

SIMULATION OF THE SOIL CONTAMINATION BY ORGANIC VAPOR

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Abstract. *The leaks of organic compounds to soil have attracted attention in studies and environmental impact assessments. This paper describes the study of the compound Toluene spread in vapor in the unsaturated zone of soil. It is released in laboratory columns containing a soil synthetic and simplified of the quartz sand classification. It is shown the experimental procedure developed in the laboratory columns, the experimental results, and an analysis by applying mathematical modeling to these results, the statistical analysis applied to the model called "Puffs" to simulate the dispersion and a discussion of the continuation of this work.*

Keywords: *leaks; propagation; soil; experiments; modeling*

1. INTRODUCTION

The current leakage of oil (gasoline, diesel, kerosene, naphtha) to the ground have attracted attention in recent years as the cause of spreading the contamination of soil and can reach the groundwater, as Santos (1998), Cordazzo (2000) and Penner (2000). In this context, the research group investigates through experimental studies and mathematical modeling of this spread in the non-saturated and saturated soil. The transport and distribution of hydrocarbon compounds in soil involves the physical phenomena such as flow by gravity, leaching, diffusion and molecular mechanics dispersion. The phenomena of distribution of compounds between the phases: solids, air, water and oil (in solid phase adsorption, solubility in the liquid phase and mass transfer to the vapor phase) and degradation processes (chemical and biological) are also present. At this stage of research is investigating the phenomena of dispersion in the non-saturated zone of the soil, Behrendt (2005) and Grathwohl et al. (2003). Experimental data are obtained on a column of soil in a laboratory scale. The compound Toluene is used as representative of petrol and quantitative values of concentration are obtained along the column. This article contains the following items: the dispersion of compounds in the non-saturated soil, the materials and methods for obtaining experimental data, the experimental results and conclusion of this phase of work.

2. SPREAD OF COMPOUNDS IN THE NON-SATURATED ZONE OF THE SOIL

The transport and distribution of hydrocarbon compounds in the soil surrounding the phenomena of spreading and flow by gravity, leaching, diffusion and molecular mechanics, as Abriola and Pinder (1985). The compounds also suffer phenomena of interaction between the stages and processes of degradation in soil. A region of soil in which the component is spreading is also an important factor in modeling the dispersion. The model should take into account whether it is the non-saturated or saturated soil. The first layers of the soil are filled with air, moisture and organic phase in its empty (non-saturated zone).

In non-saturated zone, the pore space is filled by the sum of fluids present, then:

$$\theta = \theta_w + \theta_{ar} + \theta_o \quad (1)$$

Where θ , θ_w , θ_{ar} , and θ_o is the soil porosity, the fraction of voids occupied by water, the fraction of voids occupied by air and the fraction of voids occupied by non-aqueous phase liquid (NAPL) or oil (o).

Therefore, the total concentration of component "i" in the soil is given by the relationship:

$$C_{i,t} = \theta_w C_{i,w} + \theta_{ar} C_{i,ar} + \theta_o C_{i,o} + \rho_b C_{i,s} \quad (2)$$

Where $C_{i,t}$, ρ_b , $C_{i,w}$, $C_{i,ar}$, $C_{i,o}$, e $C_{i,s}$ are the total concentration of "i" in the soil in (g of "i") (m⁻³ of the soil), the soil density in (g of the solid) (m⁻³ of the soil), the concentration of component "i" in the water phase, (g of the "i") (m⁻³ of the w), the

concentration of component "i" in the vapor phase, (g of the "i") (m^{-3} of the air), the concentration of component "i" in the oil phase, (g of the "i") (m^{-3} of the oil) and the concentration of component "i" in the solid phase in (g of the "i") (g^{-1} of the solid).

Not considering the formation of the oil phase of the layer of soil and spread predominant mechanism of organic compound, is the molecular diffusion in air. The diffusion equation, which describes the spread in the one-dimensional, saturated soil, as Grathwohl et al. (2003) and Fetter (1998), is written in the form:

$$\frac{\partial C_{i,ar}}{\partial t} = \frac{D_E}{\alpha} \frac{\partial^2 C_{i,ar}}{\partial z^2} \quad (3)$$

Where t , z and D_E are the time of release of the compound, the distance in vertical direction and the effective diffusion coefficient in air phase of soil. The diffusion coefficient is estimated by the relationship of Millington and Quirk (1961):

$$D_E = D_{i,ar} \frac{(\theta_{ar})^{10}}{\theta^2} \quad (4)$$

Where $D_{i,ar}$ and α is the coefficient of diffusion of the compound in air and the parameter that takes into account the distribution of the compound in the soil phases of air, water and soil:

$$\alpha = \theta_{ar} + \frac{\theta_w}{K_h} + \frac{K_d \rho_b}{K_h} \quad (5)$$

Where K_h and K_d are the Henry's Law Constant (dimensionless) and the distribution coefficient between solid phase and water phase.

In this work, the means of spread is limited to the length of the laboratory columns, shown in Figure 2, and the mathematical solution is applied to this contour limited as Ozisik (1993). Two analytical solutions are used: the first with the condition of fixed concentration contour at the top of the column (point of release, $z = 0$) and the USA the condition of no flow on the top and both apply the condition of flow mass at the bottom of the column. The following mathematical solutions are obtained in series:

The solution to the condition of fixed concentration, is:

$$C_{i,ars}(z,t) = 2C_{i,o} \sum_{m=1}^{\infty} e^{-D_E^2 B_m^2 t} \frac{B_m^2 + H_2^2}{L(B_m^2 + H_2^2) + H_2} \frac{(\cos(B_m L) - 1)}{B_m} \text{sen}(B_m z) \quad (6)$$

Where the constant B_m are the roots of the equation:

$$B_m \cot(B_m L) - H_2 = 0 \quad (7)$$

H_2 is the ratio of the mass transfer coefficient at the bottom of the column and the diffusion coefficient and L is the length of the column.

And the solution to non-existence of flow is (This is an intermittent release):

$$C_{i,ars}(z,t) = 2C_{i,o} \sum_{m=1}^{\infty} e^{-D_E^2 A_m^2 t} \frac{A_m^2 + H_2^2}{[L(A_m^2 + H_2^2) + H_2] A_m} \text{sen}(A_m L_i) \cos(A_m z) \quad (8)$$

Where A_m are the roots in the equation:

$$A_m \tan(A_m L) - H_2 = 0 \quad (9)$$

And L_i is the length of the release point of issue.

3. EXPERIMENTAL METHODOLOGY

3.1 Experimental Procedure for the Release of Soil Column

A quantity of the compound Toluene is released in the soil column. After a period of time the collection is held at various times of the liquid fraction of the soil. It is then determined the concentration of the compound in soil using the method of gas chromatography.

3.1.1 Materials and Equipment

The column is a steel pipe with diameter of 5 cm and height of 150 cm, filled with fine sand to simulate soil in a laboratory, as the diagram of Figure 1. Column seven shows the collection of sample points spaced 20 cm between them. The reagent Toluene p. a. compound was used as representative of a leak. Micro pipette and 10 μ L of 1 mL were also used. Gas chromatograph with a flame ionization detector and a polar column, oven and analytical balance are the equipment used.

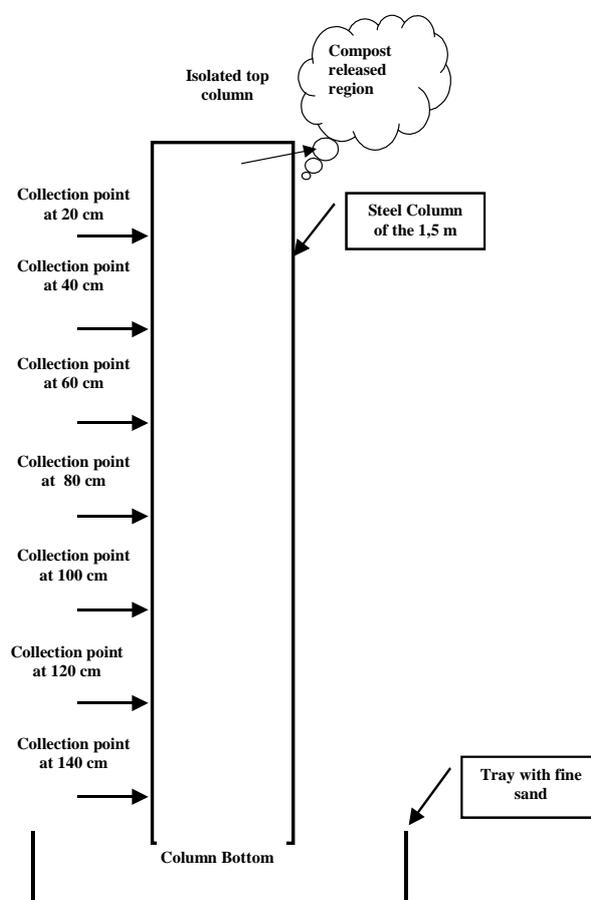


Figure 1. Schematic of laboratory column.

3.2.1 Experimental procedure

The experimental procedure consists of the following steps:

- 1) Filling of the column side (diameter 5 cm and length of 1.5 m) with fine sand;
- 2) Release of a defined quantity of toluene, representing a compound of volatile gasoline (it wanted to obtain an instantaneous release);
- 3) Daily collect of samples of soil vapor within seven points of the column. The sample is composed of a mixture of Toluene and air without the presence of solid phase;
- 4) Quantitative concentration determination of the contaminant in the sample is made. When is used the analytical procedure of the gas chromatography.

4. RESULTS

In Figures 2 and 3 is shown the result of experimental test known as the test 1. He is a release of a quantity of 1 mL consisting of Toluene in the soil column. This was sealed on top with a layer of plaster. Figures 4 and 5 show the test result 2, which was conducted under the same conditions of test 1. Figures 6 and 7 show the test 3, where the spine is soldered on top and was given 0.5 mL of Toluene. Figure 7 was placed less curved for better viewing. The graphs show the axis of the abscissa from the point of emission (top of column) against the mass concentration in ppm. The first figure of each test shows higher values of concentration, therefore presents the days closest to the issue. Figures 8, 9, 10 and 11 show results of simulation for the time of release of 1, 2, 15 and 23 days respectively for the test 3. The model of combining instant releases was used for the simulation. The statistical parameters obtained with the model are presented in Table 1.

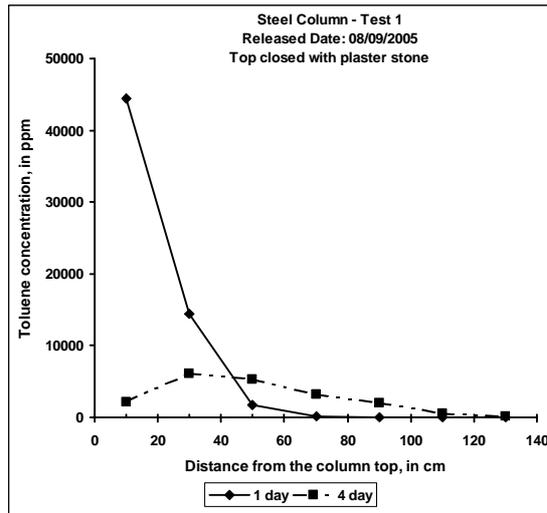


Figure 2. Experimental release on top of the soil column (Test 1).

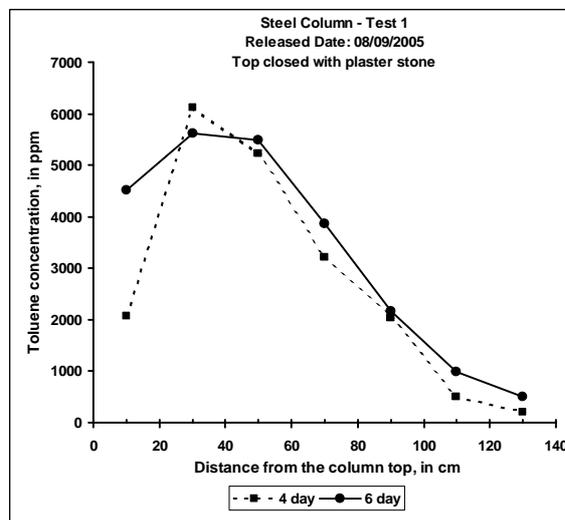


Figure 3. Experimental release on top of the soil column (Test 1).

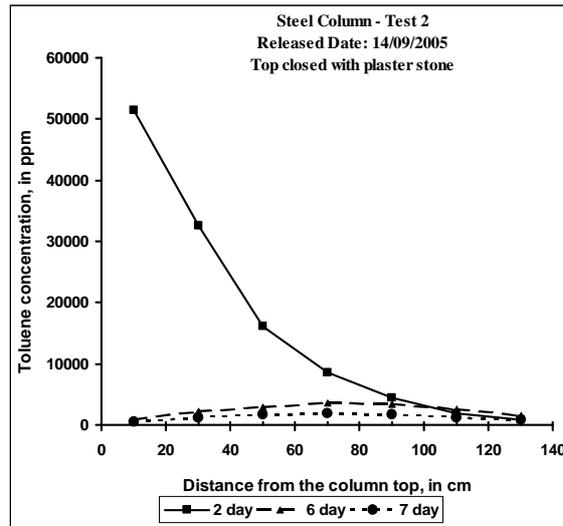


Figure 4. Experimental release on top of the soil column (Test 2).

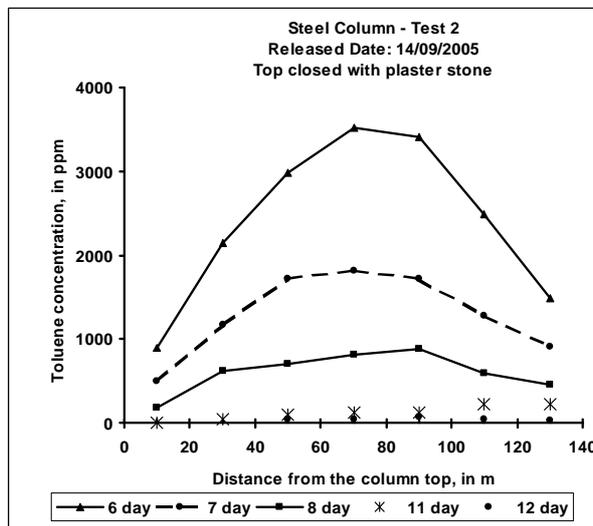


Figure 5. Experimental release on top of the soil column (Test 2).

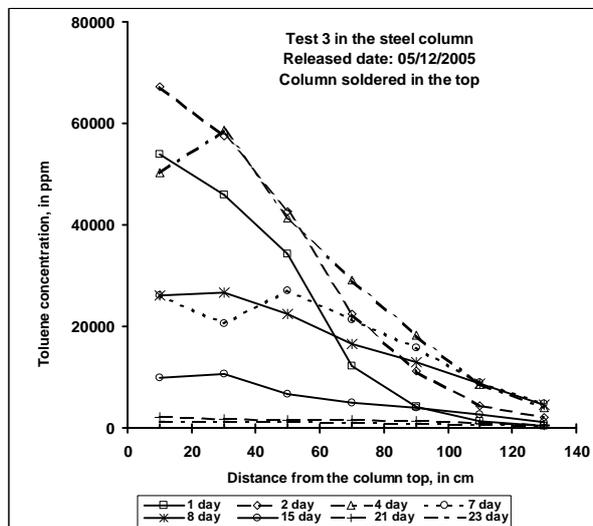


Figure 6. Experimental release with column welded at the top (Test 3).

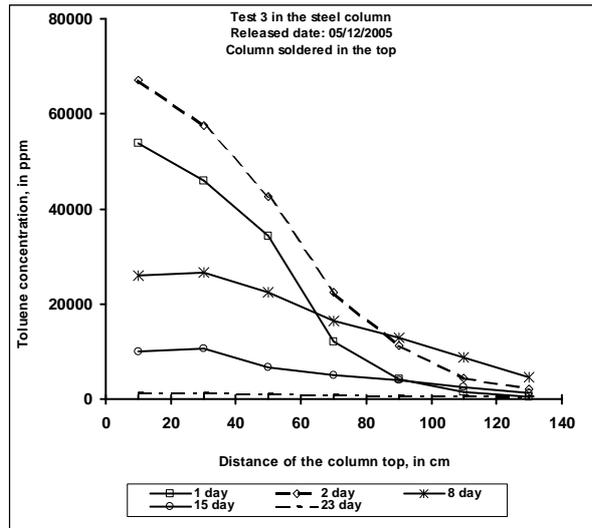


Figure 7. Experimental release with column welded at the top (Test 3).

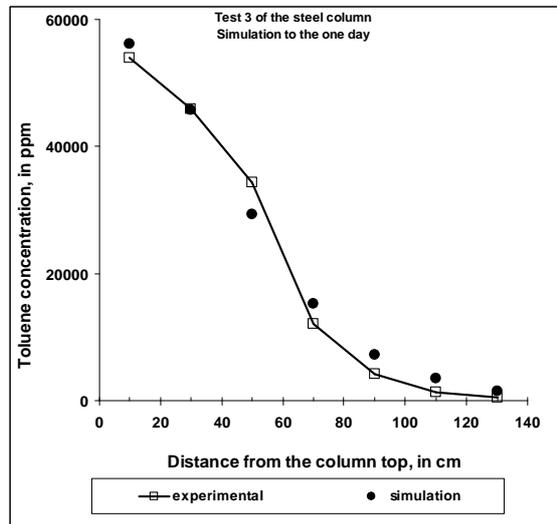


Figure 8. Simulation for the one day time period to the test 3.

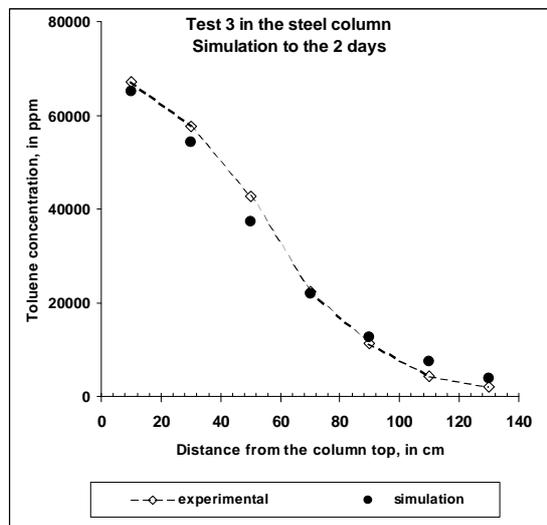


Figure 9. Simulation for the 2 days time period for the test 3.

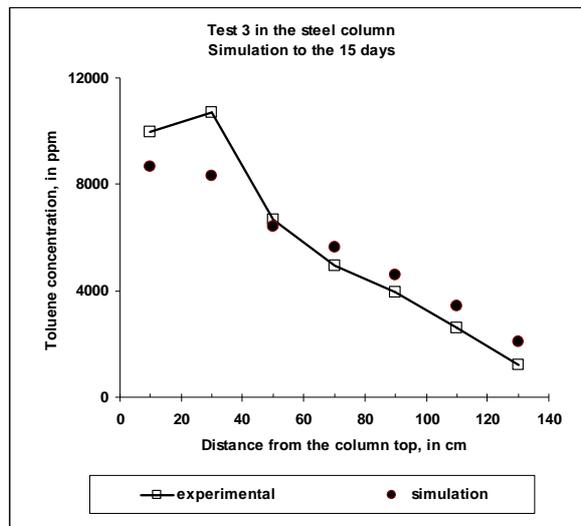


Figure 10. Simulation for the 15 days time period for the test 3.

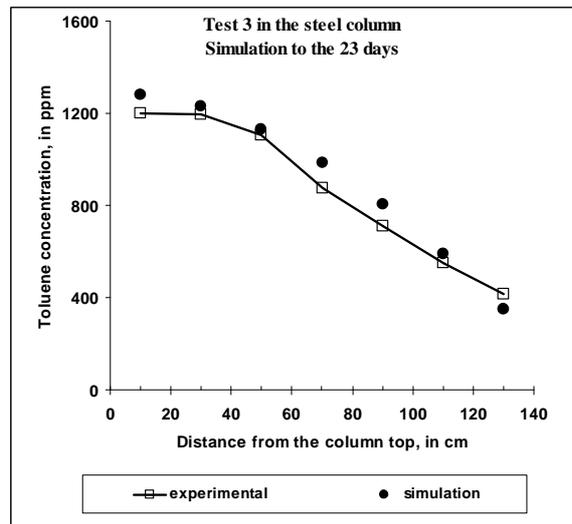


Figure 11. Simulation for the 23 days time period for the test 3.

Table 1. Statistical parameters obtained with the model of combination of "Puffs."

Statistical parameter	Value of the parameter
Fractional deviation	0,23
Dimensionless average	1,26
Dimensionless mean square standard deviation	0,36
Number of the positive simple errors obtained with the model	18
Average of the positive errors relative to the measured values	0,46
Number of the negative simple errors obtained with the model	10
Average of the negative errors relative to the measured values	-0,0937

5. DISCUSSIONS OF RESULTS

The results of tests 1 and 2 show lower values of concentration for the compound Toluene from the fourth day in the test 1 and test 2 in the sixth day (values below 10,000 ppm). Meanwhile, the test 3, with column welded on top, holds the highest concentration values by the fifteenth day. The concentration profiles were also different for the column sealed with plaster and with the lid welded. The parabolic concentration profiles for the tests 1 and 2 show an escape of Toluene on Top of the column, while test 3 shows an exponential profile with a single column at the top. The results of simulations show good agreement.

6. CONCLUSIONS

This research is developing the experimental evaluation of concentration for the fractions of petroleum compounds in the non-saturated soil. The experiments shown are the development of the technique applied to the Toluene compound. The experimental procedure has revealed to be appropriate to obtain values of concentration of hydrocarbon compounds in the gas phase in columns simulating the non-saturated soil.

Other tests should be conducted and mathematical models will be applied to a more research findings.

7. ACKNOWLEDGMENTS

The authors acknowledge the support of CNPq (project: Case No: 476858/2006-2), Laboratory of Mineral Processing, UFRGS, and the Centro Universitário Lasalle.

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