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A critical assessment of software tools for Human Health Risk Assessment: Comparative study of RBCA and Risk-net

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Alla mia famiglia, ai miei amici

O cuore, a tutti gli amici rivolgilo vario il carattere,
adattando il tuo umore a quello di ciascuno.
Imita la natura del polpo tortuoso, che sembra
tutt'uno con lo scoglio marino cui s'aggrappa.
Ora percorri una via, poi cambia colore della pelle:
vale più la destrezza che la rigidità.

Teognide, *Silloge teognidea* (vv. 213-218), traduzione di G. Nuzzo

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Introduction

Human health risk assessment represents a crucial step in the management of contaminated sites. It is the meeting point between characterization of contaminated sites and the subsequent soil and groundwater remediation. Just because the evaluation of potential adverse effects on human populations exposed to hazardous substances is a highly complex process, it deals with significant levels of uncertainty. To face this scenario, government institutions and consultancy companies rely on software tools that facilitate the quantification of risks. Among the most used programs, RBCA Tool Kit® and Risk-net® are considered as robust tools, both built on internationally accepted methods and projected to fit different regulations.

The RBCA (Risk-Based Corrective Action) Tool Kit, developed by GSI Environmental Inc., is based on the international guidelines and implements a tiered approach to site-specific risk analysis. Risk-net, developed within the Italian RECONnet framework, adapts these same international guidelines considering also the national ones (established by ISPRA) and offering a more localized application for the Italian legislative environment. Although they have common foundations, the tools present differences in terms of user-friendliness, database, fate and transport models selection and output generation.

Chapter 1 provides a general introduction to the concept of human health risk assessment, explaining its most relevant steps. While Chapter 2 offers an overview of the two tools under evaluation, focusing on their development context, structure and applications.

In chapter 3 the differences between the tools are reported analysing key technical aspects such as exposure pathways definition, chemical databases and transport algorithms. The comparison goes on in Chapter 4 with a critical evaluation, highlighting the most relevant discrepancies between the tools (and their impact on the assessment) and identifying strengths, weaknesses and selection criteria depending on the situation under consideration.

Concluding, in Chapter 5, both software are applied to practical case studies based on theoretical data, in order to perform a comparison of their behaviour while evaluating different exposure scenarios. This application is intended not only to test the programs' performance in realistic contexts, but also to investigate whether specific patterns are detected in their outputs: the aim is studying whether certain tendencies are intrinsic to each software's modelling approach.

Chapter 1 - Subject of the study

1.1 Human health risk assessment

Often individuals are exposed to harmful chemicals because of improper disposal of wastes, contamination generated by industrial activities and, more in general, anthropic processes. This dynamic has a great impact on the environment because, even if remediation processes are carried out, it is rarely possible to completely remove all the contaminants (especially in some cases, as regards the soil) and the associated cost is very high. The risk of these situations can be described as the probability of developing adverse health effects after entering in contact with such substances: for example drinking contaminated water or eating vegetables grown in a contaminated soil.

Although this is a systematic and quantitative discipline which follows defined and regulated procedures, often it has to deal with uncertainty and data gaps, that could be difficult to obtain or totally unavailable. Because of this, risk assessments must be carried out by experienced experts, so that they can carefully estimate the data where necessary.

Usually, all the environmental compartments, such as aquatic environment, terrestrial environment and air, are taken into account, although it always depends on the nature of the contaminants and the site of interest. Furthermore, during the first analysis, it is very common to divide the problem in three parts, which are sources, migration pathways and receptors: the source characterization is fundamental because it has to deal with the initial contaminants' concentrations, which rule all the subsequent study. Then the transport pathways are defined, depending mainly on the properties of the contaminants detected (solubility, volatility, degradation rate, exc..) and on the characteristics of the contaminated site and of the source. If this analysis shows that the contaminants will come into contact with receptors, it will be evaluated in which environment it will occur and the hazard that they will be exposed to.

Typically, the risk assessment process is carried out in four steps (Figure 1), defined by the environmental protection agency (EPA), that will be further discussed in the following paragraphs.

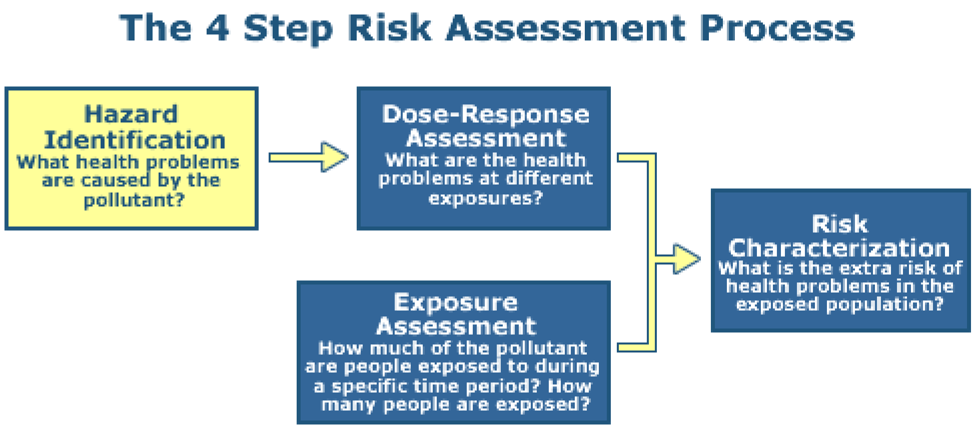

Figure 1: United States Environmental Protection Agency, https://www.epa.gov/risk/conducting-human-health-risk-assessment, April 2025

1.1.1 Hazard identification

The aim of this first step is to evaluate if the exposure to a specific contaminant can increase the risk of developing adverse effects (especially in humans), such as cancer, other diseases or birth defects. It is addressed by evaluating the properties of chemicals and their emission from their sources in the site of interest: this part can be carried out performing sampling campaigns, in order to determine the concentration and the distribution of the contaminants. The dataset used during the following steps is formed during these first surveys.

In addition, in most cases a large number of contaminants are released from hazardous wastes, up to hundreds of different chemical species. Since building a database with all relevant information would be overwhelming, the most dangerous contaminants or those present in major concentrations dictate the risk and they are identified as risk drivers.

1.1.2 Exposure assessment

An individual is said to be exposed to a contaminant when, in some way, he enters in contact with it; exposure assessment evaluates all the characteristics of this condition, such as the types of receptor exposed to the agent and frequency and duration of the exposure.

Identifying the entity, location and type of sources is of paramount importance and influences all the subsequent assessments: the effects of time variations in release rate are important and divide pulse sources, when the mass of contaminant is emitted in a single, short-lived burst (like an hazardous waste spill) and plume ones (Watts R. J & Till A. L., 2003), if the emission is continuous (as from a corroded tank). Chemicals can be transported in several ways before entering in contact with organisms, for example through atmospheric transport or transport through the subsurface till the groundwater.

In order to be able to perform the risk characterization, it is necessary to estimate the concentration of contaminant the population is exposed to, which is then used in the calculation of the chemical intake or received dose . The numerical value of the concentration term can be estimated with a sampling campaign or, more commonly (in order to low the cost of the assessment), with the use of contaminant transport models for the atmosphere, surface water and groundwater: the choice of the model has a significant impact on the final result due to the transport mechanisms the contaminant is subjected to.

Equation 1 is a general formula, used in the calculation of the chemical intake (I):

$$I = \frac{C\ x\ CR\ x\ EF\ x\ ED}{BW\ x\ AT}$$

Equation 1: Chemical intake

Where:

- I: Chemical intake. It is expressed in $mg_{contaminant}/kg_{soil}$*d if the exposure occurs via oral ingestion or dermal contact and in $mg_{contaminant}/m^3_{air}$ when there is inhalation (in this case, CR and BW are not included in the equation): these are different types of exposure route taken in account in the exposure assessment, formulas used to calculate the intake change a bit depending on the considered route.

- C: Time-averaged concentration in the exposure medium (mg/kg_{soil}; mg/L_{water}; mg/m^3_{ai}; etc..).

- CR: Contact rate (mg_{soil}/day; L_{water}/day, etc..).

- EF and ED: Exposure frequency (days/year) and duration (years).

- BW: Body weight (kg).

- AT: Averaging time (days), considered equal to the entire lifetime for carcinogenic substances and to the exposure period for the non-carcinogenic ones.

1.1.3 Toxicity assessment

Toxicity assessment includes the possible harmful effects that humans can develop once entered in contact with a contaminant. In this part of the assessment, the analysis is quantitative and the objective is to define doses considered dangerous for human health. All conclusions drawn in this context are based on epidemiological or laboratory studies. The sensitivity of a population to the adverse effects of a contaminant follows a log-logistic distribution: the limits and the rules concerning doses considered safe produced by this type of assessment are always calibrated on the most sensitive individuals, so as to protect the entire population.

Exposure is considered acute or chronic depending on its duration. In the first case the individual comes into contact with a high dose of contaminant during a relatively short time, such as inhaling smoke during a fire, while in the second one the exposure is prolonged over time with much smaller doses, like daily ingestion of water coming from a contaminated source; chronic toxicity is more difficult to evaluate, because there are less information about long term effects of contaminants than about their acute toxicity. There also are chemicals that are considered dangerous if the exposure is acute but that the body requires chronically and in small doses, such as vitamin D (Hathcock John N et al., 2007).

All the toxicological information is used to estimate a risk and to infer a critical region where the dose level begins to cause the adverse effect in the human population. The mode of action of a contaminant shows how the substance causes the effect: the way it interacts with the cells can lead to different harmful consequences, such as cancer development. According to this feature, substances can be divided into two groups:

- Threshold substances: an exposure to a dose that varies from zero to some finite value, called threshold, does not have significant toxic effects on the individual. This is represented in the following image.

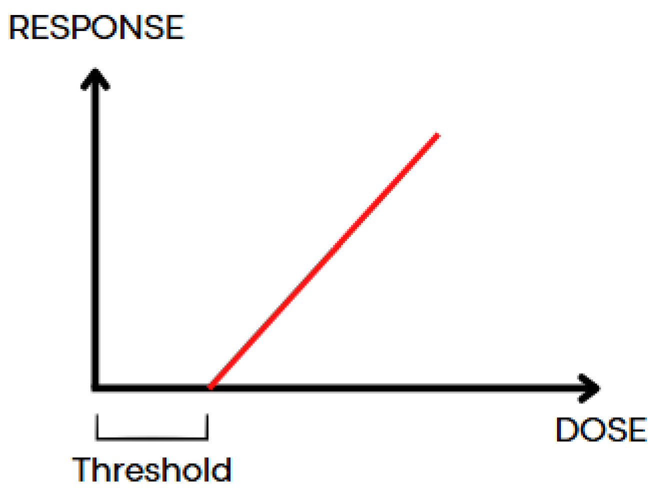

Figure 2: typical dose-response graphic of a threshold substance

Such substances cause toxic effects other than cancer (also called systemic) effects. In this case, the estimation of the risk linked to the exposure is carried out using different parameters, inferred from the scientific studies. One of the most important ones is the NOAEL (No observed adverse effect level), which represents the highest dose at which no significant increases are seen in the occurrence of adverse effect between the exposed population and its appropriate control population. Since it is not always easy to determine the NOAEL, sometimes also the LOAEL (Lowest observed adverse effect level, corresponding to the lowest tested dose giving adverse effects) can be used in this part of the risk assessment. Another parameter, called benchmark dose (BMD), can be taken into account instead of NOAEL. It is estimated with mathematical modelling and it identifies the dose of a substance that produces a predetermined change in the way an adverse effect manifest itself, compared to a background control level.

Variables such as NOAEL and BMD are used to calculate thresholds considered safe for human health, like the acceptable daily intake (ADI, daily dose that does not produce adverse effects) and the reference dose (RfD). Much reliance is placed on RfD (used for oral ingestion and dermal contact, while a reference concentration is calculated for the inhalation route), which is used by the *U.S. Environmental Protection Agency* (EPA) as official threshold and is calculated dividing the NOAEL (or the LOAEL, if a NOAEL is not available) by some uncertainty factors (UFs). These factors depend on the reliability of the studies on which the employed data are based.

$$RfD = \frac{NOAEL}{\Pi_i UF_i}$$

Equation 2: Reference dose

RfD is expressed in units of milligrams of contaminant per kilogram of bodyweight per day (mg/kg*d).

While the reference concentration (RfC) mentioned before is referred to concentration levels in the air and it is expressed in the units of milligrams of chemical per cubic meter of air (mg/m^3).

- Non-threshold substances: it is generally accepted the concept that exposure to any concentration of these substances can increase the probability of developing harmful effects, equivalent to cancer development. Hence the name, non-threshold.

The dose-response curve for these contaminants is assumed to be linear in the low dose – low response region and passes through the origin.

Figure 3: typical dose-response graphic of a non-threshold substance

The slope of this straight line becomes an important parameter, called slope factor (SF, also here for the inhalation it is different and the Inhalation unit risk, IUR, is used), used to estimate the individual's likelihood of developing cancer over his lifetime per unit of dose. Its unit measure is the inverse of a dose $(mg/kg*d)^{-1}$.

A significant question for the carcinogenic risk concerns the hazard linked to the exposure to very low concentration of contaminants: to precisely assess the effects of the low concentrations population is typically exposed to, would require chronic toxicity studies with an enormously large number of test animals. Therefore, the responses related to high doses are usually determined first and from the data obtained, the effects that lower doses might have on an individual are extrapolated.

1.1.4 Risk characterization

Risk characterization summarizes and uses all the information collected with the previous analysis with the aim of putting all the data together, in order to quantify a risk level and to assess if it is acceptable or not for the human health. A risk factor is calculated using the parameters introduced before: for example, to calculate the risk associated with the exposure to a non-carcinogen contaminant, a hazard index (HI) is employed.

$$HI = \frac{I}{RfD}$$

Equation 3: Hazard index

Where I is the intake (measured in $mg_{contaminant}/kg_{soil}*d$, as written in paragraph 1.1.2) and RfD is the reference dose (also in $mg_{contaminant}/kg_{soil}*d$, as shown before). The result of the formula is a non-dimensional number which, compared to a predetermined risk limit (equal to one in this case), provides information on the acceptability of the risk of developing systemic effects. If the value obtained is greater than one the risk is unacceptable and vice versa.

Carcinogenic risk assessment follows a similar logic, also here there is a risk factor (R), which is calculated with the following formula:

$$R = I * SF$$

Equation 4: Risk factor

The parameter R is non-dimensional and it is considered acceptable when its value is lower than 10^{-5}.

In both cases, when there is more than one contaminant the receptor enters in contact with, it is necessary to calculate HIs and Rs associated to each chemical. All these values will be summed to obtain an overall HI and R and the risk assessment will be based on them.

The choice of these risk limit values (1 and 10^{-5} adopted by the EPA) influences the subsequent remediation efforts. In fact, the target concentration, the value to which it is considered necessary to lower the concentration of the contaminant at the source, is calculated in such a way as to lower HI and R to the acceptable risk levels.

1.2 Software role in the assessment

As highlighted in paragraph 1.1, the assessment of risks to human health is of fundamental importance in many sectors. From the definition of the limits of compounds present in drinking water to the organization of remediation operations following environmental disasters: the protection of the population is at stake and it is necessary to act in order to guarantee its well-being. Tolerable levels of exposure to contaminants must be as precise as possible, in order to safeguard even the most sensitive individuals. Where there is no experimental certainty and it is necessary to resort to estimations, it is better to be conservative, within reasonable limits, since the imposition of very low limits is always associated with high costs in the processes of control and clean-up of the sites.

All these arguments make clear how important it is to approach this problem with extreme precision. Furthermore, in real cases, contamination often occurs at the site of interest in a very complex manner: there can be a large number of dangerous substances and multiple migration pathways and exposure routes; this multiplies the calculations to be made and increases the complexity of the problem.

Over the years, the development and evolution of human health risk assessment has given rise to programs capable of carrying out the necessary calculations. Through a database, where physical, chemical and toxicological parameters of the contaminants, average characteristics of the population, transport models and many other information are inserted, they are able to determine the presence of risk. They are now widely used and constitute an essential tool in this field and, precisely for this reason, there are several of them.

This is where the object of this study comes in, which aims to highlight the differences between two of the most used of this type of programs: RBCA and Risk-net. A deep comparison will be carried out in the next paragraphs.

The focus of the study is that, although the mechanism that leads to the final result is similar, these two programs have differences in the employed database, in the interface and in many other features. It is therefore interesting to make a comparison to analyse the differences, similarities, strengths and weaknesses.

Chapter 2 - Methodological approach and survey tools

The main justification for this work is the comparison between RBCA and Risk-net. Precisely because they are two programs widely used in the sector, it is interesting to compare them and reach conclusions regarding the advantages and disadvantages related to their use. The comparison will be carried out by examining all the features that are involved in the use of the programs themselves, from the database they use for the physical-chemical parameters to their interface. Chapter 3, presents an objective description of the main features of both programs, whereas chapter 4 provides a critical comparison and suggests potential improvement.

Furthermore, it can happen that these programs are used without a solid understanding of the concepts and the models they employ to reach a conclusion. And since, nowadays, almost all human health risk assessments are performed with them, this potential misuse use can lead to dangerous results: for example claiming that a scenario does not pose a risk to receptors when in fact it does. For this reason, the aim of this study is also to provide possible guidelines on the criteria for using this type of software.

But before going into the heart of the analysis, it is necessary to introduce the two programs from a general point of view.

2.1 RBCA Tool Kit ®

The acronym RBCA, which gives name to the software, stands for *Risk based corrective action*: a decision making approach employed to face environmental contamination (given by the accidental release of COCs, contaminants of concern, in the environment due to the human activity) with the aim of taking into account simultaneously the risks for the human health and for the environment with cost-effective cleanup strategies. The software, whose complete name is *RBCA Tool Kit for Chemical Releases*, has been developed by the American consulting company GSI Environmental Inc. Over the years RBCA has undergone an evolution through updates and expansions: the version that will be taken into consideration in this study is number 2.6.

The software follows a tiered risk evaluation approach, giving the user the opportunity to examine the case study through increasingly complex analysis level. These levels are commonly named tiers and they are associated with a number (from one to three), where the accuracy of the result (and the associated cost) increases with increasing number. The calculations performed by RBCA for tiers 1 and 2 (respectively Screening-level evaluation and Site-specific risk assessment) are established by the ASTM-RBCA planning process, as defined in ASTM E 2081-00 Standard Guide for Risk-Based Corrective Action (ASTM, 2004) and ASTM E-1739-95 Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites (ASTM, 2002). Also, the current U.S. EPA guidelines for human health risk assessment (U.S. EPA, 1989) are followed precisely .

Tier 3 (Detailed risk modelling) analysis can also be performed with this version of RBCA and it has been added over the years through the updates made; in fact, the software provides many additional modelling and parameter options.

A licence is required to use the RBCA Tool Kit® and can be obtained paying an annual fee (although licences are also provided to universities, for example, for educational purposes). It relies on Microsoft Excel for its operation: in particular, it only supports the 32-bit version.
All the theoretical information about the use of the program is taken from the Software Guidance Manual RBCA Tool Kit for Chemical Releases Risk-Based Corrective Action Tool Kit Version 2 (Connor et al., 2007).

2.2 Risk-net ®

Risk-net ® is a software designed with the aim of performing the calculations required for the RBCA planning process: it has been developed in Italy because of the need of creating a tool based on the Italian ISPRA (*Istituto Superiore per la Protezione e la Ricerca Ambientale*, focused on environmental protection and monitoring) guidelines, based on the same two ASTM risk assessment regulations cited above for RBCA Tool Kit. It has been conceived by Iason Verginelli (Università degli studi di Roma "Tor Vergata") and Alessandro Girelli (I.A. Industria Ambiente S.r.l.) within the Italian Network on the Management and Remediation of Contaminated Sites (RECONnet, an Italian collaborative platform where researchers, public institutions and private stakeholders work together to face the remediation of contaminated sites). The version used for the analysis performed in this study is number 3.1.1.

As for RBCA Tool Kit, it is possible both to evaluate the risk for the receptors in a contaminated sites and to estimate clean-up levels for the remediation process. The transport models employed are described in the ISPRA guidelines (Agenzia per La Protezione Dell'Ambiente e per i Servizi Tecnici, 2008) and, through them, Risk-net calculates the maximum steady state concentration at the point of exposure (for the exposure pathways selected); a daily dose is then calculated for exposed individuals and thus the risk and the remediation targets.

Unlike RBCA, this service is free and characterized by a simpler and faster use. All the theoretical information about the use of the program is taken from the RECONnet Italian Network on the Management and Remediation of Contaminated Sites USER GUIDE RISK-NET, 2019.

Chapter 3 – Comparison

3.1 Interface – main screen

RBCA

The page displayed when the program is opened is defined as main screen (Figure 4). There is a section dedicated to the *project information* where it is possible to specify general information about the site of interest. Furthermore, in *Which type of RBCA analysis?*, the user can choose between Tier 1, 2 and 3 (paragraph 2.1).

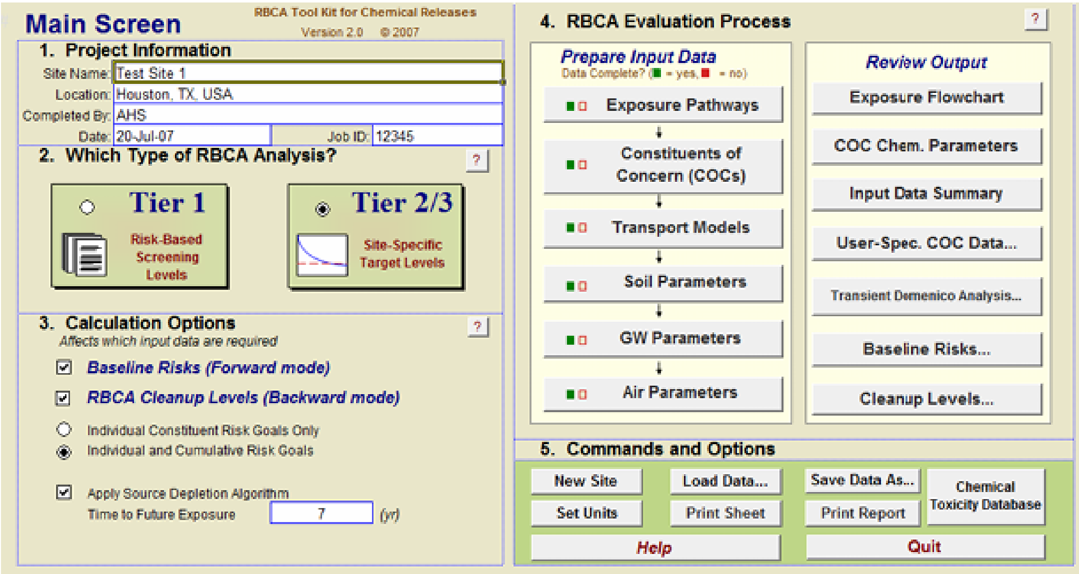

Figure 4: Main screen. Taken from: RBCA Tool Kit for Chemical Releases Manual, GSI Environmental Inc., 2007, pg. 9

In *calculation options* the user can select a forward mode option, when baseline risks are calculated based on concentrations of the contaminants specified by the user and a backward mode option to calculate cleanup levels built on risk limits (also decided by the user).

Risk goals can be set on either an individual (risk assessment will be performed by looking at the exposure to each contaminant separately) or a cumulative (combined effects of exposure to all contaminants together) basis.

Additionally, for Tier 2 or Tier 3 assessments, users have the option to use the *Source Depletion Algorithm*. This way cleanup levels are adjusted by accounting for how the source's mass naturally decreases over time (through volatilization and biodegradation for example) until a future exposure occurs.

Beyond these sections, the most relevant part of the main screen is on the left part of Figure 4 and concerns the input and output data:

- Input:

  a) Exposure pathways: discussed in paragraph 3.2.

  b) Constituents of concern (COCs): selection of the contaminants and their concentration. Here the user can provide the concentration values for each contaminant, if more than one is available. The software gives three possibilities to calculate the representative value, which will be used in the assessment:

    - Arithmetic mean.
    - Maximum value.
    - UCL95 on the mean (discussed in paragraph 5.1).

  c) Transport models: discussed in paragraph 3.4.

  d) Soil parameters.

  e) Groundwater parameters.

  f) Air parameters.

- Output:

  a) Exposure flowchart.

  b) COC chemical parameters.

  c) Input data summary.

  d) User spec. COC data.

  e) Transient Domenico analysis.

  f) Baseline risks: discussed in paragraph 3.5.

  g) Cleanup levels: discussed in paragraph 3.6.

Risk-net

A screenshot of the Risk-net main screen is shown in Figure 5. The interface consists of a sidebar from which the user has access to:

- Setup: it includes the site description (basic information about the site), the conceptual site model (selection of the exposure pathways) and the choice of receptors.

- Input: such as contaminants selection and concentration, choice of exposure factors and site parameters (about soil, air, groundwater, etc..). For the contaminants concentration Risk-net requires one value in input for each contaminant (one for each contaminated media).

- Output: where the user can check the calculated risk and site-specific target levels (SSTLs).

- Detailed results: here is conserved the more specific and complete information about the input data and the results of the estimation.

- Advanced options: model options (saturation concentration, risk limits values,..) and site characterization options (possibility to use data from advanced characterization for SSTL calculation of each exposure pathways).

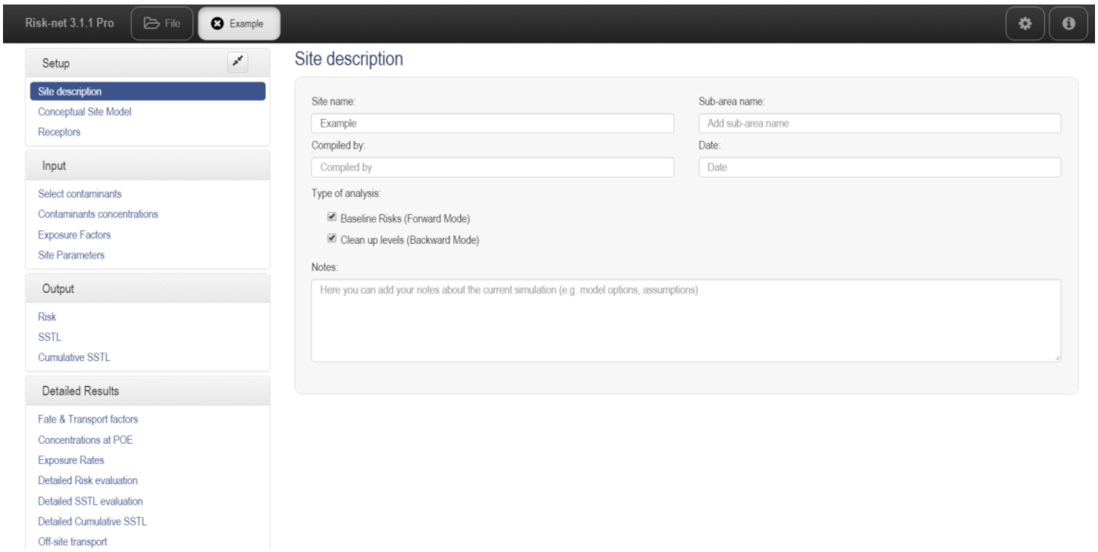

Figure 5: Main screen. Screenshotted from Risk-net.

3.2 Exposure pathway evaluation

An exposure pathway is the link between a contaminant source and a receptor (U.S. EPA, 1991). This evaluation, therefore, determines if chemicals released by the contamination source have been, are or will be in contact with individuals.

The study of an exposure pathway involves five main elements: contamination source, transport mechanism, exposure point, exposure route (i.e., the way the receptor physically enters in contact with the chemical, e.g. by inhalation, ingestion or dermal contact) and type of receptor. The approach to this step typically includes the development of a conceptual model: it can be schematic or precise as shown in the Figure 6 and 7), both taken from the Public Health Assessment Guidance Manual (2005).

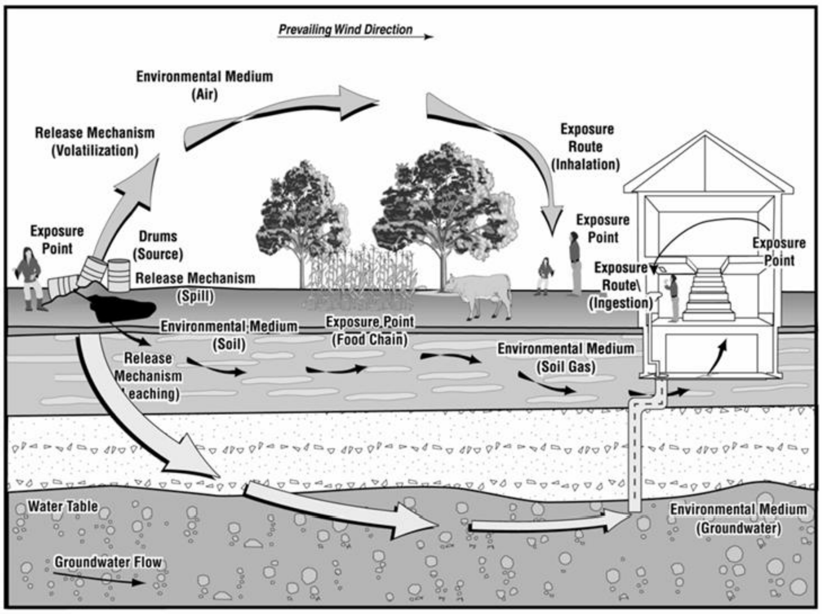

Figure 6: Site conceptual model – exposure pathway schematic. Taken from: ATSDR Public Health Assessment Guidance Manual (2005), pg. 65

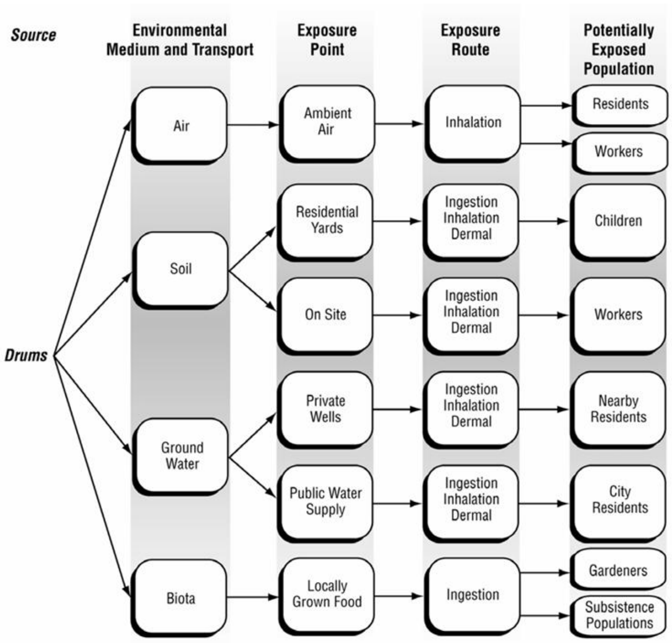

Figure 7: Site conceptual model – exposure pathway evaluation. Taken from: ATSDR Public Health Assessment Guidance Manual (2005), pg. 66

For exposure to occur the exposure pathway must be complete, which means that all the five elements mentioned before have to be present and confirmed through studies. Pathways may be partially complete, if an element is not certain or has to be confirmed: this condition requires the performance of further studies, to assess if the pathway is or could become complete in the future.

The following section describes how the two programs perform this evaluation.

RBCA

The *Exposure pathways identification* section (Figure 8) is located in the *Exposure Pathways* section of the Main Screen. Here it is possible to define the complete exposure pathways, the type of receptors (residential, commercial, etc..) for each pathway and the distance between source and receptor (downstream or downwind distance).

RBCA allows to define only on-site receptors for Tier 1 analyses and one on-site and up to two off-site receptors for Tier 2/3 analyses.

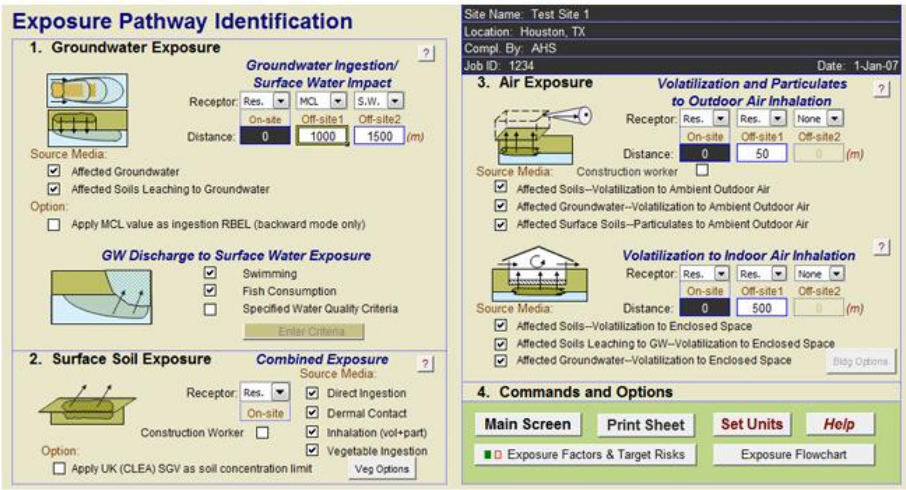

Figure 8: Exposure pathways identification window. *Taken from: RBCA Tool Kit for Chemical Releases Manual,* GSI Environmental Inc., 2007, pg. 14

The figure shows three sections:

1) Groundwater Exposure: the selectable receptors are residential, commercial, user-defined and MCL (maximum contaminant level).

For residential, commercial and user-defined receptors, the assessment is made on the basis of applicable exposure factors and target risk levels. MCL option instead, follows the drinking water criterion, which sets a specified concentration that ensures water is drinkable. This option includes the direct calculation of cleanup levels that guarantee such limit is not passed in groundwater at the receptor location.

There is an additional receptor selectable for the second off-site case, the surface water (SW) exposure pathway: it indicates exposure to surface water contaminated by discharge of groundwater, in particular through swimming and fish consumption. In this section there is also a third option selectable, *Specified Water Quality Criteria*, which requires to the user to insert applicable surface water quality criteria.

2) Surface Soil Exposure: surface soil thickness must be specified by the user (even if the major part of the models consider surface soil as the portion from zero to one meter of depth). The available receptors are the same as for groundwater exposure (except MCL, which is not present). Furthermore, it is possible to select *Construction worker* as receptor. It allows to assess excavation activities that involve contact with affected soils (the related parameters of the worker are specified on the exposure factors and target risks page of the software).

Since it is assumed that this type of exposure occurs only in the immediate area of the affected soil zone, there is not the possibility of selecting off-site receptors.

In addition, the user can apply United Kingdom CLEA (Contaminated Land Exposure Assessment) soil guideline values instead of a calculated cleanup level for backward-mode calculations, ticking the specific box. For more information about this soil guideline, the user is referred to the Contaminated Land Report (CLR), a series of documents published by the Environment Agency of England and Wales (EA, 2002).

3) Air Exposure:

<u>Outdoor air inhalation</u>

It includes the exposure to particulates and vapour from contaminated soil and underlying groundwater. There are four receptor choices: residential, commercial, user and TWA (time-weighted average). This last option automatically assumes the exposure limits as equal to occupational permissible exposure levels (PELs) or threshold limit values (TLVs), established under U.S. worker exposure criteria. TWA is similar to MCL, it does not involve the calculation of a baseline risk, but cleanup levels are determined preventing exceedance of the specified air concentration limits at the receptor location.

Also in this case the *Construction worker* option is selectable.

Indoor air inhalation

It involves the indoor inhalation of vapours emanated from affected soil and groundwater, entering buildings through foundation fractures.

Inside this window, in the lower right part, there is a *Commands and options* section, from which we can access to the exposure factors and target risk limits and to a scheme of the exposure flowchart (made automatically by the program once the exposure pathways have been selected).

Risk-net

The pathways identification can be done in the *Conceptual site model* section, present in the setup menu. The user can identify the complete pathways as shown in Figure 9.

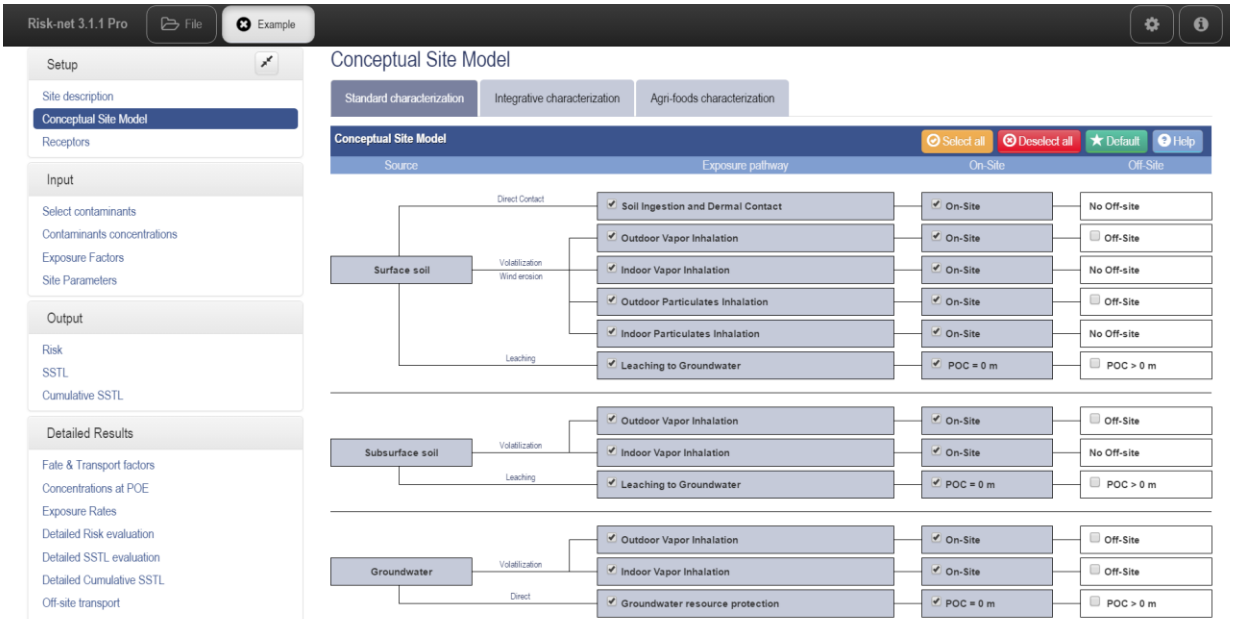

Figure 9: Exposure pathways identification window. Screenshotted from Risk-net.

Here the classification is different, in facts three sources are considered (surface soil, subsurface soil and groundwater) and for each of them it is possible to select the active exposure pathways (outdoor vapor inhalation for surface soil for example) and if the exposure occurs on-site, off-site or both. While RBCA considers the air exposure pathway separately, Risk-net classifies inhalation exposures in the group of media from which contaminated vapours arise (for example outdoor vapor inhalation for groundwater).

Surface soil is assumed to be that portion between the ground surface and the depth of one meter. For the groundwater there is also the *groundwater resource protection* option: the POC is the point of compliance where the limit values defined by the groundwater legislation (the MCL introduced for RBCA for example) must be respected. There is the possibility of activating POC = 0 m and POC > 0 m both but, if so, the cleanup levels for the protection of the groundwater resource will be computed considering POC = 0 m.

Figure 9 shows other two options that allow to assess the case study:

- Integrative characterization: it gives the possibility to select other monitoring data available in terms of ambient air, soil-gas, flux chambers or leaching tests carried out on samples collected in the surface or subsurface soil. Here the user must also define if the results of this integrative characterization should be used for on-site or off-site exposure.

- Agri-foods characterization: risk assessment for food products consumption. The products can be specified entering their names (up to ten) in this section.

3.3 Chemical parameters database

Since human health risk assessment involves a significant calculation phase, the database of physical, chemical and toxicological properties of contaminants acquires great importance.

In this section the database of the two versions of the programs object of study will be evaluated.

RBCA

It provides parameter values for 658 chemicals. The database is built from various sources. Listed below are those most commonly used for the different classes of parameters:

- Physical properties:

  a) [TX11]: Texas Risk Reduction Program, RG-366 TRRP-19, Toxicity Factors and Chemical/Physical Parameters, June 2001; (toxicity and physical/chemical properties tables dated May 24, 2011).

  All the values of this section are taken from this source, which is regularly updated;

- Miscellaneous parameters:

a) [TX11] for *soil-to-plant biotransfer factor* and *relative bioavailability factor*.

b) [H]: Howard, Handbook of Environmental Degradation Rates, Lewis Publishers, Chelsea, MI, 1989. (For *half life (first-order decay)*)

c) [S]: USEPA, Test Methods for Evaluating Solid Waste, SW-846, Third Edition, OSWER, November 1996.

d) [S2]: USEPA, Method 8270C, Revision 3, "Semivolatile Organic Compounds by GC/MS", December 1996.

e) [MC]: Nacional Primary Drinking Water Regulations, EPA 816-F-03-016, June 2003, downloaded February 2007. (*Analytical detection limits* are taken from these last three sources).

f) [LY]: Handbook of Chemical Property Estimation Methods, 1982, W. J. Lyman, (McGraw-Hill, New York), ISBN -0-07-039175-0. (For the *bioconcentration factor*).

- Dermal exposure:

a) [D]: USEPA, Dermal Exposure Assessment. Principles and Applications orD, EPA/600/8-91/011B.
For the *water dermal permeability data*.

b) [TX11] for the *absorbtion factor*;

- Regulatory standards:

a) [MC] for *maximum contaminant level.*

b) [E]: U.S. Environmental Protection Agency (EPA). (2002). National Recommended Water Quality Criteria: 2002 (EPA 822-R-02-047). Washington, DC: U.S. EPA, Office of Water.

c) [T1]: Texas Surface Water Quality Criteria, 30 TAC 307 Table 1, downloaded June 2003.

d) [T3]: Texas Surface Water Quality Criteria, 30 TAC 307 Table 3, downloaded June 2003.
These last three sources are employed for the *surface water quality criteria*;

- Toxicity parameters:

a) [TX11].

b) [EPA-I]: USEPA Integrated Risk Information System (IRIS), as of March 31,2007.

c) [EPA-OP]: USEPA. (1993). Office of Pesticide Programs: Provisional Guidance for Quantitative Risk Assessment of Polycyclic Aromatic Hydrocarbons. Office of Research and Development, EPA/600/R-93/089.

a, b and c are used as a reference for chemicals' *oral RfD*, *inhalation RfC*, *dermal RfD oral SF*, *dermal SF* and *inhalation equivalent unit risk factor*.

About the toxicity parameters, RBCA gives users the possibility to choose between values of United States, United Kingdom and Netherlands database: in this study the USA database will be used.

Special mention must be made to the so called total petroleum hydrocarbons (TPH). Oil is made up of many types of hydrocarbons with various molecular structures and properties. TPH are a summation of the identifiable hydrocarbon compounds in the oil (United States Environmental Protection Agency, 2023). There are substances included in this definition which are divided into aromatic and aliphatic and are further classified according to the number of carbon atoms present in their molecular structure. When these data are not available or cannot be collected from one source, the program draws on various documents to complete the database.

RBCA provides data for 14 TPH fractions:

- Aliphatic: seven fractions (the first two with sets of different values depending on the content of n-hexane): >C5-C6, >C6-C8, >C8-C10, >C10-C12, >C12-C16, >C16-C21 and >C21-C34. For them, RBCA relies on various documents of the TPH Criteria Working Group [TPH] (TPH Criteria Working Group. (1997–1999). *Total Petroleum Hydrocarbon Criteria Working Group Series* (Vols. 1–5). Amherst, MA: Amherst Scientific Publishers) for the physical properties and on [TX11] for all the other data (except for *bioconcentration factor* and *dermal RfD*, which are taken respectively from [LY] and [D]).

- Aromatic: seven fractions: >C5-C7, >C7-C8, >C8-C10, >C10-C12, >C12-C16, >C16-C21 and >C21-C35. Here sources employed are the same just mentioned, except for some toxicity parameters, which are taken from [EPA-I].

- An alternative grouping into >C6-C12, >C12-C28, >C12-C35 and C28-C35 is provided. In this case there is no distinction between aliphatic and aromatic compounds and the classification depends only on the number of carbon atoms. The values assigned to them come from [TX11], except for *dermal RfD*, which arises from [D].

In any case, TPH parameters (physical properties, miscellaneous parameters,..) are not always available and there is generally more lack of information than for other classes of contaminants.

Furthermore, users can edit parameter values and add new contaminants. Changes made to the standard database are displayed in yellow and can be saved with the *Save/Close DB* button.

Risk-net

It collects data for 144 contaminants. By Default, the software implements the Italian ISS-INAIL database, whose structure and content is explained in the document *Banca Dati ISS-INAIL DOCUMENTO DI SUPPORTO (2018)*. It has as main references the following international documents.

- EPA (Environmental Protection Agency). (2017). Regional Screening Levels (RSLs) – Generic Tables (November 2017). U.S. EPA.

- Texas Commission on Environmental Quality (TCEQ). (2017). Texas Risk Reduction Program (TRRP) Tier 1 Protective Concentration Levels (PCLs) Tables – March 2017. TCEQ.

- European Parliament and Council. (2008). Regulation (EC) No. 1272/2008 on classification, labelling and packaging of substances and mixtures (CLP Regulation). Official Journal of the European Union. For some toxicity parameters.

- ECHA – European Chemicals Agency. (2017). Information on Chemicals: Registered substances under REACH. Helsinki: ECHA. For some physical chemical properties.

- NIOSH – National Institute for Occupational Safety and Health. (2016). NIOSH Pocket Guide to Chemical Hazards. Cincinnati, OH: U.S. Department of Health and Human Services. In case of deficiencies of occupational exposure limit values.

- OECD – Organisation for Economic Co-operation and Development. (Various years). Screening Information Data Set (SIDS) for High Production Volume Chemicals. Paris: OECD. Also for physical chemical properties.

Risk-net as well has some TPH in its database, seventeen of them following the TPH Criteria Working Group classification (their data are taken from [TPH], used also by RBCA). The remaining seven chemicals follow a different classification, based on the guidelines of the Massachusetts Department of Environmental Protection (MADEP) (data from Massachusetts Department of Environmental Protection. Interim Final Petroleum Hydrocarbon Fraction Toxicity Values for the VPH/EPH/APH Methodology. Boston, MA: Bureau of Waste Site Cleanup, 1994).

The program also allows user to change parameters of the database (the new values will be displayed in yellow) or to insert new contaminants.

3.4 Fate and transport models

For on-site and off-site cases both, programs employ transport models to predict the concentration of contaminant the receptor is exposed to. The model can describe the transport from one medium to another (soil to groundwater for example) or from the source to off-site receptors (drinking contaminated water from the aquifer located beneath the site of contamination for example). RBCA and Risk-net give various transport options depending on the selected exposure pathways. In the following paragraphs the equations supporting these models will be discussed.

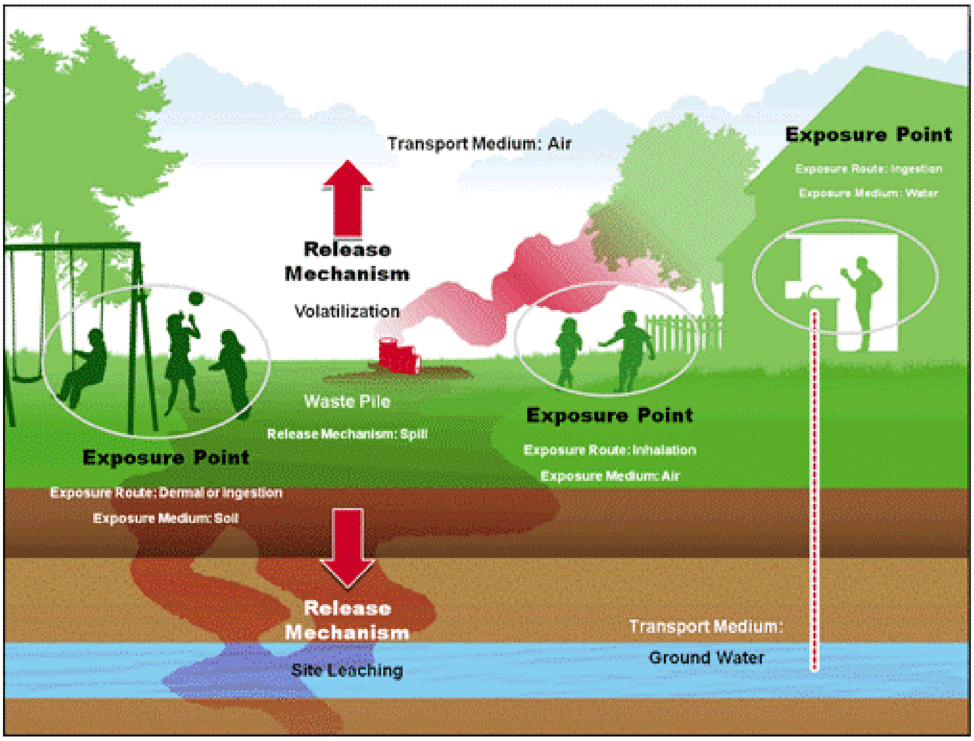

Figure 10: Fate and transport mechanisms of contaminants in the environment. U.S. EPA (June 2025, https://www.epa.gov/emergency-response-research/contaminant-fate-transport-exposure).

Equations used in the models are based on assumptions that vary depending on the phenomenon type. However, concerning RBCA, there are two main assumptions the equations are based on:

- Contaminant concentration is distributed uniformly in the source zone and constant over the exposure period.

- There is not contaminant decay, except in specific cases, for which it is specified. This is not always true for Risk-net, which often contemplates the possibility of biodegradation inserting a biodegradation factor (BDF) in the formulas.

In the following paragraphs, examining the selectable models, the parameters that have the greatest weight in the final result will be highlighted. This information relies on two documents:

- *Guía de evaluación de riesgos para salud humana en suelos potencialmente contaminados (Consejería de Agricultura, Ganadería, Pesca y Desarrollo Sostenible, Dirección General de Calidad Ambiental y Cambio Climático, Junta de Andalucía, 2019)*. [1]

- *Public Health Assessment GUIDANCE MANUAL (Update) (Agency for toxic substances and disease registry - ATSDR, 2005)*. [2]

Whenever a model uses two distinct equations to calculate one factor, the value considered is the lower of the two obtained. This criterion may seem counterintuitive, since taking the higher value would be the more conservative choice. However, each equation is already conservative under specific boundary conditions or transport scenarios. Choosing the higher value would result in an accumulation of conservatism, as both equations already incorporate safety assumptions. By selecting the lower value, the models maintain a balance between protecting human health and avoiding an excessively conservative estimation of the risk.

3.4.1 Volatilization

Volatilization is the process by which the solid or liquid phases of a contaminant present in the surface or subsurface of soil escape to the gas phase, migrating towards the air above the surface of the soil itself. It involves also volatile contaminants dissolved in the groundwater. For this phenomenon, models are based on the estimation of a volatilization factor (VF), defined as the ratio between the outdoor or indoor air concentration and the source media (soil or groundwater) concentration.

There are three specific parameters which strongly influence the result of the model employed to estimate volatilization:

- Henry's Law constant (H): It estimates volatilization from water and it is a property of the contaminant. [1] [2]

- Volumetric water content (θ_w): Ratio of volume of pore water to total volume of pore space. It affects the result because the presence of water limits the soil gas diffusion in the pores. [1]

- Effective diffusion coefficients (D_i^{eff}): Estimation of gas (or water) diffusion through the natural media. They depend on the characteristics of both the medium and the contaminant. The equations used to calculate them must be chosen carefully. [1]

The unit measure of all the volatilization factors described in this section is (mg/m^3 of air)/(mg/kg of soil), except for the groundwater volatilization factors, expressed in (mg/m^3 of air)/(mg/kg of water).

Before starting to describe how the factors are obtained, it is appropriate to present the possibilities that the programs give the user in the choice of models and how this information is organized in the interface:

- RBCA: as seen in Figure 11, the section is divided into *Outdoor* and *Indoor Air Volatilization Factors* and it involves the calculation of all factors describing volatilization (from surface and subsurface soil, from groundwater and particulate emission factor).

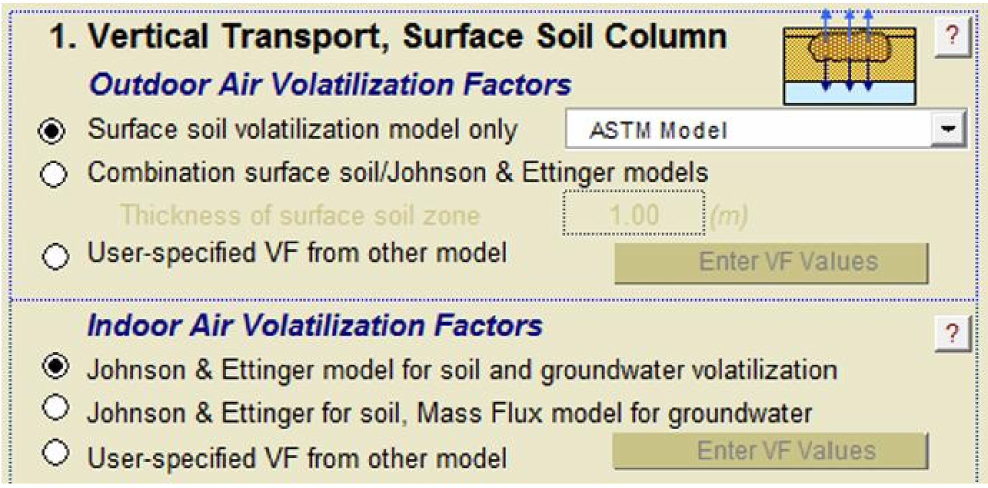

Figure 11: Transport modelling options, volatilization. Taken from: RBCA Tool Kit for Chemical Releases Manual, GSI Environmental Inc., 2007, pg. 28

Concerning Outdoor air there are three choices:

- Surface Soil Volatilization Only: the user can choose to implement the USEPA Q/C model (US EPA, 1996) and the ASTM surface soil volatilization model (ASTM, 2000) for surface and subsurface soil both. In this way, the Johnson-Ettinger volatilization model is used to estimate volatilization from groundwater (ASTM, 2000).

- Combination Surface Soil/Johnson-Ettinger Models: two different soil volatilization models (ASTM, 2000) are employed for surface and subsurface soils. In this case it is necessary to specify the thickness of the surface soil zone. For the surface soils, there is the possibility to select between the USEPA Q/C model (US EPA, 1996) and the ASTM surface soil volatilization model (ASTM, 2000). For subsurface soils (at depth greater than the specified surface soil thickness) instead, the Johnson-Ettinger volatilization model is applied (ASTM, 2000). As before, the Johnson-Ettinger volatilization model is used to assess volatilization from groundwater.

- User-Specified VF from Other Model: this option is always given by RBCA (it will no longer be reported) and it gives to the user the possibility to calculate VF with another model.

As regards Indoor air instead:

- Johnson-Ettinger Model: it uses the Johnson-Ettinger volatilization model for soils and groundwater (ASTM, 2000).

- Johnson-Ettinger Model/Mass Flux Model: the Johnson-Ettinger volatilization model is implemented for soils (ASTM, 2000) and the Mass Flux model for groundwater (McHugh et al, 2003).

- Risk-net: unlike RBCA, Risk-net does not offer the user different possible models to choose between for the calculation of the volatilization factors. For this reason, the interface of the program in this section is organised in a different way (Figure 12) and it allows to select general rules that will be applied during subsequent calculations.

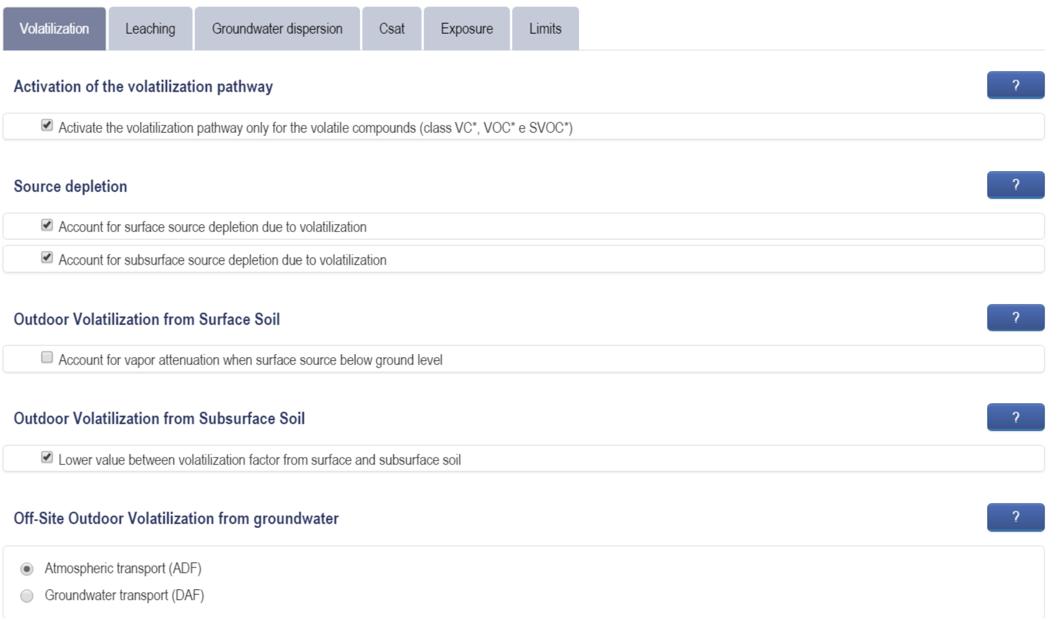

Figure 12: Model options, volatilization. Screenshotted from Risk-net.

For example, the user can decide to activate the volatilization pathway only for the volatile compounds or to account for vapor attenuation when the surface source is below the ground level.

The parameters (and the corresponding unit measure) used in the equations will be listed in tables at the end of the corresponding section. If a variable is present in more than one equation, its name will be reported only in the first one.

Surface soil to Outdoor air volatilization (VF_{ss})

RBCA

- USEPA Q/C model: simplified screening tool derived from the Johnson and Ettinger model, it offers a faster result with fewer input parameters but limited flexibility.

$$VF_{ss}(1) = \frac{2\rho_s}{\left(\frac{Q}{C}\right)}\sqrt{\frac{D_s^{eff} H}{\pi\tau(\theta_{ws} + k_s\rho_s + H\theta_{as})}} * 10^4$$

Equation 5.1: RBCA - USEPA Q/C model (1)

$$VF_{ss}(2) = \frac{\rho_s d}{(Q/C)\tau} * 10^4$$

Equation 5.2: RBCA - USEPA Q/C model (2)

Parameters
ρ_s - Soil bulk density (kg_{soil}/L_{soil})
Q - Mass emission rate from soil to air (mg/m²/s)
C - Soil concentration (mg/kg)
D_s^{eff} - Effective diffusivity in the vadose zone (cm2/s)
H – Henry’s law constant (-)
τ - Averaging time for vapor flux (yr)
θ_{ws} - Volumetric water content in vadose zone soils (cm^3 H2O/ cm^3 soil)
k_s - Soil-water sorption coefficient (gH2O/g soil)
θ_{as} - Volumetric air content in vadose zone soils (cm^3 air/cm^3 soil)
d - Thickness of affected surface soils (m)

- ASTM model: it provides a conservative estimation based on vapor diffusion in soil, without taking into account surface barriers or soil layering.

$$VF_{ss}(1) = \frac{2W\rho_s}{U_{air}\delta_{air}}\sqrt{\frac{D_s^{eff}H}{\pi\tau(\theta_{ws} + k_s\rho_s + H\theta_{as})}} * 10^3$$

Equation 6.1: RBCA - ASTM model (1)

$$VF_{ss}(2) = \frac{W\rho_s d}{U_{air}\delta_{air}\tau} * 10^3$$

Equation 6.2: RBCA - ASTM model (2)

Parameters
W - Width of source area parallel to groundwater flow direction (m)
U_{air} - Wind speed above ground surface in ambient mixing zone (m/s)
δ_{air} - Ambient air mixing zone height (m)

Risk-net

- ASTM model, the equations employed are Equation 6.1 and 6.2 (there is not the option of using the USEPA Q/C model).

However, when the factor chosen is calculated with Equation 6.1 and the depth to surface soil source (L_{sf}) is greater than zero, it is replaced with another value computed following the Jonson-Ettinger model for subsurface soils (Equation 7).

$$VF_{ss} = \frac{H\rho_s}{(\theta_{ws} + k_s\rho_s + H\theta_{as}) * \left(1 + \frac{U_{air}\delta_{air}L_{sf}}{D_s^{eff}W}\right)} BDF_{Vol} * 10^3$$

Equation 7: Risk-net - Jonson-Ettinger model for subsurface soils

Parameters
BDF_{Vol} - Biodegradation factor (-)

L_{sf} - Depth to surface soil source (m)

The Johnson & Ettinger model is more comprehensive than the others mentioned until now. In fact, it simultaneously takes into account diffusion, potential convective flow and the effects of ground covers or slabs. It gives a more precise result when dealing with site-specific risk assessments.

Surface soil to Outdoor air particulate emission (PEF)

RBCA

- USEPA Q/C model:

$$PEF = \frac{(1-V) * \left(\frac{U_m}{U_I}\right)^3 * F(x)}{Q/C} * 10^{-5}$$

Equation 8: RBCA - USEPA Q/C model

Parameters
V - Vegetation Cover Factor (-)
U_m – Mean annual wind speed (m/s)
U_I - Reference wind speed (m/s)
F(x) - Distance adjustment factor (-)

- ASTM model:

$$PEF = \frac{P_e W}{U_{air}\delta_{air}} * 10^3$$

Equation 9: RBCA - ASTM model

Parameters
P_e - Particulate emission rate (g/cm^2s)

Risk-net

- Only the ASTM model is available, with the same equation of before (Equation 9).

Outdoor subsurface Soil Volatilization (VF_{samb})

RBCA

VF_{samb} is calculated if in the *Outdoor air volatilization factors* of the transport model options, the combination between surface soil and Johnson-Ettinger models has been selected.

- Jonson-Ettinger model for subsurface soils: it calculates the factor using Equation 7 (the same used by Risk-net for the calculation of VF_{ss}, with the difference that RBCA does not take in to account the BDF_{Vol}) and another equation, which is basically Equation 6.2, with d substituted by d_s (Thickness of affected subsurface soils (m)). The lower value between the two calculated is then used.

Risk-net

In this case the equations used by Risk-net are the same employed by RBCA.

Indoor subsurface soil volatilization (VF_{sesp})

As regards the calculation of this factor and the following one (Indoor surface soil volatilization VF_{ssesp}), the models are particularly sensitive to the surface fraction of cracks in foundations or walls (the parameter η, measured in cm^2 cracks/cm^2 total area) ([1], [2]). Since it is generally difficult to be determined experimentally, it is common for the programs to rely on internationally accepted values, which are based on studies of a large number of buildings.

Also, the enclosed-space air exchange rate (ER), which quantifies the frequency of mobilization of air in an enclosed space, has a significant weight since it enhances the concentration dilution.

RBCA

For this calculation, the Johnson-Ettinger model for the indoor volatilization is used and it includes two different equations:

- The first one is split into two formulas. The program checks the convective air flow through foundation cracks (Q_s) for the choice, its presence (or absence) determines the Equation used for the calculation (10.1 or 10.2).

$$VF_{sesp} = \frac{\frac{H\rho_s}{(\theta_{ws} + k_s\rho_s + H\theta_{as})} * \left(\frac{D_s^{eff}/L_S}{ER\ L_B}\right)}{1 + \left(\frac{D_s^{eff}/L_S}{ER\ L_B}\right) + \left[\frac{D_s^{eff}/L_S}{(D_{crack}^{eff}/L_{crack})\eta}\right]} * 10^3$$

Equation 10.1: RBCA - Jonson-Ettinger model for subsurface soils (1), when $Q_s = 0$

$$VF_{sesp} = \frac{\frac{H\rho_s}{(\theta_{ws} + k_s\rho_s + H\theta_{as})} * \left(\frac{D_s^{eff}/L_S}{ER\ L_B}\right) * e^{\xi}}{e^{\xi} + \left(\frac{D_s^{eff}/L_S}{ER\ L_B}\right) + \left[\frac{D_s^{eff}/L_S}{(D_{crack}^{eff}/L_{crack})\eta}\right] * (e^{\xi} - 1)} * 10^3$$

Equation 10.2: RBCA - Jonson-Ettinger model for subsurface soils (1), when $Q_s > 0$

Parameters
L_s - Depth to subsurface soil source (m)
ξ - non-dimensional factor (-)
L_B - Enclosed space volume/infiltration area ratio (m)
D_{crack}^{eff} - Effective diffusivity in the foundations (cm^2/s)
L_{crack} - Enclosed space foundation or wall thickness (m)
η - Areal fraction of cracks in foundations/walls (cm^2 cracks/cm^2 total area)
ER - Enclosed-space air exchange rate (L/s)
Q_s - Convective Air Flow Through Foundation Cracks (cm^3/s)
A_b - Area of building foundation (m^2)

The two equations above differ in the presence of the variable ξ, which is dimensionless and quantifies the relative contribution of convective (Q_s) and diffusive transport through foundation cracks.

- The second one assumes the use of the following formula:

$$VF_{sesp} = \frac{\rho_s d_s}{L_B ER \tau} * 10^3$$

Equation 10.3: RBCA - Jonson-Ettinger model for subsurface soils (2)

It provides a simplified volatilization factor mainly driven by bulk transport parameters (soil density, source depth, attenuation factor).

Risk-net

Here it is also used the Johnson-Ettinger model for the indoor volatilization. A small variation compared to the formulas used by RBCA can be noticed: the choice between Equation 10.1 and Equation 10.2 is based on the differential outdoor-indoor pressure (Δp). Whenever its value is zero, the first Equation will be used, while in the other cases the second one. Comparing it with RBCA, which checks Q_s, it can be said that both approaches assess whether convective flow contributes to vapor intrusion, but they differ in the trigger variable: RBCA evaluates the convective air flow rate (Q_s), while Risk-Net considers the differential pressure (Δp) as the driving force.

Another difference is that in Risk-net, Equations 10.1 and 10.2 are multiplied by the BDF_{Vol}.

Equation 10.3 is not available.

<u>Indoor surface soil volatilization (VF_{ssesp})</u>

RBCA

There is not the possibility to calculate an Indoor surface soil volatilization factor.

Risk-net

This factor is calculated using the Johnson-Ettinger model for the indoor volatilization: the equation differs from the one used for VF_{sesp} only because of the presence of the depth to surface soil source (L_{sf}), which substitutes L_s.

<u>Groundwater to Outdoor air volatilization (VF_{wamb})</u>

RBCA

The Johnson-Ettinger volatilization model for compounds dissolved in the groundwater is used.

$$VF_{wamb} = \frac{H}{1 + \left(\frac{U_{air}\delta_{air}L_{GW}}{D_{ws}^{eff}W}\right)} * 10^3$$

Equation 11: RBCA - Jonson-Ettinger model for outdoor groundwater volatilization

Parameters
L_{GW} - Depth to groundwater (m)
D_{ws}^{eff} - Effective diffusivity above the water table (cm2/s)

Risk-net

Equation 11 multiplied by the BDF_{Vol} is used.

Groundwater to Indoor air volatilization (VF_{wesp})

RBCA

As explained at the beginning of the paragraph, its calculation depends on the choice that the user makes in the *Indoor Air Volatilization Factors* section:

- Johnson-Ettinger Model: Equations 12.1 and 12.2 the selection criterion regarding Q_s is the same of before.

$$VF_{sesp} = \frac{H * \left(\frac{D_{ws}^{eff}/L_{GW}}{ER\ L_B}\right)}{1 + \left(\frac{D_{ws}^{eff}/L_{GW}}{ER\ L_B}\right) + \left[\frac{D_{ws}^{eff}/L_{GW}}{(D_{crack}^{eff}/L_{crack})\eta}\right]} * 10^3$$

Equation 12.1: Jonson-Ettinger model for indoor groundwater volatilization, when $Q_s = 0$

$$VF_{sesp} = \frac{H * \left(\frac{D_{ws}^{eff}/L_{GW}}{ER\ L_B}\right) * e^{\xi}}{e^{\xi} + \left(\frac{D_{ws}^{eff}/L_{GW}}{ER\ L_B}\right) + \left[\frac{D_{ws}^{eff}/L_{GW}}{(D_{crack}^{eff}/L_{crack})\eta}\right] * (e^{\xi} - 1)} * 10^3$$

Equation 12.2: Jonson-Ettinger model for indoor groundwater volatilization, when $Q_s > 0$

- Mass Flux Model: Mass Flux model is employed (Equation 13). It evaluates the mass balance between the groundwater and vapor phases in the calculation of groundwater concentration screening levels.

$$VF_{wesp} = \frac{2wn\sqrt{\frac{D_a L v}{\pi}}}{BV * ER}$$

Equation 13: RBCA – Mass flux model

Parameters
w - Building width perpendicular to groundwater flow (m)
n - Porosity of saturated aquifer (-)
L - Building length parallel to groundwater flow (m)
D_a - Apparent diffusion coefficient (m^2/d)

v - Groundwater seepage velocity (cm/day)
BV - Building volume (m^3)

Risk-net

Only the Johnson-Ettinger volatilization model option is available, the differences that the Risk-net version has with the RBCA one are the same discussed in the paragraph about VF_{sesp}.

Equation 13 is not available.

3.4.2 Lateral air dispersion

This type of evaluation becomes necessary if there are off-site receptors: in this scenario contaminants travel from the contamination source to the site of exposure, undergoing phenomena of mixing and attenuation that reduce its concentration.

The lateral air dispersion factor (ADF) is defined as the ratio between the contaminant off-site ambient air concentration, attenuated during airborne transport, and the on-site ambient air one.

Wind speed is considered one of the most important parameters in the calculation of this factor, since it influences the distance from the source zone to which a contaminant may be transported. [2]

RBCA

To predict the concentration evolution in the atmosphere, the 3-D Gaussian dispersion model is employed. It also includes ground reflection via double exponential terms.

The dispersion coefficients (σ_i) are taken from the graphics for Dispersion Coefficients for Air Stability Classifications (EPA, 1998a).

Dispersion coefficients are computed following the Pasquill-Gifford system for stability classification, which relies on graphics providing curves that allow to obtain σ depending on the atmosphere stability class and the distance from the source.

$$\frac{C(x)_i}{C_{si}} = \left(\frac{Q}{2\pi U_{air}\sigma_y\sigma_z}\right)\exp\left(-\frac{y_{air}^2}{\sigma_y^2}\right)\left(\exp\left(-\frac{(z_{air}-\delta_{air})^2}{2\sigma_z^2}\right)+\exp\left(-\frac{(z_{air}+\delta_{air})^2}{2\sigma_z^2}\right)\right)$$

Equation 14: RBCA – 3D Gaussian dispersion model

Where the formula for the emission rate Q is:

$$Q = \left(\frac{U_{air} * \delta_{air} * A}{L}\right)$$

Equation 15: RBCA - Flow rate formula

Parameters
$C(x)_i$ - Air concentration of compound i at distance x (mg/m^3)
C_{si} - Soil concentration of compound i (mg/kg)
Q - Emission rate (mg/s)
σ_y - Transverse air dispersion coefficient (cm)
σ_z - Vertical air dispersion coefficient (cm)
y_{air} - Lateral distance from source zone (cm)
z_{air} - Height of breathing zone (m)
A - Cross-sectional area of air emissions source (m^2)
L - Length of air emissions source parallel to wind direction (m)

Risk-net

Risk-net also uses the Gaussian Plume model, even if it is less specific than the previous one: it depends only on the vertical attenuation (before also the lateral one was included, along the coordinate y) and the ground reflection is not taken into account. Equation 16 is employed to calculate an air dispersion factor.

Furthermore, the dispersion coefficients are calculated with empirical equations (Briggs, 1973).

$$ADF = \left(\frac{Q}{2\pi U_{air}\sigma_y\sigma_z}\right)[2\exp\left(-\frac{\delta_{air}^2}{2\sigma_z^2}\right)]$$

Equation 16: Risk-net – 1D Gaussian Plume model

Where the formula for the flow rate Q is Equation 15, the same used by RBCA.

3.4.3 Leaching

Leaching consists of infiltration of rainwater into the soil previous entered in contact with contaminants. It results in the formation of an eluate which flows through the unsaturated layer (vadose zone) until it reaches the groundwater, where dilution, transport and dispersion occur.

For this phenomenon, models are based on the estimation of a leaching factor (LF), defined as the ratio between the groundwater concentration impacted by soil leachate and the source zone concentration.

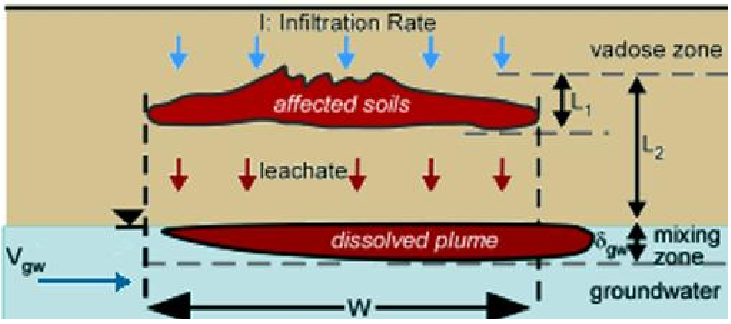

Figure 13: Leaching simplified drawing. Taken from: RBCA Tool Kit for Chemical Releases Manual, GSI Environmental Inc., 2007, pg. B-5

All the leaching factors of this section are expressed in (mg/L of water)/(mg/kg of soil).

<u>Soil leaching to groundwater (LF)</u>

RBCA

LF is estimated trough the ASTM soil leachate model (Equation 17): it assumes that the leachate mixes and contaminates the groundwater directly beneath the affected soils.

The user has the possibility to adjust the ASTM model with the soil attenuation model (SAM), that takes into account the contaminant concentration attenuation due to sorption to soils particles located between the soil source of contamination and the underlying groundwater (Connor et al., 1997. The SAM factor is the ratio between L_1, the thickness of affected soils and L_2, the distance from top of affected soils to top of water).

If SAM is selected, a first-order decay for the attenuation becomes available.

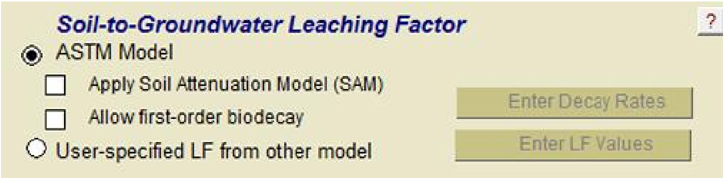

Figure 14: Transport modelling options, leaching. Taken from: RBCA Tool Kit for Chemical Releases Manual, GSI Environmental Inc., 2007, pg. 28

$$LF = \frac{K_{sw} * SAM}{LDF}$$

Equation 17: RBCA - ASTM soil leachate model with SAM adjustment

$$K_{sw} = \frac{\rho_s}{(\theta_{ws} + k_s\rho_s + H\theta_{as})}$$

Equation 18: RBCA -Soil-water partition factor

$$LDF = 1 + \frac{V_{gw}\delta_{gw}}{I * W}$$

Equation 19: RBCA – Leachate dilution factor

Parameters
K_{sw} - Soil- Water Partition Factor (mg/L water)/(mg/kg soil)
SAM - Soil Attenuation Model Factor (-)
δ_{gw} - Groundwater mixing zone thickness (cm)
V_{gw} - Groundwater Darcy velocity (cm/day)
I - Infiltration rate of water through soil (cm/year)

Risk-net

In Risk-net actually this factor is called Surface soil leaching to groundwater factor: the differences in the classification will be further explained in paragraph 4.1.4.

The ASTM model is given as first option (Equation 17 multiplied by the BDF_{LF}).

Risk-net also offers an alternative, Equation 20, which performs a simplified steady-state vertical mass balance model. It assumes instantaneous partitioning between solid and aqueous phases, advection-dominated transport, but it neglects degradation and dispersion processes.

$$LF = \frac{d * \rho_s}{I * \tau_{LF}}$$

Equation 20: Risk-net – Steady state leaching model

Parameters
τ_{LF} - Averaging time for vapor flux (yr)

Figure 15 shows some options that Risk-net offers for the leaching modelling. From this section the user can decide to activate the SAM, as in RBCA.

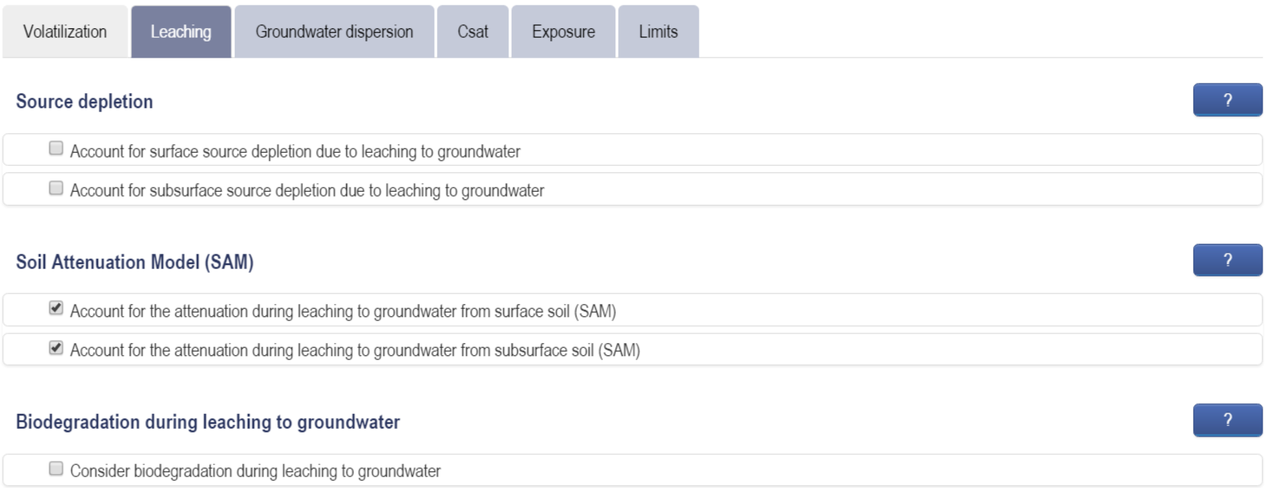

Figure 15: Model options, leaching. Screenshotted from Risk-net.

<u>Subsurface soil leaching to groundwater (LF_{sp})</u>

RBCA

There is not the possibility to calculate a Subsurface soil leaching to groundwater.

Risk-net

Risk-net gives to the users two possible equations to calculate this factor, which are the same explained in the previous paragraph (17 and 20). The difference is that the thickness of surface soil source (d) is replaced with the one of subsurface soil (d_s) and L_s with L_{sf}, as described in the paragraph about the Indoor surface soil volatilization.

3.4.4 Groundwater dispersion and attenuation

The phenomenon of groundwater dispersion and attenuation has some common features with the lateral air dispersion discussed in paragraph 3.4.2: contaminant concentrations in the flow stream are diminished due to mixing and attenuation effects.

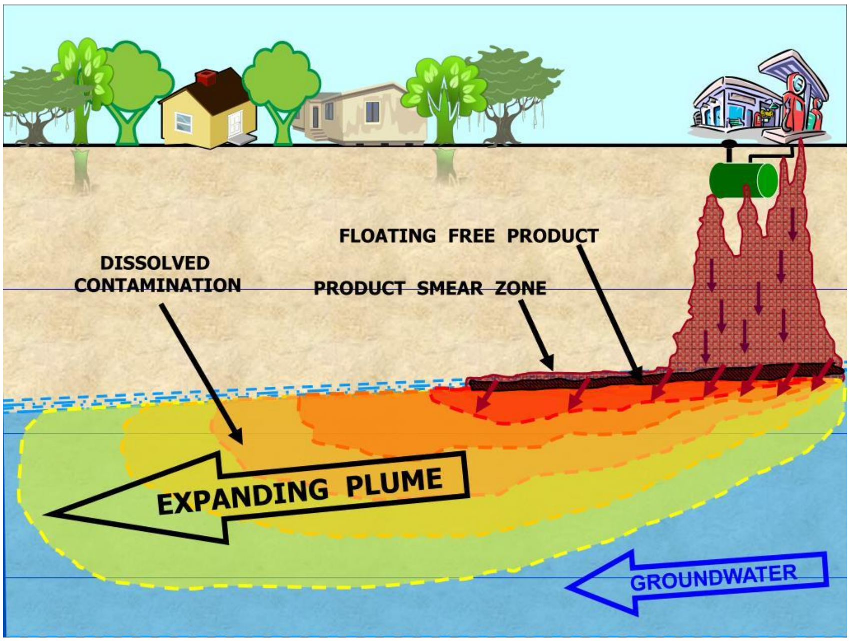

Figure 16: Groundwater dispersion and attenuation. Mike Trombetta, Monitored natural attenuation and risk-based corrective action at underground storage tank sites (June 2025, https://www.slideserve.com/madaline-leon/monitored-natural-attenuation-and-risk-based-corrective-action-at-underground-storage-tanks-sites).

This evaluation involves the calculation of a groundwater dilution attenuation factor (DAF), defined as the ratio the contaminant concentration in groundwater at the source zone and its concentration at the specific receptor location.

Since this phenomenon involves the flow of water through the soil, the determination of natural parameters of the media is fundamental. Some of the factors that particularly affect the results of the DAF calculation are listed below:

- Porosity (n): Fraction of the total soil volume that is occupied by void spaces or pores. [1] [2]

- Organic matter content (f_{oc}): part of soil composed of organic compounds, including decomposed plant and animal residues, living microorganisms and humic substances. [1] [2]

- Groundwater velocity (v): rate at which groundwater moves through the pore spaces of the aquifer material. It depends on the hydraulic gradient (i) and soil permeability (k), which are also critical parameters.

As will be further discussed, the Domenico model is employed to calculate groundwater dispersion and attenuation. In order to use it with awareness, it is customary to evaluate the groundwater velocity, which has a great impact on the outcome, to the point that that it is not recommended to use for clay soils, where the flow is slow. In facts, the model assumes media to be homogeneous and isotropic, where advection and dispersion dominate over other processes. Consequently, it is more appropriate when groundwater flow velocities are sufficiently high to ensure that advection rules contaminant migration, while dispersion provides lateral and longitudinal spreading; these conditions are not verified in low-permeability formations (such as clay layers), where groundwater velocities are extremely low and molecular diffusion becomes the dominant transport mechanism. In these contexts, the presence of fine-grained particles in the water can also promote colloidal transport, sorption and diffusion-limited processes that are not addressed by the Domenico equation. [1]

RBCA

In the *groundwater dilution-attenuation factor* section, among the transport modelling options, there are three selectable options (Figure 17):

- Domenico model with dispersion only: it represents the steady-state Domenico analytical solute transport model. It is assumed that there is no biodegradation (in the RBCA manual, Eqn. LT-1a with $\lambda = 0$, where λ is the first-order degradation rate).

- Domenico model with first-Order decay: same model of before but with biodegradation as a first-order decay process. The user has to provide first-order decay rates or half-life values for each COC (Eqn. LT-1a).

- Modified Domenico equation using electron acceptor superposition: also in this case the steady-state Domenico analytical solute transport model is used, but the process of degradation is modelled using electron acceptor superposition, the method employed in the BIOSCREEN model (Newell et al., 1996). The user has to either specify the biodegradation capacity of the groundwater flow system or provide site-specific concentrations of electron acceptors and metabolic byproducts.

The equations just mentioned will not be reported in this study, for which reference was made to the RBCA user guide, already cited above.

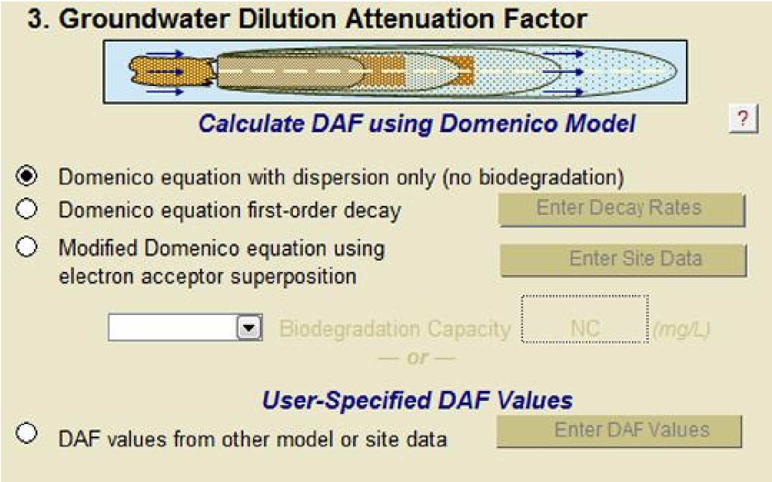

Figure 17: Transport modelling options, groundwater dilution attenuation. Taken from: RBCA Tool Kit for Chemical Releases Manual, GSI Environmental Inc., 2007, pg. 28

Risk-net

Also Risk-net uses the Domenico equations to calculate the DAF, but with some differences. In particular, it is possible to simulate the dispersion of contaminants as (Figure 18):

- DAF1: dispersion in all directions (x, y, z).

- DAF2: transversal and longitudinal dispersion in all directions, while the vertical dispersion is assumed to take place only downwards.

- DAF3: only longitudinal and transversal dispersion.

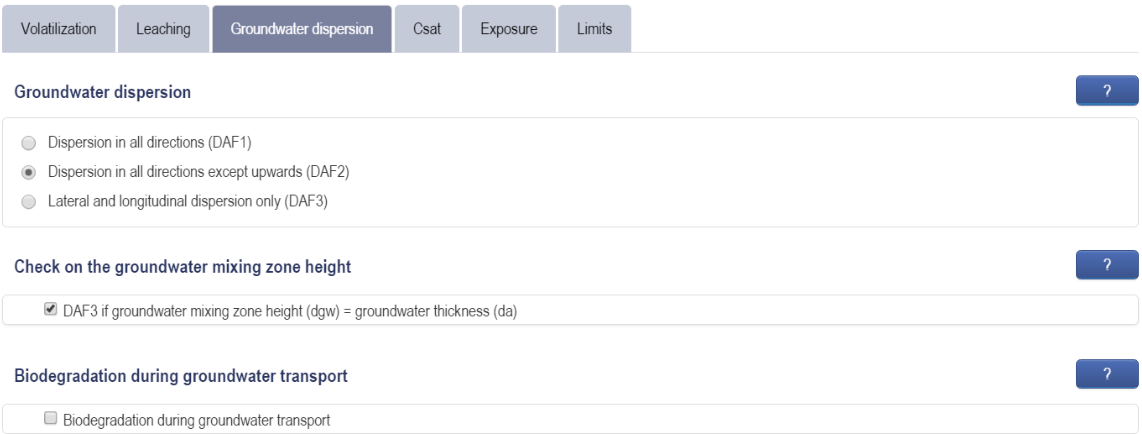

Figure 18: Model options, groundwater dispersion. Screenshotted from Risk-net.

3.4.5 Use of the factors

RBCA

After the calculation of the fate and transport factors, RBCA performs a one more step, which is relevant for the calculation of the concentration at the exposure point. In facts the program, through the use of the factors described in the previous paragraph, computes a natural attenuation factor (NAF). It corresponds to either cross media transfer or lateral transport of constituents of concern from the source area to the point of exposure.

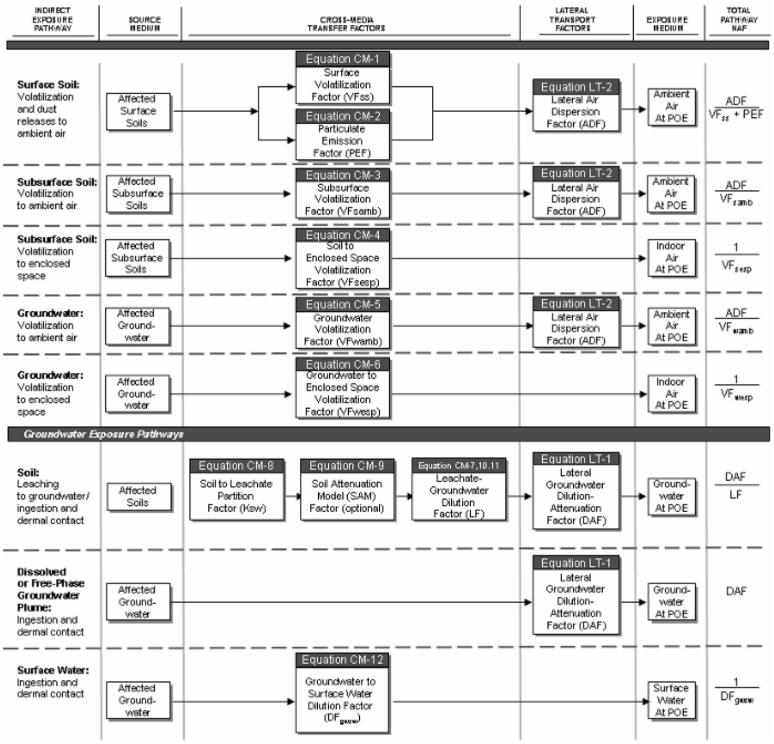

Figure 19: : NAF Calculation Schematic for Indirect Exposure Pathways. Taken from: RBCA Tool Kit for Chemical Releases Manual, GSI Environmental Inc., 2007, pg. B2

The role of this factor in the calculation of the exposure concentration will be explained in the next paragraph. Figure 19 shows how NAF is calculated in all the possible cases.

Risk-net

Risk-net instead, directly uses the fate and transport factors to calculate the concentration at the point of exposure.

3.5 Baseline risks

As explained in paragraph 1.1.4, the entire process shown in the previous section has as objective to calculate indexes that quantify the risk for the receptors.

The way hazard index (HI) and risk factor (R) are calculated by the programs is similar, this method and the consequent display of the data will be further commented.

RBCA

As written in paragraph 1.1.4, it is assumed the risk is unacceptable if the hazard index is greater than 1 and if the cancer risk factor is greater than 10^{-5} (for carcinogenic risk linked to a single contaminant the risk factor is lower, equal to 10^{-6}).

Baseline risks option, present in the main screen, becomes selectable when all the options on the left-hand side of part 4 (Figure 4) are filled with data. RBCA gives to the user the possibility to check the risks in two ways:

- By individual pathways: the calculations and the data collected for each complete exposure pathway (groundwater, surface water, outdoor and indoor air and soil) are shown.

Each section will indicate the following information (which also resumes the sequence of the calculation that the program performs in order to arrive at the final risk index) organised in tables:

- Source medium: concentration value, previously inserted in the *Constituents of Concern* section.
- NAF value: natural attenuation factor, used to estimate the change of the contaminant concentration in the transport from one medium to another.
- Exposure medium: concentration in the exposure medium, calculated by dividing the source medium concentration by the NAF. Since for soil pathways there is no NAF, source and exposure medium concentration are the same.
- Exposure multiplier (Exp): its formula varies for each medium, the following equation can be considered as generic (check Equation 1 for the definition of the variables).

$$Exp = \frac{CR\ x\ EF\ x\ ED}{BW\ x\ AT}$$

Equation 21: Exposure multiplier formula

- Average Daily Intake Rate/Average Inhalation Exposure Concentration: obtained by multiplying the Exposure Medium by the Exposure Multiplier. This value is then used for the calculation of the final risk indexes, the following table shows the criteria by which this daily intake is chosen for each exposure pathway.

Exposure pathway	**Criterion**
Groundwater	Maximum average daily intake between the ones calculated (e.g. for soils leaching to groundwater ingestion and groundwater ingestion)
Surface water	
Outdoor and Indoor Air	Total Pathway Exposure (sum of the average inhalation exposure concentrations for the surface soil, subsurface soil and groundwater vapor inhalation concentrations)
Soil	Total intake rate (combined intake rate for ingestion/dermal contact and vegetable consumption)

Table 1: Intake rate selection

- Toxicity information: carcinogenicity of the chemical, reference dose and concentration, slope factor and inhalation unit risk.
- Risk factor (R, Equation 3).
- Hazard index (HI, Equation 4).

- By all pathways: summary table of baseline risk values for all the complete pathways. The presence of unacceptable risk is highlighted through the display of a red box (Figure 20).

Return | Print Sheet | **RBCA SITE ASSESSMENT** | **Baseline Risk Summary-All Pathways**

Help

Completed By: AHS
Date Completed: 1-Jan-07 | 1 of 1

TIER 2 BASELINE RISK SUMMARY TABLE

EXPOSURE PATHWAY	BASELINE CARCINOGENIC RISK					BASELINE TOXIC EFFECTS				
	Individual COC Risk		Cumulative COC Risk		Risk	Hazard Quotient		Hazard Index		Toxicity
	Maximum Value	Target Risk	Total Value	Target Risk	Limit(s) Exceeded?	Maximum Value	Applicable Limit	Total Value	Applicable Limit	Limit(s) Exceeded?
OUTDOOR AIR EXPOSURE PATHWAYS										
Complete:	4.3E-7	1.0E-6	8.0E-7	1.0E-5	□	1.5E-2	1.0E+0	2.4E-2	1.0E+0	□
INDOOR AIR EXPOSURE PATHWAYS										
Complete:	3.9E-5	1.0E-6	4.1E-5	1.0E-5	■	4.6E-1	1.0E+0	7.6E-1	1.0E+0	□
SOIL EXPOSURE PATHWAYS										
Complete:	6.7E-6	1.0E-6	8.1E-6	1.0E-5	■	1.5E-2	1.0E+0	2.9E-2	1.0E+0	□
GROUNDWATER EXPOSURE PATHWAYS										
Complete:	8.3E-4	1.0E-6	1.6E-3	1.0E-5	■	2.0E+2	1.0E+0	2.4E+2	1.0E+0	■
SURFACE WATER EXPOSURE PATHWAYS										
Complete:	1.9E-14	1.0E-6	3.4E-14	1.0E-5	□	1.3E-9	1.0E+0	2.0E-9	1.0E+0	□
CRITICAL EXPOSURE PATHWAY (Maximum Values From Complete Pathways)										
	8.3E-4	***1.0E-6***	***1.6E-3***	***1.0E-5***	■	***2.0E+2***	***1.0E+0***	***2.4E+2***	***1.0E+0***	■
	Groundwater		*Groundwater*			*Groundwater*		*Groundwater*		

Figure 20: Baseline risk summary. *Taken from: RBCA Tool Kit for Chemical Releases Manual,* GSI Environmental Inc., 2007, pg. 49

This section shows risk values for carcinogenic and non-carcinogenic contaminants both, dividing them by exposure pathway. The *maximum value* represents the highest risk value among the ones calculated, while the *total value* indicates the cumulative risk obtained summing the risk calculated for each contaminant. In addition, among the maximum risk values for each exposure pathway the greatest value is taken, representing the general risk for the receptor. The last line of the table shows the critical exposure pathway, which is associated to the highest risk.

Risk-net

Target risk limits (HI and R) are the same used by RBCA and they are reported in the previous paragraph.

Baseline risks can be accessed clicking *Risk* on the *Output* menu. Risk values are organised in sections referred to each exposure medium: each section shows the risk linked to the single contaminant and the cumulative one.

Wherever the risk is higher than the acceptable limit, the value is highlighted in red, while if the source concentration is higher than the saturation one (or the solubility for the contamination in groundwater), it will be displayed in purple.

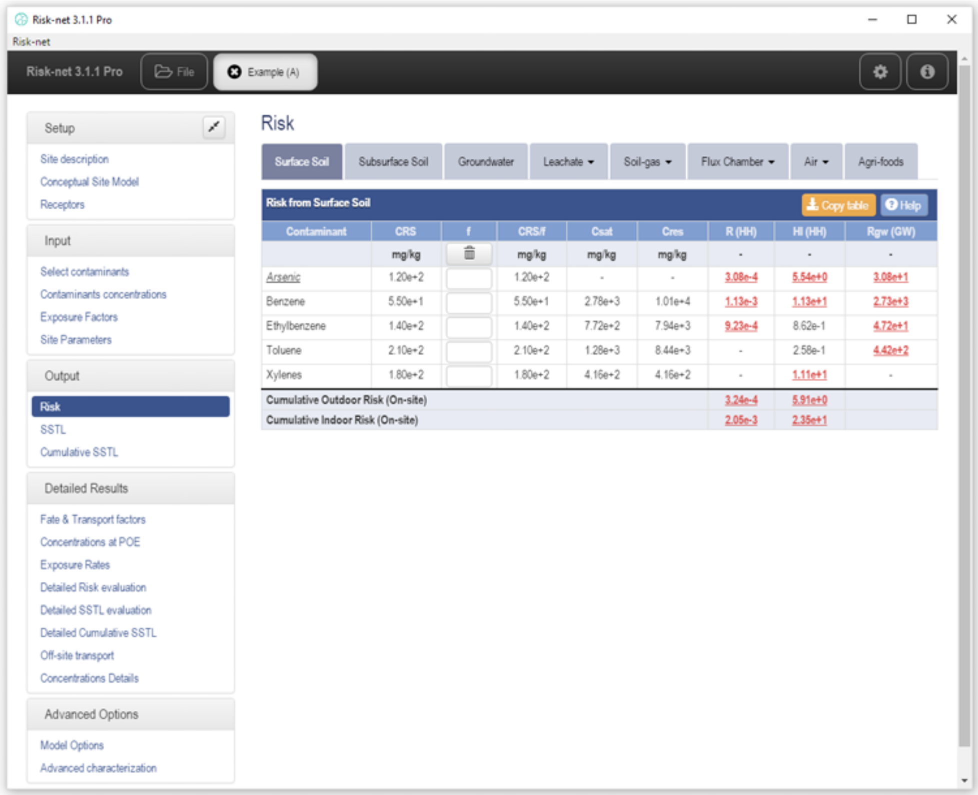

Figure 21: Baseline risk summary. *Taken from: RECONnet Italian Network on the Management and Remediation of Contaminated Sites USER GUIDE RISK-NET. (2019)*, pg. 39

In Figure 21 the risk screen is shown. It presents the following parameters:

- CRS: source concentration.

- f: reduction factor for CRS, it can be inserted by the user and it allows to calculate a target concentration, which ensures acceptable risks.

- HI and R.

- R_{gw}: risk for the groundwater resource, calculated dividing the concentration of the contaminant in the water table at the point of compliance by the reference values defined for the groundwater protection (MCL).

- Csat: saturation concentration.

- Cres: residual concentration (screening NAPL). It refers to the concentration of a contaminant remaining in the soil or groundwater that is associated with the presence of a separate non-aqueous phase liquid (NAPL). It is used as a screening value to assess whether NAPL may be present and potentially influence contaminant transport.

- Sol: contaminant solubility.

Risk-net displays risks as shown in Figure 21: HI and R are reported for each contaminant and their summatory is made defining a cumulative outdoor, indoor, on-site and off-site risk for each exposure pathway.

As mentioned in paragraph 3.4.5, the concentration at the point of exposure is calculated directly multiplying the CRS by the fate and transport factors. The rest of the procedure followed for the calculation of HI and R is the same explained for RBCA.

As Figure 22 shows, the highest risk value is chosen among the calculated ones for all the exposure routes and it is then considered as general risk. In the Risk-net user manual, similar schemes are also shown for surface and subsurface soil.

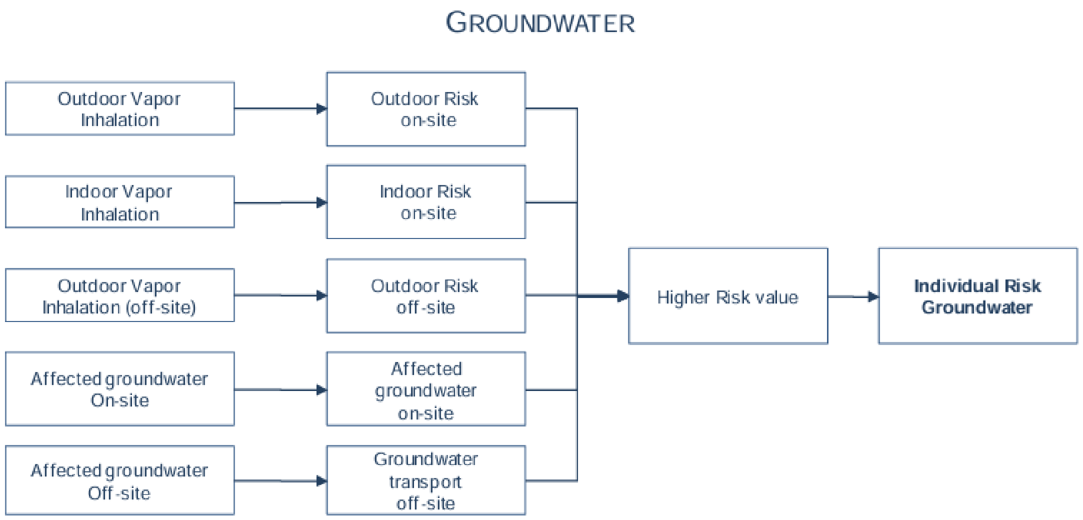

Figure 22: General risk selection process scheme for groundwater. Taken from: RECONnet Italian Network on the Management and Remediation of Contaminated Sites USER GUIDE RISK-NET. (2019), pg. 57

In this step, the main difference between the two programs lies in the organization of the exposure pathways. In facts while Risk-net calculates three general risk values respectively for groundwater, surface and subsurface soil, RBCA provides four.

3.6 Cleanup levels

Cleanup levels are defined as the hazardous constituent concentrations to which a contaminated environmental medium (e.g. soil, groundwater, surface water, sediment) must be remediated. The United States Environmental protection Agency establishes cleanup levels on a facility-by-facility basis during the remedy selection process (USEPA, 1998).

Software employed in human health risk assessment give the user the possibility to calculate such parameters.

RBCA

In RBCA the calculation of the cleanup levels starts with the determination of the Risk based exposure limit (RBEL). It is a concentration calculated for each exposure pathway and each single contaminant combining Equation 1 and 3 for the non carcinogenic contaminants (Equation 1 and 4 are used for the carcinogenic ones), as follows:

$$RBEL = \frac{HI\ x\ RfD\ x\ BW\ x\ AT}{CR\ x\ EF\ x\ ED}$$

Equation 22: General formula of the risk based exposure limit for the non carcinogens

This parameter is then used to calculate a risk based screening level (RBSL, obtained multiplying RBEL times a natural attenuation factor during across media transport) during tier 1. Then, a site specific target level (SSTL, equal to RBSL times a natural attenuation factor during lateral transport) is computed; it will be the value finally displayed by the software in tier 2 and 3.

Once these target levels are defined, RBCA calculates a constituent reduction factor (CRF) by dividing the representative concentration by the target one (which is equal to the SSTL): with this first rudimentary data, the user can calculate the values of cumulative risk, taking into account that each risk factors is calculated using the new target concentrations.

However, since these concentrations are obtained by taking into account each contaminant individually, it is not certain that they satisfy the established risk criteria; in fact, if after computing the cumulative R and HI, the result still entails a risk for the receptors, it means that the target concentrations must be further reduced and it is up to the user to understand how to adjust CRFs in order to avoid risk.

RBCA organises this information in three screens that can be checked by the user:

- Individual Constituents by Affected Media: one for each media (groundwater, surface and subsurface soil), it shows a summary of all the cleanup levels computed for the selected medium.

- Modeling Results Summary by Individual COC: one for each contaminant, it allows the user to check cleanup level values and all chemical and toxicological parameters used for their derivation.

- Cumulative Risk Worksheet: it displays the general scenario (Figure 23), with contaminant representative and target concentration and risk values divided by pathway and by on-site and off-site exposure. It is here that the first CRFs are shown and the user can iteratively change them, recalculating the risk value until the target is reached.

Return | Print Sheet | RBCA SITE ASSESSMENT | Cumulative Risk Worksheet | RBCA

Site Name: Test Site 1 | Completed By: AHS | Job ID: 1234 | Site Name: Test Site 1

Site Location: Houston, TX | Date Completed: 1-Jan-07 | 1 OF 3 | Site Location: Houston, TX

CUMULATIVE RISK WORKSHEET

Paste CRF Values | Calculate | Help

CONSTITUENTS OF CONCERN		Representative Concentration		Proposed CRF		Resultant Target Concentration		Outdoor Air Exposure: Residential (Target Risk: 1.0E-6; Target HQ: 1.0E+0)	
CAS No.	Name	Soil (mg/kg)	Groundwater (mg/L)	Soil	GW	Soil (mg/kg)	Groundwater (mg/L)	Carcinogenic Risk	Hazard Quotient
71-43-2	Benzene	2.5E+0	1.0E+0	NA	NA	2.5E+0	1.0E+0	1.1E-6	1.1E-2
100-41-4	Ethyl benzene	2.7E+0	1.8E+1	NA	NA	2.7E+0	1.8E+1		1.8E-3
91-20-3	Naphthalene	3.5E+0	2.0E+0	NA	NA	3.5E+0	2.0E+0		4.2E-2
1634-04-4	Methyl t-Butyl ether (MTBE)	1.0E+1	3.1E+1	NA	NA	1.0E+1	3.1E+1	4.9E-7	1.5E-3
108-88-3	Toluene	2.7E+0	1.2E+1	NA	NA	2.7E+0	1.2E+1		2.6E-4
1330-20-7	Xylenes (mixed isomers)	3.0E+0	2.3E+0	NA	NA	3.0E+0	2.3E+0		5.0E-3
	Cumulative Values:							**1.6E-6**	**6.1E-2**

Figure 23: Modeling Results Summary by Individual COC. Taken from: RBCA Tool Kit for Chemical Releases Manual, GSI Environmental Inc., 2007, pg. 52

Risk-net

Risk-net calculates SSTLs similarly to RBCA, Equation 21 is used to calculate the RBEL, which is divided by a fate & transport factor (FT) in order to obtain the SSTL. Also in this case, the computed value is referred to a specific exposure pathway for a contaminant.

Before getting to the final SSTL value, some steps must be carried out:

- At first, the combined effect of multiple exposure is estimated as the reciprocal of the sum of the reciprocals of the SSTL calculated for each route of exposure (as it follows, for the outdoor environments for example).

$$SSTL_{outdoor} = \frac{1}{\frac{1}{SSTL_{ing}} + \frac{1}{SSTL_{derm}} + \frac{1}{SSTL_{dusts}} + \frac{1}{SSTL_{vapors}}}$$

Equation 23: SSTL outdoor

- Then, for each media of concern, it is chosen the most conservative SSTL (the lowest one) between all values calculated for all the possible exposure pathways (Figure 24).

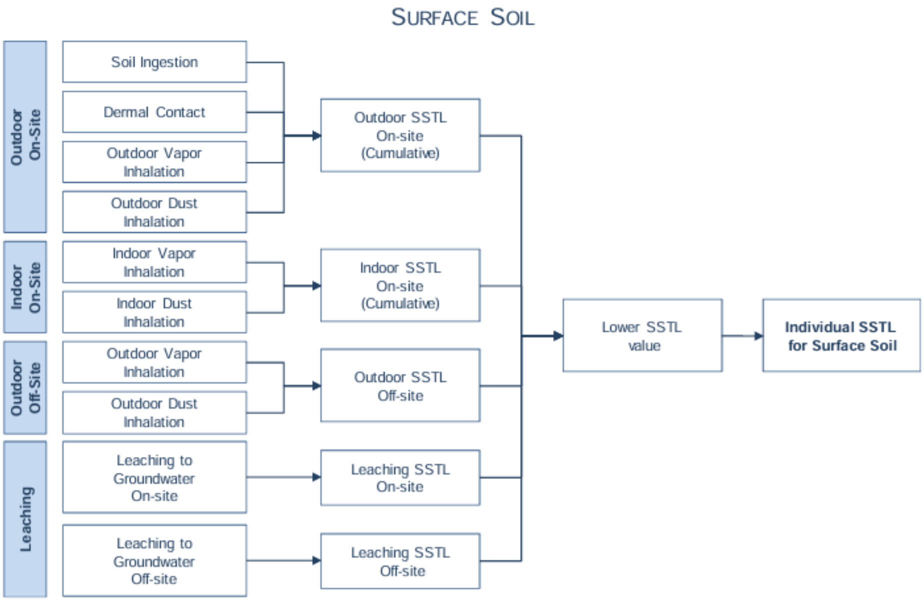

Figure 24: General SSTL selection process scheme for surface soil. Taken from: RECONnet Italian Network on the Management and Remediation of Contaminated Sites USER GUIDE RISK-NET. (2019), pg. 71

- Finally, the risk associated to the newly calculated SSTL is computed for each contaminant and these values are summed (dividing the results by indoor, outdoor, on-site and off-site exposure). As explained for RBCA, it is not sure that the computed target concentrations will avoid risk, so it could be necessary to further lower them; Risk-net gives this possibility in the *Cumulative SSTL* section (Figure 25).

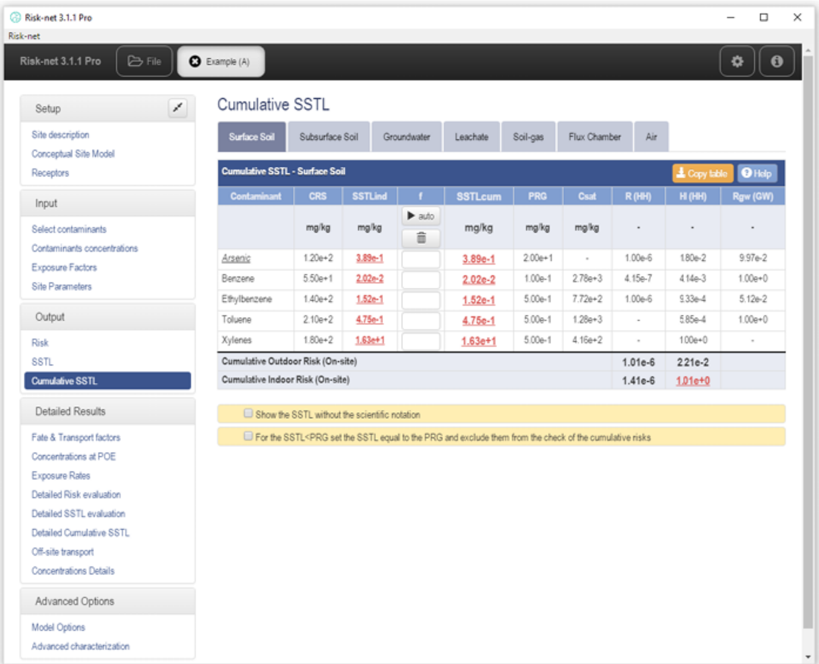

Figure 25: Cumulative SSTLs. Taken from: RECONnet Italian Network on the Management and Remediation of Contaminated Sites USER GUIDE RISK-NET. (2019), pg. 42

The fourth column of the table shown in Figure 25 includes an adjustment factor *f*, which can be used to correct the previously calculated SSTLs: SSTLind is the first value computed by default, which can be reduced by the user inserting f. The result of the ratio between SSTLind and this reduction factor is SSTLcum. By clicking *auto*, the program inserts a value equal to the number of contaminants selected and the user can iteratively change it until the target risk is avoided.

Furthermore, the contaminant for which the source concentration is higher than the calculated SSTL are highlighted in red.

Chapter 4 - Strengths and weaknesses weighed

Following the technical and methodological overview described previously, this chapter develops a critical comparison of the two risk assessment tools under analysis, through the examination of their strengths and weaknesses.

Also linking this evaluation with the application part of the next section, the study will try to identify specific scenarios in which one tool may be more adapt than the other, due to regulatory requirements, data availability or complexity of the site.

Key aspects under consideration include the transparency of calculation methods, the organization of the main screen and the way in which site-specific condition or uncertainty are managed.

4.1 Strengths and weaknesses evaluation

4.1.1 Interface and user-friendliness

Although it is not one of the fundamental characteristics for the performance of a program, it is considered important to discuss user friendliness as it determines the ease with which these tools can be used to achieve results. The two software packages are recognised and used internationally and it is interesting to analyse their differences concerning this feature.

RBCA main screen is built in order to follow the step-by-step logic of human health risk assessment: at first, information about exposure pathways and constituents of concern is required, then the user is asked to insert data about the fate and transport models and the contaminated site. This can be particularly helpful in consulting contexts, where it is important to be able to resume the assumptions made in a clear and transparent way. Anyway, this interface can also be more difficult to be understood by users without a prior experience in the field, because of the presence of sections arranged in an counterintuitive way and densely populated with data.

The order in which information is organised and requested to the user by Risk-net is similar to the one used by RBCA. Risk-net menu contains more items, because in RBCA some sections are included within the starting options of the main screen (for example the visualization the site conceptual model can be accessed through *Exposure pathways*). However, Risk-net is surely more user friendly than RBCA: its design is more intuitive and makes the understanding of the risk assessment more immediate, which can be advantageous during the tool learning process. This simplicity is partly due to the fact that the sidebar (Figure 5) provides quick access to all the categories of the risk assessment, allowing the user to find easily the information needed.

However, it is necessary to say that the ease with which a software can be used does not imply its effectiveness: in fact, it is necessary to find a good compromise between the two characteristics to ensure accuracy and reliability of results. Precision is essential and, at the same time, oversimplification can lead to the loss of critical functionalities.

4.1.2 Exposure pathways evaluation

Concerning exposure pathways evaluation, the difference between RBCA and Risk-Net is structural and it lies in their categorization. The differences reported in this paragraph in facts, have meaningful implications for how users approach risk assessment.

As explained in chapter three, RBCA organizes exposure routes primarily by the type of occurring exposure (groundwater, surface soil and air). Within these categories, the user then identifies the routes that bring the receptor into contact with contaminants (for example volatilization, ingestion and inhalation). For instance, vapor intrusion from contaminated groundwater into indoor air is classified in the *Air Exposure* category, reflecting the endpoint of the pathway.

Risk-Net approach instead, is more focused on the source: the contaminated medium (surface soil, subsurface soil or groundwater) has to be identified first and subsequently the possible exposure mechanisms arising from that medium. Connecting with the example of before, if groundwater is the source of contamination, the user has the possibility to select pathways like *Outdoor Vapor Inhalation* or *Indoor Vapor Inhalation* specifically under the groundwater section, rather than taking into account an *Air Exposure* category (as in RBCA).

This discrepancy is reflected on how users conceive the flow of contamination and the exposure. RBCA focuses more the medium of exposure, which can be a strength, since regulations assess risk at the point of contact. This approach can be convenient when quantifying exposure concentrations and doses across different media, even if, on the other hand, it requires the user to think in terms of endpoints instead of considering the original source of the contamination.

On its side Risk-net gives more importance to the origin of the contamination for this evaluation. This can be particularly advantageous for site conceptualization, as it helps to visualize how a single source can give rise to multiple exposure routes.

In general, the two programs express a different conceptual logic in this evaluation and the choice between them therefore can be based on the specific objectives and stage of the assessment process.

Another point to be discussed within this paragraph deals with off-site receptors: while RBCA gives the possibility to insert two off-site receptors in the same risk assessment, in Risk-net only one can be defined. This feature obliges the user to create two files to consider two receptors, operation that can be time-consuming if a lot of data have to be entered.

4.1.3 Chemical parameters database

One of the greatest differences between RBCA and Risk-net lies in the size of their contaminant databases. RBCA presents a list of 658 contaminants, while Risk-net includes 144. This numerical discrepancy can give the impression that RBCA is more complete or more robust from a technical point of view. However, a larger database does not necessarily mean better quality or performance in practice. Still, having more substances available in RBCA makes the software more flexible when handling complex contamination cases or site-specific pollutants. In fact, the possibility of including a wider range of potential contaminants makes the tool more flexible for the evaluation of projects.

On the other hand, Risk-net includes in its archive all the most common contaminants and the lack of data could be improved by updating its database: this possibility, which will be further discussed within the paragraph, allows the user to shape an *ad hoc* database, depending on the contaminants present at the site of interest.

Although it depends on the versions of the programs employed in this study (Chapter 2), another relevant aspect are the sources of the data used to build the two databases. As shown in paragraph 3.3 in facts, RBCA tends to rely on slightly older sources compared to Risk-net: here the argument is similar to that made above for the size of the database and, even if this difference might suggest a disadvantage given by data freshness, it does not necessarily imply a lower quality. Older sources can still be scientifically valid, especially if they are well-established and widely accepted in the field.

As regards TPH, in the following table are reported the compounds included in the database of the two programs:

Risk-net	**RBCA**
Aliphatics C5-C6 (n-hexane > 53%)	
Aliphatics C5-C6 (n-hexane < 53%)	
Aliphatics C6-C8 (n-hexane > 53%)	

<table>
<tr><td colspan="2">Aliphatics C6-C8 (n-hexane < 53%)</td></tr>
<tr><td colspan="2">Aliphatics C > 8-10</td></tr>
<tr><td colspan="2">Aliphatics C > 10-12</td></tr>
<tr><td colspan="2">Aliphatics C > 12-16</td></tr>
<tr><td colspan="2">Aliphatics C > 16-21</td></tr>
<tr><td>Aliphatics C > 16-21 (mineral oil)</td><td>-</td></tr>
<tr><td>-</td><td>Aliphatics > C21-C34</td></tr>
<tr><td>Aliphatics C > 21-35</td><td>-</td></tr>
<tr><td>Aliphatics C > 21-35 (mineral oil)</td><td>-</td></tr>
<tr><td>-</td><td>Aromatics C > 5-7</td></tr>
<tr><td colspan="2">Aromatics C > 7-8</td></tr>
<tr><td colspan="2">Aromatics C > 8-10</td></tr>
<tr><td colspan="2">Aromatics C > 10-12</td></tr>
<tr><td colspan="2">Aromatics C > 12-16</td></tr>
<tr><td colspan="2">Aromatics C > 16-21</td></tr>
<tr><td colspan="2">Aromatics C > 21-35</td></tr>
<tr><td>Aliphatics C5-C8 (MADEP)</td><td>-</td></tr>
<tr><td>Aliphatics C9-C12 (MADEP)</td><td>-</td></tr>
<tr><td>Aliphatics C13-C18 (MADEP)</td><td>-</td></tr>
<tr><td>Aliphatics C19-C36 (MADEP)</td><td>-</td></tr>
<tr><td>Aromatics C9-C10 (MADEP)</td><td>-</td></tr>
<tr><td>Aromatics C11-C12 (MADEP)</td><td>-</td></tr>
<tr><td>Aromatics C13-C22 (MADEP)</td><td>-</td></tr>
<tr><td>-</td><td>TX1105, C6-C12 (Texas Risk Reduction Program)</td></tr>
<tr><td>-</td><td>TX1105, C12-C28 (Texas Risk Reduction Program)</td></tr>
<tr><td>-</td><td>TX1105, C12-C35 (Texas Risk Reduction Program)</td></tr>
<tr><td>-</td><td>TX1105, C28-C35 (Texas Risk Reduction Program)</td></tr>
</table>

Table 2: RBCA and Risk-net available TPH (for their sources check paragraph 3.3)

Furthermore, as already mentioned, both tools offer the possibility to expand and edit the database of contaminants. In this regard, Risk-net may offer an operational advantage: as highlighted in paragraph 4.1.1, its design facilitates a quicker and more efficient integration of additional substances. This flexibility could be particularly useful in practical applications where not common contaminants need to be considered or when adapting the tool to different national or local regulatory contexts.

4.1.4 Fate and transport models

The purpose of this paragraph is to comment the differences in the contaminant fate and transport models implemented by the two programs. There is more than one model that, as has been pointed out in paragraph 3.4, is included in both software; it is significant to assess cases where the possibilities given by the programs for the estimation of the same transport phenomenon are not the same.

Different models arrive at different results influencing the final determination of risk and clean up levels. The possibility of choosing between several models can surely be an advantage: since they are all based on assumptions, there may be situations where, due to its characteristics, it is more appropriate to use one model instead of another.

In the following section, for each factor whose calculation involves differences between RBCA and Risk-net, a table with the usable models and a comment will be included.

The factors for which the tools employ the same models are not included in this paragraph.

Surface soil to Outdoor air volatilization (VF_{ss})

RBCA	Risk-net
Usepa Q/C	/
ASTM	
/	Johnson & Ettinger

Table 3: Surface soil to Outdoor air volatilization factor – available models

- Usepa Q/C: it is advantageous in scenarios where the volatilization can be assumed to be a steady-state and continuous phenomenon (e.g. for large, homogeneous contaminated sites with constant emission rates over time). It involves a simplified parameterization and this feature makes it appropriate for preliminary screening assessments or for situations where limited site-specific data are available. Moreover, the Q/C approach offers conservative estimates, providing a protective screening tool during the initial phases of risk assessment.

What has just been said is also valid for the particulate emission factor (PEF), since even in this case RBCA offers the possibility of using the Usepa Q/C model, unlike Risk-net.

- Johnson & Ettinger: this model (Equation 7) is called into question when the depth to surface soil source (L_{sf}) is greater than zero (paragraph 3.4.1). It is considered to be more appropriate in cases where a detailed site evaluation is required. It accounts for subsurface vapor transport processes including diffusion and advection and it is suitable for outdoor air exposure scenarios in residential, commercial or industrial environments.

Indoor subsurface soil volatilization (VF_{sesp})

RBCA	**Risk-net**
Johnson & Ettinger – Equation 10.1	
Johnson & Ettinger – Equation 10.2	
Johnson & Ettinger – Equation 10.3	/

Table 4: Indoor subsurface soil volatilization factor – available models

As reported in Table 4, for this factor the difference lies in one equation (10.3), since the model employed by the program is the same.

The estimation provided by Equation 10.3 is more simple compared to the other two (10.1 and 10.2). The factor is calculated with a limited set of key input parameters (soil density, source depth, enclosed-space air exchange rate,..) and it can be useful in cases where a rapid screening is required, especially when vapor intrusion data of the site are not available or difficult to obtain.

Indoor surface soil volatilization (VF_{ssesp})

The assessment of this factor is considered only by Risk-net. This difference might seem significant but it actually lies in the way surface soil is classified by the two programs:

- RBCA: surface soil thickness must be specified by the user.

- Risk-net: that portion of superficial soil up to one meter of depth.

Therefore, Risk-net splits the indoor air volatilization factor in two (VF_{sesp} and VF_{ssesp}) calculating in each case the one which complies with its classification rules (contamination source at a depth lower or greater than one meter, which is the boundary between surface and subsurface soil).

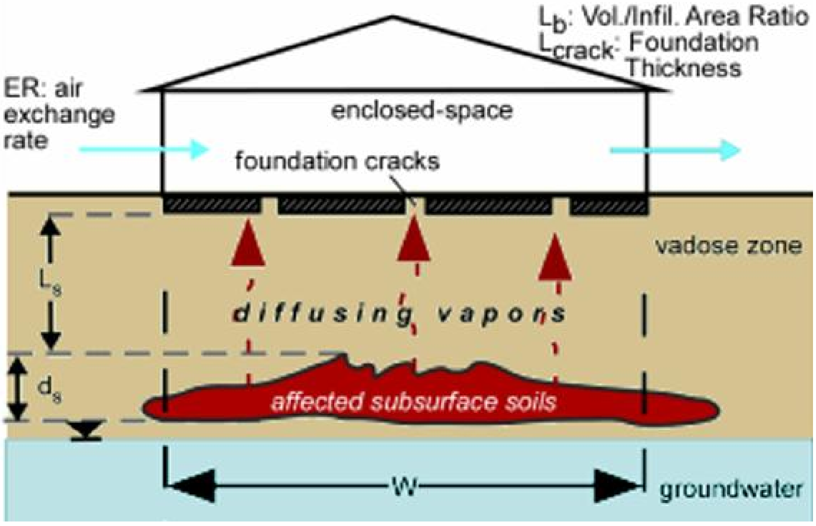

Figure 26: Indoor subsurface soil volatilization, simplified drawing. Taken from: RBCA Tool Kit for Chemical Releases Manual, GSI Environmental Inc., 2007, pg. B4

RBCA instead, does not require the surface soil depth in input and always calculates VF_{sesp} using the depth to subsurface soil source (L_s, Figure 26) provided by the user.

The difference lies mainly in the classification of the soil operated by the two programs: RBCA does not impose a rigid classification and uses the same factor in all cases, while Risk-net clearly divides surface and subsurface soil (is basically a name distinction, as the equations used for VF_{sesp} and for VF_{ssesp} are the same, only the depth of the source changes).

Groundwater to Indoor air volatilization (VF_{wesp})

RBCA	Risk-net
Johnson & Ettinger	
Mass flux	/

Table 5: Groundwater to Indoor air volatilization factor – available models

- Mass flux: the model is computationally efficient, allowing for quick evaluations of multiple scenarios or sensitivity analyses. This can be particularly useful when conducting comparative assessments across several sites or when performing preliminary evaluations to prioritize sites for further investigation. Also, taking into account both diffusion and advective transport, it provides a realistic representation of vapor migration from groundwater to the building.

Lateral air dispersion factor (ADF)

RBCA	Risk-net
3D Gaussian plume	/
/	1D Gaussian plume

Table 6: Lateral air dispersion factor – available models

- 3D Gaussian plume: accounting for both horizontal and vertical dispersion and including reflection at the ground surface, it allows for a detailed representation of the spatial distribution of airborne contaminant concentrations around the source. This model is appropriate to evaluate scenarios involving multiple potential receptor locations at varying distances both laterally and vertically from the source (Yamartino, 2008).

- 1D Gaussian plume: even if it surely has a simpler approach to the estimation (compared with the 3D version of the model), it gives significant results when the main objective is to evaluate potential exposure directly downwind of the source, on the plume centerline.

Soil leaching to groundwater (LF)

Also regarding leaching, the classification of factors operated by RBCA is different from that of Risk-net (the distinction is similar to the one implemented for indoor volatilization factors). In fact, while Risk-net, depending on the contamination source depth, defines two leaching factors (for surface and subsurface soil, for which calculation the same equation is used), RBCA resumes all the information in the Soil leaching to groundwater factor (LF).

In paragraph 3.4.3 and in this section, the Soil leaching to groundwater factor (RBCA) and the Surface Soil leaching to groundwater factor have been assessed together because in both programs they are defined by the same symbol (LF).

RBCA	Risk-net
ASTM	
/	Steady state leaching model

Table 7: Soil leaching to groundwater factor – available models

- Steady state leaching model: It is applied when the site is characterized by stable infiltration rates, without significant short term variability due to seasonal changes, fluctuating groundwater levels or weather events. It is also suitable if the contamination source has been in place for a prolonged period, allowing the system to approach steady-state conditions (Corwin et al., 2007).

Subsurface soil leaching to groundwater (LF_{sp})

This factor is not assessed by RBCA and, as explained in the section about the VF_{ssesp}, this is a matter of classification. The circumstances are the same explained for the Indoor surface soil volatilization factor.

Groundwater dilution attenuation factor (DAF)

RBCA	**Risk-net**
Domenico Model with Dispersion Only	Domenico Model with Dispersion along all the directions
Domenico Model with First-Order Decay	Domenico Model with Dispersion along all the directions (only downwards along the vertical)
Modified Domenico Equation using Electron Acceptor Superposition	Domenico Model with Dispersion along the longitudinal and the transversal direction

Table 8: Groundwater dilution attenuation factor – available models

In both cases the Domenico model is used to estimate the DAF. The equations corresponding to the first row of Table 8 very similar, even if RBCA adopts the complete form of the steady-state model of Domenico while Risk-net a simplification of the same.

As regards the other equations:

- RBCA

- Domenico Model with First-Order Decay: Fundamental if the decrease of the concentration due to biodegradation must be considered. In fact, under steady-state conditions, biodegradation (together with hydrolysis) represents the principal mechanisms of organic contaminant mass reduction during groundwater plume transport within the subsurface.
  The Domenico model implemented in the RBCA Tool Kit assumes first-order kinetics (degradation is proportional to the total concentration dissolved in groundwater and sorbed to soil through a decay rate). The value of the decay rate should be chosen carefully and it is better if it is based on site-specific field data (even if RBCA provides default literature values).

- Modified Domenico Equation using Electron Acceptor Superposition: it accounts for in-situ biodegradation via electron acceptor superposition. Instead of applying a first-order decay rate, this approach simulates biodegradation considering stoichiometric relationships between the contaminant mass and available electron acceptors (oxygen, nitrate, sulphate, methane and iron for example). This option requires the user either to specify the biodegradation capacity of the groundwater flow system or to enter site specific concentrations of electron acceptors and metabolic byproducts.

  Utilization factors are calculated for each electron acceptor: they define how much of the acceptor is consumed per unit mass of contaminant biodegraded. The biodegradation capacity for each electron acceptor is calculated by dividing its concentration by its utilization factor. A total biodegradation capacity is then assigned among individual contaminants in the plume proportionally to their mass fractions. This approach assumes that biodegradation occurs instantaneously upon mixing and it is most appropriate for readily degradable compounds, such as petroleum hydrocarbons. It is not suitable for chlorinated compounds or mixed plumes with both degradable and resistant constituents (GSI Environmental Inc., 2007).

- Risk-net

- Domenico Model with Dispersion along all the directions (only downwards along the vertical): this equation and the following one progressively simplify the Domenico Model with dispersion along all the directions. They can be applied when dispersion along the vertical direction is not significant.

- Domenico Model with Dispersion along the longitudinal and the transversal direction only.

4.1.5 Baseline risks

Both RBCA and Risk-net software implement a standardized methodology for estimating baseline risks from contaminated sites. The risk calculation formulas (for the estimation of HI and R, chapter 1) follow the same structure: they rely on the product of the source concentration, exposure intake rates, toxicological reference values (RfD and SF for example) and a series of transport and exposure factors. This shared foundation is rooted in established environmental risk assessment methods developed by the U.S. EPA and widely adopted in international guidance documents. Therefore, the difference between the two tools lies not in the nature or in the validity of the implemented equations, but in how the individual components of the calculation are computed and presented to the user.

A distinction that can influence the experience of the user is based on how the risk assessment process is communicated. RBCA displays sequentially each intermediate step leading to the final risk values. All calculation steps, from the source zone concentration specified by the user to the final risk value, are shown in a complete way. At the beginning, since RBCA's interface is considered less intuitive, it may take time to understand how the information displayed is organized. However, this arrangement makes it easier for users to understand how input parameters influence the final result and to identify where adjustments might be necessary. Conversely, Risk-net presents a cleaner, more modern interface, but abstracts some of the intermediate steps involved in the risk calculation. Users interested in understanding the detailed process behind the final results must consult the technical manual or supporting documentation, as some of the steps followed are not fully displayed within the software environment itself.

A further methodological difference between the two tools concerns how they estimate contaminant concentrations at the point of exposure. In RBCA, this estimation is performed through the use of Natural attenuation factors, which represent a composite of multiple fate and transport processes (volatilization, dilution, dispersion,.. Check paragraph 3.4). The NAF condenses all the attenuation mechanisms into a single factor: for instance, concerning indoor inhalation of contaminated vapours coming from the groundwater for an off-site receptor, RBCA would calculate a NAF which summarizes the dilution of the contaminant concentration during the transport in the aquifer and the volatilization of the vapours. Finally, the source concentration is divided by it, obtaining the concentration at the exposure.

Risk-net, in contrast, applies individual fate and transport factors directly within the risk calculation equations. For example, volatilization factors, particulate emission factors and dispersion factors are multiplied directly with the source concentration and the intake parameters. Although this approach is conceptually similar, it allows for greater flexibility in analysing the effect of each factor individually. However, it may also result in discrepancies between the two models if the values or methods used to derive these factors differ. This structural variation could become especially significant in complex exposure scenarios where multiple environmental media and transport processes are involved.

A feature common to the two programs that it is worth to mention is inhalation contact for volatile contaminants. In fact, RBCA and Risk-net consider the inhalation of contaminated soil particles also for volatile chemicals; in these cases the reference concentration and the inhalation unit risk are used for the final calculation of HI and R.

4.1.6 Clean-up levels

Both programs implement a backward calculation approach to derive clean-up levels, meaning that they base calculations on target risk thresholds to determine acceptable contaminant concentrations in environmental media.

In practice, this operation is carried out by inverting the risk assessment equations: instead of evaluating the risk from a known concentration, they calculate the concentration that corresponds to a predefined acceptable risk level. The formula used in both cases is Equation 22.

As explained in paragraph 3.6, in RBCA the SSTL calculation proceeds through multiple steps. First, the Risk-based exposure limit (RBEL) is calculated (Equation 22), variable which represents the maximum safe exposure level for a given receptor and route. Then, the Risk-based screening level (RBSL) is computed. It represents the concentration in the source medium (groundwater or soil) that would result in an exposure equal to the RBEL, considering the cross-media transfer factor describing the specific pathway. Finally, the RBSL is adjusted to derive the SSTL by applying factors such as the Natural attenuation factor (NAF) or the Dilution attenuation factor (DAF), which estimate processes like biodegradation or dispersion in the subsurface environment.

This progression (from RBEL to RBSL to SSTL) allows the user to understand how each factor (toxicity, exposure and transport) influences the final clean-up level, in case it is necessary. Anyway, this structure could result rigid when dealing with more complex site conditions. For example, scenarios of soils with contaminated layers at different depths or with simultaneous exposure pathways could be difficult to be assessed.

The approach adopted by Risk-net is slightly different. It employs a unified equation that directly computes the SSTL without passing through intermediate levels. All fate and transport processes are incorporated into the calculation using the set of factors shown in paragraph 3.4. The result is a single and integrated SSTL value that reflects both the exposure and transport behaviour of the contaminant under the conditions of the contaminated site.

Concerning cumulative exposure, Risk-net calculates cumulative SSTLs that account for multiple exposure routes (referred to the same exposure pathway) simultaneously, while RBCA evaluates each route independently and sums risks only in post-processing. Furthermore, in Risk-net SSTL derivation is integrated with regulatory compliance values (such as maximum contaminant levels, MCLs) for groundwater. This this is due to the fact that the program is designed to be aligned with the Italian regulatory context, which emphasizes compliance at specified points of compliance and requires the use of measured site data to support modelling assumptions.

4.1.7 Summary

In Table 9 are reported the most significant differences between the two tools.

	RBCA	Risk-net
Integrative characterization (Flux chamber, leaching test..)	No	Yes
Determination of the representative contaminant concentration	Arithmetic mean, maximum value, UCL95 on the mean	Direct input of the representative value
Surface soil classification	Defined by the user	Portion of the soil up to the depth of one meter
Exposure pathways classification	Endpoint classification (groundwater, soil, outdoor air and indoor air)	Source classification (surface soil, subsurface soil and groundwater)
Water recreational use (fishing, swimming)	Yes	No
Number of definable off-site receptors	Two	One
Customable database	Yes	Yes

Table 9: Most significant differences between RBCA and Risk-net

4.2 Selection criteria and application contexts

The purpose of this section is to provide some selection criteria that may guide the choice between the RBCA and Risk-net for risk assessment, summarizing and commenting the differences exposed in the chapter.

Obviously, both software follow the generally accepted logic of risk-based corrective action through exposure estimations and calculation of clean-up levels. However, each one offers unique features that make it more suitable in specific situations.

One significant difference exists regarding water use scenarios. RBCA, includes the option to evaluate recreational use and fishing activities as exposure routes through the implementation of a groundwater to surface water dilution factor (DF_{gwsw}). This factor estimates the contaminant transport process from the aquifer into a connected surface water body. It is used to consider situations in which there is human exposure through consumption of fish or incidental ingestion of water during recreational use. As long as Risk-net does not provide this feature, RBCA is appropriate for sites near lakes, rivers or coastal zones where the situation may require to evaluate this exposure pathways, especially regarding water recreational use, since it is not common to consider the ingestion of fish pathway.

Also concerning exposure pathways evaluation, Risk-net supports the use of experimental flux chamber data to estimate vapor emissions from contaminated soils, as said in paragraph 3.2. This option allows users to introduce field measurements of vapor flux, making the vapor intrusion modelling more reliable. RBCA does not include the integration of these results, relying instead on predefined attenuation models. Consequently, the use of Risk-net may be more suitable when experimental information is available, since the results obtained will be more realistic (particularly in urban sites with shallow contamination and active vapor intrusion pathways).

The above applies to the whole part of integrative characterization that Risk-net offers: in fact, it is also possible to enter data on leaching and soil gas tests carried out on samples collected in the surface or subsurface soil.

In terms of modelling instead, there are some cases in which analytical models are available in one software but not in the other. Below is a comment about these differences, since there may be situation for which a model is particularly suitable:

- Surface soil to outdoor air volatilization factor: RBCA gives the possibility to use the Q/C model developed by the U.S. EPA to estimate the volatilization contaminants from surface soil to ambient outdoor air (option absent in Risk-net). This is suitable if a conservative estimation is requested for cases in which the volatilization phenomenon can be assumed to be continuous (United States Environmental Protection Agency, 2012).

- Indoor subsurface soil volatilization factor: Unlike Risk-net, RBCA includes Equation 10.3, a refined version of the Johnson & Ettinger model, to estimate indoor air concentrations arising from subsurface contaminated soil. This is a simpler version of the model, which may be particularly useful when contamination exists directly beneath buildings and soil gas data is not available. However, in general Equations 10.1 and 10.2 (available in Risk-net) are more widely employed than 10.3 since they provide more precise results.

- Groundwater to indoor air volatilization factor: RBCA employs a mass flux model to estimate the transport of volatile chemicals from contaminated groundwater to indoor air via soil gas. This model assumes the unsaturated zone or the building foundation has no effect on the vapor transport and no mass is lost in the unsaturated zone. Cases in which this assumption can be made without significant loss of information are suitable to be assessed with this model. In Risk-net the mass flux model is not available.

- Soil leaching factor: In Risk-net a steady-state leaching model (Equation 20) is available to calculate the leaching factor. This model (not available in RBCA) includes detailed parameters for infiltration rate vertical transport and soil-water partitioning. It gives a simple estimation of the percolation process but can be useful when the aim is to obtain results that give an idea of the situation, based on the parameters of interest of the contaminated site. It is not suitable for the cases in which the groundwater table undergoes seasonal changes (Corwin et al., 2007).

- Groundwater dilution attenuation factor: RBCA provides the option to simulate groundwater plume attenuation using the Domenico analytical model. Also Risk-net uses the same model, but RBCA which includes the effect of natural attenuation via electron acceptors. This model is advantageous when evaluating long-term fate of contaminants and their degradation in the saturated zone (Aziz et al., 2002). Risk-net does not include this formulation, focusing instead on simplified attenuation factors or empirical distance-based approaches.

These modelling differences highlight how the selection of software should depend on site-specific features and data availability. RBCA offers robust capabilities for water-related exposure and Tier 2 vapor intrusion screening, while Risk-net provides higher resolution in modelling leaching, soil vapor flux and cumulative exposure across multiple pathways.

Chapter 5 - Practical application

The contaminated zone is an industrial site, located close to an urban area with residential and commercial use. Below the area there is an aquifer of regional size, at a depth of approximately 4 m. The site investigation reveals that the soil and groundwater immediately downstream of the industrial factory building are affected with phenol, arsenic and chlorinated solvents: 1,2-dichloroethane, tetrachloroethylene (PCE) and trichloroethylene (TCE). No free hydrocarbon phases have been detected.

Through the investigation of the environmental features of the site, the following geological and hydrogeological parameters have been determined:

Unsaturated zone	**Value**
Soil type	Sand
Organic carbon faction	0,007
Average annual rainfall	1465 mm
Affected area	50 m^2

Table 10: Soil unsaturated zone parameters

Saturated zone	**Value**
Soil type	Sand
Saturated aquifer thickness	5,5 m
Hydraulic gradient	0,008
Hydraulic conductivity	0,82 m/d
Organic carbon faction	0,001
Effective porosity	0,25

Table 11: Soil saturated zone parameters

The groundwater flow direction is S-SW, while the wind blows from NW to SE with an average velocity of 1,2 m/s.

In order to simplify the problem, the contamination source zone is assumed to have a square geometry, with a surface area of 50 m^2 and to extend from the ground surface to a depth of 2,5 m. The representative concentration in soil for the source zone are presented in Table 12.

Soil concentration (mg/kg)	S1	S2	S3	S4	S5	S6
Phenol	2.0E-2	4.0E-2	4.0E-2	5.0E-3	9.0E-1	< 5.0E-3
Trichloroethylene	7.0E-2	1.0E-1	7.0E-2	< 5.0E-3	9.0E-3	1.5E+1
Tetrachloroethylene	1.0E-1	< 5.0E-3	8.0E-3	5.0E+0	< 5.0E-3	2.0E+1
Dichloroethane 1,2	5.0E+0	1.5E-1	2.5E+1	< 5.0E-3	1.0E+1	2.0E+2
Arsenic	3.5E+1	2.0E-2	< 5.0E-3	9.0E-1	4.0E-2	< 5.0E-3

Table 12: Concentration of the contaminants in the soil

where S1 through S6 refer to the 6 boreholes drilled in the source zone from which soil samples were collected and analysed.

Furthermore, monitoring wells were installed in each of these boreholes and groundwater samples were collected from them. The analysis of these samples indicates that a 15m wide contamination plume exists in the saturated zone beneath the source. It presents the following values of concentration of dissolved substances:

Water concentration (mg/L)	MW1	MW2	MW3	MW4	MW5	MW6
Phenol	9.00E+0	5.00E+0	8.00E+0	1.00E-1	2.50E+0	1.70E+1
Trichloroethylene	1.20E+1	2.50E+0	1.70E+1	6.50E-2	8.50E-1	2.10E+1
Tetrachloroethylene	1.00E+0	9.00E-1	3.80E+0	1.00E-2	1.00E-1	6.50E+0
Dichloroethane 1,2	8.00E+0	2.00E+0	5.00E+0	7.00E-2	5.00E-2	1.40E+1
Arsenic	3.5E+1	5.00E+0	4.00E+0	1.00E-1	< 5.0E-3	1.00E+1

Table 13: Concentration of the contaminants in the groundwater

The following figure shows a scheme of the possible receptors and the direction of groundwater flow. A commercial area (purple in the image, the area outside the building is newly renovated and completely paved) is located approximately 50 m from the source zone while the distance to the centre of a residential area is around 100 m. Both zones have buildings with basements that are susceptible to the accumulation of gases from the subsoil. Concerning water use the commercial area is supplied by the municipal network, so receptors of the site do not enter in contact with groundwater.

Figure 27: Contaminated site scheme

In this assessment two exposure scenarios will be considered:

- On-site receptor: a worker of the factory (commercial).

- Off-site receptor: an individual working in the commercial area located 50 m downstream from the source zone (commercial).

5.1 Exposure factors and input values

Since both the versions of the programs in exam are not updated, it has been necessary to change some of the exposure factors referring to the Exposure Factors Handbook (U.S. Environmental Protection Agency, 2011) and to the OSWER Directive 9200.1-120 (U.S. Environmental Protection Agency, 2014), which explains how to update the old database.

The exposure factors used in the following assessment are listed in the table below, under the column *Currently recommended value*. They are specific for adults, children and workers: whether a parameter is specified only for the child and the adult, it is because the value for the worker either does not exist or is the same as that of the adult.

Parameter	Software default value	Currently recommended value
Averaging time, carcinogens[1] (y)	70	70
Child averaging time, non carcinogens[1] (y)	6	6
Adult averaging time, non carcinogens[1] (y)	30	20
Worker averaging time, non carcinogens[1] (y)	25	25
Child body weight[1] (kg)	15	15
Adult body weight[1] (kg)	70	80
Child exposure duration[1] (yr)	6	6
Adult exposure duration[1] (yr)	30	20
Worker exposure duration[1] (yr)	25	25
Resident exposure frequency[1] (yr)	350	350
Worker exposure frequency[1] (yr)	250	250
Child skin surface area[2] (cm^2)	2800	2370
Adult skin surface area[2] (cm^2)	5700	6030
Worker skin surface area[2] (cm^2)	3300	3525
Child soil dermal adherence factor[1] (mg/cm^2)	0,2	0,2
Adult soil dermal adherence factor[1] (mg/cm^2)	0,07	0,07
Worker soil dermal adherence factor[1] (mg/cm^2)	0,2	0,12
Child water ingestion rate[1] (L/d)	1	0,78

Adult water ingestion rate[1] (L/d)	2	2,5
Worker water ingestion rate[1] (L/d)	1	1
Child soil ingestion rate[1] (mg/d)	200	200
Adult soil ingestion rate[1] (mg/d)	100	100
Worker soil ingestion rate[1] (mg/d)	50	50
Child swimming exposure time[2] (h/event)	1	3
Adult swimming exposure time[2] (h/event)	3	3
Child swimming water ingestion rate[2] (L/h)	0,5	0,12
Adult swimming water ingestion rate[2] (L/h)	0,05	0,07
Child swimming skin surface area[2] (cm^2)	3500	6365
Adult swimming skin surface area[2] (cm^2)	23000	19650
[1]OSWER Directive 9200.1-120 (U.S. Environmental Protection Agency, 2014) [2]Exposure Factors Handbook (U.S. Environmental Protection Agency, 2011)		

Table 14: Exposure factors.

Since risk is always referred to a specific receptor, it is of fundamental importance to define the receptor exactly in the same way in the two programs. Table 14 will be the guide to complete this task.

As regards the toxicity factors, the values used by the two programs are not the same. Table 15 shows all the default values:

	RfD_ing		RfC		SF_ing		IUR	
	RBCA	**Risk-net**	**RBCA**	**Risk-net**	**RBCA**	**Risk-net**	**RBCA**	**Risk-net**
Phenol	3.00E-1	3.00E-1	-	2.00E-1	-	-	-	-
Trichloroethylene	6.00E-3	5.00E-4	1.00E-2	2.00E-3	1.30E-2	4.60E-2	2.00E-6	4.10E-6
Tetrachloroethylene	1.00E-2	6.00E-3	3.70E-1	4.00E-2	5.20E-2	2.10E-3	3.80E-7	2.60E-7
Dichloroethane (1,2)	6.00E-3	6.00E-3	7.00E-3	7.00E-3	9.10E-2	9.10E-2	2.60E-5	2.60E-5
Arsenic	3.00E-4	3.00E-4	-	1,50E-3	1.50E+0	1.50E+0	4.30E-3	4.30E-3

Table 15: Toxicity factors of the contaminants (RBCA and Risk-net)

The databases of the two programs show significant differences concerning toxicity factors. Since these parameters strongly influence the result of the risk analysis, it has been chosen to use those provided by RBCA in the following case studies. This choice was mainly driven by the fact that modifying the database in risk-net is more practical, since RBCA presented problems in changing values located in some rows of the database.

Concerning contaminants' physico-chemical parameters, their values were compared between the two software databases. They were found to be generally similar, with no significant discrepancies. Therefore, it was decided to keep the default values provided by each software, rather than standardizing them. In fact, since the differences are not substantial, maintaining the original values may lead to a realistic comparison of the average operation conditions of each tool.

For each contaminant, there are six concentration measures for both soil and groundwater. As said in paragraph 3.1, in cases like this RBCA allows the user to insert all the available values and to choose a criterion to calculate a representative value (arithmetic mean, maximum concentration, UCL95 on the mean) to be used in the assessment. On the other side, Risk-net requires only one concentration value in input.

To address the following case studies, it has been decided to use RBCA to calculate the UCL95 on the mean (the 95% upper confidence limit, representing the highest value the true mean of a dataset is expected to reach with 95% confidence) and to use the results (reported in Table 16) as representative concentrations for both software.

	UCL95 Soil (mg/kg)	**UCL95 groundwater (mg/L)**
Phenol	0,46	12,00
Trichloroethylene	7,60	16,00
Tetrachloroethylene	11,00	4,20
Dichloroethane 1,2	100,00	9,30
Arsenic	18,00	7,30

Table 16: concentration UCL95 on the mean values for the contaminants present in the site

For site parameters, as the ones concerning source geometry, soil (vadose and saturated zone), air and indoor features instead, the data provided in the explanation of the case studies and located in Tables 10 and 11 have been used for both tools.

The models employed to estimate fate and transport factors will be the same, in order to avoid that the use of different equations in the estimation of such factors influences the calculated risk. Anyway, this topic will be discussed specifically for each case.

Among the constituents of concern involved, the only one which does not have carcinogenic effects is phenol: as a result, both programs will not calculate R for it in any of the cases considered. In the following scenarios there are other cases in which, for some reason, R or HI are not computed and they will be discussed in a specific way.

Furthermore by default, both programs calculate cumulative risk values within each exposure pathway, summing the contributions from multiple exposure routes (e.g. dermal contact, ingestion and inhalation) for each contaminant. However, they do not compute a single, final cumulative risk value that estimates the total risk across all exposure pathways (Risk-net does not sum the obtained values for surface soil, subsurface soil and groundwater for example). This approach is supported by the assumption that exceeding the risk threshold in one of the environmental matrices is sufficient to ensure that the site presents an unacceptable risk to the receptor.

Anyway, it is generally recommended to perform the sum of the obtained risk values for each exposure pathway, as stated by the following guidance for Italy and the United States of America:

- *Linee guida per la valutazione del rischio cumulativo per l'ambiente e la salute* (Delibera n. 55/2019). (SNPA, 2019).

- *Risk Assessment Guidance for Superfund (U.S. EPA, 1989).*

Therefore, the risk values calculated for each exposure pathway will be summed to assess the following case studies, with the aim of obtaining a cumulative risk level to which the receptor is exposed.

5.2 On-site case assessment

The purpose of this practical section is to explain how RBCA and Risk-net perform a risk assessment, highlighting the differences in the results. Before starting the comparison, it is good to analyse in a general way the case study.

As written before the first exposure scenario is an on-site case, where workers of a factory are exposed to five harmful chemicals due to the presence of a contaminated soil area located beneath the industrial site. It is a commercial scenario and, of course, the receptors are the workers.

The soil and groundwater immediately downstream of the industrial factory building are contaminated and a contamination plume exists in the saturated zone. With this information, it is possible to perform an exposure pathway identification:

- Groundwater exposure: not considered because groundwater is not used at the site, so workers do not enter in contact with the contaminated water.

- Surface soil exposure: present since the contamination begins at the ground surface. Hence it is very likely the contact through direct ingestion, dermal contact and inhalation.

- Outdoor air exposure: since surface soil is contaminated, workers are exposed to particulates volatilization from the soil and vapour volatilization from soil and underlying groundwater, also contaminated.

- Indoor air exposure: not taken into account because the contaminated soil and groundwater are not directly beneath the industrial building. This excludes the possibility of infiltration of toxic vapours through cracks in the floor, resulting in the absence of this exposure pathway.

For this first case, the ASTM model has been chosen (paragraph 3.4.1) for the calculation of the surface soil volatilization factor and the particulate emission factor, since both programs give the possibility to use it.

Risk assessment

This comparison part (and the following ones) will be developed showing the computed risk values organized in tables, followed by some specific information about the single exposure pathway.

At the end of this section the results given by the programs will be commented.

RBCA

Outdoor air[1]	HI	R
Phenol	-	-
Trichloroethylene	$8,6*10^{-2}$	$6,1*10^{-7}$
Tetrachloroethylene	$8,5*10^{-4}$	$4,3*10^{-8}$
Dichloroethane 1,2	$1,3*10^{-1}$	$8,7*10^{-6}$
Arsenic	-	$3,7*10^{-11}$
TOTAL	$2,2*10^{-1}$	$9,4*10^{-6}$
[1]Calculated as the sum of the inhalation exposure concentrations for the subsurface soil and groundwater vapor inhalation.		

Table 17: RBCA - Outdoor air pathway risk values

- HI is not computed neither for phenol nor for arsenic because their reference concentration (RfC) is not present in the database.

- For both toxic and carcinogenic effects, dichloroethane 1,2 is the risk driver.

- The risk is acceptable (but near the limit) for this exposure pathway.

Soil	HI	R
Phenol	$1,3*10^{-6}$	-
Trichloroethylene	$5,4*10^{-4}$	$1,5*10^{-8}$
Tetrachloroethylene	$4,6*10^{-4}$	$8,6*10^{-8}$
Dichloroethane 1,2	$7,5*10^{-3}$	$1,5*10^{-6}$
Arsenic	$2,6*10^{-2}$	$4,3*10^{-6}$
TOTAL	$3,5*10^{-2}$	$5,8*10^{-6}$

Table 18: RBCA - Soil pathway risk values

- For both toxic and carcinogenic effects, arsenic is the risk driver.

- The risk is acceptable for this exposure pathway.

The baseline risk summary table (Figure 28) describes a scenario where the risk is acceptable for the receptors, all the HI and R are below the limits. The factors linked to the outdoor air are a bit higher compared to the ones of the soil exposure pathway.

BASELINE RISK SUMMARY TABLE										
	BASELINE CARCINOGENIC RISK					BASELINE TOXIC EFFECTS				
	Individual COC Risk		Cumulative COC Risk		Risk	Hazard Quotient		Hazard Index		Toxicity
EXPOSURE PATHWAY	Maximum Value	Target Risk	Total Value	Target Risk	Limit(s) Exceeded?	Maximum Value	Applicable Limit	Total Value	Applicable Limit	Limit(s) Exceeded?
OUTDOOR AIR EXPOSURE PATHWAYS										
Complete? ■	8.7E-6	1.0E-5	9.4E-6	1.0E-5	□	1.3E-1	1.0E+0	2.2E-1	1.0E+0	□
INDOOR AIR EXPOSURE PATHWAYS										
Complete? □	NA	NA	NA	NA	□	NA	NA	NA	NA	□
SOIL EXPOSURE PATHWAYS										
Complete? ■	4.3E-6	1.0E-5	5.8E-6	1.0E-5	□	2.6E-2	1.0E+0	3.5E-2	1.0E+0	□
GROUNDWATER EXPOSURE PATHWAYS										
Complete? □	NA	NA	NA	NA	□	NA	NA	NA	NA	□
SURFACE WATER EXPOSURE PATHWAYS										
Complete? □	NA	NA	NA	NA	□	NA	NA	NA	NA	□
CRITICAL EXPOSURE PATHWAY (Maximum Values From Complete Pathways)										
	8.7E-6	***1.0E-5***	***9.4E-6***	***1.0E-5***	□	***1.3E-1***	***1.0E+0***	***2.2E-1***	***1.0E+0***	□
	Outdoor Air		***Outdoor Air***			***Outdoor Air***		***Outdoor Air***		

Figure 28: Baseline risk summary table. Screenshotted from RBCA

Summing the risk obtained from each exposure pathways the results are:

- HI = 2,5E-1.

- R = 1,5E-5.

The risk is assessed to be acceptable for the toxic effects but not for the carcinogenic ones.

Risk-net

Surface soil	HI	R
Phenol	$1,2*10^{-6}$	-
Trichloroethylene	$1,6*10^{-3}$	$3,2*10^{-8}$
Tetrachloroethylene	$8,9*10^{-4}$	$1,6*10^{-7}$
Dichloroethane 1,2	$2,4*10^{-2}$	$3,3*10^{-6}$
Arsenic	$3,2*10^{-2}$	$5,2*10^{-6}$
TOTAL Accidental soil ingestion	$3,4*10^{-2}$	$5,6*10^{-6}$
TOTAL Dermal contact	$1,3*10^{-2}$	$2,3*10^{-6}$
TOTAL Inhalation	$1,2*10^{-2}$	$7,16*10^{-7}$
TOTAL	$5,9*10^{-2}$	$8,7*10^{-6}$

Table 19: Risk-net – Surface soil pathway risk values

- For both toxic and carcinogenic effects, arsenic is the risk driver.

- The risk is acceptable for this source zone.

In this case the results for each exposure route (inhalation, dermal contact and accidental soil ingestion) have been included, since the final risk values are calculated separately for each cathegory.

Subsurface soil	HI	R
Phenol	-	-
Trichloroethylene	$1,2*10^{-3}$	$8,3*10^{-9}$
Tetrachloroethylene	$4,6*10^{-5}$	$2,3*10^{-9}$
Dichloroethane 1,2	$2,2*10^{-2}$	$1,4*10^{-6}$
Arsenic	-	-
TOTAL	$2,3*10^{-2}$	$1,4*10^{-6}$

Table 20: Risk-net – Subsurface soil pathway risk values

- For both toxic and carcinogenic effects, dichloroethane 1,2 is the risk driver.

- The risk is acceptable for this source zone.

Groundwater	HI	R
Phenol	-	-
Trichloroethylene	$6,9*10^{-3}$	$4,9*10^{-8}$
Tetrachloroethylene	$6,2*10^{-5}$	$3,1*10^{-9}$
Dichloroethane 1,2	$1,4*10^{-3}$	$9,0*10^{-8}$
Arsenic	-	-
TOTAL	$8,3*10^{-3}$	$1,4*10^{-7}$

Table 21: Risk-net – contaminated vapours from groundwater pathway risk values

- Dichloroethane 1,2 is the risk driver concerning carcinogenic effects, while trichloroethylene concerning the toxic ones.

- There risk is acceptable for this source zone.

Summing the risk obtained for inhalation for each source zone the results are:

- HI = 4,3E-2

- R = 2,3E-6

The risk is assessed to be acceptable for the toxic and carcinogenic effects both.

Comment

The results of the assessment are reported in Table 22.

	RBCA	Risk-net
Total HI	2,5E-1	4,3E-2
Total R	1,5E-5	2,3E-6

Table 22: Total toxic and carcinogenic risk values resume

The analysis carried out by the two programs shows different results. In fact, they both assess toxic risk is acceptable, while, concerning carcinogenic one, RBCA assesses the presence of risk, while Risk-net does not.

Furthermore, combining the assessments made by the software, arsenic and dichloroethane 1,2 are likely to be the most harmful contaminants in this scenario.

HI and R computed by RBCA are higher than the ones calculated by Risk-net.

5.3 Off-site case assessment

Also this one is a commercial scenario, which has workers as receptors. The commercial area they work in is placed approximately 50 m downstream from the source area and the scenario presents the following exposure pathways:

- Groundwater exposure: as before, not assessed because groundwater is not used by water supply, so workers do not enter in contact with the contaminated water.

- Surface soil exposure: not present because it is assumed that contact with surface soil is evaluated only for on-site cases.

- Outdoor air exposure: active since workers are exposed to particulates volatilization coming from the contaminated site. Inhalation of contaminated vapours coming from the underlying aquifer is assessed to be neglectable, since the external area is newly renovated and completely paved.

- Indoor air exposure: taken into account given that, the underlying groundwater is contaminated and the building have basements that are susceptible to the accumulation of gases from the subsoil.

As before, models that both programs can employ have been selected: the ASTM model for the outdoor air volatilization and the Johnson & Ettinger model for the indoor air volatilization factors. The lateral air dispersion factor will be estimated with 3D Gaussian plume model by RBCA and with the 1D Gaussian plume model by Risk-net, as in this case it is not possible to select a model that they can both implement.

Risk assessment

RBCA

Outdoor air	**HI**	**R**
Phenol	-	-
Trichloroethylene	$1,8*10^{-10}$	$1,3*10^{-15}$
Tetrachloroethylene	$7,1*10^{-12}$	$3,5*10^{-16}$
Dichloroethane 1,2	$3,6*10^{-9}$	$2,4*10^{-13}$
Arsenic	-	$6,6*10^{-12}$
TOT	$3,8*10^{-9}$	$6,8*10^{-12}$

Table 23: RBCA – Outdoor air pathway risk values

- HI is not computed neither for phenol nor for arsenic because their reference concentration (RfC) is not present in the database.

- Dichloroethane 1,2 is the risk driver for toxic effects while for the carcinogenic ones is arsenic.

- The risk is acceptable for this exposure pathway, HI and R computed are well below the limits.

Indoor air	**HI**	**R**
Phenol	-	-
Trichloroethylene	$1,3*10^{-1}$	$9,2*10^{-7}$
Tetrachloroethylene	$1,4*10^{-3}$	$7,2*10^{-8}$
Dichloroethane 1,2	$1,9*10^{-2}$	$1,2*10^{-6}$
Arsenic	-	-
TOT	$1,5*10^{-1}$	$2,2*10^{-6}$

Table 24: RBCA – Indoor air pathway risk values

- HI is not computed neither for phenol nor for arsenic because their reference concentration (RfC) is not present in the database.

- R is not computed for arsenic since it does not have a VF_{wesp} (Groundwater to Indoor air volatilization factor, it is not assessed since arsenic Henry's law constant is equal to zero).

- Dichloroethane 1,2 is the risk driver for carcinogenic effects while for the toxic ones is trichloroethylene.

- The risk is acceptable for this exposure pathway.

The baseline risk summary table (Figure 29) describes a scenario where risk is acceptable for the receptors, all the HI and R are below the limits. The factors linked to the indoor air are consistently higher compared to the ones of the outdoor air exposure pathway.

BASELINE RISK SUMMARY TABLE

	BASELINE CARCINOGENIC RISK					BASELINE TOXIC EFFECTS				
	Individual COC Risk		Cumulative COC Risk		Risk	Hazard Quotient		Hazard Index		Toxicity
EXPOSURE PATHWAY	Maximum Value	Target Risk	Total Value	Target Risk	Limit(s) Exceeded?	Maximum Value	Applicable Limit	Total Value	Applicable Limit	Limit(s) Exceeded?
OUTDOOR AIR EXPOSURE PATHWAYS										
Complete? ■	6.6E-12	1.0E-5	6.8E-12	1.0E-5	□	3.6E-9	1.0E+0	3.8E-9	1.0E+0	□
INDOOR AIR EXPOSURE PATHWAYS										
Complete? ■	1.2E-6	1.0E-5	2.2E-6	1.0E-5	□	1.3E-1	1.0E+0	1.5E-1	1.0E+0	□
SOIL EXPOSURE PATHWAYS										
Complete? □	NA	NA	NA	NA	□	NA	NA	NA	NA	□
GROUNDWATER EXPOSURE PATHWAYS										
Complete? □	NA	NA	NA	NA	□	NA	NA	NA	NA	□
SURFACE WATER EXPOSURE PATHWAYS										
Complete? □	NA	NA	NA	NA	□	NA	NA	NA	NA	□
CRITICAL EXPOSURE PATHWAY (Maximum Values From Complete Pathways)										
	1.2E-6	*1.0E-5*	*2.2E-6*	*1.0E-5*	□	*1.3E-1*	*1.0E+0*	*1.5E-1*	*1.0E+0*	□
	Indoor Air		*Indoor Air*			*Indoor Air*		*Indoor Air*		

Figure 29: Baseline risk summary table. Screenshotted from RBCA

Summing the risk obtained from each exposure pathways the result are:

- HI = 1,5E-1.

- R = 2,2E-6.

The risk is assessed to be acceptable for toxic carcinogenic effects both.

Risk-net

Surface soil	HI	R
Phenol	-	-
Trichloroethylene	$1{,}5*10^{-11}$	$1{,}1*10^{-16}$
Tetrachloroethylene	$6{,}0*10^{-13}$	$3{,}0*10^{-17}$
Dichloroethane 1,2	$2{,}9*10^{-10}$	$1{,}9*10^{-14}$
Arsenic	-	$5{,}5*10^{-13}$
TOT	$3{,}0*10^{-10}$	$5{,}7*10^{-13}$

Table 25: Risk-net – Surface soil pathway risk values

- As for RBCA, HI is not computed neither for phenol nor for arsenic because their reference concentration (RfC) is not present in the database.

- Arsenic is the risk driver for carcinogenic effects, Dichloroethane 1,2 for the toxic ones.

- The risk is acceptable for this exposure pathway, HI and R computed are well below the limits.

Groundwater	HI	R
Phenol	-	-
Trichloroethylene	$4{,}0*10^{-2}$	$2{,}6*10^{-7}$
Tetrachloroethylene	$3{,}8*10^{-4}$	$1{,}7*10^{-8}$
Dichloroethane 1,2	$5{,}2*10^{-3}$	$3{,}0*10^{-7}$
Arsenic	-	-
TOT	$4{,}6*10^{-2}$	$5{,}8*10^{-7}$

Table 26: Risk-net – Contaminated vapours coming from groundwater pathway risk values

- As before, HI is not computed neither for phenol nor for arsenic because their reference concentration (RfC) is not present in the database.

- As for RBCA, R is not computed for arsenic since it does not have a VF_{wesp} (Groundwater to Indoor air volatilization factor, it is not assessed since arsenic Henry's law constant is equal to zero).

- The risk is acceptable for this exposure pathway.

Summing the risk obtained from each exposure pathways the result are:

- HI = 4,6E-2.

- R = 5,8E-7.

The risk is assessed to be acceptable for toxic and carcinogenic effects both. Risk associated with the surface soil is neglectable compared to the one associated with the exposure to contaminated vapours coming from the aquifer.

Comment

The results of the assessment are reported in Table 27.

	RBCA	Risk-net
Total HI	1,5E-1	4,6E-2
Total R	2,2E-6	5,8E-7

Table 27: Total toxic and carcinogenic risk values resume

For this second case, the programs assess the risk for the receptors is acceptable.

In both cases, outdoor exposure to particulates is negligible compared to the exposure to contaminated vapours volatilized from groundwater, so that this last pathway has the most weight in explaining the differences in the results.

For this scenario the risk indexes calculated by RBCA are greater (around three times) than the ones computed by Risk-net. This relationship had already been found in the on-site case, also in that case RBCA estimated a greater risk with equal input data.

Summarizing, even if the input data are the same for both software platforms (paragraph 5.1, toxicological parameters, physico-chemical properties, site parameters,..), a divergence has emerged in the computed risk values between RBCA and Risk-net.

Furthermore the same equations have been used to estimate the fate and transport factors:

- On-site case:

- ASTM model for the estimation of the surface soil volatilization factor (Equation 6).
- ASTM model for the estimation of the particulate emission factor (Equation 9).

- Off-site case:

- Johnson and Ettinger model for the estimation of the groundwater to enclosed space volatilization factor (Equation 12).
- Domenico model for the calculation of the groundwater dilution attenuation factor.

The only difference is represented by the calculation of the lateral air dispersion factor, for which RBCA provides a 3D gaussian model and Risk-net an 1D one. Anyway, this discrepancy has a low weight on the final result since the computed risk values for the outdoor air exposure pathway (linked to the particulates exposure, for which it is necessary to calculate the lateral air dispersion factor) are neglectable, as commented above.

However, for both scenarios, RBCA systematically produced higher estimates of risk than Risk-net for the same exposure conditions. Especially for the on-site case, for which RBCA assesses that the carcinogenic risk is acceptable, while Risk-net does not: these conclusions, which reveal an opposite result for the two risk assessments, would have important weight in a real application.

After checking all inputs and assumptions, it was observed that Risk-net applies by default two modelling options that are not activated in RBCA:
- Depletion of the contamination source due to volatilization.
- Biodegradation during transport in the aquifer.
Both processes that reduce the estimated exposure and therefore contribute, at least in part, to explain the lower risk values obtained with Risk-net.

Therefore, it has not been possible to link the difference in results to a single parameter alone, but rather to these modelling assumptions combined with structural and computational differences in how the two programs approach human health risk assessment. The way each software is designed and how it processes information has a strong effect on the results, even when the input data is nominally the same. For this reason, the differences in results may be seen as a meaningful indication of how each program works.

The comparative analysis highlights how complex the field of risk assessment modelling can be. The present work offers some insights, but the conclusions are limited by the number and type of case studies considered. To better understand the way RBCA and Risk-net work and to confirm whether the tendencies observed here are systematic features of the software, the study of multiple scenarios would be required (both on-site and off-site cases, preferably based on field data). This approach would help clarify how much of the observed differences are due to structural characteristics of the software and their default assumptions, rather than to specific site conditions.

Conclusion

The aim of this study was evaluating how two of the most used software tools for human health risk assessment differ in their structure. And, on the practical side, what these differences mean for their real-world application.

To carry out the analysis, the thesis followed a structured approach. The first two chapters provide an introductory overview of human health risk assessment and the two software tools under examination. This is followed by an objective comparison of their structure and a critical evaluation of their respective strengths and weaknesses.

The comparison revealed that, although the general approach to human health risk assessment is standardized, there are conceptual differences between the two programs; one of the greatest discrepancies concerns exposure pathway classification, for which RBCA adopts a more common exposure pathway approach, whereas Risk-net is based on a source zone approach.

The final part of the thesis instead, focuses on the analysis of two practical case studies, aimed at testing the behavior and performance of the software tools.

This practical application showed interesting results, highlighting that, even if both programs follow similar conceptual models and risk assessment logic, they lead to different outcomes under the same input conditions. In particular, in the two scenarios assessed, RBCA gave higher risk than Risk-net. This was partly because Risk-net applies by default two processes that reduce estimated exposure, and partly because of systematic differences in the way the two programs manage exposure, transport modelling and risk computation. This trend was particularly significant in the on-site case, for which RBCA determines the presence of risk and Risk-net does not.

Anyway, this study has some limitations. Firstly, the practical comparison was based on theoretical input values. In this way it is not possible to embed the variability and uncertainty of real contaminated sites. In addition, two scenarios (one on-site and one off-site case) were tested. In this way the wide range of situations encountered in professional practice cannot be fully represented. In order to be able to detect and prove a tendence in the software behaviour, the evaluation of several cases (different for exposure conditions, contaminants, receptors and site features) would be necessary.

The information gained through research, shows that the field of human health risk assessment software offers significant opportunities for further exploration. Future studies could be improved concentrating the efforts in the application part, with the aim of gathering field data to be evaluated by the tools and commenting the results obtained.

This thesis represents an initial step in the evaluation of digital instruments in human health risk assessment. By uniting theoretical comparison and practical application, it marks a starting point for research into how methodological frameworks and software design influence the outcomes of the risk assessment.

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