculations.

			Adults		
Parameter	Type	Children	Males	Females	Reference
IR_{soil}	Lognormal	m:100,sd:126	m:50,sd:16.6	m:50,sd:16.6	(Batchelor *et al.* 1998)
BW	Lognormal	m:17.2,sd:6.3	m:60.2,sd:2.9	m:53.1,sd:2.8	(China 2006)
FE	Beta	α:0.61,β:4.08	α:0.61,β:4.08	α:0.61,β:4.08	(Batchelor *et al.* 1998)
RAF	Lognormal	m:0.2,sd:0.06	m:0.07,sd:0.02	m:0.07,sd:0.02	(Batchelor *et al.* 1998; USEPA 1996a)
EF	Point	350	350	350	(USEPA 1996a)
ED	Triangular	min:1,max:6, mode:3	50%:9,90%:30	50%:9,90%:30	(Batchelor *et al.* 1998)
IR_{air}	Lognormal	50%:8.4,90%:10.9	50%:13.3,90%:17.5	50%:13.3,90%:17.5	(Finley *et al.* 1994)
PEF	Lognormal	50%:1.24E9,90%:6.2E9	50%:1.24E9,90%:6.2E9	50%:1.24E9,90%:6.2E9	(USEPA 1996a)
AT		6	30	30	(Zabin *et al.* 2008)

(Eq. 3) (USEPA 1991a), and dermal contact (Eq. 4) (Chen and Liao 2006).

$$ELCR_o = \frac{SF_0 * C * 10^{-6} kg/mg * EF * ED * IR_{soil}}{BW * AT * 365 days/yr} \quad (2)$$

$$ELCR_i = \frac{SF_i * C * BF * ED * IR_{air} * (1/PEF)}{BW * AT * 365 days/yr} \quad (3)$$

$$ELCR_j = \frac{SF_j * C * 10^{-6} kg/mg * SA * FE * RAF * EF * ED}{BW * AT * 365 days/yr} \quad (4)$$

The sum estimation of $ELCR$ ($\sum ELCR$) from multiple routes of exposure to POPs was calculated as Eq. (5) (USEPA 1991).

$$\sum ELCR = ELCR_o + ELCR_i + ELCR_j \quad (5)$$

where: $ELCR$ = Excess Lifetime Cancer Risk; SF_o = oral cancer slope factor (mg/kg d)$^{-1}$; SF_i = inhalation cancer slope factor (mg/kg d)$^{-1}$; SF_j = dermal cancer slope factor (mg/kg d)$^{-1}$; C = pollutant concentration in soil (mg/kg); EF = exposure frequency (days/year); ED = exposure duration (years); IR_{soil} = soil ingestion rate (mg/day); IR_{air} = inhalation rate (m^3/day); BW = body weight (kg); AT = averaging time (years); PEF = particulate emission factor (m^3/kg); SA = available surface area (cm^2); FE = dermal adsorption fraction (unitless); RAF = adhere factor of soil-to-skin (mg/cm^2).

Probabilistic Risk Assessment

A Monte Carlo analysis was conducted based on probability distributions for each parameter. The output of ELCR was presented as a Log-normal distribution (Figure 2), and the probability of exceedance of the specified probability of effect was calculated. A quantitative sensitivity analysis was also conducted to evaluate which parameters contributed the most variability and most significantly to risk estimates. The three parameters that contributed the most uncertainty to the ELCR were C, FE, and IR_{soil}. Greater uncertainty is contributed by the distribution of POPs concentration as a function of time. The results of the risk assessment are based on the uncertain assumption that future concentrations will be the same as those at present. Actually, the POPs concentrations will not be constant over time as a consequence of hydrologic and geochemical processes as well as massive production and by-production.

Pathway-Specific ELCR Characterization of Individual Chemicals for Local Residents

Predicted values of pathway-specific ELCR due to oral, inhalation, and dermal exposure to POPs in soils, for children and adults are shown in Table 4. Ingestion of soils was the predominant pathway of exposure to residues in soils. In fact, inhalation and dermal exposure of organic chemicals can be disregarded, especially if there was no sufficient data or not readily available for inhalation or dermal exposure under residential land use (USEPA 1991a). Based on the results of the exposure scenarios applied, children were more exposed and thus at greater risk of excess cancer from the POPs studied (Zabin *et al.* 2008), and because of relatively lesser

Table 4. Pathway-specific ELCR characterization for local residents of ingestion exposure, inhalation exposure and dermal exposure.

	PAHs		α-HCH		β-HCH		*p,p′*-DDD		*p,p′*-DDT		*p,p′*-DDE	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
						Ingestion						
Children	1.2E-07∼1.6E-04	2.3E-05	ND∼2.0E-04	3.1E-06	ND∼8.2E-06	3.6E-07	ND∼1.3E-05	2.9E-07	ND∼1.7E-06	1.1E-07	ND∼4.1E-06	1.9E-07
Adults												
Males	3.3E-08∼4.4E-05	6.4E-06	ND∼5.4E-05	8.5E-07	ND∼2.2E-06	9.8E-08	ND∼3.6E-06	7.8E-08	ND∼4.6E-07	3.1E-08	ND∼1.1E-06	5.2E-08
Females	3.8E-08∼4.9E-05	7.3E-06	ND∼6.1E-05	9.6E-07	ND∼2.5E-06	1.1E-07	ND∼4.1E-06	8.9E-08	ND∼5.2E-07	3.5E-08	ND∼1.3E-06	5.9E-08
						Inhalation						
Children	5.7E-13∼7.4E-10	1.1E-10	ND-1.7E-09	2.7E-11	ND∼8.2E-06	3.1E-12	ND∼1.3E-05	2.5E-12	ND∼1.7E-06	9.8E-13	ND∼4.1E-06	1.7E-12
Adults												
Males	4.98E-13∼6.5E-10	9.5E-11	ND∼1.5E-09	2.4E-11	ND∼2.2E-06	2.8E-12	ND∼3.6E-06	2.2E-12	ND∼4.6E-07	8.6E-13	ND∼1.1E-06	1.5E-12
Females	5.64E-13∼7.4E-10	1.1E-10	ND∼1.7E-09	2.7E-11	ND∼2.5E-06	3.1E-12	ND∼4.1E-06	2.5E-12	ND∼5.2E-07	9.8E-13	ND∼1.3E-06	1.7E-12
						Dermal						
Children	3.3E-08∼4.3E-05	6.3E-06	ND∼1.6E-05	2.4E-07	ND∼6.5E-07	2.8E-08	ND∼1.1E-06	2.3E-08	ND∼1.3E-07	8.8E-09	ND∼3.2E-07	1.5E-08
Adults												
Males	1.6E-08∼2.0E-05	3.0E-06	ND∼7.3E-06	1.2E-07	ND∼3.0E-07	1.3E-08	ND∼4.9E-07	1.1E-08	ND∼6.2E-08	4.1E-09	ND∼1.5E-07	7.1E-09
Females	1.6E-08∼2.1E-05	3.1E-06	ND∼7.6E-06	1.2E-07	ND∼3.1E-07	1.4E-08	ND∼5.1E-07	1.1E-08	ND∼6.4E-08	4.3E-09	ND∼1.6E-07	7.3E-09

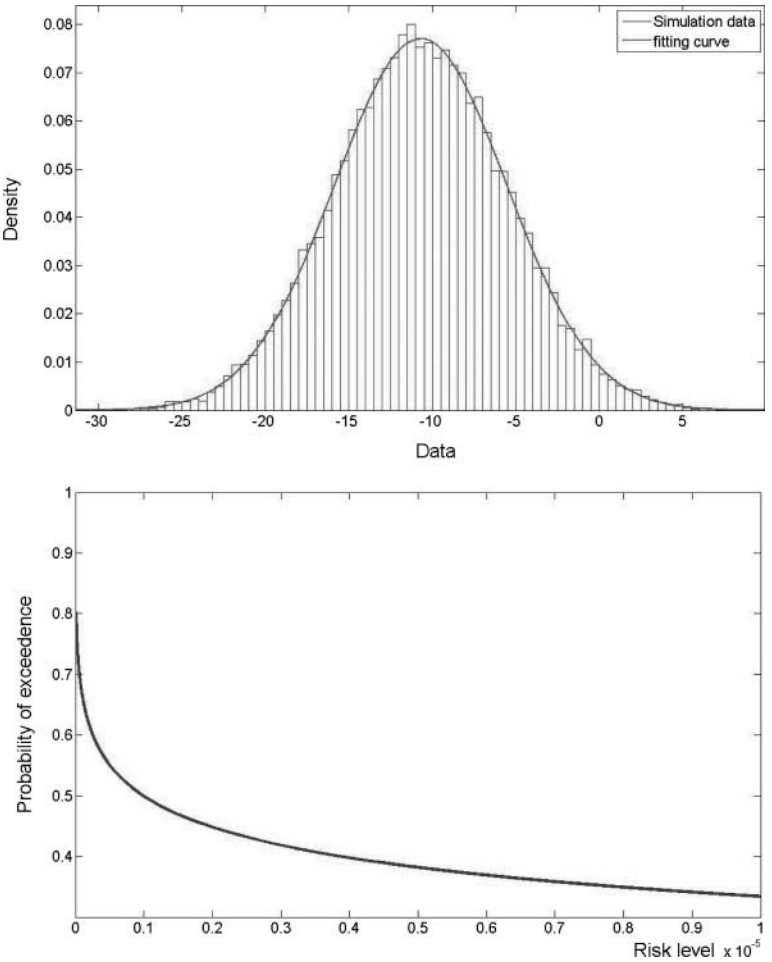

Figure 2. Distribution of ELCR and probability of exceedance to risk level.

body weight, females were predicted to have a greater risk than males for the same concentrations of residues in soils.

Chemical-Specific ELCR Characterization from Multiple Routes for Local Residents

The chemical-specific ELCR of the three classes of POPs, PAHs, HCH, and DDT as well as the sum of the three ELCR values, $\sum$ELCRs, based on intake from soil over all exposure routes were calculated (Table 5). The mean $\sum$ELCRs was estimated to be 3.41E-05, 1.06E-05, and 1.17E-05 for children, males, and females, respectively. That value exceeded the generally acceptable risk level recommended by the USEPA for carcinogenic chemicals of 10^{-6}, not being greater than 10^{-4}. However, the maximum of $\sum$ELCR was 2.87E-04 for children, which was greater than the acceptable range. The USEPA-SSLs (Soil Screening Level) approach gives a clear and unique policy of 1×10^{-6} as the acceptable individual cancer risk for individual chemicals and pathways

Table 5. Total cancer risk characterization for local residents of all exposure routes.

		Adults		Lifetime exposure	
ELCR	Children	Males	Females	Males	Females
PAHs					
5th	1.6E−06	5.0E−07	5.5E−07	7.1E−07	7.5E−07
95th	9.3E−05	2.9E−05	3.2E−05	4.2E−05	4.4E−05
Mean	3.0E−05	9.4E−06	1.0E−05	1.3E−05	1.4E−05
α-HCH					
5th	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
95th	3.9E−06	1.1E−06	1.3E−06	1.7E−06	1.8E−06
Mean	3.3E−06	9.6E−07	1.1E−06	1.4E−06	1.5E−06
β-HCH					
5th	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
95th	1.6E−06	5.1E−07	5.1E−07	7.2E−07	7.2E−07
Mean	3.9E−07	1.2E−07	1.2E−07	1.8E−07	1.8E−07
HCH					
5th	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
95th	6.0E−06	1.7E−06	1.9E−06	2.6E−06	2.7E−06
Mean	3.7E−06	1.1E−06	1.2E−06	1.6E−06	1.7E−06
p,p′-DDD					
5th	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
95th	1.2E−06	3.5E−07	4.0E−07	5.3E−07	5.6E−07
Mean	3.1E−07	8.9E−08	1.0E−07	1.3E−07	1.4E−07
p,p′-DDT					
5th	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
95th	2.8E−07	2.1E−07	2.4E−07	2.3E−07	2.5E−07
Mean	5.9E−08	3.5E−08	3.9E−08	4.0E−08	4.3E−08
p,p′-DDE					
5th	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
95th	7.3E−07	2.8E−07	3.2E−07	3.7E−07	4.0E−07
Mean	1.2E−07	5.9E−08	6.7E−08	7.2E−08	7.7E−08
DDT					
5th	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
95th	2.8E−06	8.0E−07	9.0E−07	1.2E−06	1.3E−06
Mean	6.3E−07	1.8E−07	2.1E−07	2.7E−07	2.9E−07
Total					
5th	1.7E−06	5.4E−07	5.9E−07	7.7E−07	8.2E−07
95th	1.1E−04	3.4E−05	3.8E−05	5.0E−05	5.3E−05
Mean	3.4E−05	1.1E−05	1.2E−05	1.5E−05	1.6E−05

$$Lifetime\ exposure = \frac{6 \times ELCR_{children} + 24 \times ELCR_{adult}}{30}$$

(USEPA 1996b). The Italian National Technical Regulation on Contaminated Soils (Decree No. 471/1999 of the Ministry of the Environment: Italian Ministry of the Environment 1999) gives the following indications: (1) with ELCR $< 1 \times 10^{-6}$, no risk or insignificant risk is present, and consequently no remedial action is required; (2) with ELCR $>1 \times 10^{-4}$, a remedial action is always required; and finally (3) with

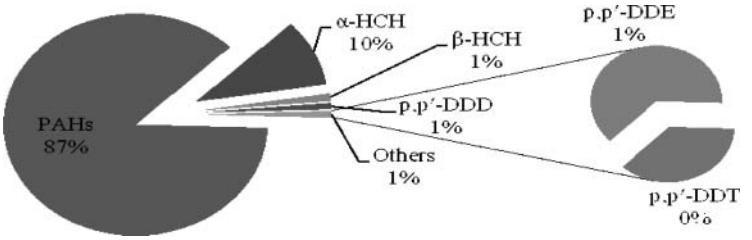

Figure 3. ELCR proportions of target chemicals in BHNA soils.

ELCR in the range of 1×10^{-6} to 1×10^{-4}, the need for a remedial action should be evaluated case by case (Zakharova *et al*. 2002). Therefore, the current concentrations of carcinogenic POPs in the BHNA soils present an acceptable cancer risk for local adults. However, there is a potential excessive risk of excess cancer for children. Thus, further investigation is necessary and measures should be taken to remedy hot spots to minimize risks of excess cancers in these areas.

Among the three POPs, PAHs, DDH, and HCH, the proportion contributed by PAHs to the ∑ELCR was greatest (87%). Due to the greater cancer slope factors, the contribution of HCH (11%) to the ∑ELCR was greater than that of DDT (2%). The relative contributions of each residue to the ∑ELCR in soils of the BHNA are shown (Figure 3).

Spatial Variation of ELCR Intake from Soil in the Study Area

The group at the greatest risk, children, were further analyzed to determine the spatial distribution of ∑ELCR. The geostatistical procedure, kriging, was used to predict values for areas that were not sampled from the data that were available (Oliver and Webster 1991). Key parameters of the semi-variogram models of POPs were selected as inputs to ArcGIS and ordinary kriging was used to do the interpolation and develop spatial distribution maps (Figure 4).

The first stage of the legend was classified as a risk for ELCR that was less than 10^{-6}, which was presented as a blank background. Except for the blank region, the potential values for ∑ELCR were greater than (10^{-6}). The darker the shading, the greater the potential cancer risk.

The spatial distribution of ELCR of PAHs in the BHNA was associated with industrial activity and urban areas. Concentrations of carcinogenic PAHs are generally less in rural soils (Wilcke 2000; Zhang *et al*. 2006a). The greatest value of ELCR for PAHs was observed in the most industrialized district, Tanggu (590.3 ng ∑PAH/g, dw), followed by Hangu (299.7 ng ∑PAH/g, dw) and Dagang (220.1 ng ∑PAH/g, dw). Carcinogenic PAHs are more associated with combustion sources, especially incomplete combustion of fossil fuels, including coal and gasoline and vehicle emissions (Rogge *et al*. 1993; Simcik *et al*. 1999). Large amounts of coal were burned as fuel at chemical parks and the number of cars has increased rapidly in the Tanggu district in recent years. In fact, only 2% of soils in the whole area had a risk for ELCR from PAHs that was less than 10^{-6}. Approximately 95% of the area had risk factors of 10^{-6} to 10^{-4}, while 3% of the area exceeded a risk factor of 10^{-4}, which was inside the chemical industrial parks.

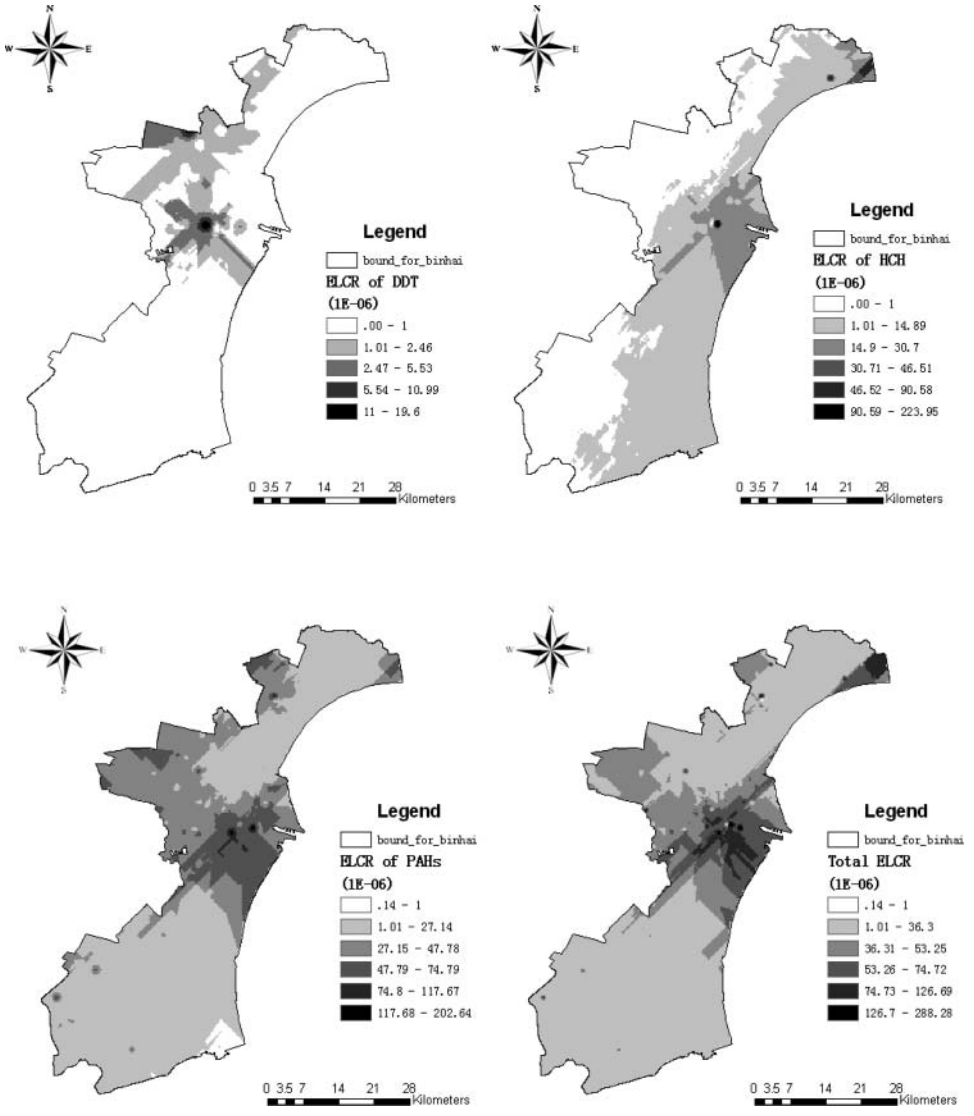

Figure 4. Spatial distribution of ∑ELCR in soils of the study area.

The spatial distribution of ELCR due to DDT in soils of the BHNA was mainly in soils of the Dagu Chemical Industrial Park, which used to be one of the main OCPs production bases. There was a significant hot spot with values of ELCR due to DDT gradually decreasing with the distance from the Dagu Chemical Industrial Park. Concentrations of DDT in soils of approximately 91% of the area resulted in ELCR values that were less than 10^{-6}. Of the remaining area ELCR values were between 10^{-6} and 10^{-4}.

The spatial distribution of ELCR resulting from HCH did not show a significant geographical trend. The soils in northeastern Hangu, near the Bohai Sea, had the greatest value for ELCR due to HCH. Areas close to the Dagu Chemical Industrial

Park also had relatively great ELCR for HCH. In approximately 85% of the study area the ELCR caused by HCH was less than 10^{-6}, while 1% of the area exceeded 10^{-4}.

Impact Factor Analysis for ELCRs of POPs in the BHNA

The three chemical industrial parks were centers of exposure of POPs to local residents, which resulted in ELCR values greater than those for background areas. To estimate the differences in effects of the three chemical industrial parks on distributions of ELCR contributed by PAHs, DDT, and HCH, sample sites close to chemical industrial parks (< 6.5 km) were selected to represent the Hangu, Dagu chemical industry sites and the Dagang oil-refinery (Wang *et al*. 2009). Comparisons among the three locations were made by use of the Kruskal-Wallis. The remaining sites (>6.5 km) were designated as being remote from the epicenters of the three regions and ELCR values in the regions were compared to the more remote or regional baseline region and Mann-Whitney U tests were employed. The three sites were significantly different in the magnitude of the ELCR ($p < .01$) (Table 6).

The $\sum$ELCRs for the Hangu and Dagu chemical industrial parks were significantly greater than that of the regional baseline area. Lindane, technical HCH, and DDT were produced in these two areas (Tao *et al*. 2006), and there were waste dumps and storage facilities for both DDT and HCB still in and around the sites. Also large amounts of PAHs were released from combustion of coal and oil at these large-scale enterprises.

There was a significant difference in ELCR contributed by DDT between the Dagu chemical industrial park and regional baseline area, but not at the Hangu chemical industrial park. It is concluded that point sources of DDT in soils of the Hangu chemical park have a small impact on the ELCR, while those at the Dagu chemical industrial park still represent a potential health risk to humans.

Table 6. Comparison of ELCR between inside each chemical industrial park and sites classified as farther away.

		Mann-Whitney test		
Residues	Kruskal-Wallis test	Hangu *vs.* Others	Dagu *vs.* Others	Dagang *vs.* Others
α-HCH	0.000	0.005	0.000	0.310
β-HCH	0.000	0.009	0.000	0.956
HCH	0.000	0.008	0.000	0.699
p,p′-DDD	0.000	0.848	0.000	1.000
p,p′-DDT	0.000	0.040	0.000	0.123
p,p′-DDE	0.000	0.013	0.000	0.899
DDT	0.000	0.026	0.000	0.781
PAHs	0.000	0.001	0.000	0.555
Total	0.000	0.001	0.000	0.585

Difference is significant at the 0.01 level.

However, there was no difference in the ELCRs contributed by PAHs at the Dagang oil-refinery region and regional baseline area. The most important industry of the Dagang oil-refinery region was a petrochemical industry, which was one of the important sources for PAHs of fewer rings than those produced by combustion and there is no OCPs production history. This result is consistent with the fact that carcinogenic PAHs of more rings were the by-products of incomplete combustion of fossil fuels (Rogge *et al*. 1993; Simcik *et al*. 1999).

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