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EXPERIMENTAL STUDY OF DISPERSION OF TOLUENE ON NON-SATURATED PHASE OF THE SOIL – PART 1

Edson Abel dos Santos Chiaramonte
Unipampa, Travessa 45, N° 1650, Bairro: Malafaia, Bagé – RS, CEP: 96413-170
edsonchi@portoweb.com.br

Jorge Rodolfo Silva Zabadal
UFRGS, Av. Osvaldo Aranha, 99 - 4° Andar, Bairro: Centro, Porto Alegre – RS, CEP: 90046-900
jorge.zabadal@ufrgs.br

Rubens Muller Kautzmann
Centro Universitário La Salle – Av, Victor Barreto, N° 2288, Canoas – RS
rubensmk@terra.com.br

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 the gaoline 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. EXPERIMENTAL METHODOLOGY

2.1 Experimental procedure for the release of soil column

A quantity of the compound Toluene is released in the soil column. It is released in the liquid phase and vaporized in the column. After a period of time the collection is held at various times of the vapor fraction of the soil (every day is performed one sample collection). It is then determined the concentration of the compound in soil using the method of gas chromatography.

2.2 Materials and Equipment

The column is a steel pipe with 5 cm of the diameter and 150 cm of the heigh, filled with fine sand which is dried in an oven to simulate dry soil in the laboratory, as the diagram of Figure 1. The column has seven sampling points spaced of the 20 cm from the top. The reagent is the Toluene p. a. compound was used as representative of the gasoline. The micro-syringes are used to sample the gas in the column. Gas chromatograph with a flame ionization detector and a polar column, oven and analytical balance are the equipment used. Chromatographic analysis method is described by Ferreira et al. (2007).

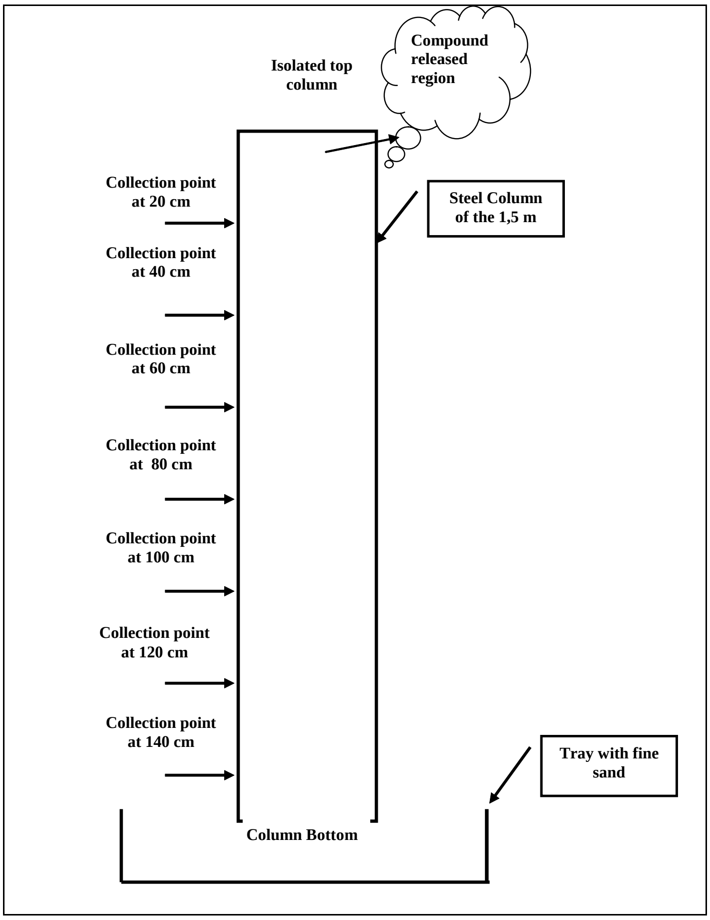

Figure 1. Schematic of the laboratory column.

2.3 Experimental procedure

The experimental procedure consists of the following steps:

1) Fills up the soil with the dry sand;

2) Releases a amount of the toluene, which is volatile compound of the gasoline (it wanted to obtain an instantaneous release);

3) Every day (at 24-hour intervals) is performed the sampling in the seven points. The sample is composed of a mixture of Toluene and air without the presence of solid phase;

4) The quantitative determination of the concentration is performed by using the analytical procedure of the gas chromatography.

3. 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:

$$\theta = \theta_w + \theta_{ar} + \theta_o \tag{1}$$

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

$$C_{i,to} = \theta_w C_{i,w} + \theta_{ar} C_{i,ar} + \theta_o C_{i,o} + \rho_s C_{i,s} \tag{2}$$

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:

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

The effentive diffusion coefficient is estimated by the relationship of Millington and Quirk (1961):

$$D_E = D_{i,ar} \frac{(\theta_{ar})^{\frac{10}{3}}}{\theta^2} \tag{4}$$

$$\alpha = \theta_{ar} + \frac{\theta_w}{K_h} + \frac{K_d \rho_b}{K_h} \tag{5}$$

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 use 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 the constant concentration is:

$$C_{i,ars}(z,t) = 2C_{i,in} \sum_{m=1}^{\propto} e^{-D_E^2 B_m t} \frac{B_m^2 + H^2}{L\left(B_m^2 + H^2\right) + H} \frac{\left(\cos(B_m L) - 1\right)}{B_m} sen(B_m z) \tag{6}$$

Where the constant B_m are the roots of the equation:

$$B_m \cot(B_m L) - H = 0 \tag{7}$$

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):

$$C_{i,ars}(z,t) = 2C_{i,o} \sum_{m=1}^{\propto} e^{-D_E^2 A_m t} \frac{A_m^2 + H^2}{\left[L\left(A_m^2 + H^2\right) + H\right] A_m} sen(A_m L_{re}) \cos(A_m z) \tag{8}$$

Where A_m are the roots in the equation:

$$A_m \tan(A_m L) - H = 0 \tag{9}$$

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

4. RESULTS

In Figures 2 and 3 is shown the result of experimental test known as the test 1. It 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.

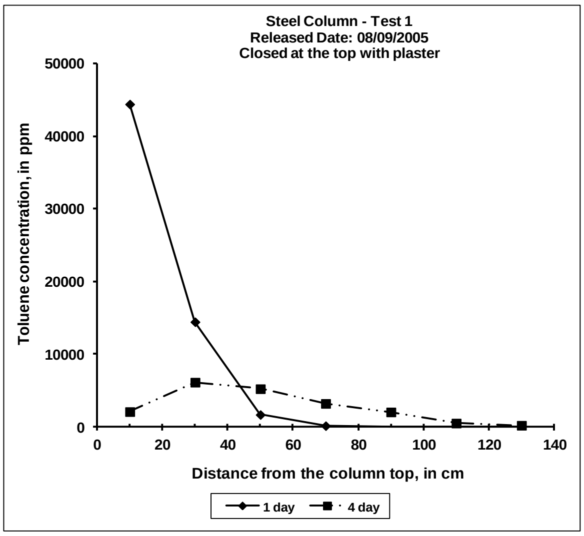

Figure 2. Experimental release on top of the soil column (Test 1).

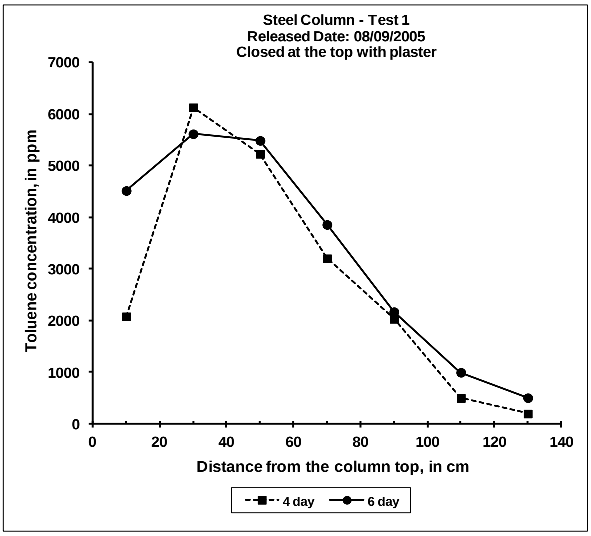

Figure 3. Experimental release on top of the soil column (Test 1).

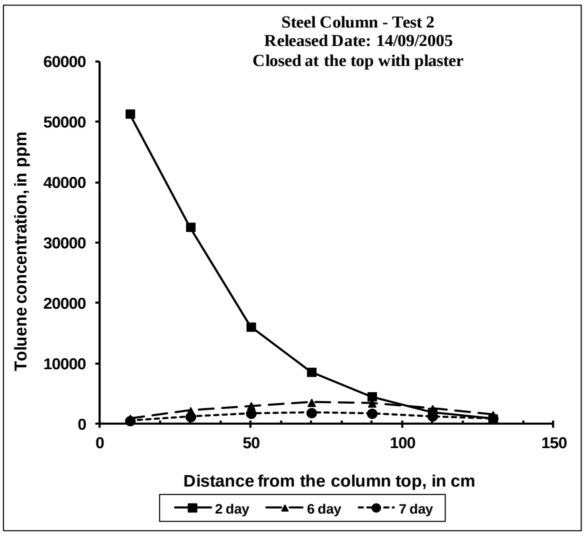

Figure 4. Experimental release on top of the soil column (Test 2).

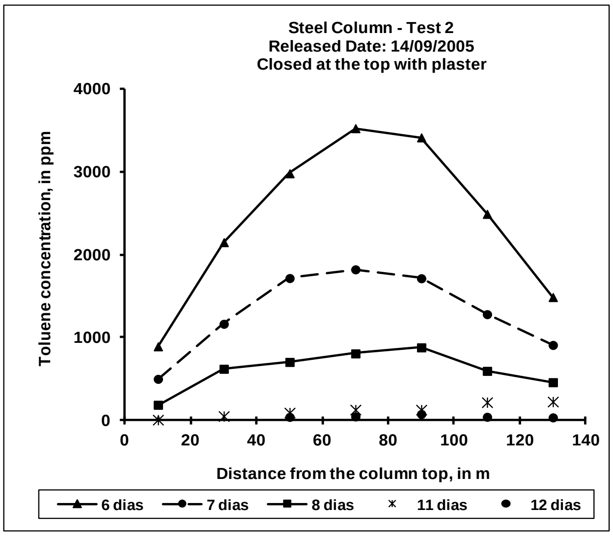

Figure 5. Experimental release on top of the soil column (Test 2).

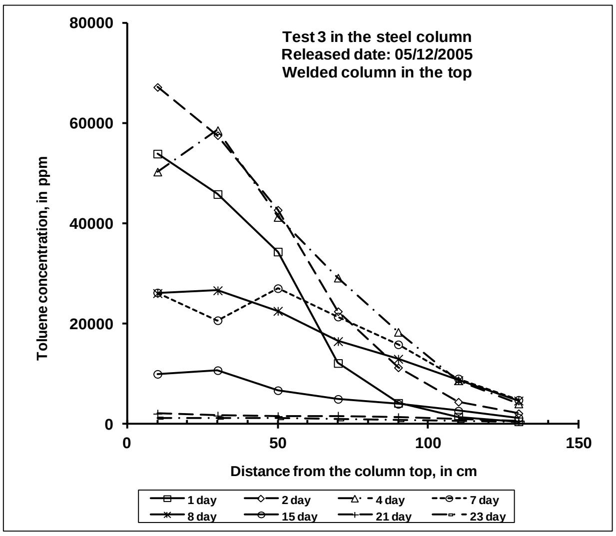

Figure 6. Experimental release with column welded at the top (Test 3).

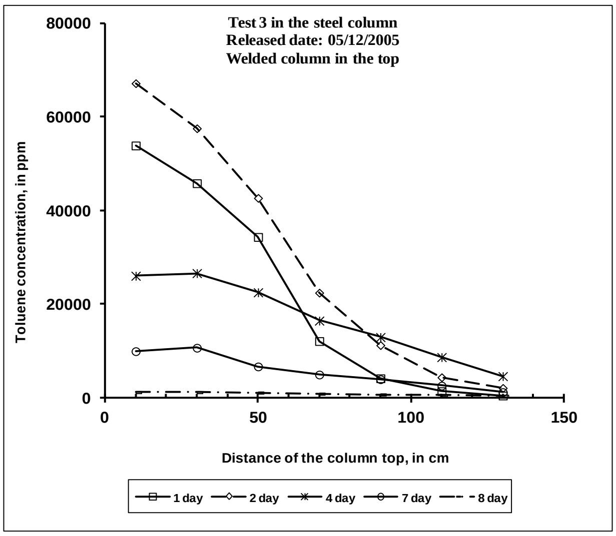

Figure 7. Experimental release with column welded at the top (Test 3).

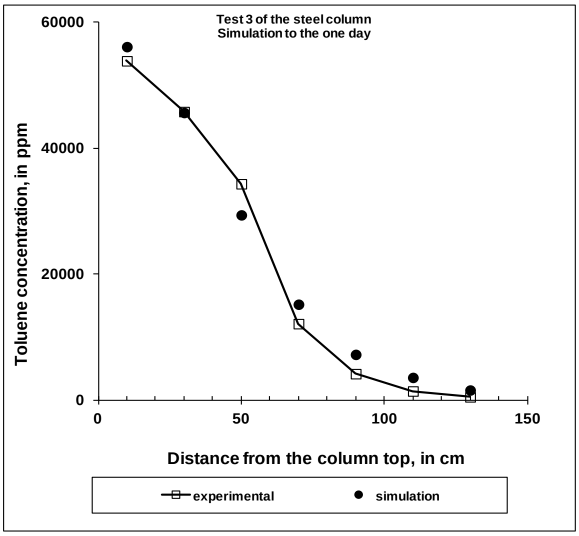

Figure 8. Simulation for the one day time period to the test 3.

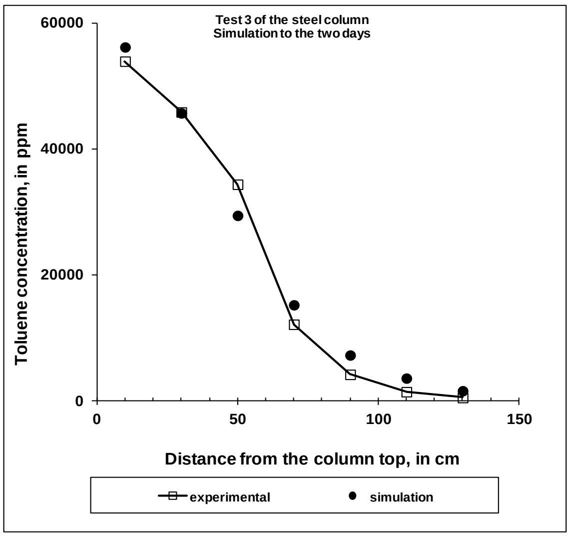

Figure 9. Simulation for the 2 days time period for the test 3.

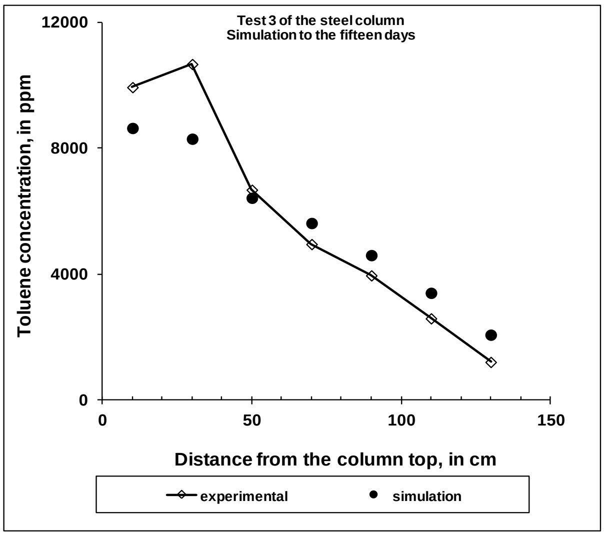

Figure 10. Simulation for the 15 days time period for the test 3.

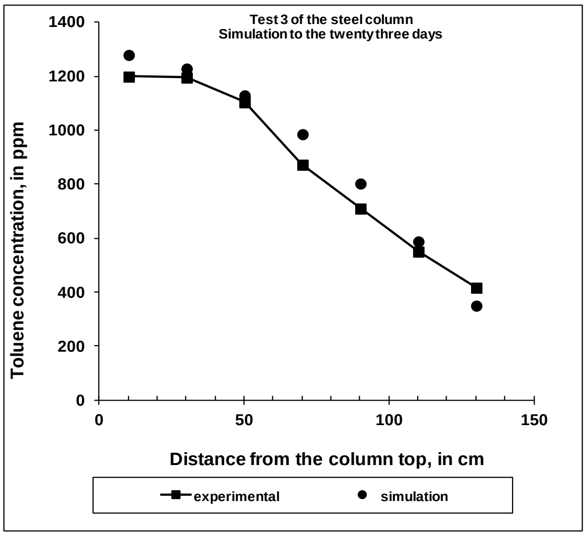

Figure 11. Simulation for the 23 days time period for the test 3.

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

1 **Statistical parameter**	2 **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. NOMENCLATURE

C_i = concentration of the component "i";
D = diffusion coefficient;
K = coefficient of the distribution;
L = length of the column;
t = time;
z = vertical distance from the top of the column;
α = the parameter of the distribution of the compound in the soil phases of air, water and soil:
θ = soil porosity or fraction of pore volume;
ρ = density;

Subscripts:
ar = air phase.
E = effective;
in = initial;
o = non-aqueous phase liquid (NAPL) or oil;
re = initial release;
s = soil;
to = total;
w = water phase;

8. REFERENCES

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9. RESPONSIBILITY NOTICE

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