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The Volatilization of Pollutants from Soil and Groundwater: Its Importance in Assessing Risk for Human Health for a Real Contaminated Site

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ABSTRACT

Pollution of different elements (air, water, soil and subsoil) resulting both from accidental events and from ordinary industrial and civil activities causes negative effects on the human health and on the environment. The present paper examines the analysis of a contaminated site, focusing the attention on the negative effects for receptors exposed to soil and groundwater contamination caused by industrial activities. The case study investigated is a contaminated area located in the industrial district of Trento North once occupied by the Italian Carbochimica plant. Pollution in that area is mainly due to contamination of soil and groundwater with polycyclic aromatic hydrocarbons. The methodology applied is the risk evaluation for human health, in terms of individual cancer risk and hazard index. In particular the attention has been focused on a specific migration way: if pollutants in the soil or in the groundwater undergo a phase change, they spread and get to the soil surface, causing a dispersion of vapors in the atmosphere. In this case risk assessment calls for the evaluation of volatilization factor. Among the different models dealing with the estimation of volatilization factor, those mostly known and used in the national and international field of Human Health Risk Assessment were chosen: Jury's and Farmer's models. A sensitivity analysis of models was performed, in order to identify the most significant parameters to estimate the volatilization factors among the wide range of input parameters for the application of models. Performing an accurate selection and data processing of the contaminated site, models for the volatilization factors calculation are applied, thus evaluating air concentrations and Human Health Risk. The analysis of the resulting estimates is an excellent aid to draw interesting conclusions and to verify if the soil and groundwater pollutants volatilization affects the human health considerably.

Keywords: *Human Health Risk Assessment, Volatilization Models, Soil Contamination, Groundwater Contamination, Cancer Risk, Hazard Index*

1. Introduction

Pollution of different elements (air, water, soil and subsoil) resulting both from accidental events and from daily industrial and civil activities, implies effects on the human health and on the environment. Through the application of the Human Health Risk Assessment methodology in a specific contaminated site, it is possible to evaluate the magnitude and probability of negative effects posed to human beings caused by exposure to contamination in various media [1]. The consolidated procedure concerning the risk analysis applies the RBCA approach [2], which refers to a step method based on three levels of assessment. In the following we refer to a tier 2 risk assessment, involving site-specific data collection and

analytical modeling of the fate and transport of contaminants across the environmental media involved (in particular unsaturated soil, groundwater and outdoor air).

Receptors exposures typically are described as contact between the chemicals of concern (COCs) and the body's exchange boundaries (skin, lung and gastrointestinal tract) across which the chemicals can be absorbed [3]. Exposure assessment also includes the identification and quantification of the multiple pathways and multiple routes that characterize the movement of a chemical from its source to an exposed individual. Frequently, in a site-specific human health risk analysis, among all the potential pathways (inhalation, ingestion and dermal exposure) and migration routes, it is possible to identify a few ones that have a predominant influence on the evaluation of

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final individual cancer risk and hazard index for a receptors group.

In the present paper the attention has been focused on the pathway of volatilization of hazardous vapors coming from contaminated soil and groundwater into open air and consequent exposure of receptors to COCs. The aims of this study are to: 1) identify the parameters that more affect the estimate of the volatilization factors and their uncertainty, 2) evaluate the importance of volatilization of pollutants from soil and groundwater in the risk assessment for human health through the application of the models to a real contaminated site case-study.

In order to reach the first objective, a selection of simple and diffusely used models for the estimation of volatilization factor in risk analysis was performed thus operating a sensitivity analysis on input parameters for the application of models; the second objective has been approached through the investigation of a case-study concerning a contaminated area located in northern Italy, where contamination of soil and groundwater is mainly due to polycyclic aromatic hydrocarbons deriving from the productive cycles in remote industrial activities.

2. Vapors Migration modeling

2.1. Volatilization Factors

In the assessment of human health risk, the estimation of transport factors is necessary, thus considering the migration of pollutants from the contamination source to the targets. When the volatilization is regarded, the transport factor is called volatilization factor (VF) and considers the attenuation phenomena occurring during migration. VF represents the ratio between the pollutants concentration in the exposure site (c_{poe}, expressed for example in mg/m^3) and the concentration at the contamination source (c_s expressed for example in mg/kg), as resulting from soil samples or calculated applying models:

$$c_{poe} = VF \cdot c_s \qquad (1)$$

Detailed models of contaminant transport in soil and groundwater include processes such as diffusion, dispersion and convection phenomena for each of the phases present in the soil. Obviously, such models include a large number of contaminated site parameters and soil-specific parameters that are often not available or not very accurate. Therefore, in most volatilization phenomena estimates, predictive models are simplified in order to allow the application of models even in situations where a few site specific parameters are available [4]. For every soil layer a different volatilization factor is identified: VF_{ss} (volatilization of outdoor vapors from surface soil), VF_{ds} (volatilization factor of outdoor vapors

from deep soil), VF_{gw} (volatilization factor of outdoor vapors from groundwater). These factors are used to estimate outdoor air concentration of volatiles by using the known chemical concentration in the groundwater and soil.

Among the volatilization models from subsurface sources into outdoor air available in literature, two models were selected, widely applied in the Risk Assessment for Human Health and Environment and suggested by EPA [1,5,6], ISPRA [7] and ASTM standard [2,8].

In detail the volatilization models selected are:
- Jury's model [9,10], assuming a contamination source with semi-infinite dimensions and time-varying concentrations (estimation of $VF_{ss,J1}$ and $VF_{ss,J2}$ for surface soil and $VF_{ds,J}$ for deep soil),
- Farmer's model [11], with steady-state assumption (estimation of $VF_{ss,F}$ for surface soil, $VF_{ds,F1}$, $VF_{ds,F2}$ for deep soil and VF_{gw} for groundwater).

These models make the following common assumptions when calculating volatilization factors: uniform and isotropic soil (fissuring-porous soil is not considered); the chemicals do not biodegrade in soil, in water solutions or in vapor phase; no transport within water, no absorption or production of the gases; the partitioning between the chemicals in the groundwater/soil matrix and vapors is linear; chemical losses by biodegradation do not occur between the groundwater/soil and the surface; for outdoor emissions, steady-state atmospheric dispersion of vapors occurs within the breathing zone.

The calculation of VF, hence the concentration of volatiles outdoors, is based on the movement of volatiles from the soil and groundwater up through the capillary zone, through the unsaturated zone, and emission into the breathing zone in outdoor air (**Figure 1**).

The models relationships are derived from simple one-dimensional or integral mass balances, based on the dif-
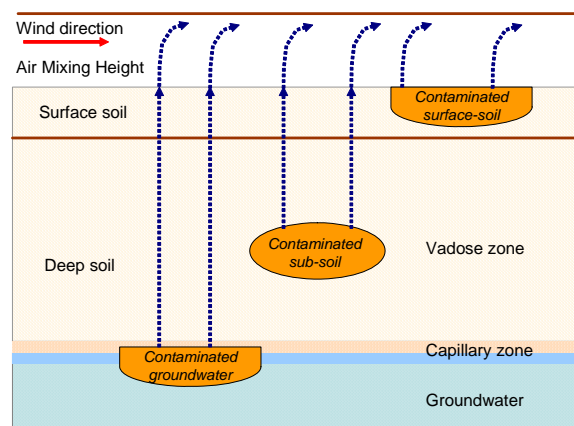

Figure 1. Conceptual model of vapors migration to outdoor air.

ferent hypothesis of the considered volatilization models.

In particular $VF_{ss,J1}$ derives from Jury's model, based on the one-dimensional application of Fick's laws considering the following assumptions and conditions: absence of boundary layer at the interface soil-air, thus assuming a perfect mixing situation in air; no water flow is considered through the soil (the pollutant's loss due to its transport into the groundwater is thus not considered and lisciviation is therefore considered apart from volatilization); the soil contaminated column of semi-infinite depth has homogeneous physical characteristics; finally a boundary condition considers that the soil concentration at the ground level must be zero.

It's worth noting that the condition of equilibrium partitioning is very rarely accomplished in the subsurface, therefore calculated soil vapor values from soil-phase data may clearly overestimate or underestimate actual soil vapor concentration.

$VF_{ss,J2}$ and $VF_{ds,J}$ are the upper limit of Jury's model and as a result are a conservative evaluation. Briefly, they consider a mass balance in which the total value of mass that can enter into the mixing volume (corresponding to the total mass of pollutants in the surface soil) is equal to the mass coming out of the mixing volume because of the aeolian transport during exposure time. Therefore the applications of these relations do not take into account the specific contaminant properties.

$VF_{ss,F}$, $VF_{ds,F1}$, $VF_{ds,F2}$, VF_{gw} are obtained in Farmer's model. This model considers an initial uncontaminated layer of soil (depth Ls) between the contamination source top and the ground level. Vapors flux is calculated applying the Fick's laws in steady-state conditions, so any time reductions in source contamination due to the volatilizing phenomena are not included. The equation $VF_{ss,F}$ is not considered since the outcome values of outdoor volatilizing factors from surface soil result extremely conservative for volatile compounds and not really conservative for the less volatile ones, when compared to the results of the equation $VF_{ss,J1}$. Despite the fact that they come from the same model, $VF_{ds,F1}$ is different from $VF_{ds,F2}$, since they apply different hypothesis: the second one considers the air flow from soil, while the first one counts it as negligible. VF_{gw} uses this last hypothesis, but it is applied to the groundwater's characteristics.

It's worth noting that these models, though widely used in risk assessment analysis, are based on simplifying hypothesis that make them not always fitting the reality of the case-studies. As an example, weaknesses and critical aspects of the models are related to water soluble compounds, contaminated source with non-homogenous properties and time-variant volatilization quantities.

Equations of volatilization factors according to Jury

and Farmer are reported in the following (see **Figure 2** for conceptual model used and **Table 1** for parameters included in the equations):

$$VF_{ss,J1} = \frac{2W \cdot \rho_s}{U_{air} \cdot \delta_{air}} \sqrt{\frac{DA}{\pi \tau}} \left[\frac{kg}{m^3} \right] \qquad (2)$$

$$VF_{ss,J2} = \frac{A \cdot \rho_s \cdot d}{U_{air} \cdot \delta_{air} \cdot \tau \cdot L} \left[\frac{kg}{m^3} \right] \qquad (3)$$

$$VF_{ds,J} = \frac{W \cdot \rho_s \cdot d_s}{U_{air} \cdot \delta_{air} \cdot \tau} \left[\frac{kg}{m^3} \right] \qquad (4)$$

$$VF_{ss,F} = \frac{\rho_s}{U_{air} \cdot \delta_{air} \cdot L} D_A A \frac{1}{L_s} = VF_{ds,F1} \left[\frac{kg}{m^3} \right] \qquad (5)$$

$$VF_{ds,F2} = \frac{\rho_s \cdot D_A}{\left(U_{air} \cdot \delta_{air} \cdot L \cdot \dfrac{L_s}{A} + D_s^{eff} \right)} \left[\frac{kg}{m^3} \right] \qquad (6)$$

$$VF_{gw} = \frac{H}{1 + \dfrac{U_{air} \delta_{air} L_{GW}}{D_{ws}^{eff} W}} \left[\frac{1}{m^3} \right] \qquad (7)$$

where the following parameters are included:

$$D_A = D_s^{eff} \cdot \frac{H}{\theta_w + k_s \rho_s + H \theta_a} \left[\frac{m^2}{s} \right] \qquad (8)$$

$$D_s^{eff} = \left(D_a \cdot \frac{\theta_a^{3.33}}{\theta_e^2} + \frac{D_w}{H} \cdot \frac{\theta_w^{3.33}}{\theta_e^2} \right) \left[\frac{m^2}{s} \right] \qquad (9)$$

$$D_{ws}^{eff} = \left(h_{cap} + h_v \right) \cdot \left(\frac{h_{cap}}{D_{cap}^{eff}} + \frac{h_v}{D_s^{eff}} \right)^{-1} \left[\frac{m^2}{s} \right] \qquad (10)$$

$$D_{cap}^{eff} = D_a \cdot \frac{\theta_{a,cap}^{3.33}}{\theta_e^2} + \frac{D_w}{H} \cdot \frac{\theta_{w,cap}^{3.33}}{\theta_e^2} \left[\frac{m^2}{s} \right] \qquad (11)$$

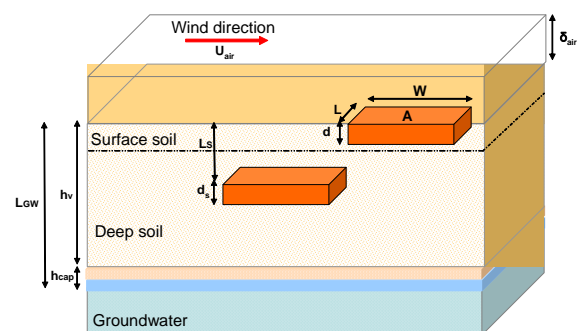In order to apply models for the volatilization factors assessment a wide set of input parameters has to be con-

Figure 2. Representation of some geometrical parameters in the scheme of conceptual model.

Table 1. List of parameters in volatilization factors models.

d	Thickness of contamination source in the surface soil	m
d_s	Thickness of contamination source in the deep soil	m
h_{cap}	Height of capillary zone	m
h_v	Height of unsaturated zone	m
L_s	Depth to subsurface soil contamination source	m
L_{GW}	Depth to groundwater ($= h_{cap} + h_v$)	m
L	Extension of contamination source in across-wind direction	m
W	Width of contamination source area parallel to wind direction or groundwater flow direction	m
A	Contamination source area	m^2
ρ_s	Soil bulk density	kg/m^3
θ_e	Effective terrain porosity in unsaturated zone	dimensionless
θ_w	Volumetric water content	dimensionless
θ_a	Volumetric air content	dimensionless
$\theta_{w,cap}$	Volumetric water content in the capillary zone	dimensionless
$\theta_{a,cap}$	Volumetric air content in the capillary zone	dimensionless
k_S	Soil-water sorption coefficient	$m^3 H_2O/kg$ soil
D_s^{eff}	Effective diffusion coefficient in soil based on vapor-phase concentration	m^2/s
D_{ws}^{eff}	Effective diffusion coefficient between the groundwater and soil surface	m^2/s
D_{cap}^{eff}	Effective diffusion coefficient through capillary zone	m^2/s
D_a	Diffusion coefficient of the substance in air	m^2/s
D_w	Diffusion coefficient of the substance in water	m^2/s
H	Henry's Law constant	dimensionless
δ_{air}	Ambient air mixing zone height	m
U_{air}	Wind speed above the ground surface in the ambient mixing zone	m/s
τ	Average duration time of vapor flux	s

sidered, characterizing geometry of contamination, the contaminated soil's and the above air's characteristics, and the physicochemical pollutants properties.

An analysis of the volatilization factors was carried out in the open literature in order to establish the most suitable transport factor for every environment section. Both for the surface soil and the deep soil, the approach proposed by standards ASTM 1739/95 [2], PS 104/98 [8] and by Handbook Unichim 196/01 [12] was adopted. Between the two evaluations $VF_{ss,J1}$ and $VF_{ss,J2}$, in particular the first equation is suggested for the less volatile compounds while the second one is used for very volatile compounds. The same choice is suggested also by the software RBCA Tool Kit [13], BP-RISC [14] and GIUDITTA [15].

As regards the deep soil both the equation $VF_{ds,F1}$ and the equation $VF_{ds,F2}$ gave nearly the same results. Following the approach suggested by Unichim Handbook 196/01 [12], the equations $VF_{ds,F2}$ and $VF_{ds,J}$ were considered. In particular $VF_{ds,F2}$ was adopted for the less

volatile compounds while $VF_{ds,J}$ for those very volatile. As a matter of fact the values supplied by the equation $VF_{ds,F2}$ were too high and thus too conservative if applied to very volatile compounds. This kind of approach is adopted by software GIUDITTA [15] and RBCA Tool Kit [13].

It's worth noting that the models analysis evidenced that the incongruous situation may occur in which the VF for surface soil value is lower than the VF value for deep soil, but the reason of this lays obviously on the different hypothesis at the basis of the two different model typologies.

Regarding saturated soil only a volatilizing factor VF_{gw} was considered. This equation is suggested by standards ASTM 1739/95 [2], PS 104/98 [8], by Unichim Handbook 196/01 [12] and by all the software examined (BP-RISC ver. 4.0, RBCA Toolkit ver. 1.2., GIUDITTA ver. 3.1 and ROME ver. 2.1).

2.2. Sensitivity Analysis of Volatilization Models

The sensitivity analysis is a common technique used in

the modeling issue to assess the effect of variability and uncertainty of parameters on the results obtained from the application of a specific mathematical model [16]. In particular, in this section the aim is the sensitivity analysis of the transport factors previously described, thus identifying the variables that mostly affect these factors and therefore the human health.

As explained in the previous section the selected volatilization factors are: $VF_{ss,J1}$ and $VF_{ss,J2}$ for surface soil, $VF_{ds,J}$ and $VF_{ds,F2}$ for deep soil, VF_{gw} for groundwater. In the analysis, a typical volatile substance (benzene) and a less volatile one (benzo(a)pyrene) are taken into account, in order to consider both the expressions for surface soil and deep soil. In particular $VF_{ss,J1}$ and $VF_{ds,F2}$ are applied for benzo(a)pyrene, while $VF_{ss,J2}$ and $VF_{ds,J}$ are applied for benzene. VF_{gw} is suitable for both compounds. A preliminary analysis of which parameters are involved in the various volatilization factors is specified in **Table 2**.

In the list, some parameters are not reported because they are not independent, but are correlated as follows: A and L ($A/L = W$); θ_a ($\theta_a = \theta_e - \theta_w$); θ_{acap} ($\theta_{acap} = \theta_e - \theta_{wcap}$); h_v ($h_v = LGW - h_{cap}$).

A brief remark has to be noted for the soil-water sorption coefficient k_s: this parameter defines the substance partitioning property between the solid phase (soil) and the water phase. It is evaluated as the partition soil-water coefficient (k_d) that corresponds to ($k_{OC} \cdot f_{oc}$) for organic compounds, where k_{OC} is the carbon-water partition coefficient and f_{oc} represents the organic carbon fraction in unsaturated soil. In this case, only f_{oc} is considered in the variability analysis, whereas the carbon-water partition coefficient is examined as a fixed parameter, as the other specific compounds properties D_a, D_w and H. **Table 3** shows all the specific compound properties utilized in the present sensitivity analysis (bold font) and in the case study after described.

The application of the sensitivity analysis to the volatilization factors attempts to provide a ranking of the model inputs based on their relative contributions to model output variability and uncertainty. As sensitivity indicators the Sensitivity Ratio (SR), also called elasticity and the Sensitivity Score (SS) are taken into account [16].

The Sensitivity Ratio (SR) is the change in model output per unit change in an input variable, as shown in the following equation.

$$SR = \left(\frac{Y_2 - Y_{ref}}{Y_{ref}}\right) \bigg/ \left(\frac{X_2 - X_{ref}}{X_{ref}}\right) \qquad (12)$$

where X_{ref} and Y_{ref} are the reference estimate for an input variable and the corresponding value of the output variable, while X_2 and Y_2 represent the value of the input variable after changing and the corresponding value of

the output variable. The sensitivity ratio assumes different values if different reference values are taken into account: for this reason estimation with minimum, maximum and mean values has been performed.

The Sensitivity Score (SS) is a variation of the sensitivity ratio approach; it may provide more information, but it requires additional information for the input variables.

This score is the SR weighted by a normalized measure of the variability in the input variable, as shown in the following equation.

$$SS = SR \cdot \frac{(X_{max} - X_{min})}{(X_{mean})} \qquad (13)$$

where X_{max} and X_{min} are the maximum and minimum values respectively, of an input variable, while X_{mean} is the mean or reference value of an input variable.

The VF estimates are considered most sensitive to input variables that yield the highest absolute value for SR and SS.

In order to evaluate these preliminary sensitivity indicators, the possible minimum, maximum and mean values assumed by the involved parameters have been examined and reported in **Table 4**. In particular the range of values taken into consideration derives from an analysis of all possible terrain typologies and environment conditions and the less and most probable values assumed by the parameters are the minimum and maximum values. For those parameters for which were not possible the evaluation of a maximum value, the sensitivity score has not been calculated.

The Sensitivity Ratio (SR, with a change of 10% in the input parameters) and the Sensitivity Score (SS) near the minimum value, mean value and maximum value has been calculated for benzene and benzo(a)pyrene.

The evaluated SR and SS are utilized to rank the involved parameter, according to ranking criteria derived from national guidelines [7]. The sensitivity score is the preferred indicator; for parameters without SS, the sensitivity ratio is taken into account. **Table 5** shows the level of sensitivity of volatilization factor for each parameter, considering an average situation among the sensitivity ratio and score estimated near minimum, mean and maximum parameters values. Obviously for SR estimations the same form of dependency of some parameters for different volatilization factors, results in a similar behavior of the sensitivity ranking.

It results that among the soil and groundwater parameters, volumetric water content (θ_w), volumetric water content in the capillary zone ($\theta_{w,cap}$) and organic carbon fraction f_{oc} are relevant for the sensitivity of volatilization factors, besides those parameters easy predictable a

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Table 2. Dependency of parameters in the volatilization factors.

	Source and site specific parameters					Soil specific parameters						Outdoor parameters			Compound specific parameters			
	d	d_s	L_s	L_{gw}	W	ρ_s	h_{ca}	θ_e	θ_w	$\theta_{w,ca}$	f_{oc}	δ_{ai}	U_{air}	τ	D	D_w	H	k_d/k_{oc}
$VF_{ss,J1}$					✓	✓		✓	✓		✓	✓	✓	✓	✓	✓	✓	✓
$VF_{ss,J2}$	✓			✓		✓						✓	✓	✓				
$VF_{ds,J}$		✓		✓		✓						✓	✓	✓				
$VF_{ds,F2}$			✓	✓		✓		✓	✓		✓	✓	✓		✓	✓	✓	✓
VF_{gw}				✓	✓		✓	✓	✓	✓		✓	✓		✓	✓	✓	

Table 3. Compound-specific parameters [1].

Compound	D_a (cm²/s)	D_w (cm²/s)	H	K_{OC} (cm³/g)	Carcinogenic/Toxic properties	Volatility
Acenaphthene	1×10^{-2}	1×10^{-5}	6.34×10^{-3}	4.9×10^3	T	+/-
Anthracene	1×10^{-2}	1×10^{-5}	2.6×10^{-3}	2.35×10^4	T	+/-
Benzene	$\mathbf{8.8 \times 10^{-2}}$	$\mathbf{9.8 \times 10^{-6}}$	$\mathbf{2.28 \times 10^{-1}}$	**62**	**C/T**	**+**
Benz(a)anthracene	5.1×10^{-2}	9×10^{-6}	1.37×10^{-4}	3.58×10^5	C/T	-
Benzo(a)pyrene	$\mathbf{4.3 \times 10^{-2}}$	$\mathbf{9 \times 10^{-6}}$	$\mathbf{4.63 \times 10^{-5}}$	$\mathbf{9.69 \times 10^5}$	**C/T**	**-**
Benzo(b)fluoranthene	2.3×10^{-2}	5.56×10^{-6}	4.55×10^{-3}	1.23×10^6	C/T	+/-
Benzo(g,h,i)perylene	4.9×10^{-2}	5.65×10^{-5}	3×10^{-5}	1.6×10^6	T	-
Benzo(k)fluoranthene	2.62×10^{-2}	5.56×10^{-6}	3.45×10^{-5}	1.23×10^6	C/T	-
Chrysene	2.48×10^{-2}	6.21×10^{-6}	3.88×10^{-3}	3.98×10^5	C/T	+/-
Dibenz(a,h)anthracene	2.02×10^{-2}	5.18×10^{-6}	6.03×10^{-7}	1.79×10^6	C	-
Ethylbenzene	7.5×10^{-2}	7.8×10^{-6}	3.23×10^{-1}	204	T	+
Fluoranthene	1×10^{-2}	1×10^{-5}	6.58×10^{-4}	4.91×10^4	T	-
Fluorene	1×10^{-2}	1×10^{-5}	2.6×10^{-3}	7.71×10^3	T	+/-
Indeno(1,2,3–c,d)pyrene	1.9×10^{-2}	5.66×10^{-6}	6.56×10^{-5}	3.47×10^6	C/T	-
Naphthalene	5.9×10^{-2}	7.5×10^{-6}	1.97×10^{-2}	1.19×10^3	C/T	+
Pyrene	2.72×10^{-2}	7.2×10^{-6}	4.51×10^{-4}	6.8×10^4	T	-
Toluene	8.7×10^{-2}	8.6×10^{-6}	2.72×10^{-1}	140	T	+
Xylenes	8.7×10^{-2}	7.8×10^{-6}	3.14×10^{-1}	196	T	+

Table 4. Range of values for parameters taken into account in the sensitivity analysis.

	Minimum value	Maximum value	Mean/Default value	Measure unit
d	0	1	0.5	m
d_s	0	n.a. (L_{GW}-1)	2	m
h_{cap}	0.1	1.92	1	m
L_s	1	n.a. (L_{GW} - d_s)	2	m
L_{GW}	1	n.a.	3	m
W	0	n.a.	30	m
ρ_s	1600	1750	1700	kg/m³
θ_e	0.28	0.426	0.353	dimensionless
θ_w	0.04	0.38	0.21	dimensionless
$\theta_{w,cap}$	0.248	0.383	0.31	dimensionless
f_{oc}	0.001	0.03	0.01	dimensionless
δ_{air}	1	5	2	m
U_{air}	0.5	4	2.25	m/s
τ	15	40	30 (residential); 25 (industrial)	years

Table 5. Sensitivity ranking of parameters for the volatilization from soil and groundwater of benzene and benzo(a)pyrene. Volatilization factors as described in 2.1.

	$VF_{ss,J1}$	$VF_{ss,J2}$	$VF_{ds,J}$	$VF_{ds,F2}$	VF_{gw}	
	Sost. B	Sost. A	Sost. A	Sost. B	Sost. A	Sost. B
d		M/**H**				
d_s			**H**			
h_{cap}					M/**H**	M/L
L_s				**H**		
L_{GW}					L	**H**
W	**H**	**H**	**H**	**H**	**H**	**H**
ρ_s	L	L	L	L		
θ_e	L			M/L	M	M
θ_w	**H**			**H**	M/L	M
$\theta_{w,cap}$					**H**	L
f_{oc}	M			**H**		
δ_{air}	M/**H**	M/**H**	M/**H**	M/**H**	M/**H**	M/**H**
U_{air}	M	M	M	M	M	M
τ	L	M/L	M/L			

Substance A: benzene; Substance B: benzo(a)pyrene;
SS sensitivity criteria:
$0 < |SS| \leq 0.5$ Low (L); $0.5 < |SS| \leq 1$ Middle/Low (M/L); $1 < |SS| \leq 1.5$ Middle (M); $1.5 < |SS| \leq 2$ Middle/High (M/H); $|SS| > 2$ High (H)
SR sensitivity criteria:
$0 < |SR| \leq 0.33$ Low (L); $0.33 < |SR| \leq 0.66$ Middle (M); $|SR| > 0.66$ High (H).

priori as the contamination source geometry (W, d, d_s, L_s) and the ambient air mixing zone heigth (δ_{air}).

As a final step of the sensitivity analysis, a Monte Carlo Simulation has been performed, assuming a Gaussian probability distribution for the variability of input parameters to derive a probability distribution of outcomes. This approach allows multiple input variables to vary simultaneously in order to rank ordering the input variables contribution to variability in the outcome estimate. The graphs (**Figure 3**) extracted by the application of the Crystal Ball software [17] show both the relative magnitude and direction of influence (positive or negative) for each variable in the calculation of Volatilization Factors (Contribution to Variance). The simulation was performed with 100,000 trails and correlated assumptions have been applied. The Gaussian probability distributions of each input parameters are set up fitting minimum, mean and maximum values or fitting values for different soil typologies [18-21]. In particular in order to build the Gaussian distribution, it has been assumed the mean of the distribution as the mean/default values as indentified before and the standard deviation as about one third of the distance between the mean and the minimum or the maximum value.

The software Crystal Ball calculates sensitivity by computing Spearman's rank correlation coefficients [22], which measure the strength and direction of association between input variables and output estimates while the simulation is running. Correlation coefficients provide a meaningful measure of the degree to which outputs and inputs change together.

If an input and an output have a high correlation coefficient, it means that the input has a significant impact on the output; positive coefficients indicate that an increase in the input is associated with an increase in the output while negative coefficients imply the opposite situation. The larger the absolute value of the correlation coefficient, the stronger the relationship. In addition, to help interpret the rank correlations, Crystal Ball computes the Contribution to Variance (as represented in the above cited graphs) that designates what percentage of the variance in the target output is due to the specific input; it is calculated by squaring the rank correlation coefficients and normalizing them to 100%.

The analysis of contribution to variance in sensitivity charts almost confirms the results obtained in the estimation of the simplified analysis with SR and SS estimation: in the case of less volatile compounds, the volumetric water content (θ_w) has a predominant role among parameters in volatilization factors from soil and groundwater, followed by f_{oc} in the volatilization from soil and L_{GW} in the volatilization from groundwater; in the case

The Volatilization of Pollutants from Soil and Groundwater: Its Importance in Assessing Risk for
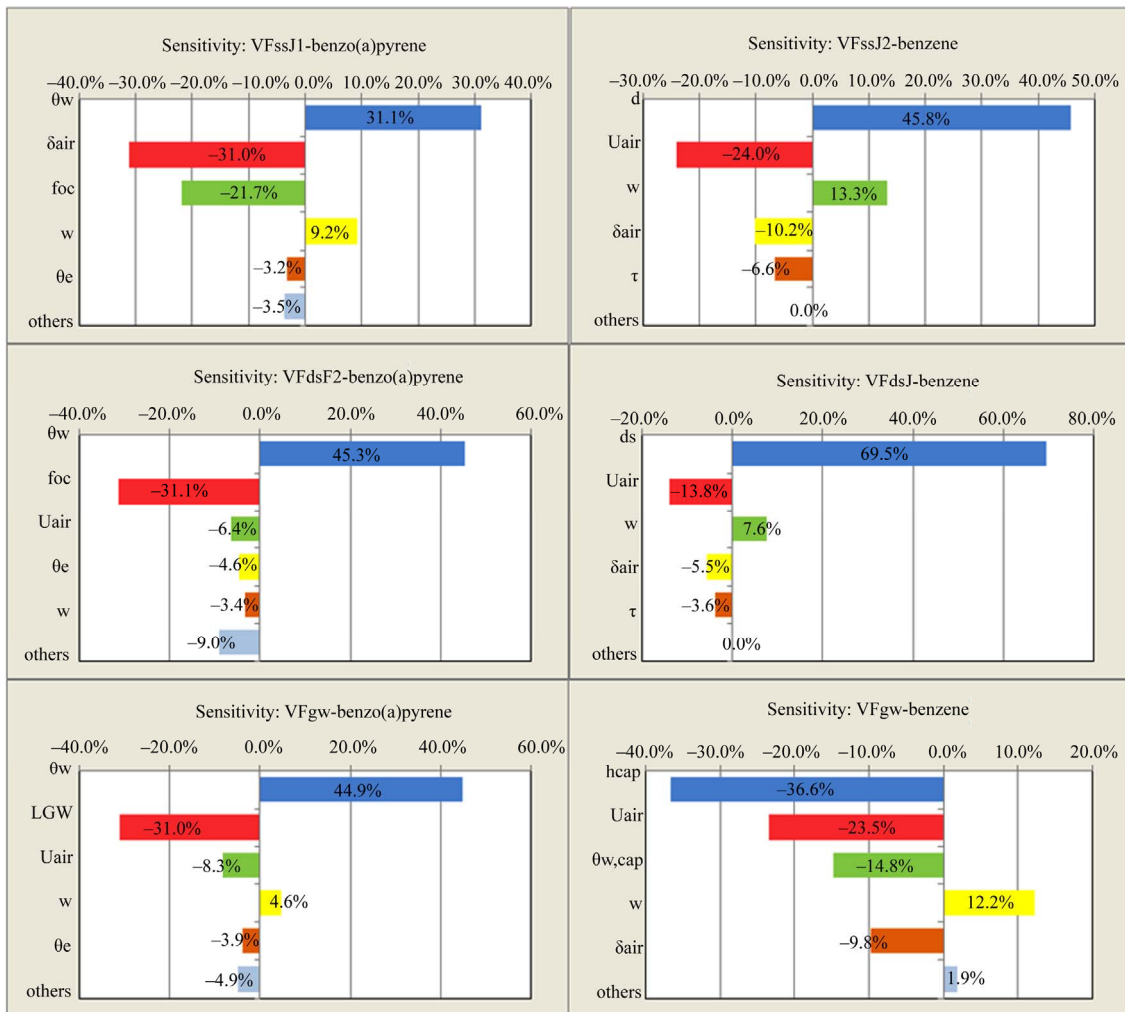Human Health for a Real Contaminated Site

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Figure 3. Sensitivity charts for Volatilization Factors resulting from Monte Carlo Simulation (Contribution to Variance).

of very volatile compounds as benzene, thickness of contamination source is the prevailing parameter in volatilization from soil, while h_{cap} in volatilization from groundwater. In both cases the dimension of the contamination source W has a medium weight in the contribution of variance differently from the high sensitivity ranking evaluated by the SR and SS evaluation; otherwise the wind velocity, which the SR and SS estimation evaluated in all cases with a medium ranking, has in the Monte Carlo analysis a medium contribute to variance for volatilization of very volatile compounds and a lower contribute for volatilization of less volatile compounds.

3. Case Study: "North Trento"

3.1. Site Description

A case study, regarding a contaminated area in Trentino Alto Adige, is hereby analyzed. The area in exam is in the self-governing province of Trento, in the abandoned

industrial area of north Trento, once occupied by the "Carbochimica Italiana" plant (42,700 m^2) which has been the last owner of the site.

The plant activity was initially tar distillation for road works and waterproofing and was then extended to the production of naphthalene, oils for wood, pitch for electrodes, phthalic anhydride and fumaric acid. In 1983, after a declining of activity and the economic inability to invest in process water depuration, the plant was closed. In the middle of the 80s plants of Carbochimica Italiana were demolished and the industrial site was dismissed.

The site is in the list of priority of the contaminated sites of national interest.

In 2001 a barrier has been realized as environmental contingency action for groundwater, in order to put a hydraulic confine for the contamination dispersion. Since September 2004 experimentations about reclamation on demonstrative scale has begun, in order to test the results

of the chemical oxidation by means of ozone technology [23].

The area is still characterized by soil and groundwater pollution as a consequence of the productive activity that took place in the area without a proper control of productive cycles. The site has been analyzed with a monitoring campaign in which a large amount of data samples have been produced: 219 surveys, 879 samples and 23,738 chemical analyses for about a hundred of chemical compounds. Among these, eighteen substances have been analyzed, extracting the ones with higher concentration, worse toxicity properties and more extensive detection.

The list of site contamination substances is reported in the **Table 3**, in which compound-specific parameters are reported. For each analyzed substance carcinogenic and/or toxic classification and volatility characteristics are reported.

Most of the analyzed compounds exceed the limit values of the contaminated sites established by national regulation for soil and for some substances groundwater limits, too.

3.2. Conceptual Model: Contaminated Site, Soil and Groundwater Characterization

The stratigraphy of subsoil in the north Trento area is characterized by a surface soil 1 meter depth of filling terrain (SS in VF calculation), the beneath deep soil of sandy loam texture and, at about 2.5 m (h_v) from terrain level, the saturated area. The piezometric oscillation of groundwater level can be considered ± 1.5 m. The monitored data samples have been set apart as contamination in surface soil and in deep soil. The surface soil and the deep soil have been considered conservatively as fully contaminated ($d = 1$ m, $d_s = 1.5$ m). Capillary height for sandy loam texture is assumed as 0.25 m [24]. The contaminated area is schematized to a rectangle of dimensions 140 m × 300 m (W parallel and L orthogonal to wind direction). The groundwater direction is the same as the wind one since both groundwater and wind direction follow the Adige Valley direction (from north-west to south-east). Wind velocity U_{air} and direction are obtained from the meteorological station of Trento-Roncafort (194 m a.s.l.). A value of 1.37 m/s has been calculated as the mean wind velocity, measuring data of a recent year with an anemometer localized at 10 m of height, so for conservative approximation a mean value of about 1 m/s has been assumed at the ambient air mixing zone height (2 m). Soil properties are assumed as those typical of sandy loam texture. As suggested in the national guidelines [7], the mean duration time of vapor flux is posed coinciding with the exposure duration of receptors. For industrial/commercial areas the considered value is 25

years.

The contamination distribution mapping has been realized arranging a georeferenced database with the concentration mean values of the different pollutants in the surface soil and in the deep soil in 171 sampling points. As regards the groundwater concentration values, a homogeneous mean distribution has been considered, taking into account a few available monitoring points in proximity of the industrial area.

The analyzed site has been subdivided in a number of cells with sides parallel and orthogonal to the wind direction, which coincides with the groundwater flux direction; the dimensions of the cells are $W = 16$ m parallel and $L = 15$ m orthogonal to wind direction. An estimation of surface soil, deep soil and groundwater contamination has been possible for each identified cell of the site, in this way allowing the calculation of the volatilization factors in the entire area. Since the soil properties are considered uniform in the analyzed contaminated site, as described above, the calculation of the volatilization factor results in a constant VF for each substance, evaluated for each cell of the site.

3.3. Volatilization and Human Health Risk Results

Volatilization factors for surface soil, deep soil and groundwater have been calculated from the conceptual model built up on the basis of the available information about the contaminated site.

The concentration of each contaminant i in air $c_{air,i}$ is conservatively calculated by summing the contribution of the volatilization from surface soil, deep soil and groundwater:

$$c_{air,i} = VF_{ss,i} \cdot c_{ss,i} + VF_{ds,i} \cdot c_{ds,i} + VF_{gw,i} \cdot c_{gw,i} \quad (14)$$

where $c_{ss,i}$, $c_{ds,i}$ and $c_{gw,i}$ are respectively the concentration of the compound i in the surface soil, deep soil and groundwater, while $VF_{ss,i}$, $VF_{ds,i}$, $VF_{gw,i}$ are the corresponding volatilization factors.

Among the VF relations, as explained before, the selection is as follows: $VF_{ss,J1}$ for the less volatile compounds and $VF_{ss,J2}$ for very volatile compounds about the surface soil, $VF_{ds,F2}$ for the less volatile compounds and $VF_{ds,J}$ for those very volatile as regards the deep soil, VF_{gw} for groundwater. The application of Jury and Farmer's models results in VF_{ss} that ranges from 1.06×10^{-8} kg/m³ (calculated for indeno(1,2,3-c,d)pyrene) to 1.73×10^{-5} kg/m³ for very volatile compounds; VF_{ds} ranges from 5.10×10^{-12} kg/m³ (calculated for indeno(1,2,3-c,d)pyrene) to the maximum value of 2.59×10^{-5} kg/m³ for very volatile compounds; finally VF_{gw} ranges from 5.77×10^{-8} l/m³ (calculated for dibenz(a,h)anthracene) to 3.97×10^{-5}

l/m^3 estimated for xylenes. The transfer factors for less volatile compounds result several orders of magnitude lower than those for very volatile ones, but the relative concentrations in air obviously depend also by the contamination levels in soil and groundwater.

As the distribution of pollutants in groundwater is considered uniform in the contaminated site, the term related to the groundwater, *i.e.* concentration in air due to volatilization from groundwater, is constant. The contribute of the polluted groundwater to the total value of air concentration is null or limited (up to 3%) for a dozen of substances, medium-level for acenapthene and pyrene (up to 11%) and naphthalene (up to 41%), and high/prevailing for those substances for which the contamination of surface and deep soil is localized in only a few monitoring points (benzene, benzo(k)fluoranthene, ethylbenzene, toluene and xylenes). Using the potentiality of the map calculation in Gis systems, the total concentration in air is calculated and mapped for each of the eighteen considered substances.

As an example in **Figure 4** Benzo(a)pyrene concentration (in μg/m^3) distribution in air due to the contribution of surface soil, deep soil and groundwater volatilization is represented, as calculated from the available data in monitored points samples.

In order to calculate the human health risk caused by the analyzed contaminated site, among all the possible exposure scenarios, the ingestion, dermal contact and outdoor inhalation scenarios are taken into account, as schematized in the conceptual model in **Figure 5**. In performing the human health risk analysis, the receptors

considered as potential targets of the contamination are industrial workers localized on the dismissed area. This choice was dictated by considerations about the actual utilization of the site: since the dismissing of the plant, the ex-industrial area was abandoned, but periodically supervised and subjected to maintenance and numerous monitoring campaigns.

In order to calculate the exposure intakes for the identified receptors, the standard procedures in human

health risk assessment have been utilized [5,16]. The exposure intakes are expressed as mass of substance in contact with the organism, normalized by time unit and body weight (mg/(kg·d)); a summary of the relations used in the procedure can be found in [25].

Human health risk assessment consists in the quantification of Individual Cancer Risk and Hazard Quotient for the exposed population, *i.e.* the computation of the upperbound excess lifetime cancer risk and noncarcinogenic hazards for each of the pathways and receptors identified in the area of interest. Cancer risk is defined as the probability that a receptor will develop cancer in his lifetime, assuming a unique set of exposure, model, and toxicity properties. In contrast, hazard is quantified as the potential for developing noncarcinogenic health effects as a result of exposure to COCs, averaged over an exposure period. It is worth noting that hazard is not a probability but, more exactly, a measure of the magnitude of a receptor's potential exposure relative to a standard exposure level.

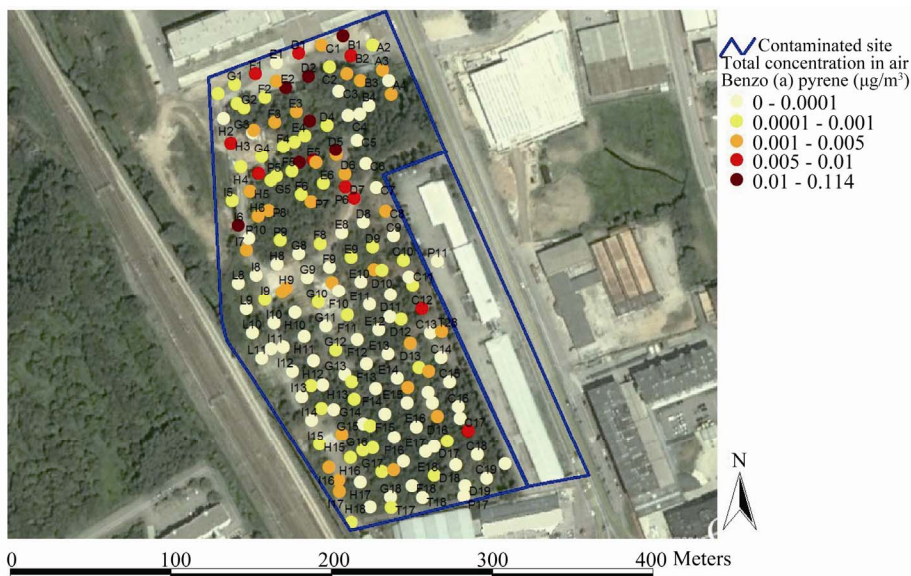The individual cancer risk of a receptor *j* set by exposure to multiple carcinogenic chemicals *i*, can be cal-

Figure 4. Benzo(a)pyrene concentration (in μg/m^3) distribution in air due to the contribution of surface soil, deep soil and groundwater volatilization.
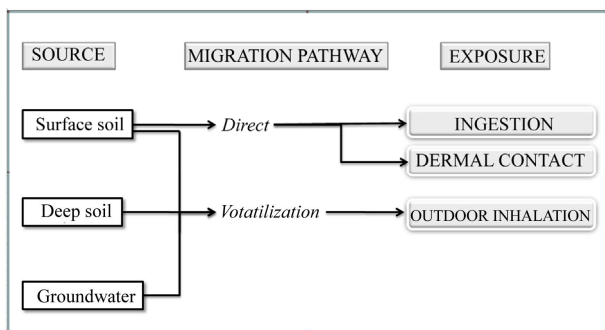
Figure 5. Conceptual model of the human health risk assessment: exposure scenarios.

culated, for low doses exposition hypothesis, through the following equation:

$$Individual\_CancerRisk_j = \sum_i LADD_{i,j} \cdot CSF_i \quad (15)$$

where:

$LADD_{ij}$ is Lifetime Average Daily Dose for a lifetime exposure of 70 years (mg/kg day) through multiple exposure pathways

CSF_i is the Cancer Slope Factor for COC i (mg/kg day)$^{-1}$. Comparing an exposure estimate to a Reference Dose (RfD), the potential for noncarcinogenic health effects resulting from exposure to a chemical is evaluated. A RfD is defined as a daily intake rate that is estimated to cause no appreciable risk of adverse health effects, even to sensitive populations, over a specific exposure duration [5]. Generally, the more the Hazard Quotient value exceeds 1, the greater is the level of concern. Based on similar COCs toxicological characteristics and additive health effects, the Hazard Quotient (HQ) for receptor j exposed to multiple chemicals i, is calculated as:

$$HQ_j = \sum_i \frac{ADD_{i,j}}{RfD_i} \quad [16]$$

where ADD_{ij} is the Average Daily Dose averaged for the exposure duration relative to the toxic i for the receptor j (mg/kg day) through multiple exposure pathways RfD_i is the COC i Reference Dose (mg/kg day) below which there are no adverse effects. The parameter values adopted for the estimation of the exposure intakes are those typically utilized for the human health risk assessment in the case of workers receptors [26]. The estimation of the exposure time and exposure frequency results from the consideration that the area is dismissed since years and that maintenance works are not requested every day. As a reasonable hypothesis, it has been considered a total number of 1500 hours of exposure for workers receptors.

Table 6 shows the carcinogenicity and toxicity values

of the considered substances utilized for the estimation of Individual Cancer Risk and Hazard Quotient, extracted from U.S. EPA IRIS Database. Summing the contribution of all the carcinogenic substances and all the toxic substances, the distribution of total individual cancer risk and total hazard quotient, respectively, has been estimated on the considered zone, as represented in **Figure 6(a)** and **Figure 7(a)**. As expected, for receptors located and directly exposed on contaminated site, total individual cancer risk has quite high values, especially in the north side of the area. The hazard quotient approaches the value of 1 only in a very limited spot of the area.

It's worth noting that the calculated cancer risk and hazard quotient values don't take into account any protection of the receptors, thus resulting excessively conservative and unrealistic. It is evident that workers usually use Personal Protective Equipment (PPE) conforming to the regulations in force for safety subject during maintenance and monitoring activities in contaminated sites. The use of PPE as gloves and masks can be taken into account in the estimation of risks by considering a reduction factor. As regards the inhalation exposure, if a mask giving protection from dust and gas with mean assigned protection factor is considered, a reduction factor of 1/30 can be supposed (EN 133, EN 529 standards). For dermal contact exposure wearing gloves (EN 374 - 2004 standard) and for ingestion exposure wearing a safety mask, a reduction factor of 1/100 can be conservatively hypothesized.

The results consequently obtained adopting the protection reduction factors are represented in **Figure 6(b)** and **Figure 7(b)**, where it is evident an average decrease of risks of about 2 orders of magnitude.

In particular for total individual cancer risk, values above the limit typically considered as threshold acceptability, 10^{-5}, are almost disappeared, while for hazard quotient, values are all reduced under 0.01 estimates.

The analysis of the contribution of pathways to both cancer risk and hazard quotient put in evidence that total cancer risk is mainly due to the dermal contribution This assessment can be used as a significant criterion to select the more appropriate PPE in order to reduce risks of exposed workers. In this specific case the inhalation pathway contribution due to volatilization of COCs from soil and groundwater does not constitute the prevailing concern of the contaminated site, but a particular regard has to be posed to dermal contact and therefore to a good choice of safety gloves during maintenance and monitoring activities on the polluted area.

Finally the analysis of the contribution of the considered substances shows that in the estimation of cancer

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Table 6. Carcinogenicity and toxicity values for the considered substances.

	inhalation CSF $(mg/kg-d)^{-1}$	ingestion CSF $(mg/kg-d)^{-1}$	dermal CSF $(mg/kg-d)^{-1}$	inhalation RfD $(mg/kg-d)$	ingestion RfD $(mg/kg-d)$	dermal RfD $(mg/kg-d)$
Acenaphtene	n.a.	n.a.	n.a.	0	0.06	0.06
Anthracene	n.a.	n.a.	n.a.	0	0.3	0.3
Benzene	0.0273	0.055	0.055	0.00855	0.004	0.004
Benz(a)anthracene	0.6	0.73	0.73	0.285	0	0
Benzo(a)pyrene	7.32	7.3	7.3	3.135	0	0
Benzo(b)fluoranthene	0.31	0.73	0.73	0.285	0	0
Benzo(g,h,i)perylene	n.a.	n.a.	n.a.	0.03	0.03	0.03
Benzo(k)fluoranthene	0.031	0.073	0.073	0.0285	0	0
Chrysene	0.0031	0.007	0.007	0.03	0.03	0.03
Dibenz(a,h)anthracene	3.1	7.3	7.3	n.a.	n.a.	n.a.
Ethylbenzene	n.a.	n.a.	n.a.	0.285	0.1	0.1
Fluoranthene	n.a.	n.a.	n.a.	0	0.04	0.04
Indeno(1,2,3-c,d)pyrene	0.31	0.73	0.73	3.14	0.03	0.03
Naphthalene	0.00012	0	0	0.02	0.02	0.02
Pyrene	n.a.	n.a.	n.a.	0.03	0.03	0.03
Toluene	n.a.	n.a.	n.a.	1.43	0.08	0.08
Xylenes	n.a.	n.a.	n.a.	0.2	0.2	0.2

Contaminated site
Total Cancer Risk without PPE
- 0.1E–07
- 1E–07 - 1E–06
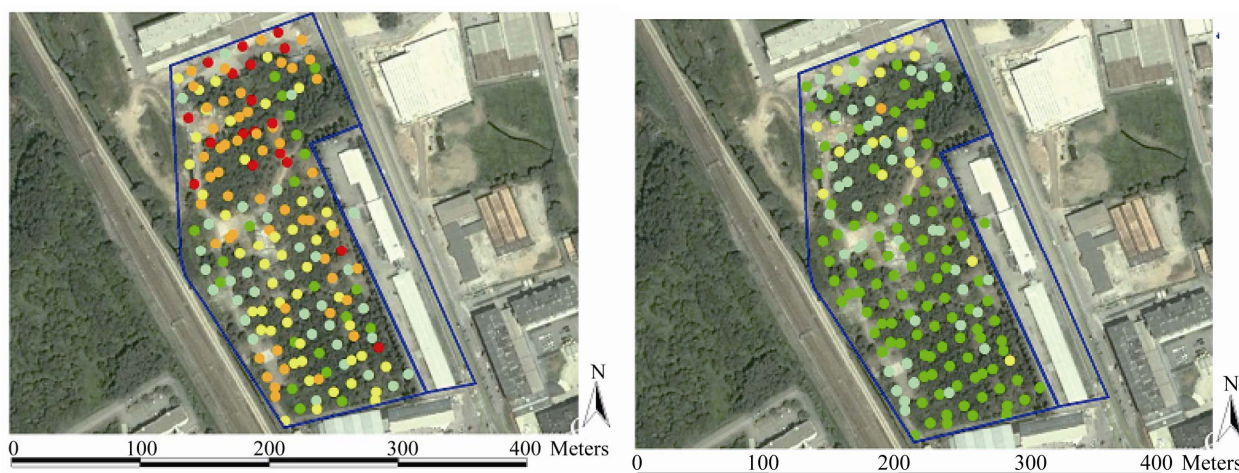- 1E–06 - 1E–05
- 1E–05 - 1E–04
- 1E–04 - 1.96E–03

Figure 6. Total Individual Cancer Risk for workers localized directly on the contaminated dismissed area, without PPE (a) and with PPE (b).
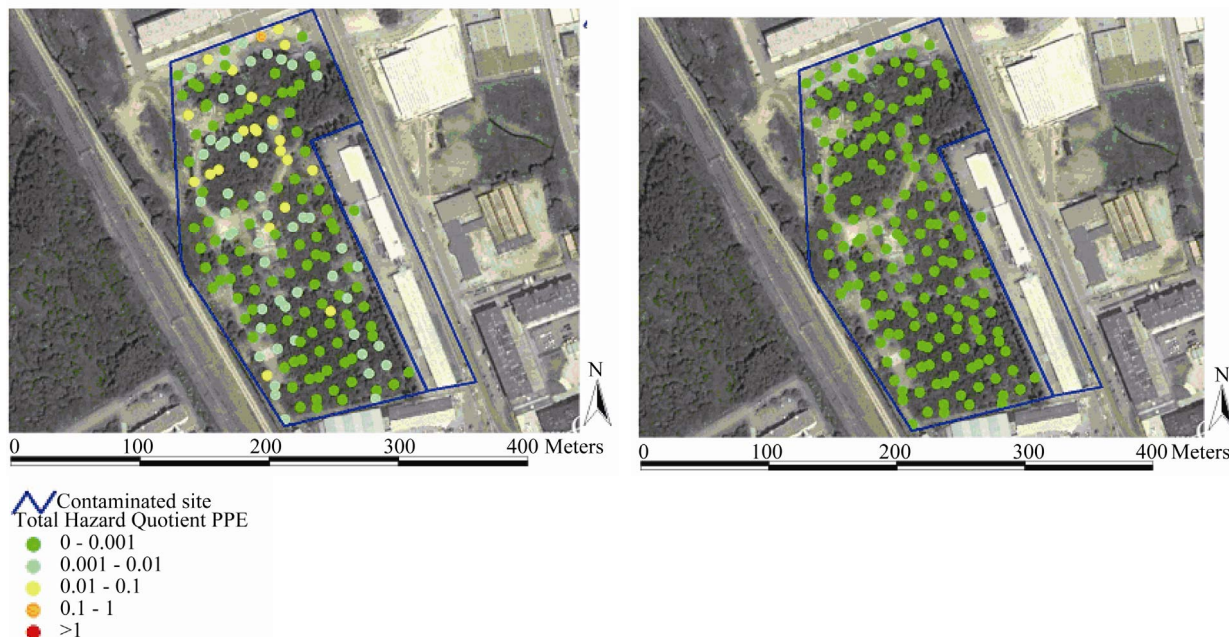
Figure 7. Total Hazard Quotient for workers localized directly on the contaminated dismissed area, without PPE (a) and with PPE (b).

risk benzo(a)pyrene is the main cause, while the hazard quotient is mainly originated by naphthalene, followed by pyrene and chrysene.

4. Conclusions

To quantify the negative effects to receptors exposed to soil and groundwater contamination, human health risk assessment methodology is usually applied, to evaluate individual cancer risk and hazard index. The paper examined in particular the dispersion of contaminant vapors through volatilization from soil and groundwater in the atmosphere. Volatilization factors have been estimated applying Jury's and Farmer's models. The sensitivity analysis of models, performed with the Sensitivity Ratio, Sensitivity Score and Monte Carlo Simulation, identified the most significant parameters: volumetric water content, thickness of the contamination source and height of capillary zone among the wide range of input parameters for the application of models. Finally a case study regarding a contaminated area located in the industrial district of Trento North was investigated. A conceptual model of the site was built up, processing the available monitored data; the concentrations of several contaminants in air were evaluated through the estimation of volatilization factors. Individual Cancer Risk and Hazard Quotient have been calculated for workers receptors localized on the contaminated site, analyzing the inhalation, ingestion and dermal pathways. In the consi-

dered contaminated site, the volatilization of compounds from contaminated soil and groundwater does not constitute the main concern: the dermal contribution results the prevailing pathway for risks and the obtained results can advise the appropriate use of PPE that enable the considerable decrease of the risks for the exposed receptors. Adopting conservative reductive factors accounting for the protection of PPE, the resulting individual cancer risks and hazard quotients are clearly below the acceptability limits.

5. Acknowledgements

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Notation

δ_{air} ambient air mixing zone height

ρ_s soil bulk density

θ_a volumetric air content

$\theta_{a,cap}$ volumetric air content in the capillary zone

θ_e effective terrain porosity in unsaturated zone

θ_w volumetric water content

$\theta_{w,cap}$ volumetric water content in the capillary zone

τ average duration time of vapor flux

A contamination source area

ADD Average Daily Dose averaged for the exposure duration

c_{poe} pollutant concentration in point of exposure

c_s pollutant concentration at the contamination source

COC Chemical of Concern

CSF Cancer Slope Factor

d thickness of contamination source in the surface soil

ds thickness of contamination source in the deep soil

DA diffusivity

D_a diffusion coefficient of the substance in air

D_{capeff} effective diffusion coefficient through capillary zone

D_w diffusion coefficient of the substance in water

D_{seff} effective diffusion coefficient in soil based on vapor-phase concentration

D_{wseff} effective diffusion coefficient between the groundwater and soil surface

foc organic carbon fraction

H Henry's law constant

h_{cap} height of capillary zone

h_v height of unsaturated zone

k_d partition soil-water coefficient

k_{OC} carbon-water partition coefficient

k_s soil-water sorption coefficient

L extension of contamination source in across-wind direction

L_{GW} depth to groundwater

L_s depth to subsurface soil contamination source

$LADD$ Lifetime Average Daily Dose for a lifetime exposure of 70 years

R_{fD} Reference Dose

U_{air} wind speed above the ground surface in the ambient mixing zone

VF_{ss} volatilization factor of outdoor vapors from surface soil

VF_{ds} volatilization factor of outdoor vapors from deep soil

VF_{gw} volatilization factor of outdoor vapors from groundwater

W width of contamination source area parallel to wind or groundwater flow direction