



## Assessment of the sanitary and environmental risks posed by a contaminated industrial site

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### ABSTRACT

Sites contaminated with hazardous material are a topical and urgent problem all over the world. In accordance with recent Italian regulations, appropriate risk assessment is required in order to determine health risks associated with contaminated sites. The paper presents a case study regarding a disused industrial plant contaminated with polycyclic aromatic hydrocarbons, heavy hydrocarbons and polychlorinated biphenyls. The site is characterized by three different topographical levels. Therefore both the characterization and the conceptual model had to be adapted to the site conditions: we divided the site into three discrete areas and we developed a separate risk assessment for each area. Besides health risk assessment, we performed ecological risk assessment for both groundwater and surface water targets, as required by Italian regulations. The future reuse scenario has not yet been defined and, consequently, risk assessment results will be useful for the remediation program. Risk assessment was supported by leaching tests and hydrocarbon “finger printing”. Leaching tests allowed us to determine site-specific soil–water partition coefficient. Hydrocarbon “finger printing” allowed us to differentiate the mobility of the different hydrocarbon groups in migration analyses. We found the site required remediation based on Italian standard. We propose a simple risk-based remediation action consisting in the replacement of the upper 1m with “clean” soil and the placement of a barrier to vapors.

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### 1. Introduction

Sites contaminated with hazardous materials are a common and burgeoning problem all over the world. Over the next 60 years there will be an increasing need to develop existing brownfield sites, and therefore innovative remediation solutions, using transferable skills and techniques from other sciences, will be required by legislation. Such solutions could include better risk assessment techniques using new methods of investigation, detection and statistical analysis together with sampling and *in situ* testing [1]. A site-specific risk assessment is an evaluation of the risk posed to human beings and the surrounding environment by exposure to site contamination in various media [2].

In Italy, health risk assessment has assumed a central role in the characterization and remediation of contaminated sites with the introduction of the new Environmental Code (D.L. 152/2006). This code defines contaminant threshold concentrations (CTCs) for many pollutants; CTCs vary according to the use of the site (residential/industrial). Wherever one or more CTCs are exceeded at a given site, a risk assessment is required. The risk evaluation process determines the cleanup levels (CLs) based on site-specific features. If the

measured contaminant concentrations are higher than the CLs, the site is defined as “contaminated” and a remediation program must be set up.

Risk evaluation is a complex task that allows us to estimate the probability that the population and the surrounding environment, exposed to the pollution from the site, will be harmed. Therefore it is a non-deterministic process that leads to non-deterministic results [3]. Several commercial and freeware software packages that assist the risk assessment procedure have been developed and reviewed over the years; each type of software adopts a slightly different modelling approach. In Italy, the national Regulatory Agency (ISPRA) has issued specific guidelines for carrying out risk analysis which are not strictly implemented by any available software.

This paper presents and illustrates the application of risk assessment procedure to a former industrial site. The soil is contaminated mainly by polycyclic aromatic hydrocarbons (PAHs), heavy hydrocarbons ( $C > 12$ ) and polychlorinated biphenyls (PCBs). The peculiar site morphology and the location of pollutant sources rendered the risk assessment particularly complex and several assumptions were necessary. The site had to be divided into three discrete areas, therefore three separate risk assessments were developed. Moreover, the type of reuse of the site was unknown so the risk evaluation had to be implemented for both an industrial/commercial and a residential scenario. The analysis was carried out following Italian legislation and guidelines, with the help of RISC<sub>4</sub> software (Spence Engineering

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### Nomenclature

CTC	contaminant threshold concentration
CL	cleanup level
PA	plant area
DA	dump area
BA	bank area
RSC	representative source concentration
ED	exposure duration
RfD	reference dose
SF	slope factor
$E$	intake rate
HI	hazard index
$R$	cancer risk
$HI_{GW}$	groundwater hazard index
$C_{POC}$	concentration at compliance point
$CTC_{GW}$	contaminant threshold concentration for groundwater
$k_d$	soil–water partition coefficient
$f_{oc}$	fraction of organic carbon
$k_{oc}$	organic carbon partition coefficient
SS	surface soil
SubS	subsoil

and BP Oil International). The choice of an appropriate and feasible tool for risk assessment is important for determining more achievable and flexible remediation goals with regard to risk. Those goals, together with the identification of main exposure pathways, have a substantial effect on the choice of remediation technology [4,5].

The study developed is a tier 2 risk assessment, involving extensive site-specific data collection and complex analytical modelling of the fate and transport of contaminants across the environmental media involved: unsaturated soil, groundwater, indoor and outdoor air, surface water.

The aims of this study were to: (1) apply the risk assessment procedure in accordance with Italian legislation and guidelines, (2) obtain information about risk level and determine soil and groundwater remediation goals and (3) evaluate the results of the analysis in order to provide information which is useful for deciding the proper remediation technique.

## 2. Site description

The site of interest is a now disused industrial plant where graphite and amorphous coal electrodes were manufactured. The productive process utilized mainly anthracite and pitch as raw materials. The industrial activity ran for over 80 years, resulting in soil pollution. The most widespread contaminants are PAHs; accidental spills from an underground tank and the scattered presence of buried waste results in localized pollution by heavy hydrocarbons. PCBs leakages from transformers were detected in the soil underneath the electrical power station. The site has a total area of 25 ha and is located close to the centre of a midsize city in central Italy, and it is therefore in an area where economic and urban revitalization is most needed. Furthermore, the site is located next to a river which could be one of the receptors.

## 3. Methodology

### 3.1. Site characterization

The property displays an irregularly shaped area bordered for about one half of the perimeter by the river bed (Fig. 1). The site is characterized by three different topographical levels: the

lowest is at approximately 109 m above m.s.l. and corresponds to the river right bank (bank area, BA, in the following text); the intermediate level located next to the river bank (at approximately 123 m above m.s.l.) consists of a dumpsite (dump area, DA). The third level corresponds to the main plant installations and buildings and lies at 139 m above m.s.l. (plant area, PA). In order to investigate the subsoil condition and collect soil samples, 35 boreholes were drilled with a roughly regular grid. In addition, two grab samples of soil were taken from the locations that were difficult to reach with the auger. Twenty-five of the boreholes were converted into groundwater monitoring wells (see Fig. 1).

The subsoil conditions are schematically depicted in Fig. 2. The upper layers of plant and bank areas consist of coarse grained layers (gravels and sands) corresponding to the different alluvial terraces of the adjacent river. The thickness of these layers ranges between 5 and 15 m. The permeability of the alluvial layer was determined by means of 3 Lefranc tests. Underneath the alluvial layers a marly-arenaceous bedrock is found. Lugeon tests were carried out to verify the hydraulic transmissivity of the bedrock. The results of hydraulic tests demonstrated that the bedrock is not fractured and acts as an aquiclude for the alluvial layers (aquifer). Two separate groundwaters were identified: the upper (less than 1 m thick) lying below the PA, the lower located in the alluvial layers next to the river bed and directly influenced by the fluctuations of the water level of the river.

A minimum of three samples from each borehole were analyzed for 10 PAHs and for heavy hydrocarbons (141 samples in total). Only six samples of soil extracted from the boreholes closest to the power station were also analyzed for PCBs. Eleven soil samples were tested to determine the fraction of organic carbon and moisture content; particle size analysis was performed on three samples. Forty-eight groundwater samples were extracted from monitoring wells and tested for PAHs, total hydrocarbon, PCBs and BTEX. Table 1 summarizes the analytical results for soil samples. Groundwater concentrations were found to be lower than the threshold concentrations (CTCs) in all samples.

To represent the distribution of contaminants in unsaturated soil the areas of influence (cells) of each borehole were defined by application of the Thiessen method.

### 3.2. Site conceptual model

The particular geomorphological configuration and geohydrological features suggested the need to divide the site into discrete areas, each with its own conceptual model [6,7]. The three areas (corresponding approximately to the three different topographical levels) were named “plant area” (PA), “dump area” (DA) and “bank area” (BA): they are shown, with the essential details, in Fig. 3. The characterization allowed us to determine or derive by correlation most of the environmental parameters necessary in the risk evaluation and summarized in Table 2. The remaining data were collected from various sources.

The site conceptual model is critical for proper implementation of the risk assessment procedure [2]. It involves three components: sources, migration pathways and receptors. In our case, the sources are polluted soil located in the unsaturated zone. Within each area, the source size and representative concentrations vary as a function of the reuse scenario (residential or industrial). In total, seven risk assessments were carried out (in one case the source within an area consists of two separate sources, for which separate analyses were necessary). If the data number was sufficiently high, the representative source concentration (RSC) was calculated using a statistical procedure (UCL of the data mean) otherwise the maximum concentration was selected as the representative value. RSCs were computed assuming for the “non-detect” value the detection limit

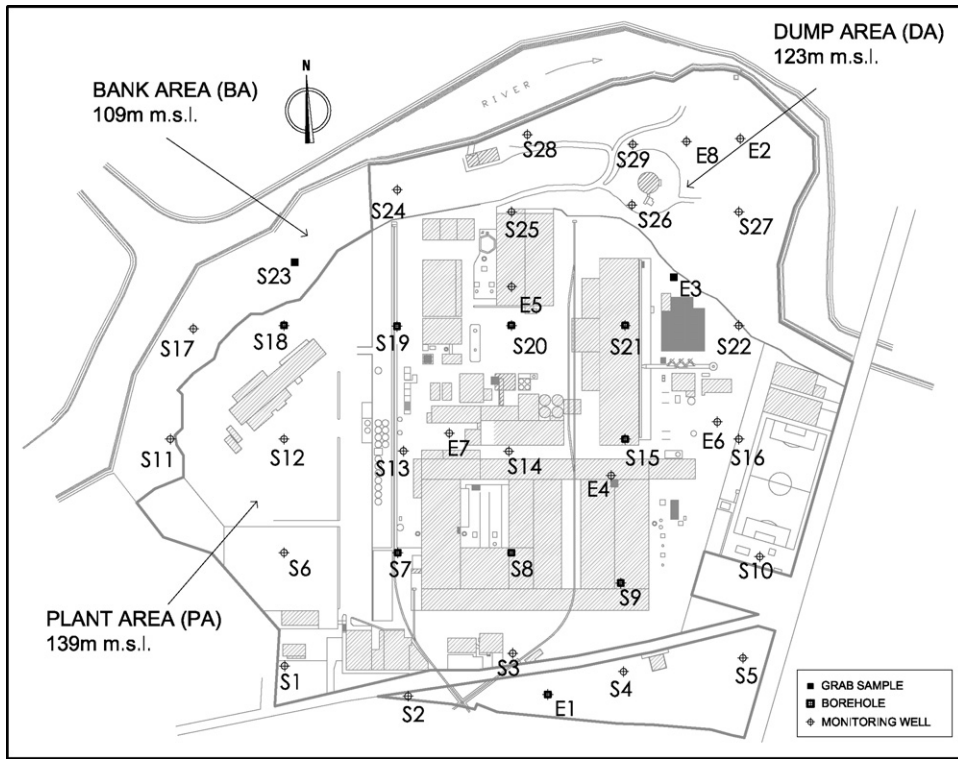


Fig. 1. Survey points location map.

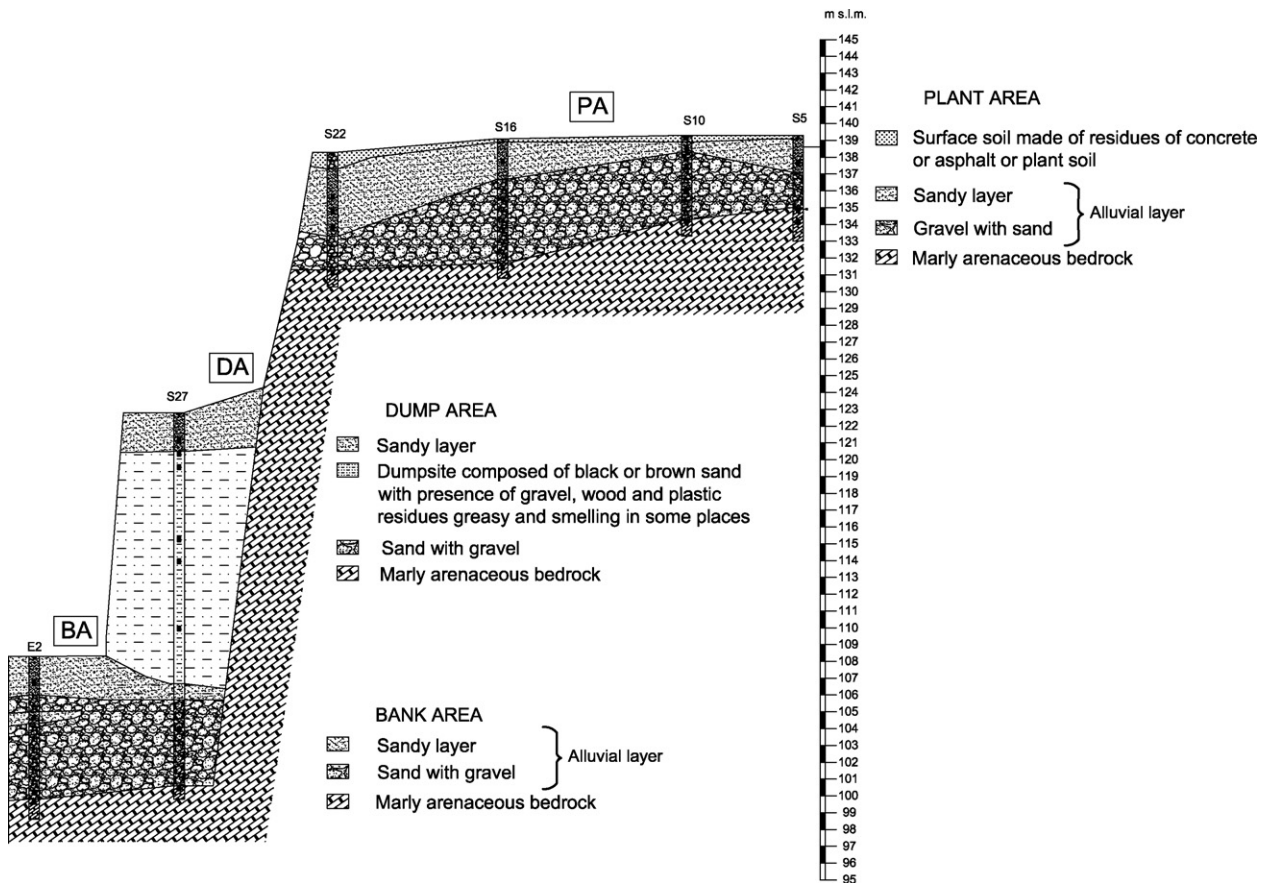
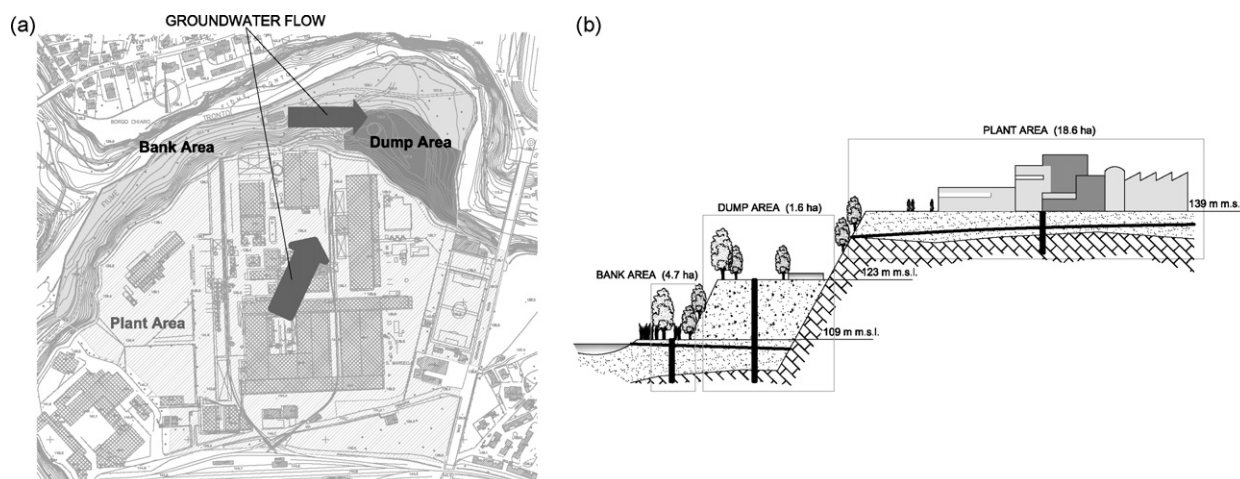


Fig. 2. Geological cross-section showing the three different topographical levels and the two groundwaters.

**Table 1**  
Summary of analytical results for soil samples.

Contaminants	Minimum (mg/kg ds)	Maximum (mg/kg ds)	Residential scenario		Industrial scenario	
			CTC (mg/kg ds)	Potentially contaminated samples (C > CTC) (%)	CTC (mg/kg ds)	Potentially contaminated samples (C > CTC) (%)
Benz(a)anthracene	<0.01	189.63	0.50	22	10.00	11
Benzo(a)pyrene	<0.01	917.78	0.10	36	10.00	11
Benzo(b)fluoranthene	<0.01	1131.1	0.50	26	10.00	12
Benzo(k)fluoranthene	<0.01	314.12	0.50	22	10.00	9
Benzo(g,h,i)perylene	<0.01	806.27	0.10	39	10.00	11
Chrysene	<0.01	602.22	5.00	13	50.00	4
Dibenz(a,h)anthracene	<0.01	718.80	0.10	36	10.00	11
Indenopyrene	<0.01	1156.85	0.10	39	5.00	13
Pyrene	<0.01	465.06	5.00	12	50.00	4
Heavy hydrocarbons	<5.00	3475	50.00	16	750.00	4
PCB	<0.05	3.41	0.06	17 <sup>a</sup>	5.00	0 <sup>a</sup>

<sup>a</sup> Total number of samples analyzed for PCBs = 6; total number of samples analyzed for PAHs and heavy hydrocarbons = 141.



**Fig. 3.** Schematics and characteristics of the three discrete areas. (a) Plan view—hatched area: plant area, grey area: bank area, dark grey area: dump area. (b) Section view.

of the analytical method, as recommended by the Italian regulatory agency [7]. Since both the mobility and the toxicity of a hydrocarbon mixture are strongly dependent on the relative amounts of the group of constituents in the mixture, “finger printing” was necessary to evaluate the contribution of the different fractions to the total concentration [6,8]. All the RSCs are summarized in Tables 3 and 4. The physical–chemical and toxicological properties of contaminants are those suggested by ISS and ISPESL (Italian National Institute for Health protection of citizens and workers) [9]. The soil–water partition coefficients were evaluated by means of leaching tests [10].

Ingestion, dermal contact (direct exposure) with soil and vapor and particulate inhalation from the soil source (indirect exposure) were considered. Migration pathways included outdoor and indoor volatilization and particulate emission. Leaching into groundwater was considered together with surface water mixing and sediment partitioning (see the conceptual model in Fig. 4).

The extensive data set collected during the characterization allowed us to determine directly most of the site-specific parameters. The use of default values, always precautionary, is often unrealistic, as shown in sensitivity analysis [3,7]. In analogy with

**Table 2**  
Environmental parameters.

Parameter	Units	Value			Data source
		PA	DA	BA	
Groundwater level	m (from g.l.)	5.4	18.2	4.3	Measured
Height of capillary fringe <sup>a</sup>	m	0.05	0.05	0.05	Correlation
Thickness of groundwater	m	0.5	1.1	3.4	Measured
Soil bulk density <sup>a</sup>	g/cm <sup>3</sup>	1.7	1.7	1.7	Literature
Total porosity <sup>a</sup>	–	0.359	0.359	0.359	Correlation
Volumetric water content <sup>a</sup>	–	0.237	0.237	0.237	Correlation
Volumetric air content <sup>a</sup>	–	0.122	0.122	0.122	Correlation
Fraction of organic carbon	–	0.00278	0.00278	0.00278	Measured
Effective infiltration	cm/year	14	14	14	Correlation
Hydraulic conductivity ( $\times 10^{-5}$ )	m/s	1.2	0.55	0.55	Measured
Hydraulic gradient	%	1.86	1.26	1.26	Measured
Dominant wind speed	m/s	0.838	0.838	0.838	Weather service

<sup>a</sup> The values are identical for the three areas because they are function of the grain size distribution (sandy gravel) that is assumed homogeneous for the entire site.

**Table 3**  
Representative source concentration for residential/recreational scenario.

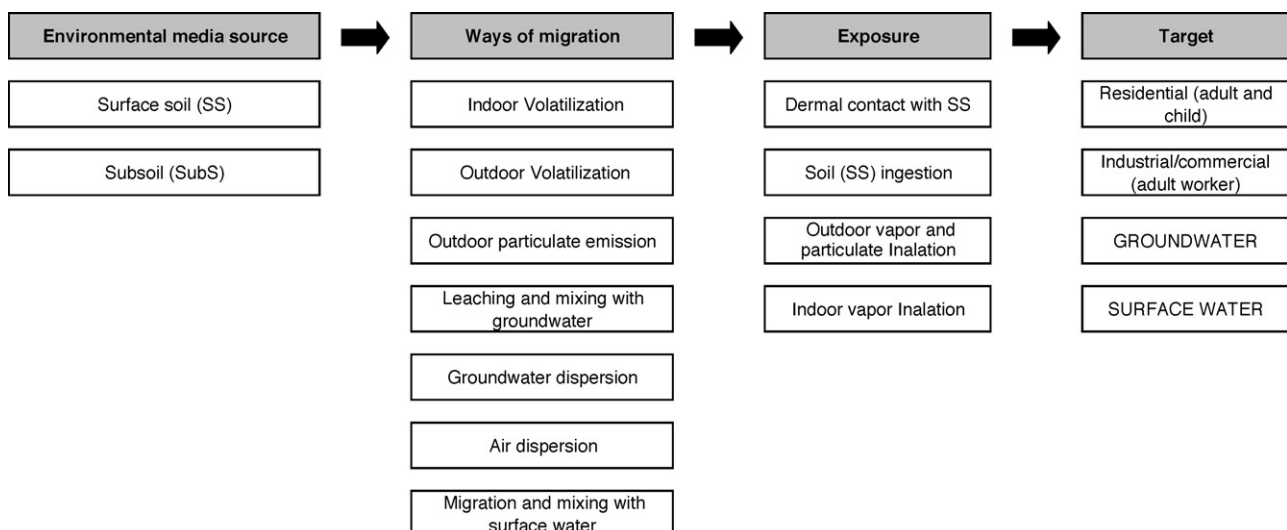
Contaminants	Plant area		Bank area		Dump area	
	SS (0–1 m) (mg/kg ds)	SubS (>1 m) (mg/kg ds)	SS (0–1 m) (mg/kg ds)	SubS (>1 m) (mg/kg ds)	SS (0–1 m) (mg/kg ds)	SubS (>1 m) (mg/kg ds)
Benz(a)anthracene	4.69	32.42	7.72	43.70	1.37	158.18
Benzo(a)pyrene	7.68	53.15	14.02	61.38	2.59	917.78
Benzo(b)fluoranthene	9.17	50.44	17.10	55.11	3.38	1131.1
Benzo(k)fluoranthene	3.51	34.30	5.50	26.11	0.90	314.12
Benzo(g,h,i)perylene	8.97	55.44	16.21	51.70	3.22	806.27
Chrysene	7.13	45.44	10.97	52.90	1.91	602.22
Dibenz(a,h)anthracene	8.17	49.16	13.40	41.65	2.52	718.80
Indenopyrene	55.23	66.92	18.98	60.86	4.05	1156.85
Pyrene	3.99	33.53	5.59	53.87	1.12	465.06
Heavy hydrocarbons	203.00	171.40	56.00	1300	8.00	3475
Aliphatic C9–C18	18.47	15.60	5.10	118.30	0.73	316.23
Aliphatic C19–C36	104.34	88.10	28.78	668.20	4.11	1786.15
Aromatic C11–C22	79.98	67.53	22.06	512.20	3.15	1369.15
PCB	3.41	–	–	–	–	–

**Table 4**  
Representative source concentration for industrial scenario.

Contaminants	Plant area		Bank area		Dump area			
	1st source		2nd source					
	SS (0–1 m) (mg/kg ds)	SubS (>1 m) (mg/kg ds)	SS (0–1 m) (mg/kg ds)	SubS (>1 m) (mg/kg ds)	SS (0–1 m) (mg/kg ds)	SubS (>1 m) (mg/kg ds)		
Benz(a)anthracene	27.80	189.63	–	70.58	7.72	43.70	–	158.18
Benzo(a)pyrene	54.07	329.17	–	18.25	14.02	61.38	–	917.78
Benzo(b)fluoranthene	58.47	308.42	–	73.97	17.10	55.11	–	1131.1
Benzo(k)fluoranthene	20.20	208.18	–	36.51	5.50	26.11	–	314.12
Benzo(g,h,i)perylene	72.70	349.25	–	18.81	16.21	51.70	–	806.27
Chrysene	35.23	267.51	–	99.53	10.97	52.90	–	602.22
Dibenz(a,h)anthracene	61.62	295.67	–	20.25	13.40	41.65	–	718.80
Indenopyrene	95.60	429.21	–	24.57	18.98	60.86	–	1156.85
Pyrene	15.58	197.10	–	76.01	5.59	53.87	–	465.06
Heavy hydrocarbons	0.00	1000.93	–	386.83	56.00	1300	–	3475
Aliphatic C9–C18	0.00	91.09	–	35.20	5.10	118.30	–	316.23
Aliphatic C19–C36	0.00	514.48	–	198.83	28.78	668.20	–	1786.15
Aromatic C11–C22	0.00	394.37	–	152.41	22.06	512.20	–	1369.15

the RSCs, site-specific parameters were calculated as UCL of the mean, if the data number was sufficiently high (>10), otherwise the most precautionary value was adopted. The receptors considered were adults and children in the residential and adult workers in the industrial/commercial scenario. In addition, for the bank area

(BA) only, the river was assumed as a potential receptor. Exposure parameters such as exposure duration, frequency, age of receptor, body weight, amount ingested and contacted, were chosen following the RME (reasonable maximum exposure) philosophy according to Italian guidelines (Table 5).



**Fig. 4.** Schematic example of the conceptual model (note: receptors and paths vary with the different areas).



**Table 5**  
Exposure parameters (ISPRA (ref.[7]) 2008).

Exposure factors	Units	Residential		Industrial Worker
		Adult	Child	
Body weight	kg	70	15	70
Carcinogen average time	years	70	70	70
Non-carcinogen average time	years	ED	ED	ED
<b>Soil ingestion</b>				
Exposure duration (ED)	years	24	6	25
Exposure frequency	days/year	350	350	250
Fraction of ingested soil	–	1	1	1
Ingestion rate	mg/day	100	100	50
<b>Soil dermal contact</b>				
Exposure duration	years	24	6	25
Exposure frequency	days/year	350	350	250
Exposed dermal surface	cm <sup>2</sup>	5700	2800	3300
Dermal adherence factor	mg/(cm <sup>2</sup> day)	1	1	1
<b>Inhalation of outdoor air</b>				
Exposure duration	years	24	6	25
Exposure frequency	days/year	350	350	250
Outdoor daily exposure frequency	h/day	24	24	8
Outdoor Inhalation	m <sup>3</sup> /ora	0.9	0.7	2.5
Fraction of soil particles in dust	–	1	1	1
<b>Inhalation of indoor air</b>				
Exposure duration	years	24	6	25
Exposure frequency	days/year	350	350	250
Indoor daily exposure frequency	h/day	24	24	8
Indoor inhalation	m <sup>3</sup> /h	0.9	0.7	0.9
Indoor fraction of outdoor dust	–	1	1	1

### 3.3. Risk evaluation tool

RISC<sub>4</sub><sup>®</sup> (Risk Integrate Software for Clean-ups ver. 4.05) was used to evaluate the potential risks. It allows an estimation of both carcinogenic and non-carcinogenic potential adverse impact on human health from different exposure pathways. The software contains vadose zone, saturated zone and air fate and transport models for estimating concentrations at the receptor point [11]. The options of the software include the modification of contaminant properties or the addition of a “new contaminant” with properties defined by the user as well as the possibility to evaluate a soil source also extended to the saturated zone and the evaluation of the effects of the groundwater level fluctuations. In the event of contaminants with carcinogenic effects, an added receptor can be considered with exposure parameters averaged between childhood and adulthood following the suggestions of the Italian Regulatory Agency. Moreover, the software offers the possibility to select the analytical transport model in an available group. For vapor emission from soil the available models are the one developed by “Johnson and Ettinger” [12], the “Dominant layer model” [13] and the “Oxygen-limited vapor model” while for leaching and mixing with groundwater, the user can choose between three models: “Vadose zone soil to groundwater” [14], “Saturated zone soil to groundwater” [15] and “Dissolved source to groundwater” [16]. For the case studied, the model chosen to consider volatilization was the Johnson and Ettinger vapor emission model. For leaching into groundwater two different methods were followed. In the case of a soil source located completely in the unsaturated zone, the “Vadose zone soil to groundwater” model was chosen. The monitoring well was positioned underneath the soil source, without any transport in groundwater. The “Saturated zone soil to groundwater” model was used in the case of contaminated samples in the saturated zone: it simulates dissolved chemical transport from a soil source zone at or near the water table taking into account possible groundwater table fluctuations. The monitoring well was again located underneath the soil source.

### 3.4. Risk characterization

Referring to the toxicity values suggested in the ISS-ISPEL Database for different contaminants (non-cancer reference doses, RfDs and cancer slope factors, SFs), toxicity and exposure assessments were integrated into quantitative expressions of risk. For each scenario, for each source and for each exposure pathway, risks due to each contaminant were divided into two categories: carcinogens and non-carcinogens. Additional lifetime cancer risk or hazard index were calculated with a procedure consisting of the following steps:

1. Evaluate the risk/hazard for each contaminant and exposure pathway (i.e. RISC<sub>4</sub> output).
2. Combine risk or hazard for each contaminant across all exposure pathways to obtain the “individual risk”.
3. Evaluate cumulative risk or hazard for each receptor by combining all individual risks or hazards previously calculated (step 2).
4. Define risks as acceptable or unacceptable.

Steps 1–4 were performed with the help of a purpose-built spreadsheet. For non-carcinogens, the hazard is evaluated by comparing (taking the ratio of) the intake rate ( $E$ ) determined from an exposure assessment with the appropriate reference dose (RfD) [17]. The ratio is called the hazard index:

$$\text{Hazard index (HI)} = \frac{\text{average daily dose}}{\text{reference dose}} = \frac{E}{\text{RfD}}$$

Pertinent RfD values are listed in the ISS-ISPEL Database (Table 6) and  $E$  was calculated by the software based on the daily dose of contaminant ingested, contacted or inhaled over a specific period of exposure (exposure duration, ED) normalized to the body weight of each receptor (BW) and the period over which exposure is averaged (averaging time, AT). The period of exposure and the averaging time may or may not be equal. For non-carcinogenic  $E$  values, the averaging time was assumed as 6 years for children and 24 years for adults (equal to ED) while 70 years (lifetime) was assumed for the added receptor to calculate cancer risk.

For non-carcinogenic effects, the acceptable range for the hazard index is less than 1, while an HI greater than 1 is unacceptable. The same criterion is assumed for both individual and cumulative HI. Additional lifetime cancer risk is defined as the probability of cancer occurring in the exposed population over a 70-year lifetime and it was determined by multiplying the intake rate ( $E$ ) by the pertinent slope factor (SF) [17]:

$$\text{Cancer risk (R)} = \text{lifetime daily dose (E)} \cdot \text{slope factor (SF)}$$

In this case, an additional lifetime cancer risk of one-in-one-million ( $10^{-6}$ ) is used as the acceptable value for individual cancer risk while for cumulative cancer risk the maximum acceptable value is  $10^{-5}$ .

In the case of unacceptable risks, a backward risk assessment was performed to derive the cleanup levels (CLs) for each contaminant and for each environmental medium. The CLs are defined as the source concentrations that ensure the respect of the acceptable risk level and must be assumed as remediation goals. They are derived by inverse application of the described procedure by fixing the acceptable risk/hazard levels.

## 4. Results

### 4.1. Forward assessment: health risk results

Forward health risk assessment was performed for each source, discrete area and scenario, for both carcinogenic and non-

**Table 6**  
Toxicological properties of contaminants.

Contaminants	CAS number	SF ing. (mg/kg-d) <sup>-1</sup>	SF inhal. (mg/kg-d) <sup>-1</sup>	RfD ing. (mg/kg-d)	RfD inhal. (mg/kg-d)
<b>PAHs</b>					
Benz(a)anthracene	56-55-3	7.30E-01	6.00E-01	–	2.85E-01
Benzo(a)pyrene	50-32-8	7.30E+00	7.32E+00	–	3.14E+00
Benzo(b)fluoranthene	205-99-2	7.30E-01	6.00E-01	–	2.85E-01
Benzo(k)fluoranthene	207-08-9	7.30E-02	3.10E-02	–	2.85E-02
Benzo(g,h,i)perylene	191-24-2	–	–	3.00E-02	3.00E-02
Chrysene	218-01-9	7.00E-03	6.10E-03	3.00E-02	3.00E-02
Dibenz(a,h)anthracene	53-70-3	7.30E+00	6.10E+00	–	1.14E-01
Indenopyrene	193-39-5	7.30E-01	6.00E-01	3.00E-02	3.14E+00
Pyrene	129-00-0	–	–	3.00E-02	3.00E-02
<b>Heavy hydrocarbons</b>					
Aliphatic C9–C18	–	–	–	1.00E-01	5.70E-02
Aliphatic C19–C36	–	–	–	2.00E+00	–
Aromatic C11–C22	–	–	–	3.00E-02	–
<b>PCBs</b>					
PCB	1336-36-3	2.00E+00	2.00E+00	2.00E-05	–

**Table 7**  
Cumulative health hazard and risk values.

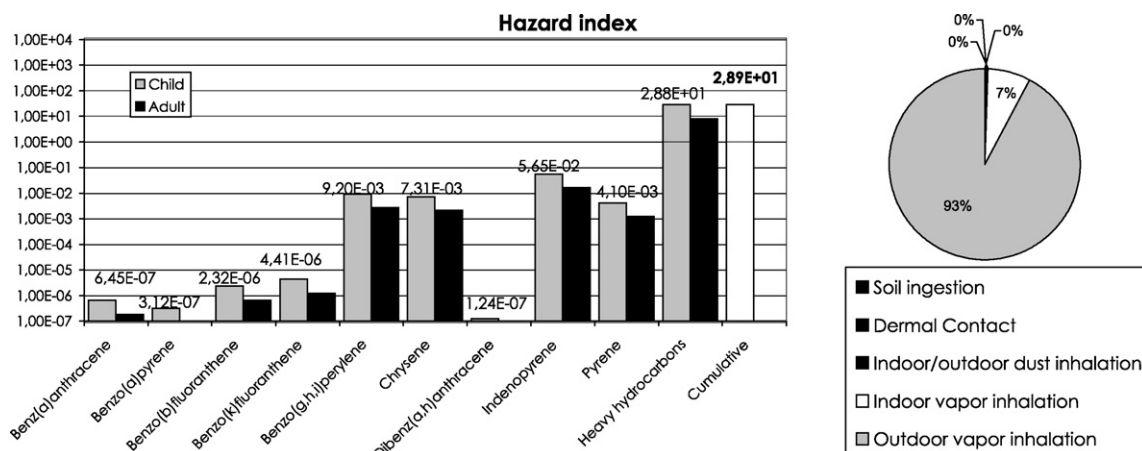
		Non-carcinogen hazard index (<1)	Carcinogen risk (<10 <sup>-5</sup> )
<b>Residential scenario<sup>a</sup></b>			
Plant area	PAHs & Heavy Hydroc. Source	2.89E+01	9.63E-04
	PCBs Source	5.23E+00	4.81E-05
Tank area	PAHs & Heavy Hydroc. Source	6.25E+01	4.88E-04
Bank area	PAHs & Heavy Hydroc. Source	5.47E+01	1.39E-03
<b>Industrial scenario</b>			
Plant area	PAHs & Heavy Hydroc. 1st Source	6.02E+00	3.17E-03
	PAHs & Heavy Hydroc. 2nd Source	7.83E-06	5.96E-08
Tank area	PAHs & Heavy Hydroc. Source	6.19E-01	9.07E-07
Bank area	PAHs & Heavy Hydroc. Source	7.94E+00	3.10E-04

<sup>a</sup> The listed values for these scenarios are those of the most sensitive receptor between adult and child.

carcinogenic effects. The hazard index for on-site receptors shows that children are, obviously, the most sensitive receptors in the case of a residential scenario. Cumulative hazard and cancer risk exceed acceptable levels in each area (see Table 7) and they are summarized in graphs like the one shown in Fig. 5. In the case of non-carcinogenic effects, for all areas, only heavy hydrocarbons exceed the individual limit value (see the example bar charts in Fig. 5) and, consequently, they are mainly responsible for the high non-carcinogenic cumulative hazard. The dominant ways of exposure are indoor and outdoor vapor inhalation (see the pie chart in Fig. 5). In the absence of “finger printing”, the total heavy hydrocarbon concentration would have been assigned to the Aliphatic C9–C18 fraction (the only fraction having inhalation RfD), result-

ing in an over-conservative high hazard value. On the other hand, individual cancer risk values exceed the target risk for each contaminant except Chrysene and the values of cumulative risk are higher than  $1 \times 10^{-5}$  in all areas. Cumulative cancer risk is primarily due to direct exposure with dermal contact contributing 73%, 37% and 70% for the plant area, tank area and bank area respectively, while soil ingestion is responsible for 27%, 14% and 26% of the cumulative risk (see the example in Fig. 6). The pie charts show the dominant ways of exposure thus giving valuable suggestions for the future remediation program (see Section 5).

For the industrial scenario two separate sources occur in the plant area, and therefore four risk assessments were performed. Hazard indexes show the same configuration as the residential sce-



**Fig. 5.** Non-cancer hazard results for residential scenario—plant area.

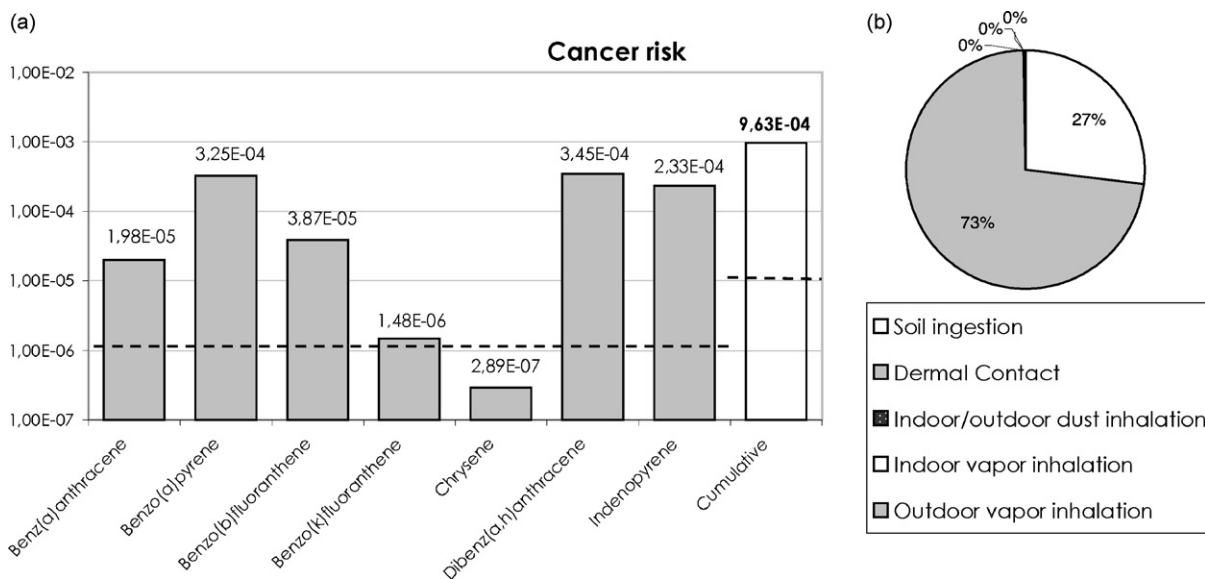


Fig. 6. Cancer risk results for residential scenario—plant area.

nario: only heavy hydrocarbons give unacceptable risk and the main way of migration is vapor volatilization. Cancer risk values exceed the acceptable limits for one of the two sources in the plant area and for the one in the bank area. The high values are mainly due to direct exposure even if, unlike the residential scenario, for the plant area 59% of the cumulative risk is due to outdoor vapor inhalation. This occurs firstly because the industrial outdoor inhalation rate is higher than the residential one (see Table 4) and secondly because the industrial RSCs are greater (see Tables 2 and 3) and the geometry of the sources is different.

#### 4.2. Forward assessment: environmental risk results

Besides health risk, environmental hazard was also calculated. The considered receptors are the groundwater bodies and the river flowing next to the bank area. In Italian regulations the groundwater resource has an intrinsic value even if it is not used for drinking water production. The groundwater hazard index ( $HI_{GW}$ ) is defined as:

$$HI_{GW} = \frac{C_{poc}}{CTC_{GW}}$$

where  $C_{poc}$  is the calculated concentration at the compliance point and  $CTC_{GW}$  is the groundwater threshold concentration. The compliance point for groundwater must be located at the property line. In some of the cases considered, the sources of contamination extend as far as the property line and hence the compliance point was located under the source. In so doing, leaching and mixing with groundwater are accounted for but dispersion and attenuation are conservatively neglected in  $C_{poc}$  calculations. Following regulatory instructions, values of  $HI_{GW}$  were determined for both residential and industrial sources. The transient groundwater transport model implemented by RISC allows the groundwater concentration versus time up to 100 years to be predicted. This feature allows us to assess if the regulatory limit will be reached within the 100-year time span.

RISC<sub>4</sub> simulations for the residential scenario predicted that for the upper aquifer, no risk of contamination exists in 100 years. For the lower aquifer, the limit concentration of heavy hydrocarbons, would eventually exceed the regulatory limit after 17 years below the DA, after 20 years below the BA; for Benzo(a)pyrene, the risk would become unacceptable after 80 years (see graphs in Figs. 7 and 8).

Calculations for the industrial scenario revealed no risk (concentration will remain undetected) for groundwater in the entire site.

With regard to surface water as an environmental receptor (river), the potential concentration was evaluated using a complete mixing model [11] in combination with the previously adopted leaching model and ignoring attenuation. This way of migration is applicable only if groundwater feeds the river and not the opposite. Although the observed piezometric level in the monitoring wells was normally lower than the river, a fictitious groundwater surge of 2 m above the river level was assumed as the worst case. A water-sediment partitioning model was also applied to evaluate concentration in sediments. Italian national regulations do not prescribe concentration limits in surface water or for sediments, hence the evaluated concentrations were compared with limits prescribed in the Regional Water Quality Plan. In any case, concentrations calculated at 100 years for surface water and sediments are well under the adopted limits.

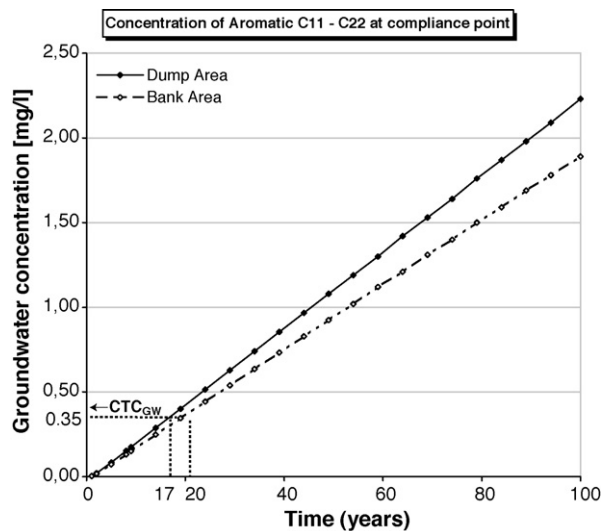


Fig. 7. Predicted concentration of aromatic fraction of heavy hydrocarbons in groundwater for residential scenario (caused by unsaturated sources in dump and bank area).



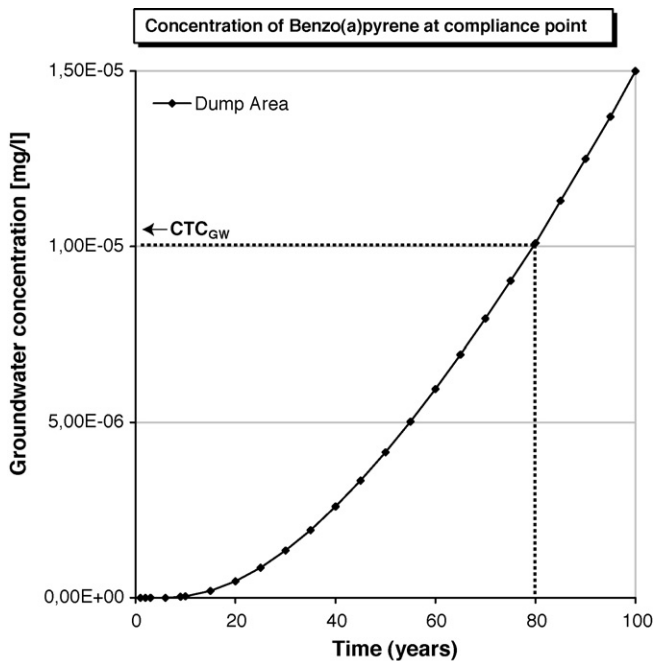


Fig. 8. Predicted concentration of Benzo(a)pyrene in groundwater for residential scenario (caused by unsaturated source in dump area).

#### 4.3. Backward assessment: cleanup levels

In the case of unacceptable risks, individual cleanup levels (CLs) were derived for each contaminant and for each environmental medium. According to Italian regulations the areas where measured concentrations are higher than CLs are effectively contaminated and require remediation. The map of contaminated areas is shown in Fig. 9 for surface soil (<1 m from ground level) and in Fig. 10 for subsoil (>1 m from ground level). If site-specific CLs are lower than regulatory CTCs then the number of contaminated samples (measured concentration < CL) may be higher than that of potentially contaminated ones (measured concentration < CTC) and vice versa. For example, in the case of the residential scenario, all measured concentrations of Benzo(g,h,i)perylene and Pyrene are lower than CLs, therefore these compounds are not a contaminant for the site (the number of contaminated samples drops to zero); in the case of the industrial scenario Chrysene is not a contaminant either. In the PA (residential scenario) the contaminated soil is mainly the surface soil (0–1 m depth) while, in the subsoil, only seven cells prove to be contaminated to a depth of 3 m. A similar situation

occurs for the industrial scenario with six cells and a maximum contaminated depth of 3 m. In the DA, the entire subsoil down to a depth of 13 m is contaminated for residential and industrial scenarios while, for the industrial scenario, the measured concentrations in the surface soil are lower than the CTC and a risk assessment was not required. In the BA, the surface soil contamination is the same for both scenarios (five cells contaminated) while, for subsoil the situation is different: for the residential scenario, the soil proved to be contaminated down to a depth of 10 m, whereas the contaminated depth was 8.5 m for the industrial scenario. The analysis revealed that the greatest contribution to the risk for subsoil was caused by heavy hydrocarbons, for which a CL of 2.2 mg/kg was calculated. This value is lower than the acceptable threshold (50 mg/kg) and even lower than the detection limit of the analytical method (5 mg/kg). Consequently, all samples with a concentration lower than the detection limit must be considered as contaminated, since a concentration equal to the detection limit is assigned to “non-detect”. The result appears contradictory in this case, since, according to the regulations, no risk evaluation is necessary if measured concentrations are lower than 50 mg/kg. This inconsistency can be due either to an overestimate of the mobility of the contaminants (heavy hydrocarbons) or an excessive threshold regulatory limit.

## 5. Discussion

Several aspects requiring further consideration and discussion emerged from the results obtained. The first aspect to notice is that, regarding the hazard for groundwater, the risk index depends on the reuse scenario. The calculated risk for groundwater depends on the RSC and the geometry of the source, that are in turn a function of the regulatory limits (CTC). However, this is in contrast with the physical reality because the risk for groundwater depends on the true concentrations and not on the representative concentration. A numerical model taking into account the real concentration distribution would probably be more appropriate for determining the risk for groundwater (tier 3 assessment).

Secondly, the study pointed out the role of “finger printing” of heavy hydrocarbons and leaching tests in the assessment results: the first one allowed us to differentiate between the mobility and toxicity of the three identified fractions, Aliphatic C9–C18, Aliphatic C19–C36 and Aromatic C11–C22. Aliphatic C19–C36 is the immobile fraction and Aromatic C11–C22 is mobile but not toxic for inhalation exposure. Without finger printing, the risk evaluation must be done by assigning the entire value of RSC to each fraction, and finally choosing the highest risk obtained.

Leaching tests are performed to determine the soil–water partition coefficient,  $k_d$ , that is a function of the compound and of

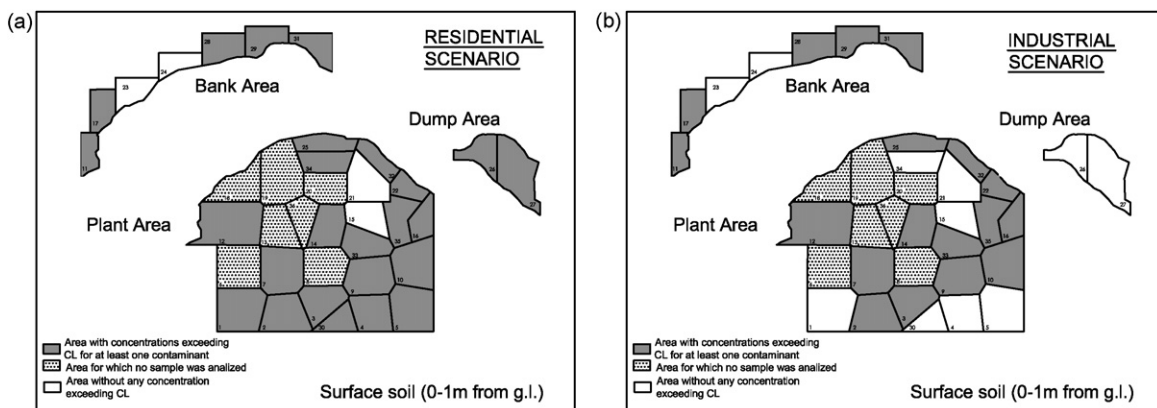


Fig. 9. Map of contamination of surface soil (0–1 m from g.l.): (a) residential scenario and (b) industrial scenario.

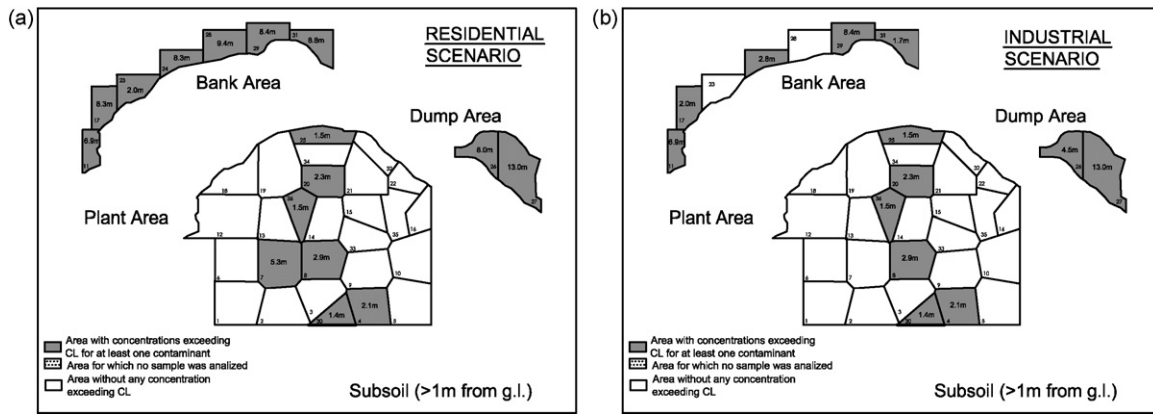


Fig. 10. Map of contamination of subsoil (>1 m from g.l.): (a) residential scenario and (b) industrial scenario.

Table 8

Calculated risks using measured or default  $k_d$  for Benzo(a)pyrene.

	R		HI for adult		HI for child	
	$k_d$ leaching test	$k_d$ database	$k_d$ leaching test	$k_d$ database	$k_d$ leaching test	$k_d$ database
Indoor inhalation	3.26E-09	1.39E-07	2.17E-10	9.27E-09	7.88E-10	3.36E-08
Outdoor inhalation	1.29E-06	5.50E-05	8.58E-08	3.66E-06	3.11E-07	1.33E-05

the characteristics of the soil. In the absence of leaching tests, our guidelines suggest calculating  $k_d$  as the product of the organic carbon partition coefficient,  $k_{oc}$ , and the fraction of organic carbon,  $f_{oc}$ . Default  $k_{oc}$  values are listed in the national ISS-ISPESL database. Measured  $k_d$  from leaching tests are significantly different from the default values. For example, Table 8 shows the effects of adopting the measured  $k_d$  or default value on the calculated risk for Benzo(a)pyrene ( $k_d$  from leaching test =  $1.15 \times 10^5$  l/kg;  $k_d$  from database =  $2.69 \times 10^3$  l/kg). Table 9 shows the impact of  $k_d$  on the calculated risk value for Aliphatic C9–C18 ( $k_d$  from leaching test =  $1.15 \times 10^3$  l/kg;  $k_d$  from database =  $1.89 \times 10^3$  l/kg).

As explained for the partition coefficient, the site-specific determination of parameters is important for performing a tier 2 analysis. A complete and in-depth characterization will even be economically advantageous because a realistic determination of environmental parameters adds reliability to the results of the analytical models applied and, eventually, increases the efficiency of remediation action.

As regards the existing migration models, different approaches are available for the same transport phenomena. For instance, with regard to leaching and mixing with groundwater, Italian guidelines suggest using a steady-state model that simulates soil–water partitioning inside the source and mixing with groundwater. In brief, the contaminant is transferred immediately to the groundwater. For certain types of contaminants with a very low  $k_d$  value, this model can closely approximate the real transfer to groundwater but not for contaminants with high  $k_d$  such as PAHs. Application of this model to the real conditions would result in immediately unacceptable concentrations in groundwater, which contrast with the experimental observations, since all monitoring wells showed PAH concentrations lower than the threshold levels. The migration model used simulates transient 1D flow and

solute transport across the vadose zone with contemporary Fick’s volatilization of part of the contaminant and a time span of 100 years. It allows us to predict the trends in the concentration versus time indicated in Figs. 6 and 7, showing no immediate risk for groundwater.

The reuse scenario of the site has not yet been defined. The results of risk assessment performed for the two possible scenarios can be of help in making decisions on the basis of risk management.

An example of risk management is illustrated in the context of calculating the CLs that ensure the respect of cumulative risk. The risk assessment procedure calculates individual CLs and remediation goals to be achieved for one given pollutant regardless of the others. However, as in the forward risk assessment, it is necessary to take into account the cumulative effect. Since the problem of calculating cumulative CLs is mathematically undetermined, one possible method to ensure respect of cumulative limits is: (1) to simulate a possible remediation, based on the migration paths (noticed in the forward assessment) and on the location of contaminated samples (obtained with the backward assessment), (2) to repeat forward risk analysis applied to the remediation scenario in order to verify the observance of acceptable cumulative risks and hazards. The example is applied to the plant area (75% of the total surface area of the site) in a future residential scenario. The remediation is shown in Fig. 11: it consists in the removal of the upper 1 m of contaminated soil and replacement with 1 m of “clean” soil. The soil in cell 20 is removed for a depth of 2.5 m, being a hotspot for heavy hydrocarbons. At the interface between surface soil and subsoil (depth = 1 m) a vapor barrier is positioned to prevent volatilization.

The site conceptual model was updated by assuming the concentration in the replaced soil equal to the detection limit and leaving the remaining concentrations unchanged. The new risk assessment

Table 9

Calculated risks using measured or default  $k_d$  for heavy hydrocarbon—Aliphatic C9–C18.

	R		HI for adult		HI for child	
	$k_d$ leaching test	$k_d$ database	$k_d$ leaching test	$k_d$ database	$k_d$ leaching test	$k_d$ database
Indoor inhalation	–	–	6.27E-01	3.82E-01	2.27E+00	1.39E+00
Outdoor inhalation	–	–	7.91E+00	4.82E+00	2.87E+01	1.75E+01

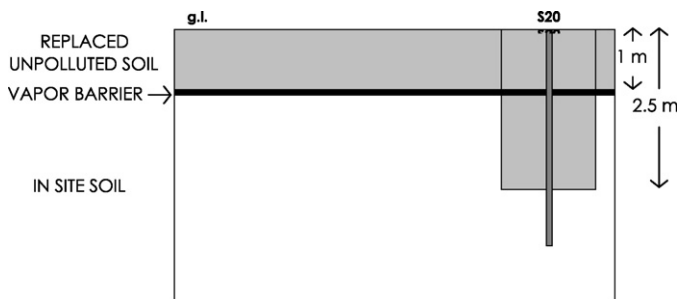


Fig. 11. Scheme of remediation scenario.

indicated no risks or hazard either for human beings or for groundwater, hence the remediation action proves to be efficient.

In order to obtain the “clean” soil to be used as replacement, the clean-up of the *in situ* contaminated soil is more environmentally sound than the use of “clean” soil from borrow pits; moreover, this strategy would allow to avoid the transport activities (with related emissions) as well as the environmental issue of disposal of the polluted soil.

The most appropriate technology for the remediation of contaminated soils must be selected following a B.A.T.E.V. (Best Available Technology Economically Viable) approach. For the given type and level of contamination and soil properties, a combination of soil washing and biological treatment appears a viable treatment option. Soil washing allows to separate the coarse grained from the fine grained fraction, to which most of the contamination is associated. Biological treatment, that will be applied only to the fine grained fraction, can be carried out by means of biopiles or bioslurries. Thermal desorption is another remediation technology applicable to organic contaminants; however, contamination levels higher than those observed in this case are usually required for the technology to be economically sustainable.

In any case, the effectiveness of a selected treatment method must be evaluated by a laboratory stage and eventually, if the treatment has proven positively in the laboratory stage, a pilot-scale stage.

## 6. Conclusions

A case study is presented with the purpose of illustrating a risk assessment procedure within the framework of Italian national legislation. Risk assessment is used for calculating cleanup goals for soil and groundwater and as a tool to help determine the most appropriate corrective actions. The conclusions of this study are summarized below.

To complete a tier 2 evaluation site-specific parameters are necessary since they provide more realistic and reliable results when fed into transport models. A comprehensive site conceptual model had to be defined taking into account the particular morphology of the site, the properties of the detected contaminants and the exposed targets.

The calculations performed indicated that health risks were higher than the acceptable levels. The main routes of exposure to contaminants were identified as vapor inhalation for non-carcinogenic contaminants and soil ingestion and dermal contact for carcinogenic ones.

As far as environmental hazard is concerned, no contamination was detected in groundwater and the transport models predicted no risk of contamination at least for the next 17 years. No hazard was estimated for surface water in the next 100 years.

Cleanup levels were determined: in some cases, they were more stringent than the regulatory threshold limits and in one case even more stringent than the detection limit. This inconsistency can be due either to an overestimate of the mobility of the contaminants (heavy hydrocarbons) and/or to a detection limit that is inappropriate for the specific case.

A possible remediation action is proposed based on the reduction of cumulative risk. Risk-based strategies allow for the identification of remedies that are both environmentally sound and cost effective.

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