

Consolidating simplified risk assessment models for pollutant leaching to and migration across groundwater

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Consolidating simplified risk assessment models for pollutant leaching to and migration across groundwater

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Abstract

The major objective of this study is to investigate simplified risk assessment models for pollutant leaching to and migration across groundwater. Data for this study were gathered through bibliographic research and experts' advice. Three European countries were selected for this investigation: Italy, United Kingdom and Walloon Region. In the first part, the procedures are compared from a theoretical point of view. The Thesis then identifies the tools used by countries and applies them on a synthetic and real case. A sensitivity analysis is performed as well. The cases have highlighted differences in terms of decision-making and shown which parameters mostly affect results. Basing on the results of this research, it can be concluded that all the countries perform Concentration based risk assessment relying on simplified analytical equations and that the way of assessing risk is quite similar. Major differences could be noticed in the choice of factors and relative adjustments for modelling leaching in the vadose zone and in the way to obtain the remedial objectives. Types of solutions for modelling the transport of contaminant across groundwater differ as well. The synthetic case study brings to light some noticeable aspects. Firstly the difficulty in choosing parameters, particularly for the saturated zone, so as to respect the mass balance between saturated and unsaturated condition. Secondly, the fact that some factors, used by countries to simplify the movement of pollutants (i.e. dilution factor), actually have a great influence on results. Therefore, their physical consistency and reliability should be further investigated by comparing results of traditional RA tools with numerical models. Finally, the sensitivity analysis has shown that Mass flux approaches may bring additional contribution to the way the presence of Risk is assessed and that research should evolve in this direction.

Key words: *Ground water, Concentration based Risk assessment, leaching, migration, analytical equations, synthetic case, Remedial objectives, Mass flux.*

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Introduction

The overall objective of this Master Thesis is to investigate simplified Risk Assessment procedures for contaminant leaching to and across groundwater for different countries.

In order to reach this objective, firstly a bibliographic review of common risk assessment procedures is performed. Secondly, the European RA tools of Italy, United Kingdom and Walloon Region are applied to a synthetic case study and a sensitivity analysis is performed as well. The same is done for a real case.

The theoretical case and the real one allow showing differences and lacks among tools and procedures.

In recent years, the concern relatively to the protection of groundwater is increased. More attention is given to the problem of groundwater pollution.

In fact the source of pollution for groundwater may come from a vast range of activities (Municipal and industrial waste disposal, metal industries, petrol, mining, agriculture). Solely in Europe, in 2014, the European Environmental Agency has classified 2, 5 million of site as potentially contaminated among with approximately 14 % are estimated to be contaminated and need remediation [34]. This is why Europe has established several Directives which the objective to protect groundwater from pollution and deterioration (Water Framework, Groundwater, Nitrates, Industrial Emissions and Landfill Directives) [41].

Globally governments and technical community have increased their awareness and search ways to assess, protect and preserve groundwater resource and human health.

Countries have made efforts for developing risk assessment procedures, which allow estimating the presence of risk for the groundwater resource and eventually obtaining remedial objectives.

These methodologies do not require entering too many data, in fact they are generally concentration based risk assessment procedures based on analytical transport models of the contaminant.

From one side, these procedures allow to simplify the problem, since only concentrations are measured and compared with proper standards. However, on the other hand, experience has shown that they may drive to incorrect estimation on the presence of risk. In fact, not only the values of concentration should be investigated but also site-specific conditions as the groundwater flow, the presence of heterogeneities and the presence of natural attenuation.

Some of these aspects are investigated along the Thesis.

The document is organised as following.

First, a general description of a typical concentration based risk assessment procedure is shown highlighting the common assumptions and conceptual choices done by countries (chapter 1). Even the critical points of traditional risk assessment and possible alternatives are presented.

Chapters 2 describes more specifically the different risk assessment procedures of Australia, Canada, Italy, United Kingdom and Walloon Region. Similarities and differences among the approaches are highlighted.

Chapter 3 gives a brief description of the tools used by the investigated European countries. The used tools are the Walloon ESR v. 2.0.4. and BIOSCREEN-AT v.1.45 tools, the Italian Risk-net v.2.1 tool and the English RT-worksheet tool v. 3.2.

In chapter 4 a theoretical case study has been developed based on the gathered knowledges of chapter 2. The same case study has been tested by the three European countries (Italy, United Kingdom and Walloon Region). The synthetic case has allowed pointing out differences among the approaches in term of decision-making.

In chapter 4 a real case study is tested for the three European countries as well. Data are given by the Environmental Belgian Company *Geolys*. For confidential reasons no much details on the location an Environmental contest are given.

Chapter 5 shows the results of the sensitivity analysis applied on the synthetic case study developed in the previous chapter. The sensitivity analysis shows the parameters, which most influence the results of the RA procedures. Moreover, it allows highlighting differences and similarities among countries.

In Chapter 6 conclusions are done. Proposals and recommendations are shown as well.

Chapter 1

Description of the general context and conceptual model for simplified RA for GW

1.1. Definition of risk assessment

The general definition of Risk Assessment (RA) given by the European commission is as following. *“The risk assessment procedure, in a general sense is the identification, analysis and evaluation of the levels of risks present in a determined situation, their comparisons against standards and the determination of an acceptable level of Risk”.*

While Risk is defined as *“the chance, probability that a person or something will be harmed, or experience an adverse effect if exposed to a hazard”.*

In addition, the hazard is *“any source of potential damage, harm or adverse effects on something (e.g. the environment) or someone”* [42] [43].

1.2. Concentration based approach

1.2.1 General procedure for assessing the presence of risk

Simplified Risk Assessment procedures for assessing groundwater pollution are generally concentration based risk assessments (cited as *C-Based* in the following parts of his document).

The process consists in comparing the measured concentration values with proper standards defined by norms, depending on specific land or groundwater use. Possible standards can be Drinkable water standards, Irrigation water standards, Fresh and marine waters standards, etc. The choice of the standard widely varies from country to country depending on the final purpose of risk assessment.

In order to be reliable, RA procedures require the selected measured values to be representative of the investigated situation and statistically consistent i.e. the Maximum value, average etc.

In the contaminated sites framework, risk assessment for groundwater can be used with two main goals:

- *Site characterization*, in order to assess the possible contamination of groundwater;
- *Clean up* values definition, in order to remediate the site up to an acceptable level.

The procedure can be simplified as following Fig.1.

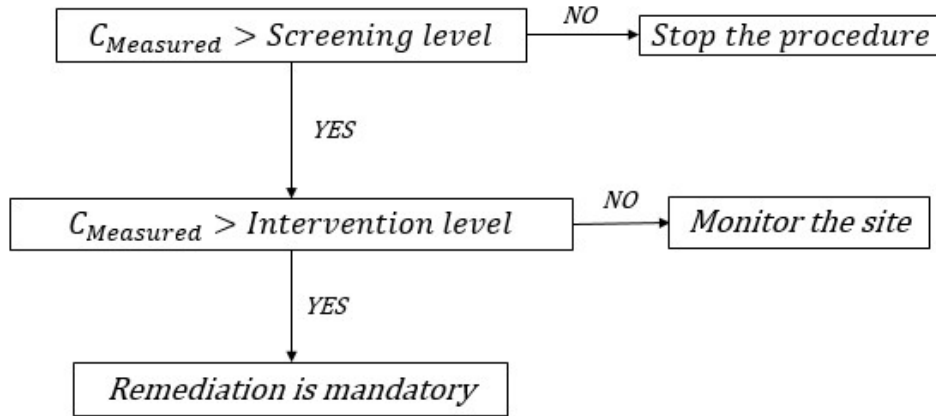


Fig. 1 General procedure to characterize the site and the presence of risk. Where $C_{Measured}$ is the measured concentration [M/M] in the soil and [M/L³] in the water. Intervention and Screening levels may be equal.

The Site characterization consists in further investigation of the site and of the level of contamination.

First, the so-called *Screening or Investigation value* is compared with the measured concentrations. The measured concentration can be both in the soil [M/M] and in the groundwater [M/L³]. If the standard is not exceeded, then it means that no pollution is present. Otherwise, it is necessary to proceed with a deeper characterization in order to estimate the extent of the contamination and its magnitude.

Then the measured concentrations have to be compared with the so-called *Intervention value*. If the *Intervention value* is not exceeded, normally the practise is a continuum monitoring of the site. Otherwise, it is mandatory by law to intervene and clean up the site down to a well-defined value. The level of remediation-acceptance can be directly defined by norms or obtained by risk assessment procedures and relative tools. The clean-up standards have to be seen as acceptable levels of controlled Risk, which has to be monitored over time. Moreover, as it is highlighted in both Verreydt (2012) and Bartlett (2013), it is often not technically and economically feasible to restore the initial condition basing on concentration standards.

Even if usually it is possible to define two main standards -*Investigations or Screening level* and the *Intervention or Remediation level*- there are no shared terminologies among the investigated countries. In some countries, the same standards are both used as *Screening values* and *Clean up values*.

1.2.2. Conceptual model choices & S-P-R approach

In order to apply the RA procedure, it is necessary to define the Conceptual Model. The model according to definition is a tool to simulate reality in a simplified way, which helps in driving conclusions of present or possible future scenarios.

The conceptual model choices, as well as the chosen parameters, have to be carefully selected due to their influence on the results. The hypothesis as well as the results have to be physically consistent.

All the investigated Risk assessment procedures are based on the so-called Source(s)-Pathway(s)-Receptor(s) approach, usually known as S-P-R approach. Indeed, the most common Conceptual Model considers the link (Pathway) between the Source(s) and the Receptor(s).

A possible simplified conceptual model is shown in Fig.2 below.

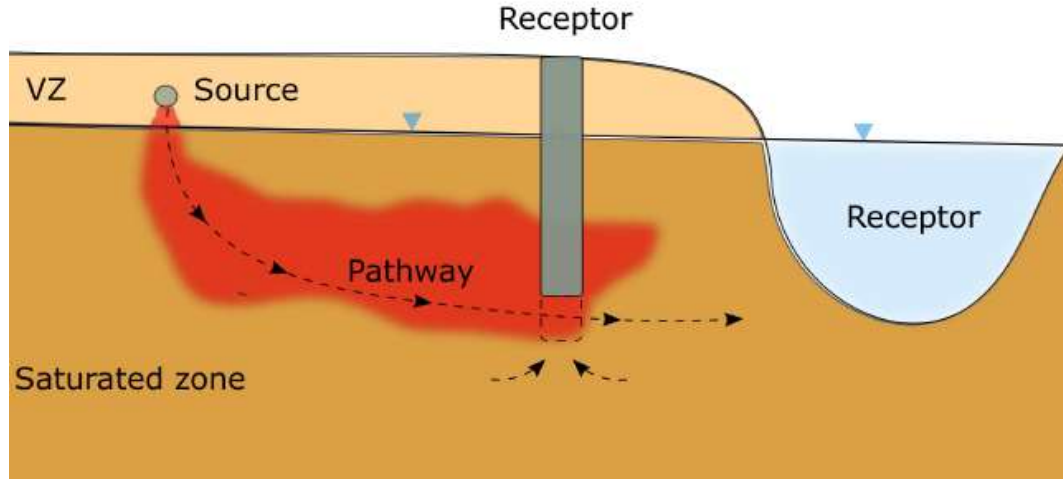


Fig. 2 Typical graphical Conceptual Model representation of RA for GW (SPR approach). Image made with Inkscape. The image is merely for explicative purpose. Scale is not respected.

A preliminary hint on pollutants behaviour is offered by the pollutant distribution between phases. This is expressed basing on distribution coefficients reflecting concentration ratio (equ.1.1).

$$K = \frac{\text{Concentration}_{\text{PHASE 1}}}{\text{Concentration}_{\text{PHASE 2}}} \quad (1.1)$$

In relation to the available phases, different constants may be found (Henry constant, adsorption constant and octanol-water partitioning constant) (Fig.3). These allow a better characterization of the site and definition of proper pathways.

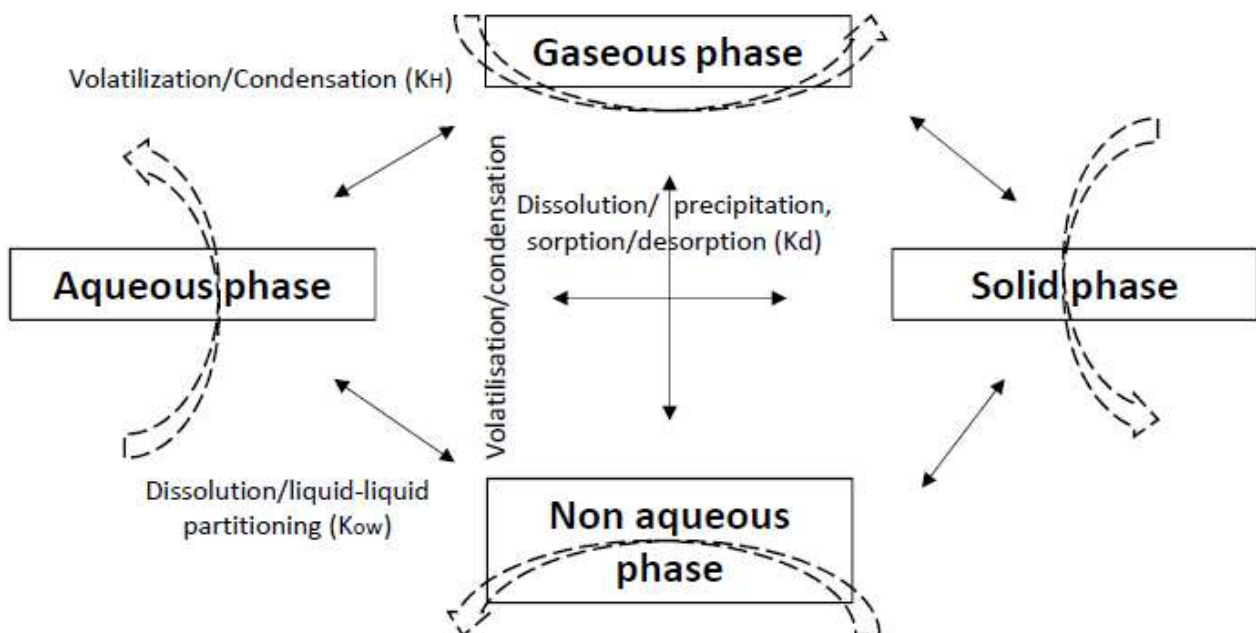


Fig. 3 Pollutants mobility and distribution between phases. [12] [13]

The reader is invited to look at figures 2 and 3 for a better understanding of the next explanation.

Looking at Fig.2 the reader can imagine to follow the path of the pollutant from the source - a pipe leak in the vadose zone (VZ) - to the chosen receptors, here represented as an extraction well and a surface body. A dotted line with arrows represents the pathway. The path starts with a vertical movement in the VZ from the pipe and continues in the saturated zone following the groundwater flow, towards the targets.

The contaminant in the vadose zone may undergo three types of mechanisms.

Firstly, it may volatilize. This mechanism is controlled by the *Henry constant* (K_H) which is used to evaluate the liquid-gas partitioning.

Secondly, the contaminant may remain partially adsorbed in the soil. The *adsorption constant* K_d is used to evaluate the Solid-liquid partitioning.

Finally, the part of pollutant that does not sorb or volatilize can start to infiltrate moving vertically in the unsaturated soil (leaching). As it moves the pollutant undergoes natural attenuation processes.

Once the pollutant has entered ground water, further mechanisms occur.

If the pollutant is soluble, it starts to dissolve in groundwater and it undergoes the mechanism of advection, dispersion, diffusion and natural attenuation. The more the pollutant is soluble, the more mobile in the water too.

If the pollutant is not degradable, it can persist in the environment and/or if decay time is long enough it can form toxic by-products.

Last but not least, if a non-aqueous phase is present then this phase may migrate across the unsaturated zone and in the groundwater table. The *octanol water partitioning constant* (K_{ow}) may be used to check the hydrophobicity of a substance.

In the end, the most dangerous pollutants for groundwater are those presenting: low sorption, high solubility, low degradation rate and form toxic by-products compounds

Summarizing the S-P-R approach is composed of the following steps.

The *source* represents the pollution starting point. While performing a risk assessment, it is essential to know if the source is point or diffusive, its spatial extension, time variability, persistence, amount/load and its eventual mobility.

Generally, typical *C-based* Risk assessment consider a not mobile point sources of contamination. The source location may vary either in soil and groundwater or in both.

The *pathways* are all the ways toward the target(s) available to the pollutant. They are strictly related to the Conceptual model choices, pollutant properties and to the target choices (Human, Animal, Ecosystem, and Groundwater).

Generally, in groundwater RA approach, mainly *Leaching* and “*Dispersion*” across ground water are considered.

Leaching represents the vertical movement of the pollutant from the source through the Vadose Zone to the groundwater table. It occurs whenever the source of pollution is located in the soil.

“*Dispersion*” instead represents the mainly horizontal movement in the saturated zone across groundwater.

Since the present study focuses on groundwater pollution, the volatilisation will not be taken into account.

The *receptors* are all possible contamination targets. One of the main objectives of Risk assessment is to determine whether the soil and/or groundwater contamination pose an unacceptable Risk for the defined receptors.

Based on Risk Assessment type (Human Health, Ecological and Groundwater risk assessment) and purpose, the receptor could be:

- *Human* (via dermal contact, incidental ingestion, vegetable/fishes ingestion, inhalation of vapours and dust);
- *Ecosystem* (plants, fishes...);
- *Groundwater*. It can be the protection of the groundwater resource itself or the groundwater can be protected in relation to its use (i.e. if the receptor is a potable well, groundwater has to be protected in order to guarantee the drinkable standards);
- *Surface water*: (it could be impacted by groundwater discharge).

Usually, while assessing risk for groundwater pollution, the considered receptors are groundwater resources, wells (for potable, irrigation or breeding purposes), piezometers or surface waters (river, lake, sea).

1.2.3 Critical points of concentration based risk assessment

Some critical points related to the investigated C-based risk assessment procedures should be noticed.

The first difficulty while dealing with polluted groundwater is the lack of clear limits. This is not an issue for soil pollution since normally the limit is represented by the boundary of the parcel.

This is the reason why concentrations in groundwater are estimated from the measured concentration in soil, taking into account the leaching mechanism.

Furthermore, even if traditional risk assessment (*C-Based* approaches) refers to point contamination, most of the real cases are represented by a diffuse contamination. In fact, groundwater degradation is usually not related to a unique source but to several ones.

In consideration of this and in order to prioritize, one of the main issues while dealing with groundwater pollution should be understanding how much of the source quantity present in the soil may be able to degrade groundwater.

Some of these aspects are investigated in the studies of Verreydt (2012), Brouyère (2012) and Bartlett (2014). Such studies show how flux based methodologies may help in dealing with the previous cited issues.

For example, the key elements of the study by Verreydt (2012) are firstly the division of the contaminated area in Risk Management Zones (RMZ) ¹with the aim of grouping groundwater contaminations coming from different sources; secondly, the computation of the maximum allowed contaminant mass discharge towards the chosen receptors (Md_{MAX}).

¹ *Risk management zones (RMZ)* are zones around one or more nearby contaminated sites, with an actual or potential impact of contaminants from the contaminated site(s) toward receptors.

While the study by Brouyère (2012) develops a regional flux-based method in order to compute a groundwater quality indicator that takes into account the additive effect of several contaminant sources with a different degradation power. This is done in order to look the groundwater quality deterioration over time and for the entire groundwater body scale.

In the Article by Bartlett (2014), the issue of loss of value² of Groundwater resources due to the presence of a polluted site is investigated. The loss of value is related to present and possible future use. In this case, differently from other articles such as Verreydt (2012) and Brouyère (2012) the study considers a point source of contamination, in an unused Aquifer.

Finally, research has highlighted that *C-based procedures* may drive to incorrect evaluation-overestimation or underestimation- of the risk.

In fact common RA approaches only rely on the value of measured concentration (high or low) to establish risks.

However, additional elements should be taken into account. The assessor should evaluate the magnitude of the flow and have an idea of the presence of possible heterogeneities in the subsoil (i.e. zone of high or low hydraulic conductivity). In fact, even if the concentration is low, it may still represent a risk when associated to high flux.

These concepts are illustrated with two example in *paragraph 1.3.2*.

All these considerations drive to the conclusion that traditional *C-based* procedures should be supported by *flux-based* methodologies, in order to better estimate the presence of risk for the groundwater resource. This is way in the following paragraph some tips on the mass flux based approach are given.

1.3 Mass flux based approach

Mass flux based approach could be an alternative or an additional contribution to the traditional C-based risk assessment. The flux-based approach might be used to monitor natural attenuation and source depletion.

1.3.1 Definitions of terms for the Flux based procedure

The visual representation of a typical way of estimating the *mass-flux approach* is shown in Fig. 4. The transects are the control planes perpendicular to the flow direction in which *Mass discharge* is measured.

² Loss of value, in the article, is defined as the impossibility of pumping, when the well is located on the polluted zone (*direct loss*) or it represents the decreasing of the pumping rate (*indirect loss*) due to the well vicinity to the contaminated plume.

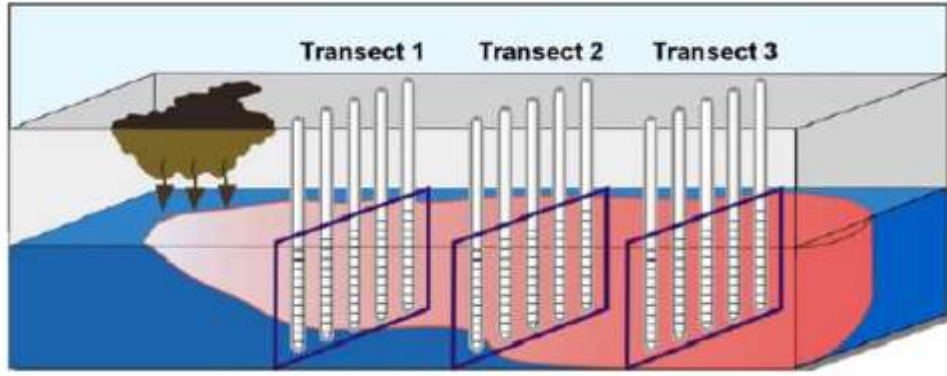


Fig. 4 Visual representation of multiple transects for measuring Mass discharge [50]

Similarly to what has been done for the concentration based risk assessment some definitions and relative equations are given. The definitions and equations come from the ITRC (2010) and the Australian technical Guidelines [20] [21].

Groundwater flux (q)

It is defined as “the velocity (speed and direction) of groundwater through a defined cross-sectional area located perpendicular to the mean direction of groundwater flow” (equ.1.2).

It is the product between the saturated hydraulic conductivity (k) and the hydraulic gradient (i). It has the dimension $[L/T]$.

$$q = k \times i \quad (1.2)$$

Mass flux (J)

It is defined as “the mass of a chemical that passes through a defined cross-sectional area located perpendicular to the mean direction of groundwater flow over a period of time” (equ.1.3). It is the product of the groundwater flux (q) and contaminant concentration (C) in a given Area. It has the dimension of $[M/L^2 \times T]$.

$$J = q \times C \quad (1.3)$$

Notice that mass flux has both a spatial and a temporal variability. Indeed, it refers to a specific area and variations both in terms of contaminant concentration and groundwater flow magnitude may occur.

Mass flux discharge (M_d)

It is defined as “the total mass of a contaminant moving in the groundwater from a given source.” It is the integral of the spatially variable mass flux estimates across a transect (J) multiplied by the representative Area (A_{cp}) (equ.1.4). It has the dimension of $[M/T]$.

$$M_d = \int_A J \times A_{cp} \quad (1.4)$$

1.3.2. Possible use of flux based methods

F-Based approach for improving C-based approach

Flux based approaches (*F-Based*) can be used together or as alternatives to *C-based* procedures.

Mass flux depends, for its definition, on:

- The level of concentration and its variation (i.e. due to sorption, redox change, attenuation mechanism etc.).
- The groundwater flow, which depends on the hydraulic conductivity and the gradient.
- The presence of heterogeneities.

These considerations are used to support the following statements.

For the traditional *C-based* approaches if in a point concentration standards are exceeded, then there is automatically risk.

On the contrary, Mass flux data could show that a real risk is not present in case the concentration is really high but associated to a low flow. Similarly, if concentration data are quite low but they are related to a big mass discharge, due to high groundwater flow, a risk may possibly be present. This is a key element. Actually, there is often the wrong idea that high concentrations are automatically associated with high risk. This is not always correct.

Simplifying and summarizing the cases that should be taken into account are shown in Table 1.

Tab 1 C-based vs F-based approaches for assessing risk [20], [21], and [50]

<i>C-based vs F-based approaches for assessing risk</i>			
<i>Concentration</i>	<i>Ground water flow</i>	<i>Possible Risk for F-Based approach?</i>	<i>Risk for C-based approach?</i>
High	High	Yes	Yes
High	Low	Maybe	Yes
Low	High	Maybe	No
Low	Low	No	No

Moreover, for the same concentration it is possible to drive to different results, depending on groundwater flow and site-specific characteristics.

In the following are given two exempla for highlighting once again the critical points of *C-based* procedures

The first example consists of two plumes with the same contaminant source concentration but with a different source load (Fig. 5).

Indeed, case A shows a greater source and a greater mass discharge through the final receptor with respect to case B (visually red lines represent mass discharge). This means that case A represents a greater risk for the downgradient receptors, compared to case B.

Notice that the same exemplum, when using *C-based* methodology, would acknowledge the same level of risk since concentrations are exactly the same.

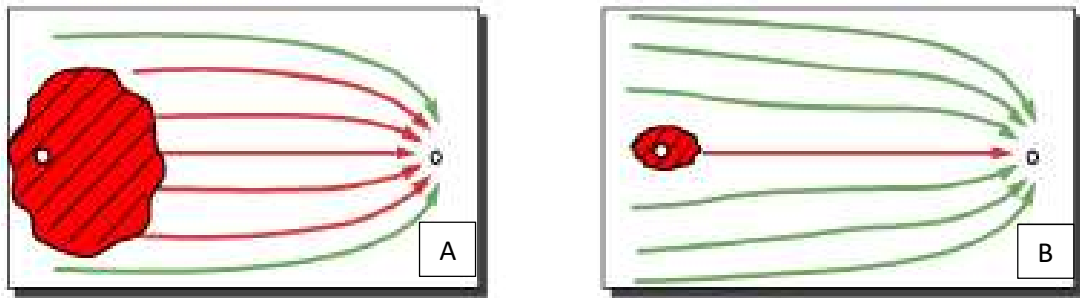


Fig. 5 Same concentration in case A and B but different risk. Case A has a large release: high max. Concentration and high mass discharge. Case B has a small release, high max. Concentration and low mass discharge [21].

The second example shows how, in many cases, while dealing with concentration based approaches, the site-specific characteristics have not been properly considered. However, these factors really do have a big influence in terms of risk evaluation for down gradient receptors.

In Fig.6 the contaminant concentration (C) and the gradient (i) have been considered as constant. They are $8 \mu\text{g/l}$ and 3×10^{-3} (-) respectively. While the hydraulic conductivity (k) expressed in m/day varies due to the presence of different lithologies.

With such hypothesis, due to the definition of Mass flux itself (equ.1.3), the greatest mass flux and consequently the greatest risk, is related to the greatest hydraulic conductivity (i.e. gravelly sand).

While just looking at the concentrations comparison, the same risk for all the three layers would be assessed.

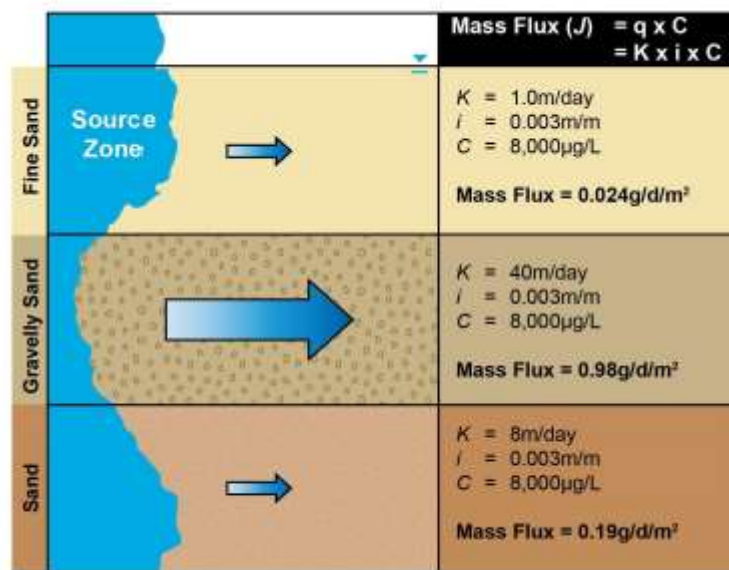


Fig. 6 Effect of hydraulic conductivity on the mass flux. Concentration is not enough for risk assessing [21] originally readapted from [50]

Based on the previous statements, it appears evident the fact that *F-based* approaches can be used in trying to estimate how much pollutant is discharged to and across groundwater. This represents a key element in the Risk management procedure.

Practically, there is the possibility of reducing the impact/ risk to the final receptor by reducing the mass flux.

F-based approach to assess compliance

The Flux based approach may be used to define an upper limit to the mass discharge.

As previously presented, this is what is done in the article Verreydt (2012). For every capture zone (which is the polluted groundwater area caught by a receptor), a maximum allowed contaminant mass discharge or upper limit (M_{d_MAX}) is computed. In the article is given the case of a static receptor (i.e. Irrigation extraction well or drinking water supply) (equ.1.5):

$$M_{d_MAX} \left(\frac{mg}{day} \right) = Risk\ level * Daily\ flux\ which\ reach\ the\ receptor \quad (1.5)$$

The risk level is a concentration (mg/m^3), which is dependent on the receptor type and exposure routes (i.e. drinking water standard).

Similarly in the Australian framework, it is suggested the use of mass flux approaches in order to demonstrate compliance in defined points [20] [21].

For traditional C-based approach risk is present every time there is an exceedance of the standard concentration; while in Australia for a potable well associated with a minimum extraction rate, located downgradient of a contaminated plume, an exceedance of the standard concentration is considered acceptable whenever the source mass discharge is such that the used criteria is not exceeded when the extraction rate is taken into account.

The acceptable mass discharge- or “upper limit”-is based on the following equation (equ.1.6).

$$Mass\ discharge = Concentration\ criterion\ for\ use * Extraction\ rate \quad (1.6)$$

F-based approach to study the evolution of the plume

Flux based methods are useful to show plume structures and evolution over time. Natural attenuation (NA) results in being one of the key elements in order to assess the presence of possible risk and its reduction. NA depends on the pollutant type, on the Aquifer characteristic and on the way the contaminant is released. Moreover, it is not always the same across the whole plume. In the external part biodegradation is more rapid.

In this context, interesting results have been obtained by the European project CORONA³. The aim of the project was to make previsions on Natural Attenuation mechanisms, by estimating the final length of the plume.

In fact using a mass balance it is possible to check whether a plume is contracting or expanding. If the source zone mass discharge is bigger than the attenuation rate then the plume is expanding. If not, then it is contracting. Steady state is reached when contaminant mass flux rate is equal to the mass attenuated by biodegradation. [52] [73].

Furthermore, in daily practice, during the estimation of mass flux approach it is necessary to take into account the presence of heterogeneities. In fact, even if the primary source of contaminant is depleted thanks to remediation or natural attenuation, a secondary source may be present in lower

³ CORONA: Confidence in forecasting of natural attenuation as a risk-based groundwater remediation strategy.

hydraulic conductivity areas and its contribution may be important (this last process is called *back diffusion*).

F-based for improving the Conceptual Model and Remediation

Flux based methods can be also used to improve the conceptual model and the remediation.

In order to enhance the conceptual model, flux based methods could be used to discover if more than a source is present, determine the mobility of the source, and whether the source mass is located in an area with either low or high hydraulic conductivity.

On the other hand, flux based approaches may be used to predict the effectiveness of a remedial method, improving the remedial techniques design, helping in choosing the proper techniques and the time needed to protect and/or restore the beneficial uses of groundwater. In fact, in the remediation context, the Natural attenuation mechanism is important.

In the article Brusseau (2008) the concept of effective source remediation based on mass discharge reduction due to max flux removal is widely described.

Chapter 2

Inventory and comparison of RA approaches

Simplified Risk Assessment procedures for polluted groundwater of Australia, Canada, Italy, United Kingdom and Walloon Region (BE) are investigated. Similarities and differences are highlighted particularly with regard to the European countries.

The choice of these specific countries has been made merely picking English speaking countries, my native country (Italy) and the country in which I am doing the Master Thesis (Belgium-Walloon Region).

2.1 Factors and assumptions made by countries to simplify the RA procedures

As described in chapter 1, risk assessment approaches build Conceptual Models based on the S-P-R approach. In Fig.7 a schematic Conceptual Model is proposed. Some of the main factors involved in the RA procedures are shown in the figure as well.

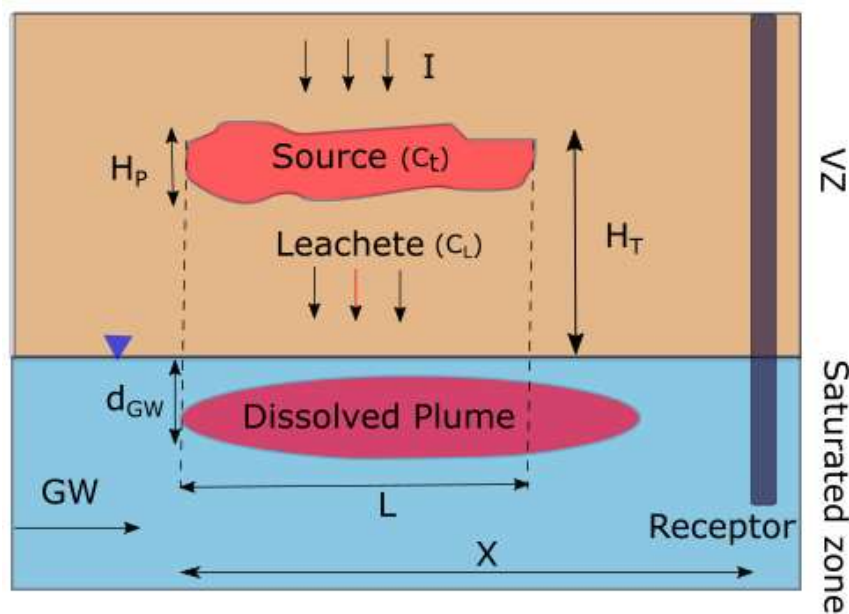


Fig. 7 Typical Conceptual Model used for estimating the movement of the pollutant from the vadose zone (VZ) towards GW and across it (inspired from Connor (1997). Some of the parameters commonly used are shown as well. Image done with Inkscape.

Where I is the infiltration rate [L/T], H_P is the thickness of the polluted VZ [L], H_T is the distance between the top of the pollution and the groundwater table [L], C_t is the total concentration measured in the soil sample [M/M], C_L is the leachate concentration [M/L^3], d_{GW} is the mixing zone thickness [L] and L is the length of the source parallel to the ground water flow [L].

When the source of pollution is in the vadose zone it may represent a risk for the below ground water due to leaching (the vertical movement of the contaminant towards the groundwater table).

Generally, when the contaminant is in the vadose zone, countries compute three main factors:

The *soil-water partition coefficient* (K_{SW} in kg/l). It takes into account the partition of the contaminant between water, air and soil. It is defined as the ratio of the leachate concentration (C_L [M/L³]) divided by the total concentration measured in the soil sample (C_t in [M/M]) (equ.2.1).

$$K_{SW} = \frac{C_L}{C_t} \quad (2.1)$$

The soil/water partition theory is based on the assumption of dealing with an infinite source, having adsorption linear with concentration, having a system in equilibrium with the adsorption and having reversible adsorption [69].

The *mass redistribution factor* (F_V (-)). It considers the possibility of adsorption of leachate by the clean soil below the source. It is the ratio between the thickness of the contaminated vadose zone with respect to the distance of the top of the source to the groundwater table (equ.2.2).

$$F_V = \frac{H_P}{H_T} \quad (2.2)$$

The *dilution factor* (DF (-)). It considers the dilution that the pollutant undergoes when it passes from the unsaturated to the saturated zone.

These factors and equations are widely illustrated for the three European countries showing similarities and differences (*paragraph 2.4.4*). They are used to assess the presence of risk for ground water due to the leaching of the contaminant.

Once the pollutant has entered the ground water, it starts to move through it towards the target(s) with a mainly horizontal movement.

In Fig.8 there is a schematic representation of the way tools generally model the transport of the contaminant in the saturated zone.

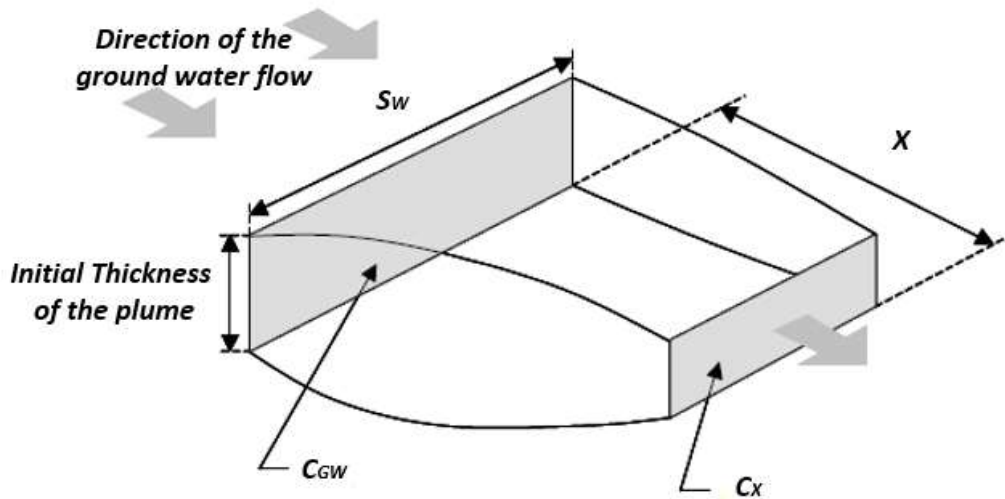


Fig. 8 Schematic representation of how tools simulate transport in the saturated zone [28] (originally from RBCA manual-Groundwater Service, 1998). Where S_w is the width of the source (length perpendicular to the GW flow) [L], C_{GW} and C_x are respectively the concentration at the source in GW and the concentration at the conformity point at a distance X [M/L³], X is the distance between the source and the receptor [L].

The release of contaminant C_{GW} [M/L³] by a perpendicular plane to the groundwater flow (*Width of the source*Initial thickness of the plume*) is represented.

The target is at a distance X [L] from the source in groundwater. The target is still represented by a vertical plane, with a concentration C_X [M/L³]. Generally tools measure C_X along the plume centreline.

The contaminant, across groundwater, undergoes the mechanism of dispersion and attenuation. In order to be conservative in some countries the biodegradation process is neglected (i.e. Walloon procedure).

As for the mechanism of leaching, a factor is computed also for the movement of the contaminant in the saturated zone. The factor is called *dilution/attenuation factor*. Such attenuation factor is defined by countries as DAF or AF. It represents the ratio of the contaminant concentration in groundwater (C_{GW} in [M/L³]) to the concentration in groundwater at the receptor point (C_X in [M/L³]) (equ.2.3).

$$AF = \frac{C_{GW}}{C_X} \quad (2.3)$$

The factor enters in the risk estimation and in the computation of remedial targets.

Definition of types of receptors by countries: On-site and Off-site

While assessing the presence of risk, countries may consider two types of receptor: *On-site* and *Off-site*. By definition, an *On-site* receptor is a receptor inside the contaminated site. If it is outside it is called *Off-site* receptor.

Figure 9 is used to clarify the difference between the two terms. In fact, the choice has an influence on the evaluation of risk and remedial objectives in the different countries.

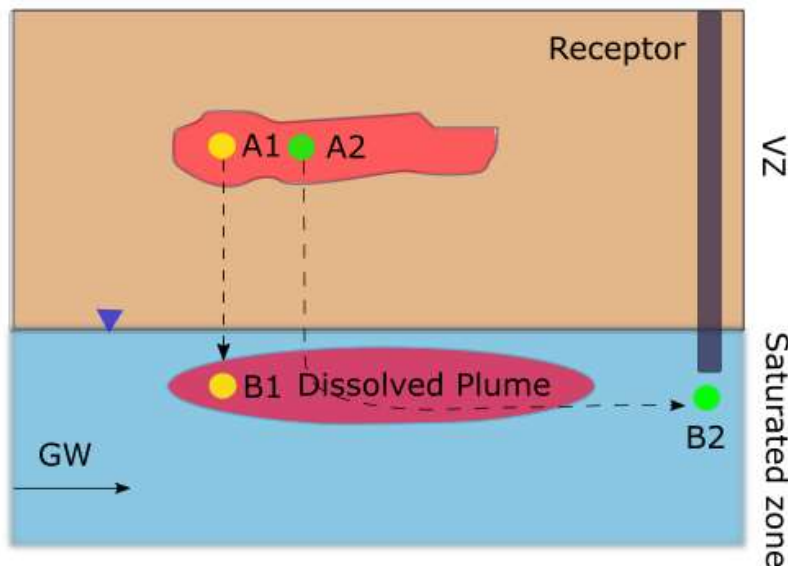


Fig. 9 Simplified model showing an On-site and Off-site receptor. Where A1 and A2 represent the remedial objective in soil [M/M] respectively when an On-site receptor (B1) or an off site receptor (B2) is considered. GW is the groundwater flow while VZ is the vadose zone. Image done with Inkscape

The letter *A* defines the remedial objective in soil [M/M] while the letter *B* defines the location of the *On-site* or *Off-site* receptor.

The remedial target A1 represents the maximal admissible concentration of pollutant in soil [M/M] in order to protect the groundwater beneath the site (location B1).

The remedial target A2 represents the maximal admissible concentration of the pollutant in soil [M/M] in order to respect standards for a receptor at a distance X downgradient of the source of contamination (location B2). In this case it is assumed that attenuation occurs during the transport of pollutant across groundwater (the *dilution/attenuation factor* is computed).

The remedial targets obtained in A1 are more conservative than the remedial targets obtained in A2.

The remedial target for groundwater at location B1 is equal to the groundwater standard, if it is interested in protecting groundwater at that location.

The remedial target for groundwater in B1 can even be the maximal admissible concentration in groundwater, which allows the respect of standards for a receptor at a distance X (location B2). In this case, the attenuation factor is taken into account to *back-calculate* this remedial concentration in B1.

In conclusion while assessing the presence of risk, countries simulate the path of the pollutant from the source zone up to the receptor.

While the pollutant is moving, it undergoes the phenomena of partitioning, dilution, dispersion, transport and attenuation, all these are taken into account by specific factors. This is done both in the evaluation of risk and in the estimation of remedial targets.

As it will be illustrated in the following paragraphs, the choices of the factors may vary between countries but the way risk is assessed is quite similar: measured concentrations are compared with the obtained remedial objectives/standards.

2.2 Countries C-Based Risk assessment procedures

2.2.1 Australia

In Australia, the National Environment Protection (Assessment of Site Contamination) Measure (NEPM) are the national technical guidelines for assessment of contaminated sites, including soil, groundwater and vapour [7] [55][56][57].

Firstly, the procedure assess the presence of contamination on the site thanks to a comparison with measured concentrations and investigation levels associated to specific land use.

If there are enough information, the procedure moves forward with a risk based assessment. This depends on the purpose of the risk assessment (i.e. human health or ecosystem) [8].

Specifically for groundwater, the process is a risk-based one and deals only with contaminations associated to a contaminated site. The aim is to protect groundwater for its “current” and “realistic” future use.

The procedure is a tiered one with the objective of minimizing the risk of adverse human health and ecosystem, which can arise from contaminated ground water from a point source [57].

The method can be divided into two basic steps: preliminary assessments and detailed assessments (Fig.10).

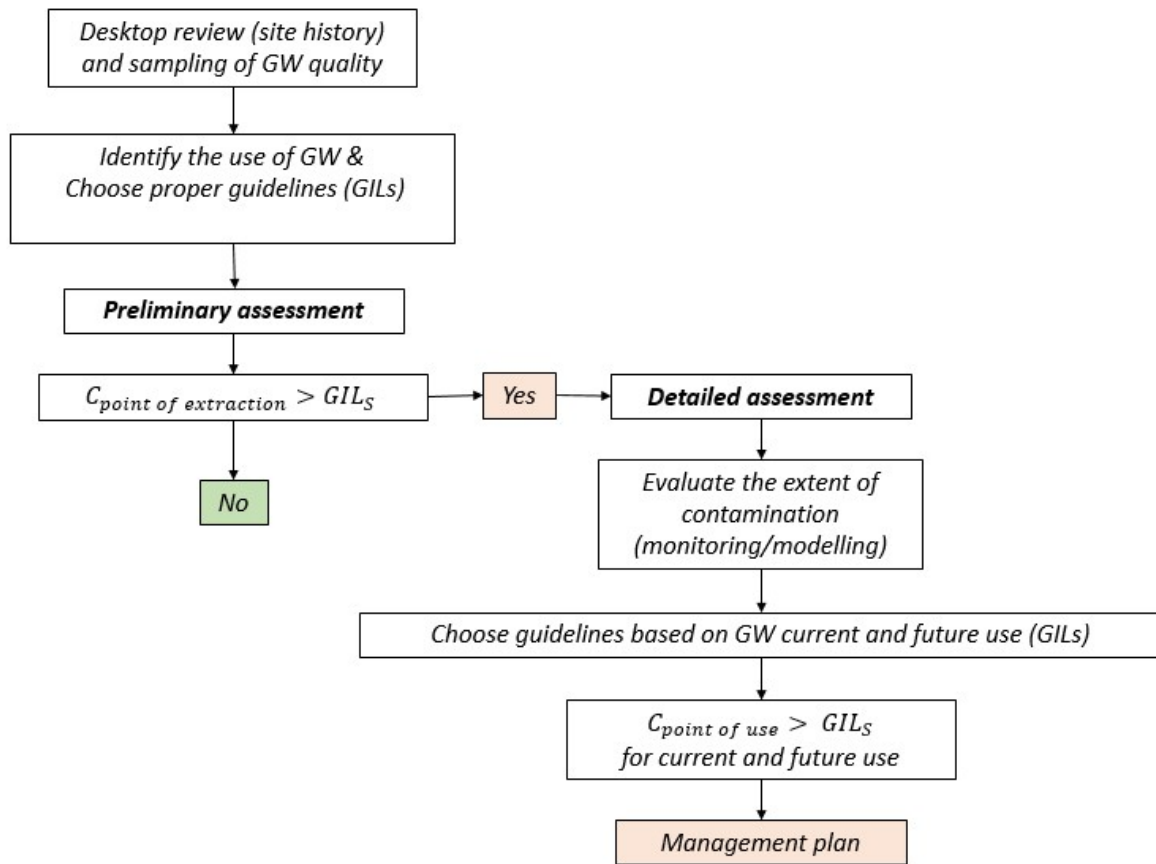


Fig. 10 Schematic Australian procedure for groundwater risk assessment. Where GILs are the groundwater investigation levels.

The assessments consist on a comparison between the *standards* or the *site-specific modified standards* with the measured concentrations. [55].

The standards are called GILs (Groundwater Investigation Levels) [55, 57]. They are defined in the Australian Quality Guidelines in relation to the groundwater use [54] [58][59]. However, each federal state could make its own modification based on the specific context.

The way to proceed differs depending on the location where the comparison is performed. Indeed, in the Australian approach, there is a differentiation between point of extraction and point of use.

The point of extraction is where a monitoring well is located. The point of use is where the groundwater is extracted and/or used (potable well, swimming pool filled by GW, stock watering, irrigation etc.).

If during the preliminary assessment, GIL is exceeded at the point of extraction further investigations and a more detailed assessment has to be performed (i.e. determine the source of contamination and the vertical and lateral extent of the plume). While if it is exceeded at the point of use an appropriate response is required and a management plan is performed.

The aim of cleaning up of polluted groundwater is to restore the protection of “*beneficial uses*” of the groundwater both *on-site* and *off-site*. In Australia, clean up values are ruled by separate guidance from regional Authorities [Australian practitioners C, E].

Notice that, even if generally, Australian *Investigation levels* (GILs) have not to be considered as clean up or response levels since they should be evaluated site-specifically, these standards are often used as trigger levels and are de facto clean-up levels.

Notice that Australia has also developed technical guidelines for the management of groundwater thanks to flux-based approaches [20] [21].

2.2.2. Canada

The Canadian guidelines for assessing contamination are found in Dillon Consulting (1999). In Fig.11 the schematic procedure is shown.

The objective of Soil quality guidelines and Groundwater quality guidelines is to protect both the environment and human health. Due to that, among all the possible guidelines, the assessor takes the lower value, in order to be on the conservative side.

The selection of the proper Canadian guideline is related to the present and future use of the site (land use and groundwater's use purpose).

The soil quality guideline and the way they are obtained can be found in reference [16]. While for groundwater quality guidelines it has to be referred to [47].⁴

However, in the Canadian norms ground water is not protected as a resource in itself, but just in relation to its use (potable groundwater, freshwater life, livestock watering and irrigation watering).

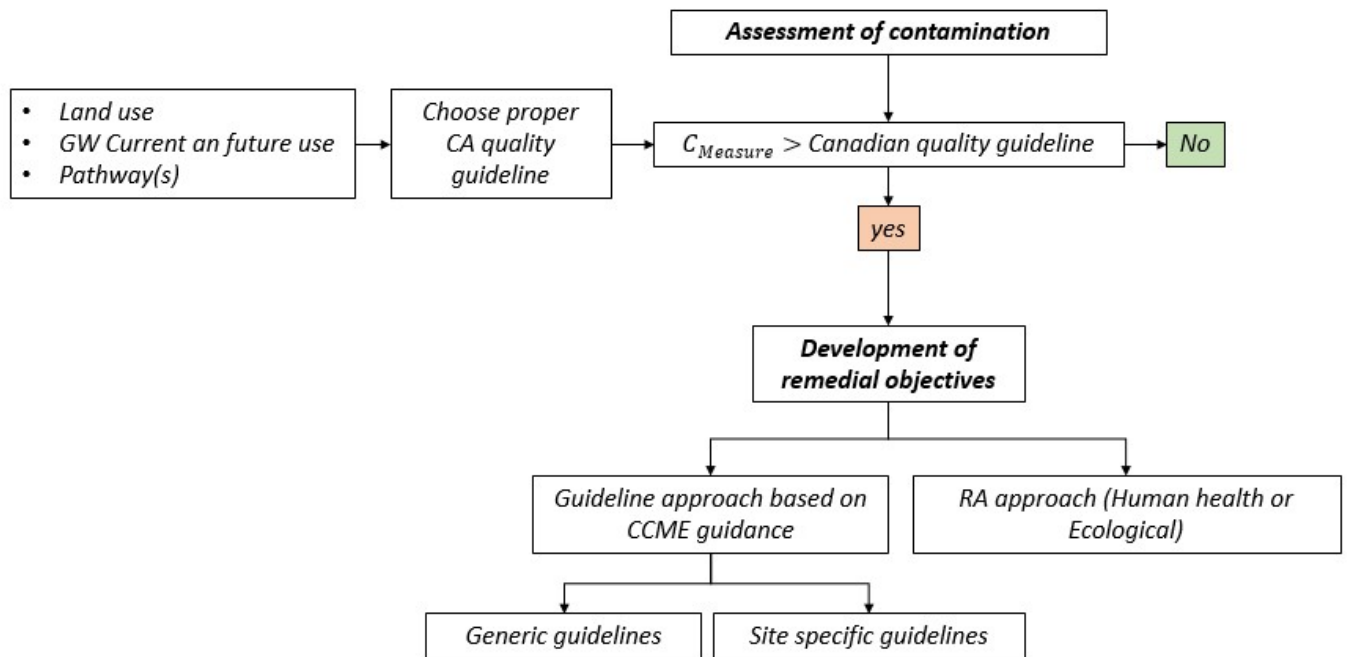


Fig. 11 Schematic representation of the Canadian RA. Where $C_{Measured}$ is the measured concentration [M/M or M/L³], CCME is the Canadian Council of Minister of Environment.

⁴ In Canada as well there is a groundwater protocol [17] but it does not contain any groundwater guidelines, just the instructions on how to derive guideline values. Canadian groundwater quality guidelines have been developed at the moment for more than 100 substances based on the methods described in the groundwater protocol [17]; In the meantime, it is referred to [47]. Notion from [Canadian environmental practitioners A].

In Canada, there are three main options for dealing with contaminated sites. It is possible to remediate up to *generic guidelines values*, to *site-specific modified guidelines* or to remediate until values defined with the risk assessment procedure. Similarly to the Australian case, the common practice is to remediate up to the lowest practicable level considering the intended land use and other factors (i.e. technological limitations).

Concerning the first two options, their values and allowed modifications are defined in reference [15] [18]. These guidelines are both screening values as well as Remediation objectives [Canadian environmental practitioners A].

The Risk assessment is only used in case of specific or really sensitive site conditions [Canadian environmental practitioners A]. Risk assessment is useful for setting site-specific remediation objectives and check the presence of Risk.

However, like in the Australian case, in Canada only the human health and ecological risk assessment is performed. In case both RA are necessary, the lowest site-specific remediation objectives between the two is chosen.

2.2.3. Italy

In Italy, contaminated sites treatment procedures and risk assessment methodology are explained in technical guidelines [1] [2] [64] based on the Italian decree D.Lgs. 152/2006 [30] [31] [32].

First, the presence of pollution in the site is assessed by comparing the measured concentration with the *Investigation standards* (defined as CSC). In case of exceedance, a further step is performed by comparing the measured concentrations with the *Remediation standards* (defined as CSR). Whenever in this step too an exceedance is found, remediation is mandatory. Otherwise, only monitoring will be performed.

Anyway, in daily practice, the Italian Software Risk-net is used [62] [63]. The procedure is schematically illustrated in Fig.12.

The Software allows directly computing the risk for groundwater resource with the so-called “*Forward procedure*”. The risk is evaluated comparing the concentration value of the contaminant in the aquifer at a defined point (conformity point) with the standard value for ground water (CSC_{GW}) defined by norms.

The conformity point is the point along the pathway where it has to be guaranteed the restoration of the initial quality of the ground water body.

In order to be acceptable, the risk has to be lower than 1.

Risk for groundwater depends on the source location (R_{ss} for shallow soil, R_{ds} for deep soil or R_{GW} for ground water) and mechanisms (leaching, “dispersion”). However, since soil risk factors are not cumulative, the most conservative value between the two is considered.

The risk factors are computed as following (equ.2.4):

$$R_{ss} = \frac{CRS * LF_{ss}}{CSC_{GW} * DAF * 10^3 \frac{mg}{\mu g}} \quad \text{a)} \quad R_{ds} = \frac{CRS * LF_{ds}}{CSC_{GW} * DAF * 10^3 \frac{mg}{\mu g}} \quad \text{b)} \quad R_{GW} = \frac{CRS}{CSC_{GW} * DAF * 10^3 \frac{mg}{\mu g}} \quad \text{c)} \quad (2.4)$$

Where CRS is the measured concentration at the source (mg/kg d.s or mg/l), LF is the leachate factor (kg/l), DAF is the dilution/attenuation factor, CSC_{GW} is the italian standard for groundwater ($\mu g/l$).

The risk factor for a polluted soil (shallow or deep) may consider that the receptor is the groundwater beneath the site (*On site receptor- case A1*) and in such a case DAF in equations 2.4 a) and b) is put equal to 1. The receptor may even be a point located at a distance X from the source (*Off site receptor- case A2*) and so attenuation in the saturated zone is considered. Obviously, the factor of risk obtained by considering an *Off-site receptor* is less conservative (higher) compared with the one for an *On-site receptor*.

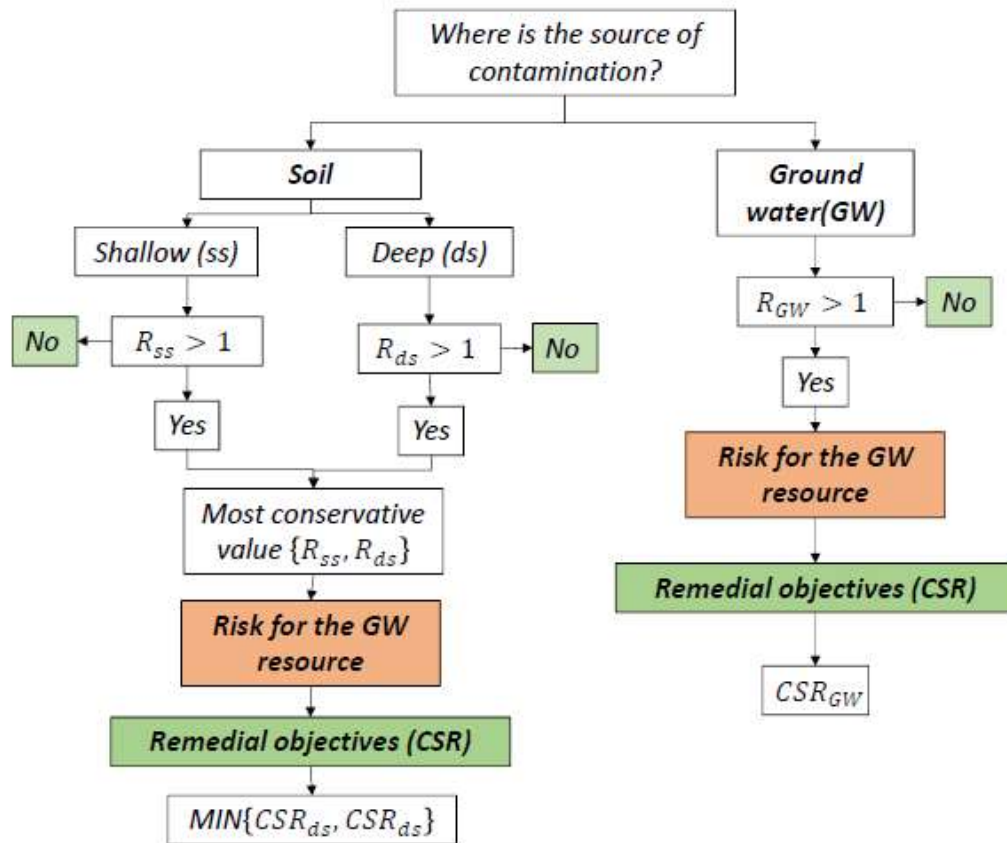


Fig. 12 Italian RA procedure for assessing groundwater pollution. Where R_{ss} , R_{ds} , R_{GW} are the risk factors computed respectively for the source of contamination in the shallow soil, deep soil and groundwater. CSR_{ss} , CSR_{ds} , CSR_{GW} are the remedial objectives computed for shallow soil, deep soil and groundwater.

Moreover, the software allows for finding the clean up values (CSR) both for soil and ground water. By definition, they are the maximal concentrations bringing to an acceptable risk in the final receptor(s). This is done by the “Backward procedure”.

For individual and cumulative migration paths CSRs are evaluated. CSR for groundwater protection are estimated considering different source locations (CSR_{ss} for shallow soil, CSR_{ds} for deep soil and CSR_{GW} for GW) and different migration paths (leaching and direct transport in groundwater). Even in this case the most conservative remedial objective is taken into account. Once again the remedial target for soil, both for deep and shallow soil, can be computed in order to protect the groundwater beneath the site (*On-site receptor- case A1*) or the groundwater at a certain distance X from the source (*Off-site receptor-Case A2*). In the second case, the *dilution/attenuation* factor is considered.

The remedial objectives are computed as following (equations 2.5):

(2.5)

$$\begin{aligned}
 \text{a)} \quad & CSR_{ss} \left[\frac{mg}{kg} - soil \right] = \frac{CSC_{GW} * DAF * 10^3}{LF_{ss}} \\
 \text{b)} \quad & CSR_{ds} \left[\frac{mg}{kg} - soil \right] = \frac{CSC_{GW} * DAF * 10^3}{LF_{ds}} \\
 \text{c)} \quad & CSR_{GW} \left[\frac{mg}{l} \right] = CSC_{GW} * DAF * 10^3
 \end{aligned}$$

Where CSR is the remedial objective (mg/kg d.s or mg/l), LF is the leachate factor (kg/l), DAF is the dilution/attenuation factor and CSC_{gw} is the italian standard for groundwater ($\mu\text{g/l}$).

2.2.4. United Kingdom

The English technical guideline for performing groundwater risk assessment can be found in reference [36]. It is one of the document supporting the English “*Model Procedures for the Management of Land Contamination*” called CLR 11 (Contaminated land research) [35].

Practically, in order to assess risk for groundwater or surface water and to obtain the remedial objectives (RT), the RT-Worksheet tool is used [36] [37].⁵ The procedure is schematically illustrated in Fig. 13.

In the methodology the definition of compliance points and target concentration (C_T), which are used to define the remedial target (RT), are crucial key elements with an impact on the results. Where the *target concentration* is the concentration at the compliance point that should not be exceeded.

⁵ Upon payment, there is also the ConSim software. It is a probabilistic software, which uses Montecarlo techniques; it helps in assessing Risk for groundwater due to leaching. The software considers the movements through the vadose zone, the degradation and the time needed to reach the water table [24].

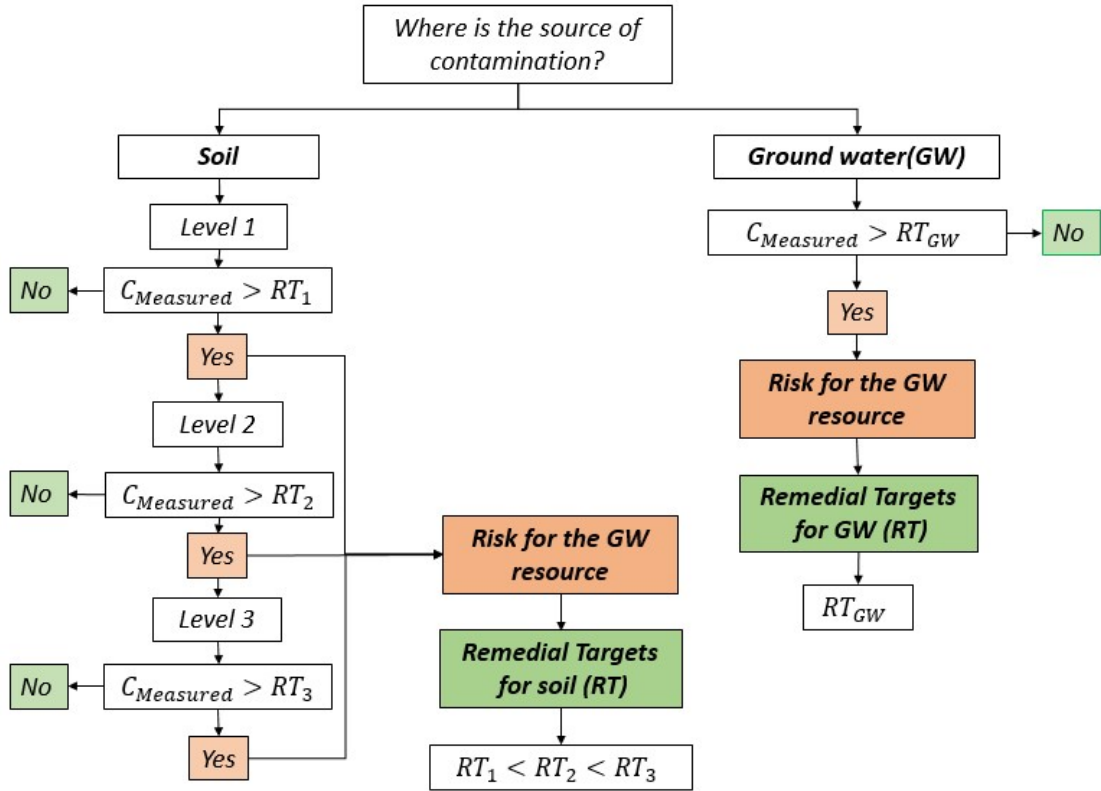


Fig. 13 English RA procedure for assessing groundwater pollution. Where RT_i is the remedial target at the i level of assessment or GW. $C_{Measured}$ is the measured concentration in soil or in groundwater.

The methodology is a tiered procedure, with the level of analysis and detail increasing at each stage.

The English methodology considers that the contamination has already occurred and that the source of contamination has been removed. The source concentration is constant throughout the simulation. As first step, it is necessary to establish where is the contamination, in the soil, in ground water or in both in order to compute proper remedial targets.

If the source of contamination is in the soil, three levels of assessment and three remedial targets can be computed.

The remedial targets for soil at level 1 and 2 consider an *On-site receptor (case A1)*. The remedial target obtained at level 3 considers an *Off-site receptor (case A2)*.

At each level, a factor is added in the computation of remedial targets (RT).

At level 1 only the *soil-water partition coefficient* is considered, at level 2 in addition to this factor *dilution* is also considered and at level 3 also *attenuation* in the saturated zone. This is why level 1 gives the most conservative remedial target.

The soil remedial targets are computed as following (equ.2.6 and 2.7):

<p>(2.6)</p> <p>a) $RT_1 \left[\frac{mg}{kg} - soil \right] = \frac{C_T}{K_{SW}}$</p> <p>b) $RT_2 \left[\frac{mg}{kg} - soil \right] = \frac{C_T * DF}{K_{SW}}$</p> <p>c) $RT_3 \left[\frac{mg}{kg} - soil \right] = \frac{C_T * DF * AF}{K_{SW}}$</p>	<p>(2.7)</p> <p>$RT_1 \left[\frac{mg}{l} - soil \right] = C_T$</p> <p>$RT_2 \left[\frac{mg}{l} - soil \right] = C_T * DF$</p> <p>$RT_3 \left[\frac{mg}{l} - soil \right] = C_T * DF * AF$</p>
--	---

Where C_T is the target concentration (GW standard) [M/L³], DF is the dilution factor (-), AF is the dilution/attenuation factor and K_{SW} is the soil-water partition coefficient.

The remedial targets obtained for a source of contamination in the soil are given in two ways (equations 2.6 and 2.7) in order to allow a comparison with measured concentration in soil [M/M] and/or a comparison with leachate tests and measured pore water concentrations [M/L³] (i.e. RT_3 in mg/l is the admissible leachable concentration).

In the English procedure, the factors of risk are not directly computed. The need for remediation of soils is done by comparing the computed remedial target with the measured soil concentration. In case the concentration on site exceeds the remedial target, it is necessary to decide how to proceed: to remediate or to continue with a more detailed risk assessment.

While considering groundwater, it is assumed that the soil does not represent a problem anymore. The approach consists in comparing the measured concentration in groundwater with the remedial target for contaminated GW.

In groundwater attenuation, dispersion etc. in the saturated zone between the identified source and the receptor is considered.

The remedial target for groundwater is obtained as following (equ.2.8):

$$RT_{GW} \left[\frac{mg}{l} \right] = C_T * AF \quad (2.8)$$

Where C_T is the target concentration (GW standard) [M/L³] and AF is the dilution/attenuation factor.

English experts have been consulted while investigating the RA methodology. [English practitioners A, B, C]

2.2.5 Walloon Region

The technical guidelines to perform risk assessment for polluted groundwater in the Walloon Region come from the guide “*Partie C: Evaluation des risques pour les eaux souterraines*” [28].

The procedure is a tiered one, divided into two main parts related to the leaching and transport of the contaminant in the saturated zone. Each part is composed of sub steps. These allow stopping the procedure whenever there are evidences that no risk is present. They are a way to avoid useless and time-consuming computations.

The procedure is schematically shown in Fig.14.

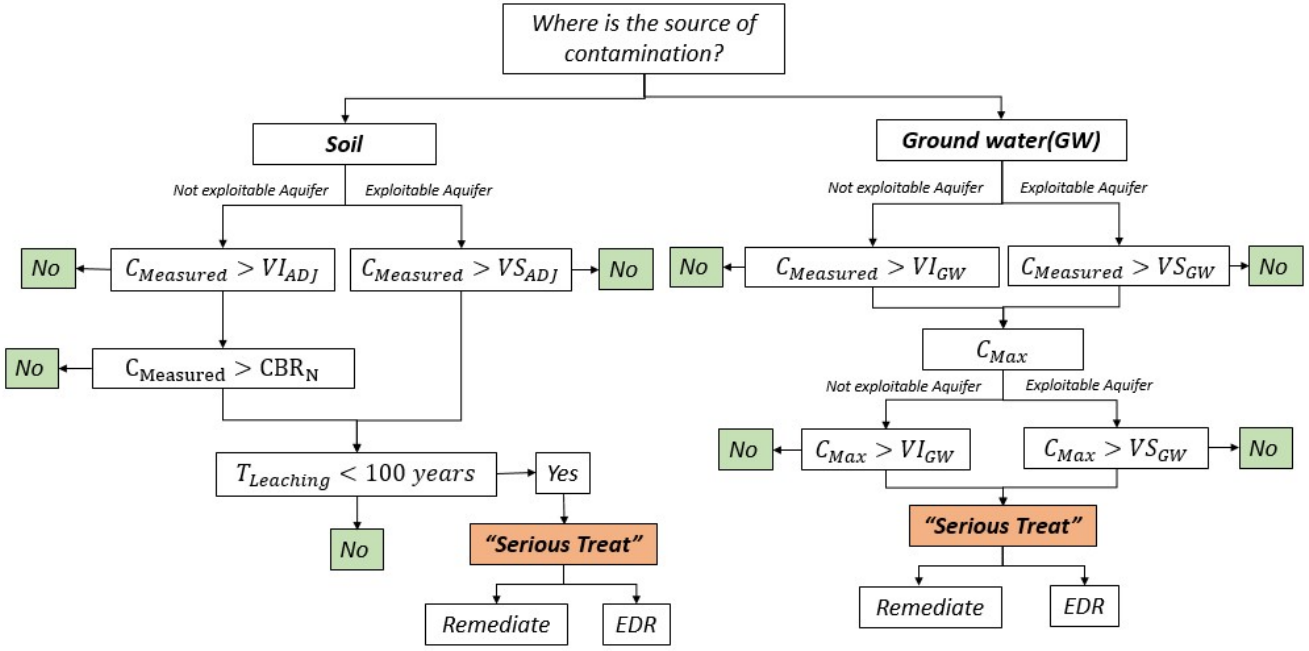


Fig. 14 Walloon RA procedure for assessing groundwater pollution. Where $C_{Measured}$ is the measured concentration in soil or groundwater, VS_{ADJ} and VI_{ADJ} are the adjusted threshold and Intervention value, CBR_N is the maximal concentration at the source to respect VI_{GW} at the receptor, $T_{Leaching}$ is the computed leaching time, VS_{GW} and VI_{GW} are the threshold and intervention groundwater standards and C_{Max} is the maximal concentration at the receptor modelled with BIOSCREEN-AT tool.

In the leaching part, the first assumption is that the point source of pollution is in the soil and it can constitute a threat for the below groundwater. The ESR tool is used [39].

First, the concentration in the soil is compared with an *adjusted limit value*. The adjusted standards vary depending if the aquifer is exploitable or not exploitable. They are the *adjusted threshold value* ($VS_{Adjusted}$) and the *adjusted intervention value* ($VI_{Adjusted}$) respectively. They guarantee the respect of ground water standards VS_{GW} and VI_{GW} .

The adjusted values are computed as following (equations 2.9):

$$VS_{Adjusted} = VS_{GW} * \frac{1}{1000} * \frac{FD_{Adjusted}}{K_{sw\ Adjusted} * F_v\ Adjusted} \quad (2.9\ a))$$

$$VI_{Adjusted} = VI_{GW} * \frac{1}{1000} * \frac{FD_{Adjusted}}{K_{sw\ Adjusted} * F_v\ Adjusted} \quad (2.9\ b))$$

Where $VS_{Adjusted}$ and $VI_{Adjusted}$ are the adjusted threshold and intervention value in soil (mg/kg) respectively, VS_{GW} and VI_{GW} are the threshold and Intervention standards ($\mu\text{g/l}$), FD is the dilution factor (-), K_{SW} is the soil water partition coefficient (kg/l) and F_v is the mass redistribution factor (-) (these three factors are combined together to form the global attenuation factor FAG (l/kg)).

Moreover, for a not exploitable aquifer, in case of exceedance of VI_{Adj} the so defined CBR_N value has to be computed as well and compared again with the measured concentration.

CBR_N is the concentration of pollutant in soil, which allows respecting VI_{GW} at compliance. This factor is computed with BIOSCREEN-AT tool taking into account the attenuation in the saturated zone (a sort of *Off-site receptor-case A2*). It is computed as following (equ.2.10):

$$CBR_N = CBR_{GW (BIOSCREEN)} * \frac{1}{1000} * \frac{FD_{Adjusted}}{K_{sw Adjusted} * F_v Adjusted} \quad (2.10)$$

Where FD is the dilution factor (-), K_{sw} is the soil water partition coefficient (kg/l) and F_v is the mass redistribution factor(-) , CBR_{GW} is the source concentration ($\mu\text{g/l}$) obtained by “*trials and errors*” with BIOSCREEN-AT tool in order to have at compliance a concentration equals to the ground water intervention value ($C_{Max}=VI_{GW}$).

In case $VS_{Adjusted}$ for an exploitable aquifer or the CBR_N value for a not exploitable aquifer is exceeded, the leaching time for reaching the GW table is estimated (equ.2.11) [annex C-5 from 29].

$$t_{Leaching} = \frac{d_{vz} * (\vartheta_w + K_d * \rho_b)}{I} \quad (2.11)$$

Where d_{vz} is the contaminant path in the vadose zone [L], ϑ_w is the volumetric water content, K_d is the adsorption constant [M/L^3], ρ_b is the bulk density [M/L^3] and I is the infiltration rate [L/T].

If the Leaching time is higher than 100 years then no risk is considered as present and the RA procedure stops. On the contrary, in case the leaching time is lower than 100 years it means that the pollutant will enter in ground water in less than 100 years. This represents a “*Serious threat hypothesis*”. This means that the assessor has to decide whether to continue with a detailed risk assessment (EDR) or to remediate the site.

In the second case the remedial objectives for soil are established depending on the pollution age (the benchmark date is 30/04/07) [26].

Notice that the key elements of the procedure for the mechanism of leaching are the *adjusted standards values*. They are adjusted basing on site-specific conditions or default values dependent on the type of aquifer [28] [29].

If the pollutant has already entered groundwater then a different tool and procedure is performed. The polluted groundwater concentration is compared with the standard. The standard is defined based on the aquifer type (VS_{GW} exploitable or VI_{GW} for not exploitable).

If the standard is exceeded the assessor uses BIOSCREEN-AT tool to simulate the maximal concentration that will be reached within 100 years avoiding degradation at the chosen target (i.e. the limit of the parcel or a well).

The simulated maximal concentration (C_{Max}) is compared again with the groundwater standard (i.e. drinking standards in case of a potable well, VS_{GW} or VI_{GW} for the limit of the parcel if it is considered respectively an exploitable aquifer or non-exploitable aquifer).

If the simulated concentration exceeds the standard, the hypothesis of a “*Serious threat*” is considered. Again, the assessor has to decide whether to perform an EDR or to remediate the groundwater.

The remedial target for groundwater depends on the purpose for which groundwater has to be protected (i.e. drinkable standards).

Thanks to a *back-modelling* procedure, the concentration in the soil, which brings to the respect of standards at the chosen receptor- may be determined too (same procedure used for the evaluation of CBR_N).

2.3 Similarities and differences between RA procedures: Extra-European vs European Countries

The major differences between the investigated Extra-European and European countries are shown in Tab.2.

Tab 2 Extra European countries major differences with European countries

<i>Extra European countries major differences with European countries</i>		
<i>Questions</i>	<i>Australia</i>	<i>Canada</i>
<i>Do they assess leaching as EU countries (K_{sw}, FD, F_V)?</i>	Only with ASLP tests	Only when developing soil-quality guidelines
<i>Do they compute Dilution/attenuation factors (DAF)?</i>	May use International DAF or compute site-specifically	Equal to 10 (BC)
<i>Do they have RA-Worksheet tools?</i>	No Only numerical models	No Only numerical models

The first difference that can be addressed between European and Extra-European countries is that Australia and Canada lack a RA procedure for polluted groundwater, considered itself as a resource. Groundwater is considered as a “pathway” that conveys water to the potential receptors (Human or Ecosystem). Looking at the Australian and Canadian guidelines [18] [47] [54] [58] [59] it is possible to notice that groundwater values are defined basing on their use: recreational, agricultural/irrigation, potable, livestock etc. Groundwater is protected in relation to the chosen final receptors. These, in fact, could eventually enter in contact with it.

Factors for modelling the pollutant movement in the vadose and saturated zone

What is most surprising is the lack of proper equations considering attenuation and dilution mechanisms both in the unsaturated and saturated zone.

For example, in Australia, it is pointed out that dilution and attenuation may occur [56] but specific guidelines, as in the European countries defining the factors that have to be computed and the modality are not given [Australian experts E, D, H].

One of the Australian practitioners consulted [Australian expert D] has said that they can also use international *dilution/attenuation* factors, if properly justified. Moreover, those factors can be computed based on site-specific cases and considerations- aquifer properties, vapour intrusion, distance to the extraction point, presence of mixing zones - which are not accepted by all jurisdiction [Australian expert D].

Even in Canada, there are no defined equations. For example, one of the consulted experts of British Columbia (BC) [Canadian environmental practitioner B] said that they apply a “*ten-fold dilution*” to the pollutant that entered groundwater. This means that instead of computing a *dilution/attenuation factor* -as European countries do- they assume that it is always equal to 10, independently from the site-specific characteristics. However, the practitioner admitted that this assumption has not a strong technical basis.

With regard to the Leaching mechanism, in Australia the pollutants leachability is assessed just by the ASLP testing⁶. To model leaching, it is possible to use any model if the assumption can be justified [Australian expert A].

In Canada, the leachability of pollutant is taken into account when *soil quality guidelines* are developed. An example on the way to assess it is given by British Columbia [10].

Notice that, at least for the Canadian case, while they have developed the *Quality guidelines*, they have taken into account some factors, which are the same as the European countries [16].

The *soil-water partition coefficient*, as well as the *dilution factor* at the interface between the unsaturated and saturated zone are computed in the same way. In terms of transport model, like in European countries, the most popular is Domenico model.

Extra-European tools for modelling the transport of pollutant

Finally, contrary to European countries, these countries do not have tools (i.e. Worksheet) for risk assessing.

For example, different Australian environmental practitioners [Australian expert B, D, E] have pointed out the fact that it is impossible to use such kind of tools, since Australia is wide and with widely different characteristics.

However, in both Canada and Australia in order to model groundwater transport, they use tools from North America (i.e. BIOSCREEN, BIOCHLOR, MODFLOW, Feflow).

2.4 Similarities and differences between RA procedures among European countries

2.4.1 European Risk assessment for polluted groundwater

Differently from Australia and Canada, European countries have well defined procedures in order to assess groundwater pollution. Groundwater is seen as a resource, which has to be protected. The groundwater quality is in compliance with the European directives (i.e. Water framework directive).

European countries develop a *Conceptual Model* based on the *Source(s)*, *Pathway(s)*, *Receptor(s)*'s procedure. Firstly considering leaching in soil and secondly considering the transport of contaminant in the aquifer to the selected receptor, for assessing migration of pollutant from soil to groundwater.

2.4.2 Definition of compliance/conformity points

The Investigated European countries procedures are all *C-based* approaches; those have defined points along the contaminated pathway where quality standard of groundwater has to be respected. The choice of proper points' location is defined in the norms depending on the receptor type.

⁶ **Australian Standard Leaching Protocol (ASLP).** ASLP tests are used to assess the leaching potential of wastes (even mine waste), sediments and contaminated soils.

These points are defined as *conformity points* in the Walloon and Italian procedures and as *compliance points* in the English procedure.

Normally, they are located between the source and the receptor. For example, if the final receptor is a well, the conformity point is the well itself. If it is the aquifer, it is a piezometer downgradient of the source.

In the English procedure, the compliance point depends on the level of the assessment [1] [30] [36] [28].

2.4.3 Standard values for European countries

Standards might be used to characterize the site and assess the presence of risk and the need of remediation. Both in soil and in groundwater.

In order to guarantee a better understanding of standards in the investigated European countries, their definitions are given in the following paragraphs and summarized in table.3.

For the Walloon procedure there are three values which can be found in references [26] [28].

The *Reference value* (VR) is the pollutant background concentration expected in the soil in the absence of any natural geological variation and without the influence of any generalized agricultural, industrial or urban activity.

The *Threshold value* (VS) is the concentration in the soil, corresponding to a level above which a characterization study is mandatory.

The *Intervention value* (VI) is the soil concentration above which an intervention has to be undertaken in the form of a remediation action, security measures and monitoring.

The Reference, Threshold and Intervention values are defined for groundwater as well.

For the Italian procedure, there are two values [1] [30] [62].

The *Contamination investigation/screening concentration value* (CSC) is the level of contamination that if exceeded, makes it necessary to proceed further with a site investigation and a site-specific risk assessment.

CSC standards can be found in annex V of Dlgs 152/2006 [30] [31]. However, from a practical point of view in the *Risk-net tool*, their definition comes from the database settled by the ISS (Istituto Superior della Sanità) [49] [62].

The *Threshold risk's concentration* (CSR) is the maximum admissible concentration at the source compatible with a tolerable level of risk at the groundwater hydric resource. It is the remediation target obtained with the “backward procedure”.

For the English procedure, there are two values [36].

The *Target concentration* (C_T) is the concentration at the compliance point that should not be exceeded. When the target concentration is met, the relevant environmental standard for the receptor(s) should also be met.

The *Remedial target* (RT) is the derived soil or groundwater concentration above which remediation is required. It can be equal to the target concentration or to the target concentration multiplied by a dilution and/or attenuation factor (depending on the level of assessment).

In simple words, it is the “concentration of the source that produces the target concentration (C_T) at the receptor” [19].

Investigation and Intervention values for European countries

Firstly, standards may be used for characterizing the site and the presence of contamination.

Such kind of value is not explicitly defined in the English procedure. However, it is known that the basic statement of the *Remedial Target Methodology: Hydrological Risk assessment* [36] is that “contamination has already occurred”. Due to this fact, probably the site is considered surely polluted and so it is meaningless to check the pollution presence with an investigation value.

For groundwater, the correspondent investigation level is the chosen target concentration.

The computed remedial targets (for both soil and groundwater) are *the intervention values*, which have to be compared with the measured concentration.

In the Italian procedure the investigation value is CSC and the Intervention value is CSR for both soil and groundwater.

In the Walloon procedure, the correspondent investigation value for soil is the threshold value (VS). While the *adjusted threshold and Intervention* (VS_{Adj} and VI_{Adj}) values in soil are used as a sort of “*intervention values*” to assess the presence of risk for below groundwater. However, additional steps have to be checked (i.e. Leaching time).

In case the pollutant is in ground water the *investigation and intervention values* are the pollutant groundwater standard and it depends on the aquifer type (VS_{GW} for an exploitable aquifer and VI_{GW} for a not exploitable aquifer). These last values are compared with measured and simulated concentrations for *screening* and *intervention* values respectively.

Remedial objectives of European countries

Remediation values differ in soil and in ground water.

Remediation values for soil can be computed or defined by norms.

In the Italian and English procedures, the clean up objectives are obtained directly with the tools. They are on one side the *Intervention value* above which it is mandatory to intervene and on the other side the *Remediation value* that has to be restored with the cleaning.

The Italian *remediation* value is CSR. In the English procedure, the remedial targets (RT) are computed for each level of the tiered approach for both soil and groundwater.

In the Walloon procedure, the clean up value for soil is defined by norms, based on the land use type and pollution age. The date of 30/04/07 is the benchmark between new and old contaminations. When dealing with a *new pollution type*, the remediation has to be completed up to the reference value (VR) or to the closest value reachable with the BATNEEC (*Best available techniques not entailing excessive costs*) [art.47 &50 from [26]].

While in case of *old pollution*, there are two possibilities. If the RA has established that no risk is present, the pollutant is left on the site as such.

If the RA has shown the hypothesis of “*Serious treat*”, the site has to be remediate up to VR or to the closest value reachable with the BATNEEC with, at least, the removal of the “*serious treat*”.

The removal of the treat is achieved upon reaching the “*minimum cleaning value*” established with the RA procedure [art.48 & 51 from [26]].

The Walloon remedial targets for polluted groundwater are defined based on the use of the groundwater (i.e. drinkable water etc.).

Tab 3 Standard values definitions in the European countries [1] [26] [28] [30] [36] [62]

European standard values						
Country	Investigation Level		Intervention value		Remedial objective	
	Soil	GW	Soil	GW	Soil	GW
Walloon Region	VS	VS _{GW} or VI _{GW}	VS _{Adj} or VI _{Adj} *	VS _{GW} or VI _{GW}	<i>f</i> (pollution age- 30/04/07)	<i>f</i> (aquifer and standard)
Italy	CSC _{SOIL}	CSC _{GW}	CSR _{SOIL}	CSR _{GW}	CSR _{SOIL}	CSR _{GW}
United Kingdom	Not explicit	C _T	RT _{SOIL}	RT _{GW} or C _T	RT _{SOIL}	RT _{GW}
*In the Walloon procedure for assessing risk due to leaching not only <i>adjusted values</i> are computed and compared with measured concentrations, but also the leaching time is evaluated.						
Where CSC is the Italian investigation value [M/M or M/L ³], CSR is the Italian intervention value and remedial objective [M/M or M/L ³], C _T is the English target concentration [M/L ³], RT is the English remedial target [M/M or M/L ³], VS is the Walloon threshold value [M/M], VS _{Adj} and VI _{Adj} are the Walloon adjusted threshold and Intervention value [M/M], and VS _{GW} and VI _{GW} are the Walloon adjusted threshold and Intervention value for groundwater [M/L ³]						

2.4.4 Factors computed by the European countries to model the leaching of pollutants and their migration across the saturated zone

Factors used to assess the mechanism of Leaching

At the beginning of the chapter a typical conceptual model with relative parameters was given. Here the same figure is proposed (Fig.15). Now discussion delves deeper into the description and the equations of factors used by the European countries for modelling all mechanisms that the pollutant undergoes from the vadose to the saturated zone.

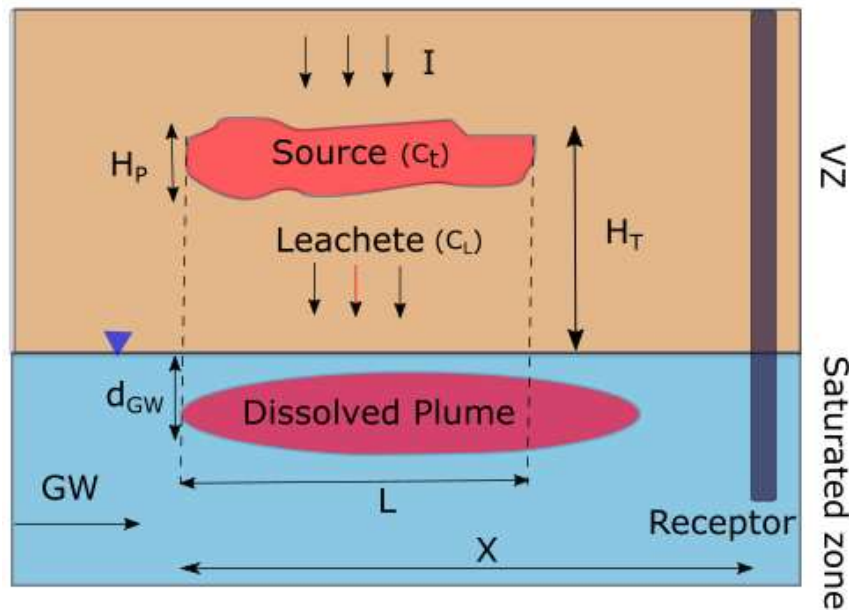


Fig. 15 Typical Conceptual Model used for estimating the movement of the pollutant from the vadose zone towards GW (inspired from Connor (1997)). Some of the parameters commonly used are shown as well. Image done with Inkscape. Where I is the infiltration rate [L/T] generally in cm/year, H_P is the thickness of the polluted VZ [L] generally in m, H_T is the distance between the top of the pollution and the groundwater table [L] generally in m, C_T is the total concentration of the source [M/M] generally in mg/kg d.s, C_L is the leachate concentration [M/L^3] generally expressed in mg/l, d_{GW} is the mixing zone thickness [L] generally expressed in m and L is the length of the source parallel to the ground water flow [L] generally expressed in m.

The investigated European RA procedures compute more or less the same factors. However, differences can still be found on the adjustments that the user may apply basing on site-specific conditions.

Considering firstly the pollutant in the vadose zone and the mechanism of leaching, three main factors are computed: the soil-water partition coefficient, the dilution factor and the mass redistribution factor.

The reader is invited to look at figure 15 for a better understanding of the factors and to follow the explanations.

1. Partition coefficient soil-water

The *partition coefficient* is defined as the ratio of the leachate concentration (C_L) and the total concentration measured in soil sample (C_i). It is computed with equation.2.1.

As shown in Tab. 4, the partition coefficient is computed exactly in the same way in all the investigated European countries. Kd is computed differently for organic or inorganic contaminants.

Tab 4 Partition Coefficient factor between European countries [1] [62] [36] [annex C-2 from [29]]

<i>Partition coefficient soil water [M/L³]</i>		
Walloon Region	Italy	United kingdom
K _{sw}	K _{ws}	Not a specific symbol
$\text{Soil – water partition coefficient} = \frac{C_L}{C_t} = \frac{1}{K_d \frac{\theta_w + \theta_g \cdot K_H}{\rho_b}} \quad (2.1)$ <p>Where: C_t: total concentration in the source* C_L: leachate concentration K_d: adsorption constant [L³/M] θ_w: Volumetric water content [-] θ_g: Volumetric air content [-] K_H: dimensionless Henry's constant [-] ρ_b: soil bulk density [M/L³]</p> <p>Observation: *C_t the total concentration in the source has not to be confused with the English target concentration C_T</p>		

However, the main difference is in the user's possibility of modifying the parameters entering in the computation of the *soil-water partition coefficient*.

In fact, the Walloon procedure, no matter whether dealing with organic or inorganic pollutant, requires correcting K_d (l/kg). This is done depending on few soil properties: % *stoniness*, *fraction of the site available for absorption*, *soil water content* and *soil bulk density*.

Moreover, if the contaminant is inorganic (i.e. heavy metals), the *partition coefficient* depends also on additional parameters: *the cationic exchange capacity (meq/100g)*, *soil pH (-)*, *clay content (%)*, *iron content which can be extracted for NH₄ oxalate (mmol/kg)*, *organic matter content (%)* and *electric conductivity of poral water (μS/m)*. The hypothesis and the way to make corrections are defined in reference [annex C-1 & C-3.1 from [29]] [39]

Notice that the Walloon ESR tool has its own specific database with some implemented values (i.e. K_{OC}).

In Italy K_d differs depending on the pollutant type (organic or inorganic chemicals). However, in practice, when using the internal software database, the user is requested to enter only the fraction of organic carbon (f_{OC}). The other data are already implemented in the dataset (i.e. K_{OC}) [1] [62].

Practically speaking notice that the databases implemented in the Italian Risk-net tool and the Walloon ESR tool are different (i.e. different organic carbon partition coefficient, different dimensionless Henry constant).

In the English procedure, K_d differs depending on the contaminant type (organic or inorganic).

The user can decide whether to enter directly the K_d 's value or to choose a modality for computing it. The computation way depends on the pollutant type. As for the Walloon case, if it is an inorganic pollutant, more data are necessary (pH (-), *sorption coefficient for ionized and neutral species* (l/kg), *acid dissociation constants* (L/kg)). [36][37][48].

2. Dilution factor

The *dilution factor* is the ratio between groundwater flow below the site (the source area) and the infiltration through the contaminated soil.

Such factor takes into account the dilution that the contaminant undergoes once it has reached the groundwater table, at the interface between unsaturated and saturated soil.

As it can be noticed in Tab. 5 the factor is computed in the same way in all European countries

However, the Walloon dilution factor must be adjusted. Two ways are available.

The first type of adjustment is based on the aquifer type. For each aquifer type, the Walloon norm has defined a specific dilution factor. The second one consists in adjusting each parameter in the equation 2.12 a) based on measurements [annex C-2 from [29]].

Notice that, if no adjustment is made the default Walloon dilution factor (FD) is equal to 30 and the lower bound is fixed to 12.

The Italian and English tools do not have default values for such factor. [1][62][36].

Tab 5 Dilution factor between European countries [1] [62] [36] [annex C-2 from [29]]

<i>Dilution factor [-]</i>		
Walloon Region	Italy	United kingdom
FD	LDF	DF*
$\text{Dilution factor} = 1 + \frac{d_{GW} * k * i}{L * I} \quad (2.12 \text{ a))}$ <p>Where:</p> <p>d_{GW} : thickness of the mixing zone [L] k: hydraulic conductivity [L / T] i: hydraulic gradient [-] L: Length of contaminated zone parallel to underground flow [L] I: Annual effective infiltration [L/ T]</p>		
<p>* The English procedure gives also the opportunity of considering the background concentration of the pollutant if present (C_u). (equation</p> $\text{Dilution factor} = \frac{(d_{GW} * k * i + L * i * C_T) - (d_{GW} * k * i * C_u)}{L * I * C_T} \quad (2.7 \text{ b))}$		

3. Mass redistribution factor (F_v) and the SAM (soil attenuation model)

The mass redistribution factor can be found only in the Walloon and Italian procedures (Tab.6) [1] [62] [annex C-2 from [29]].

The factor takes into account the contaminant mass redistribution during the leaching path from soil to groundwater. It is somehow an average of contaminant concentration on the vertical profile of the vadose zone.

The parameter is obtained as the ratio between the thickness of the contaminated source in the vadose zone (H_P) and the total thickness from the top of the contamination to the groundwater table (H_T) (equ.2.2). The worst condition occurs when the factor is equal to 1 ($H_P = H_T$).

Due to the defect of this factor, the English procedure is likely to take into account the worst condition. Notice that this lack has an influence on the choices of the conceptual model too, in fact for the English case a pollution located just on the upper part of the soil cannot be modelled.

As for the previous factors, also in this case, the Walloon procedure offers advice for the correction [annex C-2 from [29]]. The Walloon default mass redistribution factor is equal to 1.

Finally, it is necessary to highlight the fact that the Italian mass redistribution factor defined as SAM (Soil attenuation Model) is an optional parameter. The user can decide whether to consider it or not. There is not a default value.

Moreover, two mass redistribution factors can be computed, one for the deep soil and one for the shallow soil (0-1 m b. g. l.).

Tab 6 Mass redistribution factor between European countries [1] [62] [annex C-2 from [29]]

Mass redistribution factor [-]	
Walloon Region	Italy
F_v [-]	SAM [-]
$F_v = \frac{H_P}{H_T} \quad (2.2)$	$SAM = \frac{d}{(L_{GW} - L_S)} \quad (2.2 \text{ b}))$
<p><i>Where:</i> H_P is the thickness of the source in the vadose zone [L] H_T is the total thickness of vadose under contamination (from top of contamination to GW) [L]</p>	<p><i>Where:</i> d is the thickness of the source in the vadose zone [L] L_{GW} is the GW depth b.g.l. [L] L_S is the top source's depth b.g.l. [L] <i>Notice that: $d = H_P$ and $L_S - L_{GW} = H_T$</i></p>

4. “Combined factor” for the Walloon and Italian procedure

In both Walloon and Italian procedures, a “combined factor” that groups the three previously mentioned factors is given (Tab. 7).

The Italian “combined factor” is called *Leachate factor* (LF).

This transport factor allows to estimate the attenuation that the contaminant undergoes while transported from the source, located in the soil, to the groundwater table. The attenuation derives from the infiltration in the unsaturated part (VZ) and from the subsequent dilution in the superficial aquifer [1].

The LF is the ratio between the concentration that will be found in the groundwater below the source (C_{GW}) and the total source concentration in the soil (C_t) (Fig.16).

The Walloon “*combined factor*” is called *Global attenuation factor* (FAG). This factor, like in the Italian case, takes into account all the “attenuation mechanisms” that the pollutant undergoes to the ground water [annex C-1 from [29]].

The FAG is the ratio between the source concentration (C_t) and the concentration in the below groundwater below (C_{GW}) (Fig.16).

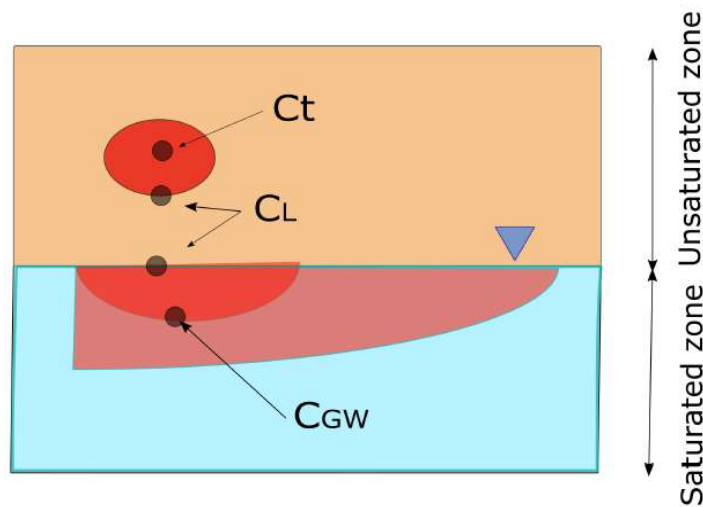


Fig. 16 Conceptual model inspired by the Italian technical guideline [1]. Where C_t is the total source concentration (mg/kg), C_L is the leachate concentration (mg/l) and C_{GW} is the concentration in groundwater below the source (mg/l). Image done with Inkscape.

From the given definitions and equations (tab.7) appears quite evident how the two “*combined factors*” are numerically one the opposite of the other.

However, they are used in the same way. In fact, the FAG enters in the computation of the *adjusted values* (eq. 2.9) as well as the LF enters in the computation of the *soil remedial objectives* (equ.2.5 a) and b)).

As shown in the Walloon and Italian procedures, these are the values, which are compared with the soil measured concentrations while assessing the presence of risk due to leaching.

Just for reminding:

$$VS_{Adjusted} = VS_{GW} * FAG \quad (2.9 \text{ a)})$$

$$CSR = CSC_{GW} * \frac{1}{LF} \quad (2.5 \text{ a) and b)})$$

Notice that the English *soil remedial target* computed at level 2 of the tiered procedure is computed similarly to these two values. The only difference is that the *mass redistribution factor* is not present.

Tab 7 “Combined factor” *f* (dilution factor, mass redistribution factor and soil-water partition coefficient) for the Italian and Walloon leaching mechanism [1] [62] [annex C-1 from [29]].

“Combined factor”		
Walloon Region	Italy	
FAG (l/kg)	LF (kg/l)	
(2.13 a))	(2.13 b))	(2.13 c))
$FAG = \frac{C_t}{C_{GW}} =$ $= \frac{FD}{K_{sw} * F_v}$ $FAG = \frac{A}{B * C}$	$LF = \frac{C_{GW}}{C_t} =$ $= \frac{K_{sw} * SAM}{LDF}$ $LF = \frac{B * C}{A}$	$LF = \frac{d * \rho_b}{I * \tau(LF)} *$
<p><i>Where</i></p> <p><i>A</i>= <i>FD</i> is the dilution factor</p> <p><i>B</i>= <i>F_v</i> is the mass redistribution factor</p> <p><i>C</i>= <i>K_{sw}</i> is the partition coefficient soil water</p>	<p><i>Where</i></p> <p><i>A</i>= <i>LDF</i> is the dilution factor</p> <p><i>B</i>= <i>SAM</i> is the soil attenuation model</p> <p><i>C</i>= <i>K_{sw}</i> is the partition coefficient soil water</p> <p><i>d</i> is the thickness of the source in the vadose zone [L]</p> <p><i>ρ_b</i> is the soil bulk density [M/L³]</p> <p><i>I</i> is the effective infiltration [L/T]</p> <p><i>τ(LF)</i> is the average leaching time [T]</p> <p><i>*Notice that this second way of computing LF is optional.</i></p> <p><i>In case both modalities for computing LF are used, the tool chooses the minimum.</i></p>	

Factors and equations to assess the migration of pollutant across ground water

1. Solute transport equation

The most used solution in order to model the transport of pollutant in the aquifer and its attenuation across groundwater along the principal flow direction is Domenico (1987). Advection, Dispersion, Adsorption and aerobic/anaerobic decay may be considered.

Normally tools predict concentration at the chosen receptor and they compute remedial targets along the centreline plume.

However, some differences among the investigated countries may be noticed (Tab.8).

Tab 8 Solutions of the transport model in the saturated zone for IT, UK and WR. [1][19][62][36][37][51]

<i>Solution for the solute transport model</i>	
Tool	Transport model
Italian Risk-net tool	Domenico (1987) (steady state) (tool for the assessor for transient state)
English RT- Worksheet	Domenico (1987) (steady and transient) Ogata banks 1961 (steady and transient)
Walloon Region BIOSCREEN-AT	Modified Domenico (transient)

In the Italian Risk-net tool, transport is modelled using Domenico (1987) approximate solution in steady state. [19]. Risk factors and remedial objectives are obtained with a steady state simulation. Risk-net tool has also the possibility to show the evolution of concentration in time but this does not enter in risk computation. It is just a tool, which may or may be not be used by the assessor.

In the English RT-Worksheet tool, transport is modelled using Ogata Banks (1961), Domenico (1987) approximate solution in transient and steady state [36] [37]. However, even if the transient state simulation can be used, English norms require that remedial targets to be computed in steady state. Finally, the RT-Worksheet tool gives the possibility to model not only centreline plumes but this choice as well does not enter in the remedial target evaluation.

In the Walloon Region to model transport, BIOSCREEN-AT uses the modified Domenico model with an exact solution in transient state [51]. The norm imposes a simulation time of 100 years without considering biodegradation.

Notice that biodegradation may be considered in the Italian and English procedures. The RT procedure suggests using Ogata Banks (1961) for first order biodegradation in a homogenous aquifer.

2. Dilution/Attenuation factor across groundwater

All the investigated European countries compute a *dilution/attenuation* factor.

The attenuation factor is the ratio between the concentration in groundwater at the source (C_{GW}) and the concentration of pollutant in the conformity point place at distance X (C_x) (Fig.8 paragraph 2.1).[62] [36] [annex C-1 from [29]].

Obviously depending on the analytical solute transport type, the computed *dilution/attenuation* factor differs. This factor is called DAF, AF and Fas in the Italian, English and Walloon procedures respectively.

In Table 9, the equations for computing the attenuation factors are shown. Notice that they refer to a steady state simulation using Domenico (1987).

Tab 9 Dilution/Attenuation factor for IT and UK (Steady state simulation) [62] [36]

Dilution/attenuation factor (shown for the IT and UK steady state case)	
Attenuation factor	Equation
(2.14 a)) $\frac{1}{DAF1} = \frac{1}{AF_{UK\ 2\ dir}}$	$= \exp\left[\frac{x}{2 * ax} * \left(1 - \sqrt{1 + \frac{4 * \lambda * ax * R}{ve}}\right)\right] * \left[\operatorname{erf}\left(\frac{Sw}{4 * \sqrt{ay * x}}\right)\right] * \left[\operatorname{erf}\left(\frac{d_{GW}}{4 * \sqrt{az * x}}\right)\right]$
(2.14 b)) $\frac{1}{DAF2} = \frac{1}{AF_{UK\ 1\ dir}}$	$= \exp\left[\frac{x}{2 * ax} * \left(1 - \sqrt{1 + \frac{4 * \lambda * ax * R}{ve}}\right)\right] * \left[\operatorname{erf}\left(\frac{Sw}{4 * \sqrt{ay * x}}\right)\right] * \left[\operatorname{erf}\left(\frac{d_{GW}}{2 * \sqrt{az * x}}\right)\right]$
$\frac{1}{DAF3}$ (2.14 c))	$\exp\left[\frac{x}{2 * ax} * \left(1 - \sqrt{1 + \frac{4 * \lambda * ax * R}{ve}}\right)\right] * \left[\operatorname{erf}\left(\frac{Sw}{4 * \sqrt{ay * x}}\right)\right]$
<p>Where:</p> <p>x is the distance from the source to the compliance point [L], ve is the effective velocity [L/T], a_x is the longitudinal dispersivity [L], a_y is the transversal/lateral dispersivity [L], a_z is the vertical dispersivity [L], λ is the biodegradation constant of first order [1/T], R is the retardation factor [-], Exp is the exponential, Erf is the error, Sw is the length of the source parallel to the flow [L] and d_{GW} is the mixing zone thickness[L].</p> <p>Note that in the Italian procedure the mixing zone thickness is always used as initial plume thickness while for the English procedure the manual puts, instead of the mixing zone thickness (d_{GW}), the “thickness of the plume” (which can be however equal to the mixing zone thickness).</p>	

In the Italian procedure there are three types of attenuation factors (DAF1, DAF2 and DAF3) while in the English procedure there are only two ($AF_{UK\ 2\ dir}$ and $AF_{UK\ 1\ dir}$)

- *DAF 1* is equal to $AF_{UK\ 2\ dir}$. This factor is computed when the vertical dispersion is allowed in two directions (up and down). This is the type of attenuation factor that should be chosen, when the source is in the middle of the aquifer’s profile.
- *DAF 2* is equal to $AF_{UK\ 1\ dir}$. This factor is computed when the source of pollution is located at the top of the aquifer and vertical dispersion is considered only in one direction (downwards). This is the type of attenuation that has to be chosen, when the contaminant is entering in groundwater. Commonly this occurs for percolation.
- *DAF 3* considers that only a transversal and longitudinal dispersion occurs. The Italian Risk-net tool considers automatically *DAF3*, every time the mixing zone thickness is equal to the aquifer thickness.

The English and Italian tools give those attenuation factors as output. The BIOSCREEN-AT tool used by the Walloon guideline does not give the *dilution/attenuation* factor as output. However, results (chapter 4.) have shown that it is equivalent to the Italian *DAF2* or to the English $AF_{UK\ 1\ dir}$.

The attenuation factor enters in the computation of remedial targets and risk factors.

Notice that the USA EPA has selected a *DAF* equals to 20 [69] while the European countries do not specify anything.

3. Equations of coefficients of dispersivity

In all the investigated European countries, the coefficients of dispersivity can be either entered by the user or computed automatically by the tool.

The implemented equations for evaluating the coefficients of dispersivity in tools depend on the distance between the source and the defined final exposition point (X [L]).

In table 10 the equations available in each tool are given (equ.2.15, 2.16 and 2.17).

Tab 10 Coefficients of dispersivity in the IT, UK and WR tools

<i>Coefficients of dispersivity in EU tools</i>		
<i>Country</i>	<i>Equation</i>	<i>Reference</i>
Italy	(2.15) $a_x = 0,1 * X$ $a_y = 0,33 * a_x$ $a_z = 0,05 * a_x$	[62] [63]
United Kingdom	(2.16) a) 10%-1%-0, 1% of X $a_x = 0,1 * X$ $a_y = 0,01 * X$ $a_z = 0,001 * X$ b) Xu & Eckstein (1995)	[37][48] [46] [23]
Walloon Region	(2.17) $a_x = 0,1 * X$ $a_y = 0,33 * a_x$ $a_z = 0,056 * a_x$	[3][23][61][67][68][70][63][28]
Where a_x = Longitudinal dispersivity [L], a_y = Transversal/lateral dispersity [L] and a_z = Vertical dispersivity [L]. X is the path (distance between the source and the receptor).		

Chapter 3

European Tools used in the RA procedures

3.1 Risk-net version 2.1

Risk-net v .2.1 software is developed by the Civil and Informatic Engineering Department of the University of Rome “Tor Vergata” in the framework of the RECONnet network [63].

The Risk-net software allows computing risk factors (*forward procedure*) and remedial objectives (*backward procedure*) for a contaminated site applying the procedure described in the technical guideline [1] in agreement with the Italian norms (*D.Lgs. 152/06 e D.Lgs. 04/08*)[30][31][32].

The Italian procedure mirrors the RBCA procedure (“Risk Based Corrective Action”) as described in the standards ASTM E-1739-95, PS-104-98 and E 2081-00. [1]

Within the software, the chemical-toxicological database of ISS-INAIL (2015) is implemented by default. The user may however select another one if desired.

The software contains analytical models for air, groundwater, and soil exposure pathways, including all models used in ASTM RBCA standards taking into account the sanitarian issue

Risk-net software has the possibility of considering source depletion due to leaching and/or volatilization, estimating the leaching time with the Green Ampt equation (however it is not used in risk evaluation), checking the mobility of the free phase.

The Risk-net v .2.1 is designed to work in Windows XP, Windows 7 and Windows 8 under Microsoft® Excel (versions 2003 through 2010). The software is incompatible with LibreOffice and OpenOffice.

The tool and relative documents can be freely downloaded at the RECONnet website:

<http://www.reconnet.net/Software.htm>

3.2 Remedial Targets Worksheet version 3.2

The Remedial Targets Worksheet v 3.2 is developed by the English Environment Agency based on the document “*Remedial targets methodology: Hydrological risk assessment for land contamination*” [36] [37][48].

The worksheet allows assessing the risk to water from land contamination, but it does not compute any risk factor. Site-specific remedial targets for polluted soil and groundwater may be found thanks to a tiered procedure.

To compute the remedial targets, the user has to introduce the concentration (target concentration) which has to be respected at the receptor. The RT-Worksheet shows the evolution of concentration in time too.

The tool does not have any database therefore the user has to enter the data manually.

RT-Worksheet has also a porosity calculator and a simple hydrological calculator for parameters who are not specifically requested in the computation of Remedial targets (i.e. GW flow velocity).

The worksheet is designed to work in Microsoft® Excel version 1997).

The RT-Worksheet and relative documents can be freely downloaded from the UK website: <https://www.gov.uk/government/publications/remedial-targets-worksheet-v22a-user-manual>

3.3 ESR-tool version 2.0.4

The ESR tool v.2.0.4 is developed by the Ram-Ses sprl in the framework of the Walloon simplified risk assessment procedure (ESR) [39].

It complies with the “*Code Wallon de Bonnes Pratiques*”.

The tool allows comparing the measured concentrations entered by the user with threshold and intervention values given by the soil decree [26].

The tool may assess the presence of risk for human health, groundwater and ecosystem.

In the present work, the ESR tool is used to assess the presence of risk for contaminant leaching. The reference document is the “*Partie C : Evaluation des risques pour les eaux souterraines*”[28].

The ESR tool is used to find soil adjusted threshold and intervention values plus the leaching time.

The tool has its own chemical-toxicological database.

The worksheet is designed to work in Microsoft® Excel environment (version 2007).

The ESR tool and relative documents can be downloaded freely at the Walloon website for the remediation of contaminated site: <https://dps.environnement.wallonie.be/home/sols/sols-pollues/code-wallon-de-bonnes-pratiques--cwbp-etude-de-risque.html>

3.4 BIOSCREEN-AT_1.43_FR_v.1.1 tool

BIOSCREEN-AT tool is developed by the US EPA. In the Walloon Region the tool is in compliance with the “*Guide de Référence pour l'Etude de Risques: Partie C*” [28].

The tool simulates the movement of dissolved pollutants in groundwater and obtains the maximal concentration at the receptor.

Thanks to a “*trials and errors*” simulation, it allows to estimate remedial objectives to protect the chosen receptor.

Traditional BIOSCREEN tool has implemented the approximate transport solution of Domenico (1987) while BIOSCREEN-AT uses an exact solution [51] [67] [68].

The tool does not have any database therefore the data have to be entered manually.

The worksheet is designed to work in Microsoft® Excel.

The BIOSCREEN-AT and relative documents can be freely downloaded from the Walloon website for the remediation of contaminated site:

<https://dps.environnement.wallonie.be/home/sols/sols-pollues/code-wallon-de-bonnes-pratiques--cwbp-etude-de-risque.html>

In appendix A Screenshots of the European tools showing requested Input and Output.

Chapter 4

Comparison of European RA approaches on a synthetic and real case study

4.1. Synthetic case study

4.1.1 Description of the synthetic case and parameters

To compare the RA procedures established by Italy, United Kingdom and the Walloon Region a theoretical case study has been built. This is done in order to highlight differences in terms of decision making among countries.

The used tools are Risk-net v 2.1 for Italy, RT-Worksheet v.3.1 tool for United Kingdom and the ESR v.2.0.4 and BIOSCREEN-AT v.1.43 tools for the Walloon Region (BE) [63][39][48].

Source-Pathway-Receptor approach

The synthetic case study is inspired by the case used by Connor (1997) developing the *Source-Pathway-Receptor* approach. In consideration of practical and conceptual differences among tools and procedures, the synthetic cases study has been slightly modified (Fig.17).

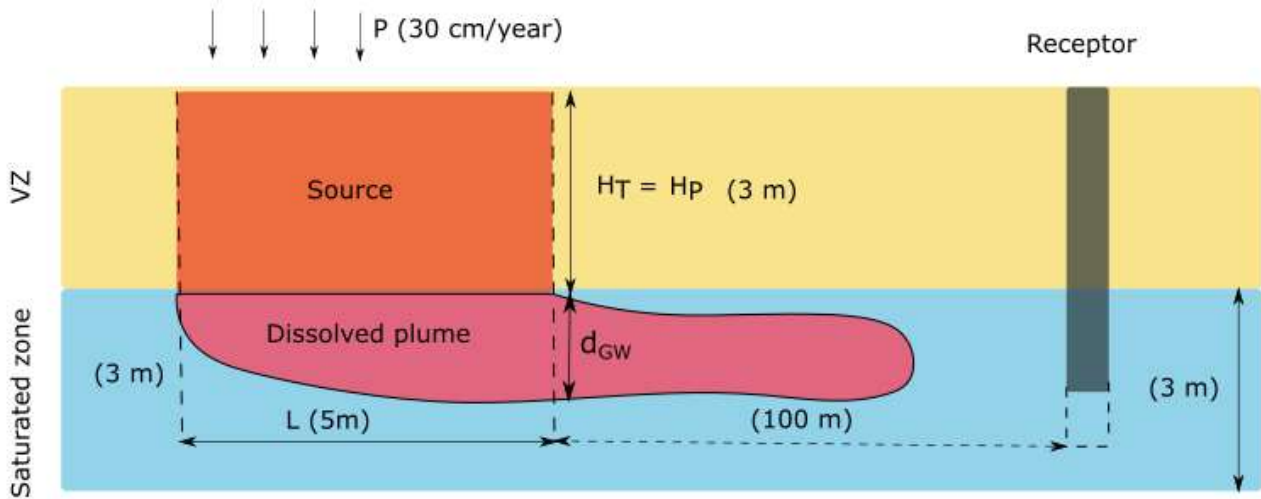


Fig. 17 Synthetic case inspired by Connor (1997). Where P is the precipitation, H_p is the thickness of the polluted soil in the unsaturated zone, H_T is the distance from the top of the source to GW table, d_{GW} is the mixing zone thickness, and L is the length of the source parallel to the GW flow.

Source

The pollutant benzene with a concentration of 1600 mg/kg d.s. is chosen as source of contamination. The value is taken from a real case study with deal on BTEX pollution in order to be realistic [13]. The source is assumed as infinite and uniformly distributed.

The source occupies an area of 25 m² with a thickness equal to the entire vadose zone.

Considering the entire vadose zone as polluted is actually not realistic but still this has been done in order to allow a better comparison among countries. In fact, the English RT-Worksheet tool does not compute the *mass redistribution factor*. Compared to the Italian and Walloon procedures it is as if the English procedure considers always a mass redistribution factor equal to 1. However this represents the worst possible condition and therefore the most conservative one.

Furthermore, the choice of benzene as pollutant is not casual.

Firstly, it is chosen for its properties since it is a pollutant with high mobility and toxicity. These characteristics may represent a threat for the groundwater resource. In Nature Benzene has a high biodegradation power too. However, in the theoretical case, this last property is not considered. This is done for proper comparison between countries as the Walloon procedure requires neglecting such detail while using BIOSCREEN-AT tool.

Secondly, the choice of benzene is made to limit the Walloon adjustments for the *soil-water partition coefficient*. Only in the Walloon procedure such adjustments are requested. The adjustments become more “data intensive” in case of heavy metals.

To avoid the Walloon adjustments for the *soil-water partition coefficient* (K_{sw}), in the correction of K_d , a *coefficient of stoniness* equals to 10^{-9} (%) is used, so that *the fraction of the site available for the adsorption* becomes equal to 1 (f_{ads}).

In fact, for equations 4.1 and 4.2 the *fraction of the site available for the adsorption* and the corrected K_d ($K_{d_{corr}}$) are obtained as following:

$$f_{ads} = 1 - \left(\frac{\% \text{ stoniness}}{100} \right) \quad (4.1)$$

$$K_{d_{corr}} = K_{OC} * f_{OC} * f_{ads} \quad (4.2)$$

Notice that to put f_{ads} equal to 1 is considered consistent since the *soil fraction of organic carbon* (f_{OC}) chosen for the synthetic case study is assumed to be already representative of the portion of the site that is available to adsorb the chosen contaminant.

In fact, the f_{OC} given in the theoretical model is considered an average value representative of the whole soil. In consideration of that, additional corrections with f_{ads} are useless.

Finally, the assumption of absence of NAPL is made.

How tools deal with the presence of NAPL

Every time the contaminant completely saturates the water and air in pores, the concentration of saturation is reached. At that condition the Non Aqueous Phase Liquid (NAPL) can form.

The Italian Risk-net tool alerts the user if the entered concentrations exceed the concentration of saturation implemented in the dataset. If desired, the tool may consider the concentration of saturation during the computation of risk factors and remedial objectives.

Once the concentration of saturation is exceeded, the free separated phase that is forming could represents an additional risk in relation to its mobility. This is why the Italian Risk net tool allows for computing the mobility of the free phase in the unsaturated and saturated soil based on the standard ASTM E 20 81. The option is available only for pollutants that are liquid at ambient temperature.

In the English RT-Worksheet tool, there is not an option as in the Italian case. However, the risk assessment procedure [36] states that the presence of NAPL has to be checked before using the RT-Worksheet. The English methodology has an additional guidance on dealing with NAPL [38].

In the Walloon methodology, the presence of a floating layer is one of the criteria for which the ESR procedure cannot be applied. For such issues a detailed risk assessment is performed. Moreover, if the NAPL on the field belongs to an historical pollution, it must be cleaned. The only exception occurs if the performed detailed risk has shown that a “*serious threat*” is not present and it is not technically feasible to remove the NAPL or there are no environmental benefits in removing it. [28][Walloon Environmental Expert B].

Pathways

The movement of contaminant is followed both for the vertical path in the vadose zone (Leaching) and for the horizontal path in the aquifer (Dispersion).

Volatilization and chemical or biological degradation of the pollutant on the other hand are not considered in the synthetic case.

Moreover, in order to apply the simplified risk procedures it has to be made the assumption of lack of colloidal transport and preferential paths (fractures).

Receptors

The receptor is groundwater. Both groundwater below the polluted site and groundwater in a “piezometer” at 100 m downgradient of the source have to be protected. The piezometer is considered to be positioned at the limit of the parcel.

Data and parameters for the Synthetic case

The entered data are given in Tab.1 appendix B.

A sand soil type with a total thickness of 3 m is assumed. The aquifer has a total thickness of 3 m too. The aquifer is assumed as unconfined with homogeneous and isotropic properties. The choice of parameters for the aquifer are made in order to respect some of the values given in the synthetic case study of the article Connor (1997).

A description of the chosen parameters for the theoretical case study and practical issues encountered using the tools is given in the following paragraphs.

1. Organic carbon partition coefficient & Henry constant

The organic carbon partition coefficient (K_{OC}) can be chosen only in the English RT- Worksheet and in the Walloon BIOSCREEN-AT tool.

In the Walloon ESR tool and in the Italian Risk-net tool such coefficient is already implemented in the database depending on the type of pollutant. For benzene the Italian K_{OC} is 146 l/kg while in the Walloon ESR tool is 74,13 l/kg (since $\text{Log } K_{OC} = 1,87$ l/kg [annex B-4 from [29]]).

The same can be said for the dimensionless Henry constant.

This value is already implemented in the Italian Risk-net tool and in the Walloon ESR tool but they differ (0,23 and 0,16 respectively)⁷, while in the English RT worksheet tool the value is entered directly by the user.

Such numerical differences have an influence on the results of the procedures.

2. *Infiltration rate*

For the synthetic case study, the infiltration rate is estimated basing on a net annual precipitation of 30 cm/year as given in the article Connor (1997). This is equal to 1, 62 cm/year.

The Italian equation for a sand texture type (equ.4.4) is used to compute the Infiltration rate [1].

$$I = 0,0018 * P^2 \text{ for Sand} \quad (4.4)$$

Where I is the net infiltration [L/T] and P is the effective rain [L/T].

3. *Density*

Soil bulk density is given by Connor (1997) and is equal to 1,7 kg/l.

In both the English RT-Worksheet and BIOSCREEN-AT tools the dry bulk density of the aquifer is requested as well. Also in this case the same value of 1,7 kg/l is used.

Density enters in the computation of the *Retardation factor*. However using a steady state simulation, the retardation factor has no influence in the computation of the concentration at compliance (i.e. Italian case). While for the transient state, the retardation may create a delay on the arriving concentration (i.e. Walloon case).

4. *Fraction of organic carbon and organic matter*

The organic carbon fraction coefficient of soil (f_{OC}) is taken from Connor (1997). and is equal to 0,006 (-).

In the Walloon ESR tool it is not directly requested in input the fraction of organic carbon but rather the organic matter. The relation between organic matter and fraction of organic carbon for an organic pollutant is given in annex C-3.1 of the Walloon guideline [29] as following. (the equation 4.5 is given for *hydrophobic organic pollutant non ionisant*).

$$f_{OC} = \frac{MO}{100 * 1,724} \quad (4.5)$$

Where MO = organic matter (%) and f_{OC} is the organic carbon fraction (-).

For the fraction of organic carbon in the saturated zone the Italian default value is instead used 0,001 (-).

⁷ In the Walloon annex B-4 from [29], the Benzene dimensional Henry constant is given (388, 6 Pa*m³ *mol⁻¹ for a temperature of 20 °C). The correspondent dimensionless Henry constant is obtained with equation 4.3 [12].

$$K_{H_{Dimensionless}} [-] = \frac{K_H \left(\frac{atm * L}{mol} \right)}{R \left(\frac{atm}{mol * K} \right) * T(K)} \quad (4.3)$$

Where K_H is the dimensionless Henry constant, R is the universal gas constant equal to 0,082058 l*atm/mol*K and T is the absolute temperature in K.

5. *Volumetric water content - Volumetric air content*

The volumetric water content and the volumetric air content depend on the soil type.

The Italian Risk-net tool may either compute them directly once the soil texture type (sand, clay etc.) is chosen [62] or the user may manually enter such values. The English RT-Worksheet requires the user to enter them.

Since the Walloon ESR tool does not allow entering them manually, the Walloon equations 4.6 and 4.7 have been used [annex C-1 from [29]].

Volumetric water content:

$$\vartheta_w = f * \left(1 - \frac{\rho}{2,6}\right) \quad (4.6)$$

Volumetric air content:

$$\vartheta_a = \left(1 - \frac{\rho}{2,6}\right) - \vartheta_w \quad (4.7)$$

Where ϑ_w is the volumetric water content [-], ϑ_a is the volumetric air content [-], ρ is the soil bulk density [M/L³] and f is the porosity fraction occupied by water (or Saturation) [-].

In order to compute the water and air content ρ equals to 1,7 kg/dm³ and f equals to 0,20 (-) are used. Such value of saturation is chosen equal to 0,20 in order to obtain the Italian water content value implemented in the Risk-net software for a sand texture type.

The obtained values are respectively $\vartheta_w = 0,068$ (-) and $\vartheta_a = 0,278$ (-).

6. *Hydraulic conductivity and hydraulic gradient*

The values of the hydraulic conductivity (10⁻⁴ m/s) and hydraulic gradient (8,82*10⁻³ (-)) have been chosen coherently with the *Darcy velocity* given by Connor (1997).

However, this hydraulic conductivity value is the typical average value given by the Walloon guideline for Walloon aquifers [annex C-2 from [29]]. In fact, such kind of value is the characteristic average hydraulic conductivity value of Walloon sand and sandstone aquifer, limestone aquifer and chalks aquifer.

7. *Effective porosity in the saturated zone*

The effective porosity in the water bearing unit can be in the range of 0,001-0,35 (-) Connor (1996). Here 0,04 (-) is used.

8. *Coefficients of dispersivity*

The coefficients of dispersivity have been chosen based on the equations already implemented in the BIOSCREEN-AT tool [61][68].

9. *Mixing zone thickness*

Since it is a synthetic case study, the mixing zone thickness is computed as following (equ. 4.8) [62] [36][annex C-2 from [29]]:

$$d_{GW} = \sqrt{0,0112 * L^2} + da * \left\{ 1 - \exp \left[\frac{-L*i}{k*i*da} \right] \right\} \quad (4.8)$$

Where L is the length of the source parallel to the groundwater flow [L], da is the thickness of the aquifer [L], I is the infiltration rate [M/T], k is the hydraulic conductivity [L/T] and i is the hydraulic gradient.

The first term estimates the mixing zone due to the vertical dispersivity, while the second term estimates the mixing height due to the seepage velocity. This parameter enters in the computation of the *dilution factor* when the mechanism of leaching is modelled

The mixing zone thickness can be either computed with *equation 4.8* or entered directly by the user. However, only in the Italian and English procedures this last choice is allowed [63] [48] [39]. In the synthetic case, a mixing zone thickness of 0,532 m is computed. In the synthetic case study the initial thickness of the plume is put equal to the mixing zone thickness. There are several reasons for this.

Firstly because of lack of real data.

Secondly because for the Italian case the initial thickness of the plume is always equal to the mixing zone thickness. By definition, the mixing zone thickness represents the amplitude of the plume in the phenomena of dispersion in the aquifer. It is the distance between the piezometric surface and the lower point of the aquifer in which pollution has been detected [66].

The Italian case uses this parameter inside the *DAF* model as a geometric parameter representing the initial thickness of the plume for the saturated part.

In the Walloon and English procedures instead, the initial plume thickness may differ with respect to the mixing zone thickness. The only exception is represented by the third level of the English tiered procedure when the contamination is located in the soil. In this case, the RT-Worksheet tool requires using the initial thickness of the plume equal to the mixing zone thickness.

4.1.2 Comparison of results given by different tools

The results of the RA procedure on the synthetic case study are shown by comparing the Italian and English procedures and the Walloon and English procedures.

This is motivated by the fact that the English RT-Worksheet tool is the most versatile one in terms of data editing and in the choice of transport models. On the other hand, the Italian and Walloon tools have their own databases and different transport solutions (the Italian tool models in steady state with an approximate solution while the Walloon tool models in transient state with an exact solution).

In the first case the English RT-Worksheet is used with the Italian values as they are given in the database of Risk-net.

In the second case the English RT-Worksheet tool is used with the values implemented in the Walloon ESR tool.

Considerations on the conceptual choices

Notice that if on one side the use of a theoretical case study allows to choose the wanted parameters and conditions, on the other hand it creates some issues in the choice of the entered parameters.

This is particularly evident when the parameters for the saturated zone are entered. In fact, one of the main issues for the theoretical case is to keep consistency between results and data of the vadose and the saturated zone.

For example, in real life the concentration in groundwater is measured. While in this theoretical case, the contaminant source in ground water is assumed equal to the “*diluted concentration*”.

The “*diluted concentration*” is the ratio between the leachate concentration and the dilution factor. The Italian and English tools give it as output. It is the estimated concentration within the receptor.

By the same token, in reality samples taken at different depths allow to define the initial thickness of the plume while in this synthetic case this is chosen equal to the mixing zone thickness for the above discussed reasons.

The initial plume thickness in reality might be higher or lower of the mixing zone thickness. In fact, it depends on the mixing zone thickness but also on the dispersion of the pollutant in groundwater. The plume thickness varies in space and time, influenced by several factors.

In conclusion, the choice of using the mixing zone thickness as initial plume thickness as well as the “*diluted concentration*” as contaminant source concentration depends firstly on the lack of real data but also on the need to respect the mass balance. In the following paragraph, the mass balance issue will be further discussed.

Finally as explained in chapter 2, it is important to highlight the fact that in the Walloon procedure the leaching and dispersion mechanism are two separated parts. In reality when the ESR tool shows that the polluted site may represent “*a severe treat*” for the groundwater due to leaching, the practice is to remediate the site or to perform a detailed risk study (EDR).

While in this study after having established the presence of risk due to leaching, it is assumed that a certain “*diluted concentration*” is in groundwater. This may represent a treat for the receptor (100 m downgradient), therefore the contaminant movement across ground water has to be checked, too.

Even in the English and Italian procedures the two mechanisms may be split and tools require entering the “measured source concentration” in groundwater.

The global Italian, English and Walloon results are in *appendix C*. This chapter mainly focuses on similarities and differences.

Considerations on the Mass Balance

As discussed above with regard to the choice of parameters, one of the main objectives is to be physically consistent in order to respect the mass balance between the unsaturated and saturated part. This means that the mass discharge due to the mechanism of leaching ($Md_{Leaching}$) has to be higher or equal to the mass discharge computed for the saturated part ($Md_{Dispersion}$). In fact, the quantity of entering pollutant has to be higher than, or at least equal to, the quantity of migrating one (equ.4.9).

$$Md_{Leaching} \geq Md_{Dispersion} \quad (4.9)$$

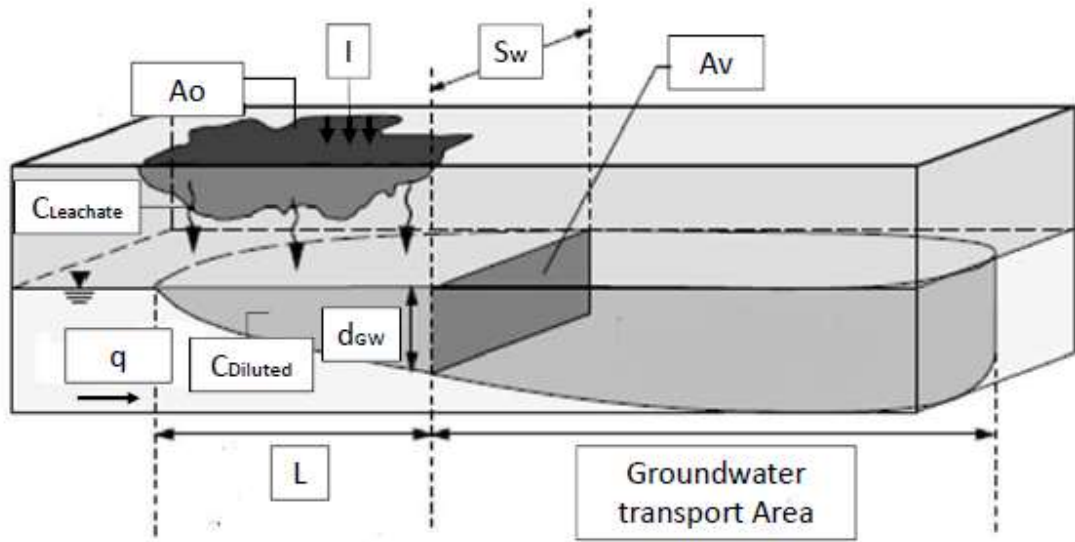


Fig. 18 Schematic representation of the factors used for computing the Mass discharge. Original image from [23].

Where I is the infiltration rate $[L/T]$, A_o is the Horizontal polluted area $[L^2]$, A_v is the vertical polluted area $[L^2]$, $C_{Leachate}$ is the leachate concentration $[M/L^3]$, $C_{Diluted}$ is the diluted concentration $[M/L^3]$ q is the GW flow $[L/T]$, Sw is the width of the contaminated source perpendicular to the groundwater flow, L is the length of the contaminated source parallel to groundwater $[L]$ and d_{GW} is the initial thickness of the plume put equal to the mixing zone thickness $[L]$.

The mass discharge is the mass per time of the contaminant through a selected area. Its dimension is $[M/T]$. It can be evaluated for both the unsaturated and saturated zone (Fig.18). The equations are as following equations 4.10 and 4.11.

$$Md_{Leaching} \left[\frac{M}{T} \right] = I \left[\frac{L}{T} \right] * A_o [L^2] * C_{Leachate} \left[\frac{M}{L^3} \right] \quad (4.10)$$

$$Md_{Dispersion} \left[\frac{M}{T} \right] = k \left[\frac{L}{T} \right] * i [-] * A_v [L^2] * C_{Diluted} \left[\frac{M}{L^3} \right] \quad (4.11)$$

Where I is the infiltration rate $[L/T]$, A_o is the horizontal contaminated area in the soil $[L^2]$, k is the hydraulic conductivity $[L/T]$, i is the hydraulic gradient $[L]$, A_v is the vertical contaminated area in

the saturated zone [L^2], $C_{Leachate}$ is the leachate concentration [M/L^3] and $C_{diluted}$ is the “*diluted concentration*” [M/L^3].

For the computation of the Mass discharge the used parameters are shown in Tab.11. The values of concentrations refer to the Walloon procedure but the same considerations remain valid also for the other two countries.

Tab 11 Parameters entered in the Computation of the mass discharge (WR)

<i>Parameters for the computation of the mass discharge (Walloon Region)</i>		
Concentration (mg/m^3)	$3,168 \cdot 10^6$ ($C_{Leachate}$)	$1,72 \cdot 10^4$ ($C_{Diluted}$)
I (m/s)	$5,14 \cdot 10^{-10}$	
k (m/s)	10^{-4}	
i (-)	$8,82 \cdot 10^{-3}$	
Ao (m^2)	25	
Av (m^2)	2,66	

The fact that the mass discharge has to be respected has an influence on the conceptual choices.

In fact looking at Tab.12 it can be noticed that the mass discharge inequality is respected only if the “*diluted concentration*” is used as the concentration within the aquifer ($0,041 > 0,040$).

On the contrary the mass discharge inequality is not respected if the *leachate concentration* ($C_{Leachate}$) is used as contaminant source concentration in groundwater for the saturated zone. This is the same concentration used for the mass discharge in the vadose zone.

This issue occurs since it is used as initial thickness of the plume the mixing zone thickness (0,532 m). The inequality would still be respected with the ground water source concentration equal to the *leachate concentration*, only if the initial plume thickness is a lower value (0,0025 m) compared to the mixing zone thickness.

This is why, in consideration of the choices made to build the synthetic case study (initial plume thickness=mixing zone thickness) the “*diluted concentration*” is used.

Tab 12 Results on the computation of the mass discharge (WR)

<i>Mass discharge (Walloon Data)</i>	
<i>Mass Discharge (mg/s)</i>	<i>Value</i>
Md _{Leaching}	0, 041
Md _{Dispersion} (input $C_{Diluted}$)	0, 040
Md _{Dispersion} (input $C_{leachate}$)	7,433

4.1.2.1 Comparison of results given by the Italian Risk-net tool and the English RT-Worksheet tool

To compare the Italian and English procedures, the English RT-Worksheet tool is used selecting the following values:

- As target concentration the Italian groundwater standard for benzene of 0,001 mg/l;
- As organic carbon partition coefficient the Italian value of 146 l/kg;
- As dimensionless Henry constant the Italian value of 0,23 (-)
- The steady state Domenico (1987) transport model;
- The same *dilution/attenuation* factor. Notice that the chosen *Dilution/attenuation* factor is $DAF2 = AF_{UK_1dir}$ where the vertical dispersion is allowed only downwards. The choice follows the advice given by the English manual [37]. Actually, such factor implies the source of contamination at the top of the aquifer and occurring percolation.

In figure 19 is schematically shown how the Italian and English procedures compute remedial targets for soil and groundwater both for an *On-site* and *Off-site* receptor. The comparable results, between the two countries, are those in the green boxes.

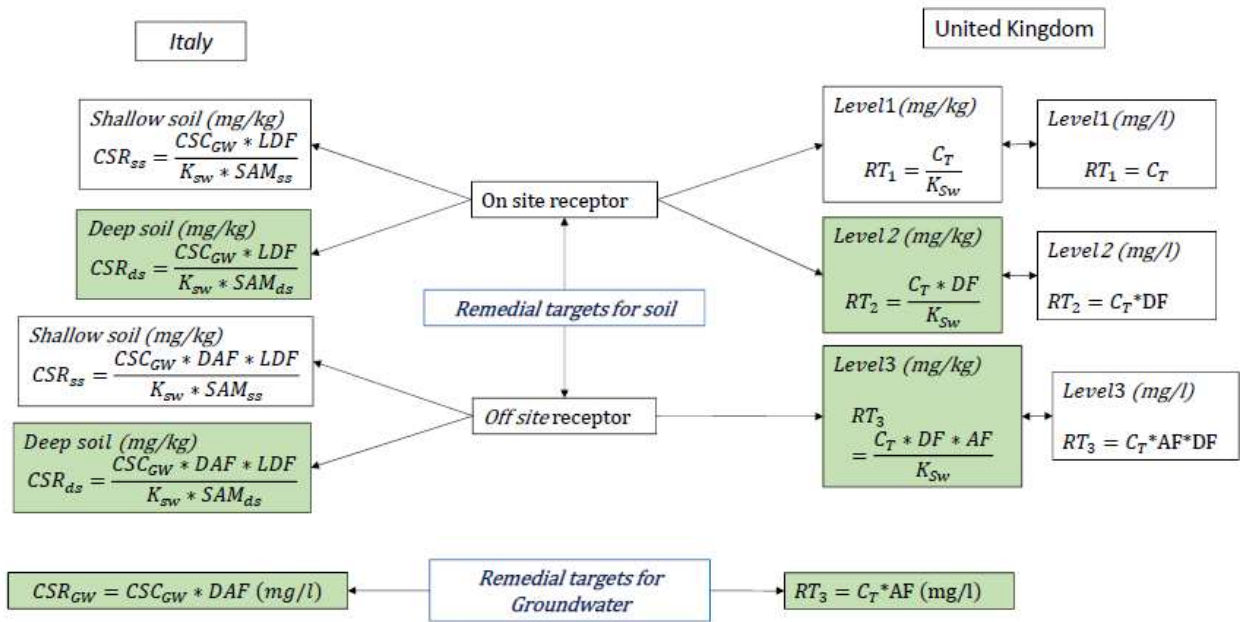


Fig. 19 Diagram showing correspondence in the way Remedial targets are computed in the Italian and English procedures [1] [36] [37] [62]

Some differences may be noticed.

Firstly, the English methodology is the only investigated procedure that gives remedial targets for soil in two ways: remedial targets which can be compared with measured soil concentrations (mg/kg) and remedial targets which can be compared with leachate tests (mg/l).

Secondly, in case the source of contamination is in the soil the results of level 1 of the UK procedure cannot be compared with anything else. At this level, the most conservative remedial target is obtained. In fact, just the partitioning between soil-water is taken into account as factor. On the contrary, in the Italian case the remedial objective for soil is computed only once considering all factors together (soil-water partition coefficient, mass redistribution factor and the dilution factor).

Thirdly, the Italian results obtained considering the source of pollution in the shallow soil cannot be compared with anything else since the UK procedure does not make the distinction between deep and shallow soil.

In Tab.13 the numerical results are given. In the last two columns is specified how, under which conditions and at which step of the RA procedure the numeric value is found.

In order to have a better understanding of results while looking at Tab 13 the reader is invited to consider figure 20.

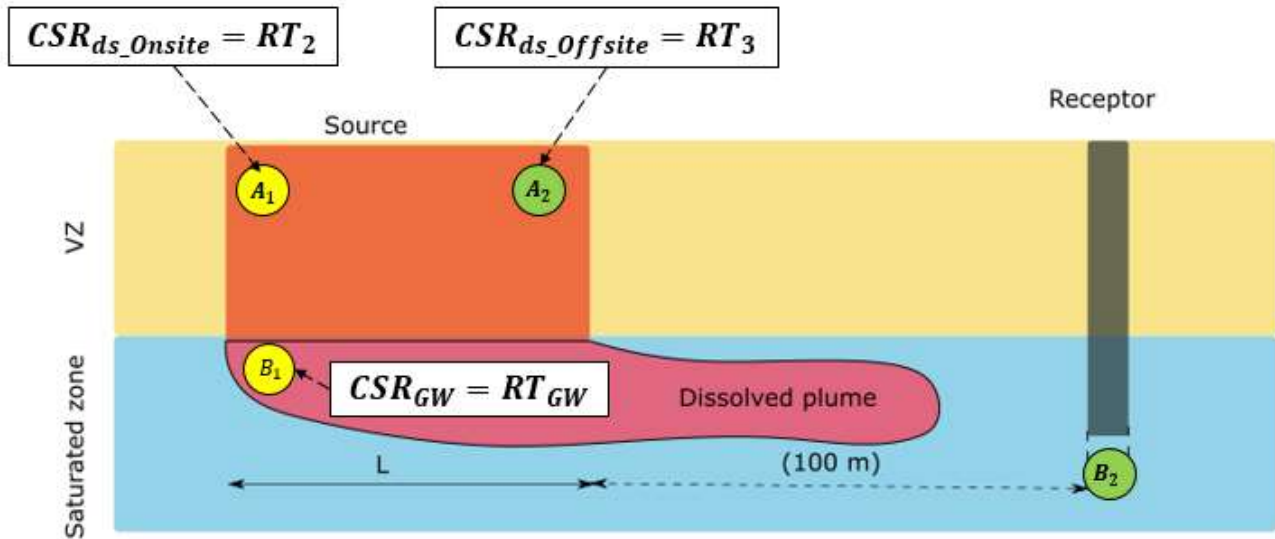


Fig. 20 Representation of the synthetic case with relative remedial objectives for the comparison among the Italian and English RA procedures. Where $CSR_{ds_On\ site}$ is the Italian remedial objective for soil [M/M] when considering an On-site receptor (case A1), RT_2 is the English remedial objective for soil computed at level 2 of the assessment [M/M], $CSR_{ds_Off_site}$ is the Italian remedial objective for soil [M/M] when considering an Offsite receptor (case A2), RT_3 is the English remedial objective for soil computed at level 3 of the assessment [M/M]. $CSRGW$ and RT_{GW} are respectively the Italian and English remedial objective for groundwater [M/L³] in order to protect the receptor at position B2.

The theoretical case study may be investigated from two different perspectives:

- To assess the risk for groundwater below the site (location B1) and to obtain the respective *soil remedial targets* for an *On-site* receptor (location A1- $CSR_{ds_On\ site}$ or RT_2 [M/M]).

Where CSR_{ds_Onsite} is the Italian remedial objective (mg/kg) found considering the source of contamination in the deep soil and RT_2 is the English remedial target for soil (mg/kg) found considering the level 2 of the English tiered procedure for a soil source of contamination.

- To assess the risk for the receptor at 100 m downgradient of the source (location B2) when the source of contamination in GW is the “*diluted concentration*”. To find the respective *soil remedial target* for an *Off-site* receptor (location A2- $CSR_{ds_Off\ site}$ or RT_3) and for groundwater at the source (location B1- $CSRGW$ or RT_{GW}).

Where $CSR_{ds_Offsite}$ is the Italian remedial objective (mg/kg) for an *Off-site receptor* found considering the source of contamination in the deep soil. RT_3 is the English remedial target for soil (mg/kg) found considering the level 3 of the English tiered procedure for a source of contamination in the soil.

These two remedial targets are computed taking into account the attenuation in the saturated zone ($DAF2=AF_{UK_1dir}$). While CSR_{GW} and RT_{3_GW} are the Italian and English groundwater remedial targets (mg/l). They represent the maximal concentration at the groundwater source (location B1) which guarantees the respect of standard at the chosen receptor (location B2).

Tab 13 Comparison of Italian vs English results on the Synthetic case study

Italian vs English procedures results in steady state			
Results	Value	Italy	United Kingdom
$C_{leachate}$ (mg/l)	$1, 7 \cdot 10^3$	Computed by the tool (4.12) $C_{Leachate} = K_{SW} * C_{Total\ source}$	Computed by the tool (4.12) $C_{Leachate} = K_{SW} * C_{Total\ source}$
$C_{diluted}$ (mg/l)	9, 24	Computed by the tool (4.13) $C_{Diluted} = \frac{C_{Leachate}}{Dilution\ factor}$	Computed by the tool (4.13) $C_{Diluted} = \frac{C_{Leachate}}{Dilution\ factor}$
Remedial objective for soil (mg/kg)	$1,75 \cdot 10^{-1}$	On site receptor $DAF=1$ (2.5 b) $CSR_{ds} = \frac{CSC_{GW} * 1}{LF_{ds}}$	Level 2 (2.6 b) $RT_2 = \frac{C_T * DF}{K_{SW}}$
	56, 3	Off site receptor (2.5 b) $CSR_{ds} = \frac{CSC_{GW} * DAF2}{LF_{ds}}$	Level 3 (2.6 c) $RT_3 = \frac{C_T * DF * AF_{UK_1dir}}{K_{SW}}$
Concentration at the receptor (mg/l) (X=100 m)	$2, 90 \cdot 10^{-2}$	Domenico (1987) Steady state simulation using $DAF2$	Domenico (1987) Steady state simulation using AF_{UK_1dir}
Remedial objective for Groundwater (mg/l)	$3, 22 \cdot 10^{-1}$	(2.5 c) $CSR_{GW} = CSC_{GW} * DAF2$	(2.8) $RT_{GW} = C_T * AF_{UK_1dir}$

The Italian Risk-net tool gives as output the factors of risk while in the English procedure, for assessing the presence of risk, the user has to compare the measured concentrations with the obtained remedial targets.

In both Countries, the presence of risk for the groundwater resource below the site (position B1) and for the receptor at 100 m (position B2) is brought to attention.

In fact, in the first case the *soil measured concentration* (1600 mg/kg d.s) is higher than the computed *soil remedial objective* for an *On-site receptor* ($1,75 \cdot 10^{-1}$ mg/kg d.s.) while in the second case the *soil measured concentration* is higher than the *soil remedial objective* of an *off site* receptor (56,3 mg/kg).

The ground water concentration at 100 m is higher ($2,90 \cdot 10^{-2}$ mg/l) than the Italian groundwater standard for benzene (1 µg/l). In fact, this is why the correspondent *ground water remedial target* (mg/l) (location B1) is lower than the used contaminant source in ground water (C_{diluted}).

Both contaminated site and groundwater have to be cleaned up till they reached the obtained remedial objectives.

4.2.1.2 Synthetic case study investigated with the Walloon procedure

The Walloon procedure in parallel to the synthetic case study for two kinds of aquifers (exploitable and not exploitable) is applied. However, notice that the chosen value of hydraulic conductivity (10^{-4} m/s) is typical of exploitable aquifers.

The procedure is applied in order to assess:

- The presence of a “*serious treat*” for the groundwater resource due to the mechanism of leaching (position B1 Fig.21).
- The presence of risk for a receptor located 100 m downgradient the source. The receptor is the limit of the parcel (position B2 Fig.21).

Notice that the Walloon procedure first establishes the presence of a “*serious treat*” for the chosen receptor and only later on it computes the remedial objectives (depending on the pollution age or type of receptor).

While looking at the table of results (Tabs 14 and 16) the reader should refer to Fig. 21. Boxes in light blue colour show the procedure when an exploitable aquifer is considered. Boxes in purple show the procedure for a not exploitable aquifer.

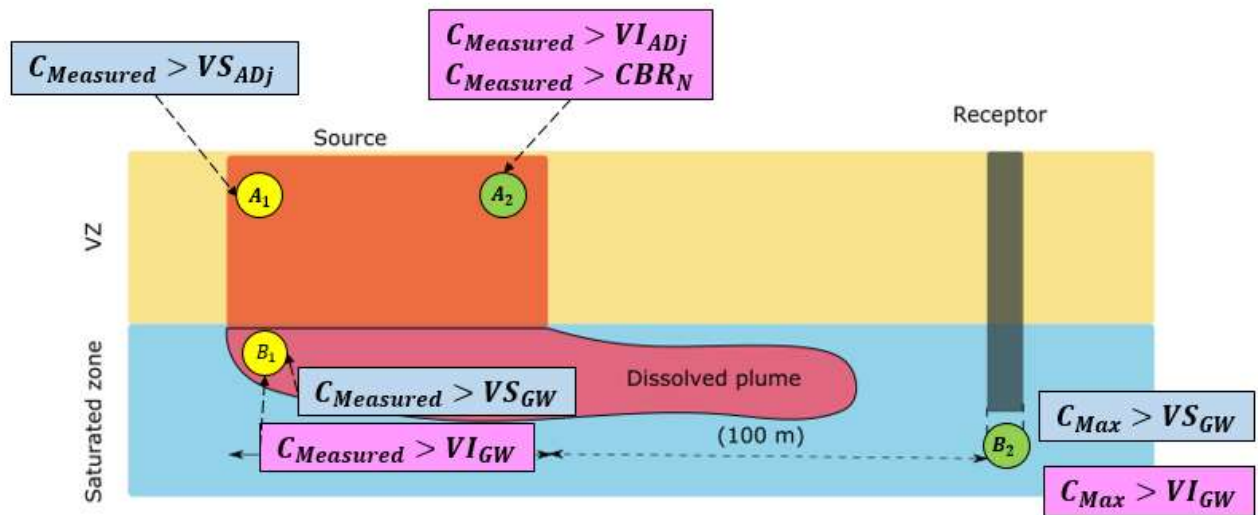


Fig. 21 Representation of the synthetic case showing the Walloon procedure. Where VI_{Adj} and VS_{Adj} are the Walloon threshold and Intervention values for soil respectively [M/M], CBR_N is the Walloon max concentration value for soil for a not exploitable aquifer [M/M], VI_{GW} and VS_{GW} are the intervention and threshold values for groundwater [M/L³] and C_{Max} is the maximal concentration at compliance computed with BIOSCREEN-AT tool.

Walloon RA procedure for the mechanism of leaching

In tab. 14, the results obtained with the ESR and BIOSCREEN-AT tool are shown. In the last two columns is specified how the numeric value is found.

Tab 14 Walloon results for the mechanism of leaching (synthetic case)

Walloon procedure Results: Mechanism of Leaching in the Vadose zone				
Results	Value Expl.	Value Not Expl.	Exploitable aquifer	Not exploitable aquifer
C leachate (mg/l)	3,17*10 ³ (WR)		Computed by the user (4.12) $C_{Leachate} = K_{SW} * C_{Total\ source}$	
Adjusted value (mg/kg)	0,93 (VS _{Adj})	3,70 (VI _{Adj})	Computed by ESR tool (2.9 a) $VS_{ADJ} = VS_{GW} * FAG_{Adj}$	Computed by ESR tool (2.9 b) $VI_{ADJ} = VI_{GW} * FAG_{Adj}$
CBR _N (mg/kg)	—	9,85*10 ²	—	Computed with BIOSCREEN (Trials and errors)+ ESR (Back-modelling) (2.10) $CBR_N = CBR_{GW} * FAG_{Adj}$

The results of the Walloon ESR (Tab.14) tool show the presence of a “*serious treat*” due to leaching both when considering an exploitable and a not exploitable aquifer. In fact, the *adjusted values* (threshold 0, 93 mg/kg and intervention 3, 7 mg/kg) by the measured concentration (1600 mg/kg d.s.) are exceeded.

In case of a not exploitable aquifer, even the computed CBR_N value is exceeded (985 mg/kg). CBR_N is the maximal allowed concentration in soil in order to respect VI_{GW} at the receptor.

For the choice of the synthetic case, the leaching time is zero, since the bottom of the source is in contact with the groundwater table.

At this stage, in real practice, the assessor should decide whether to remediate the site or continue with a more *detailed risk assessment*.

The clean up targets are dependent on the age of the pollution (Tab.15).

In case of a *new pollution* the site has to be remediated up to the reference value ($VR = 0, 1$ mg/kg for benzene) or to the closest value using the BATNEEC.

In case of an *old pollution* the remediation should be performed up to VR or to the closest value reachable with BATNEEC and at least by removing the source of risk reaching the “*minimum cleaning criteria*” found with the ESR.

The *minimum cleaning criteria* depends on the type of aquifer and receptor. When the receptor is the limit of the parcel, it can be VI_{adj} for a not exploitable aquifer (3, 7 mg/kg) or VS_{Adj} for an exploitable aquifer (0, 93 mg/kg). If the drinkable standard has to be reached then the minimum criteria would be more restrictive (drinkable standard* FAG_{Adj}).

Tab 15 Walloon Remedial targets for soil (synthetic case)

<i>Remedial target for soil (mg/kg)</i>			
<i>New pollution</i>		<i>Old pollution</i>	
Exploitable	Not Exploitable	Exploitable	Not Exploitable
VR	VR	VR or VS_{ADJ}	VR or VI_{ADJ}

Walloon RA procedure for the movement of the pollutant in the saturated zone

In the Walloon RA procedure the mechanism of leaching and the movement of the pollutant across groundwater are two separated steps.

In consideration of that, in the synthetic case study, the assumption of having measured the benzene concentration in groundwater is made. The ground water benzene concentration is $C_{diluted}$ (mg/l). The choice allows developing the RA for a contaminant concentration in groundwater by applying BIOSCREEN-AT tool.

The numerical results are given in tab.16. Once again in the last two columns is specified how the numeric value is found.

Tab 16 Walloon results for the movement of the contaminant in groundwater (synthetic case)

Walloon procedure Results: Pollutant movement in the saturated zone			
Result	Value	Exploitable aquifer	Not exploitable aquifer
C_{diluted} (mg/l)	17,21	Computed by the user (4.13) $C_{\text{Diluted}} = \frac{C_{\text{Leachate}}}{\text{Dilution factor}}$	
Concentration at compliance at 100 m (mg/l)	$6,4 \cdot 10^{-2}$	C_{MAX} obtained with BIOSCREEN-AT Modified Domenico - Transient simulation	

Even in this case the presence of “*a serious threat*” for the receptor located 100 m downgradient of the source is noticed. In fact, the maximal concentration simulated with BIOSCREEN-AT tool, avoiding degradation, (64 µg/l) exceeds the standards.

Since this receptor is considered as the limit of the parcel this value has to be compared with VI_{GW} (40 µg/l) for a not exploitable aquifer and with VS_{GW} (10 µg/l) for an exploitable aquifer. In case the receptor is a well, the comparison is done with the drinkable water standard (1 µg/l).

In consideration of this exceedance, remediation is mandatory. The clean up value depends on the use of the ground water. The numeric values are given in Tab.17

Tab 17 Walloon remedial targets for a receptor located 100 m downgradient the source (synthetic case)

Remedial target for GW (mg/l) (Receptor at 100 m)			Remedial target for soil (mg/kg) for having respected the drinkable standard at the receptor
Limit of the parcel (Exploitable aquifer)	Limit of the parcel (Not exploitable aquifer)	Potable Well	
2,55	10,60	0,40	37,40
Co values obtained with BIOSCREEN-AT Modified Domenico - Transient simulation ($C_{\text{Max}} = VS_{\text{GW}} = 10 \mu\text{g/L}$)	Co values obtained with BIOSCREEN-AT Modified Domenico - Transient simulation ($C_{\text{Max}} = VI_{\text{GW}} = 40 \mu\text{g/L}$)	Co values obtained with BIOSCREEN-AT Modified Domenico - Transient simulation ($C_{\text{Max}} = 1 \mu\text{g/l}$ drinkable water standard)	Back modelling + ESR tool (4.14) $RT_{\text{soil}} = C_O * FAG_{\text{Adj}}$

The remedial objectives are obtained with BIOSCREEN-AT thanks to a “*trial and error simulation*” of different source concentrations. It is the same procedure applied to find CBR_{GW} .

The concentration found in this way is the maximal concentration that is possible to have at the ground water source in order to respect the standard at the chosen receptor (2, 55 or 10, 6 mg/l for an exploitable or not exploitable aquifer respectively).

In case the receptor is a well, the remedial target found would be more conservative (0,402 mg/l). The assessor could even find the maximal concentration in the soil (mg/kg) allowing respect of the drinkable standard (1µg/l) at the well. This is done with a *back-modelling* procedure and it is similar to considering an *Off-site receptor* in the Italian and English procedures.

However, this *soil remedial target* (37, 4 mg/kg) differs from the Italian one (56, 4 mg/kg) (Tab.13) as in the tools two different databases are implemented (i.e. Italian K_{OC} is different respect to the Walloon K_{OC}) and the contaminant transport solutions are different too.

4.2.1.3 Comparison of results given by the Walloon ESR- BIOSCREEN AT tool and the English RT-Worksheet tool

To compare the Walloon and the English procedure, the English RT worksheet tool is used selecting:

- As target concentration (C_T) the groundwater standard for benzene VI and VS (40 and 10 µg/l respectively);
- As organic carbon partition coefficient the Walloon value 74,13 l/kg;
- As dimensionless Henry constant the Walloon value 0,16 (-)
- The transient state Domenico (1987) transport model with a simulation time of 100 years avoiding degradation;
- The English attenuation factor AF_{UK_1dir} .

A parallel comparison on the way Walloon and English procedures compute remedial targets and adjusted values is shown in Fig. 22.

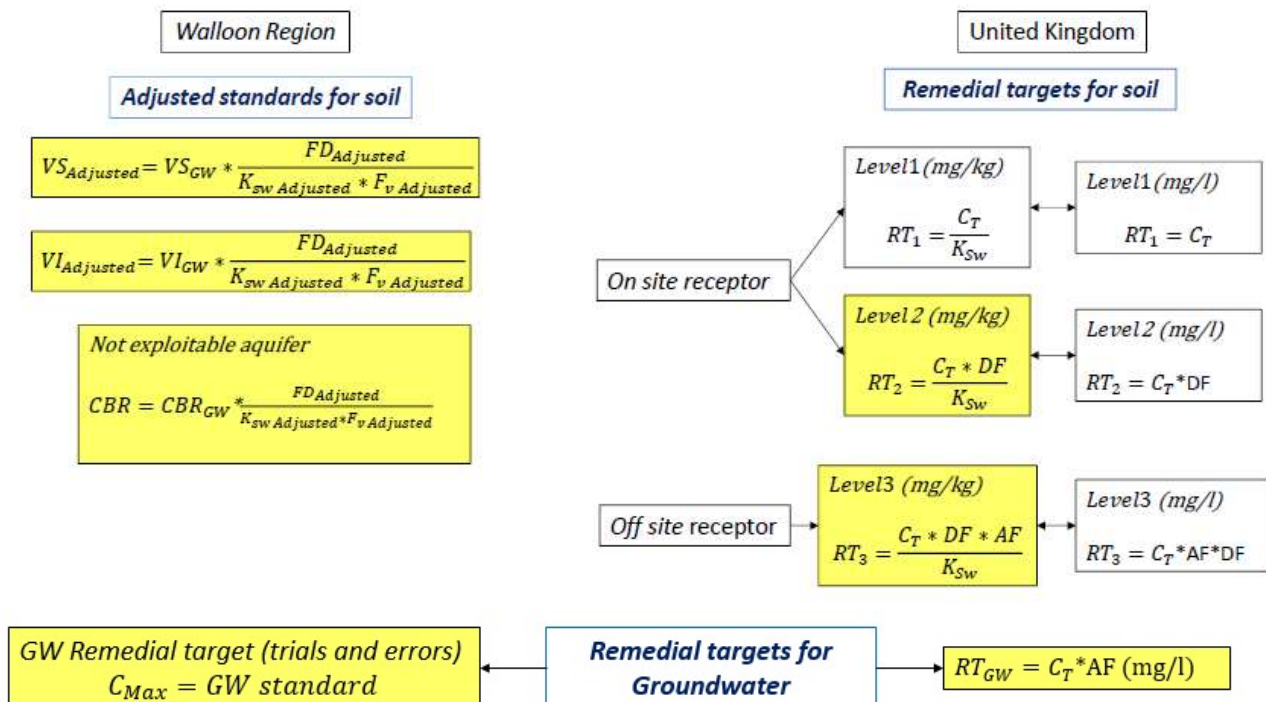


Fig. 22 Diagram showing similarities in the way remedial targets and/or adjusted values are computed in the Walloon and English procedures [28] [36] [37] [39]

Comparable results are in the yellow boxes. Further considerations regarding Walloon and English RA procedures may also be drawn.

Firstly, the Walloon procedure makes a distinction between exploitable and not exploitable aquifers while in the English procedure this is not the case. The English tool allows choosing the wanted target concentration (C_T). If desired, this can be equal to the ground water standard for an exploitable or not exploitable aquifer.

Secondly, a key element of difference between the Walloon procedure and the English one is the fact that for assessing the presence of a “serious threat” for the groundwater below the polluted site the Walloon procedure computes the *adjusted values*. These values are compared with the soil measured concentrations and in case of exceedance, also a leaching time is computed. On the contrary, in the English procedure, to establish the presence of risk only *remedial targets* are computed.

These *adjusted values* are not necessarily remedial objectives. In fact, *Walloon soil remedial targets* depend on the pollution age [26].

All this said however, the way of computing adjusted values and remedial objectives is quite similar, as shown also in fig.23.

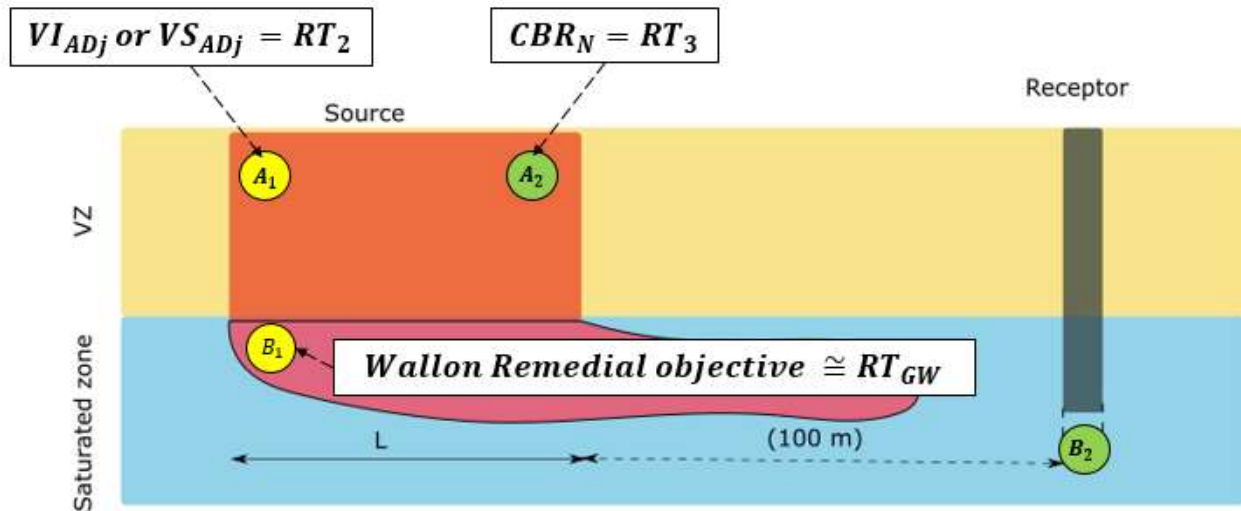


Fig. 23 Representation of the synthetic case for the comparison between the Walloon and English RA procedures.

Where VI_{Adj} and VS_{Adj} are the Walloon threshold and Intervention values for soil respectively [M/M], RT_2 is the English remedial objective for soil computed at level 2 of the assessment [M/M], CBR_N is the Walloon concentration value for soil for a not exploitable aquifer [M/M], RT_3 is the English remedial objective for soil computed at level 3 of the assessment [M/M], Walloon Remedial objective and RT_{GW} are respectively the Walloon and English remedial objective for groundwater [M/L³] in order to protect the receptor at position B2.

In Tab. 18, the numerical values obtained with the ESR and BIOSCREEN-AT tool and with the RT-Worksheet tool are shown. In the last two columns is specified how, under which conditions and at which step of the RA procedure the numeric value is found.

Tab 18 Comparison of Walloon vs English results on the Synthetic case study

Walloon vs English case			
Results	Value	Walloon Region	United Kingdom
$C_{Leachate}$ (mg/l)	3,13*10 ³ (UK)	Computed by the user (4.12) $C_{Leachate} = K_{SW} * C_{Total\ source}$	Computed by the tool (4.12) $C_{Leachate} = K_{SW} * C_{Total\ source}$
	3,17*10 ³ (WR)		
$C_{diluted}$ (mg/l)	17,21 (WR)	Computed by the user (4.13) $C_{Diluted} = \frac{C_{Leachate}}{Dilution\ factor}$	Computed by the tool (4.13) $C_{Diluted} = \frac{C_{Leachate}}{Dilution\ factor}$
	17,01 (UK)		
		Exploitable aquifer	—
Remedial targets (UK)/adjusted value (WR) for soil (mg/kg)	0,93 (WR) 0,94 (UK)	Computed by ESR tool (2.9 a) $VS_{ADJ} = VS_{GW} * FAG_{Adj}$	Level 2 when $C_T=10\mu\text{g/L}$ (2.6b) $RT_2 = \frac{C_T * DF}{K_{SW}}$
Concentration at the receptor (mg/l) (X=100 m)	6,4*10 ⁻² (WR) 5,29*10 ⁻² (UK)	C_{Max} BIOSCREEN-AT Modified Domenico – Transient simulation	Domenico (1987) - Transient simulation- Using AF_{UK_1dir}
Remedial target for the source in GW(mg/l)	2,55 (WR) 3,22 (UK)	BIOSCREEN-AT Modified Domenico - Transient simulation ($C_{Max}= VS_{GW}=10\mu\text{g/L}$)	Domenico (1987) - Transient simulation- Using AF_{UK_1dir} ($C_T=10\mu\text{g/L}$)
		Not exploitable aquifer	—
Remedial targets (UK)/adjusted value (WR) for soil (mg/kg)	3,70 (WR) 3,75 (UK)	Computed by ESR tool (2.9 a) $VI_{ADJ} = VI_{GW} * FAG_{Adj}$	Level 2 when $C_T=40\mu\text{g/L}$ (2.6 b) $RT_2 = \frac{C_T * DF}{K_{SW}}$
	9,85*10 ² (WR) 1,21*10 ³ (UK)	(Only for a not exploitable aquifer. Results of ESR + BIOSCREEN) (2.10) $CBR_N = CBR_{GW} * FAG_{Adj}$	Level 3 when $C_T=40\mu\text{g/L}$ (2.6 c) $RT_3 = \frac{C_T * DF * AF}{K_{SW}}$

Concentration at the receptor (mg/l) (X=100 m)	6,4*10 ⁻² (WR) 5,29*10 ⁻² (UK)	C _{Max} BIOSCREEN AT Modified Domenico – Transient simulation	Domenico (1987) - Transient simulation- Using AF _{UK_1dir}
Remedial target for the source in GW(mg/l)	10,60 (WR) 12,9 (UK C _t =VI _{GW})	BIOSCREEN AT Modified Domenico– Transient simulation (C _{Max} =VI _{GW} =40µg/l)	Domenico (1987) - Transient simulation- Using AF _{UK_1dir} (C _T =40µg/L)

Table 18 shows slightly different numerical values. Differences come from approximations in entering data in the RT-Worksheet tool (K_{OC}; K_H etc.) respect to the Walloon ESR tool and from the fact that as transport models, two different solutions are used. BIOSCREEN-AT uses an exact solution while the English RT-Worksheet tool uses Domenico (1987) approximate solution.

For the English procedure, risk is present since the remedial targets for soil and groundwater are exceeded. The site has to be cleaned up the computed remedial targets.

Notice that the English procedure requires computing the remedial target in steady state. In this case, even if a transient simulation is used, the steady state is reached quite soon. This means that the remedial targets found for a simulation time of 100 years are equal to the remedial targets found in steady state.

4.1.3 Conclusions of the synthetic case study

All the procedures have shown the presence of risk or “*serious treat*” for the groundwater resource for the given synthetic case study.

The results differ numerically since the implemented parameters and standards for groundwater are varied.

In fact, the Walloon ESR and the Italian Risk-net tools have their own databases with different implemented values. For example, the Italian leachate concentration is almost one half of the Walloon leachate concentration this is due to the fact that the K_{OC} values implemented in the two tools are one the double of the other (146 and 74, 13 respectively).

Looking at the groundwater standards.

The Italian procedure has in its database only a groundwater standard for Benzene (1 µg/l). This is the value used in the computation of risk factors and remedial objectives.

The English procedure allows considering the wished standard. Based on that it computes the remedial targets.

Differently from this, in the Walloon ESR tool there are two values: the threshold and intervention values for the pollutant in groundwater (for benzene 10 µg/l and 40 µg/l respectively).

They are the values used for computing the adjusted soil standards. The remedial objectives for soil and groundwater instead are not necessarily computed using these two values but even the drinkable water standard can be used.

Risk presence and remedial target estimation among the three European countries

The first element of difference is the way countries assess the presence of risk.

The Italian Risk-net tool computes risk factors. The tool gives these factors as outputs. If they are higher than 1 it means that the soil or the groundwater have to be remediated.

Risk-net tool computes also the remedial objectives. They are always computed in steady state using the Domenico (1987) solution.

Only the Italian procedure performs a division between deep and shallow soil (0-1 m b. g. l.). In consideration of that, two risk factors and two remedial objectives for soil may be computed. However, practically, when assessing the presence of risk or choosing the clean up objectives, the most conservative value between the two, in terms of either risk or remedial objective, is chosen. For the comparison with UK only the deep soil has been considered.

In the Walloon and English procedures, a risk factor is never computed.

In the English methodology, the RT-Worksheet tool computes Remedial Targets for each level of the assessment depending on the source location. Then the user compares these Remedial targets with the measured concentrations, in case of exceedance risk is present.

Remediation is necessary up to the obtained remedial targets. Remedial targets have to be computed in steady state.

The UK level 1 for source of contamination in soil obtains the most possible conservative remedial target. In fact, only the *soil-water partitioning coefficient* is considered. This is why the results of this level cannot be compared with the other two countries.

For the Walloon case, the procedure is more detailed.

Firstly, a distinction is made depending on the aquifer type (exploitable or not exploitable). For the mechanism of leaching, the measured soil concentrations are not directly compared with *remedial targets* but with the *adjusted values* found with the ESR tool. Even a leaching time may be computed in case of exceedance of those values.

If the pollution is in ground water, after having noticed that measured concentration exceeds the standard, the maximal possible concentration at the receptor is simulated with BIOSCREEN-AT tool and compared again with standards.

Differently from Italy and United Kingdom, the remedial targets for soil are not always found with the ESR tool but depend on the pollution age. In fact, the adjusted values are not necessarily the remedial objectives, even if they are computed similarly to the Italian and English Remedial targets. The remedial targets for ground water are computed with a transient simulation and a *trials and errors procedure* depending on the type of receptor (i.e. well, limit of the parcel). However, in principle, the way they are obtained is similar to the Italian and English procedure.

Summarizing the three European countries show more differences when the source of contamination is in the soil.

Only in the Walloon procedure is possible to set the difference between exploitable and not exploitable aquifer, make corrections of parameters and the adjustments of standards depending on the aquifer type or type of measurements, set the computation of the leaching time as a step for assessing risk and obtain the estimation of remedial targets depending on the site pollution age (new and old pollution).

Steady vs transient state – Approximate vs exact solution

Tools model the transport of contaminant in the saturated zone using different solutions. The difference between a steady and transient state simulation and between an exact and approximate solution is investigated.

In table 19 the comparison between the results of the measured concentration at the receptor (100 m) of the Walloon and English procedures is given.

The English procedure uses Domenico (1987) in transient state and considers the vertical dispersion only downwards. The Walloon BIOSCREEN-AT tool uses a modified version of Domenico in transient state, with an exact solution.

In the two countries the same parameters (Walloon data) and groundwater concentration ($C_{\text{Diluted}} = 17, 21 \text{ mg/l}$) are used. This is done in order to highlight the difference caused only by the use of an exact or an approximate solution.

The same can be done comparing the results given by BIOSCREEN-AT (using the Italian data as input) and the results given by the Italian Risk-net tool when a transient simulation is considered. Notice that the Italian transient simulation is just a tool for the assessor in order to see the evolution of concentration in time, but it should not be used to estimate risk factors or remedial objectives.

Tab 19 Concentration at the receptor (100 m) for different simulation time_ Walloon vs English procedures

Concentration at the receptor (100m) (mg/l) UK vs WR transient state (vertical dispersion 1 direction)		
Simulation time	$C_{100\text{ m}}$ (mg/l) (Source concentration $C_{Diluted}=17,21\text{mg/l}$)	
	BIOSCREEN-AT	RT- Worksheet ($AF_{UK_1\text{ dir}}$)
100 years	$6,40 \cdot 10^{-2}$	$5,35 \cdot 10^{-2}$
10 years	$6,40 \cdot 10^{-2}$	$5,35 \cdot 10^{-2}$
3 years	$6,4 \cdot 10^{-2}$	$5,35 \cdot 10^{-2}$
2 years	$6,4 \cdot 10^{-2}$	$5,34 \cdot 10^{-2}$
1 year	$6,2 \cdot 10^{-2}$	$4,70 \cdot 10^{-2}$

In conclusion (Tab.19) for the chosen synthetic case study using either a transient state simulation (simulation time 100 years) or a steady state simulation does not affect results. After a few years, steady state is reached anyway.

The numerical differences in results (between the Walloon and English procedures tab.19) cannot be originated by differences in the input values of parameters since they are exactly the same. The differences rather depend on the fact that the RT-Worksheet tool uses the Domenico (1987) transport model while BIOSCREEN-AT tool uses a modified version. The modified Domenico model is an exact solution while the Domenico (1987) solution is approximate.

However, notice that, the Peclet number of the synthetic case study is 10. Based on the literature reviews, the Walloon guideline [annex C-6 from [29]] states that for Peclet number higher than 6 or Peclet number equal to 10 the discrepancy between the approximate and exact solution is low and it can be considered negligible. This is particularly true when concentrations are computed along the centreline plume.

The discrepancy between the two solutions increases when the longitudinal dispersivity, the decay rate and the lateral distance increase. This last point might be an issue for the English RT-Worksheet as it allows computing concentrations not just along the centreline plumes. However, a centreline plume has always to be considered, in case remedial targets have to be computed.

Moreover, the Walloon guideline suggests avoiding Domenico (1987) model if the transport mechanism is not mainly advective.

Finally, practically speaking, for the choice of the synthetic case study it is not really important the use of an exact or approximate solution.

Factors for evaluating the movement of the pollutant in the vadose zone and consequences on the theoretical case

As described in chapter 2, the way countries model the leaching movement in the vadose zone is quite similar. The factors used and their consequences on the synthetic case are shown in Tab. 20 and summarized below.

Tab 20 Comparison of factors used for modelling the mechanism of leaching in EU countries

<i>Factors for modelling the mechanism of leaching</i>						
Country	Mass redistribution factor (SAM or Fv (-))		Soil-water partition coefficient factor (K_{sw}= kg/l)		Dilution factor (LDF or DF or FD (-))	
	Computed	Given as an output	Computed	Given as an output	Computed	Given as an output
Walloon Region	yes	yes	yes	yes	yes	yes
Italy	yes (Optional)	no	yes	no	yes	yes
United Kingdom	no	-	yes	no	yes	yes

The *mass redistribution factor* is absent in the English procedure and optional in the Italian one. In the Italian procedure two mass redistribution factors are computed, one for the deep and one for the shallow soil with a consequence in the risk factor and remedial target evaluation (in fact, two different values of leachate factors are computed).

The absence of the mass redistribution factor in the English procedure has an influence on the conceptual model choice. For example, the UK procedure cannot represent a pollution located at the top of the unsaturated zone. This is way in the synthetic case, the entire vadose zone is considered polluted.

The *soil-water partition coefficient* in all the countries is computed but only in the Walloon ESR tool is requested to adjust it based on the pollutant types and site-specific information. This is way in the synthetic case, the fraction of the site available to adsorption is put equal to 1 and benzene is chosen as pollutant.

The *dilution factor* is computed in all the countries but only the English procedure allows to consider also the background concentration of the pollutant in groundwater. Since it is a theoretical case and in order to compare the data the English background concentration is put equal to 0 mg/l.

4.2 Real case study

A real case study given during the period of internship at the Belgian Environmental company *Geolys* is proposed here. For confidential reasons the name of the location and all attributable elements of the environmental contest are avoided.

4.2.1 Scope of the RA

The study scope was to perform a simplified risk assessment following Walloon procedure. In addition to this, a comparison between the results of the different Walloon, Italian and English tools is performed. Such tools are once again ESR v. 2.0.4, Risk-net v. 2.1 and RT-Worksheet v.3.2

A Belgian quarry is due to be closed by refilling with soil. The filling soil should be taken in the area around the quarry (25 km²). Walloon norm requires the filling soil to be clean enough not to represent a risk for the groundwater beneath the quarry.

The goal is to evaluate the presence of risk for groundwater resource considering the mechanism of leaching. The investigated pollutants are heavy metals.

Representative samples of the surrounding area are taken. In order to be on the safe side in each sampling point the maximum value of each heavy metal has been set. Such concentration levels are given in table 21.

Tab 21 Heavy metals concentrations measured in samples around the quarry [44]

<i>Measured values of heavy metals</i>	
<i>Pollutant</i>	<i>Measured concentration (mg/kg d.s.)</i>
Arsenic	23
Cadmium	6,7
Chrome	58
Mercury	0,098
Nickel	58
Lead	1400
Zinc	1100

4.2.2. Description of the Environmental contest

Due to binding confidentiality agreement, a map with the exact location and characteristic of the Environmental contest cannot be shown. However, in consideration of that, a schematic

representation of the planar and transversal view of the quarry is displayed in Figs. 24 a) and b) with the purpose to help the reader in better understanding the case.

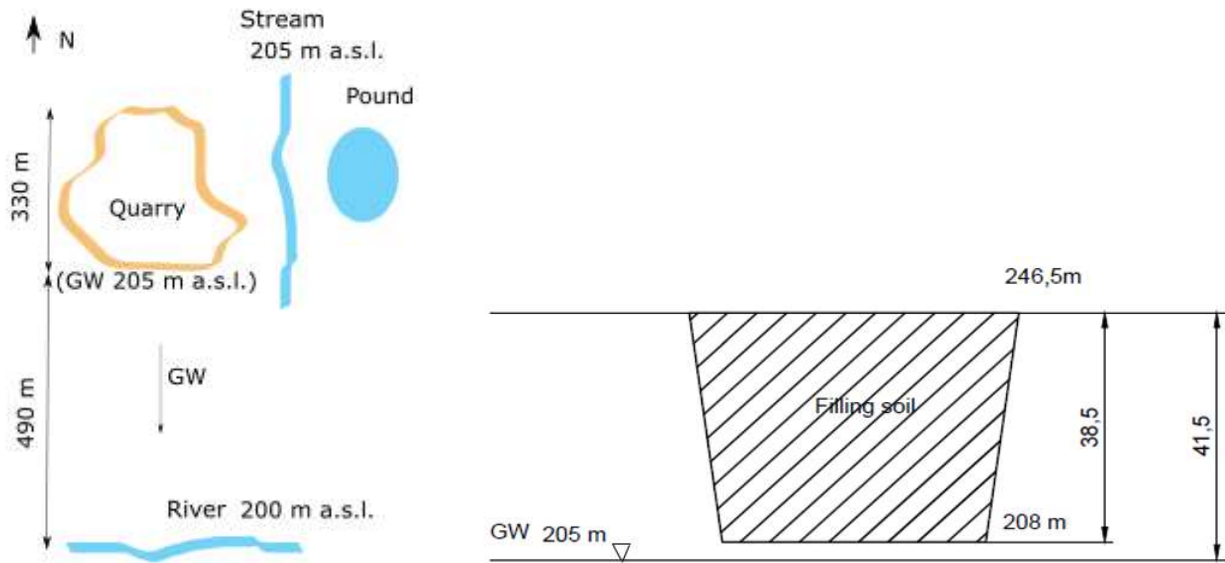


Fig. 24 a) Planar and b) Transversal schematic representation of the Environmental contest and data of the quarry.

From the hydrological point of view, the quarry is surrounded by water bodies. In the southern part of the quarry, a river flows (200 m a. s. l.). While at the East side of the quarry there are a small pound of approximately 0,023 km² and a stream (205 m a. s. l.).

From the geological point of view, the geological formation interested by the study has a total thickness of around 160 m. It is composed of two groups. The first group has a total thickness of 150 m and it is made of dolomites and limestone dolomites with nodules of limestone, dolomite and quartz. The second group has a thickness between 7 and 10 m and is of sand-limestones. Additionally underneath these two groups, there is a shale group of 7 m of thickness. This represents the lower boundary of the examined limestone aquifer.

4.2.3 Description of the parameters used in the RA tools

The input parameters required by the tools are shown in table 1 appendix D. Some of the parametric values are available from real data, others either come from literature or are the default values in the tools, finally some more ones are inferred by the Environmental contest. [45, 72].

The main assumptions are discussed below. The reader is invited to look at figures 24 a) and b).

The quarry does not have one altitude only, owing to this, in order to be on the safe side, it has been considered the minimum altitude of the quarry (208 m a. s. l.) looking at the topographic map in ArcGIS from *Geolys*. The highest altitude would have been around 265 m. a. s. l.

The filling soil altitude has been chosen looking at the final prevision made by the experts of *Geolys* (246, 5 m a. s. l. for a total thickness of about 38.5 m) [45].

The length of the quarry parallel to GW flow is chosen equal to the entire length of the quarry (around 330 m).

The groundwater level of the quarry is assumed equal to the level of the Eastern stream (205 m a. s. l.) due to the absence of data.

The hydraulic gradient is computed considering that the main groundwater flux is in the S direction, towards the southern river. The gradient is the ratio between the difference of the groundwater level in the quarry (205 m) with the southern river (200 m) and their distance (490 m) ($i = 1,02\%$). The assumption of having a negligible hydraulic gradient towards the Eastern stream is made.

4.2.4 Results and considerations of the Real case

In appendix D the results of the tools are given. Notice that, at this time, the English procedure is applied using the Italian data (i.e. values of K_d).

Presence of Risk for groundwater below the quarry

The Walloon, Italian and English procedures have shown that no risk for groundwater below the quarry is present. In fact, the Italian *risk factors* are lower than 1 and the measured concentrations (tab. D2, D3 and D4) are also below both the English *remedial targets* and the Walloon *adjusted values*. This is why in the Walloon procedure the leaching time is not computed.

Moreover, differently from the theoretical case study, the Walloon procedure has been applied adjusting the standards depending on the *type of aquifer* and on the *type of measurements* (Tab D.2). In the first case default values of a typical Walloon limestone aquifer have been used. Both ways of adjustment result in the absence of risk but the output values differ for two orders of magnitude (i.e. the Arsenic $VS_{Adjusted}$ is equal to 18636 mg/kg if the adjustment is made basing on the *type of measurements* and it is 810 mg/kg if made basing on the *type of aquifer*). This is due to the fact that the default dilution value is 33, while the computed one is 569.

However, the values found “depending on the type of measurements” are quite high. This means that probably some input parameters have to be changed (i.e. basing on additional field measurements).

Similarities and differences between the three tools in the real case

Once again, the results obtained by the three countries cannot be directly compared since the standards for groundwater and implemented parameters differ. However, based on the observations for the synthetic case study, some considerations can still be made.

The first key element of difference with respect to the synthetic case study is that now the investigated pollutants are heavy metals.

The Walloon procedure requires adjusting the *soil-water partition coefficient* taking into account several parameters (percentage of stoniness, pH, clay content, poral electric conductivity, cationic exchange capacity, etc.). These info are not available from *Geolys*'s data. In consideration of this, default values of the ESR tool have been used.

Such kind of adjustments are not required by the other two countries instead. In fact, in the Italian Risk-net tool the database has already automatically implemented the K_d values.

The option of considering an *off-site* receptor is not taken into account since the aim is to assess the presence of risk for the beneath groundwater resource.

This means that the available UK remedial targets are the ones corresponding to the first and second level of the tiered procedure. The Italian procedure in the computation of risk and remedial objectives on the other hand considers a DAF equals to one.

The Italian procedure is applied both considering shallow and deep soil. However, it has to be noticed that the real case study represents an exception with respect to traditional Italian RA. Actually, this specific study wants to assess the presence of risk for soil brought to the quarry, while normally, the soil investigated with the Italian RA is already in the site.

Finally, even if the UK RT-Worksheet is used with the Italian data, it shows different remedial objectives compared to the Italian case. This is due to the lack of the mass redistribution factor in the English procedure, moreover the tool does not require entering the depth of the groundwater table. The UK- RT procedure is unable to model the fact that between the filling soil and the ground water table there is a thickness of 3 m, which actually is the soil of the Quarry (Fig.24 b)). While the Italian procedure takes it into account through the mass redistribution factor (SAM). This is also the reason why the Italian remedial objectives are slightly less conservative (slightly higher values) compared to the correspondent remedial objectives of level 2 in the English procedure (tab. D3 and D4).

Chapter 5

Sensitivity analysis on the Synthetic case study

5.1 Description of the parameters used for the sensitivity analysis

A sensitivity analysis is conducted to see how much the RA procedures are sensitive to the selected parameters.

The parameters are shown in Tab.22. Some are arbitrarily chosen and others come from the article Connor (1996). Connor gives typical-physical ranges for those parameters.

Tab 22 Parameters used in the sensitivity analysis

<i>Parameter changes for the sensitivity analysis</i>		
<i>Parameter</i>	<i>Value</i>	<i>Reference</i>
GW depth	10 m	Chosen
Infiltration rate	$2,68 \cdot 10^1$ cm/year	Computed by the Italian tool (equ.4.4 [1]). When the net rain is 122 cm/year. Soil type dependent.
Water content	0-346	When the porosity fraction occupied by water (f) varies from 0 to 1.
Hydraulic gradient	0,001-0,1	[23]
Hydraulic conductivity	10^{-3} -1 cm/s	[23]
Soil fraction of organic carbon soil	0,001(-) - 0,03(-)	[23]
Aquifer fraction of organic carbon soil	0,03	[23]
Mixing zone thickness= Initial thickness of the plume	3 m	Chosen equal to the aquifer thickness
Effective porosity	0,35 (-) & 0,01 (-)	[23]
Coefficients of dispersivity	10%, 1%, 0.1% of pathway length	[48]
Coefficients of dispersivity	Xu and Eckstein (1995)	[48]

Parameters are being changed one at a time. However, when a parameter has an indirect or direct influence on another one this also is taken into account, to ensure consistency (Fig.25).

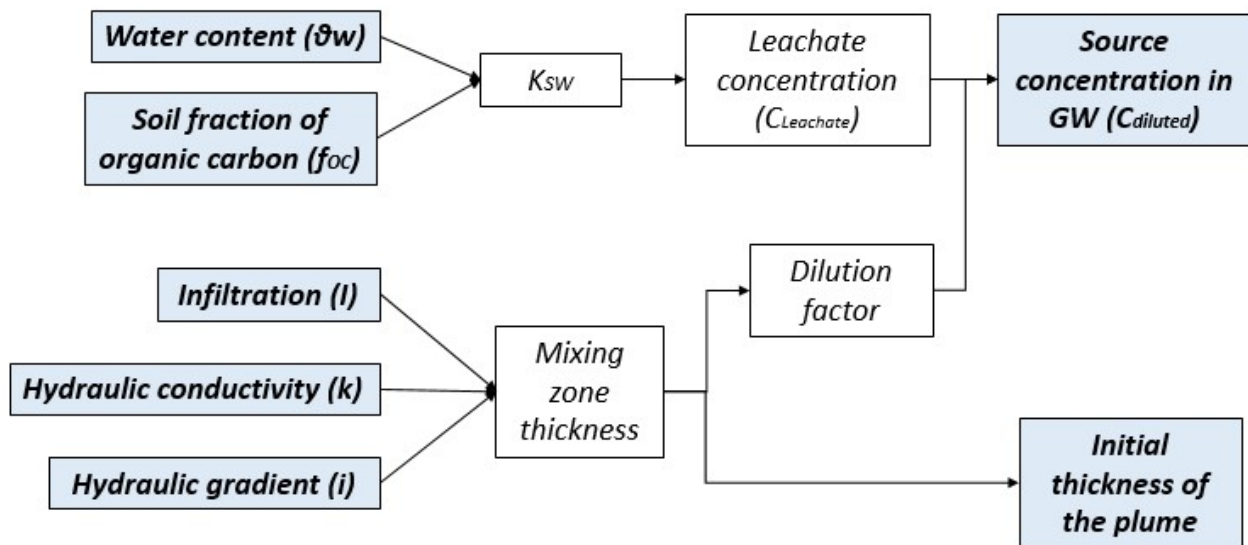


Fig. 25 Influence of parameters to other parameters

5.2 Influence of the chosen parameter in the RA procedure

Results of the sensitivity analysis are discussed for the Walloon procedure. The investigated theoretical model is still the one shown in chapter 4. An exploitable aquifer is considered. The receptor at 100 m downgradient of the source still represents a piezometer at the limit of the parcel.

Only in the occurrence of different results obtained by the Italian and English procedures, these are described. However, throughout the whole discussion, the reader has to keep in mind the different ways of performing RA, as shown in chapter 3 (i.e. Adjusted values (WR) and remedial objectives (IT) although computed similarly, have a slightly different meaning).

Results for the sensitivity analysis can be found in appendix E.

5.2.1 Variation of the depth of the groundwater table

The groundwater table has being varied from 3 m to 10 m of depth. The presence of risk for the groundwater resource for this new depth and for two sources of pollution benzene and anthracene is checked (both considered at 1600 mg/kg).

The UK RT-Worksheet does not request to input this parameter since the mass redistribution factor is absent.

The Italian and Walloon procedures however consider it. In general, it can be stated that if the GW table increases its depth then the risk is reduced and the *soil remedial targets/adjusted values* become less conservative (higher values). This is because the mass redistribution factor decreases (for the GW table at 10 m of depth it is 0,3 (-)).

Still a key difference may be noticed between the Walloon and the Italian procedure.

In fact, the Walloon ESR tool computes leaching time. The RA procedure stops in case the leaching time is higher than 100 years since the hypothesis of “*no serious threat*” has been reached. In consideration of this stopping criteria in the Walloon procedure “*a severe treat*” is found to be absent ($T_{\text{leaching}} = 356$ years) (Tab.24). On the contrary, in the Italian case risk is considered present (Risk factors both for shallow and deep soil are above 1) (Tab.23).

Notice that the Italian assessor could check the leaching time of the contaminant as well with the *Green Ampt* equation. However, this tool is only used for additional evaluations, but it is not used in the computation of risk factors and remedial objectives [62].

Tab 23 Italian results for Benzene when GW is at 10 m of depth

Italian results when the ground water table is at 10 m of depth for Benzene				
Concentration of benzene (mg/kg)	Risk for the groundwater resource (-)		Remediation objective (CSR)	
	Shallow soil	Deep soil	Shallow soil (mg/kg)	Deep soil (mg/kg)
1600	9,14*10 ² *	2,03*10 ³ *	1,75	7,88*10 ⁻¹
*The pink colour highlights the presence of risk.				

Looking at the pollutant anthracene another consideration comes to the mind.

For the Walloon procedure, risk is not present, because the “measured” concentration (1600 mg/kg) is even below the *threshold adjusted value* (5500 mg/kg). The adjusted values are so high because the correspondent *soil-water partition coefficient* is small ($K_{\text{sw}} = 8,35 \cdot 10^{-3}$ kg/l) (Tab.24).

Tab 24 Walloon Results for Benzene and Anthracene when GW table is at 10 m of depth

Walloon Adjusted values and leaching time when GW = 10 m. b. g. l.					
Pollutant	Concentration (mg/kg)	VR (mg/kg)	VS_{Adj} (mg/kg)	VI_{Adj} (mg/kg)	T leachate (years)
Benzene	1600	0,10	3,1	12	356*
Anthracene	1600	0,01	5500 *	11000	Not computed
*The green colour represents the absence of “serious treat”.					

On the contrary, for the Italian procedure such value of anthracene results in being above the value of the *concentration of saturation* implemented in the Risk-net tool (the concentration of saturation occurs whenever water and air in pores are completely saturated by the contaminant).

Different results in terms of risk and remedial targets are found with the Italian tool. This depends on the choice of the assessor in considering active or inactive the option of the concentration of saturation (see Tab.25)

In case the option is inactive (Off), the tool computes risk factors and remedial target based on the entered concentration (1600 mg/kg). In this case, risk is present.

If the option is active (On) risk is absent.

The problem is that since anthracene is solid at ambient temperature, the procedure to check the mobility of the free phase thanks to the ASTM E 20 81 standard cannot be applied. In daily practice additional field measurements should be done.

Tab 25 Italian results for Anthracene when GW is at 10 m of depth

<i>Italian results when GW depth 10 m and Anthracene is 1600 mg/kg</i>					
<i>Pollutant</i>	<i>Option</i>	<i>Factors of risk</i>		<i>Remedial objective (CSR)</i>	
		<i>Shallow soil</i>	<i>Deep soil</i>	<i>Shallow soil (mg/kg)</i>	<i>Deep soil (mg/kg)</i>
Anthracene	Off	1,77	3,93	$9,04 \cdot 10^2$	$4,07 \cdot 10^2$
	On	$4,72 \cdot 10^{-3}$	$1,05 \cdot 10^{-2}$	> Csat	> Csat
*The pink colour represents the presence of risk while the green represents the absence of risk					

Remember that in the Walloon methodology, the ESR procedure can be applied only if the NAPL is absent.

5.2.2 Variation of the Infiltration rate

The infiltration rate increases up to the value of 26, 8 cm/year (which corresponds to the rain event of 122 cm/year). The equation used to find the infiltration rate is still the one given by APAT (2008), as for the first attempt is considered a sand texture type (equation.4.4). Remember that for the same rain event the infiltration is greater for coarse materials.

By increasing the infiltration rate the *soil adjusted standards* (mg/kg d.s.) become more conservative (lower values) and consequently the possible *threat* for groundwater beneath the site increases (i.e. $VS_{Adj} = 0,06$ mg/kg while in the first attempt it was $VS_{Adj} = 0,93$ mg/kg).

This is due to the model as an increasing infiltration decreases the dilution factor (equation 2.9) but it is also physically consistent.

$$Adjusted\ value = \frac{Standard_{GW} * FD}{K_{SW} * F_v} = \frac{Standard_{GW} * \left(1 + \frac{k * i * d_{GW}}{I * L}\right)}{K_{SW} * F_v} \quad (2.9)$$

Moreover, due to the choice of the conceptual model done in chapter 4, the infiltration rate influences “indirectly” in two ways the parameters entered in the saturated part (Fig.25).

Firstly, the infiltration rate is one of the parameters used for the computation of the mixing zone thickness. The mixing zone thickness increases when the infiltration rate increases (from 0,532 to 0,577 m). The initial thickness of the plume is put equal to the mixing zone thickness.

Secondly, according to the specific choice made, the input source concentration in the saturated part is the *diluted concentration*. The *diluted concentration* depends indirectly on the changes of the infiltration rate. It is the ratio of the leachate concentration with the dilution factor. Actually the leachate concentration does not change when the infiltration rate changes but the dilution factor depends on the infiltration rate.

In consideration of these choices when the infiltration rate increases even the final concentration at the receptor increases and therefore the risk too. Consequently, the groundwater remedial targets become more conservative.

5.2.3 Variation of the water content

The influence of the volumetric water content on the risk assessment is investigated by varying the water content from the unrealistic value of 0 (-) up to 0,346 (-) using *equation 4.6* [annex C-2 from [29]]. When saturation (f) varies from 0 to 1. Notice that the residual saturation is not considered.

$$\vartheta_w = f * \left(1 - \frac{\rho}{2,6}\right) \quad (4.6)$$

This variation has a dual consequence in terms of model results and consistency with the reality.

In the RA procedure, a change of the water content has an influence on the computation of the *soil-water partition coefficient* (K_{sw}) (equation 2.1).

$$K_{sw} = \frac{C_L}{C_t} = \frac{1}{[kd + \frac{(\vartheta_w + \vartheta_a * K_H)}{\rho}]} \quad (2.1)$$

In consideration of that, a variation of the *soil-water partition coefficient* has an influence on the evaluation of the *soil-adjusted values* (equation 2.9).

$$Adjusted\ value = \frac{Standard_{GW} * FD}{K_{sw} * F_v} = \frac{Standard_{GW} * \left(1 + \frac{k * i * d_{GW}}{I * L}\right)}{K_{sw} * F_v} \quad (2.9)$$

For equations 2.1 and 2.9 by increasing the water content, the adjusted values become slightly less conservative (slightly higher values). For a water content of 0,304 (-) VS_{Adj} is 1, 2 mg/kg while in the first attempt when ϑ_w is 0,068 (-) VS_{Adj} was 0, 93 mg/kg.

Moreover, once the water content changes even the leachate concentration changes for equation 4.12.

$$C_L \left(\frac{mg}{l}\right) = C_t \left(\frac{mg}{kg}\right) * K_{sw} \left(\frac{kg}{l}\right) \quad (4.12)$$

Increasing the water content (from 0 to 0, 346) the leachate concentration decreases since the *soil-water partition coefficient* decreases at the same time (Fig.26).

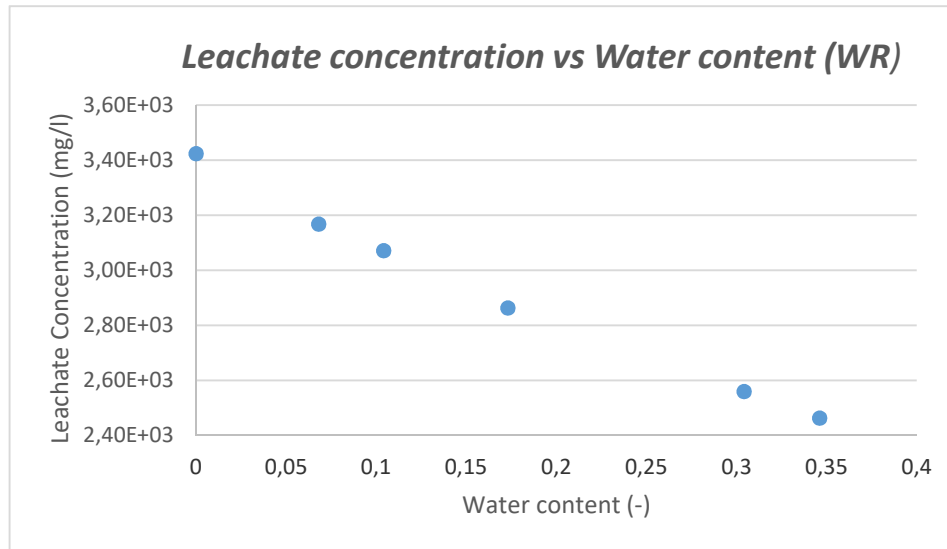


Fig. 26 Variation of the leachate concentration when the water content varies

By decreasing the leachate concentration, the quantity of pollutant entering the saturated zone (*diluted concentration*) decreases as well. This obviously drives to slightly lower values of concentration at the receptor.

For example, for water content equal to 0,304 (-) the maximal concentration at the receptor measured with BIOSCREEN-AT is 52 µg/l, while when the water content was 0,068 (-) it was 64 µg/l.

For the chosen receptor, Risk is present in any case since these values (52 and 64 µg/l) are above the standard for an exploitable aquifer (VS_{GW} 10 µg/l).

On the contrary the remedial target remains the same as in the first attempt (2550 µg/l) since it is computed with a “*trials and error*” simulation.

The same conclusion is obtained in the Italian procedure. The risk factor for the receptor at 100 m downgradient of the source is slightly reduced when the water content increases.

Looking at the mass flux another consideration may be done.

It would be expected that by increasing the water content, the flux increased as well. In fact, the water content is basically the volume of pollutant in which concentrations are diluted. This is not observed.

The mass flux for the mechanism of leaching is computed as the product between the leachate concentration and the infiltration rate.

Changing the water content, the infiltration rate remains fixed to the value of 1,62 cm/year, since it is only dependent on the rain event and texture type, while the leachate concentration decreases.

Mass flux for higher values of water content progressively gets lower because the leachate concentrations decrease (Fig.27).

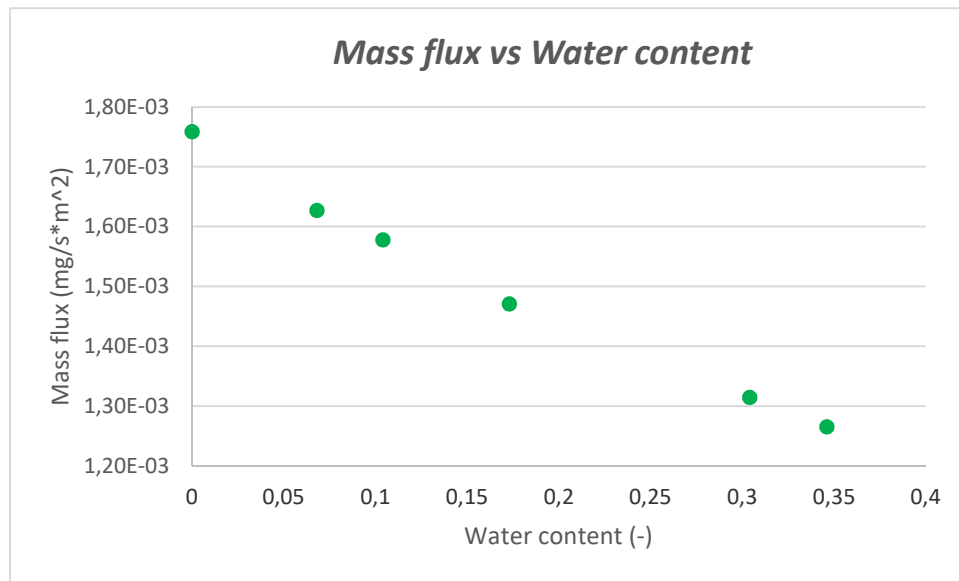


Fig. 27 Variation of the Mass flux when the water content varies

Notice that the same behaviour is observed for the mass discharge, since the source area is fixed (25 m^2).

These results are worth a few considerations.

The first consideration is that modelling the behaviour of the unsaturated zone is difficult since the unsaturated groundwater flow is a non linear problem. In fact, all the hydraulic properties of that zone depend on saturation, water content and capillary pressure.

Moreover, in reality the infiltration velocity depends on several factors: texture type, water content, temperature, organic matter etc.

Physically speaking it would be expected that for lower values of water content, the velocity of the contaminant would be reduced and consequently the pollutant should be less prone to migrate. In fact, if a rain event occurs and in case of dry condition (lower water content), the additional water would tend to fill the pores instead of migrating, therefore less water should reach the ground water table.

Moreover, in reality by decreasing the water content the capillary tension increases. The capillary pressure is the pressure needed by water to penetrate the soil. It is also true, that capillary tension is higher for fine material, which is not actually the case of the synthetic case study (sand-coarse material).

On the other hand, since water content may be seen as the volume of water in which pollutants are diluted, for higher values of water content the soluble contaminants should easily reach the groundwater and the flux should increase [25] [75] [69].

In conclusion, a possible explanation of the different behaviour between reality and the model is that it all may be due to the hypothesis under which the *soil-water partition coefficient* is estimated. In fact, this coefficient relies on the assumption of equilibrium condition in a close system. Which is never the real case.

Notice however, that from a practical point of view, changes on the water content only slightly influence the numeric values of the *adjusted standards* or *leachate concentrations* used in the C-based RA procedures.

5.2.4 Variation of the *Hydraulic gradient and Hydraulic conductivity*

The hydraulic gradient and hydraulic conductivity influence the models in the same way.

The hydraulic gradient is changed using the range given by Connor (1996) (0,001-0, 1 (-)). The hydraulic conductivity is changed basing on the default values of typical Walloon aquifers (10⁻⁵ m/s and 1cm/s) [annex C-2 from [29]].

Influence of the Hydraulic gradient and Hydraulic conductivity on risk assessment in the VZ

Looking at the mechanism of leaching it is observed that when the hydraulic conductivity or hydraulic gradient increase, the *dilution factor* increases as well. Therefore the *soil adjusted values/ remedial targets* become less conservative (higher values correspond to a lower risk) (Tab.26)

This behaviour depends on the model itself equation 2.9.

$$\text{Adjusted value} = \frac{\text{Standard}_{GW} * FD}{K_{SW} * F_v} = \frac{\text{Standard}_{GW} * \left(1 + \frac{k * i * d_{GW}}{I * L}\right)}{K_{SW} * F_v} \quad (2.9)$$

Tab 26 Variation of the adjusted values when the hydraulic conductivity or hydraulic gradient changes (WR)

<i>Adjusted standards when the hydraulic conductivity or hydraulic gradient changes</i>		
<i>Input Parameters</i>	<i>VS_{Adj} (mg/kg)</i>	<i>VI_{Adj} (mg/kg)</i>
First attempt i=8,82*10 ⁻³ and k=10 ⁻⁴ (m/s)	0,92	3,7
i =0,1 (-) and k=10 ⁻⁴ (m/s)	10	42
i = 0,001 (-) and k=10 ⁻⁴ (m/s)	0,11	0,46
i=8,82*10 ⁻³ (-) and k =10 ⁻² (m/s)	92	366
i=8,82*10 ⁻³ (-) and k = 10 ⁻⁵ (m/s)	0,10	0,41

An increase in the *dilution factor* means a reduction in risk. In fact, the dilution factor takes into account the dilution that the contaminant undergoes once it has reached the groundwater table at the interface between unsaturated and saturated soil.

If the dilution factor increases, it means that the contaminant entering in groundwater is more diluted.

The previous statement brings to a paradox. In fact, by the model (equ.2.9) it seems that aquifers, which correspond to higher values of hydraulic conductivity, can be more polluted than aquitards. Which actually is absurd since aquifers are exploited.

This result has to be kept in mind whenever the hydraulic gradient is prescribed by the hydrological context while the user may choose the hydraulic conductivity.

Influence of the Hydraulic gradient and Hydraulic conductivity on risk assessment in the saturated zone

Looking at the path of pollutant across groundwater it is possible to make other interesting observations.

In consideration of the choices in the conceptual model, the hydraulic gradient and the hydraulic conductivity influence the values of contaminant concentrations modelled in the saturated zone (Fig.25).

Firstly because both the hydraulic conductivity and the hydraulic gradient are used for the computation of the mixing zone thickness. Since the mixing zone thickness is put equal to the initial thickness of the plume when one of those parameters varies the initial thickness of the plume varies as well.

Secondly, the *diluted concentration* is used as source concentration in the saturated zone. The diluted concentration varies depending on the *dilution factor*. This last one varies as a function of the hydraulic gradient and hydraulic conductivity.

Influence of the Hydraulic gradient on risk assessment in the saturated zone

Looking at the change in the hydraulic gradient, the following has been noticed.

For the above choice, the initial source concentration differs depending on the hydraulic gradient. In fact, when the gradient is 0,001 (-) the source concentration is 138 mg/l, while when the gradient is 0,1 the concentration is 1,54 mg/l. This is because the dilution factor changes by two orders of magnitude (Tab. 27).

Tab 27 Concentration at the receptor when the hydraulic gradient varies (WR)

<i>Hydraulic conductivity vs variation of concentration at the receptor (WR)</i>				
<i>Hydraulic gradient (-)</i>	<i>Dilution factor (-)</i>	<i>Initial thickness of the plume (m)</i>	<i>Source concentration (C_{Diluted}) (µg/L)</i>	<i>Concentration at the receptor (µg/L)</i>
0,001	23	0,555	138000	513
0,1	2062	0,529	1536	6
*The pink colour represents the presence of risk while the green represents the absence of risk				

When the highest value of the gradient is used (0,1 (-)) the concentration at the receptor decreases and no risk is observed (C= 6 µg/l). This is true in the Walloon procedure.

In the Italian case instead, the computed risk factor is still above 1 (Tab.5 appendix E). The difference between the Italian and the Walloon procedure occurs because they have different GW standards and different implemented parameters for benzene. In fact, the Italian standard is always 1 µg/l while in the Walloon case for the limit of the parcel of an exploitable aquifer is 10 µg/l.

On the contrary when the gradient decreases (0,001 (-)) the concentration at the receptor increases and risk is observed in all three countries.

Influence of the Hydraulic conductivity on assessing risk in the saturated zone

Looking at the change in the hydraulic conductivity, the following has been noticed. The source concentration in groundwater varies as shown in Tab.28.

Tab 28 Leachate and diluted concentration when the hydraulic conductivity varies (WR)

Data used for sensitivity analysis in the saturated zone when the hydraulic conductivity varies (WR)				
Hydraulic conductivity (m/s)	Dilution factor (-)	Initial thickness of the plume (m)	C_{leachate} (mg/l)	C_{diluted} (mg/l)
10 ⁻⁵	20,2	0,558	3168	156,83
10 ⁻⁴	184	0,532	3168	17,22
10 ⁻³	1820	0,529	3168	1,74
10 ⁻²	18200	0,529	3168	0,17

The graph (Fig.28) shows the evolution of the concentration at the receptor for a simulation time of 100 years when the hydraulic conductivity varies between 10⁻⁵- 10⁻² m/s. The source concentration (C_{diluted}) is lower for higher values of the hydraulic conductivity since the correspondent dilution factor is higher (Tab.28).

The concentrations at the receptor associated to the higher values of the hydraulic conductivity (10⁻³ m/s and 10⁻² m/s) are below the Walloon groundwater standards (both exploitable or not exploitable aquifer (10-40 µg/l)). This means that no risk is present for the receptor 100 m downgradient.

For the same reasons as described for the hydraulic gradient, the Italian case shows risk even for the higher values of the hydraulic conductivity since the ground water standard is different.

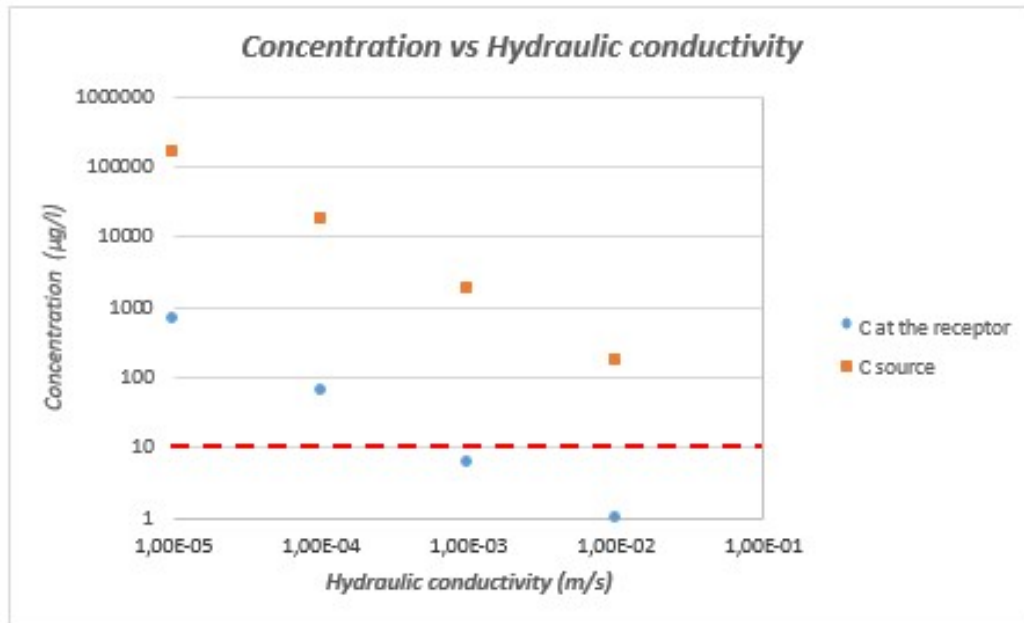


Fig. 28 Concentration at the receptor vs Hydraulic conductivity (WR)

Notice that in the Italian procedure, since the values of concentration simulated at the receptor are obtained in steady state, the assessor could make additional considerations on the time necessary to reach these values of concentration.

In fact risk differs when such value of concentration arrives at the receptor after 1 day or after 2000 years.

C-based vs F-based approaches for assessing Risk

Traditional *C-based approaches* only compute concentrations at the receptor, which have to be compared with standards by the assessor. For example, in the theoretical case, with this approach no risk has assessed for higher values of the hydraulic conductivity.

Different considerations could be expressed looking at the same problem with a *F-based approach*. In fact, the mass flux and mass discharge slightly increase when the hydraulic conductivity increases. This occurs although the initial source concentration (C_{diluted}) and initial thickness of the plume have decreased (Tab.29).

Notice that an increase of the mass flux may be associated to a potential increase of the risk, which is not addressed with the *C-based approach*.

However, remember that, this value of mass discharge is computed at the beginning of the plume, while the concentration is computed at the receptor after a simulation time of 100 years.

Much more appropriate should be the possibility of measuring mass flux data in transects along the path between the source and the receptor, in order to monitor its evolution.

Tab 29 Walloon results in term of Concentration and mass flux when the Hydraulic conductivity varies

Concentration and Mass flux & Mass discharge vs Hydraulic conductivity				
Hydraulic conductivity (m/s)	Concentration at the receptor ($\mu\text{g/l}$) (T=100 years)	C_{diluted} (mg/l)	Mass flux ($\text{mg/s}\cdot\text{m}^2$)	Mass discharge (mg/s)
10^{-5}	667	156,83	$1,38\cdot 10^{-2}$	$3,86\cdot 10^{-2}$
10^{-4}	64	17,22	$1,52\cdot 10^{-2}$	$4,04\cdot 10^{-2}$
10^{-3}	6	1,74	$1,54\cdot 10^{-2}$	$4,06\cdot 10^{-2}$
10^{-2}	1	0,17	$1,54\cdot 10^{-2}$	$4,06\cdot 10^{-2}$
*The pink colour represents the presence of risk while the green represents the absence of risk.				

In conclusion for the choices made it has been shown that:

For the leaching mechanism, higher remedial targets (and therefore lower risk) are found related to higher values of the hydraulic conductivity.

As well as for the movement of the pollutant in the saturated part, lower concentrations at the receptor (and therefore lower risk) are found for higher values of the hydraulic conductivity.

In both cases, the key element is the presence of the dilution factor.

This dilution factor is computed automatically by all the tools and cannot be changed. The procedures do not give an upper boundary for this parameter.

Only in the Walloon procedure [annex C-2 from [29]] typical values of dilution factor are given in relation of the aquifer type. For example, the dilution factor for a gravel aquifer is around 108. This maybe means that, physically speaking, the dilution factor found for a hydraulic gradient of 1 cm/s, which is 18200, is not really realistic.

Consequently, the *diluted concentration* associated to the higher dilution factors and the correspondent concentration at the receptor and mass discharge might be not really realistic as well.

Practical consideration on the choice of the hydraulic conductivity

Finally, a practical problem arises in case a lower value of hydraulic conductivity is used. This value is 10^{-8} m/s and is the lower bound limit given by Connor (1996).

For the leaching case the Walloon ESR tool does not compute the dilution factor corresponding to the hydraulic conductivity of 10^{-8} m/s (with *equation 2.7 a*) it should be 1,1) but it fixes the dilution factor to the lower bound of 12. The same problem is noticed when the hydraulic conductivity is equal to 10^{-6} m/s and 10^{-7} m/s.

This is because, for the Walloon tool, a not exploitable aquifer has a value of the hydraulic conductivity lower than 10^{-5} m/s [annex C-2 from [29]] and a default dilution factor of 12.

The Italian and English tools do not have this limit.

This is why the sensitivity analysis has been performed in the range 10^{-5} m/s to 10^{-2} m/s.

5.2.5 Variation of the Mixing zone thickness-Initial plume thickness

The manuals [62][37] state that in case the computed mixing zone thickness (equation 4.8) exceeds the aquifer thickness, the aquifer thickness is used as value for the mixing zone thickness (i.e. this is the case when k is 10^{-8} m/s). In reality, such condition may occur for thin aquifers.

Additional problems occur since for the conceptual choice the mixing zone thickness is used as initial thickness of the plume.

In the sensitivity analysis, the initial plume thickness is put equal to the aquifer thickness (for the synthetic case study 3 m).

In such a way though, the inequality of the mass discharge is not respected.

In fact, the mass discharge in the vadose zone (0,041 mg/s) is lower compared to the mass discharge in the saturated zone (0,227 mg/s). This is physically inconsistent.

Furthermore, with that choice there are also some practical problems.

The English tool gives a signal of error when the initial thickness of the plume is equal to the thickness of the aquifer (“*Dispersed plume thickness exceeds aquifer thickness reduce vertical dispersivity*”). This issue may be avoided by imposing a vertical dispersivity equal to 10^{-15} which is equivalent to neglecting the vertical dispersivity.

In the Italian procedure, no signal of error is given out, since the Italian tool has also the attenuation factor DAF3.

Finally in the BIOSCREEN-AT tool the aquifer thickness is not requested. It is like considering a infinitely thick aquifer. For this reason the initial thickness of the plume does not contrast with the thickness of the aquifer.

5.2.6 Variation of Soil fraction of organic carbon

The fraction of organic carbon is changed basing on the range given by Connor (1996) (0,03 -0,001 (-)). The value 0,001 represents the critical organic carbon content below which the partition equation is not applicable. Below the critical value, the sorption to mineral surfaces becomes significant [69].

Tab 30 Adjusted values when the soil fraction of organic carbon changes (WR)

Walloon results when the soil fraction of organic carbon varies			
<i>f_{oc} = 0,03 (MO = 5,2)</i>			
<i>First attempt Clean up values (mg/kg)</i>		<i>Clean up values (mg/kg)</i>	
VS _{Adj} = 0,93	VI _{Adj} = 3,7	VS _{Adj} = 4,2	VI _{Adj} = 17
<i>f_{oc} = 0,001 (MO = 0,2)</i>			
<i>First attempt Clean up values (mg/kg)</i>		<i>Clean up values (mg/kg)</i>	
VS _{Adj} = 0,93	VI _{Adj} = 3,7	VS _{Adj} = 0,27	VI _{Adj} = 1,1

The fraction of organic carbon (f_{oc}) represents the portion of the organic matter that is available to adsorb the investigated organic contaminant. This is why higher value of this factor is associated to the upper part of the soil.

In consideration of this, it is noticed that when the organic carbon fraction increases (0,03 (-)), the correspondent *adjusted standards* become less restrictive (their values increase compared to the first attempt). While on the contrary if the fraction of organic carbon is reduced to 0,001 (-) the *adjusted standards* become more conservative (Tab.30).

When the fraction of organic carbon changes even the leachate concentration changes (Tab. 31). If the value of the fraction of organic carbon increases (0,03 (-)) the leachate concentration decreases, since by model and definition most of the pollutant remains adsorbed in the soil.

Tab 31 Values of the leachate concentration when the fraction of organic carbon varies (WR)

Leachate concentration comparison when the fraction of organic carbon in soil changes			
Countries	$C_{leachate}$ 1 attempt ($f_{oc}=0,006$) (mg/l)	$C_{leachate}$ ($f_{oc}=0,03$)(mg/l)	$C_{leachate}$ ($f_{oc}=0,001$) (mg/l)
Walloon Region	$3,168 \cdot 10^3$	$7,08 \cdot 10^2$	$1,10 \cdot 10^4$

When the fraction of organic carbon increases, the leachate concentration decreases along with the source concentration in the saturated zone ($C_{Diluted}$).

In consideration of this, it has been observed that a lower value of concentration at the receptor is associated to a higher value of the fraction of organic carbon.

Finally, notice that for the Italian case when f_{oc} is equal to 0,001 (-) the entered concentration is above the concentration of saturation for benzene ($1,7 \cdot 10^3$ mg/kg d.s.). Different results are obtained by having either active or inactive the option of considering the concentration of saturation (Tab.5 appendix E).

Since benzene is liquid at ambient temperature, the NAPL mobility can be checked when the option of considering the *concentration of saturation* is active. For the unsaturated soil a value of $7,54 \cdot 10^3$ mg/kg d.s. is obtained and for the saturated part $8,66 \cdot 10^2$ mg/kg d.s.. Above these values, the Italian procedure assumes that the free phase becomes mobile.

5.2.7 Variation of Coefficients of dispersivity

The coefficients of dispersivity are changed basing on the equations implemented in the English RT-Worksheet [48].

Tab 32 Coefficients of dispersivity dependent on different equations

Coefficients of dispersivity for a path length of 100 m			
Dispersivity coefficient (m)	1 attempt (BIOSCREEN-AT)	10%, 1% and 0,1% of the path length	Xu & Eckstein
Longitudinal	10	10	4,42
Transversal	3,3	1	0,42
Vertical	0,56	0,1	0,042

First is considered a longitudinal, transversal and vertical dispersivity equal to 10% - 1% - 0, 1% of the distance between the source and the receptor. Then the Xu & Eckstein (1995) equation is used. The values are given in Tab. 32.

Results are shown for the modified Domenico model in transient state for a simulation time of 100 years where biodegradation is avoided (Tab.33). The source concentration in ground water is the *diluted concentration* equals to 17, 21 mg/l. The Remedial targets are obtained with a “trial and error” simulation, considering the GW standard for an exploitable aquifer.

Tab 33 Concentration at the receptor and remedial objectives f (coefficients of dispersivity) (WR)

Concentration at the receptor (100 m) for different dispersivity choices and remedial objectives (WR)					
1 attempt		10%, 1% and 0,1% of the plume length		(Xu & Eckstein (1995))	
$C_{100\text{ m}}$ (mg/l)	RT (mg/l)	$C_{100\text{ m}}$ (mg/l)	RT (mg/l)	$C_{100\text{ m}}$ (mg/l)	RT (mg/l)
$6,4 \cdot 10^{-2}$	2,5	$2,74 \cdot 10^{-1}$	$6,02 \cdot 10^{-1}$	$5,56 \cdot 10^{-1}$	$2,96 \cdot 10^{-1}$

Looking at Tab.33 is observed that the concentration at the receptor (C_{100}) is 4 (first choice) and 9 (second choice: Xu & Eckstein (1995)) times higher than the value found in the first attempt.

In conclusion, in all three countries, for higher values of coefficients of dispersivity, it is observed that:

- The concentration at the receptor is reduced.
- The attenuation factor increases.
- The remedial objectives become less conservative.

Notice that all the values of longitudinal dispersivity of Tab.32 are associated to high Peclet numbers and so the discrepancy between exact and approximate solution is still negligible.

5.2.8 Variation of the *Organic carbon fraction in the aquifer and effective porosity*

The fraction of organic carbon in the aquifer is changed with the Italian default value of 0, 03 (-). While the aquifer effective porosity is changed basing on the range given by Connor (1996) (0, 01-0, 35).

The aquifer organic carbon fraction and the aquifer effective porosity have an influence on the Retardation factor (equation 5.1).

$$R = 1 + \frac{(Kd \cdot \rho)}{n_e} \quad (5.1)$$

Where R is the retardation factor [-], Kd the partition coefficient [L^3/M], ρ the density [M/L^3], n_e the effective porosity.

For the steady state case, the retardation factor does not influence the simulated concentration at the receptor, while for the transient state it creates a delay.

However, for the specific case since in the transient simulation the steady state is reached after a few years, the retardation does not affect the results.

Notice that, this result depends on the assumption in the model of dealing with an infinite source. This is not depleted during the entire simulation time by degradation or volatilization. This choice is conservative, particularly when dealing with small sites.

5.3 Conclusions of the sensitivity analysis

Based on sensitivity analysis, some considerations can be made.

Conceptual choices influence results

As for the results of the theoretical case (chapter 4), the fact of dealing with a synthetic case study creates some problems in the choice of the entered parameters and on the way these parameters influence each other.

In fact, for the lack of real data and in order to respect the mass discharge inequality the initial thickness of the plume has been put equal to the mixing zone thickness and the *diluted concentration* is used as source concentration in the saturated zone.

These two values both depend on the variation of the *dilution factor*.

This is particularly evident when the Infiltration rate, hydraulic conductivity and hydraulic gradient have been changed.

Obviously, the diluted concentration depends on the variation of the leachate concentration too.

Considering the mechanism of leaching the use of the *dilution factor* drives to the paradox that for higher values of the hydraulic conductivities-which correspond to aquifers- the *adjusted values* become less conservative. This means that aquifers can be more polluted than aquitards and this is quite absurd.

On the other hand for the transport of the pollutant in the saturated zone, the choice of using the *diluted concentration* drives to the statement that lower source concentration in groundwater and consequently lower risk, are associated to higher values of the *dilution factor* (i.e. higher k or i). Actually such *diluted concentration* changes by several order of magnitude depending on the dilution factor. As already pointed out, the *dilution factors* found for the higher values of hydraulic conductivity and hydraulic gradient might not be realistic.

Finally, as already stated, in reality the initial plume thickness and the concentration in groundwater are directly measured.

Consideration in terms of Mass flux

As noticed, the choice of water content slightly changes the *soil adjusted values* and the *leachate concentration*.

If on the contrary the problem is approached with a “*F-based vision*”, it is noticed that the mass flux decreases with the increment of water content and this behaviour, as already discussed, seems in contrast with reality but it may be due to the assumption of equilibrium done while building the *soil-water partition coefficient*.

Finally, the mass flux may represent an additional contribution while assessing the presence of risk. As observed, in spite of reduction of the *diluted concentration* and the initial thickness of the plume, for higher values of hydraulic conductivity the mass flux, computed at the beginning of the plume, slightly increases. This means that the risk may potentially increase as well. Even if the concentration at the receptor reduces.

This highlights once again the fact that having low concentration does not always mean having low risk. However, remember that this mass discharge is computed at the beginning of the plume and it may evolve downgradient of the source.

Parameters which most influence the results of the RA procedures

In summary, based on the sensitivity analysis, the factors, which mainly influence the RA procedure, are as following:

- *Hydraulic conductivity;*
- *Hydraulic gradient;*
- *Infiltration rate;*

In fact, Darcy velocity has the greatest effect on the dilution factor, followed by the infiltration rate.

- *Organic carbon fraction in the soil;*
- *Choice of the coefficients of dispersivity.*

In case of lack of real data, they have to be chosen very carefully. Their choice in fact greatly influence the simulated concentration at the receptor and the computation of remedial targets. Among the tested equations, for the same case, the one proposed by BIOSCREEN-AT drives to less conservative results (higher remedial targets and lower concentration at the receptor).

- *Variation of the groundwater table depth.*

This parameter highlights the difference between the Walloon and the Italian procedures (i.e. leaching time and concentration of saturation).

It has also highlighted the fact that, the obtained results and the considerations made are strongly related to the pollutant type and not only to the choice of the model parameters (benzene vs anthracene).

Chapter 6

Conclusions and outcomes

The objective of the present work is to investigate simplified Risk Assessment procedures for pollutant leaching to and migration across groundwater.

The comparison has been performed firstly carrying out a bibliographic research on technical manuals and norms. The investigation has focused particularly on three European countries: Italy, United Kingdom and Walloon Region.

Then the corresponding European tools have been tested on both a synthetic and a real case.

These two cases allowed to show theoretical and practical differences among the European procedures. Moreover, they have highlighted the fact that results and conclusions are strongly dependent on the pollutant's type (i.e. benzene, heavy metals, and anthracene) even if all the other parameters in the synthetic case do not change.

What is immediately evident at first sight from the analysis of the three European RA tools is their simplicity in use.

They simulate the transport of the contaminant in the vadose and saturated zone by the use of analytical equations based on conservative and simplified assumptions. This is one of the main advantages compared to numerical models since they do not require input of too many data. This is the main reason why they are so widely used by Countries, particularly at the early stages of site investigation, when info relatively to the subsoil are limited.

The main problem of such RA tools is that they do not allow to take into account complex situations such as the presence of low permeability zones, zones of preferential flow, etc.

Moreover, Walloon ESR v. 2.0.4 and Italian Risk-net v. 2.1 tools have implemented chemical and toxicological databases, which could represent an additional advantage for the user and actually allow to save a lot of time. On the other hand, the English RT-Worksheet v. 3.2 and BIOSCREEN-AT 1.43_FR_v.1.1 leave a higher degree of freedom in terms of data editing and therefore they may be more easily adaptable to different circumstances.

However, the results of the sensitivity analysis have shown that the user has to pay great attention while entering data. This is particularly true for the *Darcy velocity*, the *infiltration rate*, the *coefficients of dispersivity* and the *fraction of organic carbon*. In fact, these parameters have a great influence on the computation of factors as *dilution factor*, *dilution/attenuation factor* and *soil-water partition coefficient*. Consequently, they have a great influence on the evaluation of risk as well.

The investigated RA procedures turned out to be quite similar in the way they assess risk. In order to estimate the presence of risk, the methodology compares *site and pollutant specific standards and/or remedial objectives* with the measured concentrations. If the presence of risk or “*serious threat*” emerges, then the clean up objective has to be estimated.

Remedial targets are always obtained taking into account the selected groundwater standard and the process of attenuation that the contaminant might undergo while moving in the unsaturated and saturated zones (partitioning, dilution, attenuation...). The only exception is represented by the Walloon case, where the clean up goals for soil depend also on the site pollution age.

Moreover, as constantly highlighted throughout the document, there are also differences among countries in terms of risk evaluation. For example, the Walloon procedure is the only one which makes a distinction between exploitable and not exploitable aquifer and computes the leaching time as a step of the RA procedure. The Italian methodology on the other hand, is the only one that makes a distinction between deep and shallow soil and that takes into account the concentration of saturation. While the English procedure is the only one that computes remedial targets for each level of the assessment.

Furthermore, the results of the synthetic case study have shown that among tools and procedures there is more discrepancy when the movement of the pollutant occurs in the vadose zone. Actually different factors and adjustments are requested by the various countries. Particularly evident is the lack of *mass redistribution factor* in the English procedure as well as the request of correcting the *soil-water partition coefficient* by the Walloon methodology. These aspects also have an influence on the way risk is estimated and on the possible conceptual choices.

Concerning the saturated zone, tools use different transport models with simulation in transient and/or steady state. For the specific synthetic case, the steady state is reached quite soon.

Moreover, the difference between an approximate and exact solution is negligible if concentrations are computed for centreline plumes and advection is high (high Péclet number).

Notice that it is not possible to recommend “the best” tool and procedure since each methodology matches its own country goals and norms.

However, as the real case has shown, under the same conditions and knowing all the parameters, the English procedure results in being the most conservative. Firstly because it assesses risk for each level of the assessment (in the first level the most conservative remedial target among all the countries is obtained) and secondly because the mass redistribution factor is always equal to 1.

On the other hand, it does not allow estimating the leaching time.

As highlighted several times, the fact of dealing with a theoretical case has caused a few difficulties in the choice of some parameters, particularly relatively to those used in the saturated zone. These are *the initial thickness of the plume* and the *source concentration in groundwater*. As a matter of fact usually these parameters are obtained by real measurements.

In the synthetic case physical coherence and respect of the mass discharge between the unsaturated and saturated zone represents a peculiar issue. This is why the *mixing zone thickness* and the so called *diluted concentration* are respectively used.

Such an issue drives to the consideration that probably a combined approach linking the mechanism of leaching in the vadose zone and the transport of contaminant in the saturated part would be more suitable. The development of such approach/tool is desirable in the next future.

The sensitivity analysis has brought to attention that *F-based approaches* may give additional elements to establish the presence of risk. In fact, as shown for example while varying the hydraulic conductivity, even if concentrations decrease, the flow may be still relevant and represent a risk. The best way to proceed might be to have the possibility of simulating and computing the mass discharge in transects located along the entire plume.

Another improvement, in the evaluation of risk could be represented by the application of the *F-based approach* to the same synthetic case in order to compare mass flux's results with those coming from the traditional RA *C-based approaches*.

However, notice that *F-based* approaches are information intensive. In fact, they require concentrations measured at different depths and at representative locations. This is why they are not so widespread.

In perspective it could also be interesting to model the same synthetic case study with a numerical model and compare the obtained results with the ones produced by the three RA tools.

This would allow to mark differences. In particular it would help to assess the reliability and influence of some factors used in the analytical procedures, such as the *dilution factor*. In fact, as emphasized throughout the whole document, the dilution factor greatly influences results and may even bring to a paradox (i.e. aquifers may result more polluted than aquitards).

The motion of the contaminants in the unsaturated and saturated zone is not well simulated by all different software. A possible alternative could be the use FEMWATER model.

FEMWATER is a three-dimensional, finite element, groundwater model. It is a suitable tool for flow and transport simulation in both the saturated and the unsaturated zone. FEMWATER is in GMS (Groundwater modelling system) [4] [5] [6] [53].

The software is developed by the U.S. Army Environmental Center and the Athens Ecosystem Research Division, Office of Research and Development, U.S. Environmental Protection Agency. The initial aim was to model salinity intrusion and other density-dependent contaminants.

In the technical report of the software [53] advice on how to model different possible circumstances (i.e. salinity intrusion, remediation etc.) is given.

For example, it is shown a possible way to model a non-point chemical spill under transient conditions. This might be the starting point for modelling the synthetic case study. In fact the exemplum in the document shows a contaminant spilled on the entire ground surface where a rainfall event occurred. The receptor is represented by a well located in the centre of the model.

Obviously while using a numerical model great care has to be paid in the choice of the grid and number of iterations in order to avoid numerical instability problems but at the same time be as accurate as possible.

Moreover, additional data of both fluids and soil for the entire mesh and for each soil and aquifer types are requested by FEMWATER. Some of them i.e. tortuosity, compressibility are not requested at all by the RA tools.

Finally, particular care has to be paid when modelling the unsaturated zone. In fact, the user has to specify three curves defining how the moisture content, relative hydraulic conductivity and water capacity vary in function of the pressure head. Generally, they refer to the van Genuchten functions (1980) [71].

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Appendices

Appendix A

Tools screenshot

Risknet-tool

The Italian Risk-net tool may be used for computing Risk factors and Remedial objectives (Fig.1). The Input parameters for the unsaturated zone are shown in Fig.2 and for the saturated zone in Fig.3. The concentrations comparison is shown in Fig.4.

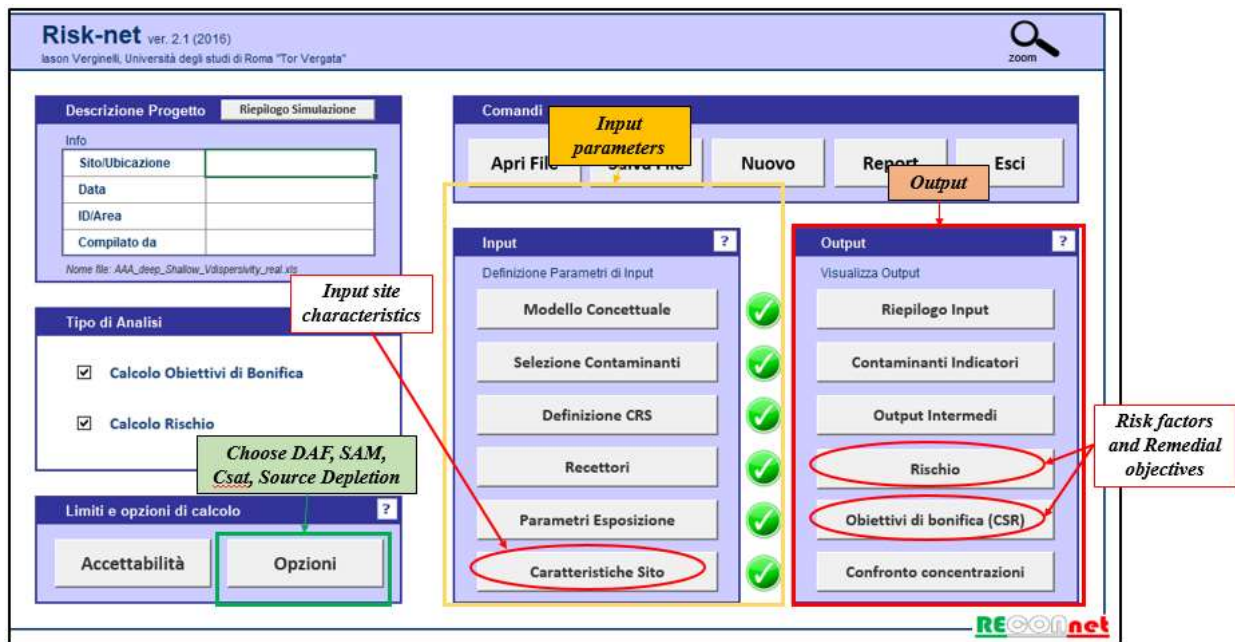


Fig. 1 Risk-net Inputs-Outputs

Zona Insatura		U.M.	Default ISpra	Default ASTM	Valore	Check
L_s (SS)	Profondità del top della sorgente nel suolo superficiale rispetto al p.c.	m	0	0	0,0	ok
L_s (SP)	Profondità del top della sorgente nel suolo profondo rispetto al p.c.	m	1	1	1,0	ok
d	Spessore della sorgente nel suolo superficiale (insaturo)	m	1	1	1,0	ok
d_s	Spessore della sorgente nel suolo profondo (insaturo)	m	2	2	2,0	ok
L_{GW}	Profondità del piano di falda	m	3	3	3,0	ok
h_v	Spessore della zona insatura	m	2,812	2,95	2,9	ok
$f_{oc, SS}$	Frazione di carbonio organico nel suolo insaturo superficiale	g-C/g-suolo	0,01	0,01	0,006	ok
$f_{oc, SP}$	Frazione di carbonio organico nel suolo insaturo profondo	g-C/g-suolo	0,01	0,01	0,006	ok
t_{LF}	Tempo medio di durata del lisciviato	anni	25	25	30,0	ok
pH	pH	adim.	6,8	6,8	6,8	ok
ρ_s	Densità del suolo	g/cm ³	1,7	1,7	1,7	ok
θ_e	Porosità efficace del terreno in zona insatura	adim.	Selezione Tessitura --- CUSTOM --- <input type="checkbox"/> Lente tra sorgente e p.c. Tessitura selezionata: --- CUSTOM ---		0,346	ok
θ_w	Contenuto volumetrico di acqua	adim.			0,068	ok
θ_a	Contenuto volumetrico di aria	adim.			0,278	ok
θ_{wcap}	Contenuto volumetrico di acqua nelle frangia capillare	adim.			0,317	ok
θ_{acap}	Contenuto volumetrico di aria nelle frangia capillare	adim.			0,024	ok
h_{cap}	Spessore frangia capillare	m	Tessitura selezionata: --- CUSTOM ---		0,1	ok
I_{ef}	Infiltrazione efficace	cm/anno	30	<input type="checkbox"/> Calcolato	1,62E+00	ok
P	Piovosità	cm/anno	---	---	122,0	ok
$\eta_{outdoor}$	Frazione areale di fratture outdoor (solo per lisciviazione)	adim.	1	1	1,0	ok

Fig. 2 Risk-net Input Parameters for the unsaturated zone

Zona Satura			Default ISPRA	Default ASTM	Valore	Check
W	Estensione della sorgente nella direzione del flusso di falda	m	45	45	5,0	ok
S _w	Estensione della sorgente nella direzione ortogonale al flusso di falda	m	45	45	5,0	ok
d _a	Spessore acquifero	m	---	---	3,0	ok
K _{sat}	Conducibilità idraulica del terreno saturo	m/s	--- CUSTOM ---		1,00E-04	ok
i	Gradiente idraulico	adim.	---	---	0,00882	ok
v _{gw}	Velocità di Darcy	m/s	7,90E-07		8,82E-07	ok
v _e	Velocità media effettiva nella falda	m/s	2,20E-06	2,20E-06	2,21E-05	ok
θ _{e sat}	Porosità efficace del terreno in zona satura	adim.	0,353	0,353	0,04	ok
f _{oc}	Frazione di carbonio organico nel suolo saturo	g-C/g-suolo	0,001	0,001	0,001	ok
POC	Distanza recettore off site (DAF)	m	100	100	100,0	ok
a _x	Dispersività longitudinale	m	10		1,00E+01	ok
a _y	Dispersività trasversale	m	3,3	<input type="checkbox"/> Calcolati	3,30E+00	ok
a _z	Dispersività verticale	m	0,5		5,60E-01	ok
δ _{gw}	Spessore della zona di miscelazione in falda	m	2	<input checked="" type="checkbox"/> Calcolato	5,32E-01	ok
LDF	Fattore di diluizione in falda	adim.	---	---	1,84E+02	ok

Fig. 3 Risk-net Input Parameters for the saturated zone

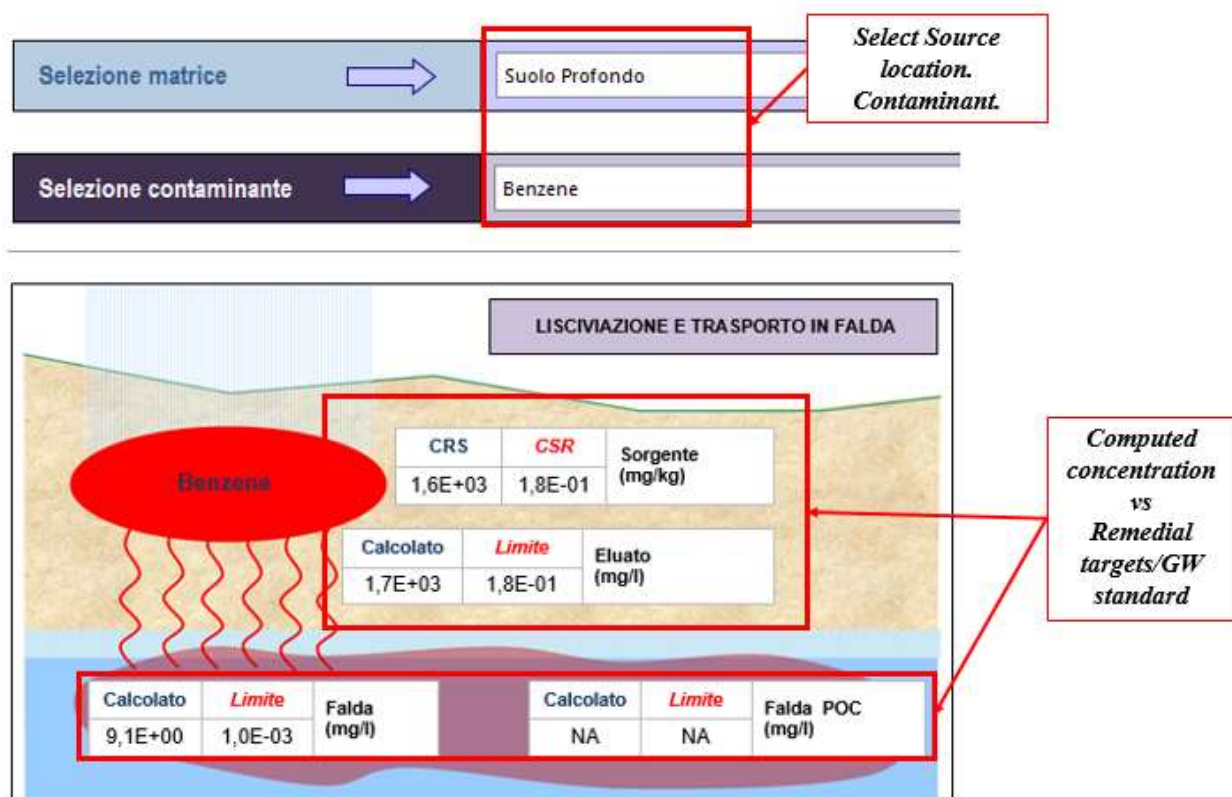


Fig. 4 Risk-net: Concentrations' comparison

RT-Worksheet tool

The English RT-worksheet is used to compute remedial targets for soil (Fig.5, 6, 7) and for groundwater (Fig.8).

Level 1 - Soil

Input parameters

Select the method of calculating the soil water Partition Co-efficient by using the pull down menu below

User specified value for partition coefficient

Contaminant	Pollutant	Value	Unit	Source of parameter value
Target concentration	C _T	0	mg/l	
Input Parameters				
<i>Standard entry</i>				
Water filled soil porosity	θ _w	0.00E+00	fraction	This sheet calculates the Level 1 remedial target for soils(mg/kg) based on a selected target concentration and theoretical calculation of soil water partitioning. Three options are included for determining the partition. The measured soil concentration as mg/kg should be compared with the Level 1 remedial target to determine the need for further action.
Air filled soil porosity	θ _a	0.00E+00	fraction	
Bulk density of soil zone material	ρ	0.00E+00	g/cm ³	
Henry's Law constant	H	0.00E+00	dimensionless	
<i>Entry if specify partition coefficient (option)</i>				
Soil water partition coefficient	K _d	0.00E+00	l/kg	
<i>Entry for non-polar organic chemicals (option)</i>				
Fraction of organic carbon (in soil)	f _{oc}		fraction	
Organic carbon partition coefficient	K _{oc}		l/kg	
<i>Entry for ionic organic chemicals (option)</i>				
Sorption coefficient for neutral species	K _{ow,n}		l/kg	
Sorption coefficient for ionised species	K _{ow,i}		l/kg	
pH value	pH		pH units	
Acid dissociation constant	pK _a			
Fraction of organic carbon (in soil)	f _{oc}		fraction	
partition coefficient used in Level Assessment	K _d	0.00E+00	l/kg	Specified value

Level 1 Remedial Target

Level 1 Remedial Target	#DIV/0!	mg/kg
	or	
	0	mg/l

Output RT1

Site being assessed:

Completed by:

Date:

Version: 1.00

Fig.5 RT-Worksheet Input and Output: Level 1-Soil

Level 2 - Soil

Input parameters

from Level 1

This sheet calculates the Level 2 remedial target for soils (mg/kg) or for pore water (mg/l)

The measured soil concentration as mg/kg or pore water concentration should be compared with the Level 2 remedial target to determine the need for further action. Equations presented in 'Hydrogeological risk assessment for land contamination' (Environment Agency 2006)

Contaminant	Pollutant	Value	Unit	Source of parameter value
Target concentration	C _T	0	mg/l	
Input Parameters				
<i>Standard entry</i>				
Infiltration	I _{inf}	0.00E+00	m/d	
Area of contaminant source	A	0.00E+00	m ²	
<i>Entry for groundwater flow below site</i>				
Length of contaminant source in direction of groundwater flow	L	0.00E+00	m	
Saturated aquifer thickness	d _a	0.00E+00	m	
Hydraulic Conductivity of aquifer in which dilution occurs	K	0.00E+00	m/d	
Hydraulic gradient of water table	i	0.00E+00	fraction	
Width of contaminant source perpendicular to groundwater flow	w	0.00E+00	m	
Background concentration of contaminant in groundwater beneath site	C _u	0.00E+00	mg/l	
<i>Define mixing zone depth by specifying or calculating depth (using pull down list)</i>				
Enter mixing zone thickness	M _z	Specify	m	
Calculated mixing zone thickness	M _c		m	
Calculated Parameters				
Dilution Factor	DF	#DIV/0!		
Level 2 Remedial Target		#DIV/0! or #DIV/0!	mg/l or mg/kg	
<i>Additional option</i>				
<i>Calculation of impact on receptor</i>				
Concentration of contaminant in contaminated discharge (entering receptor)	C _o	0.00E+00	mg/l	
Calculated concentration within receptor (dilution only)		#DIV/0!	mg/l	0

Level 2 Remedial Target

Level 2 Remedial Target	#DIV/0!	mg/l
	or	
	#DIV/0!	mg/kg

Output RT2

For comparison with measured pore water concentration. This assumes Level 1 Remedial Target is based on Target Cor

For comparison with measured soil concentration. This assumes Level 1 Remedial Target calculated from soil-water

Site being assessed:

Completed by:

Date:

Version: 1.00

Fig.6 RT-Worksheet Input and Output: Level 2-Soil

Level 3 - Soil		Input parameters			
See Note					
Input Parameters		Variable	Value	Unit	Source
Contaminant		Pollutant			from Level 1
Target Concentration		C _T	0	mg/l	from Level 1
Dilution Factor		DF	#DIV/0!		from Level 2
Select analytical solution (click on brown cell below, then on pull-down menu)					
		Ogata Banks	Equations in HRA publication		
Select nature of decay rate (click on brown cell below, then on pull-down menu)					
Approach for simulating degradation of pollutants					
		Apply degradation rate to pollutants in all phases (e.g. field)			
Enter source concentration		Variable	Value	Unit	Source of parameter value
Enter soil concentration			0	mg/kg	
Half life for degradation of contaminant in water		t _{1/2}	1.00E+100	days	
Calculated decay rate		λ	6.93E-101	days ⁻¹	calculated
Width of plume in aquifer at source		Sz	0.00E+00	m	from Level 2
Plume thickness in aquifer at source		Sy	0.00E+00	m	from Level 2
Bulk density of aquifer materials		ρ	0.00E+00	g/cm ³	
Effective porosity of aquifer		n	0.00E+00	fraction	
Hydraulic gradient		i	#DIV/0!	fraction	from Level 2 (adjusted)
Hydraulic conductivity of saturated aquifer		K	0.00E+00	m/d	from Level 2
Distance to compliance point		x	0.00E+00	m	
direction		z		m	
direction		y		m	
Time since pollutant entered groundwater		t	1.00E+99	days	time variant options only
Parameters values determined from options					
Partition coefficient		K _D	0.00E+00	l/kg	see options
Longitudinal dispersivity		α _L	0.000	m	see options
Transverse dispersivity		α _T	0.000	m	see options
Vertical dispersivity		α _V	0.000	m	see options
Parameter values should be checked against Level 1 and 2					
Calculated Parameters		Variable	Value	Unit	Source
Groundwater flow velocity		V	#DIV/0!	m/d	
Retardation factor		R _f	#DIV/0!	fraction	
Decay rate used		λ	6.93E-101	d ⁻¹	
Hydraulic gradient used in aquifer flow down-gradient		i	#DIV/0!	fraction	
Rate of contaminant flow due to retardation		u	#DIV/0!	m/d	
Ratio of Compliance Point to Source Concentration		C _{cp} /C _s	#DIV/0!	fraction	
Attenuation factor (C _s /C _{cp})		AF	#DIV/0!	fraction	
Calculated soil leachate concentration		C _o	#DIV/0!	mg/l	
<div style="display: flex; justify-content: space-between;"> <div> <p>Output</p> <p>be used if pollutant transport and degradation is best described by a first order reaction. If degradation is best described by an electron limited degradation such as oxidation by O₂, NO₃, SO₄ etc then an alternative solution should be</p> </div> <div> <p>Output RT3</p> </div> </div>					
Remedial Targets		Remedial Target	#DIV/0!	mg/l	For comparison with measured groundwater concentrations.
		Domestic - Steady state			
		Distance to compliance point	0	m	
		Concentration of contaminant at compliance C _{cp} /C _s	#DIV/0!	mg/l	Domestic - Steady state
The recommended value for time when calculating the remedial target is 9.9E+99.					

Fig.7 RT-Worksheet Input and Output: Level 3-Soil

Input parameters

Level 3 - Groundwater

Input Parameters (using pull down menu)

Variable	Value	Unit	Source
Contaminant	Pollutant		from Level 1
Target Concentration	0.00E+00	mg/l	from Level 1

Select analytical solution (click on brown cell below, then on pull-down menu)

Approach for simulating vertical dispersion: **Domenico - Steady state** Equations in HRA publication

Approach for simulating degradation of pollutants: **Simulate vertical dispersion in 1 direction**

Select nature of decay rate (click on brown cell below, then on pull-down menu)

Approach for simulating degradation of pollutants: **Apply degradation rate to pollutants in all phases (e.g. fit)**

Variable	Value	Unit	Source
Initial contaminant concentration in groundwater at plume core	0.00E+00	mg/l	
Half life for degradation of contaminant in water	3.00E+39	days	
Calculated decay rate	7.70E-101	days ⁻¹	
Width of plume in aquifer at source (perpendicular to flow)	0.00E+00	m	
Plume thickness at source	0.00E+00	m	
Saturated aquifer thickness	0.00E+00	m	
Bulk density of aquifer materials	0.00E+00	g/cm ³	
Effective porosity of aquifer	0.00E+00	fraction	
Hydraulic gradient	0.00E+00	fraction	
Hydraulic conductivity of aquifer	0.00E+00	m/d	
Distance to compliance point	0.00E+00	m	
Distance to compliance point perpendicular to flow direction	0.00E+00	m	
Distance (depth) to compliance point perpendicular to flow direction	0.00E+00	m	
Time since pollutant entered groundwater	1.00E+100	days	time variant options only

Parameters values determined from options:

Variable	Value	Unit	Source
Partition coefficient	0.00E+00	l/kg	see options
Longitudinal dispersivity	0.00E+00	m	see options
Transverse dispersivity	0.00E+00	m	see options
Vertical dispersivity	0.00E+00	m	see options

Select Method for deriving Partition Co-efficient (using pull down menu)

Entry if specify partition coefficient (option): **Soil water partition coefficient** Kd 0.00E+00 l/kg

Entry for non-polar organic chemicals (option): **Fraction of organic carbon in aquifer** f_{oc} fraction

Entry for ionic organic chemicals (option): **Organic carbon partition coefficient** K_{oc} l/kg

Entry for ionic organic chemicals (option): **Sorption coefficient for related species** K_{ow} l/kg

Entry for ionic organic chemicals (option): **Sorption coefficient for ionized species** K_{ow} l/kg

Entry for ionic organic chemicals (option): **pH value** pH

Entry for ionic organic chemicals (option): **acid dissociation constant** pK_a fraction

Entry for ionic organic chemicals (option): **Fraction of organic carbon in aquifer** f_{oc} fraction

Define dispersivity (click brown cell and use pull down menu)

Dispersivities 10%, 1%, 0.1% of pathway length

Longitudinal dispersivity ax 0.00E+00

Transverse dispersivity az 0.00E+00

Vertical dispersivity ay 0.00E+00

Note values of dispersivity must be > 0

For calculated value, assumed ax = 0.1 * x, az = 0.01 * x, ay = 0.001 * x

Ys & Eckstein (1985) report ax = 0.830 log(x^{2.44}), az = 0.010, ay = 0.0010 are assumed.

Output

Calculated Parameters

Variable	Value	Unit
Groundwater flow velocity	0.00E+00	m/d
Retardation factor	0.00E+00	fraction
Decay rate used	7.70E-101	days ⁻¹
Rate of contaminant flow due to retardation	0.00E+00	m/d
Contaminant concentration at distance x, assuming one-way vertical dispersion	0.00E+00	mg/l
Attenuation factor (one way vertical dispersion, CO/CE)	0.00E+00	

Fig.8 RT-Worksheet Input and Output: Level 3-Groundwater

ESR tool

The Walloon ESR tool may be used to compute the adjusted values (Figs 9, 10, 11) and the leaching time (Fig.12).

The user has to select the criteria (1.) and the type of adjustments (2.) depending on the type of Aquifer(2.a) or on the type of measurements (Fig.9).

Ram-Ses ESR - Evaluation Simplifiée des Risques

SELECTION A PARTIR DES CONCENTRATIONS MESUREES DANS LE SOL

USAGE retenu: **Type II - Usage agricole**

Hors zone de prévention de captage

Nom du site: **N° forage**

N° échantillon

Masquer/Afficher les paramètres non repris dans le "décret sols"

Masquer/Afficher les détails de l'ajustement

Masquer/Afficher les statistiques descriptives

Type de comparaison: **Critères Eaux souterraines**

Aquifère Calcaire (calcaires)

Ajustement selon type de nappe

VALEURS LIMITES

Critères Eaux souterraines

VR

VSN-ajustée

VIN-ajustée

Résultats intermédiaires pour l'ajustement des VSN/VIN

FD(-)

Fv(-)

K_{sw}/K_{sp}

FAG VS

FAG VS

1. Choose criteria

2. Choose Type of adjustments

2.a Choose the Aquifer

3. See Adjusted values

Fig. 9 Screenshot of the ESR tool: Adjusted values and Factors

[illegible]

Paramètres de la nappe	Sigle	Unité	Sources d'information	Paramètres à ajuster 'Type nappe'	Paramètres à ajuster 'Mesures'	Orientatio n sécuritaire	Valeurs proposées s	Justification	Etat de la Justificatio n
Paramètres pour ajustement FD									
Facteur de dilution ajusté	FD ajusté	-	GREP Annexe C-2 Eq. 2	33				Valeur fixée selon le type de nappe	
Paramètres pour ajustement Fv									
Profondeur de la nappe	dv	m	Mesure de terrain			↓		If's the level of the Fluid stream which flows between the two carriers	
Paramètres pour ajustement Ksw : ajustement Kd des métaux lourds									
pH du sol	pHeau	-	Mesure de terrain ou valeur par défaut selon type d'usage (GREP Annexe C-3-1 Tab. 1-2)			↓	6,1	default	
Contenu en MO	MO	%	Mesure de terrain ou valeur par défaut selon type d'usage (GREP Annexe C-3-1 Tab. 1-2)			↓	0,3	default	
	Paramètre d'ajustement à encoder								
	Paramètre d'ajustement à encoder - donnée obligatoire lors de l'ER								

Paramètres nécessaires au calcul du temps de lessivage (Dragun, 1988)					
Paramètre	Symbole	Unités	Valeur proposée	Valeur retenue	
Teneur en eau volumique dans la vadose	θ_v	[-]	0,22		
Densité apparente du sol à l'état sec	ρ_b	[kg/dm³]	1,45		
Infiltration efficace annuelle (I) [m/an]	I	[m/an]	0,24		
Polluants	Profondeur représentative du toit de la pollution Prt (m)	Profondeur représentative de la base de la pollution Prb (m)	Distance à parcourir pour atteindre la nappe d _{vc} [m]	Coefficient de partition sol/eau [L/kg]	Temps de résidence au sein de la vadose [an]
Arsenic	0	38,5	0		

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BIOSCREEN-AT tool

BIOSCREEN-AT requested Input parameters and Results are shown in Figs.13 and 14.

1. Input parameters

BIOSCREEN-AT 1.43_FR_v1.1 Système d'aide à la décision basé sur l'atténuation naturelle
S.S. Papadopoulos & Associates, Inc. Version 1.43 M.Karavonov (M.2007)

1. HYDROGEOLOGIE
Vitesse effective* Vs 695 (m/an)
ou
Conductivité Hydraulique K 1.0E-02 (cm/sec)
Gradient Hydraulique i 0.00882 (m/m)
Porosité efficace η 0.04 (-)

2. DISPERSION
Dispersivité Longitudinale* alpha x 10.000 (m)
Dispersivité Transversale* alpha y 3.300 (m)
Dispersivité Verticale* alpha z 0.560 (m)
ou
Longueur de la zone modélisée* Lp 100 (m)

3. ADSORPTION
Facteur de retard* R 4.2 (-)
ou
Densité apparente du sol rho 1.7 (kg/dm³)
Coefficient de Partition Koc 74.13 (L/kg)
Fraction de Carbone Organique foc 1.0E-3 (-)

4. BIODEGRADATION
Coeff. de dégradation de 1^{er} ordre* Lambda 0.0E+0 (1/an)
ou
Demi-vie du soluté t-half 0.01 (an)
ou Modèle de Réaction Instantanée
Delta Oxygène* DO 5780 (µg/L)
Delta Nitrates* NO3 17000 (µg/L)
Fer Ferreux Observé* Fe2+ 11300 (µg/L)
Delta Sulfates* SO4 100000 (µg/L)
Methane Observé* CH4 414 (µg/L)

5. GENERAL
Longueur de la zone modélisée* 100 (m)
Largeur de la zone modélisée* 5.0 (m)
Temps de Simulation* 100.00 (an)

6. SOURCE
Epaisseur de la Source 0.53 (m)
Source
Largeur (m) Conc (µg/L)
5.0 1700000
Conc. à décroissance exponentielle

7. DONNÉES DE TERRAIN POUR LA COMPARAISON
Concentration (µg/L)
Dist. à la Source (m)
0 10 20 30 40 50 60 70 80 90 100

8. CHOIX DU TYPE DE RESULTAT A AFFICHER :
Calculer l'atténuation de la C_{max} selon la distance
Calculer la dispersion du panache
Recalculer cette feuille
Restaurer les Formules pour Vs, les dispersivités, R, lambda, et autres
Lisez-moi

2. Put Simulation time=100 years & Coefficient of degradation equals to 0

3. GW objective at compliance (Chosen GW standard for comparison with C_{max})

4. Push to compute C_{max} at compliance

Fig. 13 Input parameters in BIOSCREEN-AT

Concentration en polluant dissous dans le panache (µg/L à Z=0)

	0,00	10,0	20	30	40	50	60	70	80	90	100
Sans Dégradation	1700000	141387	51161	28912	19641	14711	11697	9679	8240	7166	6335
Dégradation de 1 ^{er} Ordre	1700000	141387	51161	28912	19641	14711	11697	9679	8240	7166	6335
Données de terrain											10

Nombre de pas de temps 10 Temps Ecoulé = 100 ans

Temps Ecoulé = 100.00 ans

C_{MAX} at compliance which has to be compared with the selected GW standard

Fig. 14 BIOSCREEN-AT Simulated Max Concentration at compliance

Appendix B

Parameters for building the synthetic case

The parameters used for modelling the synthetic case study are shown in Tab.1.

Tab 1 Parameters for the synthetic case study

<i>Data for the synthetic case study</i>		
<i>Parameters</i>	<i>value</i>	<i>Reference</i>
<i>Source</i>		
Source concentration (mg/kg d.s.)	1600	Chosen from [13]
Depth of the top of the source to the ground water level (Ht) (m)	3	Chosen
Source thickness (Hp)(m)	3	Chosen
Source length (parallel to ground water flow)(m)	5	[22]
Source extension perpendicular to groundwater flow (m)	5	Chosen
Organic carbon partition coefficient (l/kg)	146 mg/l (IT) 74,13 (BE) Chosen (UK)	Tool's dependent
Dimensionless Henry constant (-)	0,23 (IT) 0,16 (BE) Chosen (UK)	[22] [39][63] (IT and BE tool is already implemented)
<i>Unsaturated zone</i>		
Rain (cm/year)	30	[22]
Infiltration rate (for 30 cm/year of rain) (cm/year)	1,62	Computed by the Italian tools based on equation 4.4 [1]
Soil bulk density (kg/l)	1,7	[22]
Soil fraction of organic carbon (-)	0,006	[22]
		Computed with Walloon ESR guideline equation 4.5 [Annex C-3 from [29]]

Organic matter (%)	1,0344	
pH (-)	6,8	Default Italian value [62]
Effective porosity in soil (-)	0,346	Computed automatically by Walloon ESR tool [39] Equations 4.6 and 4.7
Water content**(-)	0,068	
Air volumetric content**(-)	0,278	
<i>Saturated zone parameters</i>		
Saturated zone thickness (-)	3	[22]
Darcy velocity(m/s)	8,82*10 ⁻⁷	[22]
Hydraulic conductivity(m/s)	10 ⁻⁴	Based on [22] Darcy’s velocity
Hydraulic gradient (-)	8,82*10 ⁻³	Based on [22] Darcy’s velocity
Effective porosity aquifer (-)	0,04	Chosen
Fraction of organic carbon in the saturated zone (-)	0,001	Italian default value [62]
Mixing zone thickness (d _{GW}) (m)	0,532	Computed by the tools Equation 4.8 [69]
Distance of the receptor (m)	100	Chosen
Coefficients of dispersivity(m)		BIOSCREEN-AT implemented equations 2.17 [68]
Longitudinal (a _x)	10	
Transversal (a _y)	3,3	
Vertical (a _z)	0,56	

Appendix C

Results of the RA procedure on the synthetic case for Walloon Region, Italy and United Kingdom

Walloon Region results for the synthetic case

Tab 1 Walloon results for the synthetic case

Walloon Adjusted values and factors for the synthetic case-ESR tool							
Land use type	VR (mg/kg)	VS_{Adj} (mg/kg)	VI_{Adj} (mg/kg)	FD_{Adj} (-)	Fv_{Adj} (-)	K_{swAdj} (kg/L)	FAG_{Adj} (L/kg)
-	0,10	0,93	3,7	184	1	1,98	92,93
Where VR is the reference value, VS _{Adj} , VI _{Adj} are the adjusted threshold and Intervention values, FD _{Adj} is the dilution factor, Fv _{Adj} is the mass redistribution factor, K _{swAdj} is the soil-water partition coefficient and FAG _{Adj} is the adjusted global attenuation factor.							
Walloon concentration at the receptor and remedial objective for the synthetic case - BIOSCREEN-AT tool							
Concentration at the source (µg/L)		Max concentration at compliance (100 m) (µg/L)		Remedial objective for ground water at the source (mg/l)			
1,72*10 ⁵		64		10,60 (Not exploitable) 2,55 (Exploitable)			

Italian results for the synthetic case

Remediation objectives for soil and factors of risk are given both for an On-site and Off-site receptor. The dilution factor is 184 while the leachate factors are 1, 90*10⁻³ and 5, 71*10⁻³ for shallow and deep soil respectively.

Remediation objectives and factors of risk for the movement of the pollutant in the saturated zone are given for all the Italian attenuation factors (Tab.2).

Tab 2 Italian Results for the synthetic case

Italian Risk factors and remedial objectives for the synthetic case - Risk-net					
Receptor	Source concentration (mg/kg)	Risk for GW when source in the shallow soil	Risk for GW when source in the deep soil	Remedial objective for shallow soil (mg/kg)	Remedial objective for deep soil (mg/kg)
On site	1600	3,05*10 ³	9,14*10 ³	5,25*10 ⁻¹	1,75*10 ⁻¹

Off site	1600	9,47	28,4	$1,69 \cdot 10^2$	$5,63 \cdot 10^1$
Italian results for the synthetic case when the source concentration in ground water is $C_{diluted}$ (9,24 mg/l)-Risk-net					
DAF	Risk for groundwater	Remediation objective (mg/l)	Attenuation Factor (DAF) (-)	Concentration at 100 m (mg/l)	
DAF1	$1,44 \cdot 10^1$	$6,43 \cdot 10^{-1}$	$6,43 \cdot 10^2$	$1,4 \cdot 10^{-2}$	
DAF2	$2,87 \cdot 10^1$	$3,22 \cdot 10^{-1}$	$3,22 \cdot 10^2$	$2,9 \cdot 10^{-2}$	
DAF3	$7,16 \cdot 10^2$	$1,29 \cdot 10^{-2}$	$1,29 \cdot 10^1$	$7,2 \cdot 10^{-1}$	

English results for the synthetic case

English results on the synthetic case when Italian data and a steady state simulation is applied (Tab.3).

Tab 3 English results with Italian data for the synthetic case- RT-Worksheet

<i>English results for a source of contamination in the soil</i>			
<i>(Italian values f C_T=0,001 mg/l and Koc=146 L/kg)</i>			
Level	RT (mg/kg)	RT(mg/l)	
1	9,54*10 ⁻⁴	0,001 *	
2	1,75*10 ⁻¹	1,84*10 ⁻¹ *	
3	5,63*10 ¹	1,88*10 ¹ **	
*RT at level 1 and 2 for GW have to be considered as concentration values those have to be compared with pore water measure concentrations if available.			
**The RT at level 3 for groundwater has to be considered as the admissible leachable concentration.			
<i>English results for a source of contamination in GW</i>			
<i>(Italian values CT=0,001 mg/l and Koc=146 L/kg and Domenico (1987) in steady state)</i>			
Dispersion	Source concentration (mg/l)	Concentration final at 100 m (mg/l)	RT(mg/l)
1 direction	9,24*10 ³	2,87*10 ¹	3,22*10 ⁻¹
2 directions		1,44*10 ¹	6,43*10 ⁻¹

English results on the synthetic case when Walloon data and a transient state simulation is applied (Tab.4)

Tab 4 English results with Walloon data for the synthetic case- RT-Worksheet

<i>English procedure results using Walloon data</i>					
<i>(Koc = 74,13 and C_T=10 µg/L)</i>			<i>(Koc=74,13 and C_T=40 µg/L)</i>		
Level	RT (mg/kg)	RT(mg/l)	RT (mg/kg)	RT(mg/l)	
1	5,11*10 ⁻³	0,01	2,04*10 ⁻²	0,04	
2	9,38*10 ⁻¹	1,84	3,75	7,34	
3	3,02*10 ²	5,91*10 ²	1,21*10 ³	2,36*10 ³	
<i>English results for a source of contamination in GW (transient state)</i>					
<i>Target concentration (mg/l)</i>	<i>Input source for the dispersion mechanism (mg/l)</i>	<i>1 vertical dispersion</i>		<i>2 vertical dispersion</i>	
		<i>Concentration at compliance (mg/l) 100 m</i>	<i>RT (mg/l)</i>	<i>Concentration at compliance (mg/l) 100 m</i>	<i>RT (mg/l)</i>
0,04	17,01	5,29*10 ⁻²	1,29*10 ¹	2,64*10 ⁻²	2,57*10 ⁻¹
0,01	17,01	5,29*10 ⁻²	3,22	2,64*10 ⁻²	6,43

Appendix D

RA results for the real case study

Tab 1 Parameters entered in the RA tools for the real case study

<i>Parameters entered in the RA tools for the real case study (Quarry)</i>		
<i>Parameter/data</i>	<i>Value</i>	<i>Explanation</i>
Altitude of the quarry (m)	208	Topographic map
Altitude of the groundwater table (m)	205	Altitude of the stream
Depth of the ground water table (m)	3	Computed based on topography
Thickness of the filling soil (m)	38	Computation by Geolys's experts
Altitude of the filling soil	246,5	Computation by Geolys's experts
Quarry' parallel to the GW flow (m)	330	Max length from topographic map
Aquifer thickness (m)	157	Geological information
Hydraulic gradient (-)	0,0102	Computed
Hydraulic conductivity	$4 \cdot 10^{-3}$	Average value from Hydrological information
Effective porosity of the Aquifer (%)	2,5	Average value from Hydrological information
Organic carbon fraction of the aquifer (-)	0,001	Default value Risknet tool
Organic matter (%)	0,3	Default value ESR tool
Fraction of organic carbon	$1,74 \cdot 10^{-3}$	Computed with Equ.4.5 [annex C-3.1 from [29]]
Infiltration (cm/year)	0,24	Default value ESR tool
Soil bulk density (g/cm^3)	1,7	Default value Risk-net tool
Volumetric water content (-) ($f=0,2$)	0,068	Computed with equation 4.6 [29]
Volumetric air content (-)	0,278	Computed with equation 4.7 [29]
pH (-)	6,1	Default value ESR tool

Tab 2 Walloon results for the real case study (quarry)

Walloon Results for the real case study (quarry)					
Pollutant	Type of adjustment	VR (mg/kg)	VSAdj (mg/kg)	VIAdj (mg/kg)	Ksw (kg/l)
Arsenic	Measurements	12	18636	74545	3,29*10 ⁻⁴
	Type of aquifer	12	810	3240	
Cadmium	Measurements	0,2	279	1115	1,10*10 ⁻²
	Type of aquifer	0,2	12	49	
Chrome	Measurements	34	353325	706650	8,69*10 ⁻⁵
	Type of aquifer	34	15359	30718	
Copper	Measurements	14	13334	26668	4,6*10 ⁻³
	Type of aquifer	14	580	1159	
Mercury	Measurements	0,05	-	-	-
	Type of aquifer	0,05	453	1811	
Nickel	Measurements	24	10414	41655	1,18*10 ⁻³
	Type of aquifer	24	647	2587	
Lead	Measurements	25	56646	226882	1,08*10 ⁻⁴
	Type of aquifer	25	2462	9849	
Zinc	Measurements	67	94475	188949	1,3*10 ⁻³
	Type of aquifer	67	4107	8214	
The default dilution factor is 33 (-) for a limestone aquifer. The computed FD is 569 (-) and Fvis 0,93 (-)					

Tab 3 Italian results for the real case study (quarry)

Italian results for the Real case study(quarry)				
Pollutant	Risk for the groundwater resource (-)		Remediation objective (CSR)	
	Shallow soil	Deep soil	Shallow soil (mg/kg)	Deep soil (mg/kg)
Arsenic	3,6*10 ⁻³	1,38*10 ⁻¹	6,39*10 ³	1,66*10 ²

Cadmium	$1,42 \cdot 10^{-3}$	$5,44 \cdot 10^{-2}$	$4,73 \cdot 10^3$	$1,23 \cdot 10^2$
Chrome	$1,64 \cdot 10^{-7}$	$6,29 \cdot 10^{-6}$	NA	NA
Mercury	$7,92 \cdot 10^{-4}$	$3,04 \cdot 10^{-2}$	$1,24 \cdot 10^2$	3,22
Nickel	$3,6 \cdot 10^{-3}$	$1,18 \cdot 10^{-1}$	$1,89 \cdot 10^4$	$4,03 \cdot 10^2$
Lead	$6,58 \cdot 10^{-3}$	$2,53 \cdot 10^{-1}$	$2,13 \cdot 10^5$	$5,53 \cdot 10^3$
Zinc	$3,97 \cdot 10^{-4}$	$1,53 \cdot 10^{-2}$	NA	$7,20 \cdot 10^4$
Italian factors for the mechanism of leaching				
Leachate factor for the shallow soil (LFss) (kg/l)			$1,56 \cdot 10^{-6}$	
Leachate factor deep soil (LFds) (kg/l)			$6,01 \cdot 10^{-5}$	
Dilution factor (-)			569	

Tab 4 English results for the real case study (quarry)

English results (with Italian data) for the real case study (quarry)					
Pollutant	Level	RT (mg/kg)	RT(mg/l)	Italian standard ($\mu\text{g/l}$)	Kd (l/kg)
Arsenic	1 S	$2,7 \cdot 10^{-1}$	0,001	10	$2,7 \cdot 10^1$
	2 S	$1,54 \cdot 10^2$	5,7		
Cadmium	1 S	$2 \cdot 10^{-1}$	0,005	5	$4 \cdot 10^1$
	2 S	$1,14 \cdot 10^2$	2,85		
Total Chrome	1 S	$1,5 \cdot 10^4$	0,05	50	$3 \cdot 10^5$
	2 S	$8,55 \cdot 10^6$	$2,85 \cdot 10^1$		
Mercury	1 S	$5,24 \cdot 10^{-2}$	0,01	1	5,10
	2 S	$2,99 \cdot 10^1$	5,70		
Nickel	1 S	$8,01 \cdot 10^{-1}$	0,002	20	$4 \cdot 10^1$
	2 S	$4,57 \cdot 10^2$	$1,14 \cdot 10^1$		
Lead	1 S	9	0,01	10	$9 \cdot 10^2$
	2 S	$5,13 \cdot 10^3$	5,7		
Zinc	1 S	$1,17 \cdot 10^2$	3	3000	$3,9 \cdot 10^1$
	2 S	$6,68 \cdot 10^4$	$1,71 \cdot 10^3$		

Appendix E

Sensitivity analysis

Notice that the results of the sensitivity analysis for the English procedure are not reported. In fact, as shown in chapter 3, depending on the chosen parameters, results are similar to the Italian or to the Walloon procedure.

Walloon results for the sensitivity analysis

The Walloon procedure differs depending if is assessing the mechanism of leaching or the dispersion.

In Tab. 1, the results of the sensitivity analysis for the mechanism of leaching are shown. They are obtained with the ESR tool.

Where VR is the reference value, VS_{Adj}, VI_{Adj} are the adjusted threshold and Intervention values, FD_{Adj} is the dilution factor, Fv_{Adj} is the mass redistribution factor, Ksw_{Adj} is the soil-water partition coefficient and FAG_{Adj} is the adjusted global attenuation factor.

Tab 1 Walloon Adjusted values and factors for the mechanism of leaching (sensitivity analysis)

<i>Walloon Adjusted values and factors obtained with the ESR tool</i>								
<i>Parameter</i>	<i>VR (mg/kg)</i>	<i>VS_{Adj} (mg/kg)</i>	<i>VI_{Adj} (mg/kg)</i>	<i>FD_{Adj} (-)</i>	<i>Fv_{Adj} (-)</i>	<i>Ksw_{Adj} (kg/L)</i>	<i>FAG_{Adj} (L/kg)</i>	<i>T leachate (years)</i>
GW table 10 (m. b. g. l)	0,10	3,1	12	184	0,3	1,98	309,8	356
Water content 0,304 (-) (f=0,88)	0,10	1,2	4,6	184	1	1,60	115	0
Infiltration rate 2,68*10 ¹ (cm/year)	0,10	0,06	0,24	12	1	1,98	6,1	0
Hydraulic gradient 0,001 (-)	0,10	0,11	0,46	23	1	1,98	11,6	0
Hydraulic gradient 0,1 (-)	0,10	10	42	2062	1	1,98	1041,4	0
Hydraulic conductivity 10 ⁻⁸ (m/s)	0,10	0,06	0,24	12 *	1	1,98	6,1	0
Hydraulic conductivity 10 ⁻⁵ (m/s)	0,10	0,10	0,41	20,2	1	1,98	10,2	0

Hydraulic conductivity 10^{-2} (m/s)	0,10	92	366	18173	1	1,98	9178,3	0
Soil fraction of organic carbon 0,001 (-) (MO=0,1724)	0,10	0,27	1,1	184	1	1	184	0
Soil fraction of organic carbon 0,03 (-) (MO=5,172)	0,10	4,2	17	184	1	$4,4 \cdot 10^{-1}$	420,1	0
*The dilution factor equal to 12 is the limit put by the ESR tool.								

In table 2 the parameters, which have an influence on other parameters (i.e. mixing zone thickness, leachate concentration, diluted concentration) are shown.

The simulated max concentrations and remedial targets for groundwater, considering an exploitable aquifer, are shown in Tab.3. They are obtained with BIOSCREEN-AT tool.

Tab2 Mixing zone thickness and diluted concentration variation due to change in the initial parameters (Sensitivity analysis WR)

<i>Variation of the mixing zone thickness, leachate and diluted concentrations due to the change of others parameters</i>		
<i>Parameter</i>	<i>Mixing zone thickness variation (m)</i>	<i>Diluted concentration (mg/l)</i>
Hydraulic gradient 0,001 (-)	0,555	138
Hydraulic gradient 0,1 (-)	0,529	1,54
Hydraulic conductivity 10^{-5} (m/s)	0,558	156,83
Hydraulic conductivity 1 (cm/s)	0,529	0,17
Infiltration rate 0,000734 (m/day)	0,577	264
<i>Parameter</i>	<i>Leachate concentration (mg/l)</i>	<i>Diluted concentration (mg/l)</i>
Soil fraction of organic carbon 0,001 (-)	$1,10 \cdot 10^4$	59,78
Soil fraction of organic carbon 0,03 (-)	$7,08 \cdot 10^2$	3,85
Water content 0,173 (-)	$2,864 \cdot 10^3$	15,57
Water content 0,304 (-)	$2,560 \cdot 10^3$	13,91

Tab 3 Walloon Simulated concentration at compliance and Remedial targets when the sensitivity analysis is performed.

<i>Walloon Concentration at compliance and Remedial targets for GW obtained with BIOSCREEN-AT for the sensitivity analysis</i>		
<i>Parameter</i>	<i>Concentration at 100 m µg/L</i>	<i>RT (µg/l)=Co in BIOSCREEN (When CMax=VS_{GW})</i>
Soil fraction of organic carbon 0,001 (-)	223	2550
Soil fraction of organic carbon 0,003 (-)	14	250
Water content 0,173 (-)	58	2550
Water content 0,304 (-)	52	2550
Hydraulic gradient 0,001 (-)	513	2444
Hydraulic gradient 0,1(-)	6	2564
Hydraulic conductivity 10 ⁻⁵ (m/s)	667	2686
Hydraulic conductivity 1 cm/s	1	2564
Infiltration rate 0,000734 (m/day)	1067	2351
Aquifer fraction of organic carbon 0,03 (-)	64	2550
Effective porosity aquifer 0,35 (-)	64	2550
Effective porosity aquifer 0,001 (-)	64	2550
Dispersion coefficients (10%; 1%; 0,1% of path length) (Longitudinal, transversal and vertical)	274	602
Dispersion coefficients (Xu & Eckstein (1995))	556	296

Mixing zone thickness = aquifer thickness 3 (m)	355	461
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Italian results for the sensitivity analysis

The Italian results of the sensitivity analysis are shown in Tab.5. While the correspondent factors are shown in Tab.4.

For the mechanism of leaching an *on-site receptor* is chosen, instead for the movement of the pollutant across groundwater DAF2 is chosen.

Results show three risk factors for the groundwater resource and three remediation objectives (CSR).

Where CSR is the remediation objective, LDF is the dilution factor, LF is the leachate factor (*SS* stands for shallow soil and *DS* stands for deep soil) and DAF is the attenuation factor.

Tab 4 Italian factors for the sensitivity analysis

Italian factors for leaching and contaminant migration across groundwater					
Parameter	$C_{Diluted}$ (mg/l)	LDF	LF_{SS} (kg/l)	LF_{DS} (kg/l)	DAF
GW table depth 10 m b.g.l	-	184	$5,71 \cdot 10^{-4}$	$5,71 \cdot 10^{-4}$	-
Infiltration 26,8 (cm/year)	130,77	13	$2,70 \cdot 10^{-2}$	$8,09 \cdot 10^{-2}$	$2,97 \cdot 10^2$
Water content 0,304 (-)	8,15 ($C_{Leachate} =$ $1,5 \cdot 10^3$ mg/l)	$184 \cdot 10^2$	$1,71 \cdot 10^{-3}$	$5,13 \cdot 10^{-3}$	$3,22 \cdot 10^2$
Hydraulic gradient 0,001 (-)	75,22	$2,26 \cdot 10^1$	$1,55 \cdot 10^{-2}$	$4,64 \cdot 10^{-2}$	$3,09 \cdot 10^2$
Hydraulic gradient 0,1 (-)	0,83	$2,06 \cdot 10^3$	$1,7 \cdot 10^{-4}$	$5,09 \cdot 10^{-4}$	$3,23 \cdot 10^2$
Hydraulic conductivity 10^{-8} (m/s)	1545	1,1	$3,17 \cdot 10^{-1}$	$5,71 \cdot 10^{-1}$	$1,29 \cdot 10^1$
Hydraulic conductivity 10^{-5} (m/s)	84,16	20,2	$1,73 \cdot 10^{-2}$	$1,92 \cdot 10^{-2}$	$3,07 \cdot 10^2$

Hydraulic conductivity 1 (cm/s)	0,093	$1,82 \cdot 10^4$	$1,92 \cdot 10^{-5}$	$5,77 \cdot 10^{-5}$	$3,23 \cdot 10^2$
Soil fraction of organic carbon 0,001(-) ($C_{leachate}$ 1,8*10 ³ mg/l)	39 (C _{sat} Off) & 9,78 (C _{sat} On)	184	$8,13 \cdot 10^{-3}$	$2,44 \cdot 10^{-2}$	$3,22 \cdot 10^2$
Soil fraction of organic carbon 0,03(-) ($C_{leachate}$ 3,6*10 ² mg/l)	1,96	$1,84 \cdot 10^2$	$4,07 \cdot 10^{-4}$	$1,22 \cdot 10^{-3}$	$3,22 \cdot 10^2$
Mixing zone thickness = 3 m	1,65	$1,03 \cdot 10^3$	$3,39 \cdot 10^{-4}$	$1,02 \cdot 10^{-3}$	$1,29 \cdot 10^1$
Aquifer fraction of organic carbon 0,03 (-)	9,24	184	$1,90 \cdot 10^{-3}$	$5,71 \cdot 10^{-3}$	$3,22 \cdot 10^1$
Aquifer effective porosity	9,24	184	$1,90 \cdot 10^{-3}$	$5,71 \cdot 10^{-3}$	$3,22 \cdot 10^1$
Coefficients of dispersivity (10 % 1% 0,1% of the path length)	9,24	184	$1,90 \cdot 10^{-3}$	$5,71 \cdot 10^{-3}$	$7,53 \cdot 10^1$
Coefficients of dispersivity with Xu & Eckstein (1995)	9,24	184	$1,90 \cdot 10^{-3}$	$5,71 \cdot 10^{-3}$	$3,36 \cdot 10^1$

Tab 5 Italian results for the sensitivity analysis

<i>Italian Risk factors and remedial objectives in the sensitivity analysis</i>			
	<i>Risk for the groundwater resource (-)</i>	<i>Remedial objective (CSR)</i>	<i>Concentration at the</i>

<i>Parameter</i>	<i>SS</i>	<i>DS</i>	<i>GW</i>	<i>SS</i> (mg/kg)	<i>DS</i> (mg/kg)	<i>GW</i> (mg/l)	<i>receptor</i> (100m) mg/l
GW table depth 10 (m b.g.l)	9,14*10 ²	2,03*10 ³	-	1,75	7,88*10 ⁻¹	-	-
Infiltration 26,8 (cm/year)	4,31*10 ⁴	1,29*10 ⁵	4,41*10 ²	3,71*10 ⁻²	1,24*10 ⁻²	2,97*10 ⁻¹	4,4*10 ⁻¹
Water content 0,304 (-)	2,74*10 ³	8,21*10 ³	2,53*10 ¹	5,84*10 ⁻¹	1,95*10 ⁻¹	3,22*10 ⁻¹	2,5*10 ⁻²
Hydraulic gradient 0,001 (-)	2,48*10 ⁴	7,43*10 ⁴	2,44*10 ²	6,46*10 ⁻²	2,15*10 ⁻²	2,4*10 ⁻¹	2,4*10 ⁻¹
Hydraulic gradient 0,1 (-)	2,71*10 ²	8,14*10 ²	2,57	5,90	1,97	3,23*10 ⁻¹	2,6*10 ⁻³
Hydraulic conductivity 10 ⁻⁸ (m/s)	5,07*10 ⁵	1,52*10 ⁶	1,20*10 ⁵	3,15*10 ⁻³	1,05*10 ⁻³	1,29*10 ⁻²	1,2*10 ⁻²
Hydraulic conductivity 10 ⁻⁵ (m/s)	2,77*10 ⁴	8,32*10 ⁴	2,74*10 ²	5,77*10 ⁻²	1,92*10 ⁻²	3,07*10 ⁻¹	2,7*10 ⁻¹
Hydraulic conductivity 1 (cm/s)	3,08*10 ¹	9,24*10 ¹	2,87*10 ⁻¹	5,2*10 ¹	1,73*10 ¹	3,23*10 ⁻¹	2,9*10 ⁻⁴
Soil fraction of organic carbon 0,001 (-) (<i>Csat Off</i>)	1,30*10 ⁴	3,9*10 ⁴	3,04*10 ¹	1,23*10 ⁻¹	4,10*10 ⁻²	3,22*10 ⁻¹	5,6
Soil fraction of organic carbon 0,001 (-) (<i>Csat On</i>)	3,25*10 ³	9,74*10 ³	3,04*10 ¹	1,23*10 ⁻¹	4,10*10 ⁻²	3,22*10 ⁻¹	2,8
Soil fraction of organic carbon 0,03(-)	6,51*10 ²	1,95*10 ³	6,09	2,46	8,19*10 ⁻¹	3,22*10 ⁻¹	6,1*10 ⁻³
Mixing zone thickness 3 (m)	5,43*10 ²	1,63*10 ³	1,28*10 ²	2,95	9,83*10 ⁻¹	1,29*10 ⁻²	1,3*10 ⁻¹
Aquifer fraction of organic carbon 0,03(-)	3,05*10 ³	9,14*10 ³	2,87*10 ¹	5,25*10 ⁻¹	1,75*10 ⁻¹	3,22*10 ⁻¹	2,9*10 ⁻²

Aquifer effective porosity(0,35 & 0,001 (-))	$3,05 \cdot 10^3$	$9,14 \cdot 10^3$	$2,87 \cdot 10^1$	$5,25 \cdot 10^{-1}$	$1,75 \cdot 10^{-1}$	$3,22 \cdot 10^{-1}$	$2,9 \cdot 10^{-2}$
Coefficients of dispersivity (10 % 1% 0,1% of the path length)	$3,05 \cdot 10^3$	$9,14 \cdot 10^3$	$1,23 \cdot 10^2$	$5,25 \cdot 10^{-1}$	$1,75 \cdot 10^{-1}$	$7,53 \cdot 10^{-2}$	$1,2 \cdot 10^{-1}$
Coefficients of dispersivity (Xu & Eckstein (1995))	$3,05 \cdot 10^3$	$9,14 \cdot 10^3$	$2,75 \cdot 10^2$	$5,25 \cdot 10^{-1}$	$1,75 \cdot 10^{-1}$	$3,36 \cdot 10^{-2}$	$2,8 \cdot 10^{-1}$

Acronymes & Symbols

A_{CP}: Area of the control plane [L^2]

AF: Attenuation factor (UK) [-] (AF_{UK_1dir} and AF_{UK_2dir} when vertical dispersion is considered in 1 or two directions respectively)

A_O: Horizontal source area [L^2]

APAT: Agenzia per l'ambiente e la protezione dei servizi tecnici (IT)

ARPA: Agenzia Regionale per la Protezione Ambientale (IT)

a.s.l.: Above the sea level

ASLP: Australian standard leaching protocol (AU)

AU: Australia

ax: Longitudinal dispersivity [L]

ay: Transversal/lateral dispersivity [L]

az: Vertical dispersivity [L]

A_v: Vertical area [L^2]

BATNEEC: Best available techniques not entailing excessive costs

BC: British Columbia

b. g. l.: Below the ground level

BTEX: Benzene, Toluene, Ethylbenzene and Xylene

C: Contaminant concentration [M/M or M/L^3]

CA: Canada

C-Based: Concentration based

CBR_N: Maximal concentration in soil to respect VI_{GW} at compliance (WR) [M/M]

CBR_{GW}: Maximal concentration in groundwater to respect VI_{GW} at compliance (WR) [M/L^3]

C_{GW}: Concentration in groundwater below the source.

C_{Diluted}: Diluted concentration in GW [M/L^3]

C_L = C_{Leachate}: Leachate concentration [M/L^3]

C_{Measured}: Measured concentration [M/M or M/L^3]

C_{Max}: Maximal concentration simulated at compliance with BIOSCREEN-AT [M/L^3]

CORONA: Confidence in forecasting of natural attenuation

CRS: Measured concentration at the source (IT) [M/M or M/L^3]

C_{SAT}: Concentration of saturation [M/M]

CSC: Contamination investigation level (IT) [M/M or M/L^3]

CSC_{GW}: Contamination investigation level/Groundwater standard (IT) [M/ L³]

Ct: Total concentration measured in soil sample [M/M]

C_T: Target concentration (UK) [M/ L³]

CSR: Threshold risk concentration/Remedial objective (IT)

CSR_{ss}: Threshold risk concentration/Remedial objective for shallow soil (IT)

CSR_{ds}: Threshold risk concentration/Remedial objective for deep soil (IT)

CSR_{GW}: Threshold risk concentration/Remedial objective for groundwater (IT)

Cu: Background groundwater concentration beneath the site (UK) [M/ L³]

Cx: Concentration of pollutant in a conformity point place at distance X from the source [M/ L³]

d: Source's thickness in the vadose zone [L]

da: Aquifer thickness [L]

DAF: Dilution attenuation factor [-] (IT) (DAF1, DAF2 when the vertical dispersion is allowed in 2 and 1 direction, DAF3 when there is no vertical dispersion).

D. Lgs: Decreto legislative (IT) - Law decree

DF: Dilution factor (UK) [-]

d_{GW}: Mixing zone thickness [L]

ds: Deep soil

d_{vz}: Contaminant path in the vadose zone [L]

EDR: Etude détaillée des Risques

EEA: European Environment Agency

ESR: Etude simplifiée de Risque

EPA: Environmental protection agency (USA)

f: Porosity fraction occupied by water (or saturation) (WR) [-]

f_{ads}: Fraction of the site available for the adsorption (WR) [-]

FAG: Global attenuation factor (WR) [L³/M]

FAs: Attenuation factor (WR) [-]

F-Based: Flux based

FD: Dilution factor (WR)[-]

FEMWATER: Finite element groundwater model

f_{oc}: Fraction of organic carbon [-]

Fv: Mass redistribution factor (WR) [-]

GILs: Groundwater investigation Levels (AU) [M/L³]

GMS: Groundwater modelling system

GW: Groundwater

Hp: The contaminated thickness of the vadose zone (WR) [L]

Ht: The total thickness of vadose under contamination (from top of contamination to GW) (WR) [L]

I: Annual effective infiltration [L/T]

i: Hydraulic gradient [-]

ISS: Istituto superiore della sanità (IT)

IT: Italy

J: Mass flux [M/T*L²]

k: Saturated hydraulic conductivity [L/T]

Kd: Adsorption constant [L³/M]

Kd_{CORR}: [L³/M]

K_H: Dimensionless Henry Constant [-]

K_{OC}: Organic carbon partition coefficient [L³/M]

K_{OW}: Octanol-water partitioning [-]

K_{SW}-K_{WS}-K: Soil-Water partition coefficient [M/ L³]

L: Length of contaminated zone parallel to ground water flow [L]

LDF: dilution factor (IT) [-]

LF: Leachate factor (IT) [M/ L³] (LF_{ss} and LF_{ds}: Leachate factor for shallow and deep soil)

L_{GW}: GW depth b. g. l. (IT) [L]

L_s: Top source's depth b. g. l. (IT) [L]

M_d: Mass discharge [M/T]

M_{dMAX}: Max mass discharge [M/T]

M_{d_Leaching}: Mass discharge for the unsaturated zone [M/T]

M_{d_Dispersion}: Mass discharge for the saturated zone [M/T]

MO: Organic matter content [%]

NA: Natural attenuation

NAPL: Non Aqueous Liquid phase

n_e: Effective porosity

P: Effective Rain [L/T]

pH: Power of Hydrogen [-]

q: Groundwater flux [L/T]

R: Retardation factor [-] or Universal gas constant (l*atm/mol*K)

RA: Risk Assessment

RBCA: Risk based corrective action

RECONnet: Rete Nazionale sulla gestione e la Bonifica dei Siti Contaminati

RMZ: Risk management zones

RT: Remedial Target (UK) (**RT₁**, **RT₂**, **RT₃**: Remedial Target for 1, 2, 3 level of assessment for a soil source and **RT_{GW}**: Remedial Target for groundwater source) [M/M or M/L³]

RTM: Remedial Target methodology (UK)

R_{ds} , **R_{ss}**: and **R_{GW} Risk factor for** deep, shallow soil and groundwater) (IT)

SAM: Soil attenuation model [-] (IT)

S-P-R: Source(s)-Pathway(s)-Receptor(s)

ss: Shallow soil

Sw: Source's extension in the perpendicular direction of GW flow [L]

T: absolute temperature (K)

T_{Leaching}: Leaching time (WR) [T]

UK: United Kingdom

v_e: Effective velocity [L/T]

VI: Intervention value (WR) [M/M or M/L³]

VI_{Adjusted}: Adjusted Intervention value (WR) [M/M]

VI_{GW}: Intervention value for ground water (WR) [M/L³]

v_{GW}: Darcy velocity [L/T]

VR: Reference value (WR) [M/M or M/L³]

VS: Threshold value (WR) [M/M or M/L³]

VS_{Adjusted}: Adjusted Threshold value (WR) [M/M]

VS_{GW}: Threshold value for ground water (WR) [M/L³]

VZ: Vadose zone

WR: Walloon Region

X: Distance between the conformity point and the source of contamination in GW below the site [L]

Θ_a: (Volumetric) air content [-]

Θ_w: (Volumetric) water content [-]

ρ_b: Bulk density [M/L³]

τ(LF): Average leaching time [T]

% of stoniness (BE) [%]

λ: Biodegradation constant of first order [1/T]