

Lysimeter gneissic residual soil constructed and instrumented *in situ* to evaluation of biodegradation of benzene and toluene

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ABSTRACT

Accidents related to the production, storage and transportation of oil can lead to environmental contamination by hydrocarbons. The aromatics hydrocarbons (BTEX) present in the gasoline in contact with the soil water to partially dissolve contaminants being the first to reach the water table. Research indicates biological degradation as the main mechanism for minimizing the toxic characteristics of these pollutants. Given the paucity of studies *in situ* residual soils to evaluate the behavior of BTEX, this study aimed at developing a methodology for the construction, instrumentation and monitoring of a large rectangular block of undisturbed gneissic residual soil, for application of contaminant flow to assess the biodegradation of compounds of the BTEX group. Based on the satisfactory operation of the experiment, applied the horizontal flow of a contaminant solution composed of water, benzene and toluene, to evaluate the biodegradation of these compounds, along the time. The experiment was monitored for a period of 85 days and the determination of the concentration of benzene and toluene in the samples of solution collected from pre-established monitoring points in the block was made by the technique of gas chromatography. In the results of this analysis observed a decay in the concentrations of the compounds over time. The results indicate the occurrence of biodegradation of compounds benzene and toluene. This experiment can be proposed to evaluate the biodegradation of compounds in this soil type.

PRESENTACIONES TÉCNICAS

Accidentes relacionados con la producción, almacenamiento y transporte de petróleo puede llevar a la contaminación ambiental por hidrocarburos. Los hidrocarburos aromáticos (BTEX) presente en la gasolina en contacto con el agua del suelo para disolver parcialmente los contaminantes es el primero en llegar a la napa freática. La investigación indica la degradación biológica como el principal mecanismo para reducir al mínimo las características tóxicas de estos contaminantes. Dada la escasez de estudios *in situ* suelos residuales para evaluar el comportamiento de los BTEX, este estudio tiene como objetivo desarrollar una metodología para la construcción, instrumentación y seguimiento de un gran bloque rectangular de inalteradas de suelo residual gnéissicas, para la aplicación de flujo de contaminantes para evaluar la biodegradación de los compuestos del grupo BTEX. Basado en el buen funcionamiento del experimento, Aplicada que el flujo horizontal de una solución contaminante compuesto de agua, el benceno y el tolueno, para evaluar la biodegradación de estos compuestos, a lo largo del tiempo. El experimento fue supervisado por un período de 85 días y la determinación de la concentración de benceno y tolueno en las muestras de la solución recogida de los puntos de control pre-establecidos en el bloque se realizó mediante la técnica de cromatografía de gases. En los resultados de este análisis se observó una decadencia en las concentraciones de los compuestos a través del tiempo. Los resultados indican la ocurrencia de biodegradación de los compuestos de benceno y tolueno. Este experimento puede ser propuesto para evaluar la biodegradación de los compuestos de este tipo de suelo.

1 INTRODUCTION

From the oil crisis in the 70's, Brazil experienced a strong economic development and industrialization, which required large structuring of the entire productive chain of oil products from new discoveries of oil fields and the formation of several petrochemical poles, until the increase in distribution networks.

Faced with all this structure in the production logistics and marketing the oil industries live daily with environmental accidents caused by leaks and spills, and those that occur during the exploration, refining,

transportation and operations of oil storage and its derivatives (Corseuil & Marins, 1997; Silva, 2002).

The BTEX (benzene, toluene, ethylbenzene and xylenes) hydrocarbons present in gasoline, have increased mobility in water, because they are the most water soluble compounds from oil. According to Finotti et al. (2001), benzene is the most toxic and the presence of toluene at high concentrations may be toxic to microorganisms, making it difficult to biodegradation. Thus, in a possible leakage of gasoline, these compounds will be the first to percolate through the soil

and reach the water table or aquifer (Corseuil et al., 2004).

For removal of dissolved hydrocarbons in groundwater and soil has been used in a great range of techniques (natural attenuation, and bioventilation etc.). However, the natural attenuation has been noted for its efficiency and low cost. This technique is based on monitoring the decontamination of the environment by natural environmental factors (diffusion, dispersion, volatilization, sorption, biodegradation and chemical reactions) due to physical, chemical and biological agents. Among these factors, biodegradation reduces the mass of contaminant by degradation of organic compounds through the metabolism of living organisms, turning them into harmless compounds to health and, consequently, limiting the transport of petroleum hydrocarbons to groundwater (Corseuil & Alvarez, 1996; Fetter, 1993; Wiedemeier, 1996, Jacques et al. 2007; Mazzuco, 2004).

The biological activity is able to mineralize or biotransform organic compounds contaminants. Biotransformation consists on the partial degradation of compounds in one or more compounds that may or may not be less toxic than the original substance. While the mineralization represents the complete degradation of organic molecules on inorganic substances like carbon dioxide (CO₂) and water (Smith, 2002, Jacques et al. 2007; Corseuil & Marins, 1997).

The degradation of soil contaminants by microorganisms occurs if there are soil microorganisms degrading these pollutants, if the amount of pollutant is not toxic to the microbial population, if the environment is not overly acidic or alkaline, if moisture is adequate and if there are available nutrients (Mariano, 2006). Therefore, depending on the amount of microorganisms in the soil and the type of pollutant, biological activity may be important in detaining the transport of pollutants. Thus, bioremediation technique has been widely studied and used as a strategic mechanism of transformation of toxic organic compounds (eg. benzene and toluene) in less toxic products or in its disposal from the soil and aquifers.

Laboratory studies have reported the effects of various environmental factors on the biodegradation of BTEX compounds. However, most of these studies have been conducted in laboratory microreactor as microcosms and soil columns (Allayla & Mohammed, 2000).

As the field conditions can not be reproduced fully in the laboratory, especially microbial activity, it is important to carry out tests *in situ*. Thus, according to Vicente (2009), a large number of field studies for assessing the contamination of soil and groundwater by petroleum products have been developed in the Northern Hemisphere (Borden, Ontario, Canada; Cape Cod, Massachusetts, United States) and also on the Ressacada Farm (Santa Catarina, Brazil). But in all cases, the soils are sandy. The processes in tropical soils, particularly in residual soils found in Brazil, are less known, a situation that has special importance since these soils have different properties and characteristics.

Given the above, the goal of this research was to develop a methodology for construction, instrumentation and monitoring of a large lysimeter of gneissic residual soil, *in situ*, and to evaluate the occurrence of biodegradation of benzene and toluene compounds present in gasoline by analysis of gas chromatography.

2 METHODOLOGY

The experiment of this work was shown at the Experimental Geotechnics Field, at the Universidade Federal de Viçosa's campus.

2.1 Materials

The specimen used in the experiment consists of a residual soil, the highest percentage granulometric corresponds to the clay particle size, originated from gneissic rock, present in C pedological horizon, having been classified according to the Unified System of Classification (USC) as an inorganic clay very plastic .

The Table 1 presents the main results of chemical analysis and physical-chemical properties. It can be observed a low percentage of organic matter, acid pH and low effective cation exchange capacity, a characteristic usually found in most weathered soils.

Table 1. Main parameters of the physical, chemical and physicochemical characterization.

n ¹	e ²	k ³ (m.s ⁻¹)	MO ⁴ (%)	pH ⁵ (H ₂ O)	CTC _t ⁶
0,5	1,2	3,78E-06	0,64	5,29	1,05

¹ porosity; ² void ratio; ³ saturated hydraulic conductivity; ⁴ organic matter content; ⁵ effective cation exchange capacity.

According to the mineralogical evaluation, the clay soil was defined as being composed of kaolinite and gibbsite (and small amount of goethite).

The microbiology activity of soil is low.

In the experiment we used an aqueous solution prepared from the mixture of compounds benzene and toluene.

2.2 Methods

2.2.1 Constructive process of lysimeter

In 2009, in a covered area of approximately 30 m² located in the experimental field, a block of undisturbed soil was scooped up to be used in research related to the transport of contaminants *in situ*, in particular, the assessment of the degradation of organic compounds benzene and toluene existent in gasoline, in this type of soil (Figure 1).

It was established the following dimensions for lysimeter: 1.5 m of length, 0.60 m of height and 1 m of width. For the tanks were defined 1 m of length, 0.35 m of width and 0.60 m of tall.



Figure 1. Covered area for excavation of the lysimeter.

After the definition of constructive processes and instrumentation of the lysimeter, it was developed the executive project of the test, through the design tool

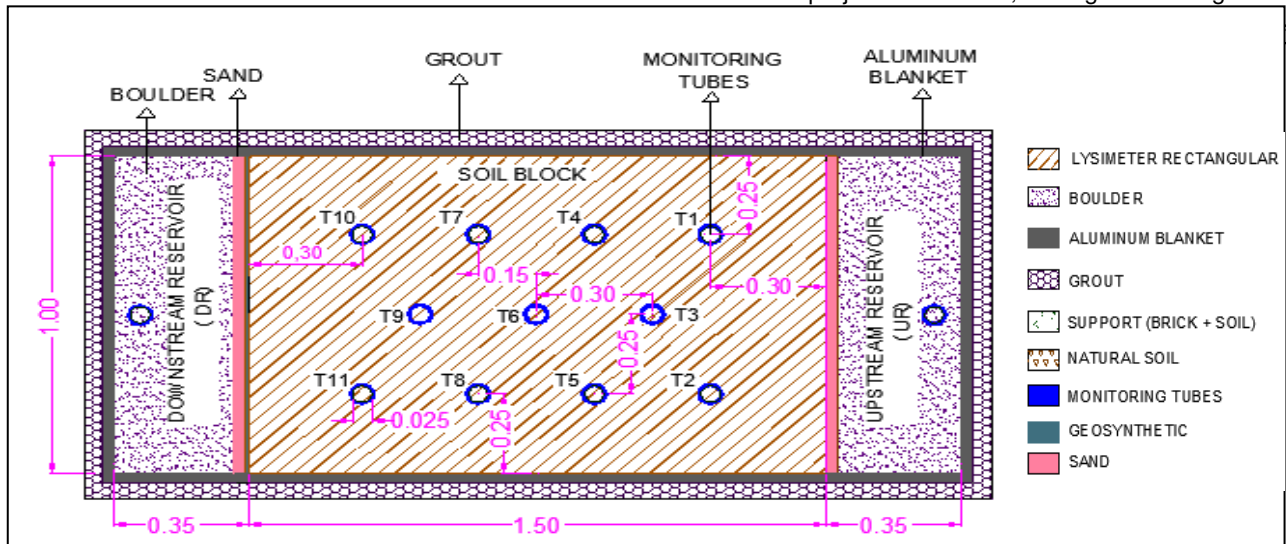


Figure 2. Plan view of the arrangement of tubes in the block and the reservoirs upstream and downstream.

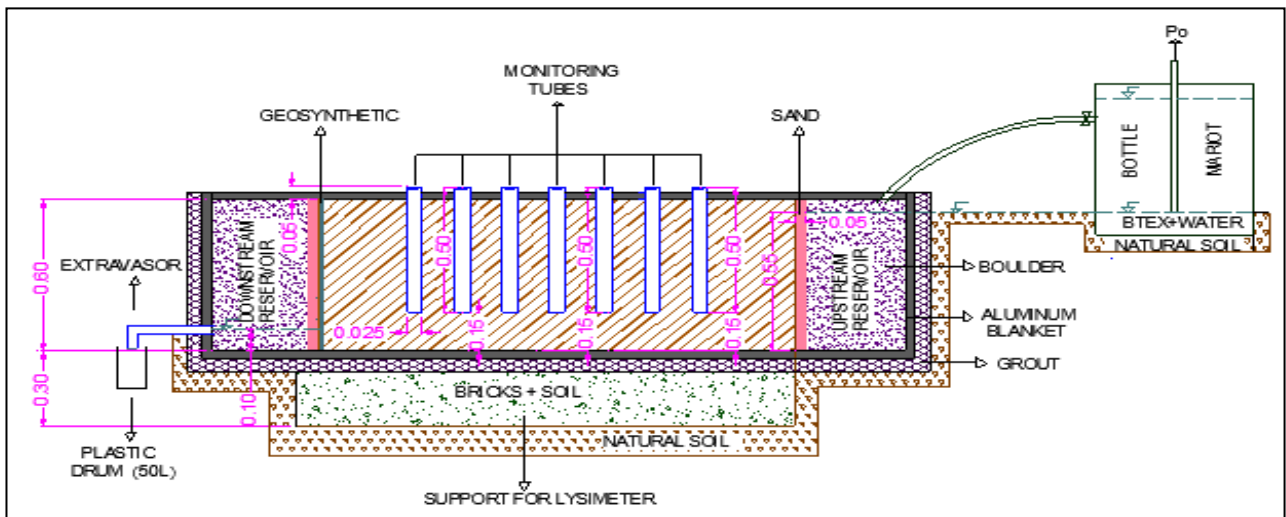


Figure 3. Longitudinal section showing the arrangement of tubes, the tanks and the Mariot bottle.

Initially, it ran up the excavation of the longitudinal laterals and of the base (Figure 4a), which was anchored with bricks and soil. Then, the lysimeter was involved with paraffin to retain its natural moisture. In Figure 4b it is possible to distinguish the materials used in the base.

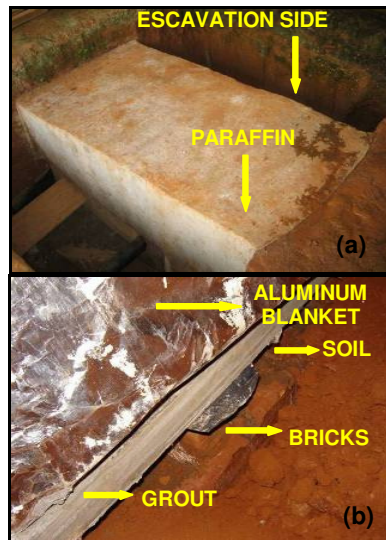


Figure 4. (a) Excavations on the sides and involvement of the block with paraffin; (b) Provision of materials used in shoring the base of the block.

The reservoirs were excavated at 0.65 m of height, 1.0 m of width and 0.35 m of length. This required the excavating 0.5 m of the block whose length resulted in a 1.50 m. In the Figure 5a it is possible to view the excavated area in order to place the reservoirs and the block wrapped with a blanket of aluminum. Then it ran up the cementation of the sides and the reservoirs, with the construction of a box in the shape of the block with 0.10 m of thickness (Figure 5b). The grout is a cementitious mass that has the property to be self compacting. Knowing that the cement could come to adsorb the hydrocarbons after contamination, the blanket of aluminum was used to prevent contact between the grout and soil.

After a week, it withdrew from the wooden forms and compacted soil to the sides to shore up the walls without reinforcement grouting, already dry, which took no armor. Also, to avoid possible preferential flow along side the contact soil-blanket aluminum, soil and bentonite were compacted in two bands of 0.10 m in width along the length of the block, as shown in Figure 5c. In the Figure 5d is an overview of the block made.

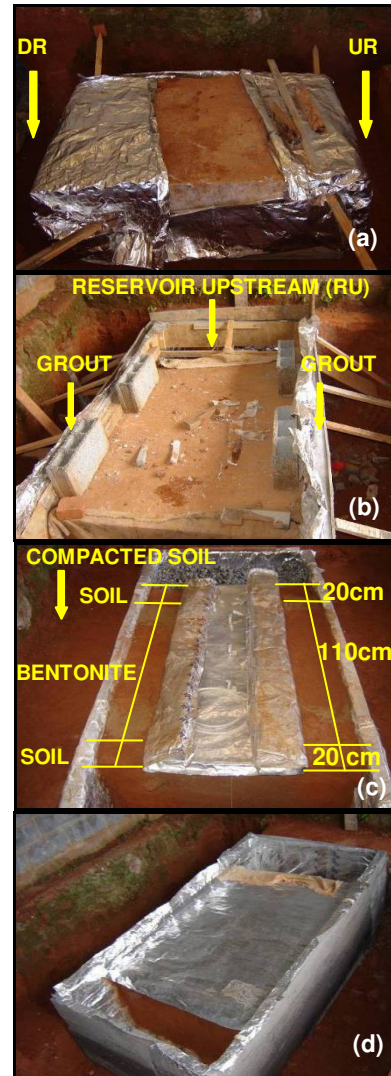


Figure 5. (a) Location of the reservoirs; (b) Groutement side of the block and the reservoirs; (c) Compaction of soil and bentonite; (d) Overview of the block.

All stages of construction, excavation, involving the lysimeter with a blanket of aluminum, cementation and shoring the base of the lysimeter were conducted with the concern to try to prevent the possible appearance of cracks in the soil.

Thereafter, the upstream and downstream reservoirs were filled with granular materials to prevent the disintegration of the block face in contact with the reservoirs due to moisture. In addition, a layer of sand was added to prevent soil clogging by gravel and a blanket of geosynthetic had the function to preventing the drift of solid particles into the downstream reservoir, as shown in the Figure 6.

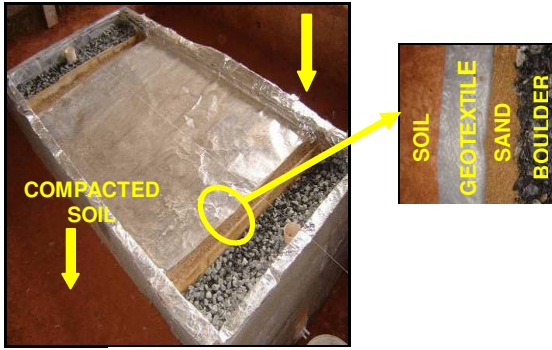


Figura 6. Reservoir filled with granular materials.
2.2.2 Monitoring tubes

✓ Confection

Eleven monitoring tubes in aluminum were manufactured. The tubes had an inch of diameter and fifty centimeters of length, and were installed along the lysimeter length, 0.15 m from the base of the block (Figure 7). Each one had a screw cap and a rubber ring attached to an aluminum bat, to make it possible to control the entry of the solution into the tube. Once opened, the solution entered the tube, passing through an aluminum screen on the base to prevent the access of solid particles. The removal of the tube solution was through a hose inserted through a small hole in the lid. Just the opening of the small hole minimized the volatilization of the compounds during sampling. Figure 8 shows the details of the aluminum pipe.

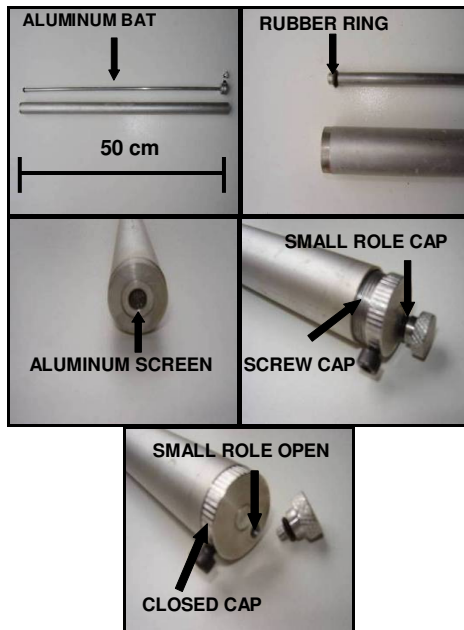


Figure 7. Details of the aluminum tubes.

✓ Installation

A metal auger with 0.7 m long and an inch in diameter

was made for the drilling of the points where the pipes were installed, positioned in the block as shown in Figure 2. The alignment of the holes was performed with a measuring tape and nylon lines, positioned perpendicular to the surface of the block. With the auger in a vertical position, each hole was performed and monitoring tubes were set up. Figure 8 illustrates the process of drilling and installation of pipes.

To maintain the level of contaminant solution contained in the upstream reservoir, it was settled a sealed stainless steel container with a capacity of 50 liters, to function as a Mariot bottle. This bottle was connected to the reservoir of amount by a silicone hose, as is presented in Figure 9. In the same figure it is possible to view the extravasor aluminum, positioned 0.10 m above the base of the downstream reservoir, a drum installed to receive the effluent coming from the extravasor; and the receiver tube of aluminum contaminant solution, positioned at 0,55 m from the base of the reservoir upstream.

The wastewater generated daily by the percolation of the contaminant solution in the lysimeter were stored in the drum, installed downstream and removed with the aid of a vacuum pump. This material was placed in canisters and then poured into a kind of small land farming.

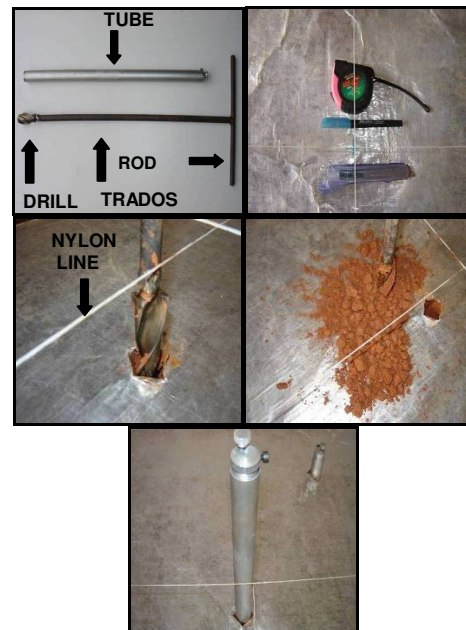


Figure 8. Drilling and installation of monitoring tubes.

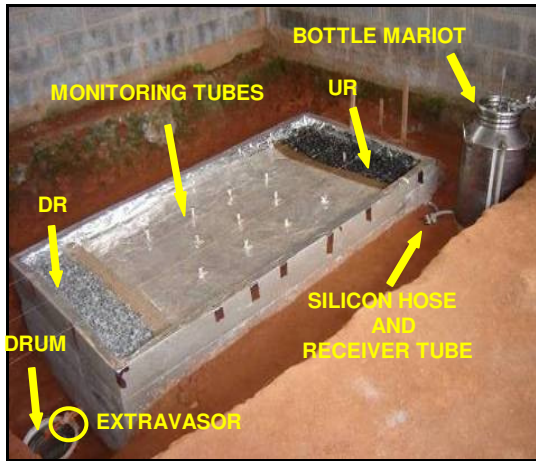


Figure 9. General aspect of the experiment.

2.2.3 Contaminant solution

It was used an aqueous solution prepared from a mixture of benzene and toluene with water from an artesian well located on the campus of UFV. The concentration of

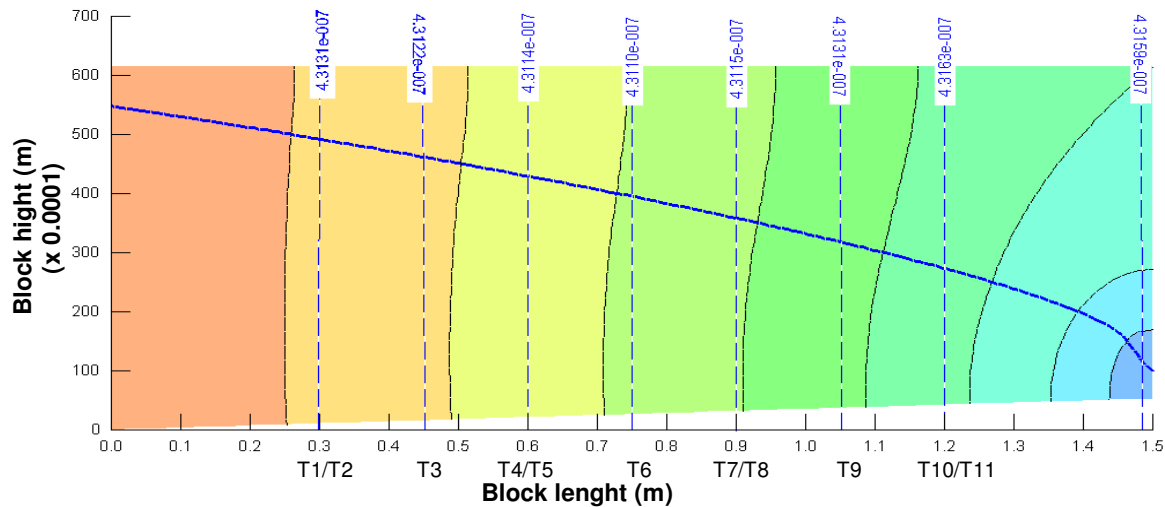


Figure 10. Position of the phreatic line and flow in different sections of pipe installation.

3.2 Analysis by gas chromatography

The process of soil contamination began on 01/09/2009. In the Figure 11 graphs, each point on the curve corresponds to a sampling day after contamination, namely: 7th; 21th; 28th, 35th, 49th; 56th, 70th and 84th days.

Based on the chromatographic analysis of gaseous phase (headspace) of contaminated effluents, it could be determined the concentrations of the compounds, benzene and toluene. Thus, it was possible to assess by means of graphs, the decreasing trend in concentrations throughout the test.

It is observed in Figures 11b and 11o that there was no trend in declining the concentration of the

each compound was set at 500 ppm. The solution was prepared daily and added to the experiment.

3 RESULTS AND DISCUSSION

3.1 Numerical simulation

We performed a numerical simulation using the computer program SEEP / W GeoSlope to predict the position of the phreatic line and the flow of water in the block. The dimensions of the longitudinal section of the block, the parameters of the water retention curve, the coefficient of permeability of saturated soil and the constant levels of water in reservoirs and downstream were provided as input data for the program. The numerically determined average flow was $4.31 \text{ E-}07 \text{ m}^3 \text{ s-}1$ (37 liters per day), while in the field, this value was $5.2 \text{ E-}07 \text{ m}^3 \text{ s-}1$ (45 liters per day). The difference between the values found can be attributed to some possible heterogeneity in the soil. In the Figure 10 there is the position of the phreatic line and the flow in different sections of pipe installation provided by the monitoring program.

compounds in the reservoirs upstream and downstream. As these reservoirs were filled with granular materials (sand and gravel), it was not expected to retain considerable amounts of the compounds studied, besides the low microbial activity.

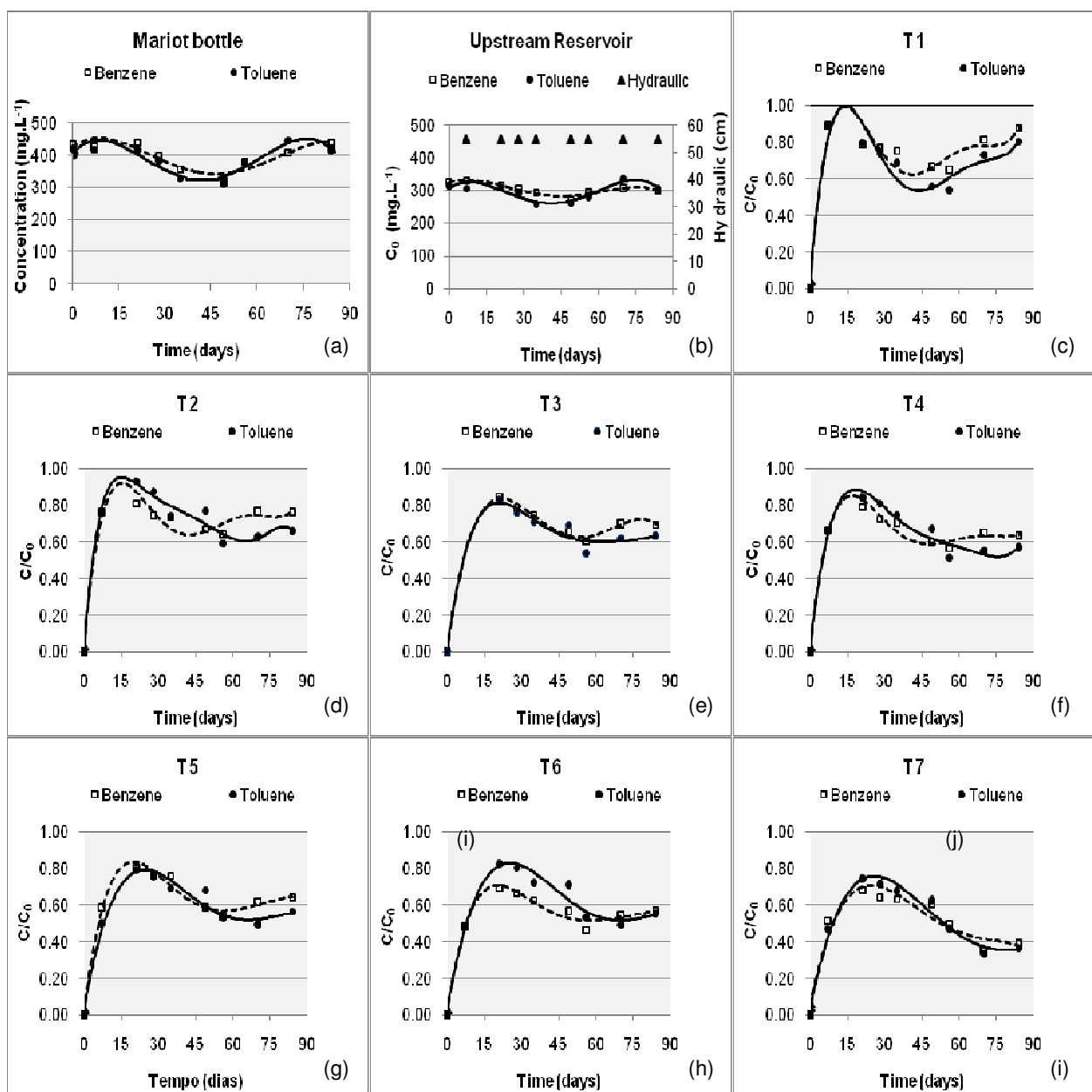
In general, it is observed in Figure 11 that after 21 days of contamination, the concentration of the compounds decreased over time in samples of all monitoring tubes, a demeanor that can be attributed to biodegradation. It is observed also a tendency to constancy of the concentration of the compounds from the 75th day, which was already provided in a situation where the source is continuous. According to the kinetic model of Monod (1949) there is a maximum rate of substrate utilization by microorganisms, from

which no longer occurs as the use of this energy source. It is also possible that the soil has reached its maximum holding capacity of the compounds.

Still, according to the graphs of Figure 11, the concentrations of benzene and toluene showed similar behavior over time. In most cases, the concentration of benzene was slightly lower than of toluene. The preferential degradation of benzene can be related to the fact that it is the compound with higher solubility and, therefore, more bioavailable to microbial attack. From the 49th day, however, there is a sharper drop in the degradation of toluene. Da Silva and Alvarez (2004) suggest that, under anaerobic conditions, this compound is preferentially degraded and that its presence inhibits the degradation of benzene.

The analysis by gas chromatography in the contaminated soil was performed only once, after 85 days of contamination. The results demonstrate that on the extraction it occurred retention of compounds in the soil by chemical processes. The results also indicate that benzene showed higher affinity with the soil.

The retention of compounds through the the soil enables the approach among soil bacteria and contaminants. However, higher concentrations of the compound retained by the soil may indicate greater difficulty of this compound to be degraded, as is the case of benzene relative to toluene.



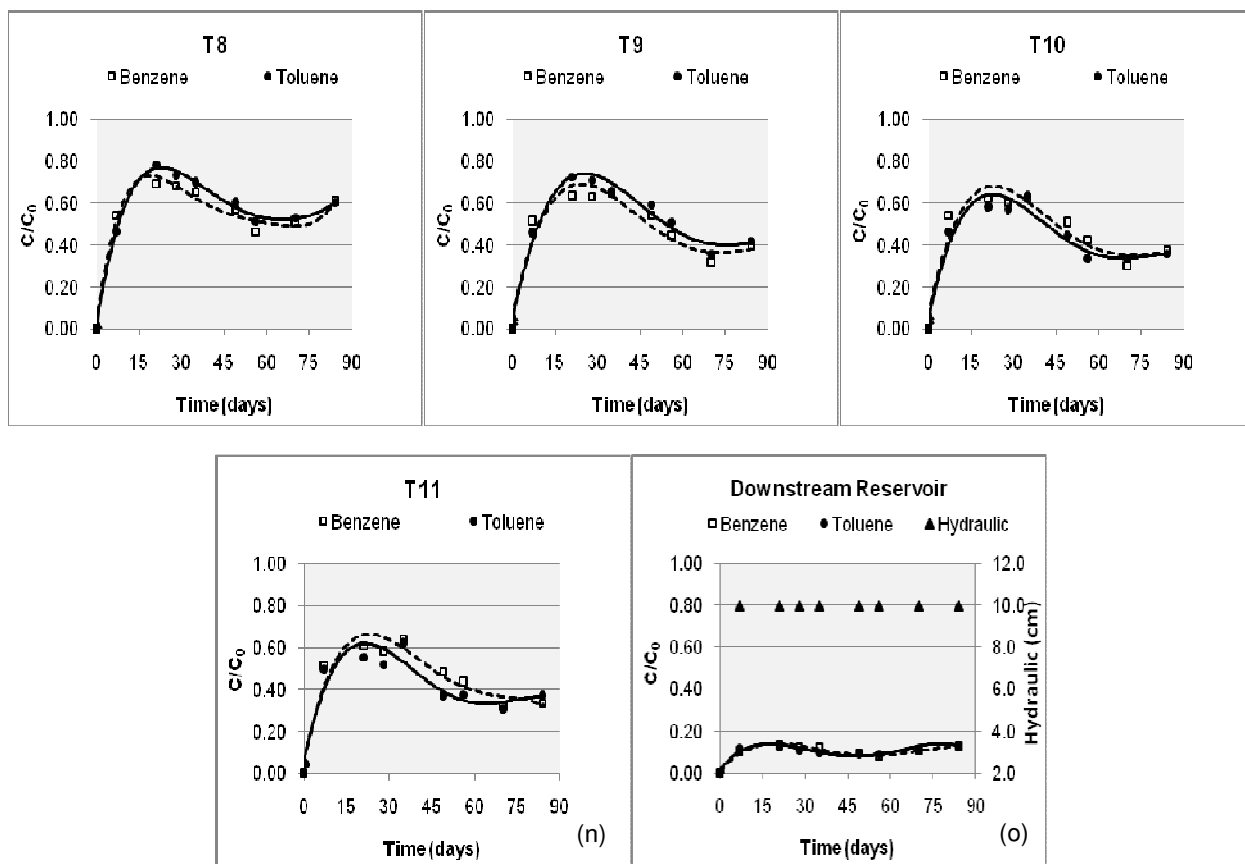


Figure 11. Graphs of the relative concentrations of benzene and toluene and hydraulic load for each monitoring point over time: (a) Mariot bottle, (b) upstream reservoir; (c) T1; (d) T2; (e) T3; (f) T4; (g) T5; (h) T6; (i) T7; (j) T8; (l) T9; (m) T10; (n) T11 e (o) downstream reservoir.

4 CONCLUSIONS

Some difficulties were encountered in the construction and instrumentation of the block of undisturbed residual soil. Among them, those considered most relevant were the construction of the cement "box" around the edge of the block and the reduction of preferential flow along side of the block in contact soil / blanket, through the compaction of bentonite.

Regarding the mounting of the experiment and analysis, it is believed they are relevant to the following observations:

- ✓ The methodology used in the excavation process and instrumentation of the pack *in situ* showed to be satisfactory.
- ✓ The compaction of bentonite on two tracks along the length of the block contributed to the substantial reduction of preferential flow.
- ✓ The aluminum tubes functioned as expected.
- ✓ The filter used in the base prevented the entry of solid particles in the samples.
- ✓ The decay profiles of the compounds benzene and toluene occurred similarly.
- ✓ The decay in the concentrations of benzene and toluene in contaminated water checked by gas chromatography analysis indicated the occurrence of biodegradation.

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