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Case Report

Assessing Risks at a Former Chemical Facility, Nanjing City, China: An Early Test of the New Remediation Guidelines for Waste Sites in China

Yanhong Zhang [1], Shujun Ye [1,*], Jichun Wu [1] and Ralph G. Stahl Jr. [2]

1 Key Laboratory of Surficial Geochemistry, Ministry of Education, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China; yhzhang618@gmail.com (Y.Z.); jcwu@nju.edu.cn (J.W.)
2 DuPont Corporate Remediation Group, DuPont Company, Wilmington, DE 19805, USA; Ralph.G.Stahl-Jr@dupont.com
* Correspondence: sjye@nju.edu.cn; Tel.: +86-25-8968-4150

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Abstract: China has recognized the need to investigate and remediate former manufacturing facilities and return the land they occupy to a new, productive use. As a result, national guidelines entitled "Technical guidelines for Risk assessment of contaminated sites" were issued in 2014 to guide site investigations, risk assessments, and remedial actions to reduce or mitigate potential exposures of people and ecological receptors to contaminants. This study was pursued to gain experience with the new guidelines at a small, former chemical manufacturing facility in Nanjing City, China. A series of investigations were undertaken to determine the locations and levels of contaminants in soils and groundwater, develop a conceptual site model, and prepare an initial estimate of risks to humans and ecological receptors. Groundwater results revealed several contaminants that were greater than the Dutch Intervention Levels, yet, surprisingly, few, if any, contaminants were found in multiple samplings of soil. Despite the limited investigations of soil and groundwater, data were sufficient to prepare initial risk evaluations for humans, both for systemic toxins and potentially carcinogenic chemicals. The site and nearby area contain industrial facilities and residential neighborhoods; hence, there were too few ecological receptors to warrant an ecological risk assessment. The new guidelines for site investigations and risk assessments proved sufficient for the purposes of this small site; however, more complex sites may require much greater levels of effort and more detailed guidelines for investigations, risk assessments, and remedial actions.

Keywords: guidelines; contaminated sites; risk assessment; China

1. Introduction

Like many nations, China has begun to recognize the need to investigate former manufacturing sites and remediate them so they can be returned to productive use [1]. In China's case, this is particularly important because many former manufacturing sites are quickly becoming isolated within large, newly developed or developing residential areas [2]. These former manufacturing facilities occupy highly desirable land that could be used for residential housing, new manufacturing, or for recreation. Without guidelines, backed by regulatory frameworks and trained staff, it is not possible to conduct the consistent, protective remediation of these former facilities, nor insure that remedial actions are overseen and tracked by trained professionals. Of additional importance to undertaking remedial actions at these facilities is the need for a risk-based decisional process. Such a process would include written guidelines for conducting qualitative and quantitative analyses of potential risks to humans and ecological receptors, as well as details on how the risk assessment should be applied in deciding what remedial action(s) are appropriate for the site under study.

The following details the investigations undertaken at this site, the lessons learned in applying the new guidelines, and suggestions on how the guidelines might be improved. We followed these steps in a risk-based decisional process to undertake, describe, and discuss our approach to work at the Luhe site: (1) Problem formulation; (2) Exposure and Hazard Assessment; and (3) Risk Characterization. Throughout the following text, we identify areas of uncertainty that we encountered while applying the new guidelines to this site. Finally, we have also provided a relatively large Supplemental Materials section that includes many of the guideline details translated from the original Chinese versions.

2. Methods

A major objective of the study was to test the newly issued Chinese national guidelines for addressing contaminated waste sites. Hence for the Luhe site, we generally followed the methods detailed in three of these new guidelines: (1) Site investigations [3]; (2) Risk assessments [4]; and (3) Remedial actions [5]. As the study began in 2011, these three sets of guidelines were still in draft form; however, after some revisions by the Ministry of Environmental Protection (MEP), they became final in 2014 and were ultimately used for this study. Later, we describe one of the major changes when the guidelines were finalized and how that impacted our risk assessment.

2.1. Problem Formulation

The location of the former manufacturing site is shown in Figure 1. The future land use plan for the site is for the eastern part to become a part of the adjacent highway, while the western part will become a municipal landscape area. These details are important for planning data collection and undertaking the risk assessment.

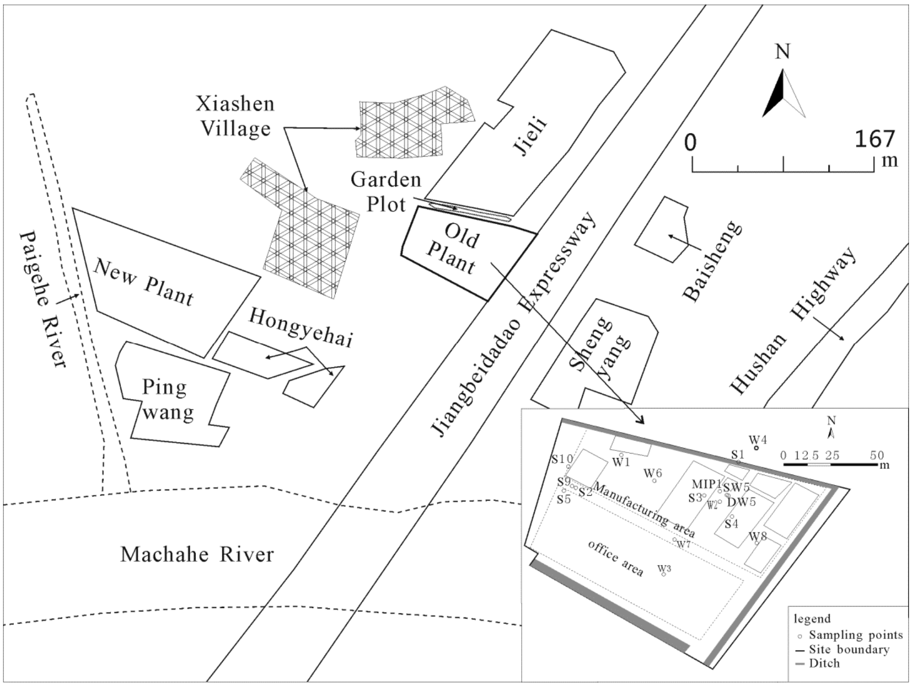

Figure 1. The schematic Location of Luhe site, Nanjing, China.

During our work, we were aware that some of the more detailed guidance and policies applicable for site investigations, risk assessments, and remedial decisions were still being developed in China. That work began before we started our project, and continues today. As a result, our initial screening of soil and groundwater data required us to augment Chinese guidelines with those from other countries, including the United States (US) and The Netherlands.

2.2. Site Setting, Operational History, and Initial Investigations

The Luhe site is approximately 1200 m^2 in size, and included several old buildings and surrounding villages (Figure 1). There are two rivers that border the site: the Paigehe River to the west, and the Machahe River, a branch of the Yangtze River, located about 300 m to the south. These two rivers are used for crop irrigation in this region of China, as well as the transportation of goods into and out of the Yangtze Delta area. Small residential villages are located just north and adjacent to the site, and residents were observed to use a small paved road to cross the site to gain access to the larger streets and nearby highway. Small vegetable gardens are present along the eastern side of this paved road, and another manufacturing complex is located to the east of those gardens. We did not attempt to collect information on operations or investigations at this adjacent manufacturing complex, and thus did not include it in this study. This highlights an important point with respect to contaminated site investigations in China—the guidelines do not yet provide recommendations for how to address potentially contaminated sites near the site under investigation.

From 1999 to 2010, the Luhe site manufactured optical brightener PF (polyester film), 2-Amino-4-methylphenol, and 2-Nitro-4-methylphenol. Unfortunately, the manufacturing history for this site does not include written details sufficient to fully understand how these substances were made and what they were used for. Available information on optical brighteners suggests that their composition can vary, largely depending on their intended use. They are sometimes referred to as fluorescent whitening agents (FWA), and can be used to enhance colors in various textiles, consumer products, paints, etc. [6]. The site ceased the production of PF in 2010, shortly before we undertook our study. The site underwent substantive physical changes during the course of our work, which complicated some aspects of our investigations.

2.3. Collection of Soil and Groundwater Samples

Three field investigations were conducted to determine the nature and extent of soil and groundwater contamination at the Luhe site. The soil sample boreholes were advanced via direct-push technology, using a Geoprobe 6620DT system. The sampling was conducted utilizing a 110 mm diameter, 1.219 m length, stainless steel macro-corer with a new, dedicated, 50.8 mm diameter, 1.219 m long, hollow plastic liner. In addition, an auger was used to collect undisturbed shallow soil samples at the target depth.

Hand bailers or mechanical pumps were used to collect groundwater from wells on the site. Groundwater sampling was performed in general accordance with US Environmental Protection Agency (USEPA) protocols [7] to minimize the potential for cross-contamination. Two groundwater samples were collected in parallel at each well location; the first was for volatile organic compounds (VOCs), followed by a second one for semi-volatile organic compounds (SVOCs).

2.4. Analytical Methodology

All soil and groundwater samples were submitted to ALS (ALS Analytical Testing (Shanghai) Co., Ltd., Shanghai, China) for "typical" chemical analysis in accordance with USEPA SW-846 methods, as presented in Supplemental Materials, Part A: Table S1. A UV-Vis spectrophotometer was used to analyze the optical brightener PF, which absorbs at 363 nm (UV 2300, Shanghai *Tianmei* Science and Technology Corporation, China). In our experience, the optical brightener PF has not been a "typical" contaminant found at contaminated sites and therefore required the use of a different analytical method to measure it in soil and groundwater samples.

2.5. Data Screening and Risk Assessment

When the study began in 2011, there were few or no guidelines available in China for conducting contaminated waste site investigations, risk assessments, or remedial evaluations and selections. However, this information gap was filled by the publication of draft guidelines, followed by final versions in 2014. These relatively new guidelines included procedures for site investigations, risk assessments, and selecting remedial actions. English translations of the models, assumptions, and many details applied to calculate various exposure, hazard, and risk parameters are shown in the Supplemental Materials, Part A.

The soil analytical data were evaluated against the Screening Levels for the Soil Environmental Risk Assessment of Sites (SLSRAS, DB11/T 811-2011) [8], Dutch Soil Quality Standards [9], and USEPA Region 9 Preliminary Remediation Goals PRGs, Version Nov. 2012) [10], respectively. The groundwater analytical data were evaluated against the Chinese Quality Standard for Groundwater (CQSG, GB/T 14848-9) [11], the Dutch Groundwater Quality Standards [9], and the USEPA Region 9 PRGs (Version Nov. 2012) [10], respectively. The use of screening criteria and standards from outside China reflected the lack of such risk-based screening values in China for our work at the Luhe site. In most instances, Dutch Target Values (DTV), which represent generally recognized safe soil and groundwater concentrations, are appropriate screening values where such values are not specified by or available in a specific country. As a result, we used the Dutch Standards (Target Values) for screening contaminants detected in soil and groundwater samples at the Luhe site. Even so, there were instances where there were no screening values readily available, including for the optical brightener PF.

3. Results and Discussion

3.1. Soils

From 2011 to 2014, three field investigations were conducted to evaluate the contamination levels at the Luhe site. For the first and second investigations, a total of nine soil samples were collected. None of the concentrations of VOCs or SVOC contaminants exceeded their applicable SLSRAS, DIV-S, or USEPA PRG screening values, where applicable screening values were available. During the third investigation, an additional 30 soil samples were collected for VOC and SVOC analysis. While low levels of ethylbenzene, chlorobenzene, 1,3-dichlorobenzene, and 1,4-dichlorobenzene were detected in soil samples collected from location S4, no contaminant was observed at a concentration above Dutch Intervention Values for Soils (DIV-S) (Table 1). Unfortunately, there are no relevant Dutch Target Values for Soil (DTV-S) for the contaminants found at the site, and SLSRAS for only a limited number of chemicals. In addition, there are not yet any applicable guidelines in China for the de novo derivation of risk-based screening values. Optical brightener PF was detected in soils at 2 mg/g from location SW5, yet this chemical does not appear to be a "typical" soil or groundwater contaminant found at former manufacturing sites that are or have been investigated, either in China or elsewhere. These results clearly demonstrate the need for China to develop risk-based screening levels for soils and groundwater, or adopt and supplement those already developed by the US, The Netherlands, or other countries.

Table 1. Contaminants in soil samples from the Luhe site, China (Unit: mg/kg in dry weight).

Sampling Points and Depth (m)	Benzene	Toluene	Xylenes	Ethyl Benzene	Chloro Benzene	1,4-Dichloro Benzene	1,2,4-Trichloro Benzene
CAS No.	71-43-2	108-88-3	1330-20-7	100-41-4	108-90-7	106-46-7	120-82-1
S4, 0.7	0.025	0.025	0.025	10.4	1.64	2.03	0.025
DW5, 8.5	0.025	0.025	0.12	0.17	0.025	0.025	1.46
DW5, 10.9	0.025	0.025	0.025	0.025	0.025	0.025	0.16
SW8, 1.5	0.025	0.025	0.025	0.025	0.1	0.025	0.025
SLSRAS	1.4	3300	100	860	64	-	-
DIV-S	1.2	320	17	110	15	19	11
DTV-S	-	-	-	-	-	-	-
PRGs	5.1	4700	280	25	130	11	26

3.2. Groundwater

All potential contaminants of concern (pCOCs) were non-detectable (detection limit = 0.5 µg/L) in the groundwater samples collected from locations W4, SW5, W6, and W7 (Table 2). Concentrations in the groundwater of all pCOCs were above Dutch Intervention Values for Groundwater (DIV-G) screening values (shown in bold type in Table 2) in samples collected from S1, S4, etc. The Dutch Target Values for Groundwater (DTV-G) were used for screening groundwater samples since there were no relevant risk-based screening values in China for groundwater contaminants.

Table 2. Contaminants found in groundwater samples at the Luhe site (Unit: µg/L).

Sampling Points and Depth (m)	Benzene	Toluene	Xylenes	Ethyl Benzene	Chloro Benzene	1,4-Dichloro Benzene	1,2,4-Trichloro Benzene
CAS No.	71-43-2	108-88-3	1330-20-7	100-41-4	108-90-7	106-46-7	120-82-1
W2, 3	0.6	0.25	0.25	2.9	2.9	39.3	**753**
W3, 3	0.25	0.25	0.25	0.25	0.25	0.25	**35.9**
S2, 3	0.25	0.25	0.25	0.25	0.25	0.25	5.5
S3, 3	0.7	0.6	0.25	6	1	14.4	**425**
S4, 3	22.1	89.1	0.25	**1200**	**638**	**1625**	**7300**
S1, 3	123	3.5	0.25	**505**	**2400**	**4117**	**4800**
W4, 3.5	0.25	0.25	0.25	0.25	6.1	16.1	5.9
SW5, 3	0.25	0.25	0.25	0.25	0.25	0.25	1.8
DW5, 10	1.2	61	**128**	**166**	42	41.9	**1353**
W7, 9	0.25	0.25	0.25	0.25	0.25	0.25	0.25
W8, 4	0.25	0.25	0.25	0.25	19	9.9	**57.4**
CQSG	-	-	-	-	-	-	-
DIV-G	30	1000	70	150	180	50	10
DTV-G	0.2	7	0.2	4	0.3	0.2	0.03
PRGs	0.45	110	19	1.5	7.8	0.48	0.4

Note: Concentrations above Dutch Intervention Values for Groundwater (DIV-G) are shown in bold type.

3.3. Conceptual Model

A conceptual model is one of the key elements of site investigations and the remediation process. It serves as both a communication tool and an illustration of contaminant movements through environmental media and the pathways by which those contaminants reach (or not) important receptors such as humans or wildlife [12,13]. It is evergreen, and updated throughout the investigation phase as new data become available. Over the course of this work, the Luhe site underwent substantial physical changes including the demolition of all site buildings and the removal of subsurface utilities. This activity tended to complicate some of our soil and groundwater investigations, because the entire surficial soils were modified by the use of heavy equipment such as excavators and hauling trucks, among others. Nevertheless, in one aspect, it was fortunate that these modifications happened during our study. It demonstrated how such sites in China may be subject to clearing and redevelopment, regardless of where they might be in relation to the investigation and identification of potential remedial actions. To our knowledge, these changes did not result in any observable changes to or impacts on the nearby residential areas.

The details above are important to the risk assessors and decision makers since they are directly related to developing the appropriate exposure scenarios that need to be considered in the human health risk assessment and for future risk communication to the local public. They also illustrate a fundamental difference in the length of time allowed for investigations and remedial actions in China compared to the process in the US, where investigations and remediation can take many years, especially on larger, more complex sites.

With respect to the groundwater, developing a site conceptual model required that the source, type, and magnitude of contamination be determined, as well as collecting data on the physical characteristics of the surficial and subsurface soils (Figure 2a). A clay layer was found at approximately four meters below the ground surface (bgs), which, fortunately, appears to be acting as a confining unit (i.e., aquitard) to the movement of groundwater and contaminants under the site. However, a discontinuous perched water zone was found above this clay layer. The apparent groundwater flow in this perched zone was found to be from northwest to southeast based on the groundwater level measurements collected from the shallow monitoring wells (Figure 2b). A semi-confined aquifer was found beneath the clay, with an apparent groundwater flow from north to south across the site based on the groundwater level measurements collected from the deeper monitoring wells.

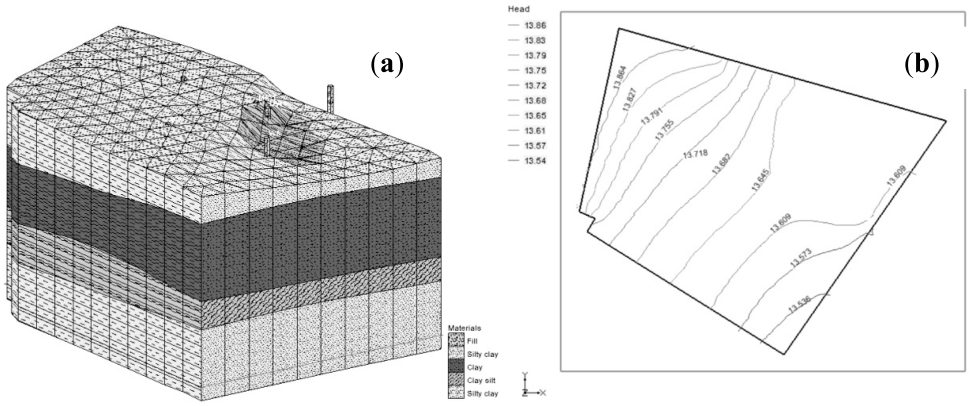

Figure 2. (**a**) The geological model for the LuHe site; (**b**) groundwater contour map of the unconfined aquifer (unit of head: m).

Figure 3 shows the details of the Source-Pathway-Exposure model for soil, based on these various field investigations. The Exposure-Routes-Receptor Model for the site is shown in Table 3. Under Chinese guidelines, contaminated land is divided into two categories: "sensitive", and "non-sensitive". Sensitive land includes land that will be used for non-industrial purposes, such as housing, recreation, etc., whereas non-sensitive land will be used for industrial purposes. In both categories, contaminated land is subject to specific input variables for estimating the potential exposure and risks to human receptors. For the Luhe site, considered non-sensitive land, exposure estimates for adults are characterized by a long exposure duration and high exposure frequency. In addition, exposure estimates are only focused on adults, both for carcinogens and non-carcinogens.

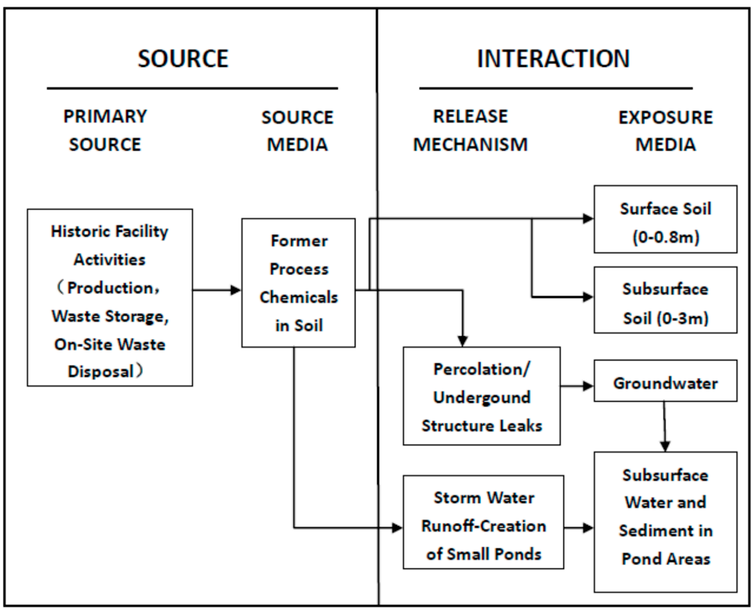

Figure 3. Source-Pathway-Exposure Model for Soil at the Luhe site.

Table 3. Exposure-routes-receptor model for the Luhe site.

Environmental Media	Protect Target	Sources	Receptor	No.	Exposure Routes
Soil	Human Health	Surficial soil	Adults	1	Oral Ingestion
				2	Dermal Contact
				3	Particle Inhalation
				4	Inhalation of Contaminants in Vapor in Outdoor Air
		Subsurface soil	Adults	5	Inhalation of Contaminants in Vapor in Outdoor Air
				6	Inhalation of Contaminants in Vapor in Indoor Air
Groundwater	Human Health	Ground-water	Adults	7	Consumption
				8	Inhalation of Contaminants in Vapor in Outdoor Air
				9	Inhalation of Contaminants in Vapor in Indoor Air

Note: This reflects the Luhe site being categorized as "non-sensitive" land, a designation similar to "industrial" in other national remediation programs.

The completion of exposure and hazard assessments for non-sensitive land presented some challenges and concerns in this study. First, this category of land use only considers potential risks to human health and does not include an evaluation of potential exposures or hazards for ecological receptors. This could be problematic because groundwater can be an important pathway for carrying subsurface contaminants to surficial areas such as ponds, lakes, rivers, and estuaries. Under that scenario, the movement of contaminants in groundwater that is later expressed in surface water bodies could potentially lead to unacceptable exposures to humans and ecological receptors. Because that potential exposure scenario is not required under the current guidelines, potential risks to humans and ecological receptors could go undetected. For our work at the Luhe site, this potential problem will be addressed in our future evaluations given that groundwater is a critical environmental media which should also be considered.

Second, this land-use category only considers human adults, but not children, as receptors that need to be evaluated. During our investigations, we observed children traversing the site using the small paved road, yet their potential exposure to contaminants in soil and groundwater were not evaluated. Hence there is uncertainty about this exposure scenario, as well as the scenario whereby wind-borne dusts that carry contaminants from the site, make their way into homes in the nearby village. This too is an issue that should be evaluated in future studies at the LuHe site.

Third, the model does not consider human exposure through the dietary ingestion route. Our investigations showed that small vegetable gardens have been and may continue to be grown adjacent to the site. In this case, there is some potential for vegetables to be contaminated through the uptake of soil-borne contaminants, or from those contaminants that might be deposited through dust settling on the vegetables. This latter point is particularly relevant in China as the rapid expansion of urban, residential areas may have taken place on former manufacturing lands that have not been properly investigated or remediated. It is also known that urban dust that settles on streets, homes, and perhaps vegetables may contain contaminants posing some level of risk to humans [14,15]. Since the potential for contaminants to reach edible crops was noted, samples of soils from the small garden plots were taken randomly and analyzed by the Supervision and Testing Center of East China Mineral Resources of Ministry of Land and Resources. Collection of the soil samples generally followed the methods outlined previously. The analytical results from sampling those soils are shown in Supplemental Materials, Part A: Table S2.

3.4. Risk Assessment

As a first step in the risk assessment process, we reviewed our results from the soil and groundwater investigations to determine which of the various contaminants would be carried forward into our initial assessment. Typically, the analytical results from sampling environmental media are screened against conservative risk-based values developed by a regulatory agency, or other groups that would be appropriate for the specific country. Those contaminants found to exceed these screening values are then carried into the more detailed risk assessment. It is at this juncture in the risk assessment for the site that we deviated from the typical approach. We elected to select final contaminants of concern (COCs) and carry them into the risk assessment based on two criteria: (1) detecting them in a media at or above the Dutch screening values (DTV); and (2) having sufficient toxicological data on the chemical for conducting the hazard (toxicity) assessment. There were limited toxicity data for both PF and no relevant Dutch screening values for PF. As a result, PF was not carried forward into the risk assessment, and thereby contributed to an uncertainty that may need to be addressed in future efforts. Chemicals that met the criteria above and which became final COCs were benzene, toluene, xylenes, ethylbenzene, chlorobenzene, 1,4-dichlorobenzene, and 1,2,4-trichlorobenzene.

3.4.1. Exposure Assessment

For non-sensitive land, the exposure rate calculations for carcinogenic and non-carcinogenic contaminants in soil and groundwater are shown in Supplemental Materials, Part A: Tables S3 and S4, respectively. The models for calculating exposure rates are found in Supplemental Materials—Part B1, and the values of the parameters used to calculate the exposure rate are listed in Supplemental Materials—Part C. As mentioned above, the values of the parameters applied to calculate the exposure rate were mostly those developed in the US, and as such they may not reflect exactly the characteristic of similar items in China. For example, they do not reflect building type and structure, and the types of soil, etc., found in China. In the future, those parameters will need to be developed and refined based on investigations and basic studies at the various contaminated waste sites in China.

3.4.2. Toxicity Assessment

The potential hazardous effects on human health via different exposure routes were analyzed, including those for carcinogens and non-carcinogens. This analysis also included an evaluation of dose-response associations and mechanisms of toxicity (hazard) for the COCs, as required and/or recommended by the Chinese guidelines. Toxicity parameters for carcinogenic effects include the inhalation unit risk (IUR), inhalation cancer slope factor (SFi), oral ingestion induced cancer slope factor (SFo), and dermal contact-induced cancer slope factor (SFd). The values of the toxicity parameters for carcinogenic effects for the COCs are shown in Supplemental Materials, Part A: Table S5. The SFi is obtained through extrapolation of IUR in Part B2; the SFd is obtained through extrapolation of SFo, also provided in Part B2.

The toxicity parameters for non-carcinogenic effects include the inhalation reference concentration (RfC), inhalation reference dose (RfDi), oral ingestion reference dose (RfDo), and dermal contact reference dose (RfDd). The values of the toxicity parameters for the non-carcinogenic effects of COCs are given in Supplemental Materials, Part A: Table S5. The RfDi and RfDd are also obtained through the Equations provided in Part B2. The toxicity values for contaminants in the new guidelines are limited, particularly for PF and 1,2,4-tricholorobenzene, which are both found at the site. It is expected that as China's national remediation program evolves, much of the data currently needed to refine these input values and support risk assessments will be obtained and incorporated into future regulatory guidelines.

The physical and chemical properties of COCs required for risk assessment calculations include the dimensionless Henry's constant (H'), air diffusion coefficient (Da), water diffusion coefficient (Dw), soil-organic carbon allocation coefficient (Koc), and water solubility (S). The values of the physical and chemical parameters of COCs are given in Supplemental Materials, Part A: Table S5. Other relevant parameters include the digestive tract absorption factor (ABSgi), skin absorption factor (ABSd), and the absorption factor for oral ingestion (ABSo).

3.4.3. Risk Characterization

Characterizing risks generally follows two approaches: the hazard quotient/hazard index, or a probabilistic approach. The Chinese guidelines provide some flexibility for this step in the risk assessment process. The risks are characterized by calculating the hazard quotient (HQ—systemic toxicity) and carcinogenic risk (CR) of COCs from samples (soils, groundwater, etc.) collected at the various sampling points. As shown in Supplemental Materials, Part A: Table S5, there are no recommended toxicity parameters for the potential carcinogenic effects of chlorobenzene. The results shown in Supplemental Materials, Part A: Tables S3 and S4, were then applied to the models needed for calculating the potential risks of the individual COCs. This included applying the results to the six exposure pathways for soils and three pathways for groundwater, as required, and are shown in Part B3.

The initial risk characterization was based on the previous results and are summarized in Table 4, which shows the concentration(s) for each COC that were applied to estimating risks. In this case, only the COCs in soils and groundwater at sampling location S4 were detected at levels above the Dutch DIV screening values. Unfortunately, the data set for this aspect of the risk characterization step was too limited for a more robust evaluation, and in the future and especially for larger and complicated sites, statistical methods will be needed for calculating more representative concentrations or ranges of concentrations of relevant COCs. This would also allow for calculating risk ranges, rather than single point estimates, something that is of interest to risk managers as they determine what action will be needed to protect human health and the environment.

Table 4. Contaminants of concern (COCs) concentrations applied for risk characterization at the Luhe site.

Parameter Symbol	Benzene	Toluene	Xylenes	Ethyl Benzene	Chloro Benzene	1,4-Dichloro Benzene	1,2,4-Trichloro Benzene
C_{sur}	0.025	0.025	0.025	10.4	1.64	2.03	1.46
C_{sub}	0	0	0	0	0	0	0
C_{gw}	0.123	0.0891	0.128	1.2	2.4	4.12	7.3

Notes: C_{sur}: Concentration of contaminants in Surficial soil, Unit: mg/kg; C_{sub}: Concentration of contaminants in Sub surficial soil, Unit: mg/kg; C_{gw}: Concentration of contaminants in Groundwater, Unit: mg/L.

The results of calculating HQ and CR are shown in Table 5. The guidelines define an acceptable risk as an HQ of 1 or less, while the acceptable level of CR (ACR) is 1.00×10^{-6} or less. The bold numbers in Table 5 highlight where the HQ or CR of an individual contaminant was greater than the acceptable risk level. In those instances, the guidelines indicate that the area where the contamination was found (around S4) should be designated as having an unacceptable risk. Among the nine different exposure routes evaluated, the groundwater consumption route was found to contribute most to the potential harm to human health for both non-carcinogenic and carcinogenic effects.

Figure 4 provides a relative contribution from the individual routes, taking 1,4-trichlorobezene as being representative of COCs. The recommended models that were used to develop these estimates are provided in Part B4. Dermal contact with soil (dcs) greatly contributes to the potential.

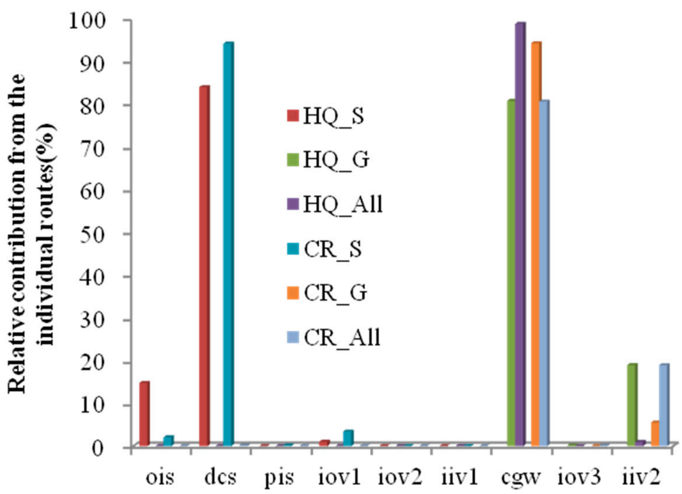

Figure 4. Relative contribution from the individual exposure routes (1,4-trichlorobenzene).

Table 5. Hazard quotient (HQ—systemic toxicity) and carcinogenic risk (CR) of contaminants for different potential human exposure routes at the Luhe site.

Parameter Symbol	Benzene	Toluene	Xylenes	Ethyl Benzene	Chloro Benzene	1,4-Dichloro Benzene	1,2,4-Trichloro Benzene
HQois	7.45×10^{-8}	6.05×10^{-6}	6.05×10^{-6}	6.29×10^{-4}	4.96×10^{-4}	1.75×10^{-4}	3.53×10^{-4}
HQdcs	2.15×10^{-4}	1.08×10^{-5}	4.30×10^{-7}	3.58×10^{-3}	2.82×10^{-3}	9.98×10^{-4}	5.02×10^{-3}
HQpis	2.33×10^{-7}	1.40×10^{-9}	7.00×10^{-8}	2.91×10^{-6}	9.19×10^{-6}	7.11×10^{-7}	2.04×10^{-4}
HQiov1	4.08×10^{-6}	2.45×10^{-8}	1.22×10^{-6}	5.09×10^{-5}	1.61×10^{-4}	1.24×10^{-5}	3.57×10^{-3}
HQiov2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HQiiv1	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HIn1	2.19×10^{-4}	1.68×10^{-5}	7.77×10^{-6}	4.26×10^{-3}	3.49×10^{-3}	1.19×10^{-3}	9.15×10^{-3}
HQcgw	1.86	6.74×10^{-2}	3.87×10^{-3}	7.26×10^{-1}	7.26	3.56	4.42×10
HQiov3	6.98×10^{-4}	3.28×10^{-6}	2.01×10^{-4}	2.31×10^{-4}	3.84×10^{-3}	2.44×10^{-4}	6.15×10^{2}
HQiiv2	1.03×10^{-1}	4.83×10^{-4}	2.96×10^{-2}	3.41×10^{-2}	5.66×10^{-1}	3.59×10^{-2}	1.06×10
HIn2	1.96	6.79×10^{-2}	3.36×10^{-2}	7.60×10^{-1}	7.83	3.60	6.70×10^{2}
CRois	5.78×10^{-10}	/	/	4.81×10^{-8}	/	4.61×10^{-9}	1.78×10^{-8}
CRdcs	1.82×10^{-9}	/	/	2.43×10^{-7}	/	2.09×10^{-7}	/
CRpis	3.79×10^{-12}	/	/	5.06×10^{-10}	/	4.34×10^{-10}	/
CRiov1	6.63×10^{-11}	/	/	8.84×10^{-9}	/	7.59×10^{-9}	/
CRiov2	0.00	/	/	0.00	/	0.00	/
CRiiv1	0.00	/	/	0.00	/	0.00	/
CRn1	2.47×10^{-9}	/	/	3.01×10^{-7}	/	2.22×10^{-7}	/
CRcgw	2.84×10^{-5}	/	/	5.55×10^{-5}	/	9.35×10^{-5}	8.89×10^{-4}
CRiov3	1.13×10^{-8}	/	/	4.01×10^{-8}	/	1.49×10^{-7}	/
CRiiv2	1.67×10^{-6}	/	/	5.91×10^{-6}	/	2.19×10^{-5}	/
CRn2	3.01×10^{-5}	/	/	6.14×10^{-5}	/	1.16×10^{-4}	/

Notes: /: no calculated value existed; HQois: HQ for route of Oral Ingestion of Soil (ois), Dimensionless; HQdcs: HQ for route of Dermal Contact of Soil (dcs), Dimensionless; HQpis: HQ for route of Inhalation of Soil Particles (pis), Dimensionless; HQiov1: HQ for route of Inhalation of contaminant vapor in outdoor air from surficial soil (iov1), Dimensionless; HQiov2: HQ for route of Inhalation of contaminant vapor inoutdoor air from Sub surficial soil (iov2), Dimensionless; HQiiv1: HQ for route of Inhalation of contaminant vapor in Indoor air from Sub surficial soil (iiv1), Dimensionless; HIn1: The hazard index (HI) for all exposure routes in soil, Dimensionless; HQcgw: HQ for route of groundwater ingestion (cgw), Dimensionless; HQiov3: HQ for route of inhalation of contaminant vapor in Outdoor air from Groundwater (iov3), Dimensionless; HQiiv2: HQ for route of inhalation of contaminant vapor in Indoor air from Groundwater (iiv2), Dimensionless; Hin2: HI for all routes in Groundwater, Dimensionless; CRois: CR for route of ois, Dimensionless; CRdcs: CR for route of dcs, Dimensionless; CRpis: CR for route of pis, Dimensionless; CRiov1: CR for route of iov1, Dimensionless; CRiov2: CR for route of iov2, Dimensionless; CRiiv1: CR for route of iiv1, Dimensionless; CRn1: The total CR for all exposure routes in soil, Dimensionless; CRcgw: CR for route of cgw, Dimensionless; CRiov3: CR for route of iov3, Dimensionless; CRiiv2: CR for route of iiv2, Dimensionless; CRn2: The total CR for all routes in Groundwater, Dimensionless.

The total risk among all soil exposure routes was as high as 84.10% on an HQ basis (HQ_S in Figure 4) and 94.30% on a CR basis (CR_S in Figure 4). For the three routes associated with exposure to groundwater ingestion, cgw contributes the largest portion (80.89%) on an HQ basis (HQ_G in Figure 4), and 94.41% on a carcinogenic risk basis (CR_G in Figure 4). Considering all nine exposure routes, the contribution from groundwater consumption (cgw) is the most significant (98.96 of HQ_All basis and 80.73 of CR_All). These results clearly illustrate that the potential for risk to humans from consuming contaminated groundwater could be problematic, and should be addressed in any proposed risk management actions.

3.4.4. Calculating Risk Control Values

The guidelines provide steps for calculating risk control values, which are those values that will be used to determine the level of remediation that might be required for sites where unacceptable risks have been estimated. Calculating soil and groundwater risk control values, based on non-carcinogenic and carcinogenic effects, follows the same process as noted for estimating risks (either HQ or CR). An acceptable HQ for an individual COC is 1 or less, and for the CR of an individual contaminant, the acceptable level is 10×10^{-6} or less. The recommended models for calculating soil and groundwater risk control values are given in Supplemental Materials—Part B4 and the relevant parameter values are given in Supplemental Materials—Part C.

The calculated risk control values for soil and groundwater based on non-carcinogenic and carcinogenic effects are shown in Table 6. When determining the soil and groundwater remediation target values at the contaminated site, the soil and groundwater risk control values should be calculated as primary reference values based on the risk assessment model. The calculated soil risk control values based on non-carcinogenic and carcinogenic effects, and groundwater risk control values based on non-carcinogenic and carcinogenic effects, are then compared (Table 6). The bold numbers are the risk control values of individual contaminants for soil and groundwater at the Luhe site, respectively. This comparison indicates that the soil remediation target value, as well as the cleanup value for ethylbenzene, is 1.65 mg/kg, and that the groundwater remediation target value is 2.15×10^{-2} mg/L. For benzene, ethylbenzene, and 1,4-dichlorobenzene, the risk control values were calculated based both on non-carcinogenic and carcinogenic effects (Table 6). These results show that the risk control values based on non-carcinogenic effects are almost two orders of magnitude higher than the risk control values based on carcinogenic effects.

Table 6. Risk control values of soil and groundwater based on non-carcinogenic effects and carcinogenic effects at the LuHe site.

Parameter Symbol	Benzene	Toluene	Xylenes	Ethyl Benzene	Chloro Benzene	1,4-Dichloro Benzene	1,2,4-Trichloro Benzene
HCVSois	6.61×10^{2}	1.32×10^{4}	3.31×10^{5}	1.65×10^{4}	3.31×10^{3}	1.16×10^{4}	1.65×10^{3}
HCVSdcs	1.16×10^{2}	2.33×10^{3}	5.81×10^{4}	2.91×10^{3}	5.81×10^{2}	2.03×10^{3}	2.91×10^{2}
HCVSpis	2.02×10^{8}	3.36×10^{10}	6.73×10^{8}	6.73×10^{9}	3.36×10^{8}	5.38×10^{9}	1.35×10^{7}
HCVSiov1	1.15×10^{7}	1.92×10^{9}	3.85×10^{7}	3.85×10^{8}	1.92×10^{7}	3.08×10^{8}	7.70×10^{5}
HCVSiov2	1.13×10^{6}	2.65×10^{8}	9.75×10^{6}	9.23×10^{7}	5.99×10^{6}	2.51×10^{8}	7.45×10^{3}
HCVSiiv1	3.32×10^{5}	5.12×10^{7}	1.20×10^{6}	9.78×10^{6}	1.18×10^{6}	3.19×10^{7}	2.24×10
HCVSn	9.88×10	1.98×10^{3}	4.72×10^{4}	2.47×10^{3}	4.94×10^{2}	1.73×10^{3}	2.04×10
HCVGcgw	2.45×10^{3}	5.75×10^{5}	2.12×10^{4}	2.00×10^{5}	1.30×10^{4}	5.45×10^{5}	1.62×10^{5}
HCVGiov3	2.25×10^{3}	3.47×10^{5}	8.16×10^{3}	6.64×10^{4}	8.00×10^{3}	2.16×10^{5}	1.30×10^{3}
HCVGiiv2	6.25×10^{-1}	1.16×10	3.39×10^{2}	1.38×10	6.65	3.93×10	1.35×10
HCVGn	6.61×10^{-2}	1.32	3.29×10	1.65	3.31×10^{-1}	1.16	1.65×10^{-1}
RCVSois	4.33×10	/	/	2.16×10^{2}	/	4.41×10^{2}	8.21×10
RCVSdcs	7.61	/	/	3.81×10	/	7.75×10	1.44×10
RCVSpis	2.58×10^{4}	/	/	3.16×10^{5}	/	7.17×10^{4}	/
RCVSiov1	1.48×10^{3}	/	/	1.81×10^{4}	/	4.10×10^{3}	/
RCVSiov2	1.44×10^{2}	/	/	4.33×10^{3}	/	3.34×10^{3}	/
RCVSiiv1	3.13×10^{-1}	/	/	9.40	/	7.26	/
RCVSn	3.00×10^{-1}	/	/	7.52	/	6.61	1.44×10
RCVGcgw	4.25×10	/	/	4.59×10^{2}	/	4.24×10^{2}	/
RCVGiov3	2.88×10^{-1}	/	/	3.11	/	2.88	/
RCVGiiv2	3.05×10^{-2}	/	/	2.16×10^{-2}	/	8.48×10^{-2}	/
RCVGn	4.26×10^{-3}	/	/	2.15×10^{-2}	/	4.34×10^{-2}	8.21×10^{-3}

Notes: /: no calculated value existed; HCVSois: Soil risk control values based on non-carcinogenic effects (HCVS) through routes of ois, Unit: mg/kg; HCVSdcs: HCVS through routes of dcs, Unit: mg/kg; HCVSpis: HCVS through routes of pis, Unit: mg/kg; HCVSiov1: HCVS through routes of iov1, Unit: mg/kg; HCVSiov2: HCVS through routes of iov2, Unit: mg/kg; HCVSiiv1: HCVS through routes of iiv1, Unit: mg/kg; HCVSn: HCVS through all the above six routes in soil, Unit: mg/kg; HCVGcgw: Groundwater risk control values based on non-carcinogenic effects (HCVG) through routes of cgw, Unit: mg/L; HCVGiov3: HCVG through routes of iov3, Unit: mg/L; HCVGiiv2: HCVG through routes of iiv2, Unit: mg/L; HCVGn: HCVG through all the above three routes in groundwater, Unit: mg/L; RCVSois: Soil risk control values based on carcinogenic effects (RCVS) through routes of Oral Soil Ingestion, Unit: mg/kg; RCVSdcs: RCVS through routes of dcs, Unit: mg/kg; RCVSpis: RCVS through routes of pis, Unit: mg/kg; RCVSiov1: RCVS through routes of iov1, Unit: mg/kg; RCVSiov2: RCVS through routes of iov2, Unit: mg/kg; RCVSiiv1: RCVS through routes of iiv1, Unit: mg/kg; RCVSn: RCVS through all the above six routes in soil, Unit: mg/kg; RCVGcgw: Groundwater risk control values based on carcinogenic effects (RCVG) through routes of cgw, Unit: mg/L; RCVGiov3: RCVG through routes of iov3, Unit: mg/L; RCVGiiv2: RCVG through routes of iiv2, Unit: mg/L; RCVGn: RCVG through all the above three routes in groundwater, Unit: mg/L.

The acceptable carcinogenic risk (ACR) of an individual contaminant for humans is 1.00×10^{-6} in the new guidelines, and perhaps deserves some reflection. For example, as China is still developing and working to undertake remediation at multiple sites around the country, one might consider whether an ACR of 1.00×10^{-6} is an appropriate value to apply at this time. Similar to remedial policies, regulations, and guidelines that began and evolved in the US and Europe, the current guidelines in China are likely to be revised over time, and it could be that setting a less stringent ACR at this time might allow more sites to be addressed, and in a shorter time period, than might be the case with a more stringent ACR. An ACR range of 1.00×10^{-4} to 1.00×10^{-5} has been applied generally for industrial sites in other countries, thus providing a less stringent but more financially practical approach. In addition, at this time, the guidelines only provide a single point estimate of potential exposure, rather than ranges or statistically-based estimates. As the experience base in remediating sites in China grows, a risk-range could be considered in determining what will be the appropriate risk control values, as well as the cleanup number, in the future.

4. Summary and Conclusions

Our work over the past three years at the Luhe site, China, has provided a useful and insightful platform for piloting contaminated site investigations, evaluating potential remedial options, and more importantly, an initial test of the new guidelines for addressing contaminated waste sites.

The Luhe site belongs to "non-sensitive land", and our application of the guidelines in this effort gave us an opportunity to determine how they perform at this relatively small site. Topic areas where the guidelines may benefit from additional work include: Future Land Use and Exposure Scenarios, co-located Contaminated Sites, Receptors (children and adults), country-specific Exposure and Screening Values, and Risk-Control Values.

4.1. Future Land Use and Exposure Scenarios

For non-sensitive land, exposures are only focused on adults, resulting in uncertainty with respect to potential harm that might arise from children that might or could frequent the site and thereby be exposed to contaminants. This is especially important given the situation at the site. Despite the site being categorized as "non-sensitive" land, we observed children using a road that went through the former site, and while not observed by us directly, could also indicate that children might also play on the former site. In addition, we observed small vegetable gardens being grown along the site. In this case, there is no provision to consider exposures through vegetables, whether for children or adults. Future revisions to the guidelines would benefit from including the flexibility to modify exposure scenarios based on direct observations at a site, especially if some portions of the "non-sensitive" land will continue to be used by children and for growing vegetables to supplement the diets of nearby residents. Because children can be more sensitive receptors, and are not included in the current guidelines, the guidelines are not sufficiently protective, something which should be corrected in the future.

4.2. Co-Located Contaminated Sites

Undertaking investigations and remediation at a contaminated site that is adjacent to another potentially contaminated site is an issue that is not unique to the site, or China for that matter. At some sites, it is not unusual to find contaminants in soil, groundwater, etc., that cannot be explained on the basis of the past operating history. The question then arises as to the source of the contamination, and who is responsible for dealing with it. Provisions in the US Superfund legislation and regulations [16] allow for investigating the potential for contaminant migration off of the site in question. Where contamination is found off-site, and clearly originates from the site under investigation, responsible parties are then obligated to continue the investigation until the contaminant levels drop to acceptable levels, or to some other pre-determined endpoint. In this case, information on potential impacts at nearby sites can be collected indirectly and evaluated. Where contaminants are found to originate from a nearby site, the owners of the nearby site then become potentially liable for addressing that contamination in connection with the work ongoing at the site under study. In our case, we observed another manufacturing site adjacent to the Luhe site, which may or may not be contributing to some of the contamination we found in soils and groundwater. The potential for this situation to occur, and how to address it, will likely require evaluation by the Chinese government.

4.3. Receptors

Our investigation provided information sufficient to develop an initial site conceptual model for the Luhe site, which helped to illustrate the various exposure pathways and receptors potentially at risk. It is noteworthy that there are no provisions in the current guidelines to include ecological receptors in the conceptual model, and as yet, none either for estimating risks to ecological receptors, regardless of the current or future use of the site. We also observed that there were no provisions to account for potential risks to groundwater itself, except for the potential for humans to be exposed to contaminants through the ingestion of contaminated groundwater. Where groundwater might connect to and be expressed in surficial water bodies, there is no provision for addressing the risks associated with this situation.

4.4. Country-Specific Exposure and Screening Values

Having technically-sound, risk-based, and country-specific screening values for soils, sediments, groundwater, etc., is another area that could require further work. This is also an area not unique to the Luhe site, or to China. It is understandable that for the time being, risk assessors will need to rely on toxicological and risk-based information already developed in other geographical regions. For the Luhe site, we were able to utilize information from The Netherlands, the US (IRIS database), and other countries, that allowed the risk assessment to proceed, albeit with the caveat that some aspects of this approach could benefit from China-specific information. It is reasonable to expect that China-specific screening, exposure, toxicological, and risk control values will be developed in the future, and similar to those in the US and Europe, undergo periodic revision as experience is gained over time.

4.5. Risk-Control Values

Perhaps one of the most vexing policy issues in national environmental or remediation programs is the level of protection that has been chosen for humans and ecological receptors. Despite over 30 years of remedial activities within the US, the debate on what level of protection should be afforded to humans and ecological receptors continues. This has been true for the 1×10^{-6} (one in a million) cancer risk level set for humans, which some believe is too conservative and others might see as too lenient [17]. In this paper, we called attention to the level of protection (1×10^{-6}) selected for humans working on or using non-sensitive sites where carcinogens have been detected. Given the current status of the national remediation program in China, we posed the question as to whether the 1×10^{-6} cancer risk level is an appropriate one, or is something that merits further discussion among policy makers, medical professionals, or other interested groups. Similar to the summary points we have mentioned already, the answer to this question rests with the Chinese government as it is a policy decision and not a technical one.

In conclusion, the work at the Luhe site has allowed us to highlight some of the more prominent issues that may require further evaluation and discussion within the Chinese government and regulatory communities. Taken collectively, the disadvantages in the new guidelines do not suggest that they need to be completely revised, but in their current form, they provide a good starting point for developing a qualitative and quantitative risk assessment system for contaminated waste sites in the nation. As more investigations and risk assessments are completed, and more remedial action experience is gained in China, the current guidelines can be revised and updated to reflect that new knowledge and experience. For that reason, these guidelines, like similar ones in the US, The Netherlands, the United Kingdom, and elsewhere, should be subject to revision on a periodic basis. It is also possible that as technical staff in the Chinese regulatory community become more experienced in contaminated site investigations, risk assessments, and evaluating remedial options, they will have the flexibility to consider each contaminated waste site on a case-by-case basis, and thus accommodate the variability in the sites across the nation.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4441/9/9/657/s1, Part A:Tables, Table S1: Lab analytical method for investigations at the Luhe site, China., Table S2: Heavy metals of soil samples in garden plot at the Luhe site, Nanjing, China (Unit: mg/kg in dry weight), Table S3: Calculation of Exposure rate based on non-carcinogenic effects of COCs at the Site, Table S4: Calculation of Exposure rate based on carcinogenic effects of COCs at the Site, Table S5: Toxicity parameters of COCs at the Site., Table S6: Physical and chemical properties, and other relevant parameters for COCs at the Site; Part B: Models, Part B1: Models for calculating exposure rate based on non-carcinogenic effects and carcinogenic effects, Part B2: Models for toxicity assessment, Part B3:Models for calculation of hazard quotient and carcinogenic risk, Part B4: Models for calculating risk control values based on non-carcinogenic effects and carcinogenic effects, Part B5: Models for analysis on risk exposure contribution; Part C: Risk-based Parameters and values; Part D: List of other Risk-based Parameters.

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