




Article

A Score Index System for a Semi-Quantitative Assessment of Inhalation Risks at Contaminated Sites

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Abstract: Risk assessment of contaminated sites is typically applied following a tiered approach with increasing levels of complexity. In the standard risk-based corrective action (RBCA) procedure issued by the American Society for Testing and Materials (ASTM), the site-specific evaluation is carried out using fate and transport models that require a relatively large amount of input data. In this work, we introduce a site-specific score index system for a preliminary assessment of the inhalation risks related to contaminants in soil or groundwater that resembles the modeling approaches typically adopted for chemical risk assessment in the field of industrial hygiene. In the developed system, a risk index for the outdoor and indoor volatilization pathways is calculated as the ratio between the calculated concentration at the point of exposure for the contaminant of concern and the corresponding acceptable concentration in air. The concentration at the point of exposure for each contaminant of concern is estimated through simple algorithms that involve a limited number of indexes that depend on the parameters that affect the exposure scenario. This qualitative assessment is then converted into a semi-quantitative approach by introducing scaling factors that were calibrated using the ASTM RBCA fate and transport models. The procedure was validated against the standard RBCA procedure by performing a simple Monte Carlo analysis with 10,000 simulations with randomly varying site-specific parameters. The developed score index system resulted in a conservative estimate of the risks, with percentages of false negatives lower than 1% and false positives lower than 15%. This means that the developed system allows one to screen out sites from further evaluations in more than 80% of cases, while ensuring a conservative estimate of the expected risks. The application to a real case study of a contaminated site confirmed the suitability of the developed approach.

Keywords: contaminated sites; risk assessment; inhalation exposure; screening analysis



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1. Introduction

Contaminants in the subsurface can pose potential long-term risks to human health [1–4]. Human health risk assessment (HHRA) plays an important role in supporting decisions about the management, remediation and reuse of contaminated sites [2,5–7]. It is defined by United States Environmental Protection Agency (U.S. EPA) as the process to estimate the nature and probability of adverse health effects in humans who may be exposed to chemicals in contaminated environmental media, now or in the future [8]. HHRA is based on a predictive approach that estimates the probability of adverse effects on human health associated with exposure to contaminants through various exposure pathways, such as soil ingestion, dermal contact with contaminated soil and inhalation of vapors and dust [3].

This risk-based approach has been encouraged since the late 1990s as an integral part of the corrective action process at sites where leaking underground storage tank (UST) systems have released petroleum products into the environment and thus created risks to human health and the environment [9].

Currently, in most of industrialized countries, the management of contaminated sites relies on a risk-based approach, where the actual pollution of the site is evaluated depending on the effective risk posed to the human health or environment [3,10,11]. HHRA results are a very useful tool because they give a rational and objective starting point for priority setting and decision making [12].

The most recognized technical references for the application of risk assessment to contaminated sites are the American Society for Testing and Materials (ASTM) risk-based corrective action (RBCA) standards for evaluating petroleum (E 1739-95) and chemical release sites (E 2081-00) [3,13–17].

The RBCA procedure is based on a tiered approach that combines information gathered during a site investigation with data on the health effects of contaminants [10], with increasing complexity in the definition of the site conceptual model and the description of the physical and chemical phenomena underlying the fate and transport of contaminants [14]. The RBCA methodology applies fate and transport models that, based on the concentration of the contaminant in soil and groundwater, estimate the concentration at the point of exposure. Tier 1 is based on very conservative or worst-case exposure assumptions. The transport of the contaminants is described through simple analytical models, and conservative default values are used for hydrogeological, geometrical and exposure data. In Tier 2, site-specific input data gathered from site investigations are used with analytical fate and transport models. In Tier 3, the transport is instead described through numerical models, relying on more detailed site-specific data [10,16]. Typically, Tier 1 is used to define contamination screening values, useful in an initial generic assessment to identify areas, contaminants, and conditions at a particular site that do not require further attention [5]. Tier 2 risk assessment is carried out for a site-specific evaluation, and is the level most commonly used because it represents a reasonable compromise between the need for a site-specific assessment and the advantage of handling a relatively easy-to-use management tool [16]. In fact, most of the HHRA tools developed worldwide are based on a site-specific quantitative risk assessment [18–23]. Tier 3 is performed only in specific complex situations.

In the intermediate level of assessment (Tier 2), which is the most used, the fate and transport models require as input a large number of geological, hydrogeological, meteorological and geometrical parameters concerning the site and the source of contamination. Furthermore, statistical elaborations of site-specific data are necessary to identify representative values of these parameters with an adequate confidence level [24,25]. As a result, applying this evaluation level requires a substantial effort from an economical and technical point of view.

This means that Tier 2 HHRA can be applied only when a detailed site characterization has been carried out; this makes its application not possible at a preliminary stage of the remediation process, e.g., when the need for preventive actions or safety measures should be assessed.

Additionally, Tier 2 HHRA can typically be carried out only by consultants with specific knowledge of the procedure and of contaminated sites, whereas it can hardly be carried out by less skilled personnel, such Health, Safety and Environment (HSE) operators, unless they are properly trained. In this regard, the much simpler Tier 1 HHRA could be of help, but it would not allow accounting for the site-specific conditions reflecting the site in which it is applied.

Therefore, the need for a simple and less expensive tool, aimed in particular at a preliminary stage of assessment, has been recognized [22,23,26].

To address this need, in this work, we developed a score index system for a semi-quantitative assessment of outdoor and indoor inhalation risks at contaminated sites. The developed approach allows the conducting of risk assessment at a preliminary stage, before

applying the Tier 2 RBCA models. Therefore, it could be used to select sites for which further risk assessment is necessary, or to assess whether preventive actions or safety measures are required. The developed score index system resembles the modeling approaches typically adopted for chemical risk assessment in the field of industrial hygiene [27–31]. In this context, the risk is assessed in terms of exposure estimation carried out through simple algorithms involving a limited number of indices that depend on the parameters affecting the exposure scenario. Compared to the RBCA Tier 2 procedure, fewer input parameters are required. This qualitative assessment was then converted into a quantitative approach by introducing scaling factors, specific for each pathway, calibrated using the ASTM-RBCA fate and transport models by performing a simple Monte Carlo analysis, so that the estimated exposure levels and the related risks can be comparable with those calculated using the equations of the RBCA Tier 2 models.

In this paper, the developed score index system, the parameters involved and the underlying assumptions are presented. Then, the calibration and validation phases, based on the comparison of risk evaluations returned by the developed system and by the RBCA Tier 2 model, are described. The calibration and validation of the model were carried out on 60 volatile organic compounds (VOCs) typically of concern for contaminated sites (e.g., BTEX, chlorinated solvents, volatile/semi-volatile polycyclic aromatic hydrocarbons, petroleum hydrocarbons) by performing a simple Monte Carlo analysis, based on 10,000 simulations randomly varying the site-specific parameters within the typical ranges expected in the field. Finally, the application of the score index system to a real case study is shown. The application of the developed approach can lead to a more sustainable management of contaminated sites, as it allows one to screen out sites from further investigations, requiring less effort in terms of site characterization while keeping the site-specific approach typical of RBCA Tier 2 models.

2. Methods

2.1. Standard RBCA Tier 2 Procedure

The equations of the RBCA Tier 2 procedure [13,14] are consistent with the current U.S. EPA guidelines for human health risk assessment to contaminated sites [6].

In this procedure, the risk for human health is calculated differently for carcinogenic and non-carcinogenic effects of the chemical of concern:

$$R = (C_{poe} \cdot IUR \cdot EF_d \cdot EF \cdot ED) / (AT_c \cdot 365 \cdot 24) \quad (1)$$

$$HI = (C_{poe} \cdot EF_d \cdot EF \cdot ED) / (RfC \cdot AT_n \cdot 365 \cdot 24) \quad (2)$$

where R [-] is the risk for carcinogenic effects, HI [-] is the hazard index related to non-carcinogenic effects, C_{poe} [mg/m^3] is the exposure concentration, IUR is the inhalation unit risk ($[\mu\text{g}/\text{m}^3]^{-1}$) of the chemical, RfC [$\mu\text{g}/\text{m}^3$] is the reference concentration of the chemical, EF_d [hours/day] is the daily exposure frequency, EF [days/year] is the exposure frequency, ED [years] is the exposure duration, and AT_c and AT_{nc} [years] are the averaging times for carcinogenic and non-carcinogenic effects, respectively. The exposure parameters valid for a commercial/industrial scenario are shown in Table 1.

Table 1. Exposure parameters used to calculate R and HI [13,14].

Symbol	Units	Value
AT_c	Years	70
At_n	Years	25
EF_d	Hours/day	8
EF	Days/year	250
ED	Years	25

The risk acceptability conditions for each chemical are $R \leq 10^{-6}$ and $HI \leq 1$ [13,14].

The exposure concentration C_{poe} [mg/m^3] corresponds to the expected contaminant concentration at the point of exposure to outdoor or indoor air, and it is calculated as:

$$C_{poe} = C_S \cdot VF \quad (3)$$

where C_S ($[\text{mg}/\text{kg}_{\text{soil}}]$ or $[\text{mg}/\text{L}_{\text{water}}]$) is the concentration of the contaminant at the source and VF ($[(\text{mg}/\text{m}^3_{\text{air}})/(\text{mg}/\text{kg}_{\text{soil}})]$ or $[(\text{mg}/\text{m}^3_{\text{air}})/(\text{mg}/\text{L}_{\text{water}})]$) is the volatilization factor that accounts for the fate and transport of the contaminant from the source to the point of exposure.

VF depends on the volatilization pathway (outdoor or indoor) and the environmental matrix. The equations defined by the ASTM standards for calculating the different outdoor and indoor volatilization factors are reported in the Supplementary Material (Tables S1 and S2). A simplified schematization of the volatilization pathways of a contaminant from the source to the receptors is represented in Figure 1.

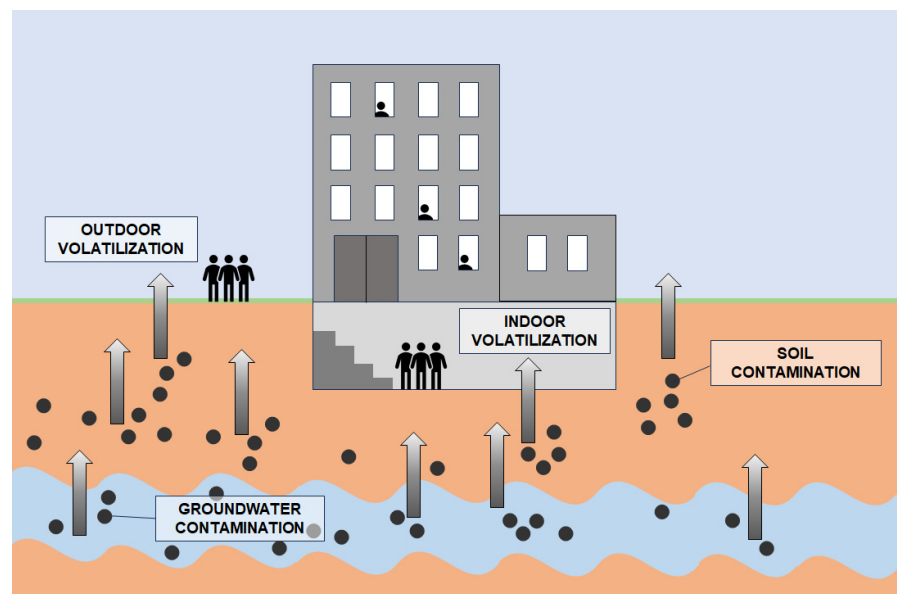


Figure 1. Schematization of the transport of contaminants from the source to the receptors.

2.2. Developed Score Index System

2.2.1. Risk Index

In the developed score index system, the risk index (RI) for the outdoor and indoor volatilization pathways is calculated as the ratio between the exposure calculated using semi-quantitative site-specific parameter indices (see the next section) and the acceptable concentration in air:

$$RI = E_{inh}/LV \quad (4)$$

where RI [-] is the risk index, E_{inh} [mg/m^3] is the calculated concentration at the point of exposure and LV [mg/m^3] the acceptable concentration limit value in air for the chemical of concern.

The limit value (LV) is the risk-based screening level in air ($RBSL_{air}$), according to the ASTM standard E 2081-00 [14] for environmental exposure, which is calculated starting from an acceptable risk level for human health and selecting the most conservative value between those obtained by applying Equation (5) for carcinogenic effects and Equation (6) for non-carcinogenic effects:

$$RBSL_{air,c} = TR \cdot AT_c \cdot 365 \cdot 24 / (EF_d \cdot EF \cdot ED \cdot IUR) \text{ carcinogenic effects} \quad (5)$$

$$RBSL_{air,nc} = THQ \cdot RfC \cdot AT_n \cdot 365 \cdot 24 / (EF_d \cdot EF \cdot ED) \text{ non carcinogenic effects} \quad (6)$$

where TR [-] is the target level for carcinogenic risks (assumed equal to 10^{-6}) and THQ [-] is the target hazard quotient for non-carcinogenic effects (assumed equal to 1).

Alternatively, the limit value (LV) can be set equal to the occupational exposure limit value (OELV), established under national regulatory frameworks or by scientific organizations, to assess the chemical risk in the case of occupational exposure [32].

Since RI is calculated as the ratio between estimated and acceptable exposure, the risk index can be considered acceptable when $RI \leq 1$.

2.2.2. Concentration in Air at the Point of Exposure

The concentration at the point of exposure for each chemical of concern, E_{inh} [mg/m^3], is calculated using semi-quantitative indices that account for the site-specific parameters, as follows:

$$E_{inh} = \left(\prod_{i=1}^n E_i \right) / K \quad (7)$$

where E_i [-] are the indices used to account for the different site-specific parameters and K [-] is the scaling factor (see Section 2.2.3) introduced to obtain quantitative results consistent with the results of the RBCA-Tier 2 model.

As discussed in detail in the following sections, the different indices (E_i) and two scaling factors (K_{OV} and K_{IV}) were defined for the outdoor and indoor volatilization pathways.

The indices are related to the site-specific parameters that mostly affect the transport of the contaminant from the source to the receptor. They have been selected from the set used by the RBCA Tier 2 models following two main criteria: (i) the sensitivity of the parameter to the final output, according to the existing literature [33,34] and (ii) the availability of the parameter at a preliminary stage of the evaluation, when a limited set of site-specific information is typically available. The indices selected for the two pathways correspond to:

- A total of 6 parameters for outdoor volatilization, compared to the 17 of the RBCA Tier 2 models [13,14];
- A total of 7 parameters for indoor volatilization, compared to the 20 of the RBCA Tier 2 models [13,14].

Site-Specific Indexes for the Outdoor Volatilization Pathway

For the outdoor volatilization pathway, the concentration at the point of exposure, $E_{inh,OV}$ [mg/m^3] is calculated as follows:

$$E_{inh,OV} = (E_M \cdot E_C \cdot E_V \cdot E_T \cdot E_S \cdot E_W) / K_{OV} \quad (8)$$

where:

- E_M is the index related to the “contaminated environmental matrix” parameter. Its value depends on the depth of the contamination: surface soil (0–1 m b.g.s), subsurface soil (>1 m b.g.s) or groundwater, according to the RBCA approach defined by U.S. EPA [5];
- E_C is the index related to the “contaminant concentration at source” parameter. Its value is equal to the representative concentration value at source, expressed as mg/kg_{soil} or mg/L_{water} ;
- E_V is the index related to the “contaminant volatility” parameter. It is calculated by Equation (9) for contamination sources in surface and subsurface soil or by Equation (10) for contamination sources in groundwater:

$$E_V = \frac{H}{K_s \left[\frac{L}{kg} \right]} \cdot D_a \left[\frac{cm^2}{s} \right] \text{ (unsaturated soil)} \quad (9)$$

$$E_V = H \cdot D_a \left[\frac{\text{cm}^2}{\text{s}} \right] \text{ (groundwater)} \quad (10)$$

where H [-] is the dimensionless Henry's law constant, D_a [cm^2/s] is the diffusion coefficient in air, K_s [(mg/kg)/(mg/L)] is the soil–water sorption coefficient. K_s is equal to K_d for inorganic contaminants (it can depend on the pH value of the soil), or to $K_{oc} \times f_{oc}$ for organic compounds (K_d [L/kg] is the soil/water distribution coefficient, K_{oc} [L/kg] the organic carbon-water sorption coefficient and f_{oc} [g/g] is the fraction of organic carbon in the soil). All these terms depend on the properties, with the exception of K_s that, for organic contaminants, also depends on the fraction of organic carbon in the soil (f_{oc});

- E_T is the index related to the “soil type” parameter. It assumes different values according to the United States Department of Agriculture (USDA) classification for the soil type, following the approach defined by U.S. EPA [5];
- E_S is the index related to the “source width” parameter. Its value is assigned by choosing, among three width ranges, the range where the site-specific contamination source width falls;
- E_W is the index related to the “wind speed” parameter. Its value is assigned by choosing among three wind speed ranges, the range where the site-specific representative value falls;
- K_{OV} is the outdoor scaling factor.

The index values E_M , E_T , E_S and E_W , and the outdoor scaling factor K_{OV} , have been defined by a calibration procedure (see next section) based on the fate and transport RBCA Tier 2 models [13,14]. The values of the different indexes are reported in Table 2.

Table 2. Outdoor volatilization indices for the application of the developed score index system.

Index	Selected Parameter	Parameter Classes	Index Values
E_M	Contaminated environmental matrix	Surface soil	10
		Subsurface soil	5
		Groundwater	1
E_C	Contaminant concentration at source	Soil concentration	$E_C = C_{\text{source,soil}} \left[\frac{\text{mg}}{\text{kg}} \right]$
		Groundwater concentration	$E_C = C_{\text{source,gw}} \left[\frac{\text{mg}}{\text{L}} \right]$
E_V	Contaminant volatility	Soil	$E_V = H \cdot D_a \left[\frac{\text{cm}^2}{\text{s}} \right] / K_s \left[\frac{\text{L}}{\text{kg}} \right]$
		Groundwater	$E_V = H \cdot D_a \left[\frac{\text{cm}^2}{\text{s}} \right]$
E_T	Soil Type	Coarse Soil (Sand, Loamy Sand, Sandy Loam)	50
		Medium Soil (Sandy Clay Loam, Loam, Silt Loam, Clay Loam, Silty Clay Loam, Silt, Sandy Clay)	5
		Fine-grained Soil (Clay, Silty Clay)	1
E_S	Source width	<50 m (small)	1
		50–250 m (medium)	5
		>250 m (large)	10
E_W	Wind speed	<1 m/s (low)	5
		1–3 m/s (medium)	2
		>3 m/s (high)	1

Outdoor Exposure

$$E_{\text{inh,OV}} \left[\frac{\text{mg}}{\text{m}^3} \right] = (E_M \cdot E_C \cdot E_V \cdot E_T \cdot E_S \cdot E_W) / K_{OV}$$

with calibrated $K_{OV} = 5000$

Site-Specific Indices for the Indoor Volatilization Pathway

For the indoor volatilization pathway, the concentration at the point of exposure, $E_{inh,IV}$ [mg/m^3] is calculated as in Equation (11):

$$E_{inh,IV} = (E_M \cdot E_C \cdot E_V \cdot E_T \cdot E_H \cdot E_{ER} \cdot E_\eta) / K_{IV} \quad (11)$$

where:

- E_M , E_C , E_V and E_T are the same of the outdoor volatilization pathway;
- E_H is the index related to the “enclosed-space volume/infiltration area ratio” parameter. Its value depends on the building type (basement, standard building and warehouse);
- E_{ER} is the index related to the “enclosed-space air exchange rate” parameter. Its value is assigned by choosing, among three air exchange rate ranges, the range where the site-specific value falls;
- E_η is the index related to the “areal fraction of the building’s cracks” parameter. Its value is assigned by choosing between three classes of structural floor conditions, corresponding to three ranges of the areal fraction of cracks;
- K_{IV} is the indoor scaling factor.

The index values E_M , E_T , E_H , E_{ER} and E_η , and the indoor scaling factor K_{IV} , have been defined by a calibration procedure (see the next section) based on the fate and transport models of the RBCA Tier 2 [13,14] (Figure 1). The values of the different indices are reported in Table 3.

Table 3. Indoor volatilization indices for the application of the developed score index system.

Index	Selected Parameter	Parameter Classes	Index Values
E_M	Contaminated environmental matrix	Surface soil	5
		Subsurface soil	2
		Groundwater	1
E_C	Contaminant concentration at source	Soil concentration	$E_C = C_{s,soil} \left[\frac{\text{mg}}{\text{kg}} \right]$
		Groundwater concentration	$E_C = C_{s,gw} \left[\frac{\text{mg}}{\text{L}} \right]$
E_V	Contaminant volatility	Soil	$E_V = H \cdot D_a \left[\frac{\text{cm}^2}{\text{s}} \right] / K_s \left[\frac{\text{L}}{\text{kg}} \right]$
		Groundwater	$E_V = H \cdot D_a \left[\frac{\text{cm}^2}{\text{s}} \right]$
E_T	Soil Type	Coarse Soil (Sand, Loamy Sand, Sandy Loam)	3
		Medium Soil (Sandy Clay Loam, Loam, Silt Loam, Clay Loam, Silty Clay Loam, Silt, Sandy Clay)	2
		Fine-grained Soil (Clay, Silty Clay)	1
E_H	Enclosed-space volume/infiltration area ratio	<2 m (Basements)	3
		2–4 m (Standard)	2
		>4 m (Warehouse)	1
E_{ER}	Enclosed-space air exchange rate	Low (<0.3 1/h)	3
		Medium (0.3–1 1/h)	2
		High (>1 1/h)	1
E_η	Areal fraction of cracks	Bad/No info (cracks > 1%)	10
		Average (cracks = 0.1–1%)	5
		Good (cracks < 0.1%)	1
Indoor Exposure			
$E_{inh,IV} \left[\frac{\text{mg}}{\text{m}^3} \right] = (E_M \cdot E_C \cdot E_V \cdot E_T \cdot E_H \cdot E_{ER} \cdot E_\eta) / K_{IV}$			
with calibrated $K_{IV} = 75$			

2.2.3. Determination of the Scaling Factor (K)

The score index system was calibrated by determining the scaling factor (K) values suitable to make the estimated exposure levels, and the related risks, comparable with those calculated using the equations of the RBCA Tier 2 model [13,14].

In particular, the calibration was based on a comparison between the exposure index E_{inh} and the exposure concentration C_{poe} estimated by the RBCA Tier 2 model. That is, the calibration was carried out on 60 VOCs typically of concern for contaminated sites with a dimensionless Henry constant greater than 10^{-3} by performing a simple Monte Carlo analysis running 10,000 simulations, randomly varying the site-specific parameters within the typical ranges expected in the field assuming a uniform distribution (see Table 4). The input and output of Monte Carlo analysis are provided in the Supplementary Material.

Table 4. Range/set of values of the selected parameters used for calibration. For more details, see the Supplementary Materials.

Selected Parameter	Unit	Range/Set of Values
Contaminated environmental matrix	-	3 classes
Contaminant	-	60 volatile chemicals (Henry's constant $H > 10^{-3}$)
Contaminant concentration at source	mg/kg _{soil} or mg/L _{water}	0.1–1000
Soil type	-	3 classes
Source width	m	10–500
Wind speed	m/s	0.5–5
Enclosed space volume/infiltration area ratio	m	1–6
Enclosed space air exchange rate	1/s	5.8×10^{-6} – 3.4×10^{-4}
Areal fraction of cracks	-	3 classes

The calibration process is detailed in the following steps and outlined in Figure 2:

1. A first tentative index value for each class of the selected parameters was set, then the calibration followed an iterative procedure;
2. For each selected parameter, a range/set of values (see Table 4) was defined, and 10,000 random combinations of these values were generated;
3. For each combination:
 - a. The corresponding index values E_i were assigned and the product of all relevant indexes E_{inh}^* was calculated;
 - b. The C_{poe} was calculated for outdoor and indoor pathways by Equations (S1)–(S6) in the Supplementary Material. For parameters not involved in the score index system, the default values set by the ASTM standard were adopted [14];
4. For each combination, an individual scaling factor K was calculated as:

$$K = E_{inh}^*/C_{poe} = \prod_{i=1}^n E_i/C_{poe} \quad (12)$$

For outdoor and indoor volatilization pathways, Equation (12) becomes, respectively:

$$K_{OV} = E_{inh}^*/C_{poe} = (E_M \cdot E_C \cdot E_V \cdot E_T \cdot E_S \cdot E_W)/C_{poe} \quad (13)$$

$$K_{IV} = E_{inh}^*/C_{poe} = (E_M \cdot E_C \cdot E_V \cdot E_T \cdot E_H \cdot E_{ER} \cdot E_{\eta})/C_{poe} \quad (14)$$

5. A tentative "best" K was chosen from the distribution of individual scaling factors;
6. For each combination, the exposure index E_{inh} (Equation (7)) was calculated using the tentative "best" K;
7. For each combination, the risk index RI (Equation (4)) and the risk, R and HI, from the RBCA Tier 2 model (Equations (1) and (2)) were calculated. The exposure parameters adopted to calculate R and HI and the limit value in air (LV) for a worker exposure are shown in Table 1. The toxicological and chemical–physical parameters of different

contaminants of concern are provided in the supplementary material (Table S4) and were taken from the database issued by U.S. EPA [35];

8. RI was compared with R and HI, according to the criteria detailed below;
9. Steps 5–8 were repeated until the choice of the final “best” K.

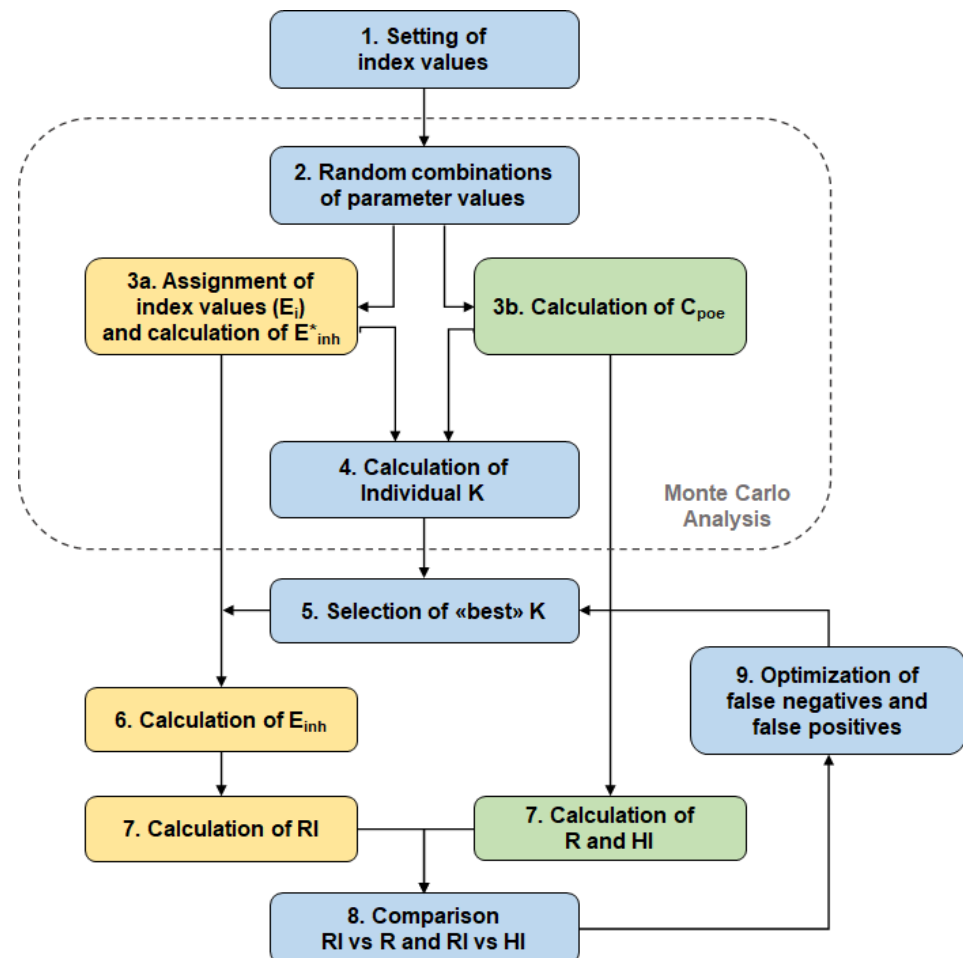


Figure 2. Procedure adopted for the calibration of the score index system.

Minimizing the differences between the risks returned by the two approaches cannot be the only criterion for the choice of the final ‘best’ K. In fact, a semi-quantitative model, as the one proposed in this work, is required to be reasonably more as conservative than the quantitative analytical model considered as a reference. For this reason, the selection of the final “best” K was also based on the analysis of acceptability or non-acceptability of the risks from the developed score index system (RI) and the risks from the RBCA Tier 2 model (R and HI) to identify the number and the type of inconsistent results.

Among inconsistent results, the case of non-acceptable RI and acceptable R and HI (false positive) is a conservative result; otherwise, the case of acceptable RI and non-acceptable R and HI (false negative) is a non-conservative result. While a lower consistency in terms of false positives can be considered tolerable, the lower consistency in false negatives should be avoided or minimized.

The K value influences the percentage of false positives and false negatives; thus, the final “best” K value was selected, minimizing the number of false negatives while keeping the number of false positives low. The iterative process was stopped with a percentage of false negatives less than 1% and a percentage of false positives lower than 15%.

At the same time, it was analyzed if false positives or false negatives fell for the most part into a specific class of a parameter. Thus, index values have been adjusted, and their

final value has been set so that false positives or false negatives were evenly distributed among the various classes.

3. Results and Discussion

3.1. Validation of the Score Index System

As previously discussed, a semi-quantitative model should be reasonably more conservative than the quantitative analytical model considered as a reference. Therefore, its reliability and conservativeness have been evaluated to analyze the quality of the output provided by the score index system. This has been performed by comparing the risk resulting from the developed system (RI from Equation (4)) with the RBCA Tier 2 model (R and HI from Equations (1) and (2), respectively) for all the random combinations generated, to find the final “best” K. Figure 3 shows the relationship between the risk index RI, calculated by Equation (4), with the final “best” K, and R and HI, calculated by Equations (1) and (2) (with R normalized to $R/10^{-6}$), respectively, for the outdoor and indoor volatilization pathway. Solid lines define four quadrants: consistent results fall into “quadrant I” and “quadrant III”, either with a judgment of non-acceptability of risk (“quadrant I”) or with a judgment of risk acceptability of risk (“quadrant III”); false negatives fall into “quadrant II” and false positives fall into “quadrant IV”. It can be observed that most of the results fall into quadrants I and III, demonstrating the consistency between the two model approaches. The discrepancies in quadrant IV are consistently higher than those in quadrant II, highlighting that the developed score index system is reliable (i.e., few false negatives) while conservative.

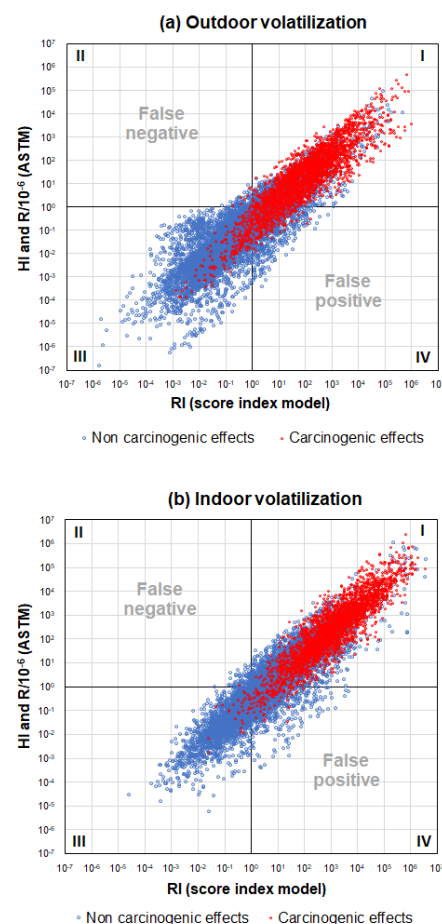


Figure 3. RI vs. $R/10^{-6}$ and HI for the selected scaling factors (K) for the (a) outdoor and (b) indoor volatilization pathway. I = consistent results-risk; II = false negatives; III = consistent results of no risk; IV = false positives.

Namely, Table 5 shows the overall percentages of consistent results, false negatives (acceptable RI and non-acceptable R or HI) and false positives (non-acceptable RI and acceptable R and HI) obtained in all simulations carried out. It can be observed that, with the selected scaling factor (K), the false negatives were lower than 1% and the false positives lower than 15%.

Table 5. Percentages of consistent results, false negatives and false positives obtained in the 10,000 random simulations.

Comparison Results	Meaning	Outdoor Volatilization Results	Indoor Volatilization Results
Consistent results	$RI \leq 1$ and $R \leq 10^{-6}$ or $HI \leq 1$ or $RI > 1$ and $R > 10^{-6}$ or $HI > 1$	84.6%	84.8%
False negatives	$RI \leq 1$ and $R > 10^{-6}$ or $HI > 1$	0.8%	0.7%
False positives	$RI > 1$ and $R \leq 10^{-6}$ and $HI \leq 1$	14.6%	14.5%

Further evidence of the conservativeness of the developed score index system is shown in Figure 4, which reports the ratio RI/R (with R normalized to $R/10^{-6}$) and RI/HI for all the 10,000 random combinations. Regardless of the risk acceptability or unacceptability judgment, the developed score system returns a RI value higher than the R or HI value estimated with the RBCA Tier 2 procedure in most cases. In particular, the ratio RI/R and RI/HI is higher than 1 in almost 90% of cases for indoor and outdoor volatilization pathways (i.e., the sum of blue shade slices in the figure).

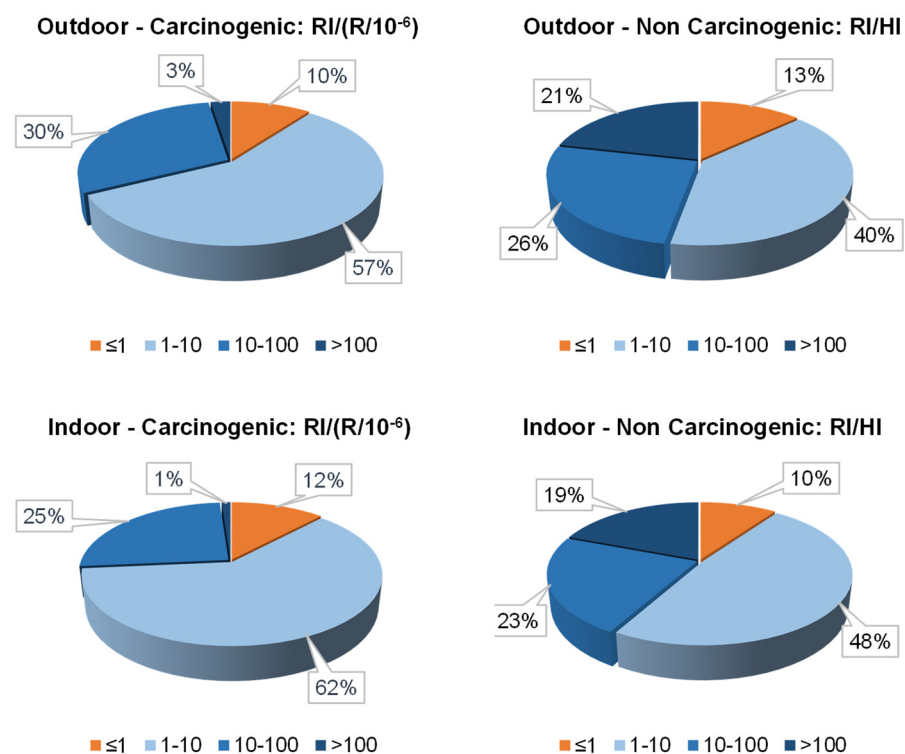


Figure 4. Percentage of the ratio of $RI/(R/10^{-6})$ and RI/HI for the outdoor and indoor volatilization pathway obtained in all simulations carried out.

3.2. Application of the Score Index System to a Case Study

The developed score index system was applied to a real case study of a contaminated site at an operative industrial plant in northern Italy. The site is characterized by VOC

contamination in both the unsaturated and saturated zone. Namely, the contaminants of concern for the two sources of contamination are as follows:

- Aliphatics C5–C8 for the source of contamination in the unsaturated soil (ID 1);
- Aliphatics C9–C12, trichloroethylene, vinyl chloride, 1,1,2,2 tetrachloroethane, 1,1 dichloroethylene and 1,2 dichloropropane for the source of contamination in groundwater (ID 2a–2f).

The main characteristics of the considered site are summarized in Table 6.

Table 6. Site-specific parameters of the case study.

Parameter	Symbol	Units	Value
Source width	W'	m	65 (Unsaturated soil) 95 (Groundwater)
Soil type	Soil type	-	Sand
Wind speed	U_{air}	m/s	1
Enclosed-space air exchange rate	ER	1/s	2.3×10^{-4}
Enclosed-space volume/infiltration area ratio	Lb	m	2.2
Areal fraction of cracks	η	-	0.01
Fraction of organic carbon in soil	f_{oc}	-	0.01
Depth to surface soil sources	L_{ss}	m	0
Depth to subsurface soil sources	L_{sp}	m	1
Depth to groundwater	L_{gw}	m	1.58
Ambient air mixing zone height	δ_{air}	m	2
Soil density	ρ	kg/m ³	1700
Averaging time for vapor flux	τ	s	7.88×10^8
Volumetric water content in vadose zone soil	θ_w	m ³ _{H₂O} /m ³ _{soil}	0.068
Volumetric air content in vadose zone soil	θ_a	m ³ _{air} /m ³ _{soil}	0.317
Enclosed space foundation/wall thickness	L_{crack}	m	0.15
Depth to base of enclosed space foundation	Z_{crack}	m	0.15
Exposure frequency	EF_d	hours/day	8
Exposure duration	EF	days/year	250

The developed score index system was applied to assess the risk for the outdoor and indoor volatilization pathways for the different contaminants of concern, using the input parameters reported in Table 6, and more in detail in the Supplementary Material. As a reference, the risks were also calculated using the standard RBCA Tier 2 procedure. The detailed results obtained by these simulations are reported in Table S3 of the Supplementary Material. The qualitative results of the two types of evaluations in terms of acceptable or non-acceptable risks are reported in Table 7.

It can be seen that, for most of the contaminants of concern, the two approaches provided consistent results. In particular, the developed score index system gave inconsistent but conservative results only in 2 out of 14 simulations (i.e., 14.3% of cases). Namely, for aliphatics C5–C8 in unsaturated soil and aliphatics C9–C12 in groundwater, the score index system predicted non-acceptable risks against the acceptable risks estimated by applying the standard RBCA Tier 2 procedure. Therefore, these results further confirmed the capability of the developed approach to filter out parameters from further evaluations in around 80% of cases, while ensuring a conservative estimate of the expected risks.

Table 7. Comparison between the developed score index system and RBCA-Tier 2 model results for the real case (black color: consistent results; red color: non-consistent results).

ID	Matrix	Contaminant	Source Concentration	OUTDOOR Acceptable Risk		INDOOR Acceptable Risk	
				Score Index System	RBCA Model	Score Index System	RBCA Model
1	Unsaturated soil	Aliphatics C5–C8	354 mg/kg	NO	YES	NO	NO
2a		Aliphatics C9–C12	7.56 mg/L	NO	YES	NO	NO
2b	Groundwater	Trichloroethylene	2.4×10^{-3} mg/L	YES	YES	YES	YES
2c		Vinyl Chloride	6.78×10^{-4} mg/L	YES	YES	YES	YES
2d		1,1,2,2 Tetrachloroethane	5.43×10^{-4} mg/L	YES	YES	YES	YES
2e		1,1 Dichloroethylene	7.38×10^{-5} mg/L	YES	YES	YES	YES
2f		1,2 Dichloropropane	2.08×10^{-4} mg/L	YES	YES	YES	YES

4. Conclusions

In supporting decisions about the management, remediation and reuse of contaminated sites, HHRA plays an important role, using a predictive approach that estimates the probability of adverse effects on human health associated with exposure to contaminants. The most-recognized technical references for the application of risk assessment to contaminated sites are the ASTM RBCA standards for evaluating petroleum (E 1739-95) and chemical release sites (E 2081-00). The RBCA procedure is based on a tiered approach that combines information gathered during a site investigation with data on the health effects of contaminants, with increasing complexity in the definition of the site conceptual model and the description of the physical and chemical phenomena underlying the fate and transport of contaminants. In this work, a score index system has been developed that allows a semi-quantitative assessment of outdoor and indoor inhalation risks at contaminated sites. Compared to the RBCA Tier 2 procedure, the developed system requires fewer input parameters (6 against 17 for outdoor volatilization, and 7 against 20 for indoor volatilization). In particular, the developed score index system requires input parameters that are typically available from the preliminary characterization of the site.

The reliability and conservativeness of the developed approach have been tested by its application to simulated and real cases. Specifically, the Monte Carlo analysis carried out by running 10,000 simulations, randomly varying the input parameters within the ranges expected in the field, showed that the system returns a percentage of false negatives lower than 1% and false positives lower than 15%. Similar results have been found by applying the system to a real case study, with 0% false negatives and 14.3% false positives. In other words, the results obtained highlighted that the developed system allows one to screen out sites from further evaluations in more than 80% of cases, while ensuring a conservative estimate of the expected risks.

In conclusion, the developed score index system can represent a sustainable tool for the management of contaminated sites, as it allows conducting a site-specific risk assessment characteristic of Tier 2 (or Tier 3) analysis foreseen by the RBCA ASTM standard, while keeping the simplicity and conservatism of the first tiers of the evaluation (i.e., Tier 1). The tool is indeed quick, and requires limited resources in terms of input data and computational efforts. The developed procedure can then be used for a preliminary risk assessment before applying the Tier 2 RBCA models to screen out cases for which further risk evaluation is not necessary, thus focusing on those where potential issues can be expected, and to assess whether prevention measures or safety measures are needed at a given site.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su151410855/s1>. Supplementary Material S1: ASTM equations and input data; Supplementary Material S2: Results of the Monte Carlo analysis. Table S1. Equations for the VF calculation [13,14]. Table S2. Overview of the parameters affecting outdoor and indoor volatilization. Table S3. Risk values obtained by the score index system and RBCA-Tier 2 model in the case study. Table S4. Chemical/physical and toxicological properties of contaminants [35].

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