Risks of airborne pollution accidents in a major conurbation: Case study of Zhangjiakou, a host city for the 2022 Winter Olympics

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Abstract: The number of airborne pollution accidents is second only to that of water-borne pollution accidents, in recorded environmental disasters. Acute casualties and public health costs have prompted many airborne pollution risk analyses. To date, few assessment methods have been carried out at regional-scale to quantify acute airborne pollution risk. Herein, a Hybrid Simulation and Risk Analysis (HSRA) approach, involving a systematic combination of simulation, risk ranking, and standardized analysis, is proposed at regional scale. Gaussian and heavy-gas models are utilized in the simulation process, and acute exposure limits preferentially adopted in the risk analysis. The case study shows that 34 of 243 townships in Zhangjiakou City of north China, one of the twin cities selected to host the 2022 Winter Olympics, are threatened by airborne risk sources. It is found that the accidental air pollution risk is comparatively higher in the Xuanhua and Wanquan conurbations. High-risk chemical enterprises (312-432 risk scores) are mostly located near urban areas with high population density where many people are vulnerable receptors to potential air pollution accidents. The resulting risk map indicates that acute airborne pollution from Zhangiiakou would not be a threat either to the proposed Olympic site at Chongli or to downwind Beijing.

Keywords: acute airborne pollution; environmental risk assessment; pollution accidents; public health; simulation

1. Introduction

Accidental pollution events occur relatively frequently in both developing and developed countries. Air pollution accidents rank the second among recorded environmental disasters. In the United States, air and water pollution accidents comprised 17% and 79% respectively of the total number of reported environmental emergencies in 2014 (NRC 2015). In China, the Ministry of Environmental Protection responded directly to 377 reported air pollution accidents over the past decade (China MEP 2006-2015), corresponding to 35% of the total number of environmental emergencies in the country. Worldwide, chemical releases into the atmosphere have caused considerable numbers of acute casualties and/or long-term health effects. In 1976, the Seveso disaster in Italy caused several hundred people to suffer chloracne and 3,300 small animals to die through the accidental release of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) from a chemical plant into the atmosphere, and approximately 80,000 animals were slaughtered to stop TCDD entering the food chain (Homberger et al. 1979). In 1984, at least 3,787 residents were killed, and more than 558,125 citizens suffered impaired health, by a leak of methyl isocyanate (MIC) gas from the Union Carbide India Ltd pesticide plant in Bhopal, India (BGTRRD 1985). In 2003, 243 people were killed and over 27,000 residents poisoned by hydrogen sulfide after a natural gas blowout accident in Kai County, Chongqing, China (China SCOEM 2005). In 2005, a leak of liquid chlorine from a crashed tanker in Huai'an, Jiangsu Province, China, killed 29 people, injured 436 people, and led to the evacuation of 10,000 people (JCX 2005). Obviously, such accidents can cause major societal and economic losses. Effective tools are thus needed to support the identification and evaluation of potential airborne pollution scenarios and the associated risks.

In the aftermath of toxic gas disasters, numerous scientific studies have been carried out on air pollution risk analysis. The European Seveso Directive (CEC 1982) and US four-step risk analysis (NRC 1983) identified and evaluated major-accident hazards for a particular dangerous substance. Accidental releases of toxic gases have been the focus of studies since the early 1980s (Pontiggia et al. 2010). Dispersion modelling, used to estimate exposure and assess the possible consequences of a gas release, provides an essential link between hypothesized accidental airborne release scenarios with regard to loss of lives and properties, and forms a critical element of risk analysis and management (Khan & Abbasi 1999). Various models, such as Gaussian model, heavy-gas model, Lagrangian particle diffusion model, and Computational fluid dynamics (CFD) 3-D models, are available to simulate concentrations and exposure durations of hazardous gas releases (Mazzola & Addis 1995; Bernatík et al. 2008; Baumann-Stanzer & Stenzel 2011; Barratt 2013). During the modelling process, it is necessary to distinguish whether the discharging gases are heavier or lighter than air (Bluett 2004). Software tools, such as ARCHIE (EFMA 1989), SLAB (Ermark 1990), DEGADIS (Havens & Spicer 1985), TRACE (SAFER Systems 1996; Hanna et al. 2008), UDM (Witlox and Holt 1999), HAZDIG (Khan and Abbasi 1999), ALOHA (Bubbico & Mazzarotta 2008; Jones et al. 2013), and SCIA (El Harbawi et al. 2008), have been widely used to model accidental airborne chemical spills. Of these, ARCHIE is designed for neutrally buoyant gases, SLAB, DEGADIS, TRACE and UDM for dense gases, and HAZDIG, ALOHA and SCIA for both. Various national exposure guidelines exist to evaluate airborne exposure levels and estimate the potential severity of accidents, but each guideline covers only a limited

number of hazardous chemicals (Planas et al. 2006). In the United States, the Department of Energy (DOE) uses Acute Exposure Guideline Levels (AEGLs) (NRC 2001; 2009), Emergency Response Planning Guidelines (ERPGs) (AIHA 2006), and Temporary Emergency Exposure Limits (TEELs) (Handbook DOE 2008), in that priority order, as the emergency exposure limits. Besides, Protective Action Criteria (PAC) (DOE 2016) specify levels of radioactive or chemical materials that threaten or endanger the health and safety of workers or the public, and are based on a dataset comprising the list of chemicals with 60-minute AEGL, ERPG, and /or TEEL values. Immediately Dangerous to Life or Health Values (IDLH) (NIOSH 2014) and the median lethal concentration (LC₅₀) have only one standard threshold, and can also be used as acute exposure limits in the absence of chemical data related to AEGLs, ERPGs, and TEELs (Chen et al. 2012).

Based on the foregoing dispersion models and exposure criteria, several accidental airborne risk analyses have been performed using overlay methods for stationary chemical plants (El Harbawi et al. 2008; Ma et al. 2012; Meng et al. 2014; Ghasemi et al. 2016), and population vulnerability analysis (Sebos et al. 2010; Anjana et al. 2018), societal risk measures (Hu 2009), matrix methods (Shao et al. 2013), and ranking-based matrix methods (Ma et al. 2015) for chemical industry parks. Accurate, quantitative risk assessments can be obtained from such simulation-based risk analyses of airborne pollution accidents, though the results are spatially limited to small areas, such as industrial parks. Further accidental airborne risk analyses have been performed at large regional-scale for natural gas pipelines using qualitative multi-criteria models (Brito et al. 2010; Alzbutas et al. 2014) and individual/societal risk measures (Jo & Ahn 2005; Han & Weng 2011), and relative risk assessment for a city (Li et al. 2014). Without detailed simulation of gas releases, these risk analyses are unable to present precise, quantitative results. Moreover, to the authors' knowledge, few analyses have been carried out on acute air pollution risk at regional scale, using dispersion models and considering pathways that involve multiple hazards and receptors. Rather more research effort has focused on chronic/accumulative air pollution risk analysis (Gurjar et al. 2010; Ragas et al. 2011; Mckenzie et al. 2012; Ishii & Yamamoto 2013; Winters et al. 2015; Wang et al. 2015; Sak et al. 2017).

The authors have previously suggested a regional-scale risk analysis method for water-borne pollution accidents (Liu et al. 2015, 2017; Dong et al. 2017), involving multiple hazards and receptors, and addressing the complicated interactions between these components. To fill the knowledge gap in regional-scale risk analysis for airborne pollution accidents at regional scale, we propose a hybrid simulation and risk analysis (HSRA) Approach. The method involves a systematic combination of a simulation process, risk ranking, and standardized analysis. Gaussian and heavy-gas models are used to simulate a hazardous gas release. In the risk analysis, acute exposure limits are preferentially adopted, and the maximum exposure distance determined. Using a ranking combination of hazard, vulnerability, exposure, and effect for acute airborne pollution accidents, multiple levels of risk are readily identified and evaluated. The method is designed to be effective as a decision-making support tool at regional-scale. The study area, Zhangjiakou City, is located in northwest Hebei Province. In addition to a large number of mine tailings ponds (Liu et al. 2015), there are many chemical enterprises sited in Zhanjiakou. The sudden release of airborne pollutants could threaten a local population of 4.68 million people, and even endanger downwind Beijing which is inhabited by 21

million citizens. Moreover, Zhangjiakou City has been selected as a host venue for the 2022 Winter Olympics. Therefore, it is important to ascertain whether acute airborne pollution from Zhangjiakou is a threat to the recommended Olympic site at Chongli or to downwind Beijing. We use HSRA to analyze acute airborne pollution hazards, residents' vulnerability and exposure to airborne toxic pollutants, and the overall risk posed to Zhangjiakou City, especially to the Olympic site. The risk map is vital to the urban development plan and to the air pollution risk management strategy, the latter involving prevention, preparation, early warning, and emergency response measures for Zhangjiakou City.

2. Methodology

Hybrid simulation and risk analysis (HSRA, which incorporates the interactions between multiple hazards and receptors, is designed to assess combined risk by integrating multiple "source-receptor-endpoint" (Liu et al. 2015) risk routes at regional scale (covering a prefecture, a province, even a nation). The new method comprises the following key procedures: airborne hazard and receptor vulnerability analyses using multi-criteria methods, simulation of fate and transport of hazardous/toxic gases using Gaussian and heavy-gas models, and airborne risk evaluation for sub-regions using a risk-ranking method combined with GIS tools. Uncertainty analysis is undertaken after the risk ranking has been established by Monte Carlo simulation.

2.1 Airborne hazard and vulnerability analyses

Generally speaking, HSRA focuses on stationary sources mostly related to industrial enterprises which produce, utilize, transport, or store hazardous/toxic airborne chemicals. Mobile sources (e.g. vehicles that transport chemicals) are excluded because of the inherent difficulty encountered to date in incorporating such hazards into the overall risk for a geographical region. The industrial enterprises hazard qualitatively describes the likelihood and severity of abrupt pollution occurrences, determined by the quantity of hazardous substances, production process safety, and risk control. Considering the inherent hazard of stressors and the operability of assessment, a risk ranking matrix, adapted from China MEP (2014), is used to evaluate the airborne hazard due to releases from industrial enterprises. The ranking matrix is determined through expert judgment, according to the ranking practices of over 40,000 national inspection records of Environmental Risk and Chemicals in Enterprises of Key Industries in China in 2010; this is jointly determined by the quotient (Q) of stock quantity to threshold quantity of hazardous substances, and the management level (M) which is related to the production process and its risk control (see Table 1). Q is the sum of each single hazardous substance quotient, which is given as:

$$Q = \frac{q_1}{Q_1} + \frac{q_2}{Q_2} + \frac{q_3}{Q_3} + \frac{q_4}{Q_4} + \cdots$$
 (1)

where q_x is the stock quantity of each hazardous substance and Q_x stands for the threshold quantity of a certain hazardous substance. Any unit storing an amount of substance above Q_x is defined as a major hazard source. M is a linear combination of four ranking criteria related to production technology, safety production control, risk prevention and control,

and the environmental emergency plan. These ranking elements are derived from risk investigation results obtained for the relevant chemical enterprises. Taking the safety production control factor as an example, in each chemical enterprise, information from four sets of ingredient documents comprising the fire prevention certificate, the permit relating to safe production, the safety assessment of hazardous chemicals, and records of major risk sources of chemical substances, is ranked according to China MEP (2014). Both Q and M are divided into 4 intervals: with the divisions set at 1, 10 and 100 for Q, and 25, 45 and 60 for M. The scale of hazard values ranges from 0 to 10, and is relative and dimensionless. The foregoing information or data are derived from the results of risk investigations carried out for the relevant industrial enterprises.

Table 1. Airborne hazard ranking matrix for industrial enterprises*

	M					
Q -	M ≤ 25	$25 < M \le 45$	45< M ≤ 60	M > 60		
Q < 1	2	2	4	6		
$1 \le Q < 10$	2	4	6	8		
$10 \le Q < 100$	4	6	8	10		
$Q \ge 100$	6	8	10	10		

^{*}Adapted from Guidebook for Environmental Risk Assessment of Accidents in Enterprises (China MEP 2014).

According to Woodman & Cowling (1987) and U.S. EPA (1986, 1998, 2003), airborne pollutants cause deleterious health effects to human beings and the ecosystem. Risk receptors that might potentially be exposed to an acute airborne pollution hazard can be categorized into three groups: human, ecosystem and agricultural economy receptors. These are denoted respectively as assessment endpoints of resident safety, ecosystem health, and property safety. The short-term, acute influence on receptors is of primary concern when toxic or harmful gases are suddenly released by accident. Three grades of 6, 4, and 2, are used to rank receptor vulnerability to acute air pollution, in accordance with national criteria or expert judgments (listed in Table 2). Human vulnerability is simply ranked according to homogeneously distributed pattern of population density (per person per km²); the larger the number of people potentially exposed the greater the vulnerability to acute air pollution hazard. Sensitive ecosystems comprise ecological nature reserves, scenic resorts, and forest parks; their vulnerability relates to their protection status. Potential economic loss caused by acute air pollution mainly affects croplands, orchards, and livestock and poultry farms; larger agricultural outputs are associated with higher level of vulnerability.

Table 2. Vulnerability ranking criteria for risk receptors

	6	4	2
Human	Population density	500/km ² < Population	Population density
пишап	$> 1000/km^2$	density $\leq 1000/\text{km}^2$	$\leq 500/\mathrm{km}^2$
Ecosystem	National level	Provincial level	Prefecture level
Agricultural	Total outputs	10,000 tons <total< td=""><td>Total outputs</td></total<>	Total outputs

2.2 Simulation of fate and transport of toxic pollutants

In accidental release situations, hazardous/toxic gases escape as jets from liquefied or compressed liquid/chemical solution containers or evaporate from liquid pools or cofferdams. Such gases can be classified as either neutrally buoyant or dense according to their excess density, specific volume, and environmental conditions. The critical Richardson number Ri_c is used to distinguish these two kinds of gases (Spicer & Havens 1989). Depending on the density of the pollutant, the wind speed, and the release rate, the critical Richardson number is given by,

$$Ri_c = \frac{H^*}{U_*^2} \frac{g(\rho - \rho_a)}{\rho_a} \tag{2}$$

where H_* is the characteristic dimension of the source, U_* is the wind friction velocity, ρ is pollutant density, ρ_a is the ambient air density, and g is the acceleration of gravity. For $Ri_c < 1$, a gas is considered to be neutrally buoyant, otherwise it is considered dense.

Two atmospheric dispersion models, the Gaussian dispersion model and the heavy-gas model were used to simulate the concentration distributions and exposure durations of accidental releases of neutrally-buoyant and dense gases, respectively (Mazzola& Addis 1995). The Gaussian dispersion model (Palazzi 1982) is given as

$$c_w^i(x, y, 0, t) = \frac{2Q'}{(2\pi)^{3/2} \sigma_x \sigma_y \sigma_z} \exp\left(-\frac{H_e^2}{2\sigma_z^2}\right) exp\left\{-\frac{(x - x_w^i)^2}{2\sigma_x^2} - \frac{(y - y_w^i)^2}{2\sigma_y^2}\right\}$$
(3)

where $c_w^i(x,y,o,t)$ is the ground-level concentration of the *i*-th vapor cloud at time *t*; He is the emission height, Q' is the volumetric emission of a vapor cloud such that $Q'=QT_R$, where Q is the emission rate and T_R is the duration of the release; x and y are the coordinates of the location of interest in the downwind and horizontal crosswind directions, x_w^i and y_w^i are the coordinates of the *i*-th vapor cloud source; and σ_x , σ_y , and σ_z are effluent dispersion parameters in the x, y, z directions, z being vertical.

When large quantities of dense toxic gas are rapidly released to the atmosphere, the heavy-gas model applies (Cox & Carpenter 1979), such that,

$$\frac{dR}{dt} = K \left(gh \frac{\rho - \rho_a}{\rho_a} \right) \tag{4}$$

where R is the exposure radius, t is the time after slumping has started, and K is a constant.

ALOHA (Areal Location of Hazardous Atmospheres, http://response.restoration.noaa.gov/aloha) is open software developed in the US jointly by the National Oceanic and Atmospheric Administration (NOAA) and the Environmental Protection Agency (EPA). ALOHA includes physical, chemical, and toxicological properties of pure chemicals and some common chemical solutions, and simulates accidental release scenarios using Gaussian neutral gas and heavy gas dispersion models. Breeze Incident Analyst (http://www.breeze-software.com/incidentanalyst/) is commercial software distributed by Trinity Consulting, and incorporates DEGADIS and SLAB dense-gas dispersion models,

and AFTOX and INPUFF Gaussian puff models. Breeze Incident Analyst is commonly used by environmental professionals to analyze the effects of air pollutant emissions and explosions. As well-established software tools, ALOHA and Breeze Incident Analyst are selected herein.

In practice, standard acute exposure limits, including AEGLs, ERPGs, and TEELs, are used as protective action criteria to assess the severity of an event involving an accidental chemical release and to devise appropriate emergency response procedures (Chen et al. 2012). AEGLs describe human health effects from rare (e.g. once-in-a-lifetime) exposure to airborne chemicals, and have been set by the U.S. Environmental Protection Agency. ERPGs recommended by the American Industrial Hygiene Association (AIHA) are used to help protect the public in the absence of AEGLs when a short-term chemical release occurs; ERPGs can be used to identify hazardous areas where a threshold concentration of toxic gas is exceeded for specified exposure duration. AEGLs and EPRGs are expressed in terms of three severity levels (1 for mild, transient effects; 2 for irreversible effects or where the ability to escape is impeded; and 3 for life-threatening effects). The dispersion of hazardous and toxic gases, under the most severe conditions of atmospheric stability class F (Pasquill 1961) and wide aperture (100 mm) leakage, is simulated using the models mentioned above. For any single risk route, the fate of hazardous and toxic gases (released from the source) weights the probability that such gases propagate to the receptor, thus producing a quantitative estimate of the complicated interactions between multiple hazards and receptors. An exposure filter (Wiegers et al. 1998) is assigned ranks 0, 0.5, or 1 to indicate low, medium, or high exposure probability. The effect filter is evaluated according to the probability that airborne exposure to the receptor causes the effect to reach a given endpoint (see Table 3).

Table 3. Effect filters for different receptors and endpoints

	Specific risk receptors					
Endpoints	Residential	Cropland,	Livestock and	Nature reserve	Scenic	Forest park
_	land	Orchard	poultry farm	Nature reserve	resort	rofest park
Resident safety	1	0	0	0	0	0
Property resilience	0.5	1	1	0	0	0
Ecosystem health	0	0.5	0	1	1	1

2.3 Airborne risk evaluation

In order to evaluate the combined acute air pollution risk, a township is treated as a sub-region, a convenient scale in terms of societal statistics and the geographical scale of plume dispersion after an acute air pollution release. The hazard ranking (H), vulnerability ranking (V), exposure filter (Ex), and effect filter (Ef) are multiplied together to calculate a risk route score (following Liu et al. 2015, 2017). The relative risk score (RS) of airborne pollution accidents in a sub-region (township) is determined by integrating all risk routes which end within the same township, in the context of receptor-oriented risk assessment. The interval breaks are determined using the Equal Interval classification method (Zald et al. 2006) placing the entire range of risk values (i.e. 75, 150, and 300) into three, equal-sized categories (low, medium and high). The relative risk score is thus defined as

$$RS_i = \sum_{i=1}^n H_{ij} \times V_{il} \times Ex_{il} \times Ef_{lm}$$
 (5)

where RS_i means the relative risk value of the *i*-th sub-region series (sub-region 1, 2, 3, etc.), H_{ij} is the hazard level of *j*-th risk source in the *i*-th sub-region series, V_{il} is the vulnerability level of the *l*-th risk receptor in the *i*-th sub-region series, Ex_{jl} is the exposure coefficient between risk source *j* and receptor *l*; and Ef_{lm} is the effect coefficient between receptor *l* and endpoint *m*. With the help of ArcGIS tools, spatial locations and scales of risk sources and risk receptors are extracted, and the overall risk of accidental air pollution mapped at regional-scale.

Uncertainty analysis is absolutely necessary in risk assessment process. Uncertainty arises from poor quality or unavailable data, which affect the derived source and receptor ranks, and exposure and effect filters (see Liu et al. 2017). Landis (2005) recommends use of Monte Carlo simulation to generate a distribution of probable risk predictions for each sub-region instead of a single point estimate (i.e. a sub-region risk score). In the present work, the Monte Carlo analysis commences by assigning discrete probability distributions to ranks and filters with medium and high uncertainty (the uncertainty level judged by data quality and availability), while retaining the original point estimates for those with low uncertainty. The designations of low, medium, or high uncertainty to each source, habitat tank, exposure, and effects filter are based on data quality and availability. Discrete probability distributions are assigned to ranks and filters with medium and high uncertainty according to criteria based on Landis WG (2005). The analysis concludes by deriving a probability distribution for the given output variable (i.e. the risk estimate) from a combination of assigned probability distributions of input variables (i.e. ranks and filters) obtained by 1000-iteration simulations using Crystal Ball® 2000 software (Decisioneering, Inc., Denver, CO, USA). The output distribution for each sub-region is then used to quantify the effects of uncertainty in input variables on the risk predictions.

3. Application to Zhangjiakou, a host city of the 2022 Winter Olympics

3.1. Overview of the study area

Zhangjiakou City is situated in northwest Hebei Province of China and upwind of Beijing (see Figure 1). The prefecture has an administrative area of 36,965 km² and comprises 4 municipal districts (Qiaoxi, Qiaodong, Xuanhua, and Xiahuayuan) and 13 counties (Zhangbei, Kangbo, Guyuan, Shangyi, Yu, Yangyuan, Wanquan, Xuanhua, Huai'an, Huailai, Zhuolu, Chicheng, and Chongli). At the end of 2014, Zhangjiakou City had a total population of 4.68 million and gross domestic product (GDP) of 135.85 billion Yuan, indicating that Zhangjiakou is relatively sparsely populated and less developed than other parts of China. In addition to the local metal and coal industry (Liu et al. 2015), several major chemical enterprises such as Shenke Chemical Co. Ltd and Xingyuan Chemical Co. Ltd have become established in Zhangjiakou, most located in areas close to where the population density is larger (labeled using blue numbers 1-16 in Figure 1). As a mountainous, semi-arid region, Zhangjiakou experiences a continental monsoon climate with prevailing northwesterly winds of maximum and average speeds of 17.7 m/s and 1.98 m/s respectively. Sensitive ecological natural reserves and forest parks (labeled

using purple numbers 1-21 in Figure 1) are situated in the prefecture, which are potentially vulnerable to airborne pollution accidents. Of particular concern are certain valleys in Chongli County that have been selected as venues for the 2022 Winter Olympic Games. Chongli County has a total population of approximately 126,000, and contains one provincial forest park. Chongli is close to two risk sources: Dongshan Comprehensive Chemical Plant (labeled S1, see Figure 1) and Jinsai Pharmaceutical Company (labeled S15, see Figure 1). Should an airborne pollution accident occur, it could pose a major threat to the Winter Olympics site in Chongli County and downwind to Beijing.

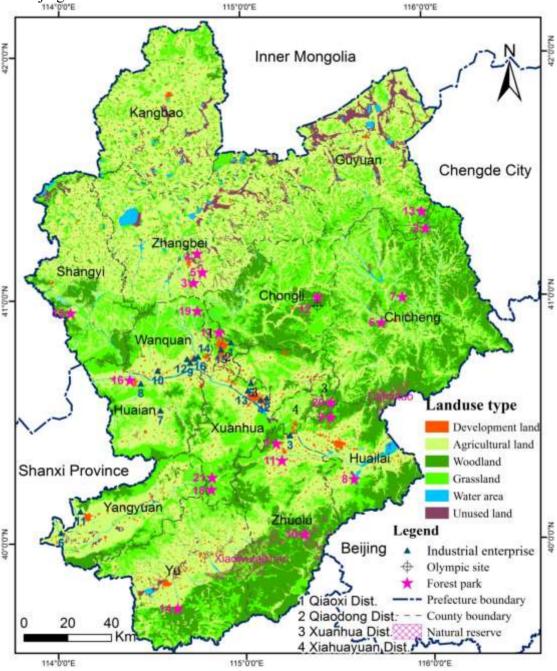


Figure 1 Risk sources, receptors, and land-use map of Zhangjiakou City,

north China

3.2 Data sources

The risk sources of chemical enterprises have been mostly derived from China's National Inspection Records of Environmental Risk and Chemicals in Enterprises of Key Industries (Environmental Risk Inspection for short), completed in 2010. A field survey was undertaken from July to September 2014 to update information on chemical enterprises in Zhangjiakou recorded in the Environmental Risk Inspection, with assistance from the local Environmental Emergency Center (EEC). Sixteen chemical enterprises that have the potential to cause air pollution accidents were identified, and included in the risk analysis for Zhangjiakou. The enterprises are labeled using blue numbers from 1-16 in Figure 1; five are located in Wanquan, four in Xuanhua District, two in each of Qiaodong District, Huai'an, and Yangyuan, and one in Zhuolu. The survey provided details for each chemical enterprise on its location, nature and quantity of chemicals involved, production technology, safety production control, risk prevention and control, environmental emergency plan, and other relevant data (such as the plan area of liquid pools or cofferdams, liquid depth, volume of storage tank, liquid temperature, etc.).

Turning to the risk receptors, details of the populations of 243 townships and the agricultural outputs (a proxy for the potential economic losses that could be sustained by croplands, orchards, and livestock and poultry farms were obtained from data listed in the Zhangjiakou City Statistical Yearbook (2013). Information on the location and spatial area of each sensitive ecosystem was obtained from data collected in 2016 by local municipal bureaus of forestry, agriculture, and environmental protection. 21 major forest parks were identified (labeled by the purple numbers 1-21, including 2 national and 19 provincial parks, see Figure 1) along with 2 national ecological natural reserves (i.e. Dahaituo and Xiaowutaishan). Plan areas of residential land, agricultural land, woodland, and administrative townships and counties were estimated from a 1:100,000 scale land-use map. This map was interpreted from the relevant remote sensing image obtained by Landsat-7 in 2010, and downloaded from the China Centre for Resources Satellite Data and Application (CRESDA) at 30 m × 30 m spatial resolution. Meteorological observations taken four times a day from 1st January 1991 to 1st January 2001 were obtained from the Zhangjiakou meteorological station (elev. 723.9m, lat. 40.78 N, long. 114.88 E) and Huailai meteorological station (elev. 536.8m, lat. 40.40 N, long. 115.50 E).

3.3 Results

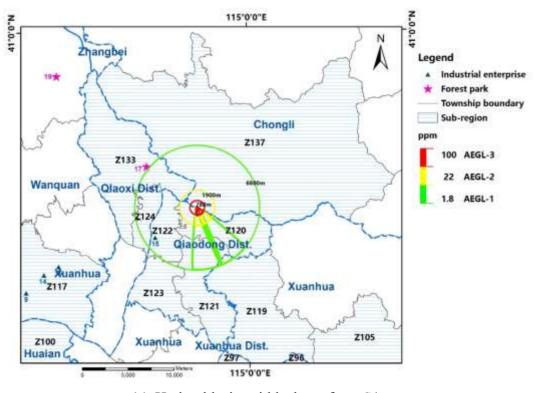
3.3.1 Airborne pollution accident modeling

To estimate the exposure distance of risk sources to receptors, simulations were carried out to predict the dispersion of relevant hazardous and toxic gases that could arise from the storage of hydrochloric acid, benzene, liquid ammonia, ammonium nitrate, and ethyne by chemical enterprises located in Zhangjiakou City. As previously mentioned in Section 2.2, ALOHA software was used for chemical solutions and Breeze Incident Analyst for pure chemicals (both neutrally buoyant gas and heavy gas). A credible accident is one within the realm of possibility and is likely to be severe enough to cause significant damage based on Maximum-Credible Accident theory (Khan, 2011). The dispersion process is fully explained below for two Maximum-Credible Accident scenarios: the leakage of hydrochloric acid from a storage tank located at risk source S1;

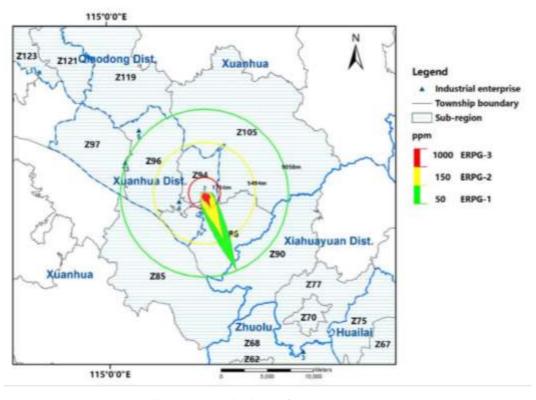
and the leakage of benzene from a tank located at risk source S2.

(1) Leakage of concentrated hydrochloric acid from a storage tank (S1)

Concentrated hydrochloric acid (otherwise known as fuming hydrochloric acid) is particularly acidic and it exists as a combination of liquid and vapor phases, the latter forming an acidic mist. Hydrochloric acid is corrosive, and damages living tissues. Its leakage would threaten human health and ecosystem safety. In risk source S1, the quotient (Q) of stock quantity to threshold quantity of hydrochloric acid is 1.6, indicating that there is a high hazard of leakage. As a typical industrial chemical solution (38% by weight), the accidental leakage and eventual dispersion of hydrogen chloride (HCl) are simulated using the ALOHA software, based on a Heavy Gas model. Table 4 lists the gas release data, where the leakage is taken to be continuous and steady. For atmospheric stability class F and a wind speed of 1.5 m/s in the NNW direction in Zhangijakou City. the dispersion of the hydrochloric acid smog, and the associated maximum exposure distance are tracked for 1 hour. The maximum average sustained release rate from an evaporating puddle of hydrochloric acid is 78.2 kg/min and the total hazardous component released amounts to 692 kg. The maximum exposure radius (see Table 4 and Figure 2(a)) for 60-min AEGL-1 (1.8 ppm) is estimated to be 6800 m, for 60-min AEGL-2 (22 ppm) to be 1900 m, and for AEGL-3 (100 ppm) to be 788 m (see Section 2.3). In this case, primary protection of risk receptors would be recommended within 6.8 km of the source (S1).



(a) Hydrochloric acid leakage from S1



(b) Benzene leakage from S2

Figure 2 Modelling of accidental release scenarios from risk sources S1 (a) and S2 (b) within Zhangjiakou City, north China

(2) Leakage of benzene from a storage tank (S2)

Benzene is highly volatile and naturally forms an organic gas at standard temperature and pressure. The escape of benzene to the atmosphere causes volatile organic compound (VOC) pollution. Benzene is poisonous to human beings and animals. In risk source S2, the quotient (Q) is 64, indicating the extremely high hazard of leakage. Here, the SLAB model in Breeze Incident Analyst software was used to model the continuous release and accidental dispersion of benzene, a dense gas. After seepage from the tank, benzene enters a cofferdam to form a liquid pool, which partly evaporates under the effect of wind, at a steady emission rate of 19460.68 g/s. Table 4 lists the release data. The release and dispersion of the benzene smog are tracked for 1 hour for the same meteorological conditions as considered in the previous case (atmospheric stability class

F, wind speed 1.5 m/s, wind direction NNW). The maximum exposure radius (see Table 4 and Figure 2(b)) for 60-min ERPG-1 (50 ppm) is estimated to be 9058.3 m, ERPG-2 (150 ppm) to be 5493.5 m, and ERPG-3 (1000 ppm) to be 1714.3 m. This implies that risk receptors must receive primary protection within a radius of 9058.3 meters from the accident source S2.

Table 4. Hypothetical gas release data for accidental leakages from hydrochloric acid and benzene storage tanks in Zhangjiakou City, north China

		Hydrochloric acid (38%)	Benzene
	CAS	7647-1-0	71-43-2
Chemical	Molecular Weight (g/mol)	36.46	78.11
Data	Ambient boiling point (K)	315.2	353.3
Data	Critical pressure (atm)	82.71	48.3
Liquid hea	Liquid heat capacity (J/kg K)	1655.85	1712
	Air Temperature (°C)	25.03	25.03
A tua a amb ami a	Ambient Pressure (mmHg)	760	760
Atmospheric	Relative Humidity	50%	50%
Data	Wind	1.5m/s from NNW	1.5m/s from NNW
	Stability Class	F	F
Release	Source type	Evaporating puddle	Evaporating pool
	Emission rate (g/s)	1303.33	19460.68
	Puddle area (m ²)	700	7500
Data	Release duration (s)	1800	1800
Data	Total mass (kg)	5000	100000
	Total hazardous component released (kg)	692	35028
	AEGL-1 (60min)	6800m	-
	AEGL-2 (60min)	1900m	-
LOC	AEGL-3 (60min)	788m	-
(Level of Concern)	ERPG-1 (60min)	-	9058.3m
,	ERPG-2 (60min)	-	5493.5m
	ERPG-3 (60min)	-	1714.4m

3.3.2 Airborne pollution accident risk map

Zhangjiakou City comprises 243 townships, each of which is treated as an assessment sub-region (labelled Z1-Z243). All sixteen risk sources (labelled S1-S16), each linked to a particular chemical enterprise, and three categories of receptors have been taken into account in determining the three risk assessment endpoints of resident safety, property resilience, and ecosystem health. Figure 3 displays the overall ranking air pollution risk map for the most urbanized districts and nearby counties in Zhangjiakou. The remaining counties are not at risk and so are left blank in Figure 3. Of the 243 townships, 34 are affected by risk sources. Relatively speaking, sub-regions Z96 and Z117 are at high risk of acute airborne pollution accidents. Nine sub-regions, Z23, Z62, Z68, Z94, Z104, Z109, Z120, Z122, and Z124, are at medium risk. The remaining

twenty-three sub-regions, Z30, Z59, Z67, Z70, Z75, Z77, Z81, Z85, Z86, Z90, Z97, Z100, Z101, Z102, Z103, Z105, Z114, Z118, Z119, Z121, Z123, Z133, and Z137, are at low risk. From the risk map, it is evident that chemical enterprises and high-risk sub-regions are mainly located in the Xuanhua, Qiaodong, Qiaoxi and Xiahuayuan districts, and Wanquan, Huai'an, Yangyuan, and Zhuolu counties.

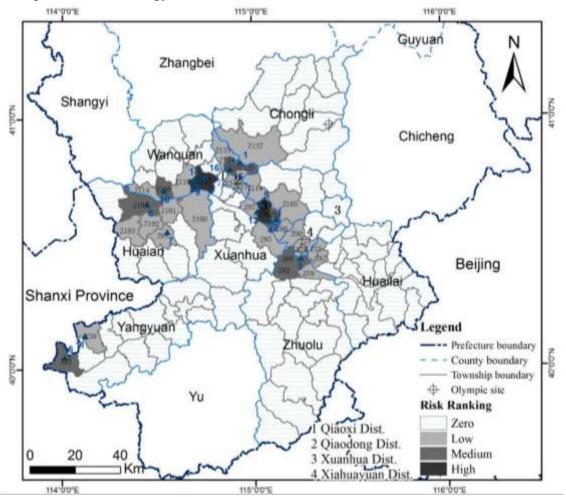


Figure 3 Risk map for airborne pollution accidents in urban areas and nearby counties within Zhangjiakou City, north China

Sources at most risk. From the results of the dispersion-simulations (see Section 3.3.1), it was found that risk sources S1, S2, S3, and S8 threaten not only their home townships but also adjacent areas. The effects of the remaining risk sources are mostly localized within their own townships. Figure 4 presents the sum risk scores for each risk source, obtained by combining every risk route originating from a particular chemical enterprise. The chemical enterprises posing greatest risk (risk score > 300) are S1 (432), S3 (408), S8 (324) and S2 (312), all of which are hazardous and capable of exporting the threat of pollution to adjacent areas. The highest risk comes from source S1, Dongshan comprehensive chemical plant, which directly threatens its relatively dense local population (Z120) and adjacent urban areas, Z119, Z121, Z122, Z123, Z124, Z133, and Z137, with exposure to acute airborne pollution should an accident occur. The second highest risk comes from source S3, Hebei Tianbao Co. Ltd, which affects seven

sub-regions, Z59, Z62, Z67, Z68, Z70, Z75 and Z77, within Xiahuayuan District, Zhuolu, and Huailai. Located in Huaian, S8 mainly impacts on four sub-regions, Z101, Z102, Z103 and Z104, in Huaian and two sub-regions, Z109 and Z114, in Wanquan. Situated in risk sub-region Z94, S2 can transmit acute airborne pollution to urban areas, Z90, Z94 and Z96, and adjacent townships, Z85, Z86, and Z105.

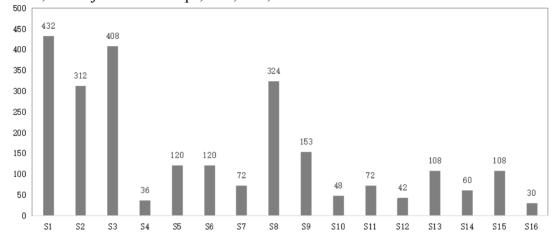


Figure 4 Risk score for each chemical enterprise in Zhangjiakou City, north China

Most vulnerable receptors. The population density of Zhangjiakou City is largest in the urban districts of Qiaoxi (Z124, Z133), Qiaodong (Z120, Z121, Z122, Z123), Xuanhua (Z94, Z96, Z97), and Xiahuayuan (Z70, Z77). By simulating the dispersion of relevant hazardous and toxic gases, the following findings are obtained for the two urban areas at greatest risk: Z96 is most susceptible to acute airborne pollution from local risk sources S4, S5, and S13 and nearby S2; urban area Z117 is directly threatened by S9, S12, S14, and S16. Across the entirety of Zhangjiakou City (see Figure 5), humans are the most vulnerable receptors and are associated with the majority of high risk scores, especially in urban areas Z94, Z96, Z120, and Z122. Forest parks located in sub-regions Z62, Z104 and Z133 are relatively significant vulnerable receptors. In terms of economic loss, sub-regions Z117, Z68, and Z96, located in Wanquan, Zhuolu and Xuanhua, respectively, are most vulnerable to damage by acute air pollution by chemical enterprises. Downwind Beijing and the proposed Winter Olympics site in Chongli are free of acute accidental airborne pollution risk from the chemical enterprises in Zhangjiakou City.

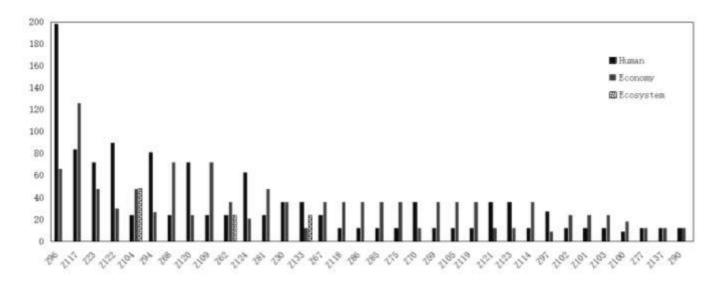


Figure 5 Risk scores for each receptor group in sub-regions of Zhangjiakou City, north China

Significantly influenced endpoints. Figure 6 displays the total risk scores for each endpoint in each sub-region, which follow similar trends as in Figure 4. Property resilience is the most significantly impacted endpoint over the majority of districts. Resident safety must be a priority, especially in high population density districts, such as urban areas Z94, Z96, Z120 and Z122. Ecosystem system health is the most importantly influenced endpoint in sub-regions Z62, Z104, Z117, and Z133, in which more attention should be paid to the ecological state should accidental air pollution occur.

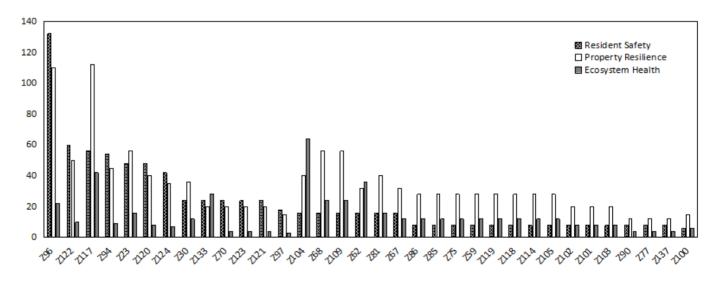


Figure 6 Risk scores of endpoints in each sub-region in Zhangjiakou City, north China

3.3.3 Uncertainty analysis

Sub-regions Z96 (264), Z104 (120), and Z118 (48) are representative of typical risk sub-regions respectively, and so are selected for uncertainty analysis. Figure 7 presents histograms of the forecast probabilities for 1000 trials, with fitted negative binomial curves superimposed. Final probability distributions correspond to the assessment values, implying that inherent uncertainty in the method of calculation has no significant effect on the risk results. The frequency distributions for Z96 are right-skewed, and so the risk levels may have been overestimated. For sub-regions Z104 and Z118, the frequency distribution follows approximately a quasi-normal curve, implying a relatively accurate assessment.

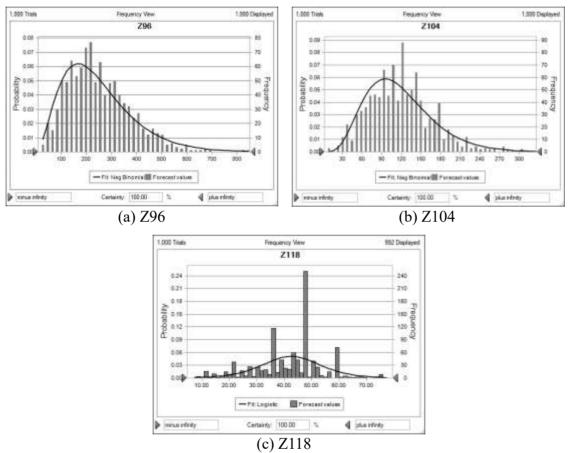


Figure 7 Results of uncertainty analysis for sub-regions of Zhangjiakou City: (a) Z96; (b) Z104; and (c) Z118.

4. Discussion

HSRA is proposed to evaluate acute accidental air pollution risk at regional-scale. As a companion method to Watershed-scale Accidental Pollution Risk Assessment (WAPRA, see Liu et al. 2017), HSRA is designed for air pollution by adopting the same idea of risk ranking and similar standardized analysis to combine cumulative risk at regional scale (covering a prefecture, a province, even a nation). Here a township is selected as the

assessment sub-region because gas leakages mostly have a scale of influence ranging from 10s to 1000s of m, as evidenced from the experience of previous gas accidents and the present exposure modeling results (see Section 3.1.1). At such scale, HSRA assesses the air pollution risk to each township arising from either interior or external chemical enterprises by using atmospheric dispersion models, an approach not undertaken in previous studies (e.g. Hu 2009; Shao et al. 2013). The method simulates dispersion of neutrally buoyant gas by means of a Gaussian model and that of dense gas by a heavy-gas model, preferentially selects acute exposure limits in sequential order of AEGLs, ERPGs, TEELs, etc., and jointly determines the maximum exposure distance for each hazardous gas release (see Section 2.3). The resulting exposure analysis is more accurate. By incorporating a standardized process and criteria similar to WAPRA (Liu et al. 2017), HSRA specifies distinct input data on air pollution risk sources (e.g. tank geometries containing liquefied or compressed gasses, and evaporation rates), meteorological conditions, and details of potentially exposed humans, flora and fauna. Using the standardized HSRA, an overall map of air pollution accident risk can be produced for a large region.

The HSRA method, with strict evaluation criteria and standards incorporated into the risk ranking procedure, has been presented as a standardized process, the aim being for this improved method to achieve wide acceptance once further applications of airborne risk assessment have been adopted. In the future, once HSRA has been applied to air pollution accident risk assessment and common ranking criteria have been established, it is likely that HSRA will be used for comparison of risk levels in different sub-regions. The Zhangjiakou case study has demonstrated that HSRA is straightforward to apply in practice and gives results that are useful in assessing potential emergency response measures. Only 34 sub-regions of Zhangjiakou were identified to be at risk, with all other sub-regions at no risk from air pollution accidents. Those sub-regions at risk were at a common risk level because of the uniformity of the stationary risk sources, all being chemical enterprises. However, applying the concept of risk ranking to Zhangjiakou, sub-region Z96 received the highest risk score (264) and sub-region Z117 the second-highest risk score (210) (Figure 4). Both these sub-regions are at relatively high risk because they are under combined threats from four chemical enterprises (Section 3.3.2) and intense population exposure (Figure 5). As the urban center of Xuanhua District, sub-region Z96 has a population density of 1500 persons per km² and four risk sources: most hazardous S5 (hazard ranking=10), S2 (hazard ranking=8), and less-hazardous S4 and S13. Sub-region Z117 comprises the capital town of Wangquan County, and contains four less-hazardous chemical enterprises (i.e. S9, S12, S14, and S16), has medium-level population density and a considerable area of susceptible croplands and farms. Nine sub-regions are at medium-risk level because one or two highly hazardous risk sources threaten urban areas which are relatively densely populated (Z23, Z62, Z120, Z122, Z94, and Z124), high economic outputs (Z68 and Z109), and sensitive ecosystems (Z62 and Z104). S1-S3 and S5-S8 are identified as the most hazardous risk sources due to their high stock quantities of hazardous and toxic chemicals and/or low management level of production processes and risk control. Of these, S2, S3, S5, and S6 have stock quantities more than 10 times the threshold value (i.e. $Q \ge 10$) of hazardous and toxic chemicals. Risk sources S1, S5, S7, and S8 have yet to construct facilities to monitor, control, and process hazardous and toxic gases or to have developed an early-warning system for leakage emergencies. Furthermore, S1-S3 and S8 have the highest risk levels because they are inherently the most hazardous and capable of exporting pollution threats to adjacent areas.

Comparing the risk analysis results between HSRA and WAPRA (Liu et al. 2017), three differences should be noted. First, the influence of an air pollution accident acts over a smaller spatial scale (10s–1000s m as opposed to 1000s–100,000s m), therefore a township and a sub-watershed are treated respectively as the assessment sub-region in HSRA and WAPRA. Second, cascading and cumulative effects are much more evident in watershed-scale risk analysis. This is because air pollution is usually restricted to the source sub-region and possibly to a downwind sub-region, whereas water pollution creates a cascade of risk as it travels downstream from one sub-watershed to the next. Third, air pollution accident risk assessment pays more attention to immediate human casualties, public health, and damage to flora and fauna, whereas water-borne risk assessment focuses on the effect on the aquatic environment and any collateral damage (i.e. to public safety by lowering drinking water quality).

It should be noted, however, that HSRA may have certain subjectivity for the ranking process in airborne hazard and vulnerability analyses. Any single "source-receptor-endpoint" may be assigned the maximum risk ranking when considering extreme situations, so HSRA may have overestimated the risk in certain areas, as indicated by the results of the uncertainty analysis. Subjectivity and overestimation of risk in the HSRA would be overcome by improving ranking criteria after progressive applications of airborne risk assessments at regional-scale have been completed in the future.

5. Conclusions

We proposed a HSRA approach to assess accidental air pollution risk at regional-scale. The approach is a companion to our previous WAPRA, adopting a similar risk ranking system and standardized analysis process. Gaussian and heavy-gas models are incorporated to simulate the dispersion of neutrally buoyant and dense gases, respectively. AEGLs, ERPGs and alternative TEELs provide acute air pollution exposure limits in priority order. Inclusion of both the dispersion models and the exposure criteria led to enhanced simulation accuracy and made the exposure analysis more reasonable. Differences between HSRA and WAPRA include the analysis scale (or size of assessment sub-region) with air pollution covering smaller areas than water pollution, the cascading of water pollution effects unlike air pollution which tends to be more localized, and the major receptors which tend to be human beings for air pollution and the environment for water pollution. From the resultant risk map in Zhangjiakou, 34 of 243 townships were identified as being at risk, the majority located in Xuanhua, Qiaodong, Qiaoxi and Xiahuayuan districts, and Wanquan, Huai'an, Yangyuan, and Zhuolu counties. Urban areas in Xuanhua District (Z96) and Wangquan (Z117) experience highest risk because of the proximity of several chemical enterprises to locations of relatively high population density. Chemical enterprises S1-S3 and S8 pose the greatest risk due to their higher inherent hazards and the relatively larger influence on their receptor sub-region(s); S5-S7 are also relatively hazardous because they contain high stock quantities of hazardous and toxic chemicals and/or have low management levels regarding chemical production and processing, and relatively poor risk control systems. HSRA indicates that the proposed Winter Olympics site in Chongli and downwind Beijing are free of acute accidental airborne pollution risk from chemical enterprises. The present results provide useful information for decision making in the context of urban development planning, air pollution risk prevention, and incident preparedness strategies.

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Author Contributions

Renzhi Liu presented the methodology and wrote the manuscript. Jing Liu & Zhijiao Zhang completed the simulation and computation works and contributed to write the manuscript. Alistair G.L. Borthwick contributed to the risk analysis. Yanpeng Cai helped to write the manuscript. Lei Dong & Xi Du contributed to prepare data.

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