

## Risk Analysis for a Contaminated Site in North of Naples (Italy)

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Exposure and risk assessment of environmental pollution deriving from releases of chemicals is a compulsory step for the remediation of contaminated sites. A site-specific risk assessment provides a systematic approach to characterise the nature and magnitude of the risks associated with the environmental health hazards, helping to determine the transport of contaminants due to natural processes and, consequently, the areas involved and the specific goals to reduce the exposure to hazardous substances. In this work, the assessment of the exposure and risk related to some pollutants detected into a contaminated site in north of Naples (Italy) is presented. A preliminary detailed characterization highlighted the presence of several heavy metals and organic compounds both into soil and groundwater. Health and environment risks for each pollutant were screened. Results showed that risks related to arsenic and benzo(a)pyrene are the highest in the area compared to the benchmarks screenings for water and soil.

### 1. Introduction

A wide range of chemicals used in industrial activities or in agriculture, may migrate from soil into the aquatic environment, affecting groundwater and representing a risk for both environment and human health (Karatzas et al., 1996).

In the context of land contamination, a risk exists when a receptor could be exposed to the contamination through one or more pathways. The level of risk is related in large part to the particular conditions and characteristics of the contaminated land, and to the circumstances of the exposition to the contamination. A site-specific risk assessment provides a systematic approach to characterise the nature and magnitude of the risks related to contamination hazards, helping to determine the transport of the pollutants due to natural processes and, consequently, the areas involved. Moreover, it helps assessing the extension of the intervention and the specific goals to reduce the exposure to hazardous substances (Critto et al., 2007; Palmeri et al., 2012). The transport of pollutants from the land surface to the groundwater is affected by a broad range of environmental factors, e.g. the variability of field and climate characteristics, the heterogeneity of the released pollutants, the presence and direction of groundwater flow, etc. (Prisciandaro et al., 2001; Citro et al., 2012; Bortone et al., 2013). To assess the risks related to any contamination, it is important to consider all the environmental compartments potentially involved (i.e. soil, groundwater, surface water and sediments), the hydro-geological characteristics of the site, the contaminant mobility, and the amounts to which receptors are exposed. One way to formalise these aspects is formulating and developing a conceptual model for the site, which is a schematic representation of the boundaries and main characteristics of the problem under analysis. The aim of the latter is to outline the relationships between contaminants, pathways and receptors, and then between hazards, exposure and environmental features. Consequently, the conceptual model is an important tool to identify the pollutant linkages and the associated risks (U.S.Navy, 2001).

In the present paper, the assessment of the exposure and risk related to some pollutants detected into a contaminated site in north of Naples (Italy) is presented. A preliminary detailed characterization highlighted the presence of several heavy metals and organic compounds both into soil and groundwater. The environmental risk for each pollutant was screened. In addition, in order to classify and display the spatial variation of risks off site, groundwater risk maps were obtained by using an analytical model, implemented ad-hoc, and a Geographical Information System (GIS).

## 2. Groundwater Risk Assessment

The primary goal of risk assessment is to obtain an accurate measure of the nature and extent of the concentration of a chemical substance(s) and the level of risk that the chemical substance(s) poses to human health and/or the environment. A range of risk criteria can be adopted to provide an indicative measure of flooding risk from groundwater sources, and to highlight the areas where a more detailed assessment of groundwater flooding risk is required. For this purpose, it is recommended using the 'source-pathway-receptor' model and to individuate the conceptual site model (CSM) of the case study. The CSM is a representation of the physical-hydrogeological system with a detailed description of the groundwater dynamics. It needs to identify the complete and potential pathways between the source and the receptor and generally contains the following information:

- assessing the source and properties of the chemical substance (solubility, partitioning, toxicity, etc);
- identifying and confirming the beneficial uses in the vicinity of the site;
- determining the groundwater flow direction and the potential exposure of the receptors to the chemical substances (e.g. if the site is located hydraulically down-gradient of a sensitive receiver etc.);
- assessing the impact on water quality in the receiving environment by comparing to water quality criteria;
- evaluating the volatilisation pathways for volatile chemical substances.

These assessments are important in defining the remediation goals including the degree and timing of the remediation. Risk assessment for groundwater resources is performed by comparing, for each desired contaminant, the concentration calculated at the so called "exposure point" with the regulatory benchmarks ( $C_{lim}$ ) reported for the groundwater protection, as shown by Eq(1).

$$Risk = \frac{C(x, y, z)}{C_{lim}} \leq 1 \quad (1)$$

The ratio between the two concentrations provides a numerical definition of risk for groundwater resources, whose acceptability limit is set equal to 1.

### 2.1 Transport model

The risks related to contaminated soil and groundwater in a suburban area depend on the potential extent of the exposure and on the physical-chemical properties and concentrations of the pollutants at a point of interest termed as "exposure point" at some distance off the site.

The concentration at the point of exposure  $C_{poe}$  is predicted from the concentration in the contamination source ( $C_s$ ) by Eq(2):

$$C_{poe} = FT \cdot C_s \quad (2)$$

Where  $FT$  is the transport factor, which takes into account the physical and chemical properties of the constituent, the mechanism of releases of pollutants to environmental media, the physical and chemical properties of the media through which the migration occurs and the interactions between the constituent and the medium along the migration pathway. The transport factor used for describing the contaminant transport in the unsaturated zone is the Leaching Factor ( $LF$ ).  $LF$  allows for the prediction of the attenuation phenomena involved in the contaminant transport from the source located in the vadose zone to the groundwater table due to its infiltration through the vadose zone and the subsequent dilution in groundwater. This factor is simply defined as the ratio between the contaminant concentration in the groundwater right below the contamination source located in the vadose zone ( $C_{Lmf}$ ) and the concentration in the contamination source itself ( $C_s$ ) (Figure 1a), which represents also the concentration at point of exposure  $C_{poe}$  (APAT, 2006). The equation for estimating  $LF$  is given by Eq(3):

$$LF = \frac{k_{ws} \cdot SAM}{LDF} \quad (3)$$

Where  $k_{ws}$  is a coefficient that considers the partition of the contaminant between aqueous, air and solid phase in the vadose zone, while  $SAM$  is the Soil Attenuation Model accounting for the distance that the contaminant

has to travel before reaching the water table and  $LDF$  is the Leachate Dilution Factor, which describes the dilution of the contaminant concentration when the contaminant is transferred from the leachate to groundwater (as a function of the groundwater flow velocity and the contaminant source dimension in the vadose zone).

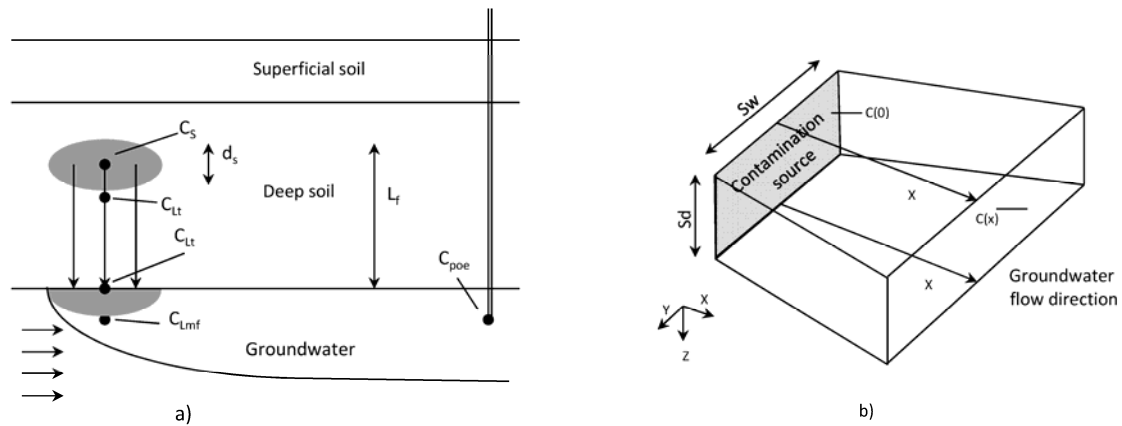


Figure 1: Contaminant transport in the vadose zone and groundwater a) Conceptual model of the leaching process; b) Source geometry in groundwater for Domenico Solution.

Mathematical models with different degrees of complexity can be used to describe the mechanism of transport and diffusion of pollutants in environmental media (soil, water, and food chain) (Bell, 2002). Regardless of their complexity, such models aim at estimating the  $C_{poe}$  taking into account natural attenuation processes like dilution, volatilization, dispersion and biological degradation.

The equation describing the chemical transport in the saturated zone is Eq(4):

$$R \frac{\partial C}{\partial t} = -\nabla(C \cdot v_e) + \nabla[(D_h + D_m)\nabla C] - k_d C \quad (4)$$

Where  $C$  is the contaminant concentration,  $R$  is the retardation factor,  $v_e$  is the seepage velocity,  $D_h$  and  $D_m$  are the hydrodynamic dispersivity and the diffusion, respectively, and  $k_d$  is the adsorption coefficient. The retardation factor can be evaluated by Eq(5):

$$R = 1 + k_d \frac{\rho_s}{\theta_e} \quad (5)$$

Where  $\rho_s$  is the bulk density of the soil and  $\theta_e$  is the effective porosity of the soil. For organic components,  $k_d$  can be evaluated as  $k_d = K_{oc} f_{oc}$ , where  $K_{oc}$  is the soil organic carbon/water partition coefficient and  $f_{oc}$  is the fractional soil organic carbon content. One of the most used analytical solution for the continuous release is the Domenico solution (Domenico and Schwartz, 1998). This is a three-dimensional analytical solute transport model that assumes a vertical plane source oriented perpendicular to groundwater flow to simulate the release of organics to groundwater, as shown in Figure 1b. Considering the steady state solution and supposing that the whole aquifer thickness is interested by the contamination, that results in no vertical dispersion (Domenico and Schwartz, 1998), the Domenico equation can be written according to Eq(6):

$$\frac{C(x)}{C_0} = \frac{1}{4} \exp \left[ \frac{x}{2a_x} \left( 1 - \sqrt{1 + \frac{4\lambda R a_x}{v_e}} \right) \right] \cdot \left[ \operatorname{erf} \left( \frac{S_w}{4\sqrt{a_y x}} \right) \right] \quad (6)$$

Where  $a_x$ , and  $a_y$  are the dispersivities in the bi-dimensional space directions ( $x$ ,  $y$ ),  $\lambda$  is the biodegradation coefficient,  $S_w$  is the source dimension along the  $y$  direction (Figure 1b) and  $\operatorname{erf}(x)$  is the error function defined by Eq(7):

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \quad (7)$$

### 3. Case study

The groundwater risk assessment procedure was applied in a coastal urban area in Castel Volturno, town in north of Naples (Campania, Italy). This area was selected since it is very close to many sensitive receptors like schools, theatres and sport complexes. Data were collected from the site characterization of the case study. The source area is of about 87.500 m<sup>2</sup>, located between two lakes and not far from the sea (2km) (Figure 2). The groundwater aquifer is located at a depth of 2.6m from the land surface and confined by an aquitard (25m). The groundwater flux lines are East-West oriented as reported in Figure 2. The site characterization showed the presence of a large number of pollutants, both inorganic and organic, and present both in soil and in groundwater. The highest concentrations were found for arsenic and benzo(a)pyrene, in both the top and deep soil and groundwater. Risk analysis procedure was applied via considering the maximum pollutant concentrations in the whole domain and taking into account two scenarios: Risk/case1 in which were considered only the concentration values measured into groundwater, and Risk/case2 in which were considered the concentration values obtained from the leaching process through the upper soil into groundwater. In particular, in Table 1 the maximum values measured for top soil,  $C_{TS}$ , for deep soil,  $C_{DS}$ , and groundwater,  $C_G$ , with the concentrations estimated via considering the leaching process,  $C_L$ ; and the groundwater regulatory benchmarks,  $C_{lim}$ , for arsenic and benzo(a)pyrene are reported. Arsenic and benzo(a)pyrene concentrations in water were determined according to ICP-MS and GC-MS techniques, respectively. The determination of Arsenic and benzo(a)pyrene concentrations in soil required a preliminary extraction step, followed by ICP-AES and GC-FID techniques. The geological composition of the saturated zone in the study area can be described with a permeability (K) of  $5.66 \times 10^{-4}$  m/s. The values of the parameters used in the risk analysis procedure and the main hydrogeological source area properties are listed in Table 2 and Table 3, respectively.

As no site-specific data were available, and following a conservative principle, the biodegradation coefficient ( $\lambda$ ) equal to zero was assumed.

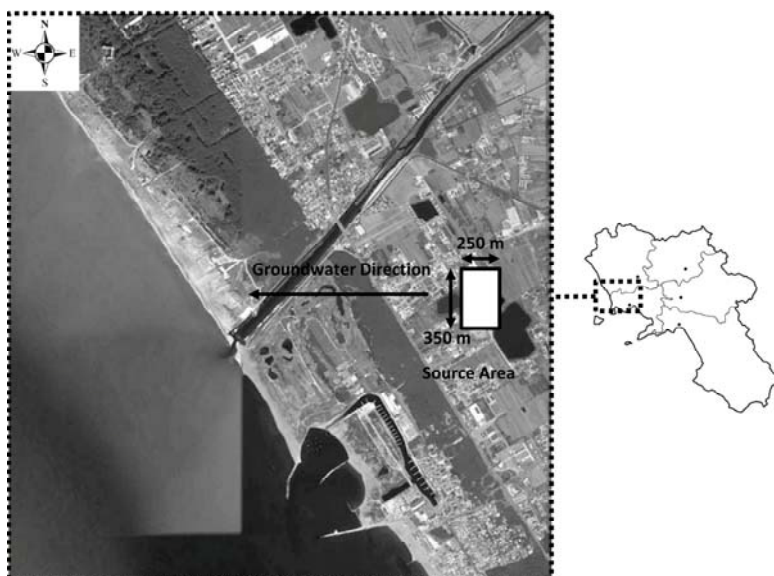


Figure 2: Study area with the location of the polluted area.

Table 1: Maximum contaminant concentrations and regulatory benchmarks

Pollutants	$C_{TS}$ [mg/kg <sub>ds</sub> ]	$C_{DS}$ [mg/kg <sub>ds</sub> ]	$C_L$ [µg/l]	$C_G$ [µg/l]	$C_{lim}$ [µg/l]
Arsenic	14.2	320	1,370.8	11.2	10
Benzo(a)pyrene	2.3	16.2	0.2	0.03	0.01

Table 2: Risk analysis parameters

Pollutants	LF Top soil	LF Deep soil	R	$k_d$ [cm <sup>3</sup> /g]
Arsenic	$5.09 \times 10^{-3}$	$6.79 \times 10^{-3}$	$1.26 \times 10^2$	$2.80 \times 10^1$
Benzo(a)pyrene	$1.47 \times 10^{-5}$	$1.98 \times 10^{-5}$	$4.34 \times 10^4$	$9.69 \times 10^3$

Table 3: Source area properties

$S_w$ [m]	$\theta_e$	$K$ [m/s]	$v_e$ [m/s]
350	0.35	$5.66 \times 10^{-4}$	$9.53 \times 10^{-7}$

The integration of these data provided the risk mapping for groundwater of the area studied, represented as iso-risk contours (Al-Adamat et al., 2003). The risk mapping provided the risk frequency for a specific type of damage at a given point of the area, by considering the actual distributions of risk and environmental conditions. In particular the cumulative risk was computed.

#### 4. Results

The risk assessment for groundwater was evaluated first taking into account only the groundwater contamination transport (Risk/case1), and then also considering the contaminant leached from the polluted soil into groundwater (Risk/case2), the latter computed both with top soil and deep soil concentration values. The highest risk values obtained for each investigated pollutant and cumulative, for both the cases considered, are reported in Table 4. As shown, both the single and cumulative maximum values calculated are much higher than the acceptable risk set equal to 1, showing values of 4.2 in the first case and 156.4 in the second one. Iso-risk contours were also obtained and reported in Figure 3 and Figure 4.

Table 4: Highest risk values for groundwater contamination transport and leaching transport

Pollutants	Risk/case1	Risk/case2
	Groundwater	Groundwater + leaching
Arsenic	1.1	137.1
Benzo(a)pyrene	3.1	19.4
Cumulative	4.2	156.5

Figure 3 represents the risk contours based on the values obtained in the area for the Risk/case1 while Figure 4 represents those for the Risk/case2. Figure 3 shows that a not acceptable risk ( $Risk > 1$ ) was assessed for an exposed area of about 4.5ha. An acceptable risk for the aquifer ( $Risk < 1$ ) was registered starting from distances from the source area of about 290m and 180m, along and perpendicularly the groundwater flow rate direction, respectively. Differently, in Figure 4 a not acceptable risk was assessed for an exposed area of about 235ha. The acceptable risk for the aquifer was evaluated starting from distances from the source area of about 2,700m and 1,200m, along and perpendicularly the groundwater flow rate direction, respectively. The comparison between the two analyzed cases highlighted highest individual and cumulative risk values and a widest exposed area for the Risk/case2, resulting, as expected, as the worst scenario. Moreover, arsenic showed a higher risk than benzo(a)pyrene in Risk/case2, while the opposite scenario was found evaluating only groundwater contamination transport, in agreement with leaching pollutant concentration. Results agree with simulations by Trolborg and co-workers (2009), according to which the groundwater risk level is affected by unsaturated zone leaching.

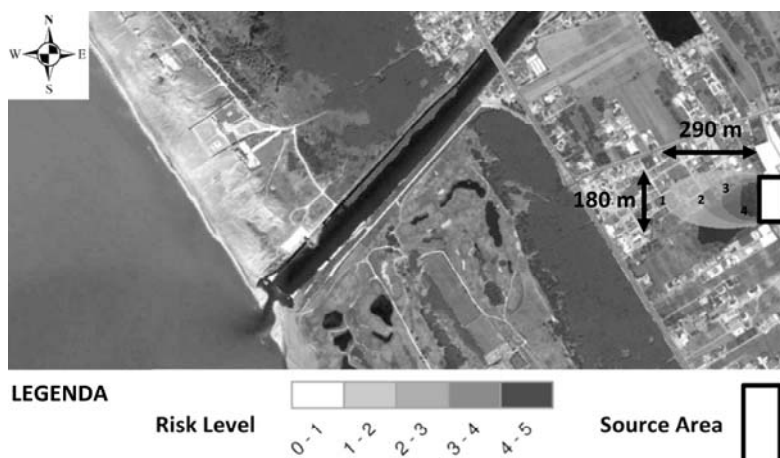


Figure 3: Risk mapping in the groundwater (Risk/case1).

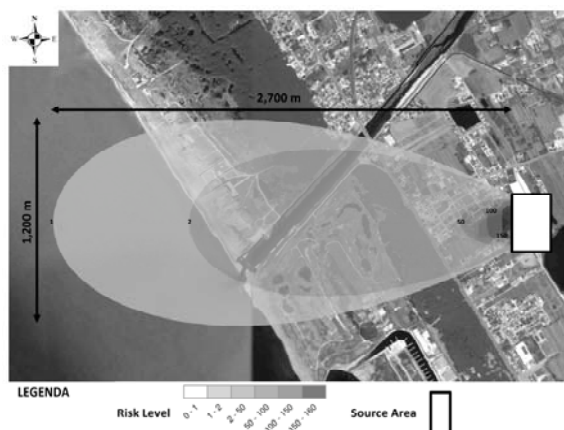


Figure 4: Risk mapping in groundwater with leachate from top soil and deep soil (Risk/case2).

## 5. Conclusions

In this work, a methodology for the risk analysis of polluted sites was presented and the assessment of the exposure and risk related to some pollutants detected into a contaminated site in north of Naples (Italy) was carried out. A preliminary detailed characterization of the site highlighted the presence of several heavy metals and organic compounds both into the soil and groundwater. The environmental risk for each pollutant was screened. Both the vadose and groundwater transport were considered, mapping the risk related to the contaminants in the area studied. Results showed that arsenic and benzo(a)pyrene had the highest concentration and risk in the area, compared to the benchmark screenings for water and soil, as they reached distances of more than 2.5km along the groundwater direction. Increments of both individual and cumulative risk values of both contaminants, and exposed area extensions were obtained by considering the additional leaching phenomenon.

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