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**MODELING AND SIMULATION FOR VOCs EXTRACTION BY AN
SVE SYSTEM**

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Dedicated to my Parents:

Marisela

And

Fermín

For always being a guidance in my life. Thank you for all your love and support through easy and very difficult times.

With respect and love for you.

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To my Grandparents, for your unconditional love and support.

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ABSTRACT

Volatile organic compounds (VOCs) are highly toxic substances and it has been demonstrated that they can be found in the atmosphere and soil, producing adverse health effects in human beings. Throughout many years, some soil remediation technologies have been developed. Soil vapor extraction (SVE) is the one being used nowadays for VOCs removal of the unsaturated or vadose zone from soil. This technique is low cost and efficient, although if a good system design is not done, the success of the technique is jeopardized. Models and simulations have been developed as tools that will help provide enough information to a better understanding of the process. Moreover it will enable the possibility of evaluation of contaminant degradation and feasibility of the technique in a hypothetical site under certain characteristics. This paper intends to develop a simulation exercise of the SVE process using a mathematical model, evaluate the feasibility of such model and the extraction of vapors from soil matrix. This was accomplished under certain restrictions and considerations in an approximately 30 days of an SVE operating system.

Key words: *Soil vapor extraction, unsaturated zone, volatile organic compounds, mathematical model, simulation.*

RESUMEN

Los compuestos orgánicos volátiles (COV) son sustancias altamente tóxicas y se ha demostrado que se puede encontrar en la atmósfera y el suelo, produciendo efectos adversos a la salud de seres humanos. A lo largo de muchos años, algunas tecnologías de remediación del suelo se han desarrollado, la extracción de vapores del suelo (EVS) es la que se utiliza en la actualidad para la eliminación de compuestos orgánicos volátiles de la zona no saturada o zona vadosa del suelo. Esta técnica es de bajo costo y eficiente, aunque si el sistema no es bien diseñado, el éxito de la técnica está en peligro. Modelos y simulaciones se han desarrollado como herramientas que ayudarán a proporcionar información suficiente para una mejor comprensión del proceso. Por otra parte, permitirá la posibilidad de evaluar la degradación de contaminantes y la viabilidad de la técnica en un caso hipotético bajo ciertas características. Este trabajo se propone desarrollar un ejercicio de simulación del proceso de extracción de vapores del suelo mediante un modelo matemático, evaluar la viabilidad de este modelo y la extracción de vapores de una matriz de suelo. Esto se logró, con determinadas limitaciones y consideraciones en un aproximado de 30 días de un sistema operativo SVE.

Palabras clave: *extracción de vapores del suelo, zona no saturada, compuestos orgánicos volátiles, modelo matemático, simulación*

Zusammenfassung

Flüchtige organische Verbindungen (VOC) sind sehr giftige Stoffe, die in der Atmosphäre und im Boden gefunden werden können. Es ist bekannt, dass VOCs Gesundheitsschäden beim Menschen hervorrufen. Im Laufe der Zeit haben sich unterschiedliche Bodensanierungsmethoden entwickelt. Heutzutage wird die Methodik der Bodenluftabsaugung (SVE) für die Entfernung von VOC aus der ungesättigten oder gesättigten Bodenzone verwendet. Diese Technik ist kostengünstig und effizient, jedoch muss der Systemaufbau angemessen durchgeführt werden, um den Erfolg der Technik zu gewährleisten. Um genügend Informationen zu liefern und um ein besseres Verständnis zu ermöglichen, wurden spezielle Modelle und Simulationen als Hilfswerkzeuge entwickelt. Unter bestimmten Eigenschaften werden darüber hinaus die Bewertung des Schadstoffabbaus und die Umsetzbarkeit der Technik in einer hypothetischen Annahme ermöglicht. In dieser Arbeit wird mit Hilfe eines mathematischen Modells ein Simulationsmodell für den SVE Prozess entwickelt. Außerdem wird die Durchführung eines solchen Modells, sowie die Gewinnung von Dämpfen aus der Bodenmatrix bewertet. Unter festgelegten Einschränkungen und Berücksichtigungen wird dies bei Durchführung des SVE-Betriebssystems in ungefähr 30 Tagen erreicht.

Stichworte: *Bodenluftabsaugung, ungesättigte Zone, flüchtige organische Verbindungen, mathematisches Modell, Simulation*

1. INTRODUCTION

1.1 Thesis Structure

This text is divided into chapters. The first one is the Introduction, where you can find background information and general information about the topic. Thus, the main reason of why this research has been done and a hypothesis, which it is intended to be proved or neglected. The objectives, divided into general and specific.

Chapter 2 includes general concepts, which are needed to have a foundation and develop a better understanding of some processes. A summary of the remediation techniques can be found, what is a volatile organic compound and their physical and chemical properties. Some important soil properties, the concept of unsaturated zone and the contaminant transport mechanisms that are taken place in that zone.

Chapter 3 contains more detailed information regarding the soil vapor extraction technique.

Chapter 4 is about some concepts about modeling and simulation, including a table with available commercial software's that can be used for simulating different processes and the technique.

Chapter 5, include general information regarding numerical methods,

Chapter 6, 7 and 8, is the detailed information from where the simulation exercise was done, conclusions and recommendations regarding the same topic.

Finally the references, a list of tables and figures are shown at the last part of the work.

1.2 Background

Natural resources exploitation has been an activity done for thousands of years now. This was since humans have noticed that their necessities can be very much fulfilled by nature. Natural resources have been continuously depredated and degraded in large scale and the situation has not stopped at all in the last century. Such disturbances have seriously damage both, biotic and abiotic resources mostly due to anthropogenic factors. It is important to notice that the damages are definitively not in the same scale but rather important to the living and natural conditions of any ecosystem. In addition to, human health can be harmed by these factors.

In last years oil derivates have been playing the main role of providing humans with goods or resources that improves life quality, such as energy and synthetic products. On the other hand a high dependence has been developed around this not renewable resource and it was not until recent years that has been realized the consequences of using and processing this material. Pollution caused by oil and its derivates is not only observed in oil producer countries since the later use of the compounds generates it as well. This means that contamination is an everyday issue worldwide.

Production and usage of pesticides, paints, gasoline, dissolvent among some other factors may provoke soil and groundwater contamination; but the main reason is due to hydrocarbon leakages coming from underground storage tanks (Galán Huertos, et al, 2003). These spills may occur by accident or deliberately, by failures or deficient processes, and either human or technical faults. According to the Environmental Protection Agency (EPA) in the United States by 1993 more than 10% or 295.000 underground storage tanks have had leakages (US Army Corps of Engineers, 2002). Table 1 shows some industries that because of their processes and products may generate soil and groundwater pollution.

Asbestos	Chemical products and derivatives	Explosives	Fabrics and gas storage	Metallurgies
Oil production and storage	Pesticides production	Pharmaceutical products	Solid residues treatment	Petrochemical industry
Paints	Polymers and coverings	Smelting	Industrial dumps	Mining and extractive industries

Table 1.1 Contaminant Industries. Source. (Galán Huertos, et al, 2003)

Every raw material used and every generated product by any of these industries has got in its chemical structure organic compounds, which can be among some others volatile or semi volatile, this is according to its physical properties. These have been demonstrated (by different studies) to be health harmful.

Volatile Organic Compounds (VOCs), are components of petroleum fuels, such as gasoline, paints, etc and can frequently be found in soil and groundwater as pollutants (USGS-U.S. Geological Survey., 2007) It is mentioned by EPA that several of them are currently known to cause cancer in humans, but the health effects may vary according to every compound. This means that each one of them has different toxicity levels and the repercussions can go from a simple headache to no observed effect at all (US EPA, 2009).

In order to extract these compounds from soil different techniques might be used, but the most effective and commonly applied one for this specific situation is the Soil Vapor Extraction (SVE) also called according to Pedersen and Curtis as vacuum extraction, in situ vaporization or soil venting (Pedersen, et al, 1991). The SVE is a technique used to remove VOCs from the unsaturated zone from soil in the most efficient and not expensive way (US Army Corps of Engineers, 2002). This technique basically works by extracting the vapors from the unsaturated zone and in order to obtain better results it can also be induced air flow in order to promote the volatilization of the contaminant. After the contaminant is been extracted an off gas treatment is needed before releasing the vapors to the atmosphere. This technique has also limitations or disadvantages, for example it is not capable of cleaning up some semi volatile organic compounds, the fact that an off gas treatment may be used implies extra costs, it only works in unsaturated soils, etc. Moreover this technique as some many others requires an adequate design of the system to enhance a successful performance.

Modeling is a useful tool that will help predict the performance and feasibility of the technique (David L. Jordan, 1995). Diverse models have been developed by various

authors such as Johnson, Mansour, Falta, Benson among some others. Each of them have different approaches, some are used as screening tools to be able to determine if the technique is a viable solution, others as flow and transport models that will help in the design of the system and evaluate its performance (Paul C. Johnson). Also Geographical Information Systems (GIS) may be another very useful tool, it can be able to provide graphic information to a better understanding of the process. One of its characteristic is that the data can be integrated as a whole and be visualized in various forms, this way will help with the decision making process, in this case whether or not make use of the SVE technique (Environmental Systems Research Institute, Inc. (ESRI)).

Worldwide this technique has been pretty much applied. Just an example of its application, in the United States at the North Fire Training Area (NFTA) Luke AFB, Arizona the application of SVE was needed for the cleanup of two fire training pits. The place was polluted with various hydrocarbons, including benzene, toluene, xylene, ethylbenzene (BTEX) and methyl ethyl ketone (MEK) since 1973. Years later between 1981 and 1989 it was determined this pollution. After establishing the cleanup goals the remediation began in October 1991 until December 1992. In total 12,000lbs were cleaned up in a period of 30 weeks of operation. The removal rate was 40lbs/day; one extraction well was constructed in each pit with 35 foot screen to depths up to 57 feet. Finally a thermal oxidizer was used as an off gas treatment of the extracted vapors. By November 1992 samples were taken at the site and demonstrated that contaminants were removed from the site (US EPA, 1995).

In order to enhance the understanding of the techniques performance and evaluate its feasibility, further research is needed to be done, in areas such as modeling, which so far it has been demonstrated that is a valuable tool before applying this procedure.

1.3 Justification

The actual situation regarding to contamination in close relation to hydrocarbon spills or leakage is more alarming, reflected in shocking environmental consequences. Finally environmental liabilities are generated, which are translated in a danger to the biota and surrounding populations.

Based on the previous context and in the need to understand better and evaluate the feasibility of the usage of simulation in order to predict the extraction of a certain contaminants by SVE technique, programs and simulations have been developed. All this with the use of mathematical models and its simulation will provide enough information to a better understanding of the process. Moreover it will enable the possibility of evaluation of contaminant degradation and feasibility of the technique in a hypothetical site under certain characteristics.

1.4 Hypothesis

Using mathematical modeling and simulation, it is possible to predict and evaluate contaminant degradation under certain conditions during the application of a soil vapor extraction (SVE) operating system.

1.5 Objectives

1.5.1 General

Develop a simulation exercise of the process using a mathematical model in order to evaluate contaminant degradation by the use of such predicting tools for an SVE operating system in VOCs contaminated soils.

1.5.2 Specific

- Development of a mathematical model, taking into account operational conditions, soil and contaminant characteristics.
- Simulation exercise making use of the mathematical model.
- Evaluation of the system performance.

2. GENERAL CONCEPTS

2.1 Remediation techniques

According to the EPA, 2001, the treatment term, correspond to all operation or operations that modify the composition of a dangerous substance or contaminant by physico-chemical, thermal or biological actions in order to reduce the toxicity, mobility or volume of the contaminated material. The varieties of factors which will determine the success or not of the treatment are mention next.

According to the Environment Natural Resources and Fishing organism in Mexico (SEMARNAP, because of its initials in Spanish) in 1996, the toxic effects of hydrocarbons in the atmosphere and therefore the selection of the best remediation technology will depend on:

- The amount and composition of petroleum.
- The frequency and exposure time.
- The physical state of the spill.
- The characteristics of the site where the spill have happened.
- Environmental variables like temperature, humidity and oxygen.
- The use of dispersing chemicals (its use is restricted).
- The sensitivity of the specific biota of the impacted ecosystem.

Remediation technologies can be classified based on the place where the activity is being carried out (INE, 2007). This is In-situ and Ex- situ. The first term is related to the remediation activity that is being done in the same place or site which is polluted, without the need of removing or excavating. The second one is about the activity which needs excavating, dredging, removing or extracting the contaminated soil to be treated either in-site or off-site (CENAPRED/SEGOB). Each type of technology has its own disadvantages, it is certain that In-situ technology allows the treatment of the contaminated soil without having to excavate or to remove, but it is also true that the treatment requires of greater time and represents bigger difficulties of verification in the effectiveness of the treatment. With Ex-situ technology, happens just the opposite, it is required little treatment time, excavation and extraction of the contaminated soil to carry out the treatment (Volke Sepúlveda, et al, 2002).

Another classification is based on the type of treatment. They can be biological, thermal and physico-chemical (Volke Sepúlveda, et al, 2002). Properly speaking of

biological treatments, these make use of microorganisms that are naturally in soil or are added for natural attenuation or in the best scenario for the complete degradation of the polluting agent. The thermal treatment implies the elimination of the contaminant compound in the site by providing enough heat to destroy it. Finally, the physico-chemical techniques, use the physical and chemical features of the own polluting agent or the soil for their removal (CENAPRED/SEGOB) (Volke Sepúlveda, et al, 2002).

In relation to the physico-chemical treatments, according to the EPA, diverse types of technologies can be found to apply in dependence of the polluting agent that needs to be removed. The different technologies are:

- Chemical oxidation.
- Electrokinetic remediation.
- Bioventing.
- Soil washing
- Soil vapor extraction.
- Flushing.
- Solidification/Stabilization.
- Solvent extraction.

Chemical oxidation

Chemical oxidation is a remediation technique which makes use of adding (as its name says) chemical substances that can be able to oxidize organic contaminants present in soil and turn them into carbon dioxide or into compounds that can be easily degraded. According to Amarante in 2000, there are two ways to inject the chemical substance, the first one is near to the contaminated zone and with the groundwater extraction too or just injecting with no extraction. There are some oxidants that are more frequently used; just to mention some, ozone, hydrogen, permanganate, persulfate, among some others. The radical per sulfate is the most use, just because it is more stable than the other ones under different conditions, it reacts faster, etc. (Hamberg, 2009). This technique has got some limitations and it directly depends on some factors like the amount or level of contamination, the organic matter content and how the particles are distributed (Andreottola, et al, 2009).

Electrokinetic remediation

Electrokinetic remediation is an in situ technology which can remove metals and organic contaminants from soils with low permeability, mud, sludge and marine dredging (Federal Remediation Technologies Roundtable (FRTR)). This technology is based in passing direct current through the polluted soil, this way some contaminants will move toward a place where it can be removed (Sandia National Laboratories). The application of current help mobilize the charged species, this way ions and water will move to the electrodes and the positive charged compounds will move to the cathode. The organic compounds will move to the anode (FRTR).

There are two mechanisms which determine the transport of the contaminant towards either both electrodes; this is electromigration and electroosmosis (FRTR). The first one makes reference to the particles that are mobilized through the substrate, while in the other hand the electroosmosis regards to the transport of a liquid which contains ions to a stationary charged surface (FRTR). The path and velocity of mobilization of ionic species will highly depend on particle charge, in magnitude and polarity, on the other hand the non ionic species will also be transported with the electroosmosis induced water flow (Federal Remediation Technologies Roundtable (FRTR)).

Bioventing

This technique is based on the issue of bringing the microorganisms' enough oxygen for them to be able to biodegrade the contaminant (US Army Corps of Engineers, 2002). This technique does not represent very expensive costs, furthermore it has been used for 20 years now and it is commonly used for contaminated sites with hydrocarbons (Roudier).

The airflow is induced in the unsaturated zone, slow enough to allow contaminant residence time and not to permit volatilization losses out of the zone where the treatment is being done (US Army Corps of Engineers, 2002). The efficiency of this method can reach 90%, but it highly depends on the homogeneity of the soil and the agents in soil, also the biodegradation can be also limited by the need of some nutrients like nitrogen and phosphorous (Roudier).

This system consists in one or more extraction or injection wells, monitorized in the unsaturated zone, blowers or vacuum pumps and perhaps air injection or pressure venting wells (US Army Corps of Engineers, 2002).

Soil Washing

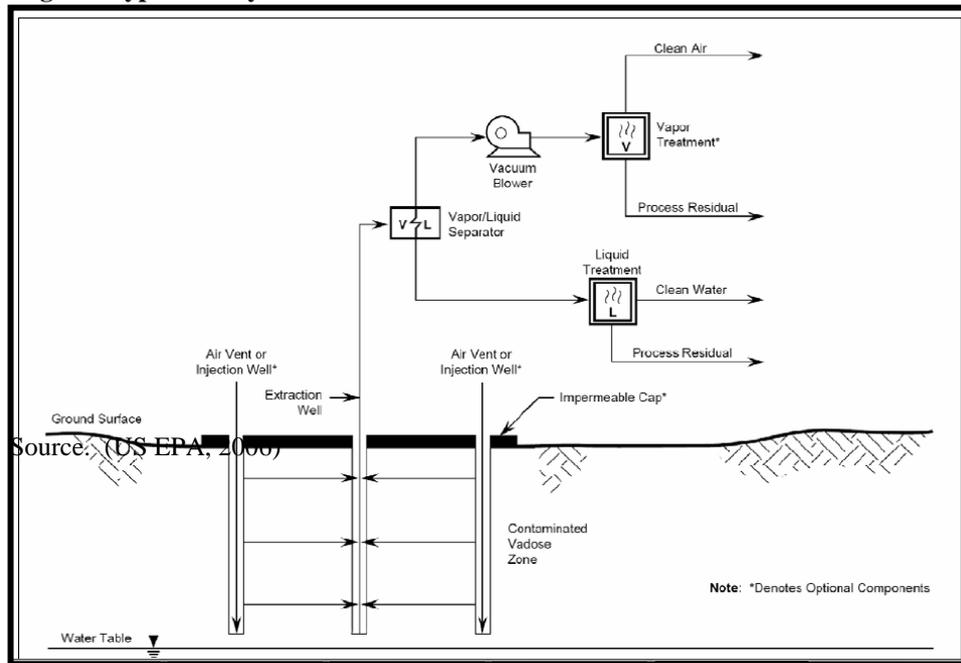
Soil washing is common technique that makes use of chemical and physical properties in order to detach contaminated particles from clean ones (Mulleneers, 2001). The washing is done mostly with water and sometimes after the washing is needed an extra treatment which will finally do the job (US EPA, 2001), also by adding some chemical substances will ensure the technique. Washing ex situ guarantee that the whole contaminated soil is treated, this is because with this technique soil is removed and heterogeneities in it do not matter (Roudier). A variety of chemical compounds can be clean up by this technology, such as fuels, metals, SVOCs, also some VOCs and pesticides that can be attached to soil (US EPA, 2001). The duration of the remediation is short to medium term (Federal Remediation Technologies Roundtable (FRTR)). An efficiency of almost 95% is got from the application of this technology.

Soil Vapor Extraction

The SVE is one of the most efficient and less expensive methodologies at the moment. As it was mentioned, it is frequently used for the In-situ removal of VOCs of the soils unsaturated zone, that can possibly be held in pores by capillary forces or material that has been absorbed by fine particles of the soil and occupy the majority of the spaces of pores (US EPA, 2006)/ (Fetter, 1999).

The technique (fig 5) consists of one or more monitored wells of extraction in the unsaturated zone of the soil, with blowers, suction pumps and sometimes also include air injection or wells with venting pressure, low permeability in the surface of soil, an air/ water separator and an off-gas treatment system. The airflow is induced in the unsaturated zone creating a pressure gradient through the air injection from wells or trenches in the subsurface. The SVE gas flow assures the evaporation of non-aqueous phase liquids (NAPLs), volatilization of polluting agents dissolved in pore water, and desorption of polluting agents of surface of soil particle (US Army Corps of Engineers, 2002).

Fig. 2.1 Typic SVE system



Flushing

This technique is used for both inorganic and organic pollutants. It is based on introducing to the contaminated site some solvents or water in the unsaturated zone. Flushing is used to remove inorganic as well as organic contaminants like VOCs, pesticides, etc. The methodology of the technology is first to infiltrate or inject the solution, as the solution moves through the media it solubilizes the contaminants and move within it. Afterwards the fluid is recovered and treated. The used solution is then reused until the goal has been achieved or when it is no longer removing and solubilizing the contaminant. The effectiveness of the method depends on the hydrologic conditions of the zone and it better performs in permeable soils. In addition to, the costs of the technology can be high and in the presence of various contaminants its performance is slow and usually takes a long time. On the other hand it represents an advantage, because of the issue that the soil surface of the site is not greatly affected (Miller, et al, 2007).

Solidification/Stabilization

Solidification regards to make the contaminant immobile by introducing some agents like limes, phosphates, etc. The contaminant can be encapsulated either in fine particles or in bigger blocks (Hamberg, 2009). Stabilization makes reference to the issue

that the material will be less dangerous or toxic and that can be found in a more stable form (Volke Sepúlveda, et al, 2002).

This technology can be done either in-situ or ex-situ. For the ex-situ form the material needs to be excavated, this means to take away the contaminant and have it have a disposal. The in-situ way there is no need to excavate so the material is left on the site. Inorganic contaminants are the most treated ones with this technique; for VOCs is not a recommended process, because of the fact that these compounds are volatilized and therefore cannot be immobilized.

Solvent extraction

This technique works by extracting from the soil organic and inorganic compounds by using an extraction liquid, which usually uses organic solvents in order to remove the contaminant from the soil. This fluid should certainly need an afterward treatment in order to destroy the contaminant (Volke Sepúlveda, et al, 2002). The effectiveness of the technique depends on the close interaction of the solution and soil.

2.2 Volatile Organic Compounds (VOCs)

Organic compounds are those that contain carbon and hydrogen in their molecules structure. Carbon is an element able to unite to other carbons by means simple, double or triple bonds (Bedient, et al, 1999). Organic compounds, the simplest ones, are those only formed by carbon and hydrogen and united by simple bonds are called alkenes.

Volatile organic compounds are by definition any compound which structure is formed by carbon and hydrogen and are in the atmosphere as gases, but under regular temperature and pressure can be found as liquids or solids (Derwent) and according to Breus and Mishchenko this type of contaminants at least in soil matrixes have not been very much studied yet.

VOCs are organic compounds, provokers of great amount of ground contamination. These compounds are emitted in gas phase of solids or liquids, originated by the use of various products that emit these toxics, such as paints, fuels, pesticides, apparatuses like copier machines and printers, permanent adhesives, just to mention some examples (US EPA, 2009). VOCs are toxic substances, although the degree of toxicity of each specie will vary based on its chemical composition, the exposure time to the polluting agent, among others factors. The importance of the study of these contaminants are according

to Derwent, relies on the fact that present adverse health effects to human health such as cancer, the augmentation of greenhouse effect, they are environmental accumulated and persistence, contribute to stratospheric ozone diminution, among others. Moreover and making emphasis on soil contamination, these pollutants seriously deteriorates soil properties and makes the remediation or cleaning complicated.

There are hundreds of compounds that fit within this category such as benzene, toluene, dichloroethane, xylene as so many others. According to the capability of these compounds to be found in gas phase, they can be VOCs and SVOCs (Hamberg, 2009). These chemicals are characterized because of having some properties such as been volatile, for example low molecular weight and high vapor pressures makes them this way and also helps to be easily removed from soil.

VOCs are released to soil in form of non-aqueous phase liquids (NAPLs). In dependency of the physical and chemical properties of each NAPL, it will be absorbed in soil, dissolved in ground water or volatilized in vapor of the soil. The NAPLs are classified in dense liquids in non-aqueous phase and light liquids in non-aqueous phase (LNAPL-less dense than water) and (DNAPL-denser than water) (US EPA, 2006). One characteristic which distinguishes the DNAPLs of the LNAPLs is that the first ones sink in permeable soils in the saturated zone and unsaturated zone up to the last layer and the second ones sink through the unsaturated zone and will float in the water table and migrate to the lowest part of it, of course this is related to the density and viscosity of the contaminant. The equilibrium between the liquid and vapor phase NAPLs phases is governed by Raoult's Law (US EPA, 1991). Compounds which have affinity for soil organic matter will move slowly. According to Falta VOCs normally got low solubility around 50 to 2000 mg/l. This will be shown in "high Henry constants and high partitioning into the gas phase from the aqueous phase" (Falta, 2006). Henry's Law governs the equilibrium between the aqueous and vapor phase (US EPA, 1991).

In the unsaturated zone VOCs can be distributed in four different phases vapor or gaseous, dissolved in pore water or aqueous, free liquid (NAPL) and adsorbed phase or solid, this is in dependence of the physical and chemical properties of the contaminant (Johnson, et al, 1990)/ (US Army Corps of Engineers, 2002). The next figure shows the VOCs partitioning.

Fate of vapor phase contaminants are really difficult to predict and can be mixed with air and water (US EPA, 1996); as they move rapidly, the speed and the trajectory is

not controlled with ground-water gradients. When NAPLs volatilize, a vapor plume is formed which in its way towards the surface leaves contamination where they can be available for its inhalation or even explosion as it introduces in buildings structure. But these not only migrate towards the surface also to ground-water, due to an increase in the water table and recharge by infiltration (Bedient, et al, 1999).

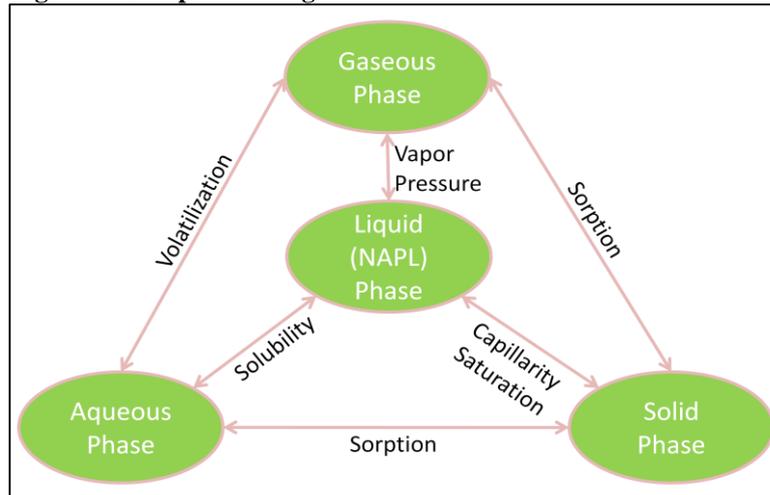
Aqueous phase contaminants can be found in soil moisture above the capillary fringe and below the water table. On normal bases this compounds are very soluble and can be able to move great distances away from where the release of the pollutant took place. They also represent a small percentage of the total released mass. This is the main probable way where the contaminant can be in close contact to humans and the environment (US EPA, 1996).

Liquid or NAPL phase, can also be called free liquid phase. They can saturate the media so that they can be accumulated in the water table and mobilize towards wells or excavations, and this is because of their volume. And it is this volume characteristic which makes the difference between this phase and the residual or solid one. These two phases can actively contribute to the contaminant mass in the vapor phase through evaporation and aqueous phase through dissolution. Sorption will contribute only to the solid phase (US EPA, 1996).

Solid or residual phase contaminants do not travel to far away from the source of where the contamination was first released. They can occupy more than 50% of the pore space in the form of sediments. They can persist in the environment and be a continuous form of groundwater contamination in the case that the compound is very soluble (US EPA, 1996).

Contaminants distribution is determined by the interaction of its chemical and physical properties such as solubility and volatilization besides soil properties, such as heterogeneity, permeability and many others (US EPA, 1996). On the other hand there are some processes that will establish the pollutant fate, such as advection, volatilization, desorption, biodegradation, and diffusion as well as how the contaminant is going to be accumulated in the ecosystem and environment (some of these mechanisms are going to be described in further pages) (US Army Corps of Engineers, 2002)/ (Breus, et al, 2005).

Fig. 2.2 VOCs partitioning



Source. (US Army Corps of Engineers, 2002)

2.3 Physical-Chemical Properties

As it has been mentioned before among some other factors the physical and chemical characteristics of the VOCs will help define the partitioning and disposition of the compound in this case in soil matrix.

Table 2, shows some VOCs and their physical characteristics. The most important property is the vapor pressure. Low molecular weight and high vapor pressures makes the compound more volatile and it is this property the one that causes that these are easily removed from soil.

It is mentioned by the US Army Corps of Engineers that the partition into vapor at equilibrium is pointed out by the vapor pressure, Henry's law and boiling point of the compound. In which will be dissolved in water also in equilibrium is given by the solubility and how will it be adsorbed or attached to soil is indicated by the adsorption coefficient. While the contaminant is heavier, less soluble and less volatile it is and the higher probability of these to persist within the soil matrix.

Some of the other properties that are not shown in the next table, but that also have an impact in the compound distribution and transport and are important as well are Raoult's Law which provides an approximation of compounds vapor pressure of a NAPL mixture, such as petroleum product, the soil distribution coefficient, indicates the tendency of the compound in solution to adsorb to the surface of particles of soil or

organic matter and biodegradation which varies according to each compound (US Army Corps of Engineers, 2002).

Physical Properties of VOCs

COV	PM (g/mol)	Pf (°C)	Pe (°C)	Pv (mmHg)	dv	γ (kN/m ³)	Sol (mg/l)	Csat (g/m ³)	H (m ³ atm/mol)	log Kow
Benzene	78.11	5.5	80.1	76	2.77	9	1780	319	5.49x10 ⁻³	2.1206
Chlorobenzene	112.56	-45	132	8.8	3.88	11	500	54	3.70x10 ⁻³	2.98
Ethylbenzene	106.1	- 94.97	136.2	7	3.66	8.67	152	40	8.43x10 ⁻³	3.13
Chloroethane	62.5	-153	-13.9	2548	2.15	9.12	6000	8521	6.4x10 ⁻²	---
Tetrachloroethene	165.83	-22.5	121	15.6	---	16.3	160	126	2.85x10 ⁻²	2.5289
Trichloroethene	131.5	-87	86.7	60	4.54	14.6	1100	415	1.17x10 ⁻²	2.42
Dichloromethane	84.93	-97	39.8	349	2.93	13.27	2000	1702	3.04x10 ⁻³	---
Toluene	92.1	-95.1	110.8	22	3.14	8.67	515	110	6.44x10 ⁻³	2.2095

Table 2.1 Physical Properties of VOC's. Source. Modified, (Ingeniería Civil y Medio Ambiente, 2004).

Where:

- PM: Molecular weight of the compound. High molecular weights will be better adsorbed than low ones.
- Pf: Melting point. It is when the liquid and solid phase of a compound is in equilibrium; this is when the vapor pressure of both phases is the same. The solid becomes liquid.
- Pe: Boiling point. The temperature in which the compound in liquid phase is able to become vapor. In other words, it is the temperature at which the liquids vapor pressure is equal to the atmospheric pressure. When inducing vacuum the pressure in pores filled by air will decrease, resulting in low boiling points and in an augmentation of the capacity of volatilization (US EPA, 2006).
- Pv: Vapor pressure. This is related to the tendency that particles have to escape from the liquid or a solid. It indicates the evaporation rate of a liquid. VOCs have high vapor pressure, which gives them the particularity of being volatile.

- d_v : Vapor density. It is the weight of a volume of vapor or gas compared to the weight of a same volume of dry air at the same temperature and pressure. A d_v lower than 1 means that the vapor is lighter than air and will tend to move upwards. On the other hand a d_v higher than 1 means that the vapor is heavier than air and will move downwards toward soil.
- Specific weight. Weight of a certain substance divided between the occupied volume of it.
- Sol: Solubility. It is the maximum concentration of a compound that can be dissolved in water. The higher the solubility of the VOC, the harder it will be for it to remain adsorbed in soil and will be easily transported towards the aqueous dissolution.
- C_{sat} : Saturation concentration. It is the maximum concentration that can be able to be dissolved in air.
- H: Henrys constant. It describes the tendency of a compound to volatilize. The higher the value of H the higher tendency the compound has to volatilize and as well the higher concentration will be found in the off gas stream (US EPA, 2006).
- Log K_{ow} : Octanol-water partition coefficient. It is a measure of how the contaminant can be distributed between two immiscible dissolvent. It is very much used to estimate the distribution of the compound in animals' fat tissue; the bigger the coefficient the highest tendency contaminant will have to bioaccumulate.

2.4 Soil Properties

There are some characteristics of the soil that will determine the fate and transport of the contaminant. This is such as the pore space, fractures in soil or channels in which the fluid can move through. It is also important to remember that soils with high water infiltration rates will allow soluble compounds to move far away from the spill (Pedersen, et al, 1991).

The next table shows the significance of the some properties of the geologic media and how it affects for the free product recovery, this means hydrocarbon in its liquid phase.

Property	Significance
Porosity	Porosity is required for calculation of the amount of free product and immobile (residual) product. The relevant parameter for determining recoverable free product is the “drainable” or “effective” porosity, which is always less than total porosity.
Permeability	Permeability controls the rates of groundwater flow and free product migration. It is also used to calculate pumping rates required for hydraulic control.
Anisotropy	Anisotropy is a condition of the geologic media in which measurement of a property like hydraulic conductivity depends upon the direction of measurement. Anisotropy can cause groundwater flow to not be in the same direction as the hydraulic gradient.
Heterogeneity	Heterogeneous media often provides preferential pathways for fluid migration-these pathways are difficult to locate and to characterize.

Table 2.2 Properties of geologic media. Source. (US EPA, 1996)

But there are two relevant properties of soil, permeability and porosity. Permeability makes reference to how the contaminant is going to move or transported in soil. The second one is related in the capacity of the fluid to be held in the media. So if the soil does not have few pores the fluid cannot be retained, but permeable since in this case the polluting agent can pass through it (Price, 2003).

Permeability characteristic is going to determine the rates of groundwater flow and free product migration. Intrinsic permeability is a concept related to hydraulic conductivity, which is the measure of the facility that geologic media has got to have water of contaminant to pass through it. Soils with a high hydraulic conductivity are also highly permeable and in consequence can easily have fluids such as water and some hydrocarbons transmitted through it. This important characteristic will help determine the rate at which the soil vapors can be extracted from the media (US EPA, 1996). So hydrocarbons will tend to move through the most permeable pathways and will avoid zones where permeability is low (US EPA, 1996).

Porosity makes reference to the amount of water or contaminant that can be contained per unit volume. Normally most aquifers porosity varies between 25 to 35% (Bedient, et al, 1999).

There are other characteristics beside porosity and permeability that will influence the contaminant transport, which are listed below:

- Saturation is the volume of the fluid per volume of the pore space in soil.
- Wetting and nonwetting phases. The first one means the fluid that is nearest to the solid phase, while the second one is regarding the fluid that it is far from the points of the interparticle.
- Residual water saturation is the volume fraction of the water that cannot flow by the action of the capillary forces.
- Residual NAPL saturation is the degree of NAPL saturation that remains in the soil, is subjected to drainage until the NAPL fills the pore spaces that are discontinuous.
- Capillary pressure between two phases is the difference between pressures of wetting and nonwetting phases.
- Capillary pressure head-saturation curves can give useful information for the design of the SVE. It reflects the distribution and size of the pore, as well as the energy associated with the water table in several saturation levels.
- Permeability is the measurement in which the porous medium can transmit water, air or any other fluid.

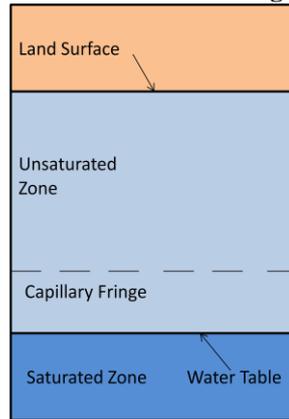
- Hydraulic conductivity is the measurement of the facility in which the porous medium can transmit a certain fluid, such as water or contaminant.
- Air permeability, is the ability of vapors to flow through the porous medium.
- Peclet number is the dimensionless number that relates the effectiveness of mass transfer by advection to the effectiveness of mass transfer by diffusion.
- Humidity, which is the amount of water retained in soil particles or voids.
(US Army Corps of Engineers, 2002).

2.5 Unsaturated zone

Concerning the vertical distribution of the water in soil, two important zones can be distinguished, the unsaturated and saturated zone these two divided by the water table. The thickness of this zone varies in dependence of the area, for example if the water table is high, it can be from a few feet or in arid regions of hundreds of feet depth. Here water is held by surface forces and water passes down to the water table as a gravitational flow (Charbeneau, 2000).

According to Tindall the unsaturated zone is also known as the vadose zone and zone of aeration. The unsaturated zone is the one that goes right from the surface to the water table and pores are full with atmospheric air, water and perhaps contaminants and it holds solid, liquid and gas phases. This zone is divided as well in 3 zones; the first of them is the zone of soil moisture, which extends up to the zone where roots of plants, grasses and superficial roots of superior plants and evapotranspiration processes are important. Roots of plants are important for contaminant transport in agricultural lands, because of the fact that will eventually lead to further polluted crops. The following zone is the intermediate one, located right under the zone of soil moisture. This zone is well known as zone of transition, since the fluid infiltrates and happens to go through this region, to later move up to the water table. The capillary zone, begins where the intermediate zone ends right up to the surface of the water table. In this zone pores can be actually filled with water or contaminant, this means can be saturated. The water table is the intermediate division between the unsaturated and the saturated zone, and directly depends on the amount of precipitation and amount of fluid that infiltrates through the soil. Subsequent to the water table is the saturated zone, where the fluid fills all the pores.

Fig. 2.3 Vertical distribution of groundwater

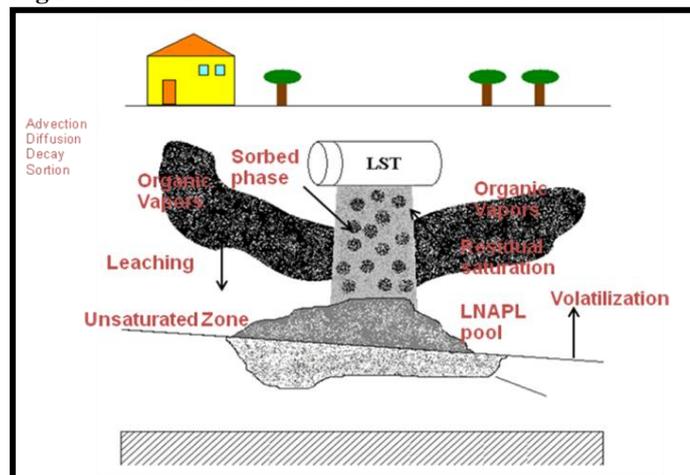


Source. (USGS-U.S. Geological Survey, 2006)

The study of this zone is difficult since a lot of processes are taken place there. A lot of investigations have been done and it has been found out that obviously the unsaturated zone is not an isolated system. Compounds in their different phases can easily move through soil matrix by leaching to the groundwater or escaping in the form of gases to the atmosphere. Various disciplines are required in order to have a better understanding of this zone, such as chemistry, physics, mathematics, engineering, soil chemistry, hydrology, mineralogy, soil-plant-water relations and also computer science (Tindall, et al).

The next figure shows the unsaturated zone contamination, provoked by leaching underground storage tanks.

Fig 2.4 Contamination in the unsaturated zone



Source. (Bedient, et al, 1999)

2.6 Contaminant Transport Mechanisms in Unsaturated zone

Contaminants can be transported from kilometers or just centimeters away from the point where they were first released. How far are they going to travel depend on the some contaminant characteristics and the flow of water or air that will transport them along with (Ramaswami, et al, 2005).

The unsaturated zone has been constant study, since the contaminants mobilizes in this region before achieving ground-water.

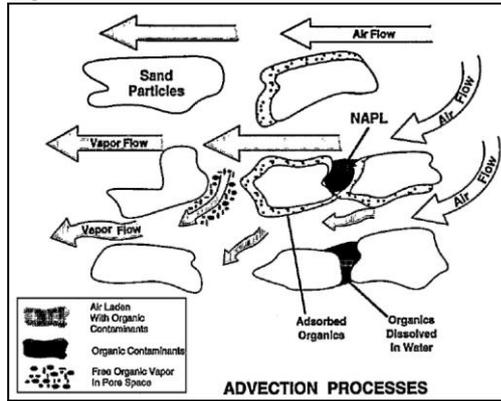
One of the strongest contaminants in soil and ground-water are organic vapors. In comparison with liquid phase compounds vapors move rapidly, their speed and trajectory is not controlled with ground-water gradients. When NAPLs volatilize, a vapor plume is formed which in its way towards the surface leaves contamination where they can be available for its inhalation or even explosion as it introduces in buildings structure. But these not only migrate towards the surface also to ground-water, due to an increase in the water table and recharge by infiltration (Bedient, et al, 1999).

There are three contaminant transport mechanisms, which are advection, diffusion and dispersion, governed by water transport, soil heterogeneities and molecules movement respectively.

The advection process represents the movement of the contaminant along with the groundwater flow at the speed of filtration in the space of the pore. Diffusion is caused by molecules movement and dispersion is caused by heterogeneities in the soil and creates pathways and variations in the flow speeds (Bedient, et al, 1999). Both diffusion and dispersion mean the combination of contaminants due to difference in their concentration.

According to (Charbeneau, 2000) advection is the main process for contaminant mass transport. When the fluid moves through the media, could be either gaseous or liquid phase, it takes with it contaminant present in the zone, this is due to advection. The next figure shows the advection process in the unsaturated zone. In this case airflow is drawn in and the contaminant will move along in the same direction.

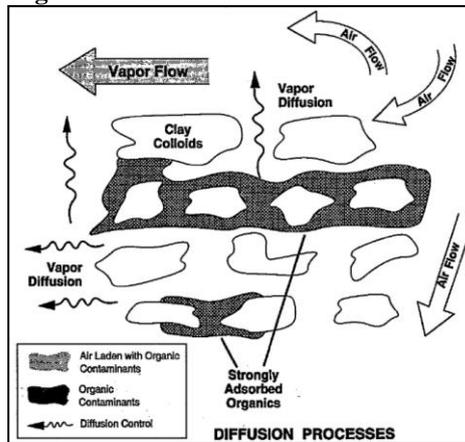
Fig 2.5 Advection Process



Source. (US EPA, 1991)

Diffusion process is described by the random movement of molecules. This is that the transport can take place from bigger to lower concentration zones. It is also defined as Ficks transport since the equation that can describe the process is prevailed by Fick's law.

Fig 2.6 Diffusion Processes



Source. (US EPA, 1991)

3. SOIL VAPOR EXTRACTION TECHNIQUE

3.1 SVE Concepts and bases

SVE is an effective technique for the removal of some compounds, such as VOCs from the unsaturated zone of soil. This is a cheap technique in comparison to some others, thus the ability of it to extract efficiently VOCs are some of the reasons which is one of the most worldwide used remediation technology nowadays. It is mentioned in the US EPA Off gas treatment text, that especially in Europe it is a widely used technique and in Germany it is a standard protocol. It is also important to mention that the SVE system can be in operation in dependence of the previously established remediation goals and quantity of contamination and type of contaminant; running time of the technique can go from six months up to many years.

Before going into more details of the technique, the next table shows advantages and disadvantages according to USEPA in 1994.

Advantages	Disadvantages
Proven performance; readily available equipment, easily installation. Minimal disturbance to site operations.	Concentration reductions greater than about 90% are difficult to achieve. Effectiveness less certain when applied to sites with low permeability soil or stratified soils.
Short treatment times: usually 6 months up to 2 years under optimal conditions. Cost competitive: \$20-50/ton of contaminated soil.	May require costly treatment for atmospheric discharge of extracted vapors. Air emission permits generally required.
Easily combined with other technologies, such as air sparging, bioremediation and vacuum enhanced dual phase extraction. Can be used under buildings and other locations that cannot be excavated.	Only treats unsaturated zone soils, other methods may also be needed to treat saturated zone soils and groundwater.

Table 3.1 Advantages and disadvantages of SVE technique. Source. (US EPA , 1994)

This technique is also known as soil venting, vacuum extraction or in situ vaporization, and it is classified among the in situ technologies (Pedersen, et al, 1991)/ (ERG-Environmental Remediation Group, 2007). It is able to reduce concentrations of volatile and semivolatile compounds held in the unsaturated zone and might reduce the movement of them.

The increasingly fame of this technology relies on the issue that it can treat large areas of polluted soil in relatively low costs. The next table shows the costs according to the Federal Remediation Technologies Roundtable (FRTR) for an SVE system in dependence of the size of the site, quantity of contamination and the hydrological factors.

	Small Site		Large Site	
	Easy	Difficult	Easy	Difficult
Per cubic foot	\$36	\$42	\$11	\$27
Per cubic meter	\$1275	\$1485	\$405	\$975
Per cubic yard	\$944	\$1100	\$300	\$722

Table 3.2 SVE Costs. Source. (Federal Remediation Technologies Roundtable (FRTR))

Some chemicals that can be treated by this method are those shown in the next table; obviously the efficiency of the extraction will highly depend on the compounds physical properties among some other considerations that are needed to be taken into account (US EPA, 2006).

Halogenated and nonhalogenated VOCs	Gasoline, jet fuels, lighter fuel oils	Toluene	Chlorobenzene
SVOCs	Kerosene	Ethylbenzene xylene (BTEX)	Chloroform
Metil-isobutil cetona	Benzene	Styrene	Carbon tetrachloride
Tetrachloroethene	Trichlorethene	Vinyl Chloride	Trichloroethane
Dichloroethene	Methylene chloride	Acetone	Metyl isobutyl ketone (MIBK)

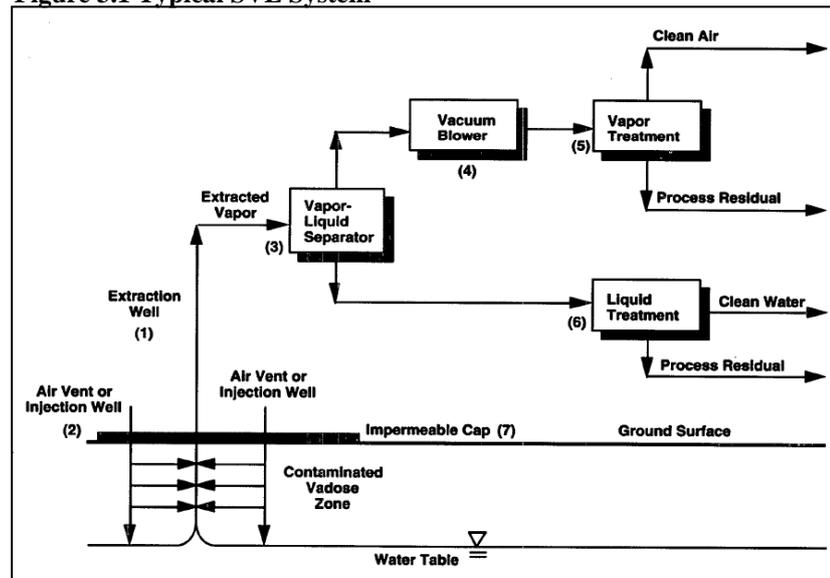
Table 3.3 Compounds that can be removed by SVE

This technology has variants, but it normally operates in a simple manner. This technology consists in applying vacuum through some wells and inducing air flow in some others. Vacuum will create a gradient pressure, provoking the vapors of the contaminant mass to move toward the extraction wells. When airflow is induced in soil, this will pass through high air permeability zones. Airflow after being induced will end up in contaminants desorption attached to soil particles, volatilization of them when

dissolved in groundwater and NAPLs phase contaminant evaporation (US Army Corps of Engineers, 2002). After the contaminant extraction, the vapors are needed to be treated before releasing them into the atmosphere. Carbon adsorption is commonly used for this purpose, even though there are different off gas treatment that can be used for every specific situation; these technologies are in further pages described.

The next figure shows a SVE system with the components of it. It consists of injection and extraction wells along the contaminated area, there can be one or more of them installed in the zone. There are also injection wells, from which airflow is going to be drawn into soil matrix, there can also be one or more of this type of wells. A vapor-liquid separator can also be installed; nevertheless it is optional equipment. This equipment can be used to enhance a better performance of the further gas or liquid treatments. It is also found vacuums or air blowers, this in order to reduce gas pressure in the extraction wells. A vapor and/or liquid treatment can also be used. It is been already told that off gas treatment is a must, since some regulations tells it so in some countries, these technologies are explained in further pages. Finally an impermeable layer can be used. This layer has different purposes such as minimize water infiltration from the surface, because water can fill pores and this way reduces airflow. It can also increase the radius of influence (this term is going to be described ahead), this way preventing short circuiting. At last, this layer can also prevent air losses and/or inlets that may affect the process (US EPA, 1991).

Figure 3.1 Typical SVE System



Source. (US EPA, 1991)

There are many factors that may affect the success of an SVE system such as, contaminant characteristics, soil properties, site conditions and the design of the system. So soil and contaminant characteristics plus operating data through equations will help determine the amount of extracted contaminant and extraction time.

Among the parameters of the design of the system there are others that have to be taken into account in order to make an appropriate SVE design and are mentioned in the list below.

- Radius of influence
- Wellhead vacuum
- Vapor extraction flow
- Initial vapor concentrations
- Required remedial cleanup time
- Extraction and injection wells
- Well orientation, placement and construction details

Explaining the terms above, the radius of influence (ROI) is the distance from the extraction well for an effective removal of the contaminant when vacuum is applied. It is an important factor since it will enhance the adequate pollutant extraction and it will

help determine number and space between extraction wells. According to US EPA in their Evaluation of the SVE System Design, ROI can range from 5 to a 100 feet, this is depending on the soil type. Wellhead vacuum is the needed pressure located at the top of the extraction well in order to produce the wanted extraction flow rate. The vapor extraction flow rate, makes reference to the volumetric flow rate of the vapor that is going to be extracted from the extraction well. This factor will help to meet the desired time of the operation of the system. The three mentioned factors have close relation between them; this is for example, a change in the extraction rate will end up in wellhead vacuum and ROI adjusts. The initial pollutant concentrations and the required remedial cleanup time will help determine the development of the technique and the system design. Finally the table below shows the site conditions that have to be fulfilled in order to determine the well orientation (US EPA , 1994)

Well Orientation	Site Conditions
Vertical extraction well	<ul style="list-style-type: none"> • Shallow to deep contamination (5-100 feet). • Depth to groundwater >10feet.
Horizontal extraction well	<ul style="list-style-type: none"> • Shallow contamination (<25feet). More effective than vertical wells at depths <10feet. Construction difficult at depths >25feet. • Zone of contamination confined to a specific stratigraphic unit.

Table 3.4 Site conditions to be fulfilled in a well orientation. Source. (US EPA , 1994)

3.2 Blowers

Selection of type and size of blower should be based on the required vacuum to reach the previous design vacuum pressure at the extraction wellheads and the total flow rate. The flow rate constraint should be based on the sum of the flow rates from each vapor extraction well participating in the process. According to the US EPA there are basically three types of blowers that can be used in an SVE system.

- Centrifugal blowers.
- Regenerative and turbine blowers.
- Rotary lobe and other positive displacement blowers.

3.3 Extraction/Injection Wells and Wells Distribution

The SVE system can use vertical or horizontal extraction wells and the selection of which is going to be used, highly depends on the site conditions and needs. For example the closer the wells are located, the fastest removal of the contaminant, of course this is not a rule and it might not work; well material have to be also chosen in dependence of the type of contaminant. Regarding to the injection wells, they are used to enhance the extraction of the contaminant, these are optionally part of the system design, but it is recommended because of the mentioned fact. In order to know how the wells are going to be distributed there are some formulas that can be applied. As an example the contaminated area can be divided by the area of influence of one well and obtain the amount of them that are needed.

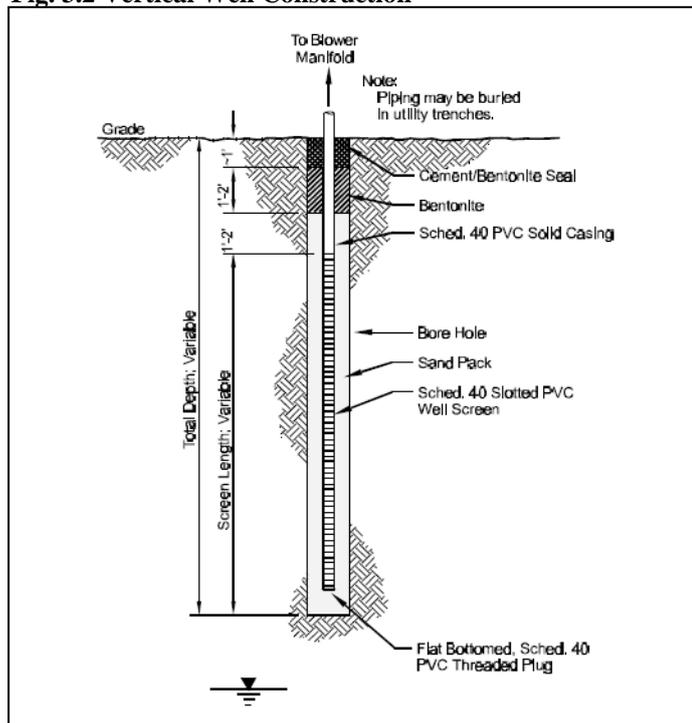
Extraction wells are normally designed to go through the unsaturated zone up to the capillary fringe. When groundwater is not too deep or if the contaminant is located in not so profound layers, the extraction wells can be horizontally located (US EPA, 1991). Air injection wells help to have less dead zones, minimize upwelling and increase pressure gradients (US Army Corps of Engineers, 2002).

Location and number of injection or extraction wells depends on the specific site characteristics, such as soil characteristics, air permeability and profundity of the contamination and physical and chemical properties of the contaminants. So the design of well distribution has to let air flow in the contaminated zone, also is intended to pull off an enough air exchange rate that will help fulfill an adequate cleanup of the site. In addition an analysis of air velocities as well as travel times to the extraction wells at different flow rates are needed to establish the better spacing. Injection wells should be located so that the contamination heads to the extraction wells and not to areas with any contamination at all. (US Army Corps of Engineers, 2002).

As US Army Corps establish it is important to take into account the next considerations to make the right decision regarding wells geometry and flow rates:

- Geometry of the contaminated zone.
- Air permeability and horizontal to vertical permeability ratio.
- The desired air exchange rate.

Fig. 3.2 Vertical Well Construction



Source. (US EPA , 1994)

3.4 Off Gas Treatment

An off gas treatment is necessary in most cases after the gases of the compounds are been extracted from soil by the technique. It is important to remember that the VOCs are hazardous compounds that can provoke serious health damages such as cancer just to mention one example (US EPA, 2006). So the main objective of this part of the process is to improve the gas quality before releasing it to the atmosphere because of safety, health or any other main concerns.

The VOC vapors extracted from soil matrix by SVE present low or rather medium concentrations of the compounds in the flows. As there are some factors that influence the movement of the contaminant in the soil, the gas generated after applying the technology is influenced also by the distribution of the compounds, type and soil characteristics. In order to select the overall right treatment including the off gas treatment the following characteristics have to be taken into account:

- Soils with small amounts of VOCs present lower off gas concentrations that will diminish quickly.

- If the site contains large quantities of NAPL will have elevated off gas concentrations for large periods of time that will only be diminished when the NAPL phase is removed.
- Sites with high permeable soils help the off gas concentrations to diminish quicker than in soils with lower permeability; this is because the VOC are better removed from permeable soils.
- If the spill were of mixtures it is needed to adapt with the pass of time the technology, this is due to the fact that more volatile compounds are been extracted the first.
- Chemical compounds concentrations in air have different lower explosive limit (LEL). When the compound has low LEL concentrations will need diluted air in order to prevent explosive air streams. (US EPA, 2006).

The off gas normally has almost 100 percent of humidity, so some technologies does not always apply. For example, carbon adsorption is less effective when humidity is high, but some others can be perfectly applied in these cases such as the biofiltration.

According to EPA in 2006 the classification the treatment technologies can be divided in thermal, adsorption, biological and some new technologies that are being applied, such as non thermal plasma treatment.

The thermal treatment is a commonly used technology that works by combusting or oxidizing VOCs to byproducts like water and carbon dioxide. According to the US EPA Off Gas Treatment, it includes thermal oxidation systems. These type of systems are used because it can guarantee high destruction and removal efficiencies (DRE) of VOC, quantified in almost a 99 percent of the SVE gas stream. The next table shows the type of compounds that can be destroyed using this technology including non halogenated VOCs, SVOCs at different concentrations.

Alcohols	Esters
Aliphatics	Ketones
Aromatics	Fuel Hydrocarbons

Table 3.5 Types of compounds that can be destroyed.
Source. (US EPA, 2006)

Adsorption treatments are the ones can separate the contaminants by using a certain type medium that will work for the compound. It is said that well designed adsorption systems are capable of reaching from 95 to 98 percent DRE where initial concentrations range among 500 to 2000 ppmv and with lower concentrations can be higher than 98 percent. The most commonly used adsorbent is granular activated carbon (GAC). GAC can treat a great variety of VOCs, although it is not efficient enough for VOCs with characteristics such as high polarity for example alcohols or high vapor pressures like vinyl chloride or methyl terbutyl ether (MTBE). As it has already been said high humidity streams diminishes also the performance of the usage of GAC. Another two types of adsorbents commonly used are the zeolites and polymers.

In the Off Gas Treatment text by the US EPA in 2006 it is mentioned that biofiltration can be used for dilute VOC stream concentrations by using organisms to metabolize the chemicals attached in the off gas. When this system is well designed and applied can achieve sometimes more than 95 percent DRE. It can work the most effectively for vapor streams coming from SVE remediated USTs located in gas stations containing compounds such as benzene, toluene, ethylbenzene and xylene (BTEX). As well this type of treatment has got limitations; the effectiveness can be affected when parameters such as moisture content, temperature, pH and nutrient levels vary.

In the emerging technologies are included photocatalytic and photolytic, non thermal plasma, membrane separation, gas absorption and vapor condensation technologies. All these technologies have not been very much used so far for SVE off gas treatment. Photocatalytic and photolytic are very good for halogenated and non halogenated VOCs, alcohols, ethers, ketones, aldehydes and aromatic and aliphatic hydrocarbons, on the other hand non thermal plasma, which makes use of UV light and electrical energy to destroy the contaminants, is effective for a various compounds including chlorinated and aromatic VOCs (US EPA, 2006).

4. MODELING AND SIMULATION

4.1 Basic Concepts

Modeling techniques are used for the creation of a representation of some process in a certain time or space, object or phenomenon of the real world. The objective of modeling is to help understand the phenomenon and their behavior, based on assumptions and restricted to some conditions; the results are going to be approximated since it is an ideal representation and therefore are not exact. Its foundation regarding to environmental modeling is mainly mass balance, since this will help determine, loss, accumulation and distribution or contaminant in different matrixes. This tool is not only used in areas such as science and technology, moreover they are fully used in government and business areas, where are used to have a better understanding of a portion of reality, sometimes called a system (Dekking, et al). Some examples of the application of modeling in environmental applications are wind tunnels that have been used to investigate pollutant dispersion and deposition, scale-model waterways for flow and circulation studies, and bench-scale soil columns that have been used to study the transport of pollutants in soils and groundwater (Ramaswami, et al, 2005).

Whether a model is a good one or not will depend in the detail that is driven into it. When too little detail is included in the model there is always the risk of omitting some interactions and finally will end up failing in the objective of having a better understanding of a certain process. On the other hand, if too much detail is included in the model it might become too complicated and also failing in the same objective of understanding (Bellinger, 2004).

According to US Army Corps, Analytical and numerical models can be used to:

- Determine applicability of various SVE configurations during the technology screening process.
- Aid in design of pilot test programs.
- Extrapolate pilot test data to design of full-scale systems.
- Estimate airflow rates and contaminant concentrations to aid in equipment specification.
- Optimize the numbers and locations of air extraction and injection points.
- Estimate the time that will be required to meet remedial objectives.

There are two different kinds of modeling, physical and mathematical modeling. In general terms, for the elaboration of the mathematical model it is required to define or to establish the real problem, to identify the dependent and independent variables, formulate the model, apply to mathematic laws for their solution and conclusions, later the resulting data will be compared with the real ones. If the data have significant differences, the process is reinitiated fitting the model. A mathematical model can be represented by functions or relations and are classified like linear, quadratic or exponential.

The importance of mathematical models relies on the fact that this will help reveal relations which sometimes are not evident between variables and in some situations where there is no possibility to try out the real thing, models will help to provide information and sometimes conceptual framework in order to help the decision making process with its possible consequences either good or not. In other words the advantages of modeling can be condensed under the next three statements:

- Low cost to analysis of several alternatives,
- Possibility to get more information and more details
- Possibility to simulate situations which are physically difficult

Models can be static or dynamic. Static models do not highlight the time parameter and it does not play a main role, on the other hand dynamic models time is taken into account and it is an important variable and many others are involved and in constant change as they are time functions describing temporal trajectories or movements, such as the case of contaminants held in soil.

Bedient mentions a protocol design by Anderson and Woessner for proposing a model and it is as follows:

- Establish the purpose of the model.
- Develop a conceptual model of the system.
- Select the governing equation and a computer code.
- Design the model, which includes boundary conditions and parameters.

- Calibrate de design model, with the main purpose to verify if the design model actually can reproduce real processes.
- Determine the effects of uncertainty on model results. This means to make a sensitivity analysis of the model parameters.
- Verify designed and calibrated model with different cases to reproduce them.

According to Ronald Lacking W., Karsten Press and Dwayne A. Chesnut, during soil vapor extraction, the mathematical models of gas flows and transport of contaminants are useful tools for the design and evaluation of vapor extraction systems. Frequently, these models are based on numerical solutions of mass balance equations and a number of numerical simulators have been developed for modeled of gas flow and chemical transport, in the unsaturated zone. There are models available that may simulate pressure distributions and airflow, contaminant and some other vapor concentrations and others that can simulate both, pressure distributions and vapor concentrations (US Army Corps of Engineers, 2002).

A great number of models exist to analyze the viability of the implementation of certain remediation technique. Models like the Hypervent that Johnson mentioned in 1991, can help to determine the permeability of the site, the radius of influence of extraction wells, the flow speed and mass removal, using semi-analytical or numerical methods (Bedient, et al, 1999). Some models work to predict if the remediation is going to work as expected. For example they can simulate mixtures of several components and thus to know which one of them are still in the site after the SVE (Bedient, et al, 1999). In addition, mathematical modeling, can provide information about partitioning, degradation, pathways predictions, this will help to the problem assessment (Sims, 1990).

Simulation is the manipulation of a model in order to have it operating such as in real time or space and will allow observe the interactions among variables that otherwise cannot be seen. It is develop under the concern of having a good understanding of a certain real system or process. It is very useful to simulate a situation when in some cases it is too expensive or dangerous to take it out to the real world before knowing the possible consequences (Bellinger, 2004).

Simulation is a tool which reproduces the operation of a natural system, which has as objective, the study and analysis about the system, but using different conditions. It is a reproduction of a system represented by a model therefore it allows to experience with it, getting a prediction about its performance using different values in the input variables of the process.

Chemical engineers use some techniques in modeling such as: adimensionalization and scaling, averaging, appropriate choice of independent variables. However, physical insight is gained as a consequence of such manipulations. A further step is transforming model results into useful tools for real life situations (Rodrigues, et al, 2005).

4.2 Types of Models

According to Rutherford Aris, there are six different types of models; among them you can find:

- Verbal models and mechanical analogies
- Finite models
- Fuzzy subsets
- Statistical models
- Difference and differential equations
- Stochastic models

The first type of model is not a mathematical model as its name properly says, but it can be described as one because it keeps some characteristics of them. This can be called as soft models since it does not have quantitative predictions. It is said that for social purposes a rigid model is not useful.

Finite models make possible to transform theory and database theory problems to ones with mathematical logic. It has its concept under graphs, databases, computations and its application inside the physical and social sciences.

Fuzzy subsets is a type of mathematical model based on the idea whether the statement can be completely true or completely false.

Statistical models make use of mathematical equations that will help describe the behavior of a certain situation or object by random variables and its association with

probability distributions; the model can utilize one or various equations. The goal of this model is to construct it on the basis of the output and therefore make a conclusion of the desired phenomena.

The difference and differential equations is base in the use of an equation for an unknown function. It is the commonly used type of model in physical sciences. On the other hand difference equations are suitable when the dependant variable is discrete.

Finally the stochastic model is the one for estimating probability distributions of the many possible outputs by permitting the variation of the income values taking into account time steps.

4.3 Commercial Software's

With the pass of years a lot of different models, either digital or analytical have been developed in order to simulate different processes such as, pressure distributions, vapor transport and also extraction.

The unsaturated zone has been a focal point for developing various software's that in their structure incorporate complex mathematical solutions for solving the model but with a friendly interface. A great part of them require a lot of information in order to provide the adequate output information, even though they are very commonly used in different areas of science.

Simulation of the design and operation of SVE systems can be easily visualized when the use of specific software is used. For example this tool may be useful when interested in knowing how much vacuum to apply or knowing the best well orientation and even when is the correct time to turn on and off the system. The models used can also help simulate the contaminant partitioning, it is important to point out that the equations that better describe the process are nonlinear and difficult to solve. These factors combine to make modeling of SVE processes a research task.

There are lots of commercially available software's that can be used for different approaches. Selection of the adequate model will depend on what type of process is desired to be modeled and its outputs. The next table shows some models, their description and how they operate

MODEL NAME	MODEL DESCRIPTION	MODEL PROCESS
SCREENING MODELS		
HyperVentilate (1991) Paul C. Johnson, Available from EPA	A screening model that can be used to determine the potential feasibility of SVE for remediation at contaminated sites. The flow equation is solved analytically. The transient one-dimensional multicomponent contaminated transport equation is solved by finite difference.	Steady-state, radial, confined air flow to a vapor extraction well. Transient, mass balance approach, volatilization based on Raoult's law.
BioSVE (1998) Scientific Software Group, Washington D.C.	A screening model based on Johnson's model Hypervent (1991) that evaluates different remediation schemes such as SVE, Vacuum Enhanced Recovery and Bioventing. Models recovery versus time of up to 250 components partitioned between water, vapor, NAPL and soil.	Equilibrium partitioning between phases is assumed. Nonequilibrium partitioning may be incorporated using an efficiency factor. Oxygen limited biodegradation based on instantaneous reaction. Kinetics effects handled using a bio-efficiency factor. Can simulate recovery of the free floating product along with bioventing the unsaturated zone.
AIR FLOW MODELS		
MODAIR (1996); P3DAIR (1989) Guo Zheng Scientific Software Group , Washington D.C	MODAIR simulates airflow based on MODFLOW, the groundwater code. P3DAIR simulates the advective movement of vapors in the unsaturated zone. It is a particle tracking program for calculating air flow paths and travel times. The two models are used together for SVE system design.	Air flow and pressure calculations are computed by MODAIR. Vapor extraction wells can be specified as pressure controlled or volumetric rate controlled. P3DAIR calculates the travel times and pathlines for each particle along the x, y and z coordinates and initial and final positions of particles captured by sources/sinks. It can be used in 2D or 3D, steady-state or transient.
MULTIPHASE MODELS		
T2VOC (1995) R.W. Falta Karsten Pruess Stefan Finsterle Alfredo Battistelli	Three-dimensional, finite difference model for simulating flow and transport of organic contaminants in non-isothermal, heterogeneous, multi-phase systems.	Flow and transport of air, water and a VOC are simulated. Interphase mass transfer include evaporation and boiling of NAPL, dissolution of NAPL into the aqueous phase, condensation of VOC into the NAPL, equilibrium partitioning between the gas, aqueous, and NAPL phase, and condensation of water vapor from the gas phase. Accounts for heat transfer due to conduction, multiphase convection, and gaseous diffusion.
Bioventing (1997) Sistemas Ambientales y Tecnologías, Inc. Blacksburg, VA.	Finite difference, one dimensional, multiphase, multicomponent model for evaluation of design options for air-based in situ remedial technologies.	Air flow rates are calculated. Contaminant composition and recovery versus time is calculated. The model considers leakage from the ground surface, equilibrium partitioning, oxygen-limited biodecay, air turnover rates and their effect on recovery. The model computes costs for design options.
Source. (Bedient, et al, 1999)		

Table 4.1 Some models for unsaturated zone analysis.

5. NUMERICAL METHODS

5.1 General Concepts

Numerical methods are techniques from which some problems can be solved by using easy operations. There are a lot of types of these methods, but still have a common characteristic among them, which is making lots of arithmetic calculations using tools as computation.

The most regular mathematical formulations according to Bedient for making approximations of partial differential equations of flow and transport are:

- Finite differences methods.
- Finite element methods.
- Method of characteristics.
- Collocation methods.
- Boundary element methods.

Finite difference methods are easily understood and it is the most popular method for simulating groundwater flow and transport issues in both saturated and unsaturated zones.

On the other hand finite element methods operate also as the finite difference method by dividing the flow into elements but here they may vary in size and shape. Opposite as the finite difference it is needed a deep understanding in formal mathematics to keep up with the procedure.

The method of characteristics is suitable for solving hyperbolic equations; it was developed mainly to simulate advection process transport.

Collocation methods have in the advantages of the finite element method plus it not required integration procedures. Finally the boundary element methods, is a variant or the finite element method, and very used for the solution of elliptic equations. It is able to reduce a 2 or 3D problem to a one or two dimension solution (Bedient, et al, 1999).

There are different algorithms that may help get to a solution, such as polynomial roots, matrixes and vectors, interpolation and approximation and differentiation a numerical integration (ITESM).

In the polynomial roots, there can be found, Search by Increases, Bisection Method, Newton-Raphson Method and Secant Method. Different approaches can be pursued, that will vary in dependence of what is wanted to have as an output after applying them in a specific situation. Each of these methods are described below.

5.2 Search by Increases

It is used in order to find out polynomial real roots in subintervals. This technique search for intervals (a_k, b_k) , so that the function value will be negative either in a or b and positive in the other point.

For each subinterval (a_k, b_k) :

- Evaluate the function in both points a_k y b_k .

If $|f(a_k)|$ is equal to zero o smaller in relation a small number (ϵ) then a_k is a root.

If $|f(b_k)|$ is equal to zero o smaller in relation a small number (ϵ) then a_k is a root.

If $f(a_k)*f(b_k)$ is negative then the root between the subinterval is estimated.

5.3 Bisection Method

This is a method where an interval (a, b) is analyzed. The point in the middle of a and b is calculated by:

$$xMid = \frac{(a + b)}{2}$$

There are three possibilities when evaluating $f(xMid)$: if $f(xMid)$ equals zero, then $xMid$ is the root, or it can be found either left or right of $xMid$.

Bisection (a,b)

Calculate $xMid$

If $|f(xMid)|$ is zero or less than a small number (ϵ) then

$xMid$ is the root

or

If $f(a)*f(xMid) < 0$ then

bisection(a,xMid)

or

bisection(xMid,b)

5.4 Newton-Raphson Method

It is based in the use of a tangent line for an approximation of $f(x)$, near points where the functions value is zero.

- Choose an initial value (x_0)
- Calculate the next approximation x_1 using the formula:

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$$

- If $|x_n - x_{n+1}| < \epsilon$ then x_{n+1} is a root
If not, go back to step 2.

5.5 Secant Method

Involves finding a root with two initial approximations and using iteration. A problem of the Newton-Raphson method is the derivate evaluation, which can be approximated by a secant line, where:

$$f'(x_c) = \frac{(f(x_{n-1}) - f(x_n))}{(x_{n-1} - x_n)}$$

This derivate approximation can be substituted in Newton-Raphson equation.

- Choose an initial value (x_0)
- Calculate the next approximation x_1 using the formula:

$$x_{n+1} = x_n - \frac{f(x_n)(x_{n-1} - x_n)}{f(x_{n-1}) - f(x_n)}$$

- If $|x_n - x_{n+1}| < e$ then x_{n+1} is a root.
If not, go back to step 2.

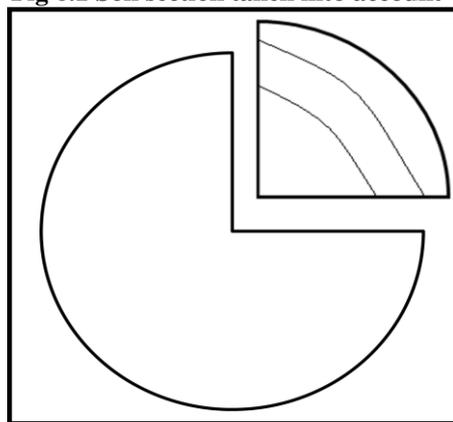
6. METHODOLOGY (MODEL DEVELOPMENT)

6.1 Conceptual Model

A hypothetical spill of toluene and benzene is being simulated in order to find out these compounds extraction by making use of an SVE system. It is assumed that the spilled took place in the unsaturated zone of a sandy soil formation. This model is only taking into account the equilibrium distribution equations for both compounds. Volumetric flow rate is considered to be air plus hydrocarbon vapors into the vacuum well. Some assumptions where, made such as that the contaminant is distributed uniformly along a certain amount of soil. It is supposed that an advective-diffusion process is taking place in the zone. It is also assumed that the vapor, free-liquid, sorbed and dissolved phases are always in equilibrium. Vapor phase behaves as an ideal gas, free liquid phase behaves as an ideal mixture and soil moisture phase is nonideal (Johnson, et al, 1990). It is desired to observe the total removal mass loss along time.

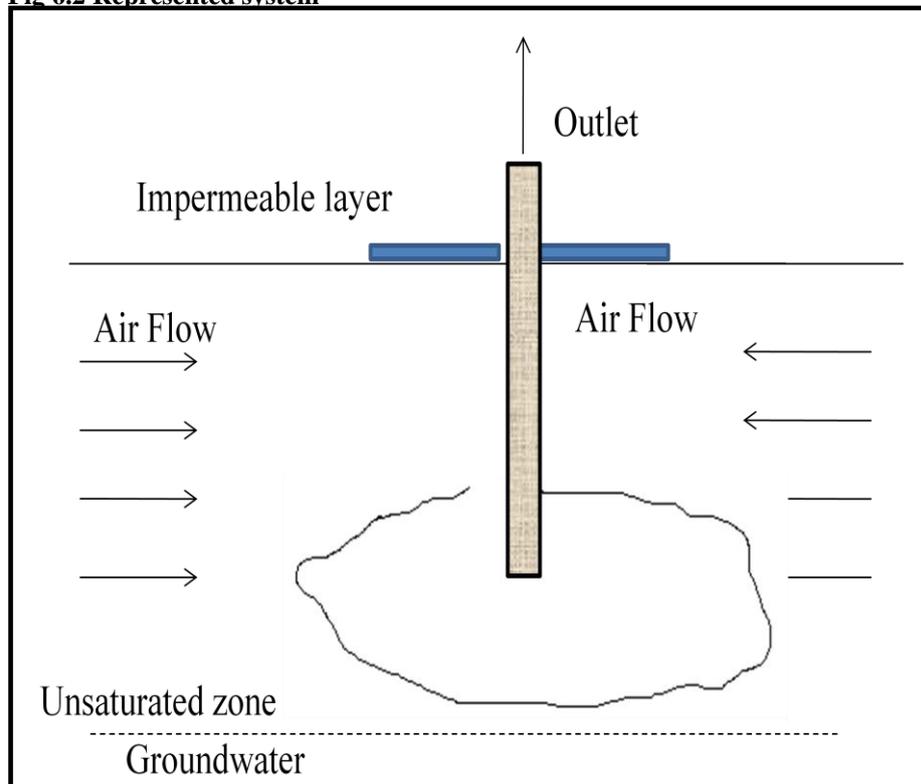
Only a small section of soil is taken into account for this model and simulation; it is divided itself in three more parts where the contaminants are distributed from small to bigger amount, just as the next figures shows it.

Fig 6.1 Soil section taken into account



In a more graphic way, the next figure shows the simulated system.

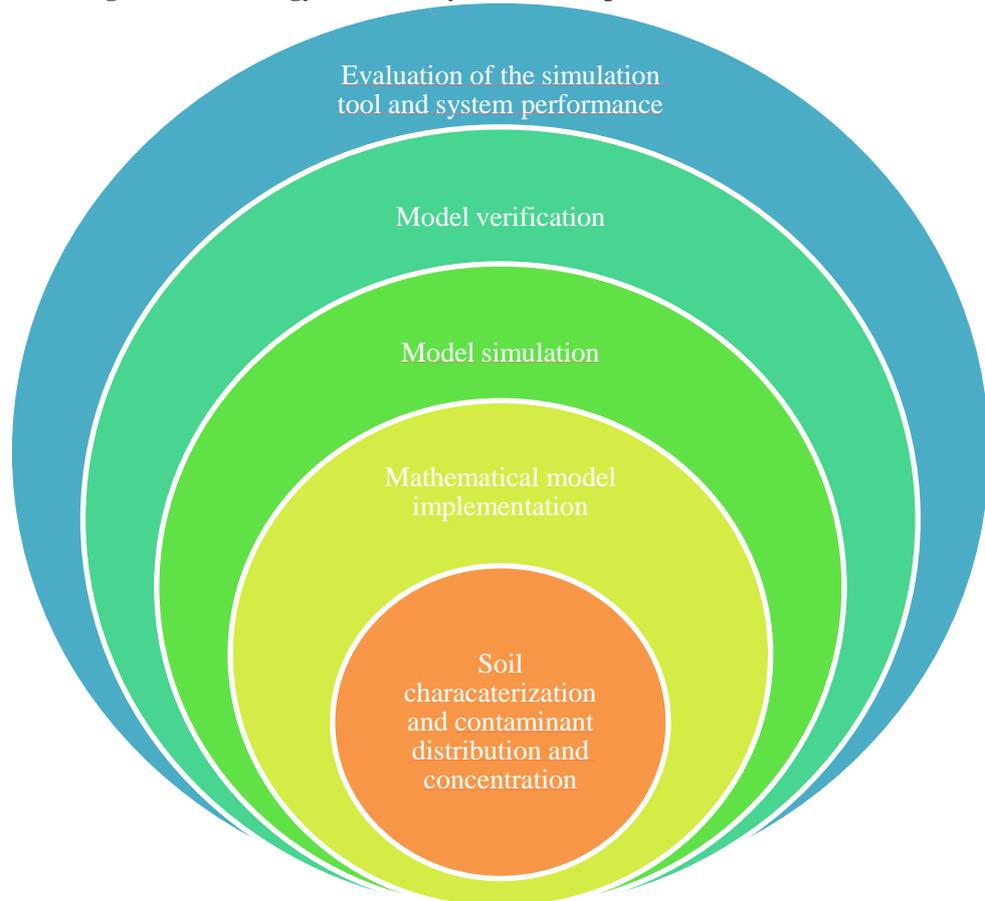
Fig 6.2 Represented system



6.2 Methodology Description

A general diagram has been developed to have an overall overview of what it is needed to be done in order to approach and fulfill the general and specific objectives of this work.

Fig 6.3 Methodology for an analysis of a SVE process



The first step for developing this work a bunch of conditions and assumptions were needed to be established in order to make the model run correctly. The underlying characteristics under which the program has been developed and are going to be further described, but it is important to mention that the considerations of the operational parameters are ones used on normal bases in an actual remediation processes; were mainly based on the text written in the by (Johnson et al, 1990).

The zero dimensional model has been developed to simulate contaminant degradation during site remediation of an SVE technique with a constant airflow

injection during 24 hours operation. It is desired to find out how the contaminants respond to such an operation. Moreover an evaluation of the use of excel as a simple simulation tool is going to be done.

The main equations that govern the degradation process are also part of the paper written by the same author.

For this project two compounds were taken into consideration, toluene and benzene. Both of them are VOCs that can be easily removed from soil matrix by SVE technique, this is the main reason because of why they were both chosen for this simulation exercise.

The equations used for the development of the project are the following ones. This first equation represents the total mole balance for the component i, in this case either toluene or benzene.

$$\frac{dM_i}{dt} = -QC_i - B_i \quad \dots (1)$$

In this equation M_i represents the total amount of moles of i in the soil in each phase in which the compound is distributed; this means either vapor, aqueous, liquid or solid phase. t is the variable defining time in hours. Q is the volumetric flow rate of air including the hydrocarbons vapors in the vacuum well. C_i is the molar concentration of each component i that is incoming into the vacuum well. B_i denotes the rate of degradation of i due to biological or chemical processes, in this case desorbed.

As Johnson did in his article, it is assumed that the vapor, liquid, solid and aqueous phases are in all time in equilibrium, in order to obtain a relationship between M_i and C_i , which is given by the next equation:

$$M_i = \frac{z_i P \epsilon V}{RT} + M^{HC} + y_i M^{H_2O} + k_i y_i \frac{M_{soil}}{M_{w,H_2O}} \quad \dots (2)$$

Where:

z_i = mole fraction of i in the vapor phase.

x_i = mole fraction of i in the liquid or free liquid phase.

P = total pressure in the pore vapor in atm.

ϵ = void fraction occupied by vapor.

V = volume of contaminated soil in cm^3 .

R = gas constant ($82.1 \text{ cm}^3 \cdot \text{atm/molK}$)

T = absolute temperature in soil in K.

M^{HC} = total moles in free-liquid phase.

y_i = mole fraction of i dissolved in soil moisture.

$M^{\text{H}_2\text{O}}$ = total moles in soil moisture phase.

k_i = sorption coefficient for i component.

M_{soil} = total mass of contaminated soil in g.

$M_{\text{w,H}_2\text{O}}$ = molecular weight of H_2O (18g/mol).

Sorption coefficients can be calculated with the following expression:

$$k_i = 0.63 k_{\text{ow},i} f_{\text{oc}} \frac{\text{gm}_i/\text{gm}_{\text{soil}}}{\text{gm}_i/\text{ml}_{\text{H}_2\text{O}}} \dots (3)$$

Where:

$k_{\text{ow},i}$ = is the octanol-water partition coefficient.

f_{oc} = is the organic carbon fraction in soil.

Activity coefficients that are also needed in the formula can be estimated from the solubility values of the compounds, this is:

$$\alpha_i = \frac{1}{y_i} = (55.55 \text{ moles/l}) M_{\text{w},i} / S_i \dots (4)$$

All phases can be related by the next equation:

$$z_i P = x_i P_i^V = \alpha_i y_i P_i^V = C_i RT \quad \dots (5)$$

Where P_i^V is the component vapor pressure in its pure form.

This next equation was used in order to determine the mole fraction of component i in the liquid phase.

$$x_i \left\{ \frac{P_i^V}{RT} + M^{HC} + \frac{M^{H_2O}}{\alpha_i} + \frac{k_i M_{soil}}{\alpha_i M_{w,H_2O}} \delta(M^{H_2O}) \right\} = M_i \quad \dots (6)$$

Where if,

$$\delta(M^{H_2O}) = 0 \text{ if } M^{H_2O} = 0$$

$$\delta(M^{H_2O}) = 1 \text{ if } M^{H_2O} > 0$$

In order to determine M^{HC} needed in the previous equation, it is required to calculate it iteratively for various sets of M_i values under the constrain that the sum of all x_i for every component is equal to 1.

The next expression was used in order to determine the distribution of the component i in dissolved in soil moisture or which it is the same in the aqueous phase. So that if all the products $\alpha_i y_i$ calculated are less than unity for some given M_i then the equilibrium distribution does not include a liquid phase.

$$\alpha_i y_i = \frac{M_i}{\left[\frac{P_i^V \epsilon V}{RT} + \frac{M^{H_2O}}{\alpha_i} + \frac{k_i M_{soil} \delta(M^{H_2O})}{\alpha_i M_{w,H_2O}} \right]} \quad \dots (7)$$

This is the solution for equation 1, with a given set of time in this case given in hours. This is solved iteratively, calculating for each time step a new set of values of M_i and in consequence new x_i values.

$$M_i(t + \delta t) = M_i(t) - \delta t \frac{Q x_i P_i^V}{RT} \quad \dots (8)$$

It is important to know that a typical vacuum well vapor flow rate (Q) is 9440cm³/s, but as Johnson in its paper did, it is assumed that only a 25% of the air will actually flow through the contaminated soil. This and other considerations are summed up in a further table.

Another assumption is that the contaminated zone is covered with an impermeable layer that is supposed to be located in the soil surface in order to enhance no air losses or inlets during the SVE technique process.

As it was mentioned before the two used compounds were benzene and toluene and their physical properties for both components are seen below.

	Formula	Molecular Weight (g/mol)	Pi (20 c, atm)	Tb (1 atm, c)	Si (20 c, mg/l)	Kow
Benzene	C ₆ H ₆	78.1	0.1	80	1780	135
Toluene	C ₇ H ₈	92.1	0.029	111	515	490

Table 6.1 Physical properties for Benzene and Toluene.

This next table shows the soil and contaminant input data, some of them are based in the same article from Johnson and some others proper assumptions:

Volume (cm3)	40000000
Soil Density	2500
Runiv (cm3*atm/molK)	82.1
Temp (K)	293
foc	0.01
vfobv	0.4
Delta(MH2O)	1
Q (cm3/hr)	8.49E06
MW H2O (g/mol)	18
Msoil (g)	100000000
Mbenzene (g)	1400000
Mtoluene (g)	600000

Table 6.2 Soil and contaminant input data.

The first step was to develop the mole balance for the compounds, as following:

$$M_T = M_{Dry} + M_{Humid} \dots (9)$$

It is said that soil moisture quantity is 10% by dry soil weight,

$$M_{Humid} = 0.10M_{Dry} \dots (10)$$

So,

$$M_T = M_{Dry} + 0.10M_{Dry}$$

$$M_T = 1.10M_{Dry}$$

Taking into account that $M_T = 100000000g$, it is that,

$$M_{Dry} = 90909090.9g$$

$$M_{Humid} = 9090909.09g$$

Calculating mol numbers for each compound:

$$n_{H_2O} = \frac{M_{Humid}}{M_{w,H_2O}} \dots (11)$$

If,

$$M_{Humid} = 9090909.09g \quad M_{w,H_2O} = 18g/mol$$

$$n_{H_2O} = 505050.505mol$$

Making the same calculus for both compounds it is that:

$$n_{Benzene} = 17925.7mol \quad ; \quad n_{Toluene} = 6514.66mol$$

And,

$$n_{Total} = 529490.899mol$$

These are some results of the calculus made before making use of the main distribution equations and the total mole balance.

	Benzene	Toluene
Activity coefficient (α_i)	2437.33427	9934.28155
K_i	0.8505	3.087
Mole No.	17925.7362	6514.65798
$\alpha_i Y_i$	8.10268303	3.62635944
C_i	3.0401E-06	3.2593E-07

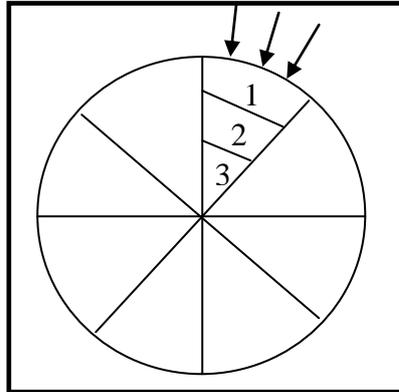
Table 6.3 Calculations

At this point one of the restriction is applied $\alpha_i y_i < 1$ there is no free phase. In this case there is, so the use of equations 6, 7 and 8 are solved iteratively and simultaneously.

This figure illustrates the contamination in a certain zone and its corresponding distribution; since it is a zero dimensional model the simulation of this model is only

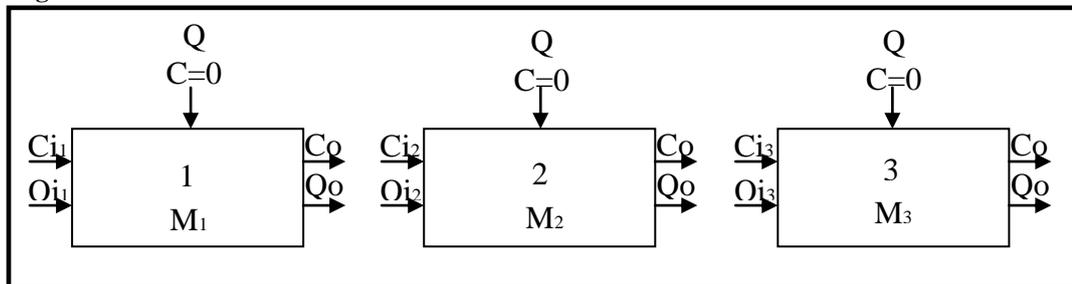
given in one point of the contaminated zone. This zone is divided into three subzones in a way that the mole number in each compartment goes from the smallest to the biggest, this way the degradation of the pollutant is going to be done like it was in a continuous stirred tank reactor.

Fig 6.4 Soil contaminated section and flow inlet



Having a close look to the compartments the figure is seen this way:

Fig 6.5 Contaminant distribution and flow inlets



The arrows demonstrate the direction of the input of clean injected air and this next table explains the mole distribution of each compound in every compartment and the corresponding x_i fraction.

	Benzene	Fraction	Toluene	Fraction
M_{i1}	2560.81946	0.14285714	977.198697	0.15
M_{i2}	6530.08963	0.36428571	1302.9316	0.2
M_{i3}	8834.82714	0.49285714	4234.52769	0.65

Table 6.4 Mole distribution of each compound.

According to this previous set of moles and taking into consideration the restrictions for x_i , the new amount for M^{HC} is 22300mols.

Based on the previous, the mole balance for determining the pollutant degradation it is like the following equations:

$$M_1(1) = M_1(0) + \Delta t Q_{i_1} C_{i_1}(0) - \Delta t Q_{o_1} C_{o_1}(0) \dots (12)$$

$$M_2(1) = M_2(0) + \Delta t Q_{o_1} C_{o_1}(0) - \Delta t Q_{o_2} C_{o_2}(0) \dots (13)$$

$$M_3(1) = M_3(0) + \Delta t Q_{o_2} C_{o_2}(0) - \Delta t Q_{o_3} C_{o_3}(0) \dots (14)$$

These same equations are needed to be solved iteratively for every set of new values in the different in each increase of time which is 1hr.

After calculating in every time step the new values for the equilibrium between phases, graphics will show the degradation tendencies for both components. Such results and contaminant behavior are going to be described in the next chapter.

Two more simulations were done in order to see the behavior of the same system under little differences, such as an increase in the benzene and toluene mass and a variation in the fraction of organic carbon and augmentation of the volumetric flow.

Volume (cm3)	40000000
Soil Density	2500
Runiv (cm3*atm/molK)	82.1
Temp (K)	293
foc	0.01
vfov	0.4
Delta(MH2O)	1
Q (cm3/hr)	8.49E06
MW H2O (g/mol)	18
Msoil (g)	100000000
Mbenzene (g)	2000000
Mtoluene (g)	900000

Table 6.5 Data with mass variation

Volume (cm3)	40000000
Soil Density	2500
Runiv (cm3*atm/molK)	82.1
Temp (K)	293
foc	0.075
vfov	0.4
Delta(MH2O)	1
Q (cm3/hr)	9.85E06
MW H2O (g/mol)	18
Msoil (g)	100000000
Mbenzene (g)	2000000
Mtoluene (g)	900000

Table 6.6 Data with foc and Q variation

7. RESULTS

The simulation exercise done for the extraction and degradation of toluene and benzene from soil matrix by a continuous SVE operating system helped visualize the behavior of both compounds under the restrictions mentioned in the previous chapter.

The table below is just a short glimpse of the results of the simulation process, after only 5hrs of the operating system. It is clearly seen that both compounds after calculating for each time step the new equilibrium, the behavior of them have a diminish tendency in every phase. This procedure was done until 936hrs, which equals 39 days of operation.

Time (hr)	Phase	Benzene (mol)	Fraction	Toluene (mol)	Fraction
0	Air z	1579.3976	0.08810782	61.5388903	0.00944622
0	Water y	59.5923836	0.0033244	2.3780775	0.00036503
0	Free x	13109.0001	0.73129494	1761.28548	0.27035732
1	Air z	1579.55583	0.08820224	61.5097878	0.0094538
1	Water y	59.47678542	0.003321178	2.372020722	0.00036457
1	Free x	13110.31338	0.73207859	1760.452548	0.270574252
2	Air z	1576.48741	0.08811653	61.3839844	0.00944413
2	Water y	59.3612467	0.00331795	2.367169328	0.000364197
2	Free x	13084.84548	0.731367181	1756.851968	0.270297413
3	Air z	1573.42057	0.08803078	61.2583182	0.00943445
3	Water y	59.24576758	0.003314721	2.362323224	0.000363824
3	Free x	13059.39072	0.730655448	1753.255315	0.270020593
4	Air z	1570.99753	0.08798095	61.1582225	0.0094287
4	Water y	59.1303482	0.003311491	2.357482407	0.000363451
4	Free x	13039.27948	0.730241907	1750.390505	0.269856014
5	Air z	1570.5017	0.08803911	61.1345145	0.00943473
5	Water y	59.01498871	0.003308259	2.352646875	0.000363078
5	Free x	13035.16408	0.730724577	1749.711967	0.27002848

Table 7.1 Short glimpse of results of simulation process

The numbers above are better understood with the use of graphics. The next two figures below show the aqueous phase for both compounds and its behavior in the same period of time. This clearly shows a tendency for a decrease of the presence of the contaminant in soil matrix, almost reaching a value of zero along the process. According to Raoult's Law, which establishes the relation between the vapor pressure of each component in an ideal solution is dependent of the vapor pressure of every

compound and the molar fraction of it in the solution. By taking a look to the graphics, benzene and toluene respectively, it is clear that this law explains the tendency of the contaminant fall with every time step along the solution of the mathematical model was done. So as the gaseous phase of the compounds increases, the pressure of each one of them decreases as well as the molar fraction in every time step. Particularly in this case of the aqueous phase, an asymptotic tendency with the pass of time is observed.

Figure 7.1 Simulation results of Benzene in aqueous phase

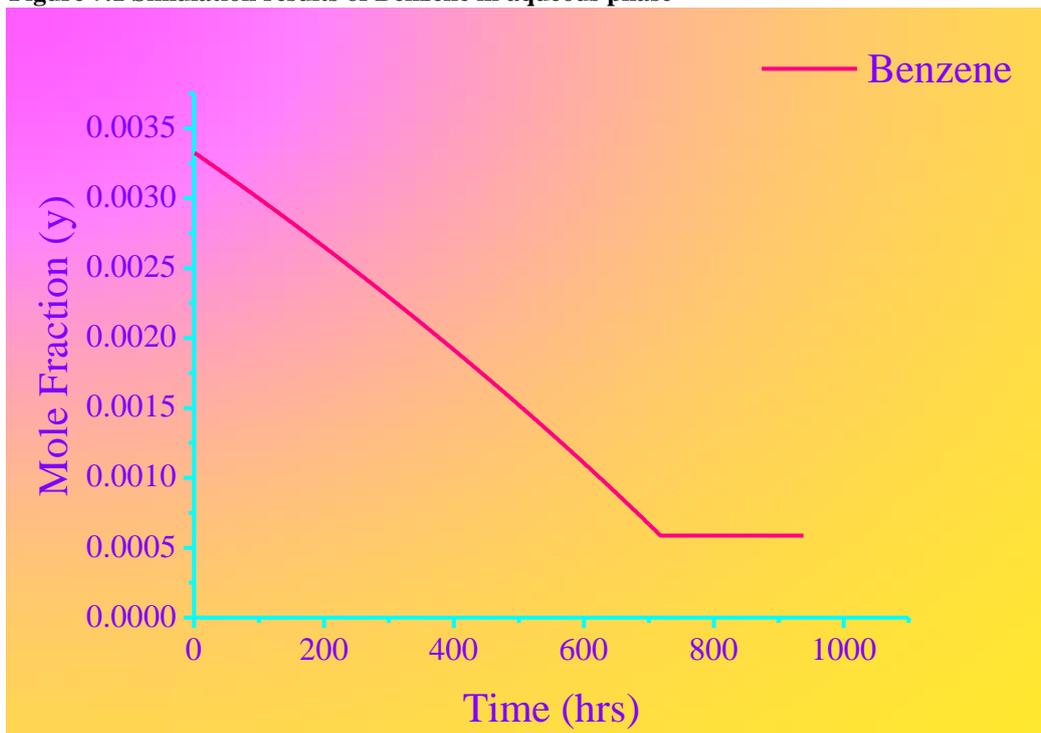
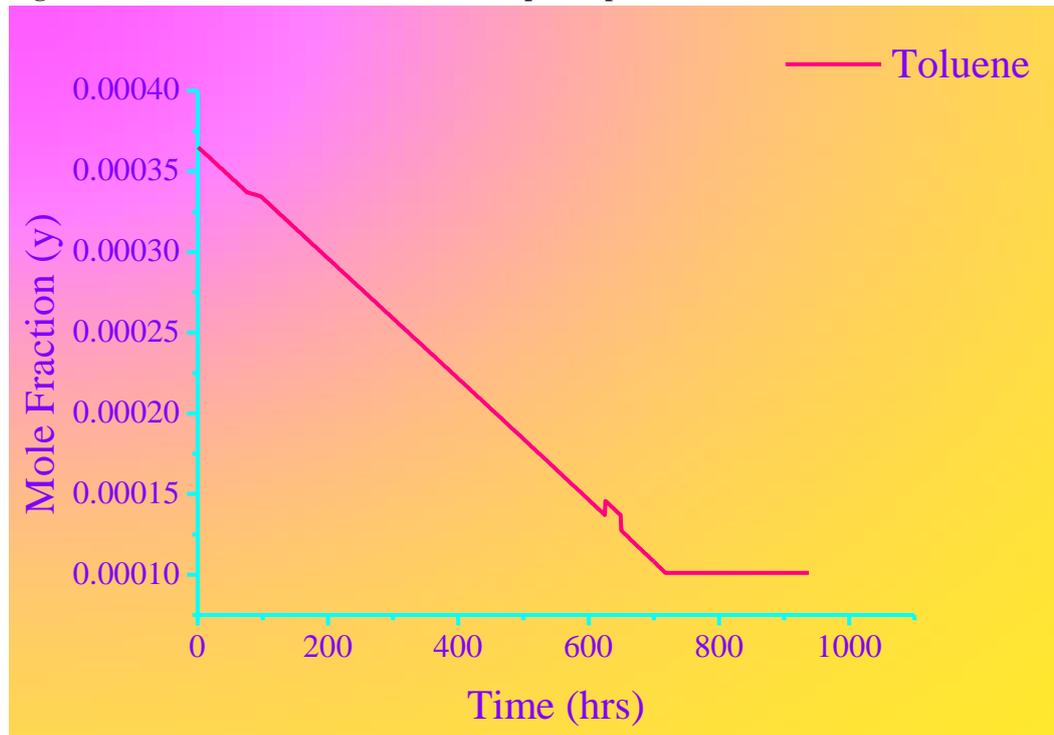


Figure 7.2 Simulation results of Toluene in aqueous phase



Graphic number 7.2 shows an abnormal behavior approximately between the hours 616 and 657. This behavior might be explained with the issue that at that point the value of the quantity of hydrocarbon moles was bigger than the previous value of it and after a few more operation hours it fits again to the expected tendency.

On the other hand, graphics 7.3 and 7.4 show the behavior of benzene and toluene respectively, but both in the free liquid phase.

It is seen that while the concentration of benzene decreases, toluene increases. This is explained because the capacity of the benzene to volatilize is high, meaning that the Henrys constant of the benzene is bigger than the one of the toluene. The process acts like this, while the benzene is being extracted, the toluene occupies the free spaces left by the benzene. This does not mean that the quantity of toluene moles increases, but certainly the concentration does. This same tendency is shown along the whole process. The free liquid phase does not exist up to the 39 days of operation, but yes until the day 29, where the benzene and toluene in this phase is exhausted. Meanwhile the partitioning between the other phases still exists.

Figure 7.3 Simulation results of Benzene in free liquid phase

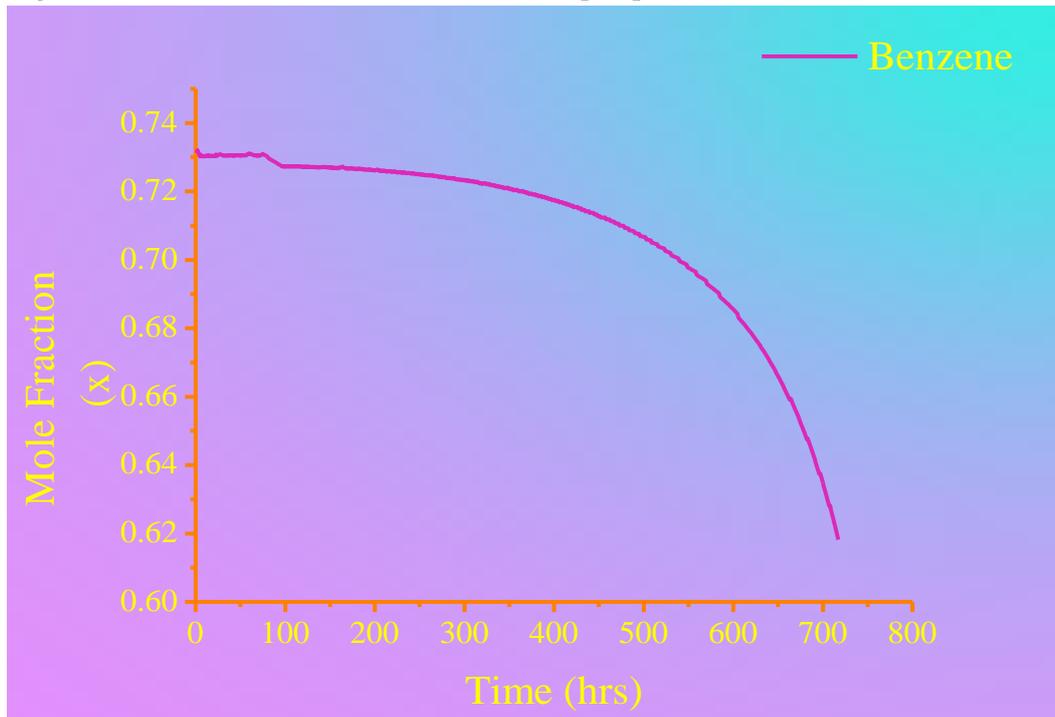
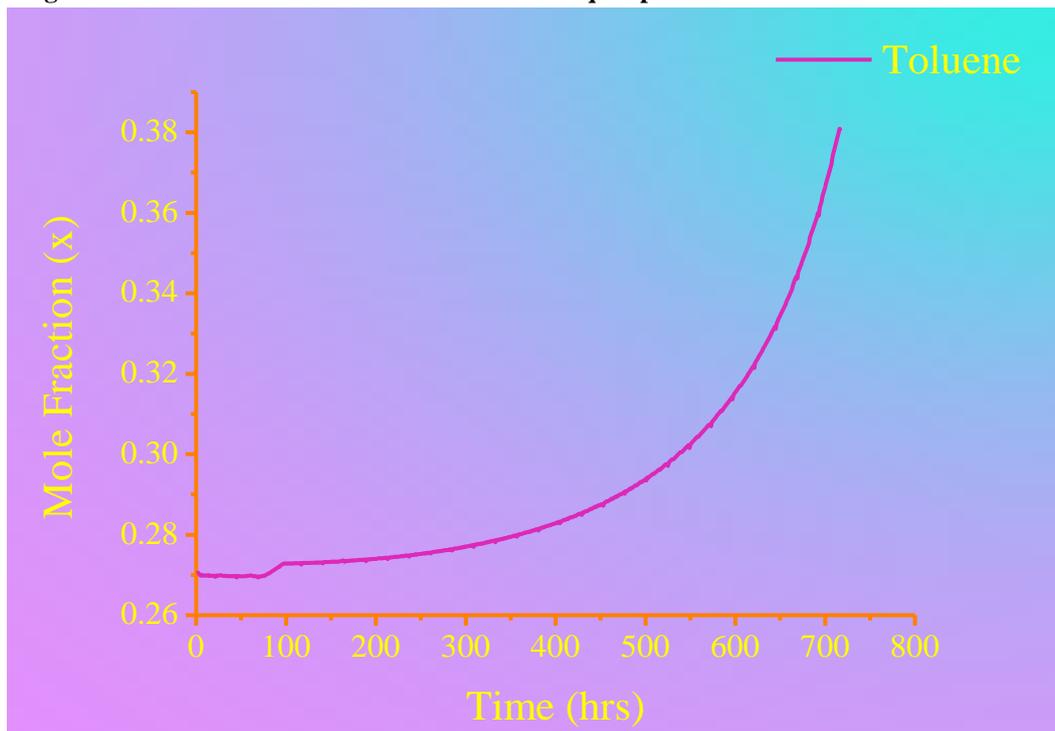


Figure 7.4 Simulation results of Toluene in free liquid phase



These next figures will show the mole quantity for benzene and toluene in their two phases, free liquid and aqueous phase respectively. These clearly shows the decrease of moles in soil matrix for each compound as the SVE system operates in 39 days.

Figure 7.5 Simulation results of mole quantity for Benzene

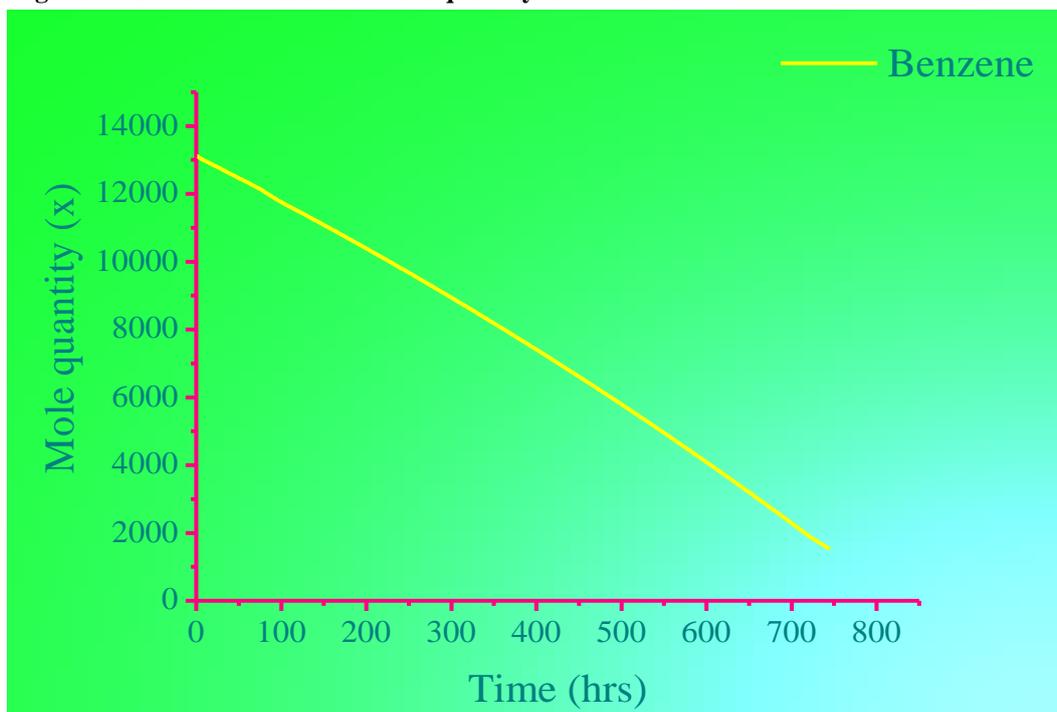


Figure 7.6 Simulation results of mole quantity for Toluene

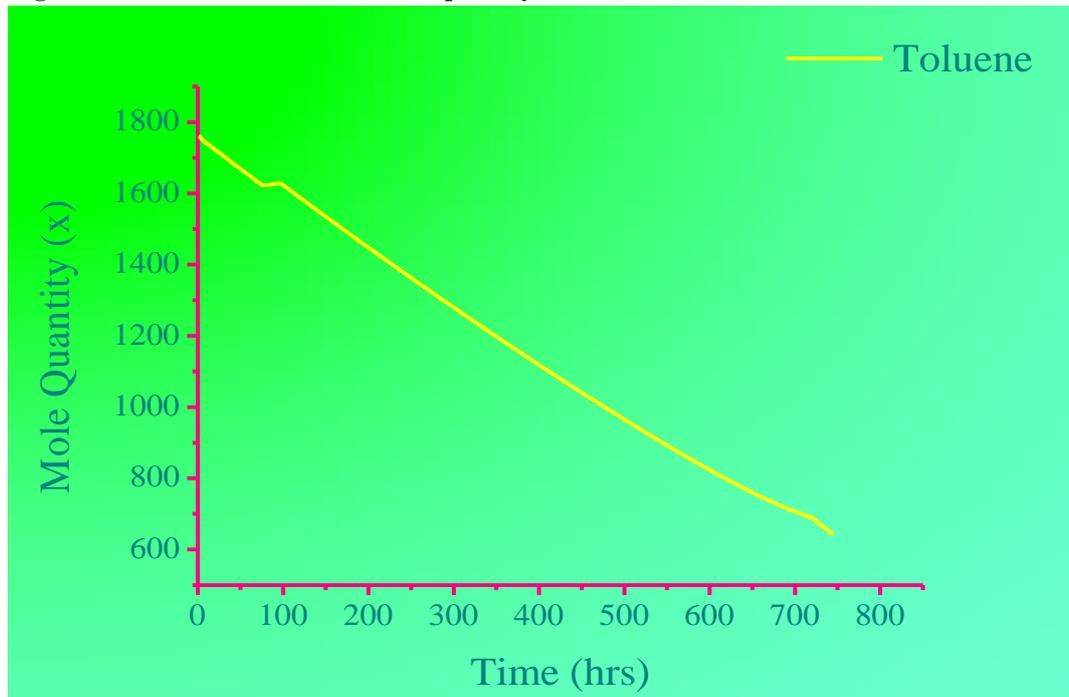


Figure 7.7 Simulation results of amount of moles for Benzene

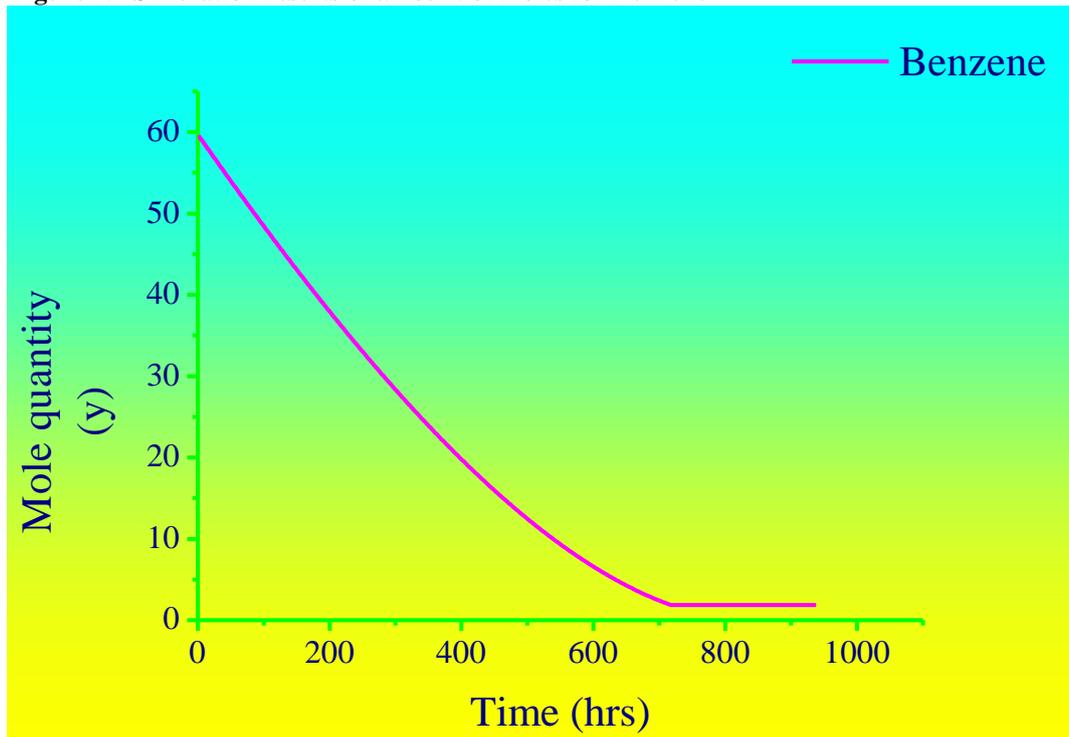
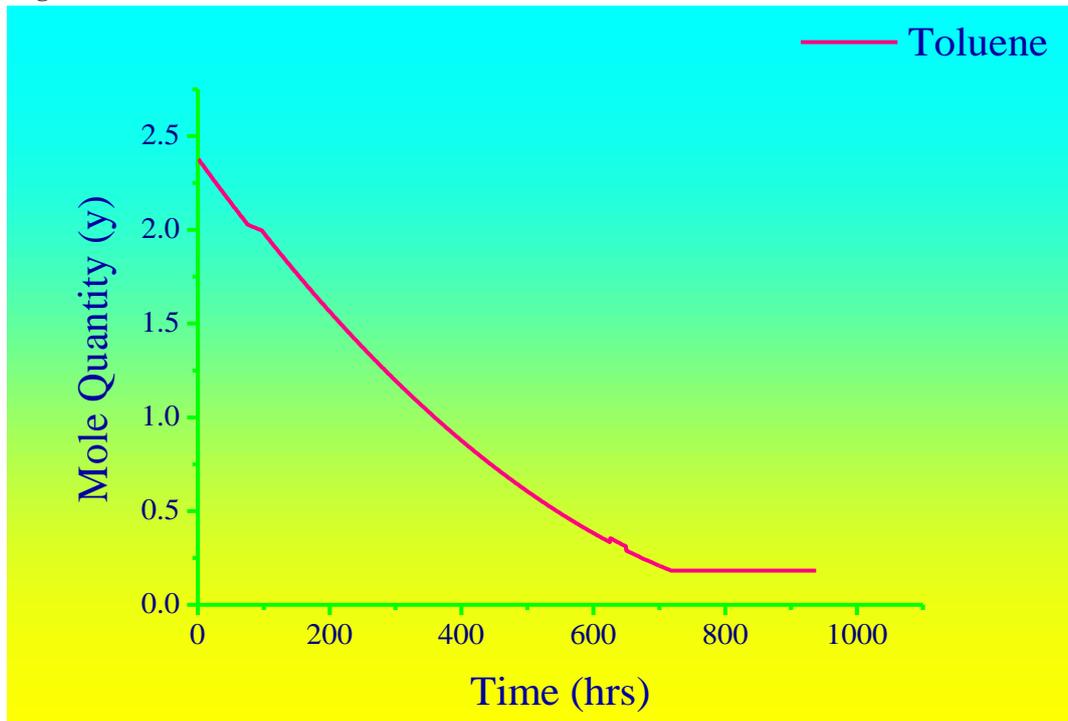


Figure 7.8 Simulation results of amount of moles for Toluene



The two last graphics shows finally the amount of moles of benzene and toluene which after the hours of operation end up in a asymptotic line, which can be translated to a favorable extraction of contaminants from soil matrix.

As a summary it can be said that after making use of the corresponding equations and running the simulation process, the previous graphics have shown the behavior of both contaminants as time runs and the extraction technique showed favorable for these type of contaminants under that specific case. It is important that each time step corresponds to 1hr. Finally the extraction process of the pollutant ended up by approximately after 936hrs, which corresponds to 40 days of an uninterrupted SVE operating system. The conditions of operation of this technique were described in the previous chapter.

It is important to notice that the partitioning of both components at the beginning of the process where between the four different phases; this means between the gaseous, liquid, solid and aqueous phase. These phases were eventually disappearing as time goes by.

After making the previous simulation two more simulations were run under small variations of parameters, as mentioned in the previous chapter. Also graphics were generated in order to see the systems behavior under such changes.

For the second simulation where only the amount of benzene and toluene were increased not really big change was observed at all. The system showed only one hour

difference when the free liquid phase disappeared. Graphics generated by this simulation were omitted from these results as they showed no significant difference at all in comparison with the ones obtained in the first exercise.

In the last simulation done it was observed that neither both compounds presented free liquid phase. This means they were only distributed along aqueous, air and adsorbed phases. After some hours of operation variations between numbers were little, so that the simulation under those conditions worked.

8. CONCLUSIONS AND RECOMMENDATIONS

In this chapter the conclusions that have been achieved after the evaluation of the results obtained once the simulation process of the SVE technique has been done; moreover advantages and disadvantages of the developed model and finally the recommendations that have been achieved along the work, including the simulation process are going to be described and discussed in the next sentences in order to have an understanding of its future application and methodology usage.

As it has been mentioned before, this model has been developed under certain conditions and restrictions. This means that any change of any of this pre-established operating conditions and restrictions that might want to be applied can probably produce different outputs that would be convenient to be evaluated before the use of it and this way the user can establish whether the model can be used or not. It is highly recommended the study of the model operation and its characteristics before applying it to real situations. This with the main objective of a better understanding of the process in order to generate the correct and expected results.

On the other hand, this model has correctly worked and has fulfilled the generated expectations while the development of the model and by which it was designed in the first place. It is important to emphasize that the simulation as an effective tool for the determination of the degradation and/or extraction of the compounds used in this simulation exercise, in this case benzene and toluene.

It is also important to take into account that the possibility of the modification of this model is feasible. This means that in dependence of the necessities of the model user, it can be added for example other compounds and their particular characteristics, obviously if needed.

Another highlight of the process needed for the solution of the model and that also was a big consideration, is that the contaminant is distributed in three different compartments. This explanation can be seen in the chapter where the methodology was fully described.

The constant study and comprehension of the processes that are taken place in soil matrix and compounds partitioning, is needed, in order to make a good use of the mathematical model, equations that will guide the development of the technique.

It is highly recommended, for the simulation itself and generation of the mathematical model, to apply or search of a real study case. This is with the main goal

to obtain the validation of it and will eventually guarantee the onwards use of it where an SVE system is taken place.

Another consideration is that the processes do not act or behave individually, so during the development of the model it is not correct to consider the system as a whole.

This work was based under certain assumptions and making some other considerations, this means that the model was working (in a kind of way) under ideal conditions. This fact limits the further application of the model for a real site case, but it certainly has fulfilled the expectations and requirements for which it was created in the first place.

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ANNEX A

Suelo

Volumen (cm³)	40000000
Densidad Suelo	2500
Runiv (cm³*atm/molK)	82.1
Temp (K)	293
foc	0.01
vfov	0.4
Delta(MH₂O)	1
Q (cm³/hr)	8.49E+06
PM H₂O (g/mol)	18

Masa Contaminada

Msoil (g)	100000000
Mbenceno (g)	1400000
Mtolueno (g)	600000

Tiempo

Incremento de tiempo (hr)	1
----------------------------------	---

Propiedades

	Benceno	Tolueno
PM (g/mol)	78.1	92.1
Pi (20 c, atm)	0.1	0.029
Tb (1 atm, c)	80	111
Si (20 c, g/l)	1.78	0.515
Kow	135	490

Parametros

	Benceno	Tolueno
Coef de actividad (α_i)	2437.33427	9934.28155
K_i	0.8505	3.087
No. Moles	17925.7362	6514.65798
$\alpha_i Y_i$	8.10268303	3.62635944
C_i	3.0401E-06	3.2593E-07

Restriccion

$\alpha_i Y_i < 1$ No hay fase libre

	Benceno	Fraccion	Tolueno	Fraccion
M_{i1}	2560.81946	0.14285714	977.198697	0.15
M_{i2}	6530.08963	0.36428571	1302.9316	0.2
M_{i3}	8834.82714	0.49285714	4234.52769	0.65

Balance

$$M_T = M_{\text{Dry}} + M_{\text{humid}}$$

$$M_{\text{humid}} = 0.10 M_{\text{Dry}}$$

M_{Dry}	90909090.9
$M_{\text{humid}} = M_T - M_{\text{Dry}}$	9090909.09

$n_{\text{H}_2\text{O}} = M_{\text{humid}} / P_{\text{M}_{\text{H}_2\text{O}}}$	505050.505
No. Moles totales	529490.899

Moles HC fase libre	22300
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ANNEX B

		Benceno			Tolueno			Benceno y Tolueno	
		o	Fraccion	C_i	Fraccion	o	o y	Tolueno	
						y		y	
C	5.04195	M ₁ (1	2555.77	0.14271	1.53527	974.431	0.14976	1.15524	0.54241
<i>i</i>	393)	75	436	497	5	609	711	359
C	12.8569	M ₂ (1	6522.27	0.36420	2.04703	1300.16	0.19982	2.94815	0.72373
<i>i</i>	825)	46	316	329	44	988	917	156
C	17.3947	M ₃ (1	8830.28	0.49308	6.65285	4231.76	0.65040	3.99141	2.35559
<i>i</i>	41)	94	248	821	05	403	408	331
		M _T (1	17908.3			6506.35			
)	415	1		65	1		
		$\alpha_i Y_i$	8.09482			3.62173			
			036			847			
		2225	24462.3	0.73207		24046.4	0.27057		
MHC		0	211	859		733	425		
					1.00265				
					284				
								Benceno	Tolueno
								o y	y
C	5.03691	M ₁ (2	2550.74	0.14257	1.53288	972.898	0.14968	1.15297	0.54156
<i>i</i>	462)	06	165	081	7	364	036	032
C	12.8540	M ₂ (2	6514.45	0.36412	2.04529	1299.65	0.19995	2.94462	0.72344
<i>i</i>	689)	74	049	209	20	571	571	633
C	17.4026	M ₃ (2	8825.74	0.49330	6.65699	4227.14	0.65036	3.98935	2.35302
<i>i</i>	939)	08	786	357	88	065	803	623
		M _T (2	17890.9			6499.69			
)	388			95			
		$\alpha_i Y_i$	8.08695			3.61803			
			41			288			
		2225	24462.3	0.73136		24046.4	0.27029		
MHC		0	211	718		733	741		
					1.00166				
					459				
								Benceno	Tolueno
								o y	y
C	5.03187	M ₁ (3	2545.70	0.14242	1.53203	971.366	0.14960	1.15069	0.54070
<i>i</i>	769)	87	9	694	6	114	588	752
C	12.8511	M ₂ (3	6506.63	0.36403	2.04657	1299.13	0.20008	2.94109	0.72315
<i>i</i>	512)	82	771	998	75	146	129	991
C	17.4106	M ₃ (3	8821.18	0.49353	6.65654	4222.53	0.65031	3.98729	2.35046
<i>i</i>	486)	13	33	955	89	741	708	01
		M _T (3	17873.5			6493.04			
)	282	1		30	1		
		$\alpha_i Y_i$	8.07908			3.61432			

		424			753				
		2225	24462.3	0.73065		24046.4	0.27002		
MHC		0	211	545		733	059		
					1.00067				
					604				
								Bencen	Tolueno
								o y	y
C	5.02684	M ₁ (4	2540.68	0.14228	1.53119	969.835	0.14951	1.14842	0.53985
<i>i</i>	314)	19	642	256	4	859	368	518
C	12.8482	M ₂ (4	6498.81	0.36395	2.04786	1298.62	0.20020	2.93755	0.72287
<i>i</i>	294)	68	48	7	08	712	591	231
C	17.4186	M ₃ (4	8816.61	0.49375	6.65610	4217.93	0.65027	3.98523	2.34789
<i>i</i>	05)	09	878	69	06	429	12	494
		M _T (4	17856.1			6486.38			
)	095	1		69	1		
		$\alpha_i Y_i$	8.07121			3.61062			
			079			244			
		2224	24452.3	0.73024		24036.4	0.26985		
MHC		0	211	191		733	601		
					1.00009				
					792				
								Bencen	Tolueno
								o y	y
C	5.02181	M ₁ (5	2535.66	0.14214	1.53034	968.305	0.14943	1.14615	0.53900
<i>i</i>	096)	01	391	768	1	6	375	332
C	12.8453	M ₂ (5	6490.99	0.36387	2.04915	1298.10	0.20033	2.93401	0.72258
<i>i</i>	033)	33	178	317	20	269	958	352
C	17.4265	M ₃ (5	8812.02	0.49398	6.65566	4213.32	0.65023	3.98316	2.34533
<i>i</i>	632)	96	432	562	41	131	041	075
		M _T (5	17838.6			6479.73			
)	830	1		12	1		
		$\alpha_i Y_i$	8.06333			3.60691			
			374			759			
		2220	24412.3	0.73072		23996.4	0.27002		
MHC		0	211	458		733	848		
					1.00075				
					306				
								Bencen	Tolueno
								o y	y
C	5.01678	M ₁ (6	2530.64	0.14200	1.52950	966.775	0.14935	1.14388	0.53815
<i>i</i>	114)	33	146	23	6	335	609	193
C	12.8423	M ₂ (6	6483.16	0.36378	2.05043	1297.58	0.20045	2.93048	0.72229
<i>i</i>	732)	77	864	847	11	819	231	354

C i	17.4345	M ₃ (6	8807.43	0.49420	6.65522	4208.71	0.65018	3.98108	2.34276
	232)	75	99	57	93	846	469	751
		M _T (6	17821.2			6473.07			
)	485	1		60	1		
		$\alpha_i Y_i$	8.05545			3.60321			
			309			298			
			2219	24402.3	0.73030		23986.4	0.26986	
MHC		0	211	956		733	36		
					1.00017				
					316				

							Bencen	Tolueno	
							o y	y	
C i	5.01175	M ₁ (7	2525.63	0.14185	1.52865	965.246	0.14927	1.14162	0.53730
	369)	15	908	64	9	066	071	101
C i	12.8394	M ₂ (7	6475.34	0.36370	2.05172	1297.05	0.20058	2.92694	0.72200
	389)	00	538	291	80	359	408	238
C i	17.4424	M ₃ (7	8802.83	0.49443	6.65478	4204.11	0.65014	3.97900	2.34020
	849)	44	554	716	63	575	405	523
		M _T (7	17803.8			6466.42			
)	060	1		12	1		
		$\alpha_i Y_i$	8.04756			3.59950			
			885			862			
			2217	24382.3	0.73019		23966.4	0.26981	
MHC		0	211	324		733	113		
					1.00000				
					437				

							Bencen	Tolueno	
							o y	y	
C i	5.00672	M ₁ (8	2520.62	0.14171		963.719	0.14918	1.13935	0.53645
	86)	48	677	1.52781	1	791	76	056
C i	12.8365	M ₂ (8	6467.51	0.36362	2.05300	1296.53	0.20070	2.92340	0.72171
	004)	02	2	648	28	892	492	003
C i	17.4504	M ₃ (8	8798.22	0.49466	6.65434	4199.51	0.65010	3.97691	2.33764
	485)	05	123	999	49	317	848	391
		M _T (8	17786.3			6459.76			
)	555	1		68	1		
		$\alpha_i Y_i$	8.03968			3.59580			
			1			45			
			2214	24352.3	0.73037		23936.4	0.26987	
MHC		0	211	619		733	129		
					1.00024				
					748				

							Bencen	Tolueno	
							o y	y	
C	5.00170	M ₁ (9	2515.62	0.14157	1.52696	962.192	0.14910	1.13709	0.53560
i	586)	31	452	31	2	512	676	058
C	12.8335	M ₂ (9	6459.67	0.36353	2.05428	1296.00	0.20083	2.91986	0.72141
i	577)	84	851	918	55	416	481	649
C	17.4584	M ₃ (9	8793.59	0.49488	6.65391	4194.91	0.65006	3.97482	2.33508
i	139)	56	697	419	53	073	798	355
		M _T (9	17768.8			6453.11			
)	971	1		29	1		
		$\alpha_i Y_i$	8.03178			3.59210			
			955			062			
			2212	24332.3	0.73025	23916.4	0.26981		
MHC		0	211	903		733	875		
					1.00007				
					778				

							Bencen	Tolueno	
							o y	y	
C	4.99668	M ₁ (1	2510.62	0.14143	1.52611	960.666	0.14902	1.13483	0.53475
i	547	0)	64	234	569	0	227	818	108
C	12.8306	M ₂ (1	6451.84	0.36345	2.05557	1295.47	0.20095	2.91632	0.72112
i	109	0)	45	49	101	60	931	377	178
C	17.4663	M ₃ (1	8788.95	0.49511	6.65347	4190.31	0.65001	3.97273	2.33252
i	811	0)	99	276	977	74	842	255	414
		M _T (1	17751.4			6446.45			
		0)	307	1		95	1		
		$\alpha_i Y_i$	8.02389			3.58839			
			451			699			
			2209	24302.3	0.73044	23886.4	0.26987		
MHC		0	211	178		733	908		
					1.00032				
					086				

							Bencen	Tolueno	
							o y	y	
C	4.99166	M ₁ (1	2505.63	0.14129	1.52526	959.140	0.14893	1.13258	0.53390
i	743	1)	47	023	777	8	938	188	204
C	12.8276	M ₂ (1	6444.00	0.36337	2.05685	1294.94	0.20108	2.91278	0.72082
i	6	1)	85	117	197	44	437	179	587
C	17.4743	M ₃ (1	8784.31	0.49533	6.65304	4185.72	0.64997	3.97063	2.32996
i	501	1)	32	86	673	12	625	218	569
		M _T (1	17733.9			6439.80			
		1)	564	1		64	1		

		$\alpha_i Y_i$	8.01599			3.58469			
			585			36			
		2207	24282.3	0.73032		23866.4	0.26982		
MHC		0	211	378		733	648		
					1.00015				
					025				
								Bencen	Tolueno
								o y	y
C_i	4.98665	M ₁ (1	2500.64	0.14114	1.52441	957.616	0.14885	1.13032	0.53305
	174	2)	81	818	935	4	644	785	348
C_i	12.8247	M ₂ (1	6436.17	0.36328	2.05813	1294.41	0.20120	2.90923	0.72052
	049	2)	04	732	205	07	936	888	878
C_i	17.4823	M ₃ (1	8779.65	0.49556	6.65261	4181.12	0.64993	3.96852	2.32740
	209	2)	56	45	507	67	421	688	818
		M _T (1	17716.4			6433.15			
		2)	741	1		38	1		
		$\alpha_i Y_i$	8.00809			3.58099			
			36			044			
		2204	24252.3	0.73050		23836.4	0.26988		
MHC		0	211	633		733	698		
					1.00039				
					331				
								Bencen	Tolueno
								o y	y
C_i	4.98163	M ₁ (1	2495.66	0.14100	1.52357	956.092	0.14877	1.12807	0.53220
	838	3)	64	62	041	8	344	608	539
C_i	12.8217	M ₂ (1	6428.33	0.36320	2.05941	1293.87	0.20133	2.90569	0.72023
	456	3)	03	336	126	49	425	504	051
C_i	17.4902	M ₃ (1	8774.98	0.49579	6.65218	4176.53	0.64989	3.96641	2.32485
	935	3)	70	044	48	39	23	663	163
		M _T (1	17698.9			6426.50			
		3)	838	1		16	1		
		$\alpha_i Y_i$	8.00018			3.57728			
			775			753			
		2201	24222.3	0.73068		23806.4	0.26994		
MHC		0	211	901		733	765		
					1.00063				
					666				
								Bencen	Tolueno
								o y	y
C_i	4.97662	M ₁ (1	2490.68	0.14086	1.52272	954.570	0.14869	1.12582	0.53135
	736	4)	98	429	097	1	04	657	777

C _i	12.8187	M ₂ (1	6420.48	0.36311	2.06068	1293.33	0.20145	2.90215	0.71993
	821	4)	82	927	958	69	906	028	105
C _i	17.4982	M ₃ (1	8770.30	0.49601	6.65175	4171.94	0.64985	3.96430	2.32229
	68	4)	75	644	591	29	054	143	603
		M _T (1	17681.4			6419.84			
		4)	855	1		98	1		
		α:Y_i	7.99227			3.57358			
			828			486			
MHC	2200	24212.3	0.73026		23796.4	0.26978			
	0	211	809		733	157			
				1.00004					
				966					

							Bencen	Tolueno	
							o y	y	
C _i	4.97161	M ₁ (1	2485.71	0.14072	1.52187	953.048	0.14860	1.12357	0.53051
	866	5)	82	244	103	2	731	933	063
C _i	12.8158	M ₂ (1	6412.64	0.36303	2.06196	1292.79	0.20158	2.89860	0.71963
	145	5)	40	507	703	68	378	459	041
C _i	17.5062	M ₃ (1	8765.61	0.49624	6.65132	4167.35	0.64980	3.96218	2.31974
	443	5)	71	249	842	35	89	129	138
		M _T (1	17663.9			6413.19			
		5)	793	1		85	1		
		α:Y_i	7.98436			3.56988			
			522			242			
MHC	2197	24182.3	0.73045		23766.4	0.26984			
	0	211	012		733	225			
				1.00029					
				236					

							Bencen	Tolueno	
							o y	y	
C _i	4.96661	M ₁ (1	2480.75	0.14058	1.52102	951.527	0.14852	1.12133	0.52966
	23	6)	16	065	057	2	417	435	396
C _i	12.8128	M ₂ (1	6404.79	0.36295	2.06324	1292.25	0.20170	2.89505	0.71932
	427	6)	77	075	359	46	842	799	858
C _i	17.5142	M ₃ (1	8760.91	0.49646	6.65090	4162.76	0.64976	3.96005	2.31718
	225	6)	57	86	231	58	741	62	768
		M _T (1	17646.4			6406.54			
		6)	650	1		76	1		
		α:Y_i	7.97644			3.56618			
			854			022			
MHC	2195	24162.3	0.73032		23746.4	0.26978			
	0	211	988		733	943			

1.00011

931

								Bencen	Tolueno
								o y	y
C	4.96160	M ₁ (1	2475.79	0.14043	1.52016	950.007	0.14844	1.11909	0.52881
i	826	7)	00	894	961	0	098	163	776
C	12.8098	M ₂ (1	6396.94	0.36286	2.06451	1291.71	0.20183	2.89151	0.71902
i	667	7)	95	631	927	03	297	047	557
C	17.5222	M ₃ (1	8756.20	0.49669	6.65047	4158.17	0.64972	3.95792	2.31463
i	025	7)	34	475	76	99	605	616	493
		M _T (1	17628.9			6399.89			
		7)	428	1		71	1		
		$\alpha_i Y_i$	7.96852			3.56247			
			826			826			
			2192	24132.3	0.73051	23716.4	0.26985		
MHC		0	211	17		733	029		

1.00036

199

								Bencen	Tolueno
								o y	y
C	4.95660	M ₁ (1	2470.83	0.14029	1.51931	948.487	0.14835	1.11685	0.52797
i	653	8)	34	728	814	7	774	118	204
C	12.8068	M ₂ (1	6389.09	0.36278	2.06579	1291.16	0.20195	2.88796	0.71872
i	866	8)	92	176	406	38	743	203	138
C	17.5301	M ₃ (1	8751.48	0.49692	6.65005	4153.59	0.64968	3.95579	2.31208
i	844	8)	01	096	428	56	483	117	311
		M _T (1	17611.4			6393.24			
		8)	126	1		71	1		
		$\alpha_i Y_i$	7.96060			3.55877			
			438			653			
			2190	24112.3	0.73039	23696.4	0.26979		
MHC		0	211	06		733	741		

1.00018

801

								Bencen	Tolueno
								o y	y
C	4.95160	M ₁ (1	2465.88	0.14015	1.51846	946.969	0.14827	1.11461	0.52712
i	712	9)	18	57	615	2	445	298	679
C	12.8039	M ₂ (1	6381.24	0.36269	2.06706	1290.61	0.20208	2.88441	0.71841
i	023	9)	69	708	796	52	181	268	6
C	17.5381	M ₃ (1	8746.74	0.49714	6.64963	4149.01	0.64964	3.95365	2.30953
i	681	9)	58	722	236	31	374	121	225

92

		M _T (1	17593.8			6386.59			
		9)	745	1		75	1		
		$\alpha_i Y_i$	7.95267			3.55507			
			688			504			
			2188	24092.3	0.73026		23676.4	0.26974	
MHC			0	211	897		733	446	
						1.00001			
						343			
								Bencen	Tolueno
								o y	y
C	4.94661	M ₁ (2	2460.93	0.14001	1.51761	945.451	0.14819	1.11237	0.52628
<i>i</i>	003	0)	52	418	366	6	111	705	202
C	12.8009	M ₂ (2	6373.39	0.36261	2.06834	1290.06	0.20220	2.88086	0.71810
<i>i</i>	138	0)	26	229	097	44	61	243	944
C	17.5461	M ₃ (2	8742.00	0.49737	6.64921	4144.43	0.64960	3.95150	2.30698
<i>i</i>	537	0)	06	354	184	22	279	63	232
		M _T (2	17576.3			6379.94			
		0)	283	1		82	1		
		$\alpha_i Y_i$	7.94474			3.55137			
			577			378			
			2185	24062.3	0.73045		23646.4	0.26980	
MHC			0	211	025		733	549	
						1.00025			
						573			
								Bencen	Tolueno
								o y	y
C	4.94161	M ₁ (2	2455.99	0.13987	1.51676	943.934	0.14810	1.11014	0.52543
<i>i</i>	524	1)	35	272	066	8	772	337	772
C	12.7979	M ₂ (2	6365.53	0.36252	2.06961	1289.51	0.20233	2.87731	0.71780
<i>i</i>	211	1)	63	737	309	16	03	127	17
C	17.5541	M ₃ (2	8737.24	0.49759	6.64879	4139.85	0.64956	3.94935	2.30443
<i>i</i>	412	1)	43	99	272	30	198	642	334
		M _T (2	17558.7			6373.29			
		1)	742	1		94	1		
		$\alpha_i Y_i$	7.93681			3.54767			
			106			276			
			2183	24042.3	0.73032		23626.4	0.26975	
MHC			0	211	775		733	247	
						1.00008			
						021			

Bencen Tolueno

							o y	y	
C _i	4.93662	M ₁ (2	2451.05	0.13973	1.51590	942.418	0.14802	1.10791	0.52459
	275	2)	69	133	715	9	428	195	389
C _i	12.7949	M ₂ (2	6357.67	0.36244	2.07088	1288.95	0.20245	2.87375	0.71749
	242	2)	80	234	431	66	442	921	277
C _i	17.5621	M ₃ (2	8732.47	0.49782	6.64837	4135.27	0.64952	3.94720	2.30188
	305	2)	71	633	5	55	131	158	53
		M _T (2	17541.2			6366.65			
		2)	121	1		11	1		
		$\alpha_i Y_i$	7.92887			3.54397			
			273			196			
MHC	2179	24002.3	0.73081		23586.4	0.26992			
	0	211	316		733	806			
				1.00074					
				122					

							Bencen	Tolueno	
							o y	y	
C _i	4.93163	M ₁ (2	2446.12	0.13959	1.51505	940.903	0.14794	1.10568	0.52375
	256	3)	53	001	314	9	079	278	055
C _i	12.7919	M ₂ (2	6349.81	0.36235	2.07215	1288.39	0.20257	2.87020	0.71718
	231	3)	77	719	464	95	844	624	266
C _i	17.5701	M ₃ (2	8727.69	0.49805	6.64795	4130.69	0.64948	3.94504	2.29933
	218	3)	89	28	869	97	077	176	819
		M _T (2	17523.6			6360.00			
		3)	419	1		31	1		
		$\alpha_i Y_i$	7.92093			3.54027			
			079			14			
MHC	2178	23992.3	0.73038		23576.4	0.26976			
	0	211	544		733	058			
				1.00014					
				602					

							Bencen	Tolueno	
							o y	y	
C _i	4.92664	M ₁ (2	2441.19	0.13944	1.51419	939.389	0.14785	1.10345	0.52290
	466	4)	86	875	861	7	725	587	767
C _i	12.7889	M ₂ (2	6341.95	0.36227	2.07342	1287.84	0.20270	2.86665	0.71687
	179	4)	54	192	407	03	238	239	137
C _i	17.5781	M ₃ (2	8722.90	0.49827	6.64754	4126.12	0.64944	3.94287	2.29679
	149	4)	97	933	379	56	037	698	203
		M _T (2	17506.0			6353.35			
		4)	638	1		56	1		
		$\alpha_i Y_i$	7.91298			3.53657			
			523			107			
MHC	2175	23962.3	0.73056		23546.4	0.26982			

ANNEX C

Time (hr)	Phase	Benzene (mol)	Fraction	Toluene (mol)	Fraction
0	Aire z	1579.3976	0.08810782	61.5388903	0.00944622
0	Agua y	59.5923836	0.0033244	2.3780775	0.00036503
0	Libre x	13109.0001	0.73129494	1761.28548	0.27035732
1	Aire z	1579.55583	0.08820224	61.5097878	0.0094538
1	Agua y	59.47678542	0.003321178	2.372020722	0.00036457
1	Libre x	13110.31338	0.73207859	1760.452548	0.270574252
2	Aire	1576.48741	0.08811653	61.3839844	0.00944413
2	Agua	59.3612467	0.00331795	2.367169328	0.000364197
2	Libre x	13084.84548	0.731367181	1756.851968	0.270297413
3	Aire	1573.42057	0.08803078	61.2583182	0.00943445
3	Agua	59.24576758	0.003314721	2.362323224	0.000363824
3	Libre x	13059.39072	0.730655448	1753.255315	0.270020593
4	Aire	1570.99753	0.08798095	61.1582225	0.0094287
4	Agua	59.1303482	0.003311491	2.357482407	0.000363451
4	Libre x	13039.27948	0.730241907	1750.390505	0.269856014
5	Aire	1570.5017	0.08803911	61.1345145	0.00943473
5	Agua	59.01498871	0.003308259	2.352646875	0.000363078
5	Libre x	13035.16408	0.730724577	1749.711967	0.27002848
6	Aire	1568.07569	0.0879891	61.0344332	0.00942897
6	Agua	58.89968923	0.003305026	2.347816627	0.000362705
6	Libre x	13015.0282	0.730309565	1746.847572	0.269863598
7	Aire	1566.29142	0.08797509	60.9598307	0.00942714
7	Agua	58.78444992	0.003301791	2.34299166	0.000362332
7	Libre x	13000.21875	0.730193239	1744.712395	0.269811128
8	Aire	1565.14827	0.08799713	60.9106772	0.00942924
8	Agua	58.66927092	0.003298555	2.338171972	0.000361959
8	Libre x	12990.73063	0.730376192	1743.305588	0.269871286
9	Aire	1563.36115	0.08798302	60.8360904	0.0094274
9	Agua	58.55415237	0.003295317	2.333357562	0.000361586
9	Libre x	12975.89753	0.730259028	1741.170864	0.26981875
10	Aire	1562.21527	0.08800503	60.7869541	0.00942951
10	Agua	58.43909442	0.003292078	2.328548428	0.000361214
10	Libre x	12966.38672	0.730441783	1739.764548	0.26987908
11	Aire	1560.4253	0.08799082	60.712383	0.00942767
11	Agua	58.3240972	0.003288837	2.323744567	0.000360841
11	Libre x	12951.52998	0.730323775	1737.630272	0.269826477
12	Aire	1559.27668	0.08801281	60.6632638	0.00942979
12	Agua	58.20916086	0.003285595	2.318945978	0.000360468
12	Libre x	12941.99646	0.730506331	1736.224446	0.26988698
13	Aire	1558.12686	0.08803482	60.6141588	0.00943191

13	Agua	58.09428555	0.003282351	2.314152658	0.000360095
13	Libre x	12932.45291	0.730689009	1734.819027	0.269947653
14	Aire	1555.68972	0.08798411	60.5141654	0.0094261
14	Agua	57.9794714	0.003279106	2.309364606	0.000359723
14	Libre x	12912.22468	0.730268092	1731.957149	0.269781566
15	Aire	1554.53683	0.08800604	60.465066	0.00942822
15	Agua	57.86471856	0.00327586	2.304581819	0.00035935
15	Libre x	12902.65572	0.730450118	1730.551888	0.269842245
16	Aire	1552.73984	0.08799155	60.3905385	0.00942638
16	Agua	57.75002718	0.003272612	2.299804297	0.000358977
16	Libre x	12887.74069	0.73032988	1728.418862	0.269789435
17	Aire	1551.58421	0.08801346	60.3414559	0.0094285
17	Agua	57.63539739	0.003269362	2.295032036	0.000358605
17	Libre x	12878.14896	0.730511698	1727.014083	0.269850287
18	Aire	1549.78437	0.08799887	60.2669438	0.00942666
18	Agua	57.52082934	0.003266111	2.290265035	0.000358232
18	Libre x	12863.21025	0.7303906	1724.881494	0.269797408
19	Aire	1547.9832	0.08798421	60.1924442	0.00942481
19	Agua	57.40632317	0.003262859	2.285503292	0.000357859
19	Libre x	12848.26059	0.73026897	1722.749266	0.269744458
20	Aire	1546.82329	0.08800605	60.0807032	0.00941711
20	Agua	57.29187904	0.003259605	2.280746804	0.000357487
20	Adsor k	12838.63334	0.730450246	1719.55116	0.269524312
21	Aire	1545.01928	0.08799129	60.0688965	0.00942509
21	Agua	57.17749707	0.003256349	2.275995571	0.000357114
21	Libre x	12823.66	0.730327748	1719.213245	0.269752466
22	Aire	1544.49983	0.08804978	60.0452965	0.00943122
22	Agua	57.06317741	0.003253092	2.27124959	0.000356742
22	Libre x	12819.34858	0.730813158	1718.537797	0.269928064
23	Aire	1542.04975	0.08799825	59.9453804	0.00942537
23	Agua	56.94892022	0.003249834	2.266508859	0.000356369
23	Libre x	12799.0129	0.730385438	1715.678129	0.26976058
24	Aire	1540.88433	0.08802003	59.8963502	0.00942751
24	Agua	56.83472563	0.003246574	2.261773376	0.000355997
24	Libre x	12789.33997	0.730566283	1714.27485	0.26982196
25	Aire z	1539.7177	0.0880418	59.847334	0.0094297
25	Agua y	56.7205938	0.00324331	2.25704314	0.00035562
25	Libre x	12779.6569	0.73074725	1712.87197	0.26988351
26	Aire	1538.5499	0.0880637	59.798332	0.0094318
26	Agua	56.6065248	0.00324005	2.25231815	0.00035525
26	Libre x	12769.9638	0.73092833	1711.4695	0.26994524
27	Aire	1536.737	0.0880486	59.723882	0.00943
27	Agua	56.4925189	0.00323678	2.2475984	0.00035488

27	Libre x	12754.9175	0.7308034	1709.33869	0.26989209
28	Aire	1534.9229	0.0880335	59.649445	0.0094281
28	Agua	56.3785762	0.00323352	2.24288389	0.00035451
28	Libre x	12739.8603	0.73067793	1707.20824	0.26983886
29	Aire	1533.1075	0.0880183	59.57502	0.0094262
29	Agua	56.2646967	0.00323025	2.23817462	0.00035413
29	Libre x	12724.7922	0.73055191	1705.07815	0.26978555
30	Aire	1531.2907	0.0880031	59.500607	0.0094244
30	Agua	56.1508808	0.00322698	2.23347058	0.00035376
30	Libre x	12709.7131	0.73042535	1702.9484	0.26973217
31	Aire	1530.1155	0.0880247	59.451628	0.0094265
31	Agua	56.0371284	0.00322371	2.22877178	0.00035339
31	Libre x	12699.9587	0.73060518	1701.54659	0.26979409
32	Aire	1528.2959	0.0880094	59.37723	0.0094247
32	Agua	55.9234399	0.00322044	2.22407822	0.00035302
32	Libre x	12684.8559	0.73047772	1699.41726	0.26974064
33	Aire	1526.475	0.0879939	59.302844	0.0094228
33	Agua	55.8098152	0.00321717	2.21938988	0.00035265
33	Libre x	12669.7421	0.73034971	1697.28828	0.26968711
34	Aire	1525.2954	0.0880155	59.253883	0.009425
34	Agua	55.6962545	0.00321389	2.21470677	0.00035227
34	Libre x	12659.952	0.73052896	1695.88699	0.2697492
35	Aire	1523.4716	0.088	59.179511	0.0094231
35	Agua	55.5827581	0.00321062	2.21002889	0.0003519
35	Libre x	12644.8145	0.73040005	1693.75842	0.26969561
36	Aire	1522.2893	0.0880216	59.130566	0.0094253
36	Agua	55.469326	0.00320734	2.20535624	0.00035153
36	Libre x	12635.0014	0.73057907	1692.35758	0.26975788
37	Aire	1520.4627	0.0880059	59.056209	0.0094234
37	Agua	55.3559583	0.00320406	2.20068881	0.00035116
37	Libre x	12619.8402	0.73044925	1690.22942	0.26970421
38	Aire	1519.2776	0.0880275	59.007279	0.0094256
38	Agua	55.2426553	0.00320078	2.1960266	0.00035078
38	Libre x	12610.004	0.73062803	1688.82903	0.26976666
39	Aire	1517.4481	0.0880117	58.932936	0.0094237
39	Agua	55.1294171	0.0031975	2.19136961	0.00035041
39	Libre x	12594.8191	0.73049729	1686.70127	0.26971291
40	Aire	1515.6173	0.0879959	58.858605	0.0094218
40	Agua	55.0162438	0.00319421	2.18671784	0.00035004
40	Libre x	12579.6233	0.73036599	1684.57386	0.26965909
41	Aire	1514.4279	0.0880174	58.809693	0.009424

41	Agua	54.9031355	0.00319093	2.18207128	0.00034967
41	Libre x	12569.7512	0.73054418	1683.17398	0.26972172
42	Aire	1512.5942	0.0880014	58.735376	0.0094221
42	Agua	54.7900925	0.00318764	2.17742994	0.0003493
42	Libre x	12554.5316	0.73041196	1681.04697	0.26966783
43	Aire	1511.402	0.0880229	58.68648	0.0094243
43	Agua	54.6771148	0.00318435	2.17279381	0.00034892
43	Libre x	12544.6365	0.7305899	1679.64753	0.26973064
44	Aire	1509.5654	0.0880068	58.549619	0.0094124
44	Agua	54.5642026	0.00318106	2.16816288	0.00034855
44	Adsor k	12529.3932	0.73045675	1675.73048	0.26938884
45	Aire	1508.3705	0.0880282	58.563296	0.0094246
45	Agua	54.451356	0.00317777	2.16353717	0.00034818
45	Libre x	12519.475	0.73063444	1676.12191	0.26973966
46	Aire	1506.5311	0.0880121	58.489006	0.0094228
46	Agua	54.3385753	0.00317448	2.15891666	0.00034781
46	Libre x	12504.2079	0.73050037	1673.99569	0.26968561
47	Aire	1505.3333	0.0880335	58.440141	0.009425
47	Agua	54.2258604	0.00317119	2.15430136	0.00034744
47	Libre x	12494.2665	0.73067781	1672.59713	0.26974879
48	Aire	1503.491	0.0880172	58.365864	0.0094231
48	Agua	54.1132117	0.00316789	2.14969126	0.00034706
48	Libre x	12478.9757	0.73054279	1670.47129	0.26969466
49	Aire z	1501.6475	0.0880009	58.2916	0.0094212
49	Agua y	54.0006292	0.00316459	2.14508636	0.00034669
49	Libre x	12463.6739	0.7304072	1668.34579	0.26964046
50	Aire	1500.4454	0.0880222	58.242752	0.0094234
50	Agua	53.888113	0.00316129	2.14048666	0.00034632
50	Libre x	12453.6965	0.73058402	1666.94772	0.26970382
51	Aire	1498.5989	0.0880057	58.168501	0.0094215
51	Agua	53.7756634	0.00315799	2.13589216	0.00034595
51	Libre x	12438.371	0.73044748	1664.8226	0.26964954
52	Aire	1497.394	0.088027	58.119667	0.0094237
52	Agua	53.6632804	0.00315469	2.13130285	0.00034558
52	Libre x	12428.3705	0.73062404	1663.42496	0.26971308
53	Aire	1495.5447	0.0880104	58.04543	0.0094218
53	Agua	53.5509642	0.00315139	2.12671874	0.0003452
53	Libre x	12413.0212	0.73048655	1661.30022	0.26965873
54	Aire	1494.337	0.0880317	57.996611	0.009424
54	Agua	53.438715	0.00314808	2.12213982	0.00034483
54	Libre x	12402.9974	0.73066285	1659.90301	0.26972245

55	Aire	1492.4849	0.088015	57.922387	0.0094221
55	Agua	53.3265329	0.00314478	2.11756608	0.00034446
55	Libre x	12387.6243	0.7305244	1657.77865	0.26966802
56	Aire	1491.2744	0.0880362	57.873583	0.0094244
56	Agua	53.2144181	0.00314147	2.11299754	0.00034409
56	Libre x	12377.5773	0.73070044	1656.38186	0.26973193
57	Aire	1490.0626	0.0880574	57.824793	0.0094266
57	Agua	53.1023707	0.00313816	2.10843418	0.00034372
57	Libre x	12367.52	0.73087657	1654.98546	0.26979602
58	Aire	1488.8497	0.0880787	57.776016	0.0094289
58	Agua	52.9903908	0.00313485	2.103876	0.00034335
58	Libre x	12357.4523	0.73105282	1653.58944	0.2698603
59	Aire	1486.9915	0.0880618	57.701808	0.0094269
59	Agua	52.8784785	0.00313154	2.09932301	0.00034297
59	Libre x	12342.0296	0.73091266	1651.46553	0.26980579
60	Aire	1485.7757	0.088083	57.653046	0.0094292
60	Agua	52.7666342	0.00312823	2.0947752	0.0003426
60	Libre x	12331.9386	0.73108864	1650.06993	0.26987026
61	Aire	1483.9147	0.088066	57.57885	0.0094273
61	Agua	52.6548578	0.00312491	2.09023256	0.00034223
61	Libre x	12316.4921	0.7309475	1647.94639	0.26981566
62	Aire	1482.0524	0.0880489	57.504665	0.0094254
62	Agua	52.5431495	0.00312159	2.0856951	0.00034186
62	Libre x	12301.0347	0.73080577	1645.82317	0.26976099
63	Aire	1480.1887	0.0880317	57.430492	0.0094235
63	Agua	52.4315095	0.00311828	2.08116282	0.00034149
63	Libre x	12285.5664	0.73066344	1643.70029	0.26970623
64	Aire	1478.3238	0.0880145	57.35633	0.0094216
64	Agua	52.319938	0.00311496	2.07663571	0.00034112
64	Libre x	12270.0873	0.73052052	1641.57773	0.2696514
65	Aire	1477.1005	0.0880356	57.307587	0.0094238
65	Agua	52.208435	0.00311164	2.07211377	0.00034074
65	Libre x	12259.9341	0.73069507	1640.18265	0.26971605
66	Aire	1475.2327	0.0880182	57.233437	0.0094219
66	Agua	52.0970007	0.00310831	2.067597	0.00034037
66	Libre x	12244.4312	0.73055115	1638.06045	0.26966114
67	Aire	1473.3635	0.0880008	57.1593	0.00942
67	Agua	51.9856354	0.00310499	2.0630854	0.00034
67	Libre x	12228.9174	0.73040664	1635.93858	0.26960614
68	Aire	1472.1359	0.0880217	57.048098	0.0094119
68	Agua	51.874339	0.00310166	2.05857897	0.00033963

68	Adsor k	12218.7279	0.73058051	1632.75591	0.26937599
69	Aire	1470.2639	0.0880042	57.036446	0.0094203
69	Agua	51.7631118	0.00309834	2.05407769	0.00033926
69	Libre x	12203.1903	0.730435	1632.42241	0.2696159
70	Aire	1469.0334	0.0880251	56.987731	0.0094226
70	Agua	51.6519539	0.00309501	2.04958158	0.00033889
70	Libre x	12192.9774	0.73060858	1631.02817	0.26968093
71	Aire	1467.1586	0.0880075	56.913618	0.0094207
71	Agua	51.5408654	0.00309168	2.04509064	0.00033851
71	Libre x	12177.416	0.73046206	1628.907	0.26962577
72	Aire	1465.9253	0.0880284	56.864918	0.0094229
72	Agua	51.4298466	0.00308835	2.04060484	0.00033814
72	Libre x	12167.1797	0.73063536	1627.51316	0.26969099