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# A soil and groundwater remediation program using risk analysis as a design tool

## Programme de rémédiation de sols et des eaux souterraines utilisant l'analyse de risque comme outil de décision

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### ABSTRACT

A risk-based remediation approach was developed as a design tool to support the decision-making process and re-examine remediation goals at an industrial site contaminated with chlorinated organics. This strategy is becoming a common practice in Brazil, as enforced by most environmental agencies and regulators. The risk-based approach demanded the assessment of contaminant exposure pathways as well as groundwater mass transport analysis, taking into account the intrinsic degradation pathways and other natural attenuation mechanisms. It was also emphasized the premise that groundwater transport modeling is inherently complex due to geological matrix and DNAPL characterization which determines the final contaminant concentrations at points of compliance and/or exposure. The Domenico's analytical solution for the advective-dispersive transport equation was used and its input parameters were assumed to be normally distributed. Risk analysis results indicate that vinyl chloride is responsible for the most elevated calculated risk at the site. Therefore, the understanding of the mechanisms of formation of this compound is a key factor to promote the best remedial action to be adopted. As the pump-and-treat system is not sufficient to eliminate the free-phase DNAPL source and achieve site closure, other remediation alternatives are being considered, such as soil vapor extraction and enhanced bioremediation in order to achieve the calculated SSTLs (site specific target levels).

### RÉSUMÉ

Une stratégie de rémédiation fondée sur l'analyse de risque a été développée pour réexaminer les objectifs et les critères de rémédiation adoptés sur une surface industrielle sous l'impact des composés organiques et chlorés. Cette stratégie devient une pratique commune au Brésil, selon ce qui a été demandé par la majorité des agences régulatrices et environnementales. L'analyse de risque introduit une évaluation des possibles voies d'exposition ainsi qu'une analyse des transports de contaminants en considérant les processus de dégradation naturelle du composé dans le milieu hydro-géologique. Il est remarquable que le modelage du transport dans des eaux souterraines soit essentiellement complexe du fait des hétérogénéités de la matrice géologique et de la caractérisation du DNAPL. Ces facteurs sont déterminants pour le calcul des concentrations finales du contaminant sur le point d'exposition. La solution analytique de Domenico a été utilisée pour l'équation advection-dispersion de transport et ses paramètres d'entrée ont été pris comme normalement distribués. Les résultats de l'analyse de risque ont indiqué que le composé chlorure de vinyle est le responsable des indices élevés de risque calculés sur la surface. De cette façon, la compréhension de la formation de ce composé dans le milieu physique est un facteur clé pour l'élaboration de la meilleure alternative de rémédiation. Comme le système de retenue hydraulique n'est pas efficace pour éliminer la source de contamination, d'autres traitements complémentaires sont en voie d'adoption, telles que l'extraction de gaz du sol et la bioremediation de façon à atteindre les buts de traitement basés sur le risque.

Keywords : risk analysis, groundwater remediation, FOSM method, natural attenuation, vinyl chloride

## 1 INTRODUCTION

The primary objectives of a soil and groundwater remediation plan is to minimize health and environmental risks within an acceptable timeframe by assuming an appropriate cost-benefit relation. Based on an understanding that environmental cleanup to the level of drinking water standards is unfeasible in most site scenarios, regardless of the remediation action employed, the use of risk-based approaches, along with natural attenuation, is becoming common worldwide. Under favorable geochemical conditions, natural attenuation of groundwater contaminants can result in significant cost savings over other remedial options. Even the most sophisticated in-situ methods may not be able to completely remove the organic and heavy metal compounds within an acceptable timeframe. As such, instead of evaluating the optimal removal rates, it is more important to certify whether a certain technology applied is capable of cleaning up the aquifer to regulatory standards and at what cost.

In North America, a number of attempts have been made to define protocols for the cleanup decision-making process. The

best known is the Risk Based Corrective Action (RBCA) approach. It is based on the theoretical principles of Risk Assessment Guidance for Superfund (RAGS), developed by the United States Environmental Protection Agency (USEPA 1989), to be used in remedial investigation/feasibility study (RI/FS) processes at Superfund sites. The RBCA protocol establishes a tiered approach of gradual response in site characterization and remediation efforts to soil and groundwater remediation. Site characterization efforts are directed at collecting only the information that is needed for each stage or tier (Brady et al. 1998). Details on the RBCA protocols are found at ASTM E2081-00 (ASTM 2000) for chemical releases, in general, and ASTM E1739-95 (ASTM 1995) for petroleum release sites.

This widely recognized approach to calculate risk involves a four-stage process (USEPA 1989): i) data collection and hazard identification: the characterization of chemicals of interest from potential contaminant sources; ii) exposure assessment: pathways or environmental routes by which chemicals from the site can reach potentially exposed populations (receptors);

characterization of potential receptors; and characterization of exposure routes: ingestion, inhalation and dermal contact; iii) toxicity assessment: determination of numerical indices of toxicity to calculate risk; and iv) risk characterization: the estimation of the magnitude of risk as well as the uncertainty of the estimate. Since this approach demands the assessment of contaminant exposure pathways as well as groundwater mass transport analysis, it should take into account the intrinsic degradation pathways and other natural attenuation mechanisms. It should also be remembered that groundwater transport modeling is inherently complex due to geological matrix and DNAPL characterization which determine the final contaminant concentrations at points of compliance and exposure (Nobre et al. 2006).

Another application of risk assessment in site remediation is the establishment of cleanup standards. It is a way to define, objectively, "how clean is clean" and "what is safe." These standards may guide site remediation actions and promote site closure. It is an inverse procedure, that is, the process starts with a definition of acceptable risk and works back to the level of contamination that will produce the acceptable risk level (LaGrega et al. 1994). It is expected that cleanup decisions and site characterization reflect a balance between cost and health-risk reduction.

This work presents a remediation program in which risk analysis is being incorporated at an advanced stage to evaluate its performance. Due to the absence of potential receptors downgradient of the source, the establishment of cleanup standards (site-specific target levels) was not required. The Domenico's analytical solution for the advective-dispersive transport equation was used and its input parameters were assumed to be normally distributed. The first order second moment method (FOSM) was applied as a tool to estimate the mean risk and its variance. Thus, instead of a deterministic single output, the risk resulting from this procedure was assumed to be a Gaussian type. The risk zones were then calculated based on a 95th percentile of confidence and mapped in accordance with site specific conditions, contaminant biodegradation potential and risk analysis results.

## 2 METHODOLOGY

Mathematical models are needed to simulate contaminant concentration values at various exposure pathways and routes. For the advective-dispersive transport equation, the Domenico (1987) analytical solution was chosen and adjusted to consider parameter uncertainties, by applying a probability density function (pdf) for each variable. In this way, it was possible to replace a deterministic risk response with one that is also a pdf. The most conventional way to carry out this procedure is by using the iterative Monte Carlo method. Another alternative is the first order second moment method (FOSM), which requires less computational effort (Nobre 1992). This method was applied here as a tool to estimate the mean risk and its variance.

The Johnson-Ettinger (1991) model was used in order to simulate contaminant partition and movement from groundwater liquid phase to the vapor phase. The Foster & Chrostowski (1986) model was also implemented to estimate the exposure vapor phase concentrations attributed to bathing water and irrigation water. The RBCA guide ASTM (1999) recommended the use of these two models.

### 2.1 First order second moment method (FOSM)

The main hypothesis implied by this procedure is that all important information about the stochastic nature of the system can be expressed with the mean and the variance. The ideal case to be portrayed by this method occurs when the pdf of the response has a Gaussian shape. It is the objective to investigate the uncertainty of a selected system response function (or

performance measure), due to the uncertainty in a system parameter. The estimate of the mean and variance are obtained by utilizing a multidimensional Taylor series expansion of a system response about the mean values of the parameters. A detailed description of the method is found in Nobre (1992) and Sykes & Thomson (1988). Since the parameters are described as pdf, not just scalar values, the risk calculation returns, not a single value, but a pdf as well. By incorporating the FOSM method in the risk analysis, it was possible to choose confidence intervals for the results, for instance the 50th and 95th percentile of confidence. The corresponding risk zones are related to these confidence intervals (R50 and R95). Figure 1 explains, in a schematic form, the definition of risk (or protection) zones according to the percentile selected for the pdf solution.

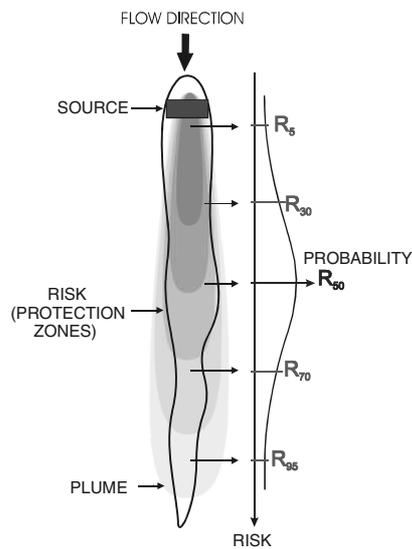


Figure 1. Schematic risk zones according to confidence intervals.

## 3 SETTING DESCRIPTION

Risk analysis was carried out based on the RBCA protocol, at an inactive industrial site contaminated with chlorinated organics, particularly 1,2 dichloroethane (1,2 DCA). The free-phase DNAPL source control is currently being achieved by a hydraulic system of four extraction wells. Risk analysis (tier 1) was performed by considering 20 contaminants detected in groundwater, including chlorinated organics and benzene. Exposure routes considered were ingestion, inhalation and dermal contact. For the transport analysis, a long-term simulation time of 30 years was adopted.

The aquifer is mostly composed of granular material consisting of sandstones and bedded shale sequences of the tertiary formations. A semi-continuous shale layer at 60m depth retains most of the DNAPL free-phase. Groundwater levels of the unconfined aquifer range between 9 to 13 meters. The regional hydraulic gradient was measured at 0.6%. The hydraulic conductivity (K) was considered to be a sensitive parameter, with a mean value of  $2.0 \times 10^{-5} \text{ m.s}^{-1}$  and variance equal to  $3.88 \times 10^{-8} \text{ m}^2.\text{s}^{-2}$ .

We simulated the secondary source geometry with an area of  $50 \times 50 \text{ m}$  at 5 m in depth. Groundwater concentrations at the source were attributed according to recent analytical results (2005-2006). For each compound, the mean and the variance were calculated, as indicated in Table 1. According to Domenico (1987), at time  $t = 0$  (initial conditions), the source presents the maximum concentrations, and in the rest of the domain, the concentration is zero. Source depletion with time was not simulated, which is a conservative assumption. The parameters in Table 1, dispersivity and source depth, from the mass transport equation, were considered as normally distributed pdf.

Table 1. Analytical results and parameters considered as pdf.

Contaminant	Mean (mg/L)	Variance (mg/L) <sup>2</sup>
VC	3,80E-02	1,11E-02
1,2 DCA	1,52E+01	3,96E+02
cis-1,2 DCE	1,46E-02	2,83E-04
trans-1,2 DCE	5,36E-03	4,20E-05
1,4 Dioxane	3,36E-02	1,33E-03
1,1,2 TCA	1,59E+01	4,97E+02
TCE	4,78E-02	4,21E-03

Parameter	Symbol	Mean Value	Standard Deviation
Dispersivity (m) (x-dir)	$\alpha_x$	9.78E+00	4.97E+00
Dispersivity (m) (y-dir)	$\alpha_y$	9.78E-01	4.97E-01
Dispersivity (m) (z-dir)	$\alpha_z$	1.12E-02	5.71E-03
Source depth (m)	Z	5.00E+00	

#### 4 RISK ZONES MAPPING AND RESULTS

The conventional risk assessment methodology states that the incremental risk is calculated by the estimated concentration and a downstream fixed point at a considered time (ASTM 2000). This procedure, yet reasonable to quantify risk at that very point, does not allow for risk evaluation at surrounding areas. To handle this difficulty, we suggest evaluating risk not at a fixed point, but in zones of equal values. Since risk quantification was carried out by the FOSM method, it was also possible to select confidence intervals to the results.

For the groundwater transport simulations, a first order degradation decay of the various plumes were considered and constant concentration values were attributed to the source, as indicated in Table 1. The RBCA protocol was also applied according to the orientations of ASTM E2081-00 (ASTM 2000), for the procedures to estimate the risk values throughout the domain, which was necessary to map the protection/risk zones in the direction of flow. Figure 2 presents the final horizontal projection of the risk zones based on a 95th percentile of confidence. These were estimated considering the sum of risks attributes to the various contaminants. The transverse distances were augmented by 50% due to the greater uncertainties and preferential pathways. Four zones were delineated: one relative to the Hazard Quotient of 1.0 and three relative to the Carcinogenic Risks of  $1 \times 10^{-4}$ ,  $1 \times 10^{-5}$  and  $1 \times 10^{-6}$ . That means an incremental risk of 1 in 10,000 to develop cancer, 1 in 100,000 and 1 in 1,000,000, respectively. These are protection areas that must be considered in terms of land use priorities.

Figure 3 presents the contribution of the compounds in calculating risk. Risk analysis results indicate that vinyl chloride (VC) is responsible for the highest calculated risk at the site (96%). Therefore, understanding the mechanisms of formation of this compound is a key factor to promote the best remedial action. Vinyl chloride is present at the site as a metabolic by-product from the degradation pathway of chlorinated organics, primarily 1,2 DCA, 1,2 DCE and PCE, as dissolved forms in groundwater. Under natural temperature and pressure conditions, VC is always present in the vapor phase. It can be produced under biotic or abiotic conditions. In general, however, microorganisms under reducing conditions mostly mediate VC production.

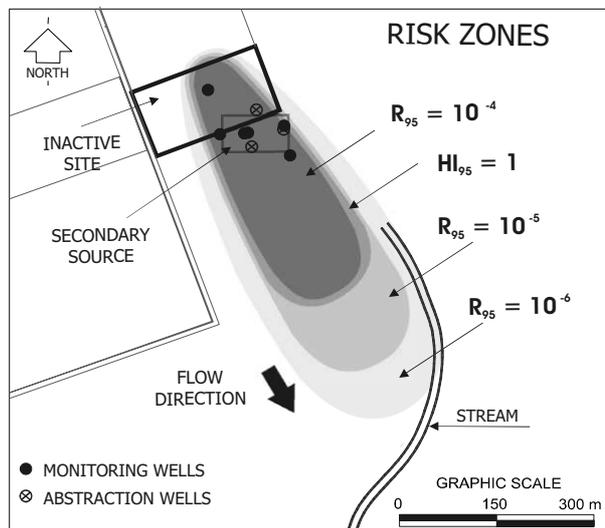


Figure 2. Risk/protection zones for 95th percentile of confidence.

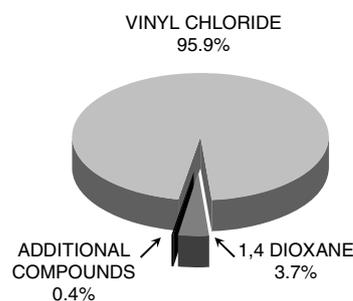


Figure 3. Contribution of compounds in risk estimation.

Monitored natural attenuation for the dissolved plume has been proposed at a distance downgradient from the containment area, as there is clear evidence that natural processes are taking place. 1,2 DCA is probably biodegrading into vinyl chloride as well as ethene and ethane, under the site sulfate-reducing conditions. The detection of VC seems also to be related to the process of reductive dechlorination of PCE and dichloroethene isomers. The concentrations of the latter compounds have been significantly reduced over the years. We estimated the biodegradation parameters from a seven-years site-specific database, which were monitored in accordance with USEPA protocols (Wiedemeier et al. 1998).

The Pearson correlation coefficient ( $r$ ) was calculated in order to measure the linear relationship between three major contaminants (1,2 DCA, cis 1,2 DCE and PCE) with their metabolic by-products and the parameters associated with intrinsic biodegradation. Figure 4 presents the correlation results for the monitoring well PE-03, with the highest concentrations detected at this site. The best correlations were between the contaminants and the byproducts VC and ethene+ethane, along with sulfate and dissolved oxygen. Methane, though normally considered a good indicator for 1,2 DCA natural degradation processes (Nobre & Nobre 2004; Nyer et al. 1996), was not produced at high concentration levels. Values of the Pearson coefficient were highest between 1,2 DCE and its by-products. Negative values of  $r$  indicate that while ethene+ethane is being produced, daughter products are being depleted.

Regression methods were used to obtain first-order degradation rates to adjust field data. Contaminant half-life values ( $t^{1/2}$ ) equal to 10.5, 7.7 and 2.3 months were obtained for PCE, 1,2 DCA and benzene, respectively. The results match with field results found in the literature. Groundwater at the site varies from aerobic (background) to sulfate reducing only at source areas. Groundwater redox conditions range from -150 mV to +450 mV and pH around 4.0. Biostimulation, through

the proper selection and delivery of nutrients along with substrates, is required to accelerate mass removal rates at areas beyond or below the abstraction well capture zones, in deeper zones of the aquifer.

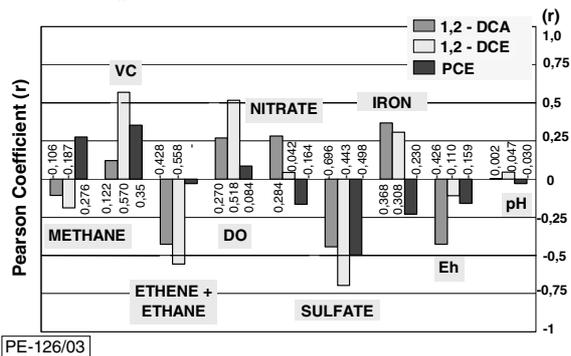


Figure 4. Pearson correlation results for the well PE-03.

Figure 5 shows the historical evolution of major contaminants and metabolic compounds in two wells: PE-03 and PM-03, located downgradient and upgradient of the secondary source, respectively. PM-03 is far from the abstraction wells and more representative in terms of intrinsic degradation processes. 1,2 DCA concentrations are orders of magnitude higher with respect to the other contaminants. Benzene, initially detected at the PM-03 at high concentrations, is now depleted and was probably used as a substrate (electron donor) to promote reductive dechlorination of the chlorinated solvents to occur.

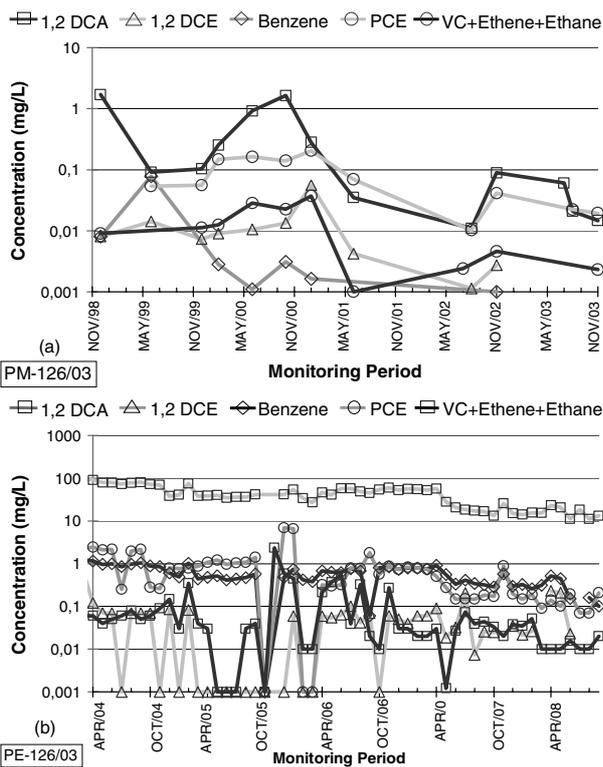


Figure 5. Historical evolution of major contaminants and metabolic compounds.

5 CONCLUSIONS

Risk analysis was conducted for a contaminated site impacted with chlorinated solvents and benzene in order to evaluate alternative risk based alternatives for site remediation. Risk/protection zones were mapped for

groundwater based on a 95th percentile of confidence with respect to the input parameter uncertainties and relative to a Quotient Hazard of 1 and Carcinogenic Risks of 10E-04, 10E-05 and 10E-06. The uncertainties in transport model parameters, such as hydraulic conductivities and dispersivities, along with conceptual model variables (source geometry and concentration) were evaluated by the use of the first order second moment method (FOSM). These protection areas can be used as a decision making tool for land use planning. Groundwater well capture zones, for instance, must not overlap these areas in future developments.

The risk analysis results indicate that vinyl chloride is responsible for the highest calculated risk at the site (96%). It is therefore a priority to understand the formation of this compound. We verified that dissolved PCE and 1,2 DCA plumes, at the secondary source, are responsible for the formation of VC together with ethene and ethane. Statistical correlations by the Pearson coefficient were also estimated. The best correlations were between the contaminants and the metabolic products VC and ethene+ethane along with sulfate and dissolved oxygen. Methane, though normally considered a good indicator for 1,2 DCA natural degradation processes, was not produced at high concentration levels at this site. Therefore, as the pump-and-treat system is not sufficient to eliminate the free-phase DNAPL source and achieve site closure, other remediation alternatives are being considered, such as enhanced bioremediation and soil vapor extraction.

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