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2. Detailed human risk assessment arising from groundwater contaminated by chlorinated hydrocarbons (DNAPLs)

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Abstract. Human health risk assessment is the basis for groundwater contamination and remediation goals definitions. Chlorinated solvents have a high toxicity for humans, even at low concentrations, and are important soil and groundwater pollutants. The main objective of this work is to assess the human health risk derived of exposition to a contaminated groundwater using a commercial Risk Analysis model (RBCA) and taking into consideration different exposure factors. A case study was used. Some risk differences were observed using specific exposure factors in different countries, which were explained by differences in life style.

Introduction

Chlorinated solvents are a type of DNAPLs (Denser-than-water Non Aqueous-Phase Liquids) that include: Tetrachloroethene (PCE), 1,1,1

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Tricloroethane (111TCA), 1,1,2 Tricloroethane (112TCA), 1,2 Dichloroethane (DCA), Chloroethane (CA), Trichloroethene (TCE), cis-1,2-Dichloroethene (c-DCE), trans-1,2-Dichloroethene (t-DCE), Vinylchoride (VC), Carbon tetrachloride (CT), Chloroform (CF), Dichloromethane (DCM), and Chloromethane (CM).

They have been produced and utilised widely since the beginning of the 20th century. The typical uses were: dry cleaning (mostly tetrachloroethene), metal degreasing, pharmaceutical production, and pesticide formulation [1]; they were also used in the rubber industry and as coating products [2]. Their importance as soil and groundwater contaminants was not recognised until the 1980s.

Thereby since 1970, chlorinated solvents have been less and less used in order to preserve the environment. They are now under control by REACH (European Regulation on Restriction, Evaluation, and Authorization of Chemicals) [3].

These solvents have a high toxicity, even at low concentrations [1]. The major target organ of these compounds is central nervous system; other targets are skin and mucus membranes, heart, eyes, lung, liver, and kidneys. An acute toxicity can be observed on these organs that results in: ravage of the central nervous system (depression, reversible mood, and behavioural changes, impairment of coordination,…). PCE can cause irritation of the upper

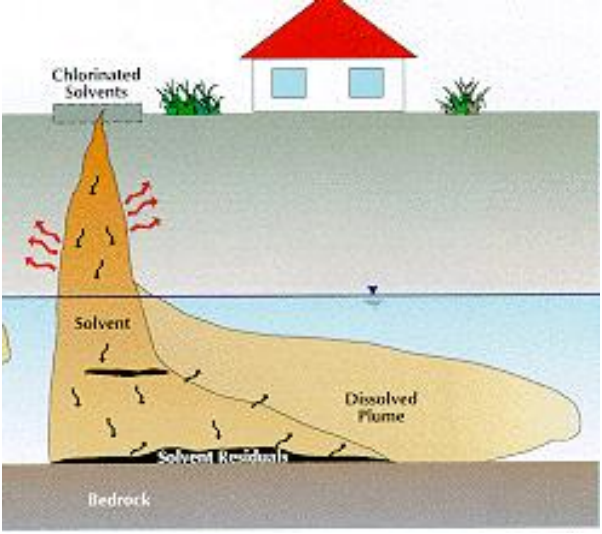


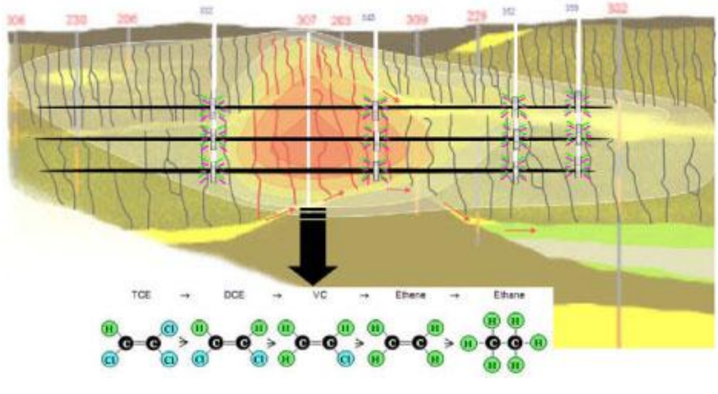
Figure 1. Fate of chlorinated solvents in the media.

respiratory tract and eyes, kidney dysfunction, headache, sleepiness and unconsciousness. The liver toxicity is particularly due to carbon tetrachloride. Heart excitability or irritation of the nose and throat are consequences of TCE exposition. High concentrations of TCE have caused numbness and facial pain, unconsciousness, irregular heartbeat, and death. CF causes depression, rapid and irregular heartbeat, as well as liver and kidney damage [4]. A chronic toxicity has all been stated on all the targets organs, as well as a potential carcinogen effect [2]. VC is admitted to produce angiosarcoma [5]; indeed, IARC (International Agency for Research on Cancer) classifies: VC in the group 1, carcinogenic to humans, [6]; TCE, in group 2A, probably carcinogen to humans; PCE, CT, CF and DCM in group 2B, possibly carcinogen to humans, and TCA in group 3, unclassifiable by its carcinogenicity to humans [7,8].

There may be a natural attenuation of such a contaminants by physical (volatilization), chemical (dilution, absorption, dispersion) and biological processes (biodegradation). The above mentioned processes contribute to the diminution of risk for the human health [4].

Some microorganisms as *Dehalococoides* spp. are able to use chlorinated solvent as electron acceptors during the dehalorespiration and dechlorinate them. Sometimes, biotransformation of the initial compounds produces other compounds more toxic or more persistent at the media [4].

The first exposed people are usually the workers in the industries but, due to the dispersion in groundwaters, the population can be also exposed during long time through the consumption of drinking water, representing an important public health issue locally.

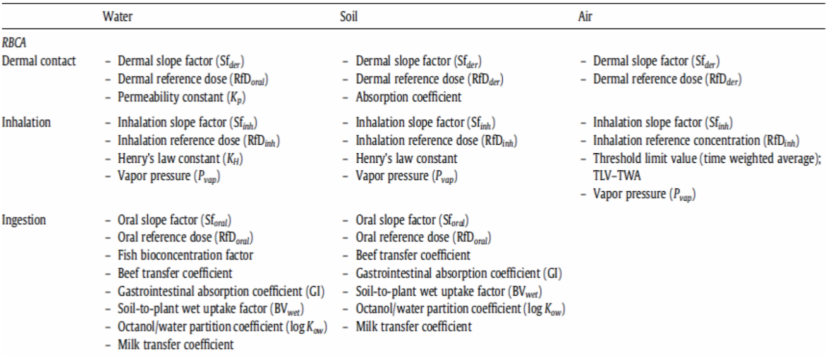


(Source: Danish Environmental Project No. 1295, 2009) [9]

Figure 2. Natural attenuation of chlorinated solvents at the media.

RBCA (Risk Based Corrective Action) is a tool developed by the American Society of Testing and Materials (ASTM) for determining the amount and urgency of necessary actions for a polluted site regarding human health [10]. This model is used to identify exposure pathways and receptors at a site, determine the level and urgency of response required, determine the level of surveillance appropriate for a site, and incorporate risk analysis into all phases of the corrective action process [11]. RBCA combines contaminant transport models and risk assessment tools to calculate baseline risk levels and derive risk-based clean-up standards for a full array of soil, groundwater, surface water, and air exposure pathways. Environmental site managers, regulatory authorities, and consultants around the world have increasingly turned to Risk-Based Corrective Action (RBCA) for the management of contaminated soil and groundwater [12].

Table 1. Main exposure related parameters.



	Water	Soil	Air
RBCA			
Dermal contact	- Dermal slope factor (Sf_{der}) - Dermal reference dose (RfD_{oral}) - Permeability constant (K_p)	- Dermal slope factor (Sf_{der}) - Dermal reference dose (RfD_{der}) - Absorption coefficient	- Dermal slope factor (Sf_{der}) - Dermal reference dose (RfD_{der})
Inhalation	- Inhalation slope factor (Sf_{inh}) - Inhalation reference dose (RfD_{inh}) - Henry's law constant (K_H) - Vapor pressure (P_{vap})	- Inhalation slope factor (Sf_{inh}) - Inhalation reference dose (RfD_{inh}) - Henry's law constant - Vapor pressure (P_{vap})	- Inhalation slope factor (Sf_{inh}) - Inhalation reference concentration (RfD_{inh}) - Threshold limit value (time weighted average); TLV–TWA - Vapor pressure (P_{vap})
Ingestion	- Oral slope factor (Sf_{oral}) - Oral reference dose (RfD_{oral}) - Fish bioconcentration factor - Beef transfer coefficient - Gastrointestinal absorption coefficient (GI) - Soil-to-plant wet uptake factor (BV_{wet}) - Octanol/water partition coefficient ($\log K_{ow}$) - Milk transfer coefficient	- Oral slope factor (Sf_{oral}) - Oral reference dose (RfD_{oral}) - Beef transfer coefficient - Gastrointestinal absorption coefficient (GI) - Soil-to-plant wet uptake factor (BV_{wet}) - Octanol/water partition coefficient ($\log K_{ow}$) - Milk transfer coefficient	

The main objective of this work is to assess the human risk of contaminated groundwater by chlorinated hydrocarbons using the RBCA model that is widely regarded as a useful one for specific scenarios. Site-specific consideration allows for attenuation process to be taken into account along the pathway from the source of groundwater pollution. Secondary objectives are: to verify the correct toxicological and exposure values to be used to fit the model, to establish different exposure scenarios, and to identify data gaps.

1. Study area

The pollution episode studied was detected in 1996 at an industrial plant inside a chemical complex, but it is not well known when the episode started.

Two chlorinated methanes were associated with the episode: carbon tetrachloride (CT) and chloroform (CF), stored independently at the site. Repeated leaks and spills are responsible for the current situation. The area is located at a small sedimentary basin. Characterization studies, monitoring, and control of groundwater's quality began in 1996. 196 m^2 of the soil were then affected by contamination of CT, CF, DCM, 1,1,1,2 PCA, 1,1,2,2 PCA, 1,1,1 TCA 1,1,2 TCA, PCE, TCE, 1,1 DCE, tDCE, and cDCE, from 0.5 to 6 m of depth.

Concerning the water, the polluted plume is supposed to be 4 m thick and big of 2 m. Concentrations recorded at the groundwater, ranged between 15 and 22,600 μg/L for CF, and between the detection limit and 86 μg/L for CT [13]. Six samples were taken from a well for analysis; every sample was analysed by triplicate. The methodology used for chlorinated solvent characterization has been gas chromatography because, being sensible, specific and applicable, it is the most performing method, with a detection limit of 0,01-0,1 μg L^{-1}[14,15].

2. Exposure assessment

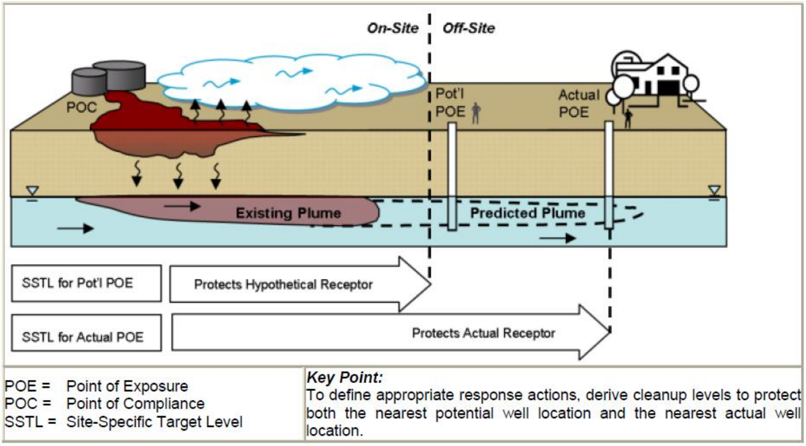
The following equation has been used to model the exposure rate (E):

$$E = (CR \times EF \times ED) / (BW \times AT) \qquad [1]$$

Which depends on the entrance via (ingestion, inhalation, dermal contact) rate (CR), the exposure frequency (EF), the exposure duration (ED), the body weight (BW), and the average time of exposure (AT).

Due to the presence of an operating industrial plant at the polluted area, the first receptors are regular and temporary workers. Exposure point primarily for on-site workers involved in excavation, digging, and other activities that turn over the soil or that are in touch with groundwater. Workers can be exposed principally by inhalation of the compounds in the outdoor air, but national legislations use to oblige also to take into account: accidental ingestion of contaminants in soil, and inhalation of contaminated dust in air.

No residents are present at the affected area, but to take into consideration population that could be exposed outside the area (residents and visitors who dig holes for planting trees, installing swimming pools, or other uses) it has been considered that the residential population can be exposed 500 m far from the area (Point of Exposure 1, POE1) and 1,000 m far from the characterised area (POE 2); if contaminated groundwater is being supplied as drinking water, then the residents may be exposed via ingestion, inhalation (from volatilization during shower), and dermal contact (when taking a shower/bath).



POE = Point of Exposure
POC = Point of Compliance
SSTL = Site-Specific Target Level

Key Point:
To define appropriate response actions, derive cleanup levels to protect both the nearest potential well location and the nearest actual well location.

Figure 3. Points of exposure (POE) considered at the modelisation.

3. Toxicity assessment

For non-carcinogenic compounds, the RfD is the used reference, which is an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure to the human population, including sensitive subgroups, that is likely to be without an appreciable risk of deleterious effects during the lifetime. The RfD is generally expressed in units of milligrams per kilogram of body weight per day (mg/kg/day). The RfD is determined for all routes of exposure by using the following equation:

$$RfD = NOAEL / (UF \times MF) \qquad [2]$$

RfD is usually derived from an experimentally determined "no-observed-adverse-effect level (NOAEL) which is the experimentally determined dose at which there was no statistically or biologically significant indication of toxic effects of concern. Uncertainty Factors (UF) and Modifying Factors (MF) are used, based on a professional judgment [16].

For the carcinogenic exposure this is done by quantifying how the number of cancers observed in exposed animals or humans increases with the dose. Typically, it is assumed that the dose-response curve for cancer has no threshold (i.e., there is no dose other than zero that does not increase the risk of cancer), arising from the origin and increasing linearly until high doses are reached. Thus, the most convenient descriptor of cancer potency is the slope of the dose-response curve at low doses (where the slope is still linear). This is referred as the Slope Factor (SF), which is expressed as risk of cancer per unit dose.

4. Individual risk analysis

For the non-carcinogenic compounds it's represented by the Hazard Ratio (HR):

$$HR = E / RDf \qquad [3]$$

If HR is higher than 1, they is a risk because the exposure dose is higher than the exposure dose without significant effect.

For the carcinogenic compounds which don't have threshold, the following equation is used:

$$R = E \times SF \qquad [4]$$

Where:
R = Risk, a unitless probability (e.g., 2×10^{-5}) of an individual developing cancer;
E = chronic daily intake averaged over 70 years (mg/kg-day);
SF = slope factor, expressed in (mg/kg-day).

The most widely used value of acceptable risk is 10^{-5}, what means that one new case of cancer due to this compounds exposure every 100,000 people is accepted.

5. Cumulative risk analysis

The risk commonly used for the case by case risk assessment is the cumulative risk, which takes into account all the compounds together. The cumulative risk for carcinogens (sum of risk for all chemicals and all complete exposure pathways) must not exceed $1\text{x}10^{-4}$ or $1\text{x}10^{-5}$, according different legislations.

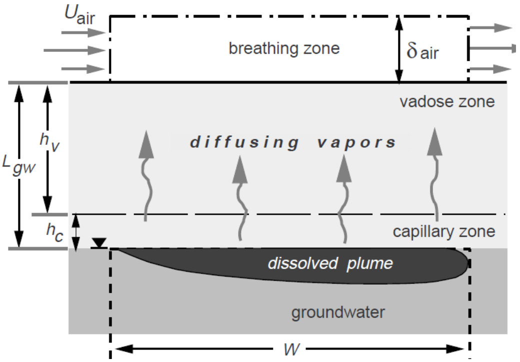
For non-carcinogenic compounds, the site-wide hazard index, which is the sum of hazard quotients for all chemicals and all complete exposure pathways, must not exceed 1.0.

6. Pollutant transfer and degradation

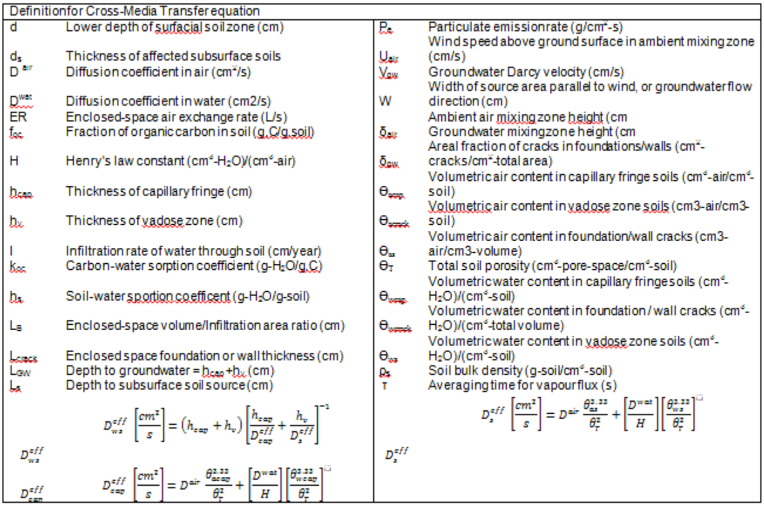
Pollutant transfer and degradation contribute to contaminants depletion, which results in less risk. Risk analysis considers a constant concentration value for the contaminant/s throughout the entire exposure period, which is a very conservative assumption.

Cross media transfer factors: To take in account the transfer of pollution between media, as for example, volatilisation of chlorinated solvent from the groundwater to the outside air, the used model applies the following equations:

Groundwater Volatilization Equation



$$VF_{wamb}\left[\frac{(\frac{mg}{m^3}-air)}{\frac{mg}{L}-H2O)}\right]=\frac{H}{1+\left[\frac{U_{air}\delta_{air}\,L_{GW}}{WD_{ws}^{eff}}\right]}\times 10^3$$



Definitionfor Cross-Media Transfer equation	
d	Lower depth of surfacial soil zone (cm)
d_s	Thickness of affected subsurface soils
D^{air}	Diffusion coefficient in air (cm²/s)
D^{wat}	Diffusion coefficient in water (cm2/s)
ER	Enclosed-space air exchange rate (L/s)
f_{oc}	Fraction of organic carbon in soil (g.C/g.soil)
H	Henry's law constant (cm³-H₂O)/(cm³-air)
h_{cap}	Thickness of capillary fringe (cm)
h_v	Thickness of vadose zone (cm)
I	Infiltration rate of water through soil (cm/year)
k_{oc}	Carbon-water sorption coefficient (g-H₂O/g.C)
k_s	Soil-water sportion coefficent (g-H₂O/g-soil)
L_B	Enclosed-space volume/Infiltration area ratio (cm)
L_{crack}	Enclosed space foundation or wall thickness (cm)
L_{GW}	Depth to groundwater = $h_{cap}+h_v$ (cm)
L_s	Depth to subsurface soil source (cm)
P_e	Particulate emissionrate (g/cm²-s)
U_{air}	Wind speed above ground surface in ambient mixing zone (cm/s)
V_{gw}	Groundwater Darcy velocity (cm/s)
W	Width of source area parallel to wind, or groundwater flow direction (cm)
	Ambient air mixing zone height (cm
δ_{air}	Groundwater mixingzone height (cm
δ_{gw}	Areal fraction of cracks in foundations/walls (cm²-cracks/cm²-total area)
θ_{acap}	Volumetric air content in capillary fringe soils (cm³-air/cm³-soil)
θ_{acrack}	Volumetric air content in vadose zone soils (cm3-air/cm3-soil)
θ_{as}	Volumetric air content in foundation/wall cracks (cm3-air/cm3-volume)
θ_T	Total soil porosity (cm³-pore-space/cm³-soil)
θ_{wcap}	Volumetric water content in capillary fringe soils (cm³-H₂O)/(cm³-soil)
θ_{wcrack}	Volumetric water content in foundation / wall cracks (cm³-H₂O)/(cm³-total volume)
θ_{ws}	Volumetric water content in vadose zone soils (cm³-H₂O)/(cm³-soil)
ρ_s	Soil bulk density (g-soil/cm³-soil)
τ	Averaging time for vapour flux (s)

$$D_{ws}^{eff}\left[\frac{cm^2}{s}\right]=\left(h_{cap}+h_v\right)\left[\frac{h_{cap}}{D_{cap}^{eff}}+\frac{h_v}{D_s^{eff}}\right]^{-1}$$

D_{ws}^{eff}

$$D_{cap}^{eff}\left[\frac{cm^2}{s}\right]=D^{air}\,\frac{\theta_{acap}^{3.33}}{\theta_T^2}+\left[\frac{D^{wat}}{H}\right]\left[\frac{\theta_{wcap}^{3.33}}{\theta_T^2}\right]$$

D_{cap}^{eff}

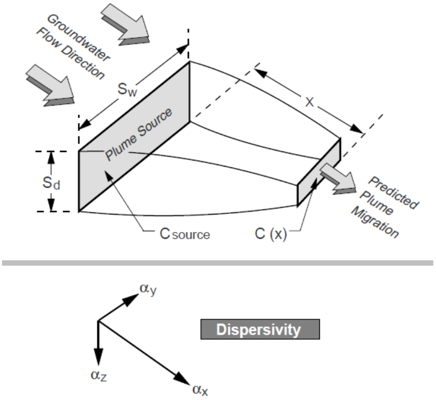
$$D_s^{eff}\left[\frac{cm^2}{s}\right]=D^{air}\,\frac{\theta_{as}^{3.33}}{\theta_T^2}+\left[\frac{D^{wat}}{H}\right]\left[\frac{\theta_{ws}^{3.33}}{\theta_T^2}\right]$$

D_s^{eff}

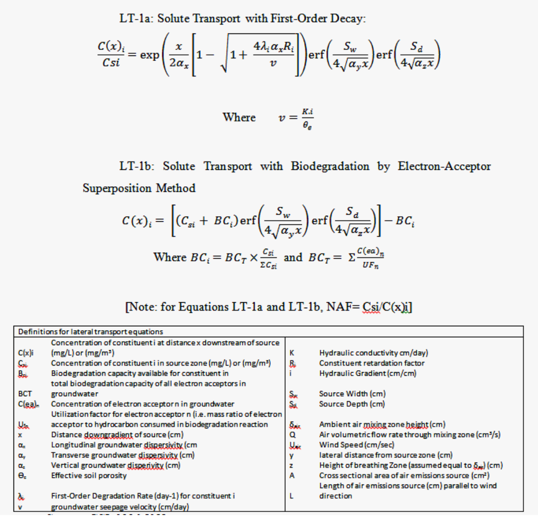
(Source: GSI, 1996) [17]

Lateral Groundwater transport equation

To account for attenuation of affected groundwater concentrations between the source and the receptors, this model considers a partially or completely penetrating vertical plane source, perpendicular to groundwater flow, to simulate the release of organics from the mixing zone to the moving groundwater.



Lateral Groundwater Dilution Attenuation Factor



LT-1a: Solute Transport with First-Order Decay:

$$\frac{C(x)_i}{Csi} = \exp\left(\frac{x}{2\alpha_x}\left[1 - \sqrt{1 + \frac{4\lambda_i \alpha_x R_i}{v}}\right]\right)\mathrm{erf}\left(\frac{S_w}{4\sqrt{\alpha_y x}}\right)\mathrm{erf}\left(\frac{S_d}{4\sqrt{\alpha_z x}}\right)$$

Where $v = \frac{K.i}{\theta_e}$

LT-1b: Solute Transport with Biodegradation by Electron-Acceptor Superposition Method

$$C(x)_i = \left[(C_{si} + BC_i)\mathrm{erf}\left(\frac{S_w}{4\sqrt{\alpha_y x}}\right)\mathrm{erf}\left(\frac{S_d}{4\sqrt{\alpha_z x}}\right)\right] - BC_i$$

Where $BC_i = BC_T \times \frac{C_{si}}{\Sigma C_{si}}$ and $BC_T = \Sigma \frac{C(ea)_n}{UF_n}$

[Note: for Equations LT-1a and LT-1b, NAF= Csi/C(x)i]

Definitions for lateral transport equations			
C(x)i	Concentration of constituent i at distance x downstream of source (mg/L) or (mg/m³)	K	Hydraulic conductivity cm/day)
C_{si}	Concentration of constituent i in source zone (mg/L) or (mg/m³)	R_i	Constituent retardation factor
B_{si}	Biodegradation capacity available for constituent in	i	Hydraulic Gradient (cm/cm)
BCT	total biodegradation capacity of all electron acceptors in groundwater	S_w	Source Width (cm)
$C(ea)_n$	Concentration of electron acceptor n in groundwater	S_d	Source Depth (cm)
UF_n	Utilization factor for electron acceptor n (i.e. mass ratio of electron acceptor to hydrocarbon consumed in biodegradation reaction	δ_{air}	Ambient air mixing zone height (cm)
x	Distance downgradient of source (cm)	Q	Air volumetric flow rate through mixing zone (cm³/s)
α_x	Longitudinal groundwater dispersivity (cm	U_{air}	Wind Speed (cm/sec)
α_y	Transverse groundwater dispersivity (cm)	y	lateral distance from source zone (cm)
α_z	Vertical groundwater disperivity (cm)	z	Height of breathing Zone (assumed equal to δ_{air}) (cm)
Θ_e	Effective soil porosity	A	Cross sectional area of air emissions source (cm²)
λ_i	First-Order Degradation Rate (day-1) for constituent i	L	Length of air emissions source (cm) parallel to wind direction
v	groundwater seepage velocity (cm/day)		

Source: GSI, 1996 [17].

The general experience is that these substances may be, under different environmental conditions, adaptively degraded.

The estimated half-lives for chlorinated solvents should therefore be considered, being in accordance with “the realistic worst-case concept”, in order to establish the realistic exposition level.

Table 2. Half life of chlorinated solvents in groundwaters.

COMPOUNDS	**Half time life (days)**			
	CAS	**Model value**	Min	Max
CT	56-23-5	360 [a]	7 [b]	360[b]
CF	67-66-3	1800 [a]	1825 [b]	
CM	74-87-3	546 [c]	14 [b]	56 [b]
DCM	75-09-2	56 [a]	14 [b]	56 [b]
PCE	127-18-4	720 [a]	360 [b]	720 [b]
TCE	79-01-6	1653 [a]	321 [b]	1653 [b]
tDCE	156-60-5	2880 [a]	2880 [a]	
cDCE	156-59-2	2875 [c]	2880 [a]	
VC	75-01-4	2880 [a]	56 [b]	2850 [b]
1,1,1 TCA	71-55-6	730 [a]	140 [b]	546 [b]
1,1,2 TCA	79-00-5	730 [c]	136 [b]	730 [b]
1,2DCA	107-06-2	360 [a]	100 [b]	360 [b]
CA	75-00-3	56 [a]	14 [b]	56 [b]

a: Data from the RBCA model
b: Data bank of environmental properties of chemicals (EnviChem), 2013 [18].

7. Data used to fit the model

Physicochemical parameters and toxicological data of contaminants

The verification of the properties’ data in the model is important for the validity of the results. The variability in parameter values may have a significant effect on the predicted contaminant’s behavior and ultimately on the estimated human exposure. So, it has been decided to take into account the maximum and the minimum values, and to make the average of the different values found in bibliography to have a complete extent.

From different data bases, such as Reaxys, and IRIS [16,19], or toxicological reviews of the EPA [20,21], we built a data base with maximum, minimum and average values for: Solubility, Vapor pressure, Henry’s constant, Partition Coefficient octanol/water, Coefficient Koc, and Coefficient of diffusion in air and in water (see Table 3).

Table 3. Physicochemical parameters of contaminants.

		Chloromethane				Chloroethene					Chloroethane			
Propriety		CT	CF	CM	DCM	PCE	TCE	tDCE	cDCE	VC	1,1,1 TCA	1,1,2 TCA	1,2DCA	CA
CAS		56-23-5	67-66-3	74-87-3	75-09-2	127-18-4	79-01-6	156-60-5	156-59-2	75-01-4	71-55-6	79-00-5	107-06-2	75-00-3
Molecular weight		153,8	119,38	50,49	84,9	165,8	131,4	96,94	96,94	62,5	133,4	133,4	98,96	64,51
Solubility (mg/L)	Max	805 [a]	7920 [a]	7250 [a]	15400 [a]	200 [a]	1198 [e]	6300 [e]	4930 [a]	2760 [a]	1330 [a]	4420 [a]	8700 [e]	20000 [a]
	Average	799	4360	6025	14200	175,5	1149	6300	4215	2180	1232,5	4410	8700	12870
	Min	793 [e]	800 [e]	4800 [e]	13000 [d]	151 [e]	1100 [a]	6300 [a]	3500 [e]	1600 [e]	1135 [e]	4400 [e]	8700 [a]	5740 [e]
Vapour pressure P ·C (mmHg) (20-25C)	Max	115,25 [e]	198 [a]	4310 [c]	455 [a]	18,4 [a]	9000 [e]	395 [e]	202,52 [e]	2800 [a]	124 [a]	25,2 [a]	81,3 [a]	1400 [e]
	Average	113,625	196,09	4037,5	442,2	18,2384	4536	373,5	188,758	2730	122,5	24,1	80,025	1300
	Min	112 [a]	194,18 [e]	3765 [a]	429,4 [d]	18,077 [e]	72 [a]	352 [a]	175 [a]	2660 [e]	121 [e]	23 [e]	78,75 [e]	1200 [a]
H	Max	1,25 [d]	0,15 [a]	1,44 [a]	0,09[a]	0,8 [e]	0,43[a]	0,39 [a]	0,19 [a]	3,49 [a]	0,75 [e]	0,038[a]	0,05 [a]	0,21 [a]
	Average	1,223608	0,148581	0,899661	0,09041915	0,782444	0,4250855	0,1983233	0,09519035	2,30094	0,732502	0,03767731	0,0466548	0,1106535
	Min	1,197 [a]	0,1446 [e]	0,361 [c]	0,0898 [d]	0,765[a]	0,422 [d]	0,0067 [e]	0,0029 [e]	1,11 [d]	0,715 [a]	0,0374 [d]	0,0401 [d]	0,0093 [e]
Log Koc	Max	2,27 [a]	1,67 [a]	0,778 [a]	1,25[d]	2,19 [a]	2,22 [d]	1,72 [d]	1,55 [d]	1,27 [d]	2,04 [a]	1,7 [d]	1,5 [e]	1,25 [a]
	Average	2,155	1,635	0,739	1,16	2,19016585	2,095	1,71	1,506199	1,16	2,03	1,7	1,37	1,25
	Min	2,04 [e]	1,6 [d]	0,7 [c]	1,07 [a]	2,19	1,97 [a]	1,7 [a]	1,46 [a]	1,04 [a]	2,02 [b]	1,7 [a]	1,24 [a]	1,25 [e]
Log Kow	Max	2,73 [d]	1,97 [e]	1,0865 [a]	1,34 [a]	2,965 [a]	2,71 [d]	2,07 [a]	1,86 [e]	1,62 [a]	2,77[a]	2,05 [e]	1,83 [a]	1,578 [a]
	Average	2,58605	1,7455	0,99825	1,29525	2,8177	2,59155	2,065	1,86	1,56165	2,6246	2,03105	1,6508	1,4888
	Min	2,4421 [a]	1,521 [a]	0,91 [c]	1,25 [d]	2,67 [d]	2,47 [a]	2,06 [e]	1,86 [a]	1,5 [d]	2,48 [e]	2,01 [a]	1,47 [d]	1,4 [e]
Coeficient Diffusion Air (cm2/s)		0,078 [a]	0,104 [a]	0,126 [a]	0,101 [a]	0,072 [a]	0,079 [a]	0,0707 [a]	0,0735 [a]	0,106 [a]	0,078 a	0,0792 [a]	0,104 [a]	0,15 [a]
Coeficient Diffusion water (cm2/s)		0,0000088 [a]	0,00001 [a]	0,0000065 [a]	0,0000117 [a]	0,0000082 [a]	0,0000091 [a]	0,0000119 [a]	0,0000113 [a]	0,000123 [a]	0,0000088 [a]	0,0000088 [a]	0,0000091 [a]	0,0000118 [a]

a : Data base from RBCA model

b: US-EPA. Toxicological review of 1,1,1-Trichloroethane (CAS No. 71-55-6) In Support of Summary Information on the Integrated Risk Information System (IRIS). Aug 2007.

c: US-EPA. Toxicological review of methyl chloride (CAS No. 74-87-3) In Support of Summary Information on the Integrated Risk Information System (IRIS). June 2001.

d: US- EPA, Integrated Risk Information System, review, 2010.

e: Elsevier. Reaxys. 2013. Elsevier Information Systems GmbH.

The same process has been accomplished to collect the toxicological data from IRIS [16] and other reviews or articles [22]. Concerning the toxicological properties, Reference Dose (RfD) and Reference Concentration (RfC) for different routes of entry has been used to determine the potential of a toxic effect. Slope factors (SF) and Unit risks level (URL) have been used to determine the development of excess number of cancers in receptors [23].

Exposure parameters

The exposure factors change according to the social behavior, which is different from one place to another, from one gender to the other, or according to the age. For example, children have usually hand-to-mouth activities; at the adolescence, they stop this behavior but they are still in contact with higher amounts of soils (through playing football or other games) than adults [24]. So it is interesting to differentiate the risk evaluation for each subpopulation group. Indeed, males and females (as children/adults) do not have the same food needs or body weights.

Exposure parameters for different countries have been checked. Concerning quantity of food ingested, exposure time, the maximum available values or the 95th percentile have been chosen, in order to have the worst scenarios. If the specific exposure parameter was not available, the default value of the RBCA model has been used.

Groundwater parameters

A minimum of three wells in the aquifer have been necessary for triangulation of water levels and to indicate groundwater flow direction. Other parameters are shown in Table 5.1.

Air parameters

It has been also needed to characterize air parameters, the dimension of the zone, and also the dispersion taxes (see Table 5.2).

Table 4. Toxicological parameters.

		Toxicological parameters																	
		RfD TDSI oral (mg/kg/day)			RdE TDSI derma (mg/kg/day)			RfC TCA inhalation equivalent (mg/m3)			Oral Slope factor equivalent			Derma Slope factor equivalent			Unit risk factor equivalent for inhalation (µg/m3)		
		Max	Average	Min	Max	Av	Min	Max	Average	Min	Max	Average	Min	Max	Av	Min	Max	Average	Min
Chloromethane	**CT**	4 E-3 [b]	2,35 E-3	7 E-4 [a]	4 E-3 [b]	2,35 E-3	7 E-4 [a]	0,1 [b]	5,10E-02	2 E-3 [q]	0,13 [q]	0,1	7 E-2 [b]	0,13 [q]	0,1	7 E-2 [b]	3 E-6 [b]	9,0E-06	1,5 E-5 [d]
	CF	1 E-2 [b]	1 E-2	1 E-2 [a]	1 E-2 [b]	1 E-2	1 E-2 [a]	Not establish by EPA			3,1 E-2 [g]	1,85 E-2	6,1E-3 [d]	3,1 E-2 [g]	1,85 E-2	6,1E-3 [d]	2,3 E-5 [d]	1,4E-05	5,3E-6 [l]
	CM	-		-	-		-	9 E-2 [b]	9 E-2	9 E-2 [q]	1,3 E-2 [q]			1,3 E-2 [q]			1,8 E-6 [h]		1,8 E-6 [q]
	DCM	6 E-2 [a]	3,3 E-2	6 E-3 [b]	6 E-2 [a]	3,3 E-2	6 E-3 [b]	3 [q]	1,53	0,6 [b]	7,5 E-3 [d]	4,75 E-3	2 E-3 [b]	7,5 E-3 [d]	4,75 E-3	2 E-3 [b]	4,7E-7 [d]	2,4E-07	1 E-8 [b]
Chloroethene	**PCE**	1 E-2 [a]	8 E-3	6 E-3 [b]	1 E-2 [a]	8 E-3	6 E-3 [b]	0,27 [q]	0,155	4 E-2 [b]	0,54 [g]	0,27	1.5E-3 [b]	0,54 [g]	0,27	1.5E-3 [b]	1.9 E-7 [b]	3,9E-07	5,8E-7 [d]
	TCE	6 E-3 [a]	3,19 E-3	3,7 E-4 [b]	6 E-3 [a]	3,19 E-3	3,7 E-4 [b]	1,9E-3 [b]			4.6 E-2 [b]	2,4 E-2	2,1 E-3 [g]	4.6 E-2 [b]	2,4 E-2	2,1 E-3 [g]	4.1E-6 [b]	1,7E-06	1,7E-6 [d]
	tDCE	2 E-2 [b]	2 E-2	2 E-2 [a]	2 E-2 [b]	2 E-2	2 E-2 [a]	In discussion [b]		0,793 [q]	-		-	-		-	-		-
	cDCE	1E-2 [a]	6 E-3	2 E-3 [b]	1E-2 [a]	6 E-3	2 E-3 [b]			0,793 [q]	-		-	-		-	-		-
	VC	3 E-3 [b]	3 E-3	3 E-3 [a]	3 E-3 [b]	3 E-3	3 E-3 [a]	0,1 [b]	0,1	0,1 [q]	1,9 [d]	1,33	7.5E-1 [b]	1,9 [d]	1,33	7.5E-1 [b]	8,4E-5 [d]	4,4E-05	4.4E-6 [b]
Chloroethane	**1,1,1 TCA**	2 [a]	1,1	0,2 [q]	2 [a]	1,1	0,2 [q]	1 [d]	1	1 [q]	-		-	-		-	-		-
	1,1,2 TCA	4 E-3 [b]	4 E-3	4 E-3 [a]	4 E-3 [b]	4 E-3	4 E-3 [a]	Not establish by EPA			5.7E-2 [b]	5.7E-2	5.7E-2 [q]	5.7E-2 [b]	5.7E-2	5.7E-2 [q]	1.6E-5 [b]	1.6E-5	1.6E-5 [l]
	1,2DCA	-		-	-		-	2,42 [q]			9.1E-2 [b]	9.1E-2	9.1E-2 [q]	9.1E-2 [b]	9.1E-2	9.1E-2 [q]	2.6E-5 [b]	2.6E-5	2.6E-5 [q]
	CA	0,4 [q]	0,4	0,4 [a]	0,4 [q]	0,4	0,4 [a]	10 [b]	10	10 [q]	-		-	-		-	-		-

a: Data from the model

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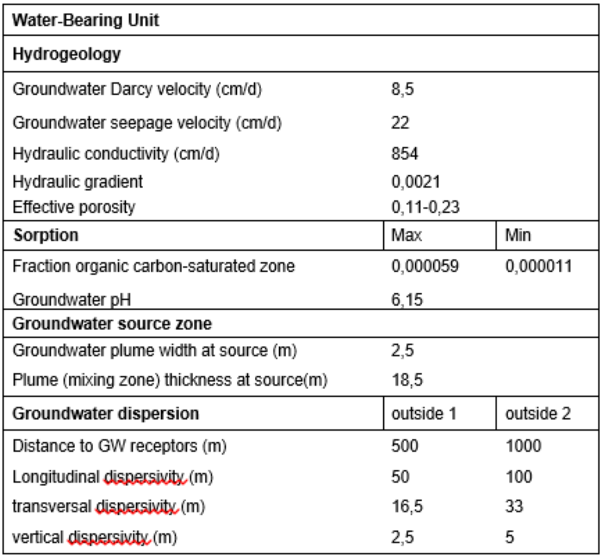
q: GSI Environemental Inc, GSI Chemical properties Database, 2010.

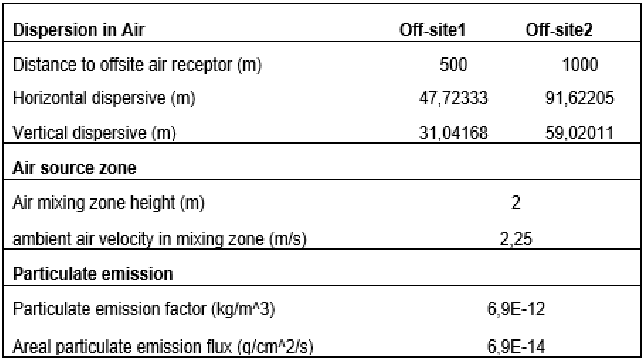
r: Department of Environmental Toxicology University of California Davis, Final draft report Intermedia Transfer Factors for Contaminants Found at Hazardous Waste Sites TRICHLOROETHYLENE (TCE) Risk Science Program (RSP), California, 1994, 46 pp. ALL THESE REFERENCES MUST BE AT THE FINAL REFERENCE LIST. HERE, ONLY NAMES AND YEARS MUST APPEAR.

Table 5.1. Water parameters to fit the RBCA model.



Water-Bearing Unit		
Hydrogeology		
Groundwater Darcy velocity (cm/d)	8,5	
Groundwater seepage velocity (cm/d)	22	
Hydraulic conductivity (cm/d)	854	
Hydraulic gradient	0,0021	
Effective porosity	0,11-0,23	
Sorption	Max	Min
Fraction organic carbon-saturated zone	0,000059	0,000011
Groundwater pH	6,15	
Groundwater source zone		
Groundwater plume width at source (m)	2,5	
Plume (mixing zone) thickness at source(m)	18,5	
Groundwater dispersion	outside 1	outside 2
Distance to GW receptors (m)	500	1000
Longitudinal dispersivity (m)	50	100
transversal dispersivity (m)	16,5	33
vertical dispersivity (m)	2,5	5

Table 5.2. Air parameters to fit the RBCA model.



Dispersion in Air	**Off-site1**	**Off-site2**
Distance to offsite air receptor (m)	500	1000
Horizontal dispersive (m)	47,72333	91,62205
Vertical dispersive (m)	31,04168	59,02011
Air source zone		
Air mixing zone height (m)	2	
ambient air velocity in mixing zone (m/s)	2,25	
Particulate emission		
Particulate emission factor (kg/m^3)	6,9E-12	
Areal particulate emission flux (g/cm^2/s)	6,9E-14	

8. Results

Thanks to the risk analyses applied according exposure parameters considerations made in different countries, we have had a large view of different scenarios, with different exposure parameters for the potential on site receptors.

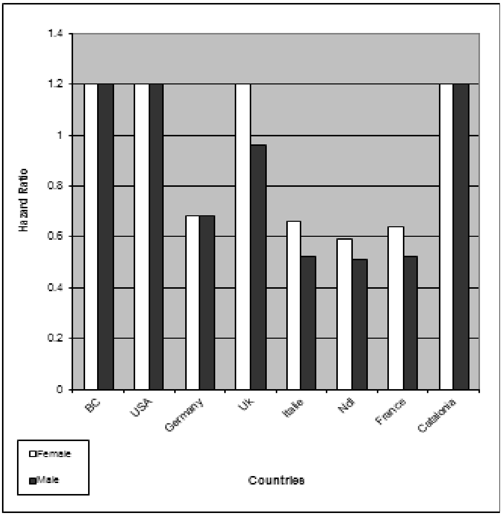


Figure 4. Hazard Ratio from the exposition of males and females working at the polluted area and exposed to polluted groundwater according to exposition default values applied at each country.

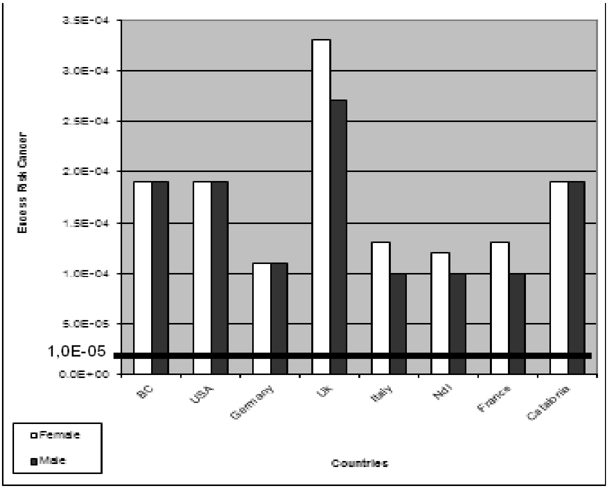


Figure 5. Excess risk of cancer from the exposition of males and females working at the polluted area and exposed to polluted groundwater according to exposition default values applied at each country.

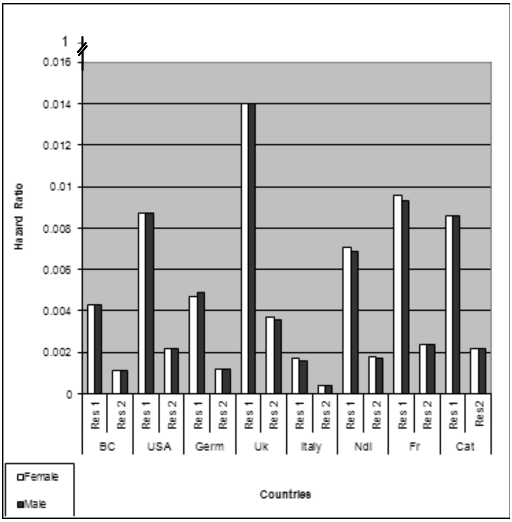


Figure 6. Hazard risk from the exposition of males and females living at the polluted areas and exposed to the polluted groundwater according the exposition default values applied at each country.

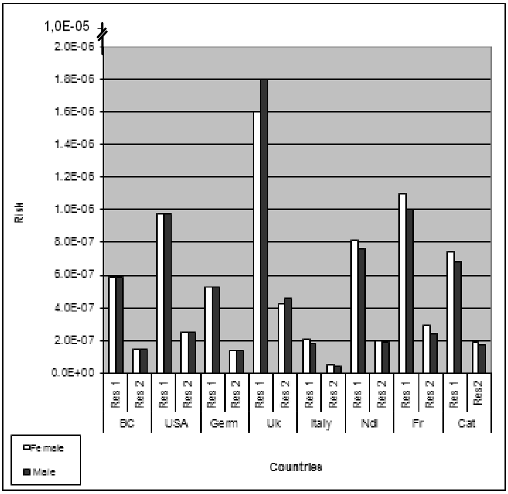


Figure 7. Excess risk of cancer from the exposition of males and females living at the polluted areas and exposed to the polluted groundwater according the exposition default values applied at each country.

The variation of the calculated risk between female and male depends on the exposure parameters which can differ from one gender to another, when considering specific exposure parameters (body weight, dairy products ingestion,…). The parameter which changes the most is the body weight. For example, for Catalonian female body weight is statistically 55 kg, whereas for male is 70 kg; or, 70 and 83.2 kg respectively in UK. Indeed, as female have a lower body weight than male and that body weight is on the denominator of the excess risk equation, a lower body weight increase the risk. Vegetable uptake or skin surface are also changing between male and female. Indeed, the UK exposure factors, for the consummation of water polluted for the receptor residential the risk is higher for men than for women. This can be explained by differences in the water uptake for man (3.17 L) and woman (2.27 L), so male is more exposed and that means a higher risk.

Conclusion

This work was focused on the value of the real exposure time and exposure parameters in a particular industrial region and on contamination of chlorinated solvent DNAPL's, but it can be extrapolated to different scenarios. Differences in human exposure factors data, including anthropometric and sociocultural data (e.g., body weights, skin-surface areas, and life expectancy), behavioural data (e.g., non-dietary ingestion rates, activity/time use patterns, and consumer product use), factors that may be influenced by the physiological needs of the body, metabolic activity, and health and weight status (e.g., water and food intake, and inhalation rates), and other factors (e.g., building characteristics) can lead to variations in calculated risk.

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