

Soil Clean-Up Levels for Residential and Industrial Land Use in Mexico: A Case Study Applying RBCA on a Site Contaminated by Hydrocarbons

Rosa M. Flores-Serrano
Instituto de Ingeniería, UNAM,
Apartado Postal 70-472, Ciudad Universitaria, 04510 México D.F., México,
rfs@pumas.iingen.unam.mx

ABSTRACT

RBCA (Risk Based Corrective Action) framework was applied in two contaminated sites located on the east coast of Mexico in order to assess the risks of the exposed population to the hydrocarbons and metals found on the soil and groundwater, as well as to obtain the soil clean-up concentration levels required to protect these populations. Soil physical and chemical properties of both sites were similar, differences were observed on hydraulic conductivity, depth to the water table, extension of the contaminated area, and land use (one was classified as industrial and the other one as residential). Almost in all cases hydrocarbon and metal soil concentrations were greater on the industrial site, and soil clean-up concentrations were less restrictive on this site.

A 2^k factorial design was applied to determine the factors (Hydraulic Conductivity, Depth to the Water Table, Contaminated Area, and Land Use) and their interactions that posed the main influence on the soil clean-up concentrations obtained with RBCA Tool Kit for one of the contaminants present at the sites. The contaminant analysed was MTBE, because of its great potential of contaminating groundwater and its adverse health effects. The results showed that the main influence on the soil concentrations obtained with RBCA Tool Kit are Land Use x Depth to Water Table, followed by the interaction of Hydraulic Conductivity x Depth to water Table.

INTRODUCTION

When applying Health Risk Assessment it is well known that the nature of the receptors (residential or industrial/commercial land use) makes a difference on site specific soil concentrations; sites with residential land use provide more restrictive soil concentrations than the ones assessed as industrial/commercial land use. This is because on a residential scenario is considered the most sensible part of the population, which are babies and kids (less than 15 years old) with low bodyweights, longer time of exposure, and playing activities that suppose a more intimate contact with contaminated media. Nevertheless, there are other factors that influence the results obtained, such as the geohydrological properties of the subsoil.

A Health Risk Assessment (Tier 2) was applied in two sites located on the east coast of Mexico using RBCA (Risk Based Corrective Action) framework through the GSI (Ground Water Services Inc.) RBCA Tool Kit for Chemical Releases v 1.3, 2001 software. One was classified with a residential land use (Site 1) and the other one as industrial/commercial (Site 2). The sites were contaminated with hydrocarbons and some metals, and were located near from each other, so they had similar characteristics, the only differences were observed on On-Site land use, hydraulic conductivity, depth to water table, and contaminated area. In spite of the contaminants presented higher concentrations on the industrial site, the site specific soil clean-up concentrations were less restrictive in this site, which was attributed mainly to the nature of the receptors as explained in the paragraph above, but it was also recognized that hydraulic conductivity, depth to water table, and contaminated area might have had an influence on the results obtained.

To visualize the magnitude of the effects of these properties (land use, hydraulic conductivity, depth to water table, and contaminated area) on the site specific soil clean-up concentrations obtained, it was applied a 2^4 factorial design, in which each one of the four properties mentioned was considered as a factor of influence, and each of these factors was considered at two levels: high and low. This provided 16 different combinations of factors. Each one of these combinations of factors was supplied as an input to the RBCA software, obtaining 16 different responses (site specific soil clean-up concentrations), which were analysed to figure out the main influences or effects.

This paper presents the results obtained with this statistical tool, indicating which are the factors and their interactions that have the more important influence on the soil clean-up concentrations.

SCENARIOS EVALUATED

At the residential site (Site1) the On-Site receptors were children (0-6 years old), and for the industrial/commercial site (Site 2) the On-Site receptors were workers of a refinery facility, including construction workers with digging activities.

Both sites were contaminated with hydrocarbons (BTEX, Acenaphtene, Anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Dibenzo(a,h)anthracene, Phenanthrene, Fluoranthene, Fluorene, Indene(1,2,3,c,d)pyrene, Naphtalene, and Pyrene), metals (Iron, Nickel, Lead, Vanadium, and Zinc), and MTBE (Methyl Tertiary-Butyl Ether), which is a synthetic additive originally introduced to replace lead as an octane-enhancer and anti-knocking agent in gasoline, and now is used as an oxygenate to reduce automobile carbon monoxide emissions (1).

Due to the lack of space only one of the contaminants present at the site is analysed. The contaminant selected was MTBE because of its great potential of contaminating ground water (the solubility of MTBE in water at 25° C is approximately 5,000 mg/L of a gasoline that is 10% MTBE; and approximately 50,000 mg/L when is pure) (2), and its dangerous characteristics (U.S.EPA and other organizations have not classified MTBE as to its human carcinogenicity, but it is related to animal carcinogenic effects and other systemic effects) (3, 4). Table 1 shows the toxicological information used to assess this compound.

The exposure pathways considered were air and groundwater migration (soil to air by volatilisation or particulate migration, and leaching from soil to groundwater). The exposure routes considered were inhalation and dermal contact with vapours, and ingestion of groundwater contaminated by the soil to groundwater pathway.

Both sites were located nearby a neighbourhood at 1239 m down gradient from the sites, so the Off-Site receptors were classified as residential land use. The depth of contaminated soil was 1 m (0-1 m depth).

Soil characteristics common to both sites are shown on table 2. Table 3 shows the factors that suppose a difference on site specific soil concentrations.

FACTORIAL DESIGN AND RBCA SOFTWARE

Design of experiments (DOE) is a statistical technique for organizing and analysing experiments (5), unlike one-factor at a time experiments (OFAT) it has the

advantage that allows to vary several factors simultaneously and determine the impact or effect of two or more factors on a response (6, 7). It has been used mainly to evaluate parameters of variability on science laboratory experiments, or industrial processes, but it can also be applied to computer models. Each experiment may require that multiple replications of the simulation be run. The factors are the parameters that are varied (independent variables that are under the experimenter's control), while the responses are the dependent variables or outcome measures of interest (5).

A conventional and very useful form of DOE is the 2^k factorial design, where each of k factors is allowed to take on two values, a low or minus value and a high or plus value. This design has been shown to be not only economical but also effective at revealing interaction effects. Each combination of factors is called a design point. The entire design is often summarized as a design matrix, with the design points arranged sequentially in the first column, the value of factor k (- or +) indicated in column $1+k$. The response is shown in the final column (5). In some cases of software simulation runs there are multiple replications run at each design point in order to compute the response, which might be the mean value for the number of replications made, in other cases only one run is needed to obtain the response for the desired design point, which is the case of the present application.

For this case it was applied a 2^4 factorial design, in which each one of the four properties mentioned was considered as a factor, and each of these factors was considered at two levels: high (+) and low (-). This provided 16 different design points or combination of factors. Each one of these combinations of factors was supplied as an input to the RBCA software, obtaining 16 different results (site specific soil clean-up concentrations), which were analysed to figure out the main effects. The factorial design was solved with the help of Minitab v.13.32 statistical analysis package

The – and + values of each factor considered on this exercise are shown on table 4. The design matrix obtained for this application is shown on table 5 where the first column identifies the experiment or design point and the last column shows the response (site specific soil clean-up level for MTBE in mg/kg) obtained with RBCA software (higher concentrations correspond to situations with lower risks). This matrix was entered to Minitab.

The geohydrological input parameters for each run of RBCA software are the ones shown on table 2, as well as the correspondent combination of factors shown on table 4. The Toxicological parameters used are shown on table 1. Table 6 presents the exposure information used on RBCA runs. The Target Hazard Quotient was set to 1 (maximum allowable dose = reference dose). It is important to mention that soil clean-up concentrations obtained with RBCA correspond to the soil to ground water leaching pathway (ingestion of water contaminated through this pathway), which means that these concentrations were the most restrictive compared to the ones obtained through the inhalation, dermal contact, and soil ingestion routes.

RESULTS AND DISCUSSION

Results obtained from the analysis of the design matrix with Minitab package are shown on table 7, and figure 1. Table 7 shows the effects of each factor as well as their interactions; this results are better understood through the Pareto chart shown on figure 1. The Pareto chart displays the absolute values of the effects and any effect that past the reference line is significant, so from figure 1 it is observed that, contrary to what was expected, apparently the main single effect is not the land use, but the depth to water table, and land use is the second single effect in importance, but due to the interaction between these two variables it is more appropriate to analyse their interaction as will be shown later; another important interaction, but less remarkable, is the one between hydraulic conductivity (K) and depth to water table. All other effects and interactions are not significant for the response, as it is shown on figure 2, which shows data means of the interactions for MTBE soil concentrations. From figure 2 it can be observed that the lines are parallel in all cases except for the Land Use x Depth to Water Table interaction, and the Hydraulic Conductivity x Depth to Water Table interaction (where non-parallelism is almost imperceptible).

Figure 3 shows the two way interaction plot for the Land Use x Depth to Water Table interaction, and the Hydraulic Conductivity x Depth to Water Table interaction. The values on the corners of the squares correspond to the mean value of the design points that matches the combination of interest. From this figure it can be observed that the deeper the water table is the higher the concentration allowed, which is because if the water table is shallow then it would take less time for the contaminant to get to the groundwater, so it is expected a more restrictive soil concentration for the site with the shallower water table in order to reduce the risk of contamination and exposure. It is also observed that the more restrictive soil MTBE concentration (figure 3a, mean value = 0.225 mg/kg) is obtained for the Low Depth to Water Table x Residential Land Use combination, and the less restrictive concentration is obtained for the High Depth to Water Table x Industrial/commercial Land Use (figure 3a, mean value = 3.95 mg/kg); it is also observed that a change of land use from residential to industrial when the water table is deeper (14 m) may allow an increment of 2.3 mg/kg on the acceptable soil clean-up concentration, while at a shallower depth (1 m) will only allow an increment of 0.305 mg/kg on the acceptable soil clean-up concentration. These results probably have to do with the fact that MTBE is a contaminant with a very high water solubility (5,000 mg/L of a gasoline that is 10% MTBE; and 50,000 mg/L when is pure), and low affinity to soil particles ($\log K_{oc} = 1.08$, approximately), so it tends to migrate very fast through the porous media.

The interaction of Depth to Water Table x Hydraulic Conductivity (Figure 3b) shows a less dramatic difference: in both cases (deep and shallow depth to water table) a change of Hydraulic Conductivity on one order of magnitude (3.47×10^{-3} cm/s, and 5.79×10^{-4} cm/s) will produce only a difference of 0.01 mg/kg on the soil clean-up concentration for the shallow Depth to Water Table, and of 0.1 mg/kg for the higher Depth to Water Table. But the effect of Depth to Water Table for both Hydraulic

Conductivities is of 2.47 and 2.36 mg/kg. This means that the important fact is to prevent MTBE contact with ground water, a higher distance between contaminated soil and water table helps with that.

Figure 2 also shows that in the cases of Land Use x Hydraulic Conductivity, and Land Use x Contaminated Area interactions, the response depends on Land Use, no matter what the values of Hydraulic Conductivity and Contaminated Area are, in both cases the change of land use produces a response that goes from 0.91 mg/kg (mean value) for the residential land use, to 2.21 mg/kg (mean value) for the industrial/commercial land use. For the Hydraulic Conductivity x Contaminated Area interaction, the response depends on Hydraulic Conductivity better than on Contaminated Area, the response (soil concentration) is slightly lower when Hydraulic Conductivity is higher (low mean value = 1.56 mg/kg; high mean value = 1.86 mg/kg), which makes sense because the higher the value of Hydraulic Conductivity the higher the risk of groundwater contamination, so it is expected a more restrictive soil concentration in order to reduce that risk. For the Contaminated Area x Depth to Water Table interaction, the remarkable effect depends on depth to water table, no matter what the contaminated area is (concentration mean value ranges from 2.8 mg/kg for the deeper value, to 0.38 mg/kg for the shallow one).

CONCLUSIONS

The application of the 2^4 factorial design to determine the magnitude of the effects of the factors: Land Use, Hydraulic Conductivity, Depth to Water Table, and Contaminated Area, on the response (site specific soil clean-up concentrations obtained with RBCA Tool Kit for chemical releases) for the sites describe on this paper, and the contaminant MTBE, lead to the following conclusions:

- Apparently the main single effect on the response is not the Land Use, but the Depth to Water Table, and Land Use is the second single effect in importance.
- The main factor interactions in order of importance are Land Use x Depth to Water Table, and Hydraulic Conductivity x Depth to Water Table, because a change of land use from residential to industrial when the water table is deeper (14 m) may allow an increment of 2.3 mg/kg on the acceptable soil clean-up concentration, while at a shallower depth (1 m) will only allow an increment of 0.305 mg/kg on the acceptable soil clean-up concentration; on the other hand the interaction of Depth to Water Table x Hydraulic Conductivity shows a less dramatic difference: in both cases (deep and shallow depth to water table) a change of hydraulic conductivity on one order of magnitude (3.47×10^{-3} cm/s, and 5.79×10^{-4} cm/s) produces only a difference of 0.01 mg/kg on the soil clean-up concentration for the shallow Depth to Water Table, and of 0.1 mg/kg for the higher Depth to Water Table. But the effect of Depth to Water Table for both Hydraulic Conductivities produces a difference of 2.47 and 2.36 mg/kg, for the higher and lower water table, respectively. These results can be related to the high water solubility of MTBE.

- The more restrictive soil MTBE concentration is obtained for the Low Depth to Water Table (-) x Residential Land Use (+) combination, and the less restrictive concentration is obtained for the High Depth to Water Table (+) x Industrial/commercial Land Use (-).
- The less important factor on the response is Contaminated Area.

Table 1. Toxicological information for MTBE

Parameter	Value
Inhalation RfC (mg/m ³)	3.0 (8)
Oral RfD (mg/kg/d)	0.01 (9)
Dermal RfD (mg/kg/d)	0.008* (10)

RfC = reference concentration for systemic effects; RfD = reference dose for systemic effects; *Extrapolated from the oral RfD considering a gastrointestinal absorption factor of 0.8 (11)

Table 2. Soil characteristics common to sites 1 and 2

Characteristic	Value
Soil type	Silty sand
Bulk density (g/cm ³)	1.377
Real density (g/cm ³)	2.475
Porosity (dimensionless)	0.44
Fraction of Organic Carbon (dimensionless)	0.0057
pH	7.06
Hydraulic gradient (dimensionless)	0.00094

Table 3. Factors that suppose a difference on site specific soil concentrations for sites 1 and 2

Factor	Site 1	Site 2
Land Use	Residential	Industrial/Commercial
Hydraulic Conductivity (cm/s)	5.79x10 ⁻⁴	3.47x10 ⁻³
Contaminated Area (m ²)	67984	32785
Depth to Water Table (m)	14	1

Table 4. High (+) and low (-) values for each factor considered for the 2⁴ factorial design

Factor	Value	
Land use	(+) Residential	(-) Industrial
Hydraulic conductivity (K) (cm/s)	(+)3.47 x 10 ⁻³	(-)5.79 x10 ⁻⁴
Contaminated area (m ²)	(+) 67984	(-) 32785
Depth to water table (m)	(+) 14	(-) 1

Table 5. Design matrix for the 2⁴ factorial design

Experiment	Land Use	K	Area	Depth WT	MTBE (mg/kg)	Concentration
1	-	-	-	-	0.52	
2	-	+	-	-	0.54	
3	-	-	+	-	0.52	
4	-	-	+	+	3.9	
5	-	-	-	+	3.9	
6	-	+	+	-	0.54	
7	-	+	-	+	4.0	
8	-	+	+	+	4.0	
9	+	-	-	-	0.22	
10	+	+	-	-	0.23	
11	+	-	+	-	0.22	
12	+	-	+	+	1.6	
13	+	-	-	+	1.6	
14	+	+	+	-	0.23	
15	+	+	-	+	1.7	
16	+	+	+	+	1.7	

Table 6. Exposure information used on RBCA health risk assessment for both sites

Parameter	Adult- Residential	Children- Residential	Adult- Industrial/Com	Adult- Construction
Averaging time for non-carcinogens (year)	30	6	25	1
Body weight (kg)	70	15	70	70
Exposure duration (year)	30	6	25	1
Exposure frequency (days/year)	350	350	250	180
Skin surface area (cm ²)	5800	2023	5800	2900
Ingestion rate of water (L/day)	2.0	2.0	2.0	2.0
Ingestion rate of soil (mg/day)	100	200	50	100
Inhalation rate (m ³ /d)	20	20	20	10

Table 7. Estimated effects of factors and their interactions on soil concentrations of MTBE (mg/kg)

Factor	Effect
Constant	--
Land Use	-1.3025
K	0.0575
Area	0.0000
Depth WT	2.4225
Land Use x K	-0.0025
Land Use x Area	-0.0000
Land Use x Depth WT	-0.9975
K X Area	-0.0000
K X Depth WT	0.0425
Area x Depth WT	-0.0000
Land Use x K x Area	0.0000
Land Use x K x Depth WT	0.0025
Land Use x Area x Depth WT	-0.0000
K x Area x Depth WT	0.0000
Land Use x K x Area x Depth WT	-0.0000

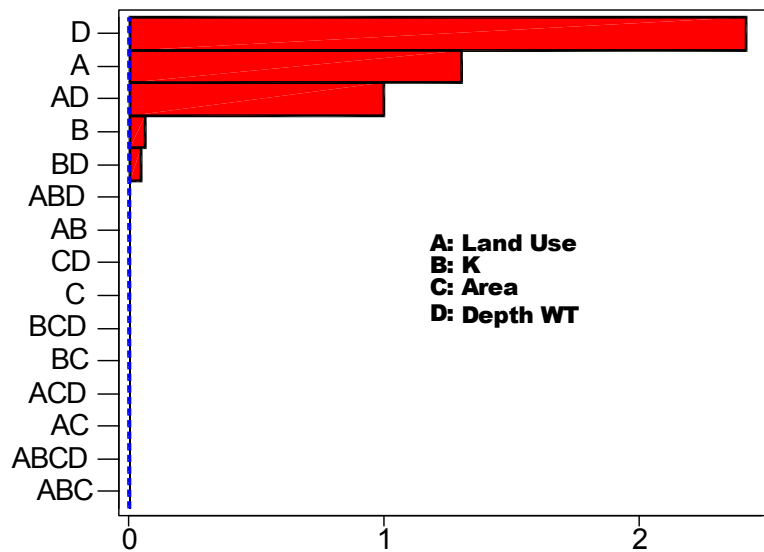


Figure 1. Pareto Chart showing significant effects (Reference line at $\alpha = 0.05$).

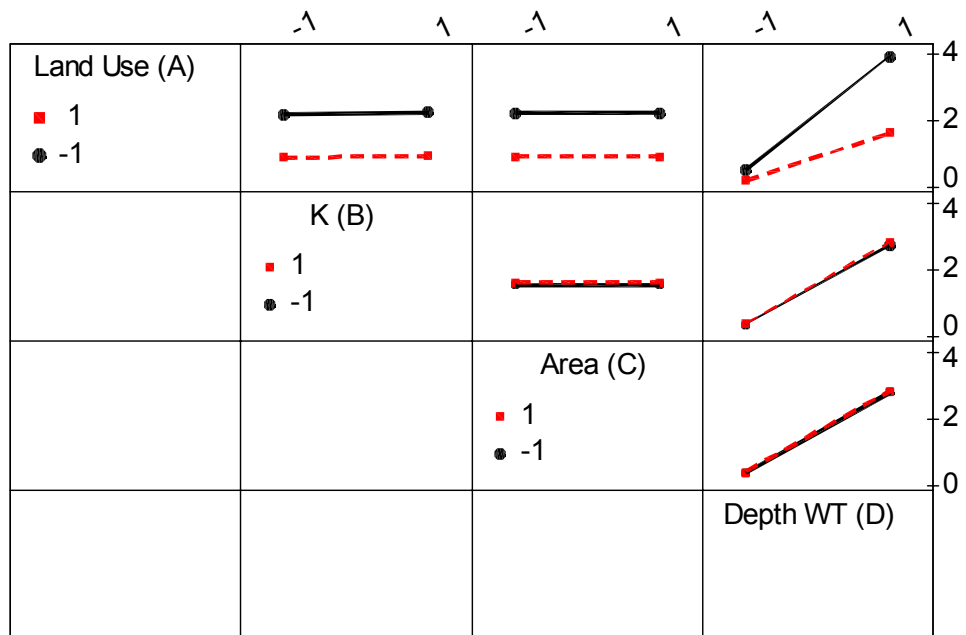


Figure 2. Interaction Plot (data means) for MTBE soil concentration (mg/kg).

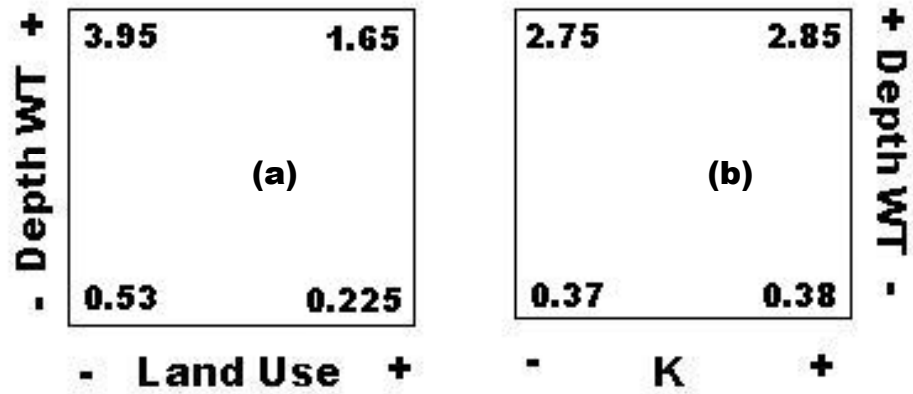


Figure 3. Two way interaction plot for the (a) Land Use x Depth to Water Table interaction, and (b) the Hydraulic Conductivity x Depth to Water Table interaction. Values on the corners of the squares correspond to the mean concentrations of MTBE (mg/kg) of the design points that matches the combination of interest

REFERENCES CITED

1. U.S.EPA, "Methyl Tertiary-Butyl Ether (MTBE)", <http://www.epa.gov/mtbe/gas.htm> (2003).
2. Wilks University, "Methyl Tertiary Butyl Ether", <http://www.earthisland.org/bw/MTBEfacts.shtml> (2003).
3. Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological profile for methyl tert-butyl ether (MTBE), Atlanta, GA, Department of Health and Human Services, Public Health Service (1996).
4. Penn State University (PSU), "Methyl tert-Butyl Ether", <http://www.personal.psu.edu/users/r/x/rxs334/MTBE.html> (2002).
5. Wakeland, W., Martin, R.H. and Raffo, D., "Using Design of Experiments, Sensitivity Analysis, and Hybrid Simulation to Evaluate Changes to a Software Development Process: A case Study" in proceedings of the Pro Sim '03 Workshop, Portland, Oregon, Portland State University (2003).
6. Box, G.E.P., Hunter, W.G. and Hunter, J.S, Estadística Para Investigadores. Introducción al Diseño de Experimentos, Análisis de Datos y Construcción de Modelos, México D.F., Reverté Ediciones, S.A. de C.V. (1999).
7. Czitrom, V., "One-Factor-at-a-Time versus Designed Experiments", *The Am. Stat.*, **53**, 126-131 (1999).
8. U.S.EPA Integrated Risk Information System (IRIS), "Methyl Tert-Butyl Ether (MTBE) (CASRN 1634-04-4)", <http://www.epa.gov/iris/subst/0545.htm> (2002).
9. Texas Risk Reduction Program (TRRP), "Rule (30 TAC 350), Toxicity Factors Table", Texas Commission of Environmental Quality (Texas Natural Resource Environmental Commission), <http://www.tnrcc.state.tx.us/permitting/remed/techsupp/pcls0403.xls.exe> (2002).
10. Ground Water Services Inc. (GSI), RBCA Tool Kit Chemical Releases v.1.3, Houston, Groundwater Services Inc. (2001).

11. Risk Assessment Information System (RAIS), "Chemical-Specific Factors", [http://
risk.lsd.ornl.gov/tox/tox_values.shtml](http://risk.lsd.ornl.gov/tox/tox_values.shtml) (2002).