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A Comparison of deterministic and probabilistic approaches for assessing risks from contaminated aquifers: An Italian case study

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Abstract

In this article we consider the methods of deterministic and probabilistic risk analysis regarding the presence of chemical contaminants in soil, water and air, with a broader meaning than usual for the latter, as we extended the probabilistic treatment to the parameters that influence the transport to a greater extent, in particular hydraulic conductivity and partition coefficient. These parameters, to which only one value is assigned, are considered here as random variables. The objective of the study reported herein was to demonstrate that application of the probabilistic method of risk assessment is preferable to the use of the deterministic method. Both methods yield contaminant removal levels that will reduce adverse effects on human health and the environment, but results from the deterministic method are typically more conservative than necessary, and are thus more costly to achieve. In addition, we found it essential to consider the importance of random variables (the parameters influencing the flow and the transport), such as the hydraulic conductivity and the partition coefficient, when assessing health risks. Both methodologies of health risk analysis, deterministic and probabilistic, were applied to a site in southern Italy, contaminated by heavy metals. The results obtained confirm the purposes of this study.

Keywords

Risk analysis, deterministic approach, probabilistic approach, Monte Carlo simulation, soil contamination

Introduction

The presence of fugitive industrial chemicals in soil, water and/or air presents risks to human health and the environment. Scientists apply risk analyses to quantify the risks and to evaluate the significance of the risk (Harms-Ringdalh, 2001; Khadam and Kaluarachchi, 2003). One says that a person is 'at risk' when he/she is 'exposed' to a 'danger' and the magnitude of the risk is a function of the degree of hazard presented by the substance and of the magnitude of exposure (Bonomo and Andreottola, 2000; US EPA, 1989). The assessment of the risks at sites contaminated with industrial chemicals is mainly based on modeling of the subsurface system, including forecasting its evolution in the risk context by two different approaches: deterministic and probabilistic.

Usually, risk analysis is carried out in connection with environmental and human health (Covello and Merkohofer, 1993; Harms-Ringdalh, 2001; Kaplan, 1997). Our study refers, in particular, to health risk, namely to the risks that may endanger human health. In effect, by the term 'dangerous' one refers to the possibility that a substance produces negative effects in the body, and by the term 'risk' to the probability that in a given situation a dangerous substance produces damage or otherwise (Bonomo and Andreottola, 2000; Kolluru, 1996; NRC, 1993; OTA, 1993; US EPA, 1989,).

Several authors (Benekos, et al., 2007; Bennett et al., 1998; EPA, 1986, 1996; Peck et al., 1998) stress the importance in risk assessment of a proper characterization of the variability and uncertainty in the transport and fate of contaminants (hydro-dispersive parameters), as well as in the dose–response effects (toxicological parameters).

Deterministic risk analysis consists of assigning a single representative value to each exposure parameter (input), which appears in the risk equation, and, as a result, leads to a unique risk value (output). This approach turns out to be very limited as a single value assignment clearly involves a stiffness, which often leads to overestimating the risk and, consequently, to conservative decisions, which are reflected in a higher remediation cost.

Probabilistic risk analysis considers the degree of variability and uncertainty of each parameter in the risk equation through an estimation based on stochastic methods such as, for instance, Monte Carlo simulations (Bennett et al., 1998; Cohen et al.,

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1996; Dettinger and Wilson, 1981; James and Oldernburg, 1996; McKone and Bogen, 1992). The uncertainty analysis using Monte Carlo simulation can be very useful when the values obtained with the deterministic method are not very realistic. In the probabilistic approach each parameter in the risk equation is assigned a probability density function that describes the behavior of the risk in probabilistic terms. Thus, the probabilistic risk analysis may provide more information than the traditional deterministic approach through the curves of probability distributions, which evaluate intervals of possible values of the risk, each one with a specified probability.

In this article we consider the risk analysis and compare the deterministic and probabilistic approaches, including in the latter as random variables not only the toxicological parameter, as in the procedure usually followed, but also the characteristic parameters of the aquifer. Thus, we demonstrate the greater reliability of the probabilistic methodology, which provides more realistic results for the remediation work.

The study area we considered corresponds to that of a former chemical industry called Pertusola Sud Crotone. The area has been declared of 'national interest' owing to the high concentrations of heavy metals in it.

Risk analysis theory

For the considered study area we determined the risk values by both approaches for all receptors (children, adults and workers), but in the present study we show only the results relative to the adults—ingestion and dermal contact being the exposure routes we consider. In this article the definition of risk given by US Environmental Protection Agency (US EPA, 1989) was assumed, which considers a linear relation between the exposure and risk for both carcinogenic and non-carcinogenic (toxic) substances. Therefore, the risk is defined as:

$$R = ADI \times T \tag{1}$$

where ADI is the average daily intake ($mg^{-1}kg^{-1}.d^{-1}$) of the examined dangerous substance and T the toxicity factor concerning to the contaminant.

For non-carcinogenic substances the toxicity factor T is expressed in terms of maximum permissible dose (chronic reference dose) as $T = 1/RfD$ ($mg^{-1}kg^{-1}.d^{-1}$) and afterwards it is indicated as R_{tox}. For carcinogenic substances the factor T is expressed in terms of carcinogen potential (slope factor) as $T = SF$ ($kg^{-1}d.mg^{-1}$) and is indicated as R_C. These definitions are valid for all environmental matrices (water, air, soil).

For carcinogenic substances the shape of correlation curve sketched in Figure 1 shows the existence of a no-effect threshold, which can be interpreted as the typical behavior of these substances. This model allows the SF to be estimated as the slope of the initial linear range of the curve. For non-carcinogenic substances the correlation curve sketched in Figure 1 shows the trend dose–response and the maximum acceptable limit dose for the considered substance. The corresponding model shows the existence of a threshold value; however, for safety, the RfD value is always less than this.

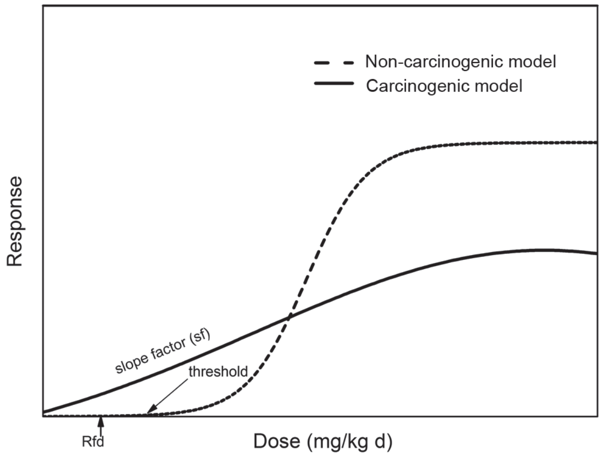

Figure 1. Typical dose–response curves for a carcinogenic and non-carcinogenic substance.

Therefore, equation (1) can be written for carcinogenic and non-carcinogenic substances, respectively:

$$R_C = ADI \cdot SF \tag{2}$$

$$R_{tox} = \frac{ADI}{RfD} \tag{3}$$

Moreover, to determine the risk value it is necessary to also know other important parameters: the value of the concentration at the point of exposure (C_{POE}), the migration pathways and the exposure modality.

The concentration at the contamination source can be known by in situ experimental measurements. If the receptor is not located at the source of the contamination, but at some distance from it, it is necessary to evaluate the concentration value of the contaminant at the point of exposure. To determine this value, appropriate flow and transport mathematical models should be used. In fact, the flow models verify whether the receptor is involved from the groundwater flow and therefore affected by the contamination. To describe the flow in a homogeneous and anisotropic porous media the following equation is used (Bear, 1979):

$$\operatorname{div}\left(\mathbf{K} \cdot \operatorname{grad} h\right) = S_s \frac{\partial h}{\partial t} \tag{4}$$

where $\mathbf{K}$ represents the tensor of hydraulic conductivity (LT^{-1}), h is the hydraulic head (L), t the time (T) and S_s the specific storage term (L^{-1}). These models are based on the following general mass transport equation (Bear, 1979):

$$\operatorname{div}\left(\mathbf{D} \cdot \operatorname{grad} C - C\mathbf{q}\right) = R\frac{\partial C}{\partial t} + \lambda C \tag{5}$$

where C is the mass of solute per unit volume of porous medium in the liquid phase (ML^{-3}), $\mathbf{q}$ the average velocity (LT^{-1}), $\mathbf{D}$ is the tensor of hydrodynamic dispersion (L^2T^{-1}), R is a retardation factor ($R = 1 + \beta$, with β constant and depending from the particular adsorption isotherm) (0) and λ is a decay constant (0).

Of course, both the flow and the transport model require a knowledge of the initial and boundary conditions of the system examined. In deterministic risk analysis of contaminated sites the so-called upper confidence limit (UCL) criterion can be used to estimate the C_{POE}. UCL is the estimated value of the concentration at the exposure point for a fixed significance level, obtained from the data set sampled in situ.

The typical exposure modalities for a receptor that can be exposed via the groundwater are those due to ingestion of water, dermal contact and inhalation of volatile particles—consequences of the use of contaminated water (US EPA, 1989). However, in this study only the first two exposure pathways were considered. For all the considered receptors (adults, children and workers) and for the considered two exposure pathways, dermal contact R_{DC} and ingestion of water R_{IW}, respectively, the risk value is given as follows:

$$R_{DC} = ADI \cdot T = \frac{C_{POE} \cdot SA \cdot AF \cdot ABS \cdot EF \cdot ED}{BW \cdot AT} \cdot T \tag{6}$$

$$R_{IW} = ADI \cdot T = \frac{C_{POE} \cdot IR \cdot EF \cdot ED}{BW \cdot AT} \cdot T \tag{7}$$

where C_{POE} is the concentration of the chemical of concern in water at the point of exposition (ML^{-1}), SA is the superficial contact area (L^2), P_c is the skin permeability constant (LT^{-1}), EF and ED are the exposure frequency (0) and exposure duration (T), respectively, IR is the ingestion rate (L^3T^{-1}), AF is the adhesion factor equal to 1 (ML^{-1}), ABS is the absorption factor equal to 1×10^{-3} (0) and, finally, BW is the body weight (M). These parameters and their corresponding values are those set by the US EPA (1989) on the basis of numerous studies of international institutions. They are determined by the land use and the safety factor, one for each route of exposure (US EPA, 1989) and specifically by the reasonable maximum exposure (RME) that represents the largest reasonably possible exposure, considering 95% of the exposed population and form the most likely exposure (MLE), which represents the statistically most likely average exposure for the population. Carcinogenic risk (R_C) and non-carcinogenic (toxic) Risk (R_{tox}) can be determined taking into account equations (1), (2), (3), (6) and (7). In the presence of more than one route of exposure for a given pollutant, the risk is additive. Total carcinogenic risk (R_{CT}) for one contaminant is given by the sum of dermal contact R_{DC} and ingestion of water R_{IW} carcinogenic risks exposure pathway. Likewise, total non-carcinogenic risk (R_{toxT}) is given by the sum of dermal contact R_{DC} and ingestion of water R_{IW} non-carcinogenic risks. According to international agencies, the carcinogenic total risk (R_{CT}) may be considered null or negligible if $R_{CT} < 1 \times 10^{-6}$ and remediation action is not required. Some remediation actions can be suitable if $1 \times 10^{-6} < R_{CT} < 1 \times 10^{-4}$, while for $R_{CT} > 1 \times 10^{-4}$ remediation action is required. For non-carcinogenic risk no adverse effects are expected for human health if $R_{toxT} < 1$.

In the deterministic approach, each parameter, involved either in the risk determination or in the flow and transport description by models, is represented with a single value (mean, median, mode, etc.), usually obtained by field sampling and measurement. For these reasons and owing to causes linked to cost and time required, the available values are usually limited in number, so that the one assumed for the single parameter is affected by this limitation.

In the probabilistic approach, the considered parameters assume the values corresponding to the fixed probability. In fact, it is possible to generate synthetic data sets (e.g. by the Monte Carlo method) for each of these parameters. In this way it is possible to describe each of these data sets by a probabilistic density function and thus assign a probability value to each value of the data set relative to the considered parameter. This method takes into account the values obtained by the field measurements because the synthetic data sets are generated with the same characteristics (mean, variance, etc.) as the experimental data sets. Nevertheless, the probabilistic method allows much more extensive data sets to be obtained than those related to the measurement values and, consequently, provides a more accurate description.

Case study of the chemical industrial district of Crotone

Regarding the town of Crotone (Figure 2), because of the high death rate owing to respiratory sicknesses and pulmonary cancer in this town, the World Health Organization carried out an epidemiological study, the conclusions of which encouraged more in-depth research on the hypothesis that an environmental factor could have caused the anomalous clinical framework.

A wide collection of soil and groundwater samples, especially those taken within the area of the Pertusola plant and in the inland agricultural area, showed a high level of soil and water contamination by heavy metals (arsenic, cadmium, mercury, lead, zinc, copper), with concentrations much higher than the threshold values of the Italian regulation (D. Lgs. 152/2006).

The study area from which the abovementioned soil and groundwater samples were obtained is located to the north-east of Crotone, 2 km distant. It includes an industrial district, located on the Ionian coast, and an inland, wide agricultural area, the subsoil of which is suspected to hide one of the largest archaeological deposits of the Hellenic age, when the city of Crotone was an important crossroads of the Magna Grecia civilization (Figure 2a). The industrial district includes the Pertusola plant for zinc, cadmium, copper, lead sulfate and silver. The plant is currently almost inactive. The agricultural area is delimited by the Esaro River to the south and by the Passovecchio River to the north. Its orography is prevalently a plain and slightly hilly.

In the Pertusola area 90 drilling bores of different depths were executed and many of them were completed to install wells and a network of 21 piezometric observation points. Several pumping tests were carried out in order to estimate the subsurface

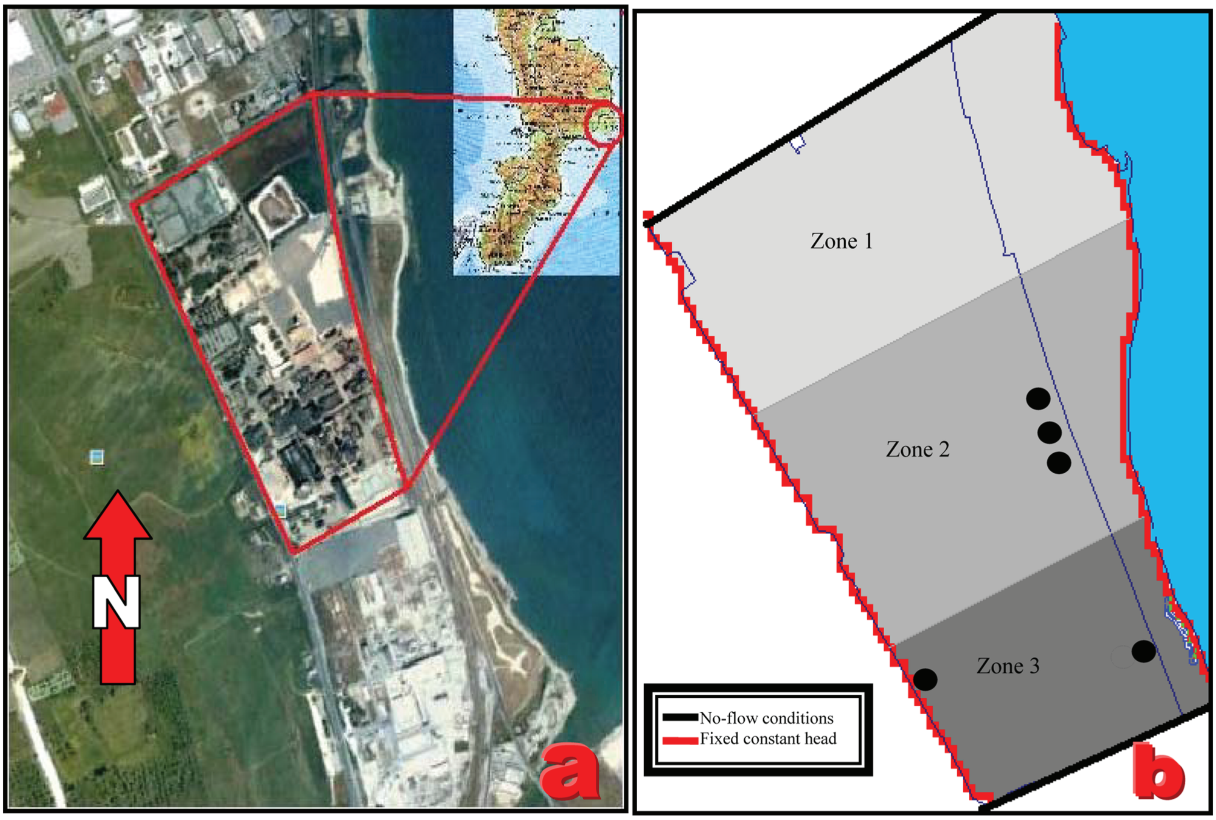

Figure 2. (a) Location of the Pertusola area in Crotone (Italy). (b) Conceptual model and zones of the area examined with different hydraulic conductivity and the heavy metal contamination sources (black dots).

hydraulic properties and a number of geo-electrical surveys were executed. The hydro-geological and geophysical tests showed that (1) the subsoil of the study area includes a basic formation consisting of clay and loam soil and an upper formation consisting of sand and sandstone; (2) the alluvial deposits, produced by the erosion of the surrounding hills, consist of lightly silty sands mixed with gravel elements, and show very high hydraulic conductivity (10^{-3} m/s); and (3) the groundwater system consists of a phreatic aquifer characterized by a mean thickness of around 30 m, with a shallow water table (3–6 m from the ground surface). Soil samples were collected in the Pertusola area. Table 1 shows the highest observed concentrations of heavy metals in the soil, such as arsenic, cadmium, copper, mercury, lead and zinc compared with threshold values according to Italian regulations. Groundwater sample analysis showed strong contamination by heavy metals such as cadmium, zinc and arsenic, while copper, mercury and lead showed acceptable or low concentrations.

Regarding the statistical and sensitivity experimental data analyses and their reliability, see Rivera et al. (2008) and Decreto Ministeriale (1999).

Table 1. Groundwater maximum concentrations of heavy metals.

Heavy metal	Source area (µg/kg)	Italian threshold value (µg/kg)
Arsenic	55	10
Cadmium	20,300	5
Copper	150	1000
Mercury	1	1
Lead	490	10
Zinc	7,875,000	3000

Modeling contaminant transport and health risk

In order to investigate on the fate of a contaminant in the aquifer it is necessary to apply a flow and transport model for the aquifer analyzed. Regarding the flow model, GW Vistas program (Ruskauff, 1998), which works with a finite-difference approach, was used. The coastal aquifer was schematized as a two-dimensional unconfined aquifer with a heterogeneous and isotropic porous medium. The aquifer of the area was appropriately discretized by a grid of 100 rows and 96 columns. The single cell has dimensions of 12 m × 9.6 m, and a thickness of 28 m.

Referring to the Pertusola area a solute reactive transport model was used in order to study cadmium, arsenic and zinc transport into the underlying unconfined aquifer. The transport model is based on the following hypotheses: (1) heterogeneous and isotropic porous medium, (2) continuous emission of contaminant from two point sources located to the lixiviation and stocking zones of Pertusola plant, (3) steady state two-dimensional flow

Table 2. Characterization of the probability density functions (PDF) for the hydraulic conductivity and partition coefficients.

Parameter			PDF	Mean	SD	Min.	Max.
Hydraulic conductivity (m/d)	Zone	North	Lognormal	3.41	0.27	2.0	100
		Central	Lognormal	20.2	17.67	8.0	100
		South	Lognormal	22.5	37.44	10.0	100
Partition coefficient (L/kg)	Contaminant	Arsenic	Lognormal	3.2	0.70	0.3	4.3
		Cadmium	Lognormal	2.7	0.80	0.1	5.0
		Zinc	Lognormal	2.7	1.00	0.1	5.0

Table 3. Input values of concentration and longitudinal and transversal dispersivity for arsenic, cadmium and zinc used in the numerical model.

	Zone		Arsenic	Cadmium	Zinc
Input values of concentration (mg/L)	1		1240	196	37,500
	2		–	312	–
	3		–	314	–
α_L (m)	Whole area	5	5 zone a	10 zone b	5
α_T (m)	Whole area	0.5	0.5 zone a	1 zone b	0.5

domain and (4) reactive contaminant on the solid matrix according to the Langmuir isotherm. The conceptual model of the system studied was developed considering the following boundary conditions (Figure 2b): (1) no flow conditions along the north and south sides of the area, (2) along the west side, in zone 1, the hydraulic head had values between 1.6 m and 1 m, in zone 2 it was constant and equal to 1 m, and in zone 3 it had values between 1 m and 1.1 m and (3) on the east side its value was fixed equal to 0 m along the coastline.

For deterministic risk analysis, the flow and transport simulation model kept fixed the values for hydraulic conductivity and partition coefficient. For the hydraulic conductivity we used the values measured by pumping tests and for each contaminant's partition coefficient those of Jerry and Allison (2000). Natural recharge (rain) is considered constant all over the area, with a k value of 2.74×10^{-4} (m/d) (Straface et al., 2007).

Instead, for the probabilistic risk analysis, the values of these parameters were defined by the Monte Carlo method and the relative probability density function as discussed above. The probabilistic density functions of the hydraulic conductivity for each zone are characterized in Table 2, together with the mean value, the SD, and the minimum and the maximum value of each examined sample.

In Table 2 the probabilistic density functions of the partition coefficient are also characterized for the substances examined.

As pollution sources three points were considered for cadmium, whereas for the other two pollutants just one point source was considered. As we are addressing tranport of heavy metal in groundwater the exposure points are located along the coastline.

In Table 3 the concentration values and the longitudinal and transversal dispersivity values used as input in the model are presented. The longitudinal dispersivity was calculated according to the equation proposed by Xu and Eckestein (1997), in which these parameters are a function of the characteristic distance (L) from the pollution source:

$$\alpha_L = 0.83\left[\log\left(L\right)\right]^{2.414} \tag{8}$$

while the transversal dispersivity was considered 10% of the longitudinal ones. The values of these parameters are shown in Table 3; for cadmium, the area was divided into two zones (a and b).

For deterministic analysis the risk was calculated considering the C_{PE} as a single representative value. The flow and transport were simulated by the numerical model considered, obtaining a C_{POE} value for each of the exposure points.

Subsequently, a single value of C_{POE}, determined by UCL, was calculated using the specific model ProUCL 3.0, assuming a significance level equal to 95% (US EPA, 2004). In the case of the probabilistic calculation, the value of C_{POE} was determined from the probability density function generated by the utilized numerical model.

Results and discussion

Equations (6) and (7) were used to determine the carcinogenic and non-carcinogenic risk values, for the $n^{\text{-th}}$ migration pathways and the $m^{\text{-th}}$ contaminant indicator of the area under study for both the deterministic and probabilistic methods. Deterministic risk calculation was performed by assigning a single value to each parameter affecting the phenomenon as described in equations (6) and (7). The assigned values are according to the receptors (adults, children and workers), to the land use (residential, commercial and industrial), to the safety factor selected (RME and MLE) (Spence and Walden, 2001) and to the flow and transport in the porous media. Probabilistic risk analysis was

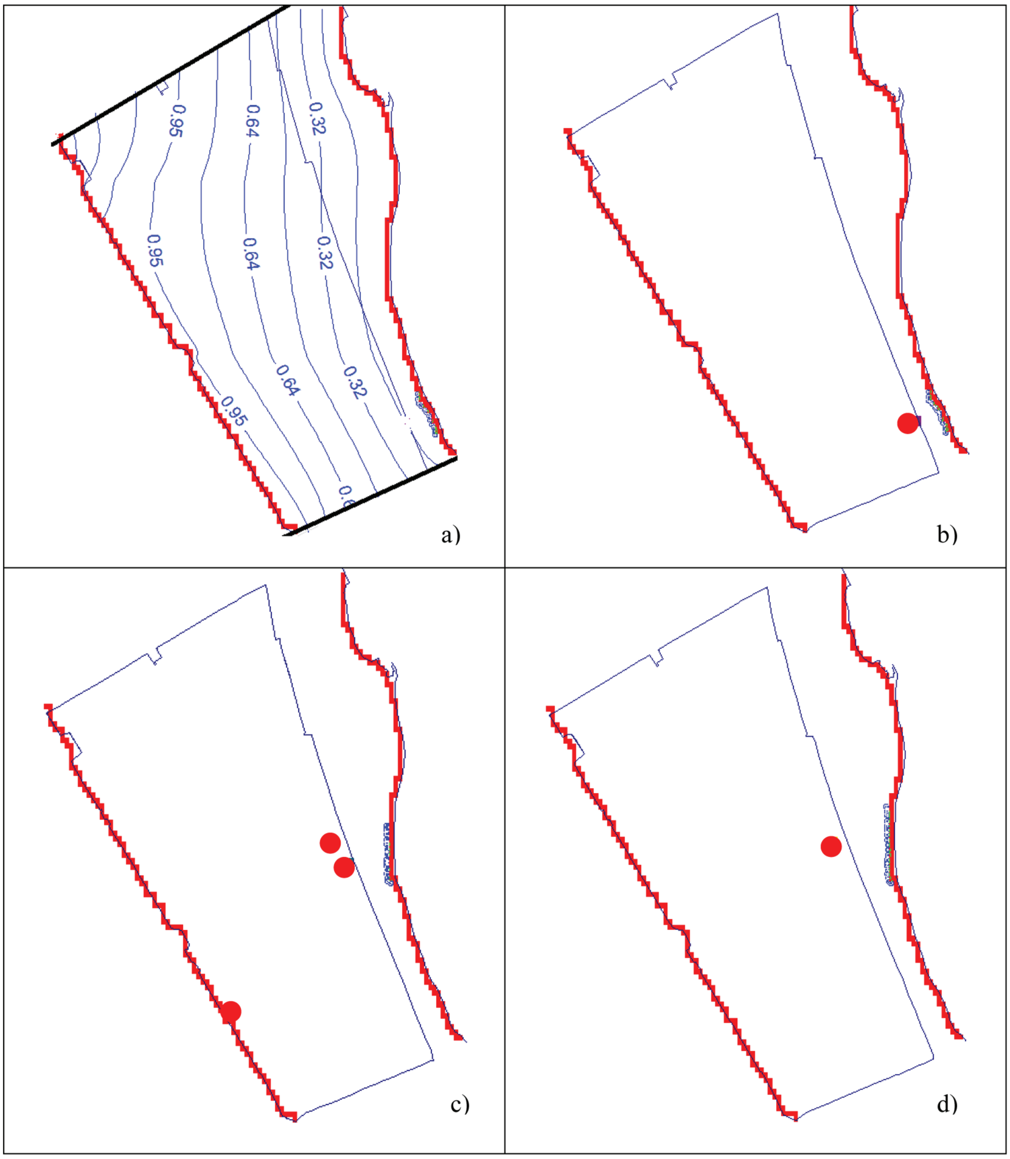

Figure 3. (a) Piezometric distribution for the area of Pertusola Sud and contamination sources by (b) arsenic, (c) cadmium and (d) zinc.

performed using the program SimLab 2.2, based on the Monte Carlo method. This program is able to evaluate multiple input models selected probabilistically. This method is based on an algorithm that generates a series of numbers between their uncorrelated parameters, which follows the probability distribution describing the investigated phenomenon. The Monte Carlo simulation calculates a number of possible manifestations of this phenomenon, with the weight of the probability of such an event. Once one has calculated this random sample, the simulation performs 'measures' of the quantities of interest on the sample. The Monte Carlo simulation is well done if the mean value of these measures on the achievements of the system converges to the true value.

In the examined case, for each parameter a set of 1000 synthetic values is generated by the Monte Carlo method, taking into account the experimental data. The value of each parameter was determined setting a probability value equal to 0.95. In Figure 3(a) it is shown that the groundwater flow direction is towards the coastline. In Figure 3(b–d) the contamination sources are shown for arsenic, cadmium and zinc, respectively.

The simulation of contaminant transport in the aquifer was carried out a large number of times, ranging from 100 to 10,000 days. However, here the results of the calculation of risk analysis were shown for concentration values corresponding to 1500, 4500 and 10,000 days (Figure 4).

The breakthrough curves (concentration versus time) are shown in Figure 4 for each fixed exposure point and for each considered contaminant. These curves indicate that the maximum value of concentration is reached for all three considered contaminants after about 500 days.

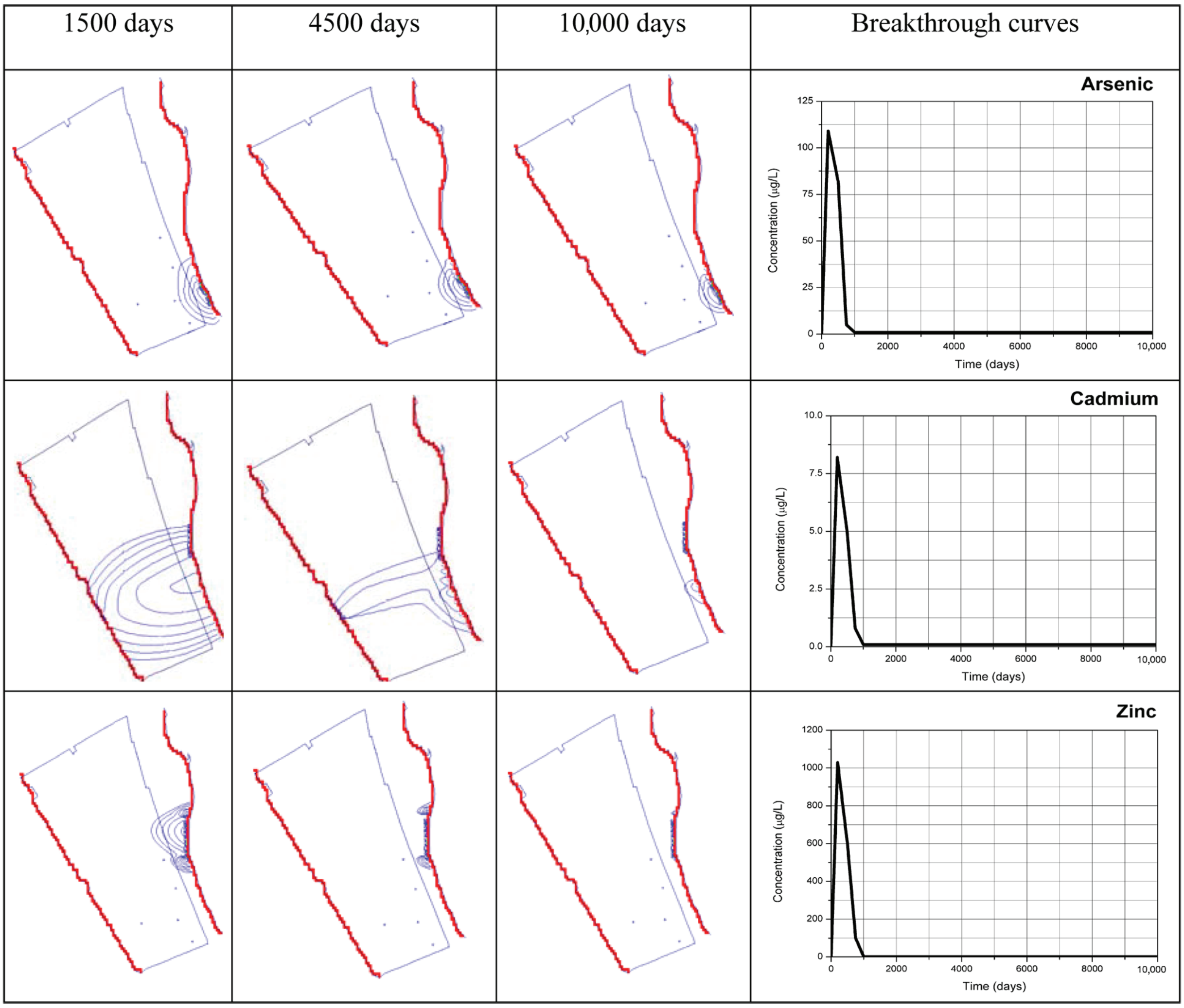

Figure 4. Arsenic, cadmium and zinc concentration lines, and corresponding breakthrough curves for 1500, 4500 and 10,000 days.

Table 4. Values of C_{POE} in groundwater used for the risk analysis.

Contaminant	Time (days)	UCL	Expected value	SD	Distribution type	Min.	Max.
As (mgL^{-1})	1500	3.46E-01	2.39E-01	3.63E-02	Lognormal	9.30E-02	1.00E+00
	4500	1.16E-01	5.99E-02	3.97E-03	Lognormal	1.10E-02	2.00E-01
	10,000	2.46E-02	1.52E-02	3.81E-04	Lognormal	3.90E-03	7.40E-02
Cd (ml^{-1})	1500	2.69E+00	1.67E+00	5.40E+00	Lognormal	5.20E-01	9.90E+00
	4500	4.04E-04	3.31E-04	1.88E-07	Lognormal	2.30E-04	3.40E-03
	10,000	3.16E-07	3.06E-07	3.76E-15	Lognormal	3.00E-07	9.10E-07
Zn (mgL^{-1})	1500	1.91E+02	1.09E+02	1.75E+04	Lognormal	6.18E+01	6.79E+02
	4500	8.70E-02	4.17E-02	5.25E-03	Lognormal	2.30E-02	4.40E-01
	10,000	1.16E-08	5.62E-09	9.23E-17	Lognormal	3.90E-09	7.40E-08

UCL = upper confidence limit.

The C_{POE} values for deterministic and probabilistic approach are reported in Table 4. The results of deterministic and probabilistic risk analysis were obtained by equations (6) and (7). From the analysis of the different risk scenarios one finds that in the deterministic case the risk measurement evaluated using RME exposure parameters is greater than that evaluated with MLE exposure parameters, which are less conservative than the former. Probabilistic risk analysis shows that even in the case of

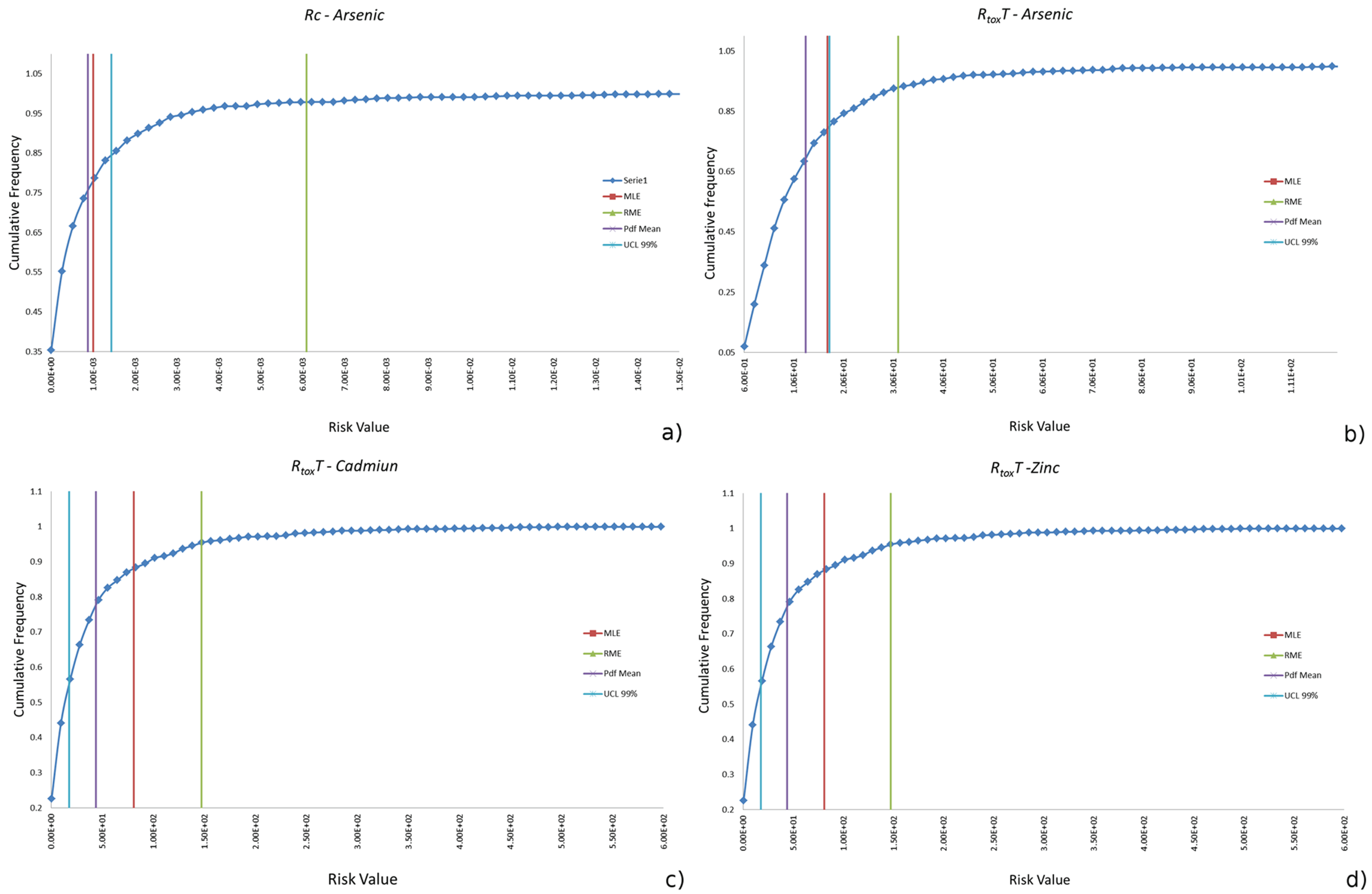

Figure 5. Risk probability curves for adults, at a time of 1500 days. In each graph the following results are shown: (a) for the deterministic approach the risk values and the probabilities corresponding to the reasonable maximum exposure (RME) and most likely exposure (MLE) values; (b) for the probabilistic approach the probability value corresponding to 99% upper confidence limit (UCL) and the average probability.

Table 5. Clean up values determined for adults at a time of 1500 days.

Contaminant	RME	UCL 99%	Percent of reduction
Clean-up of arsenic	3.46E-01	8.18E-02	23.62
Clean-up of cadmium	1.35E-01	8.18E-02	60.73
Clean-up of zinc	1.03E-01	3.27E-02	31.69

an absolute value that exceeds the risk limit, the frequency of hazardous cases may be low (especially for a confidence interval value larger than 95%). This limit could be considered acceptable as level of risk and a limit value of 99% was here considered.

As the aim of the present study is only to compare the deterministic and the probabilistic methodologies, in the following only the results for adults and for a time of 1500 days are shown. These results are compared in Figure 5, where the trend of the probability versus risk for arsenic, cadmium and zinc is shown. For arsenic both carcinogenic (Figure 5a) and non-carcinogenic (Figure 5b) risk were taken into account. In Figure 5 (c, d) the analogous probability curves in terms of R_{tox} are presented for cadmium and zinc, which are not carcinogenic substances.

A general result of this analysis is that in all cases the RME risk is overestimated with respect to that corresponding to a 99% UCL; as a matter of fact, these values differ by at least one order of magnitude. The highest risk values correspond to 1500 days; this result is certainly the consequence of the fact that the C_{POE} value for this time is the largest in comparison with those relative to the other times (4500 and 10,000 days).

In an RME scenario these values were calculated for both types of risk: carcinogenic and non-carcinogenic. The carcinogenic risk value (R_C) obtained for each contaminant was assumed as the acceptable level of risk because it corresponds to higher values of the target concentration. The values presented in Table 5 could be considered acceptable for ‘adults’ and reasonable goals for remedial work, which brings the risk to an acceptable value.

These results show that the concentration values corresponding to clean-up levels, determined using a probabilistic methodology, are much lower than those determined on the basis of a deterministic methodology; consequently, the remediation cost based on the former method is lower than the latter. This fact is easily understood if one thinks that a higher level of risk, such as that which occurs with the deterministic method, involves a more extensive and detailed clean up, which certainly leads to higher costs. This result is not limited to this case, but it is valid in all cases.

Conclusions

In this article the risk analysis for a specific site using both a deterministic and a probabilistic methodology was carried out. The comparison of deterministic (MLE and RME) and probabilistic (estimated average value, 99% UCL) risk values, with reference to a probability density function of the risk, indicates some relevant results. In the case of arsenic pollution, both for carcinogenic and non-carcinogenic risk (with the sole exception of workers receptors at 10,000 days) was over the acceptable limit for all cases of times and receptors. We remind the reader that among the pollutants arsenic is the only one that can provoke cancer risk. A difference of at least one order of magnitude between RME and 99% non-parametric UCL was found. This is a safe value for deterministic and probabilistic methodology, respectively. This provides evidence on the overestimation of risk by the deterministic method. For the 1500 day concentration we obtain higher risk values than for 4500 and 10,000 days. This can be understood observing the breakthrough curves of each pollutant (see Figure 5). Maximum concentration values of the three pollutants under study are approximately 500 days (~1.36 years). The estimated risk at the point of maximum concentration is the value to consider for a condition of extreme caution.

The probability density function that provides the largest dispersion around the mean is that of cadmium in the case of noncancer risk (R_{tox}), whereas the lowest dispersion is that of arsenic in the case of carcinogenic risk (R_C). The small variance is a good indicator of the reliability of the concentration clean-up level. Clean-up levels calculated assuming a maximum exposure scenario (RME) for the risk are overestimated.

Assuming the RME values for the deterministic and probabilistic cases for the exposure rates, the clean-up levels in the probabilistic scenario are lower than those corresponding to the deterministic risk. The comparison of the values of the clean-up level in the deterministic (RME) and in the probabilistic case (99% UCL) for the considered contaminants shows that the probabilistic methodology leads to a reduction of target concentration equal to 23.62%, 60.73% and 31.69%, for arsenic, cadmium and zinc, respectively. It must be emphasized that the results obtained by the probabilistic method always respect the limits of the law; therefore, the protection of human health is always guaranteed, even if one accepts the risk levels lower than those for the deterministic case and if one considers some of the conservative assumptions for the latter (Bolster et al., 2009; Korre, 1999; Rodriguez-Martin et al., 2006; Tartakovsky, 2007). For this reason, regulatory agencies may require application of both approaches to risk assessment, but cannot require that the landowner clean up to the point of satisfying the most conservative results in a context of higher, often not sustainable, costs.

This study shows the benefits of using the probabilistic method of risk assessment in lieu of the deterministic method when setting remedial objectives in a contaminated property.

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References

Bear J (1979) hydraulics of groundwater. New York: McGraw-Hill.

Benekos I, Shoemaker C and Stedinger J (2007) Probabilistic risk and uncertainty analysis for bioremediation of four chlorinated ethenes in groundwater. Stochastic Environmental Research and Risk Assessment, Vol. 21, pp. 375–390.

Bennett DH, et al. (1998) On uncertainty in remediation analysis: variance propagation from subsurface transport to exposure modeling. Reliability Engineering and Systems Safety. Northern Ireland: s.n.

Bolster D, Barahona M, Dentz M, et al. (2009) Probabilistic risk analysis of groundwater remediation strategies. *Water Resources Research* 45: W06413.

Bonomo L and Andreottola G (2000) *Criteri dell'analisi di rischio. Siti Contaminati: Indagini, analisi di rischio e tecniche di bonifica*. Milan: Grafiche GSS.

Cohen JT, Lampson MA and Bowers TS (1996) The use of two stage Monte Carlo Simulation Techniques to caracterize variability and uncertainty in risk analysis. *Human And Ecol. Risk Asses* 2: 939-971.

Covello VT and Merkohofer MW (1993) Risk assessment methods, approach for assessing health and enviromental risk. New York: Plenum Press.

Decreto Ministeriale (1999) n. 471. *Gazzetta Ufficiale della Repubblica Italiana – Serie Generale* n. 293 del 15/12/99.

Decreto Legislativo (2006) n. 152 Norme in materia ambientale. Gazzetta Ufficiale n. 88 del 14 aprile 2006 – Supplemento Ordinario n. 96.

Dettinger MD and Wilson JL (1981) First Order Analysis on uncertainty in numerical model of flow groundwater part 1. Mathematical Development. *Water Resour Res* 17: 149–161.

EPA (US Environmental Protection Agency) 1(986) Guidelines carcinogenic risk assessment. *Federal Register*. Vol. 51, pp. 33992–34003.

Harms-Ringdalh L (2001) *Safety Analysis. Principles and a Practice in Occupational Safety*. 2nd ed. London: Taylor & Francis.

James AL and Oldernburg CM (1996) Linear and Monte Carlo Uncentainty analysis for subsurface contaminant transport simulation. *Water Resour*. 33: 2495–2508.

Jerry D and Allison D (2000) *Partition Coefficients for Metals in Surface Water, Soil, and Waste*. s1.: US Environmental Protection Agency.

Kaplan S (1997), The Words of Risk Analysis. *Risk Analysis* 17: 407–417.

Khadam IM and Kaluarachchi JJ (2003) Multi-criteria decisional analysis with probabilistic risk assessment for the management of contaminated ground water. *Environmental Impact Assessment Review* 23: 683–721.

Kolluru RV (1996) Risk assessment and management. A unified approach. In: RV Kolluru, et al (eds) *Risk assessment and management handbook for enviromental, health and safety professionals*. New York: McGraw-Hill.

Korre A (1999) Statistical and spatial assessment of soil heavy metal contamination in areas of poorly recorded, complex sources of pollution. Part 1: factor analysis for contamination assessment. *Stochastic Environmental Research and Risk Assessment* 13: 260–287.

McKone TE and Bogen KT (1992) Uncertainties in health - risk assessment: an integrated case study based on tetrachloroethylene in California groundwater. *Regul. Toxicol. Pharmacol*. 15: 86–103.

NRC (1993) *Risk-assessment in the federal government: managing the process*. Washington DC: National Academy Press.

Peck A, et al. (1998) Consequences of spacial variability in aquifer properties and data limitation for groundwater modeling practice. Institute of Hydrology IAHS Press. s.l.: IAHS Publication No 175.

Rivera MF, Migliari E, Fallico C and Troisi S (2008) Análisis de riesgo para sitios contaminados. Aplicación a un caso de interés italiano. *Revista Latinoamericana de Hidrogeología* 6: 69–77.

Rodríguez Martín JA, López Arias M and Grau Corbí JM (2006) Heavy metals contents in agricultural topsoils in the Ebro basin (Spain). Application of the multivariate geoestatistical methods to study spatial variations. *Environmental Pollution* 144: 1001–1012.

Ruskauff G (1998) Stochastic MODFLOW, MODPATH & MT3D. s.l.: Virgina, USA: Gregory J Ruskauff & Environmental Simulation Inc.

Spence LR and Walden T (2001) RISC4 User's Manual. Pleasanton, California: Spence Engineering and Sunbury: BP Oil International.

Straface S, Migliari E, Ruga F, et al. (2007) Stima dell'incertezza parametrica mediante un approccio Bayesiano. Un caso reale. In: Franchini M and Bertola P (eds) *Atti del convegno on Approvvigionamento e distribuzione idrica: esperienze, ricerca e innovazione*, Ferrara, 28–29 Giugno, Vol. 1, pp. 273–285. Perugia: Morlacchi Editore.

Tartakovsky DM (2007) Probabilistic risk analysis in subsurface hydrology. *Geophysical Research Letters* 34: L05404.

US EPA (US Environmental Protection Agency) (1989) *Risk Assessment Guidance for Superfund. Evaluation Part A*. Vol. 1. EPA/540/1–89/002. s.l., Human Health. Washington: US EPA.

US Environmental Protection Agency (1996) Summary Report for Workshop on Monte Carlo Analysis.

US EPA (US Environmental Protection Agency) (2004) *A Statistical Software. National Exposure Research Lab*. Washington: US EPA.

Xu M and Eckestein Y (1997) Statistical Analysis of the relationships between dispersivity and other Physical properties of porous media. *Hydrogeology Journal* 5: 4–20.