

**Biodegradation of Toluene (an LNAPL)
Under Varying Temperature and Fluctuating
Water Conditions**



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Title: Biodegradation of Toluene (an LNAPL) under varying temperature and fluctuating water conditions

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Abstract

Groundwater contamination occurs when there is spill of substances which are harmful to humans and the environment. One of the most common groundwater contaminant is Non-aqueous phase liquids (NAPL). These substances are notorious as they do not mix with water and are able to persist in nature causing long term harm. They are broadly classified as Light (LNAPL) or dense (DNAPL) based on their relative density with water. BTEX (Benzene, Toluene, Ethylene benzene and Xylene) is an example of a LNAPL which is commonly found in gasoline and diesel fuels.

Microbes present in the environment are able to utilize contaminants as food to degrade them to non harmful daughter components. This technique is termed as biodegradation and proves to be a promising remediation method. There are various environmental factors which affect the degradability of microbes such as soil temperature and water table fluctuations. A study of these factors was done in batch and column experiments. They were replicated for field conditions in a semi-arid coastal region. Toluene was used as a representative of the LNAPL in the experiments.

Several batch experiments were run to investigate the effect of temperature on degradation rates. Results from the constant temperature experiments indicated that degradation was highest in summer. The increase in degradation rate was two times for every 10°C increase in temperature. In addition, fluctuating temperature experiments were done to account for the diurnal change of temperature. The results showed that microbes were able to overcome the effect of temperature changes even in case of extreme weather conditions and continued thriving though taking slightly longer time.

Column experiments were done to investigate the effect of fluctuating water conditions on degradation. Results showed that water table fluctuations brought residual LNAPL higher in the unsaturated zone from a LNAPL lens present on the water table. In absence of fluctuations LNAPL lens remained at the same place. The difference between LNAPL concentrations of live and sterile columns and consumption of oxygen in the live columns indicated biodegradation going on in the saturated as well as the unsaturated zone.

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1. Introduction

1.1 Background

Groundwater makes about twenty percent of world's fresh water supply, which is about 0.61% of the total of world's entire water. This makes it the largest and most reliable resource of all fresh water resources. Currently as much as eighty percent of drinking water resources in major parts of the world come from groundwater. However, due to increasing population, changes in land use pattern such as urbanization and rapid industrialization there is a lot of pressure and changes in the quality of this important resource. Groundwater pollution occurs when any undesirable substance seeps through the ground and enters the source of groundwater. Even naturally occurring minerals such as Arsenic, Selenium, and Boron might be harmful to humans when present in drinking water sources. One of the most common ways of groundwater pollution is by leakage of underground storage tanks. Any contamination that reaches groundwater sources might be difficult to remediate as the movement of water underground is usually slow with little turbulence, dilution or mixing. This can make the contamination undetectable for years while it is causing harm.

1.2 Problem Definition

One of the most notorious groundwater contaminants can be Non Aqueous Phase Liquids (NAPLs). These liquids are organic liquids such as dry cleaning fluids, fuel oil and gasoline which have very low solubility in water and are considered a potential carcinogen if they enter the human body. As they do not mix with water, they form a separate phase when found. NAPLs are classified as light or dense NAPL based on their relative density. Examples of Light NAPLs are aromatic hydrocarbons such as BTEX, gasoline and that of Dense NAPLs are chlorinated solvents like TCE, PCE.

When there is a spill of NAPL from an underground storage it migrates vertically under the influence of gravity up to the water table. During this process small droplets called blobs are left behind trapped behind in pores. Once the NAPL reaches the water table if it is lighter than water (LNAPL) then it forms a layer on the water table and moves in the direction of groundwater flow (Pinder and Celia, 2006).

If the NAPL is heavier than water (DNAPL), then it moves downward under the influence of gravity through the water table until it reaches a formation that stops its flow. The problem associated with NAPL contamination is that they are very difficult or impossible to remove once they enter the ground. Hence, this type of contamination can persist for hundreds of years slowly dissolving from the residual phase to the groundwater.

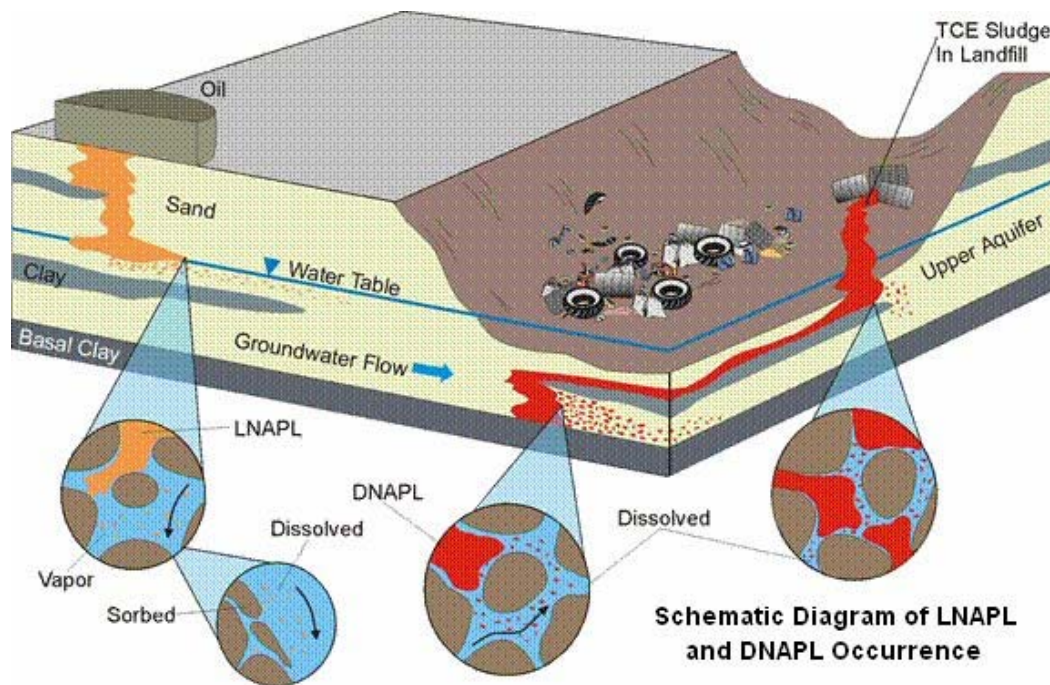


Fig 1: Picture of LNAPL and DNAPL spill in the subsurface.

1.3 Research Objectives

The main objective of this study was to see the impact of soil temperature variations and water table dynamics on fate and transport of toluene (a LNAPL) using lab experiments.

The specific research objectives were:

- To study the impact of temperature on biodegradation rate of toluene.
- To investigate the effect of varying soil-water temperature on biodegradation of toluene.
- To study the fate and transport of toluene under constant and varying water table conditions.

1.4 Scope of the work

This research looked at the impact of soil temperature variations and water table dynamics on fate and transport of toluene. At first it was determined if toluene could be aerobically biodegraded by the bacteria's present in the natural groundwater. Then the effect of fluctuating temperature on biodegradation was investigated. The final part was to study the effect of water table dynamics with column experiments. All gas and liquid samples were analyzed with a gas chromatograph.

1.5 Organization of the Dissertation

The chapter Literature Review focuses on research done and literature available on the topics of biodegradation of LNAPL, temperature effects on degradation, water table dynamics and the fate and transport of LNAPL under constant and dynamic water table conditions. Details about the batch and column experiments are written in chapter Research Methodology. The experimental results obtained and discussions are elaborated on the fourth chapter and finally the conclusion of the research and future recommendations are written in the fifth chapter.

2. Literature Review

2.1 Overview of remediation techniques

Remediation means removal of contaminants from environment such as soil, groundwater, surface water etc. It is classified into various categories in different ways among which a major category is based on the location of the treatment (US EPA, 2001):

a) Ex-situ remediation: The extraction of highly contaminated material from the site and its treatment away from the site is known as Ex-situ remediation. Examples of Ex-situ treatment methods are as following:

1. Soil Excavation, Soil Washing and Incineration: These methods involve excavating soil from a contaminated site to clean it by washing. It can also be disposed into a landfill site after the harmful contaminants are removed or incinerated. This method is expensive and not suitable for small areas.
2. Activated Carbon Treatment and Air Stripping: The first method involves letting the contaminated air and water to pass through activated carbon filter on which harmful chemical sorbs. It doesn't destroy the contaminants and generates waste in terms of spent carbon which has to be further treated or disposed. Air stripping involves forcing air through contaminated soil to remove harmful chemicals.
3. Chemical Dehalogenation and Solvent Extraction: These methods involve using different processes such as mixing, heating or even solvents to remove harmful halogens or other contaminants present in soil.
4. Thermal Desorption: It involves using heat to remove harmful chemicals present in the soil to gas. The gas itself is collected and further treated before release and the clean soil can then be returned to the site.

b) In-situ remediation: The treatment of contaminants at the site itself is known as In-situ remediation. The examples of in-situ remediation are chemical oxidation, permeable reactive barrier (PBR), pump and treat, soil vapour extraction, air sparging, monitored natural attenuation, bioremediation and phytoremediation etc.

1. Chemical Oxidation and Permeable Reactive Barriers: In these methods chemical oxidants are pumped into a wall of reactive barriers placed on site which reacts with pollutants present in the groundwater to convert them into non-harmful products.

2. Pump and Treat: This is a common method for cleaning up groundwater in which pumps are used to bring polluted groundwater to the surface where it is cleaned more easily.

3. Soil Vapour Extraction and Air Sparging: Soil vapour extraction removes harmful chemicals, in form of vapour, from soil above the water table. The vapour is extracted from ground by applying a vacuum to pull them out. Air sparging uses air to help remove harmful vapour from polluted soil and groundwater below the water table. When air is pumped underground, the chemicals evaporate faster, which makes them easier to remove.

4. Monitored Natural Attenuation: This method relies on natural processes to clean up or attenuate pollution in soil and groundwater. It is less disruptive to the environment and is also a cheaper alternative but on the other hand might take longer.

5. Bioremediation and Phytoremediation: Using natural processes or plants to remove contaminants from polluted soil and groundwater is termed respectively as Bioremediation/Phytoremediation. The latter one works best for sites with low amounts of pollution. Bioremediation is discussed in detail in the following chapter.

Both the in-situ and ex-situ methods have their own advantages and disadvantages. Most of the ex-situ remediation techniques are more expensive as compared to the in-situ methods. They are also more complex to design as they involve disposing the waste properly and filling up the excavated site. However, in-situ remediation techniques are generally slower because stimulatory substrates have to slowly diffuse through heterogeneous sites. At the same time they are less expensive and less intrusive.

2.2 Process of Biodegradation

The process of using microbes to degrade environmental contaminants to non-harmful or less harmful products is termed as microbial Biodegradation. It can occur aerobically or anaerobically. Aerobic or oxidative degradation occurs when the pollutant is oxidized using oxygen, nitrogen, iron, sulphate and manganese by the microbes and the pollutant acts as electron donor. Anaerobic or reductive degradation occurs when pollutant is reduced by the microbes. Mostly LNAPLS are degraded aerobically while DNAPLS are degraded anaerobically.

There are certain characteristics of the contaminants like: chemical solubility (compounds with greater aqueous solubility are generally more available to degradative enzymes), volatility (enhances the influx of materials being removed), viscosity (determines the spreading and dispersion of pollutants and thus the surface area available for microbial attacks), density (this determines fluid movement in the subsurface), chemical structure (if there are groups or substitutes in the molecule which affects degradation or the structure is such that the compound is in a physical state where degradation is slowed down), toxicity (end products of degradation might be toxic or due to contaminant overloading) and its concentration (very low or high concentrations might not be ideal for degradation) which make it susceptible to undergo degradation (Roberts, 1998).

Further, biodegradation also requires certain environmental conditions for it to occur which are: presence of microorganisms capable of degrading a particular contaminant, accessibility of organism to target pollutant, availability of electron acceptors and donors, availability of nutrients, adequate pH, adequate temperature and absence of inhibitory substance (Alvarez *et al.* 2006). The environment influences biodegradation by regulating both the bioavailability of the compound and the activity of the degraders (Roberts, 1998). Temperature is one of such an environmental factor and was the first topic of interest for this research.

2.3 Temperature effects on Biodegradation

Soil temperature is one of the most important factors controlling microbiological activity and the rate of organic matter decomposition (Sims and Bass, 1984). Temperatures of both air and soil affect the rate of biological degradation in soil (JRB Associates, Inc., 1984). Microbial metabolism accelerates with increment of temperature up to an optimum value at which growth is maximal (Alvarez *et al.* 2006). Increasing temperature decreases viscosity of petroleum hydrocarbons and increase their solubility in soil aqueous phase. There is decrease in adsorption with rising temperature, which makes more organics available for the microorganisms to degrade (JRB Associates, Inc., 1984). Also, higher temperatures increase evaporation of short-chain alkanes and other low-molecular-weight hydrocarbons, which usually cause solvent-type membrane toxicity to microorganisms (Atlas, 1994). For an example, in a study done by Corseuil and Weber (1994), it is suggested that degradation rates can double or triple due to temperature increment of 10°C.

On the other hand, decrease in temperature can slow down degradation but it is not lethal to micro-organisms. Low temperatures reduce the fluidity and permeability of the cellular membrane, which hinders nutrient and contaminant uptake (Alvarez *et al.* 2006). Also, it can lengthen the acclimation period and delay onset of biodegradation. It generally decreases microbial enzymatic activity - i.e. the 'Q 10' effect (Zhou and Crawford, 1995). Biodegradation can take place even at a low temperature like that of 5°C, but hydrocarbons are degraded more slowly at lower temperatures (Parr *et al.* 1983).

In a study done by, Deeb *et al.* (1998) the temperature effects and substrate interactions during the aerobic biotransformation of BTEX mixtures were looked upon. The study found out that cell growth on Toluene increased with temperature from 7°C to 35°C, decreased sharply at 36°C to 40°C and was entirely inhibited above 45°C. Also, cell growth on toluene increased fourfold from 20°C to 35°C. In this way environmental changes can affect the growth of microbes and thus alter degradation rates. After undergoing an abrupt change in the environmental conditions microbes take some time to get acclimatized. This is seen in the lag phase of development. Survival of microbe maybe hindered by abiotic and biological stress as fluctuating or extreme temperatures (Gentry *et al.* 2004).

Similarly, when microbes are exposed to such repeated changes in the environment they can slowly adjust to it. It was of great interest to see how such sudden but repeated changes in environment could impact degradation. Hence, the second topic of interest for this research was to investigate the consequence of abrupt environmental change. Specifically, in this case sudden but repeated increase/decrease of temperature affect upon the degradation of a LNAPL was looked upon.

There can be various reasons for changes in soil temperatures such as seasonal difference in temperature, diurnal variations or even the temperature gradient that exists in soil. One very important factor that affects soil temperature is the pore water content. Variations in groundwater level directly change soil-water temperature and consequently degradation rates. Study to see an area subject to fluctuations in water table show change in the degradation rates was fascinating. Hence, the final topic of interest for this research was to look at the effect of water dynamics on biodegradation and this is discussed in detail in the following text.

2.4 Water table dynamics and its impact on biodegradation.

Natural groundwater level is rarely at a fixed depth. It undergoes fluctuations which are termed as seasonal, tidal or long term fluctuations. Seasonal fluctuations cause due to difference between recharge and withdrawal between various seasons. Tidal fluctuations occur mostly in coastal areas due to stage variations in water bodies. It can occur diurnally with one high and one low tide or semi-diurnally with two high and low tides. Long term fluctuations occur when there is a change in deep groundwater which is not easily recharged through the surface. Fluctuations caused by these different factors can modify, or even reverse horizontal and vertical gradients and thus alter groundwater flow directions. In areas influenced by tides, hydraulic gradients can change as tidal level changes (Nielsen, 2006).

Variations of groundwater not only cause changes in the soil surrounding it, but also impact LNAPL layer if it is present on the water table. When water table falls, LNAPL lying on top will also follow the water table. As the LNAPL moves down it will leave a trail of LNAPL in the unsaturated zone in form of isolated ganglia. Subsequently, when the water table rises the LNAPL will also move upwards and leave behind trapped amount of LNAPL in form of

disconnected blobs in the saturated zone. A part of the residual LNAPL in the unsaturated zone will be mobilized again when the water table rises. If the water table fluctuates again in such a case where there is already a smeared zone the situation gets more complicated as the residual saturation above and below the water table is different. Trapping of NAPL in the pores occurs due to difference in the wettability order of different liquids. In this situation with three phases in the system water is the wetting phase, NAPL is the intermediate wetting phase and air is the non-wetting phase. (Mayer and Hassanizadeh, 2005)

In an area subject to water table fluctuations down at the pore level, the water either enters into or is released from storage from pores. This means that when water level lowers, pores that were originally saturated will be partially filled with air/oxygen. Similarly, when water level rises the pores that had air will be saturated with water. This phenomena leads to various changes in the soil such as: temperature changes, introduction of air in the saturated zone and intermittent supply of water in the unsaturated zone etc. Sinke *et al.* (1998) investigated the effects of fluctuating water table on redox dynamics and transport of 4-nitrobenzoate and toluene. Results showed that columns with fluctuating water table were subject to spatial and temporal variation in the redox conditions. Similarly, Oostrom *et al.* (2000) investigated the oxygenation of anoxic water in a fluctuating water table system experimentally as well as numerically. Results showed that zones with entrapped air saturations formed during imbibitions. It also led to significant amounts of dissolved oxygen to be transported deeper into the flow cell. Results from the numerical simulations also agreed with the experimental ones.

Overall, water table dynamics can impact biodegradation of pollutants in several ways by introduction of air/oxygen in that area or even by changes in temperature. Hence, it was of interest to explore these ideas.

2.5 Overview of existing studies

In a study done by Oostrom *et al.* (2006), the behavior of a viscous LNAPL under variable water table conditions was investigated both experimentally and numerically. Two viscous volumes of LNAPL were released into the unsaturated zone in a flow cell having unsaturated as well as saturated zone. The LNAPL migrated downward and accumulated on top of the capillary fringe reducing it by 0.04 m (22%). After 30 days the drainage of LNAPL from the unsaturated zone was seen quite less and it left behind residual saturation. When the water table was rapidly raised, the LNAPL pool moved up in a delayed manner following the same path and leaving behind entrapped amount in the saturated zone. Numerical simulations were also able to predict the movement of the LNAPL in a similar way. The results of this work showed that viscous mobile LNAPL subjected to variable water table conditions does not necessarily float on water table and may not appear in an observation well.

Similarly, Rainwater *et al.* (1993) studied biodegradation of diesel fuel under cyclic water table movement using column experiments. It was observed that the columns with water table movement had 15% less residual diesel than the static ones.

Also in a field study done by Lee *et al.* (2001), the attenuation of petroleum hydrocarbons mostly comprised of Toluene (a LNAPL), in the smear zones was investigated. The study site in a shallow unconfined aquifer was subjected to seasonal water table fluctuation. The results showed that concentrations of toluene in soil, groundwater, and soil gas were markedly decreased above or below water table. Soil gas concentrations of toluene and its respiration gases indicated vertical and seasonal variations.

Dobson *et al.* (2007) studied the effect of water table fluctuation on dissolution and biodegradation of a multi-component, LNAPL. Results showed that the fluctuation in the water table increased the vertical extent of the source zone by a factor of 6.7. It also led to enhanced biodegradation activity shown by the amount of consumption of electron acceptors. However, there was enhanced dissolution of the LNAPL components due to the water table fluctuation which was even up to 20 times.

Most recently Robinson *et al.* (2009) investigated the effect of tidal influence numerically on biodegradation of BTEX. The results showed that significant biodegradation of BTEX occurred in smearing zone leading to a reduction in total mass transported from aquifer to ocean.

Thus, it can be concluded from the above discussed papers that variation of water level in a region polluted with LNAPL leads to a complex situation of smearing of the LNAPL in the unsaturated and saturated zone. This situation is in a way beneficial when compared to areas without water level variation as it helps in dissolution and biodegradation of the LNAPL and thus helps to reduce the total amount present.

3. Research Methodology

3.1 Materials and Methods

Batch experiments and column experiments were run during the research. Clean sand having grain size between 0.1 mm and 1 mm was used for all the experiments. The sand (Quartz sand H31) was obtained from Sibelco, Belgium. Natural groundwater was collected from a BTEX contaminated site from A&G Milieutechniek situated in Harlem, The Netherlands. The collected groundwater was left open under ventilated hood to remove all the volatile components and was later used as primary source for microorganisms. Toluene (Merck) was used as LNAPL representative for all the experiments. Both headspaces as well as liquid samples were analyzed using Gas Chromatography (GC). Two types of Gas Chromatographs were used: 1)Agilent Technologies 6850 and 2)Varian Star 3600CX. For the batch experiments as concentrations were expected in range lower than 1mg/L Varian Star 3600CX GC was used. For the column experiment concentrations were expected in higher range so it was measured in Agilent Technologies 6850.

3.2 Batch Experiments

The main goal of the batch experiments was to look at the effect of varying soil-water temperature on biodegradation of toluene. For this, first some preliminary experiments were run for presence of toluene degraders in the groundwater. After confirmation of microbes in the groundwater two sets of batch experiments were conducted under constant and varying temperature conditions. The constant temperature batches were performed at room (21°C) temperature along with a low (10°C) and high (30°C) extremes which may correspond to spring and/or autumn, winter, summer conditions at most of the arid and semi-arid polluted sites. The batch experiments under these constant temperatures were repeated 2-3 times to minimize the gap whenever there was a sudden decrease in toluene concentration in a short span of time.

For the fluctuating temperature experiments three sets of batches were assembled to investigate the effect of diurnally varying temperature during three different seasons. The first set was for the winter season by maintaining day and night temperature at 21°C and 10°C for 14 and 10 hours respectively. Second case was for summer season during which

a day and night temperature of 30°C-21°C for 14 hours and 10 hours respectively were maintained. The last set of experiment was performed to see the effect of weather extremes on toluene degradation during which the batches were put under 30°C-10°C for 14 and 10 hours respectively. All of the batch experiments were run in triplicates for both live and sterile sets.

For batch experiments, 120 ml glass bottles (Alltech) and viton stoppers (Rubber B.V., Hilversum, The Netherlands) together with crimp seals (Wheaton, The Netherlands) were used. For live batch experiment 10 grams of the sand was first weighed and put in the bottles then 15 ml of the groundwater added. After closing the bottle with viton stopper and crimp seals air tightly, 40 µL of toluene stock was injected through the stopper with a gas tight syringe (SGE). They were then thoroughly shaken for some time to ensure complete mixing. Sterile controls were made in same way but with 14 ml of groundwater and 1ml of 10g/L HgCl₂ (Mercury Chloride) to kill the microbes present and ensure that the final concentration were same in both live and sterile batches. Toluene stock used during batch experiments was prepared by over saturating distilled water with pure phase and storing in an inverted bottle. As Toluene was extracted from the bottom it would always have concentration in its solubility limit of 500mg/L. The concentration of the stock was measured before the starting the experiments.



Fig 2: Picture of the live and sterile batches.

All batch experiments were prepared in similar way and then incubated in dark at different temperature according to the experiment type. During incubation the bottles were placed on lying position on an orbital platform shaker with 150 rpm. The constant temperature batches at 10°C were put in a refrigerator with required temperature together with the shaker installed inside. The 21°C batches were put in lab with fixed room temperature. The batches for 30°C were incubated in a water bath in upright position to prevent possible contamination. For the fluctuating temperature cases batches were moved between fridge, fixed temperature lab and the water bath according to the temperature requirement dependent on the experiment type.

3.3 Sample analysis

For the constant temperature batches liquid samples were taken out periodically from the bottles using 1ml syringes and 0.6 mm disposable needles (Terumo). Gas samples were taken out with air tight (luer lock syringes, SGE) and measured by hand injections in Varian Star 3600CX GC. Only liquid concentrations were analyzed in case of variable temperature batches. Liquid samples from all the batch experiments were put in 1.5 ml vials (Grace Discovery science) with 5µL of (1g/L) HgCl₂ to kill bacteria and prevent further degradation in the vial itself. They were placed on auto sampler (Varian 8200 CX) for analysis. This GC has a Stabilwax DB column of 0.32 mm diameter, 30 m length and film thickness 1 µm with a UV lamp and PID detector (200°C). The detection limit of this GC was from 0 to 1mg/L.

The concentration in all of the batches were below 1mg/L so a seven point standard calibration curve was prepared with concentration range from 0 to 1mg/L. The areas obtained from GC were then used in the calibration curves to get the exact concentration present in the samples. Similarly, for gas calibrations also seven point calibration curves was made with concentration ranges from 0-2 mg/L. Results from all the batch experiments are presented on chapter 4 and the calibrations curves are listed in appendices C.

3.4 Column experiments

The primary aim of the column experiments was to investigate the fate and transport of toluene under constant and varying water table conditions. Two sets of columns were designed for this purpose; water table was kept constant in the first set while it was fluctuated in the second setup. Each setup was made with a pair of sterilized and live columns to quantify biodegradation of toluene.

The dynamic water level case setup was used to demonstrate tidal fluctuations of groundwater in coastal areas. As the research corresponds to Jeddah a semi-diurnal case was chosen with two high tides and two low ones in a day. Hence, the water level in the column was changed for a fixed height every six hours. In the setup of the static water level case, it was kept at a fixed level. The details about the design and the setup of the column experiments can be found in following chapters.

3.5 Column design

The designs of both dynamic and static water level setups are described below.

3.5.1 Dynamic water level design:

In this setup one main column and two side/auxiliary columns were used. The main column was filled with sand and was used to investigate the effect of water level change. The auxiliary columns were used to store extra volume of water which came out of the main column whenever water level was lowered or to provide extra volume of water as the water level was raised. The sand in the main column was filled up to a certain height leaving some headspace free. This headspace was connected to a balloon to provide extra oxygen and also flexible area needed for storage of air. Thus, the headspace at atmospheric pressure was unaffected from lowering/raising of water table. Toluene pool was created right above the average water level in the sand column. The lowermost port of the sand column was connected to inner auxiliary column which in turn was connected to the outer auxiliary column. Figure 3 shows the schematic diagram of the column setup. Groundwater in the saturated zone was circulating at a rate of 1ml/hour.

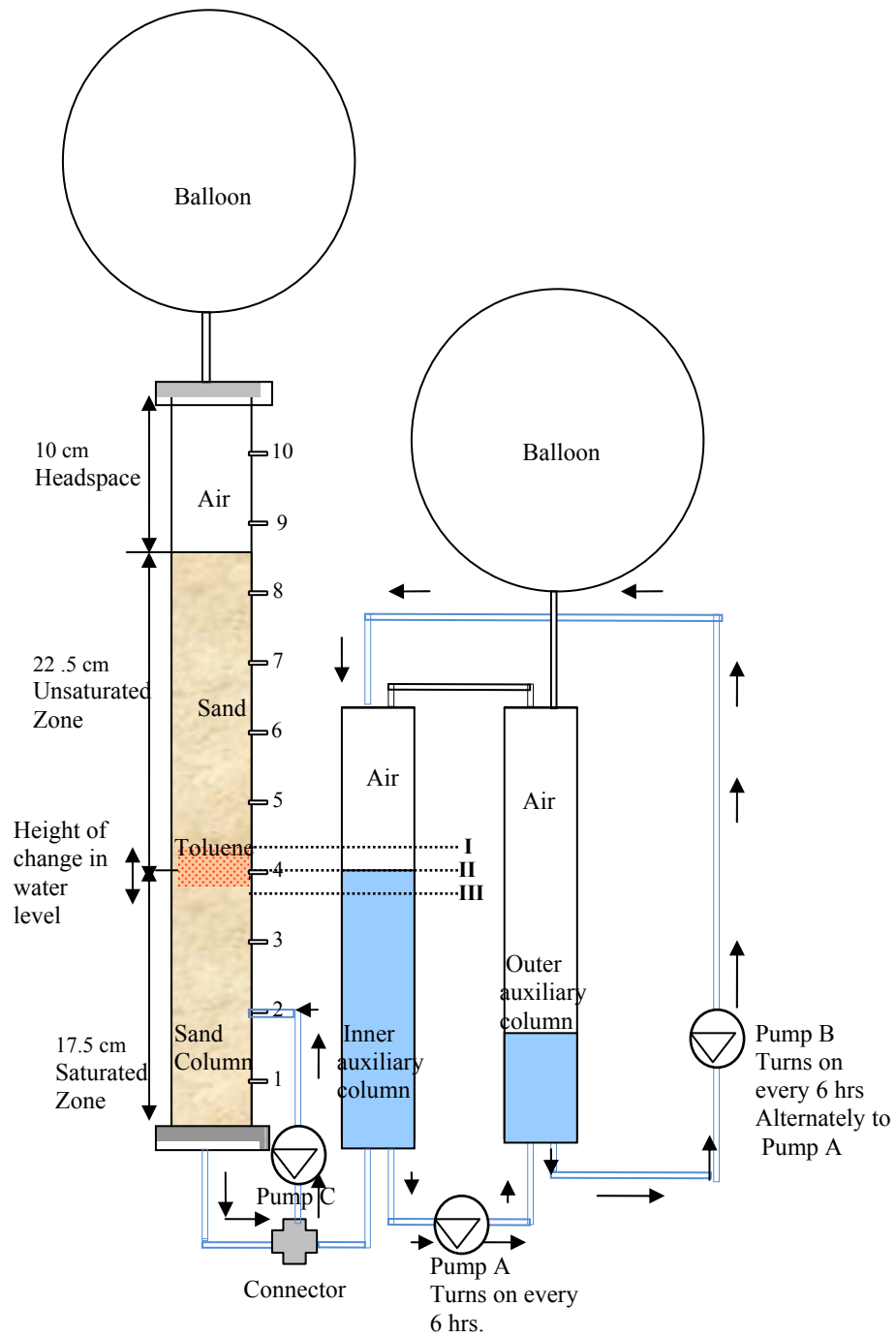


Fig 3: Schematic diagram (1:5) of the column setup used for dynamic water level case scenario.

At first, the water level in the sand column and the inner auxiliary column was maintained at level II. For lowering the water level to position III, pump A was turned on for a specific time needed to pump out the water from the inner to the outer one. As a result, the water in the sand column drained slowly downward and reached level III. Similarly, when the water level in the sand column had to be raised from position III to II, Pump B was used to pump water back from the outer to the inner auxiliary column. This increased the water height in the inner auxiliary column such that the water level in the sand column went up slowly. The time taken by both the pumps to change position from II to III, then back from III to II, II to I and then finally from I to II were recorded. This was then used to setup a 24 hour automatic timer switch (Gamma digital timer) for changing the water level once every six hours. The last Pump C was used to circulate water continuously in the sand column at a very slow rate such that there was no stagnation.

The headspaces between the two auxiliary columns were interconnected and also a balloon was placed on top of the outer auxiliary column. These balloons prevented pressure reduction or built up in the system. The setup was made airtight to prevent loss of Toluene. An experiment was also performed to see if toluene adsorbed onto the balloon surface. For this 10ml vials with balloon pieces were closed with air inside and toluene in gas phase was injected. They were then stored and measured for a couple of days to see if the concentration changed. Results showed that it didn't adsorb on the balloon surface.

3.5.2 Static water level design:

The design of static water level case setup was relatively simpler than the above mentioned case. One sand column an auxiliary column was used for this purpose. The figure of the setup is given below.

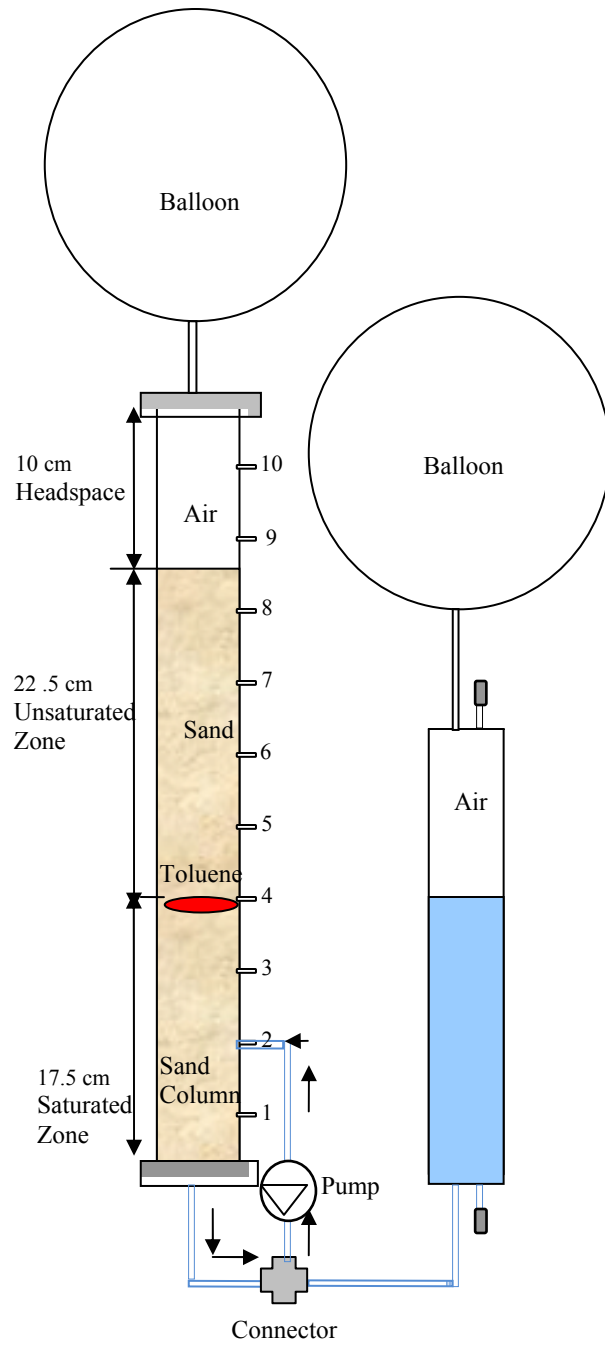


Fig 4: Schematic diagram (1:5) of the column setup used for the static water level case scenario.

3.6 Experimental setup

Column experiments were performed in four glass columns which were 50 cm in length and 4.5 cm inner diameter. These columns had 10 equally spaced ports with 5 cm gap in between and 2.5 cm on the first and last ports. The columns had stainless steel top and bottom lids with an inlet in the middle for liquid flow. Between the lid and the column opening, a glass porous plate (Schott Duran, Por1) was placed to prevent the soil flow out of the column. To make the column airtight a viton-o-ring (Eriks Alkmaar, The Netherlands) was placed between lid and POM (Delrin) ring around the column and secured with bolts. The top and the bottom lids were connected with two rods and fixed together with bolts. The sampling ports in the columns were fitted with Teflon septa (Alltech) to make them airtight.

The columns fitted with PVDF Serto connection around the side ports together with the bottom cap was first checked for leakage by filling water. Packing of the column was done under saturated conditions with groundwater by putting in a layer of sand and mixing until 40 cm leaving a headspace of 10 cm free. The filling of sterile column was done similarly but with groundwater made sterile by putting in 100mL Mercury Chloride (10g/L HgCl₂) per liter of groundwater. The columns were then left in saturated conditions by clamping the tube in the bottom port until the side setups of auxiliary columns were ready.

Firstly, in case of the dynamic water level setup two auxiliary columns were placed on stands on the right of the sand column. The auxiliary columns were 30cm in length and 5cm in diameter, with 2 upper and 2 lower ports. The lower right port of the inner auxiliary column was connected to the lower port left port of the outer auxiliary column with a pump (Master flex). For all of these connections viton tubing (Cole Parmer) was used. Also the lower right port of the inner auxiliary column was connected to the upper left port of the inner auxiliary column with another pump. Then the sand column was connected to the lower left port of the inner auxiliary column via a T-connector and was allowed to drain up to 17.5 cm which was at the 4th port in the column. The sand column and the inner column were mounted on same height such that the saturated water level in the sand column would be the same as in the inner auxiliary column. The excess water in the inner auxiliary column was pumped out such that the final water height was 17.5cm

in the sand column. This would allow fixed height change of water level (2.5cm above and below from port 4) in the sand column by adjusting the water level in the inner auxiliary column. Balloons pumped with air were connected on the top of the sand column and on upper right port of the outer auxiliary column. Second set was made exactly in the same way but with a sterile column. Finally, a peristaltic pump with tygon tubing (Ismatec) was used to circulate water within the sand column at a very slow rate to make sure that there was no stagnation in the sand column. For this water was taken out from the T-connector in the bottom port and was injected through the first port of the sand column as the bottom portion of the column had a porous plate and this would have minimum disturbance in the column. The setup of static water level case was prepared in the same way. There was only one auxiliary column present in this case so the remaining 2 ports left were closed. Both the setups can be clearly seen in fig 5.



Fig 5: Picture of the column setups with the static water level (left) and dynamic water level (right).

After the setup was ready it was run for two days prior to toluene injection to make sure that the water level change was going according to the plan. Then, 5 ml of pure phase Toluene prepared before with Sudan Red B (Fluka) was injected through port 4 of the sand column. This was done when the water level in the sand column was at port 4 such that it would form a layer right above the water level.



Fig 6: Injection of toluene in the column.

3.7 Sample collection and analysis

Sampling was done from the column everyday starting right before the injection of Toluene. For the later part of the experiment sampling was done on alternate days. Gas samples were taken out from the ports 7, 8, 9 using air tight (1 ml, luer lock syringes, SGE) and 0.8 mm disposable needles (Terumo). The needles were then changed with 0.5mm (Terumo) with the valve closed before injection into the vials such that there was only a small opening in the rubber of the cap. They were then injected in 10ml vials (Grace discover science) prepared before gas sample collection with 1ml water, 0.5 g of

table salt (NaCl) and closed with caps (Grace discover science) to make it airtight. Liquid samples were extracted with same needle but with a different syringe (1ml, SGE). They were then put in 1.5ml vials and closed right after to prevent loss from volatilization. 5µL of 1g/L of (1g/L) HgCl₂ was added in all the vials to prevent further degradation in the vial itself.

The caps of 10ml vials are designed to prevent leak of volatile components. In preliminary tests it was observed that toluene concentration in gas samples decreased significantly after overnight storage. On the other hand, no significant change in concentration was seen in liquid samples until 3 days of storage. Therefore, gas samples were measured the very same day of extraction while the liquid samples were sometimes stored in a refrigerator. Both gas and liquid samples from the column experiment were measured using the Agilent Technologies 6850 GC. This GC has Agilent J&W gas column with 0.32 mm diameter, 30 m length, film thickness 0.25 µm and a FID detector (250°C). A 12 point calibration curve was prepared with concentrations ranging from 0-100mg/l. Since this curve was not linear in the entire concentration range it was divided in 3 different regions with polynomial equations to get the correct areas. These calibrations curves are listed in appendices C.

4. Results and discussion

Graphical presentations of all experimental results and their discussion are presented in this chapter.

4.1 Preliminary batch result

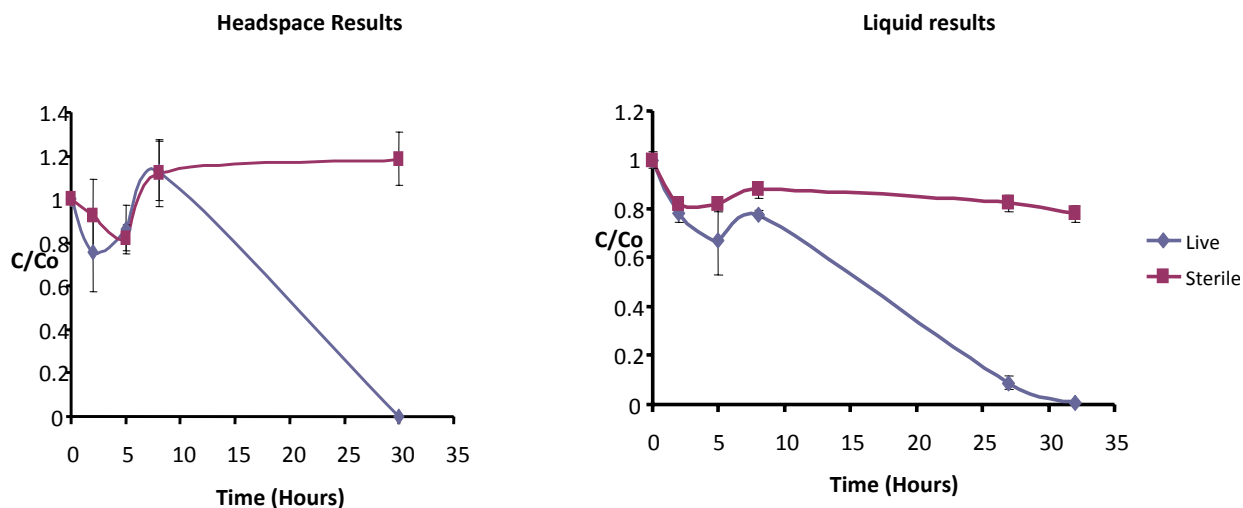


Fig. 7: Concentration of toluene in groundwater batches over time.

It can be seen in Fig. 7 that the concentration of toluene added to the batches declined over time in both headspace and liquid. Hence, it was concluded from this experiment that the microbes present in the groundwater were able to degrade toluene. Thus, the groundwater collected could be used for further experiments.

4.2 Constant temperature batches

Concentration of toluene decreased in both the headspace and liquid over time in all the live batches at different times depending on the temperature. In the sterile batches concentration remained to around eighty percent of the original concentration which might have been due to abiotic degradation. The batch experiments at each temperature were repeated 2-3 times to sample the gap whenever there was a sharp reduction in

toluene concentration. Also, the concentration of toluene was normalized with initial concentration such that differences in initial concentration between the batches were canceled out. Detailed graphs are presented below.

4.2.1 Set 1: 10° C batches

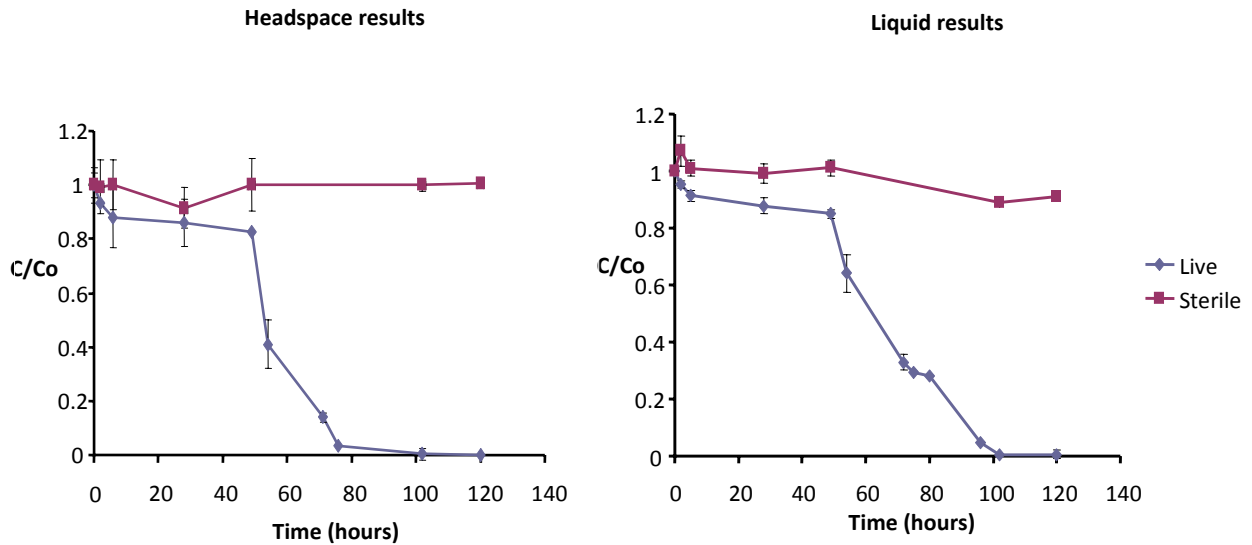


Fig 8: Change in concentration of toluene in headspace and groundwater at 10° C.

It can be seen in Fig. 8 that the concentration of toluene declined in live batches at around 76 hours in headspace measurement. However, in the liquid it has remained until 96 hours. This is type of result is not seen in other constant temperature batches which are presented later in the report. This could have been due to measurement error.

4.2.2 Set 2: 21° C batches

The concentration of toluene degraded faster i.e. around 49 hours in case of 21° C batches. It can be seen in Fig. 9 that both headspace and liquid concentrations have similar trends of degradation in this case.

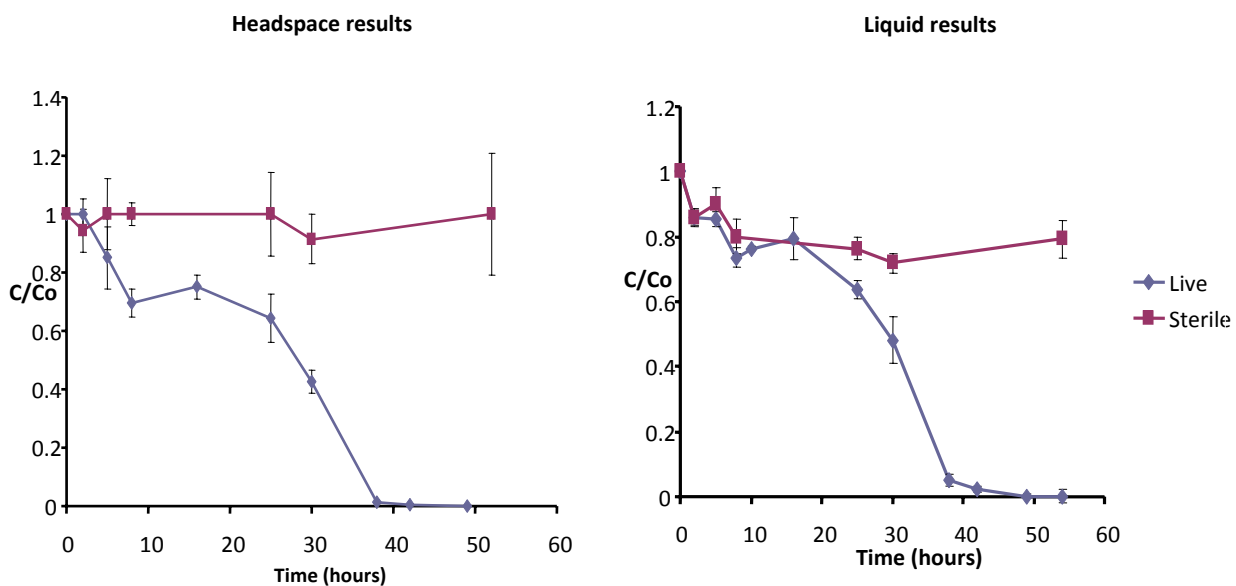


Fig. 9: Change in concentration of toluene in headspace and groundwater at 21° C.

4.2.3 Set 3: 30° C batches

The batches of 30° C showed the fastest degradation rates over time as seen in Fig. 10. Around 21 hours the concentration of toluene decreased completely.

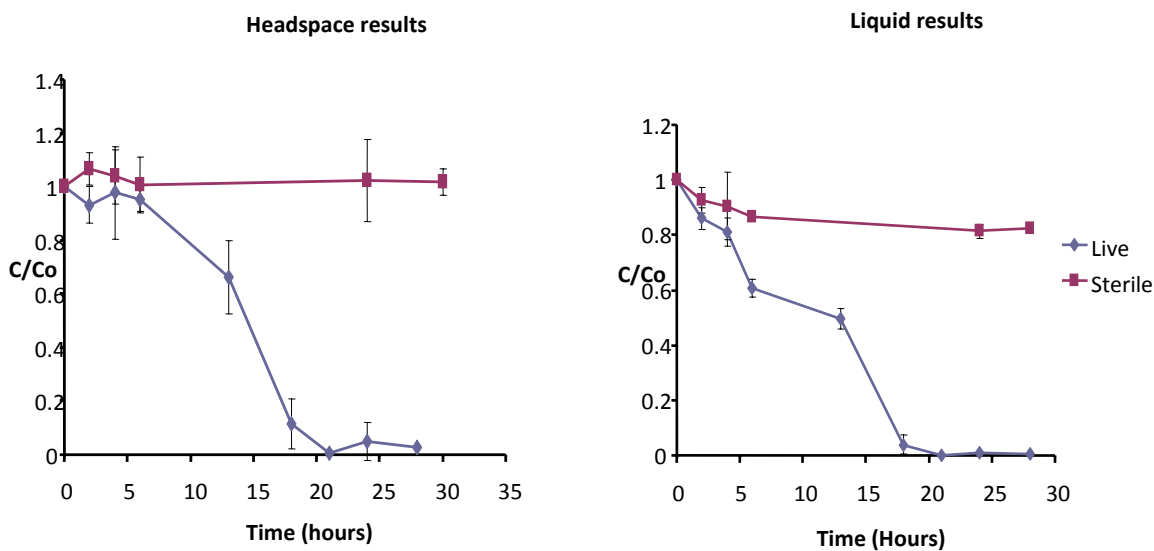


Fig. 10: Change in concentration of toluene in headspace and groundwater at 30° C.

4.3 Variable temperature batches

It was seen in the experiment of the variable temperature batches that even when microbes were exposed to change in the environment (fluctuating temperature); they were able to survive and continued growing by degrading toluene. For the sterile batches there was a distinct trend of fluctuating concentration seen. This is because the samples were taken in two different temperatures alternatively. With high temperature Henry's constant i.e. the ratio of the concentrations in air and water is higher. Thus the high and low values of concentrations were seen.

4.3.1 Winter case: 21° C to 10° C

In winter case batches it took 62 hours for the toluene concentrations in live batches to degrade. The time taken is much lower when compared to 10° C batches (91 hours) and longer when compared to 21° C batches (37 hours).

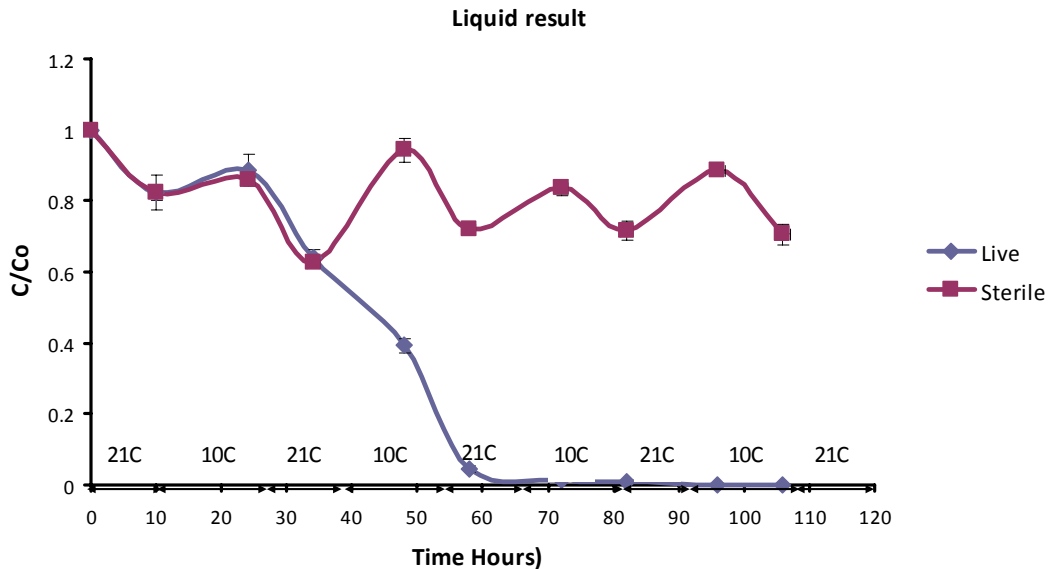


Fig. 11: Toluene concentration in 21° C to 10° C batches.

4.3.2 Summer case: 21° C to 30° C

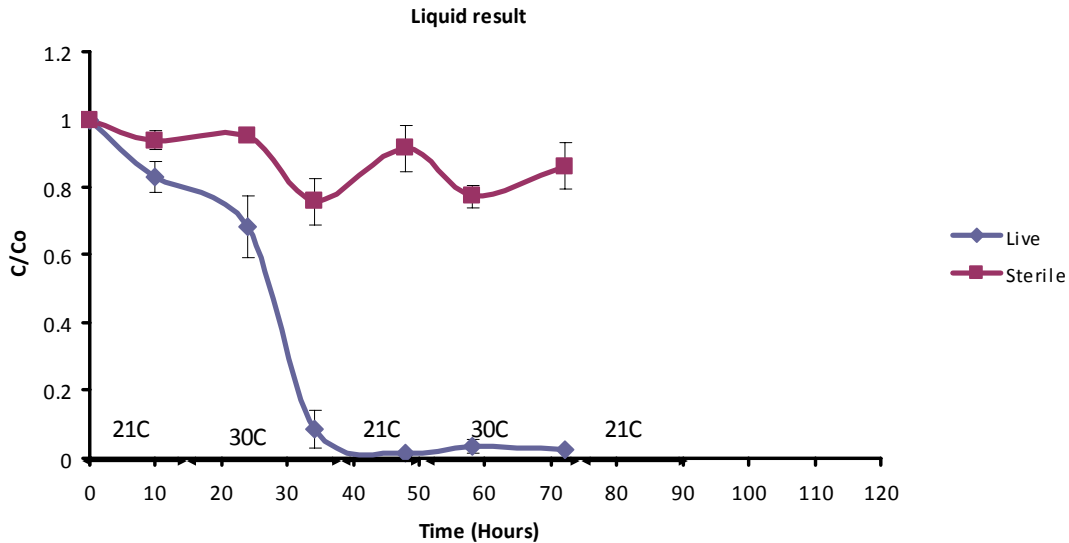


Fig. 12: Toluene concentration in 21° C to 30° C batches.

For summer case batches after 10 hours rapid degradation started and it took 40 hours for toluene concentrations to degrade (Fig. 12). This was different when compared to the winter case of 21°C to 10°C batches, where it took 24 hours to start the rapid degradation even though both the experiments began at same temperature. Overall, the time taken is longer when compared to 30° C batches (17hours) and similar to 21° C batches (37 hours).

4.3.3 Extreme case: 10° C to 30° C

The result of the extreme case batch is presented in Fig. 13. The batches for 10°C to 30°C behaved much different than expected and showed a faster degradation rate. In this case it took around 48 hours for toluene concentration to degrade. When compared to the individual constant temperature batches the time taken is less than half the duration as that of 10° C batches (91 hours) and longer than double the time taken by 30° C batches.

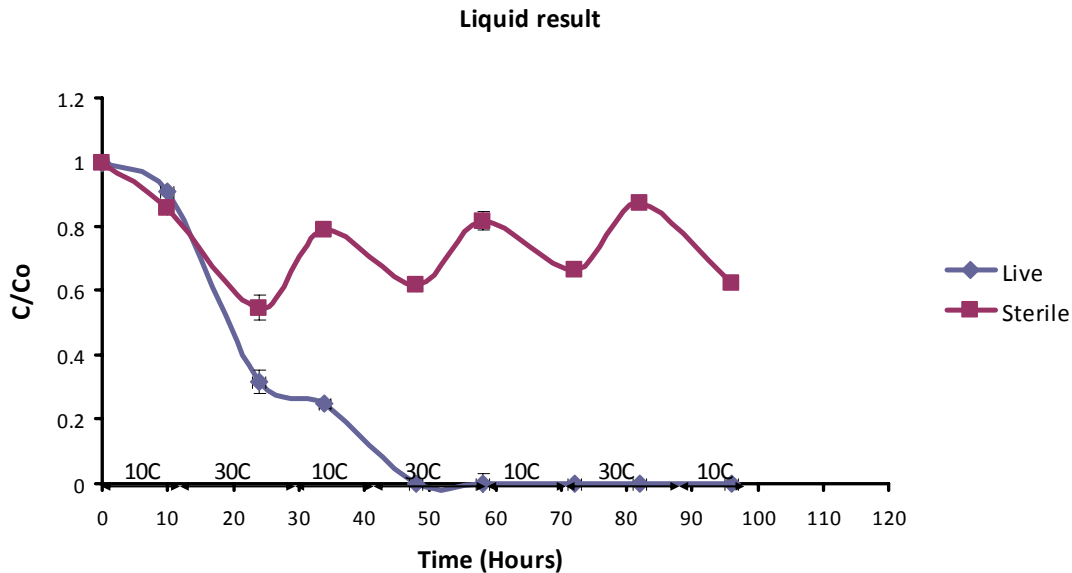


Fig. 13: Toluene concentration in 10° C to 30° C batches.

4.4 Summary of the batch experiments

A plot of all the constant temperature live batches shows that with decrease in temperature there is an increase in both the lag time and total time required for degradation (Fig. 14). Similar plot of live batches for variable temperature case can be seen in Fig. 15. A sudden change in the slope of concentration curve was considered for measuring the lag phase. A summary of the lag phase for different temperature batches are listed in Table 1. The concentrations in all the batches are lower than 1mg/L so first order kinetics formula was used to calculate the degradation rates. From the degradation rate calculated it can be seen that with decrease in temperature there is a decrease in degradation rates. The degradation rates in case of variable temperature batches were close to the lower temperature in summer and winter cases. In extreme case batches it was close to the higher temperature.

Table 1: Summary of the degradation time for the batch experiments.

	Cases					
	Constant temperature			Variable temperature		
	10°C	21°C	30°C	21°C to 30°C	21°C to 10°C	10°C to 30°C
Total time (hrs)	102	49	21	40	72	48
Lag time (hrs)	49	16	0	10	24	10
Effective time (hrs)	53	33	21	30	48	38
Degradation rate (hr ⁻¹)	0.054	0.120	0.248	0.112	0.081	0.187

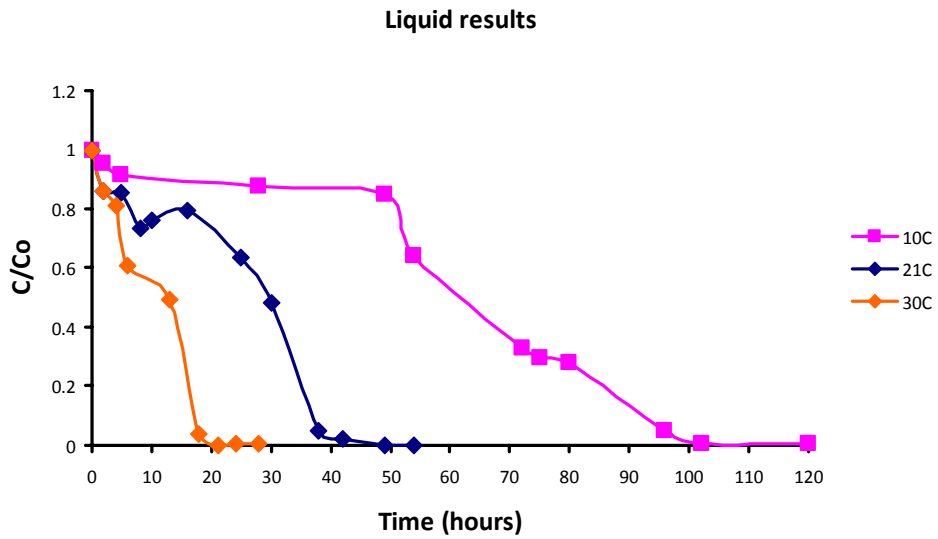


Fig. 14: Toluene concentration in liquid phase for constant temperature live batches.

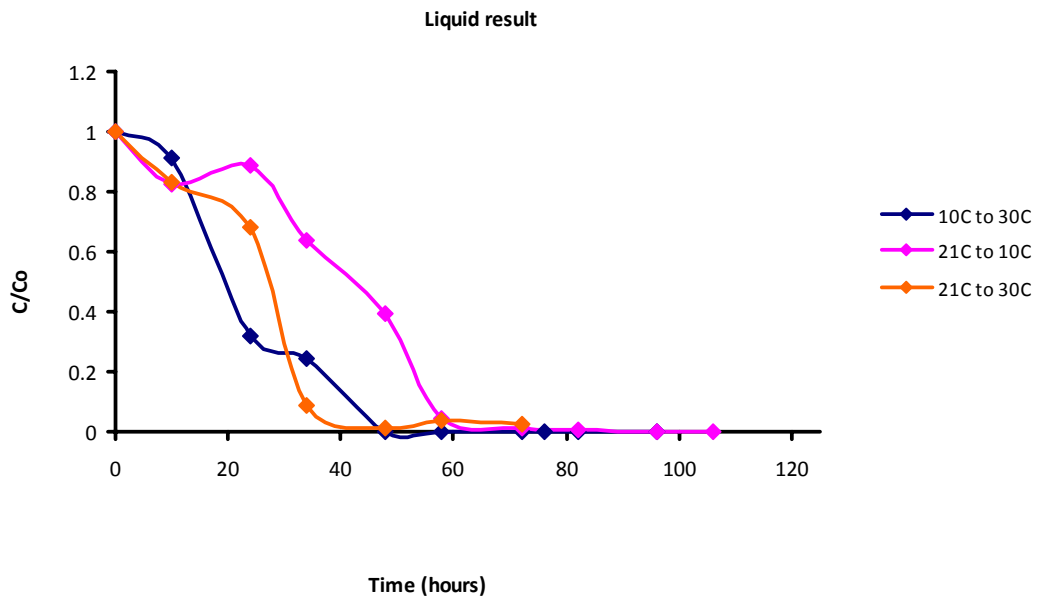


Fig. 15: Toluene concentration in liquid phase for variable temperature live batches.

4.4 Column results

Detailed results of the column experiments are presented in this chapter. Individual cases are discussed below.

4.4.1 Dynamic-water-level setup

A series of pictures taken for the live column and the sterile column of the dynamic water level setup are presented below.

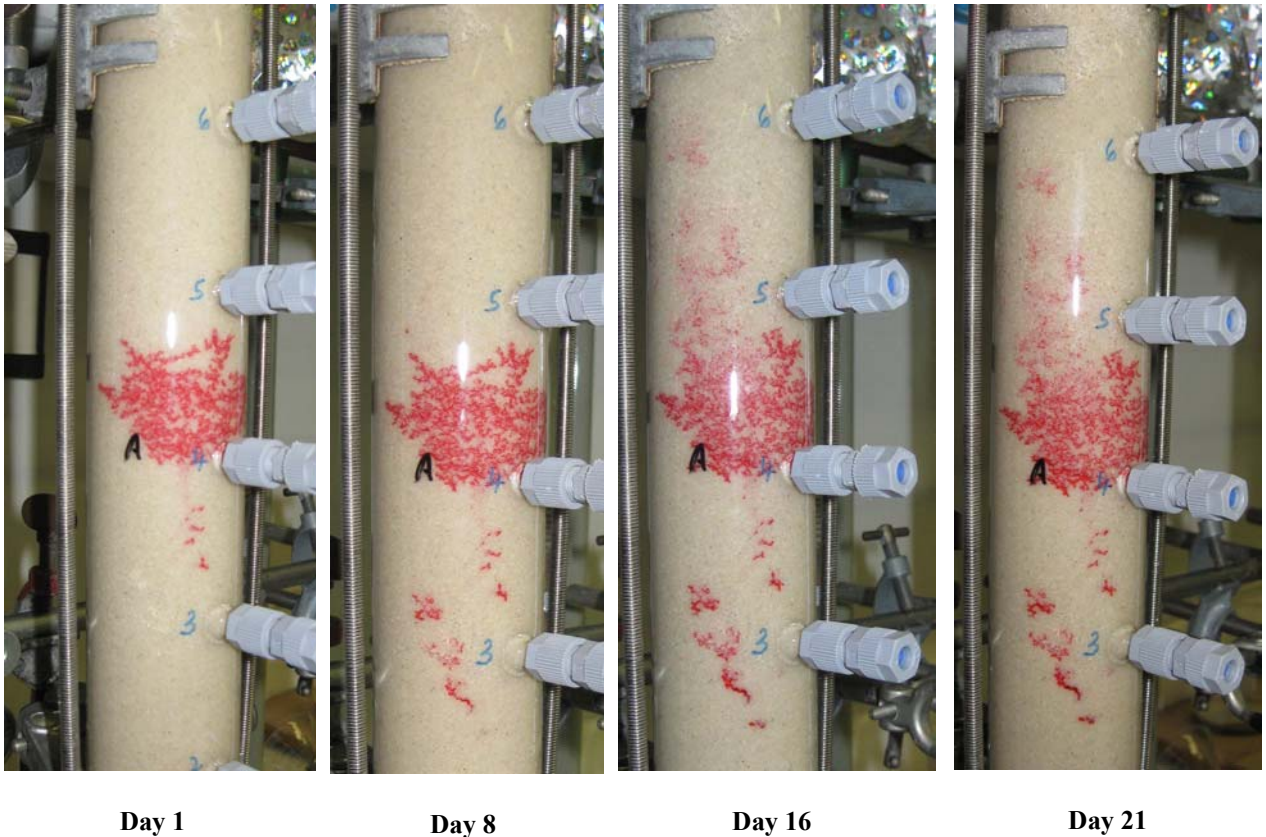


Fig. 16: Pictures of the live column for the dynamic-water-level setup.

The first picture shows toluene lens right after injection into the column. It can be seen that most of toluene has remained right above the water level which is at port 4 of the column. Note that there is a little bit of toluene that is seen below port 4. This can be because toluene was injected with a syringe. Over time it can be seen that toluene has spread much above and below port 4 even if water table was fluctuating only 2.5 cm above and below.

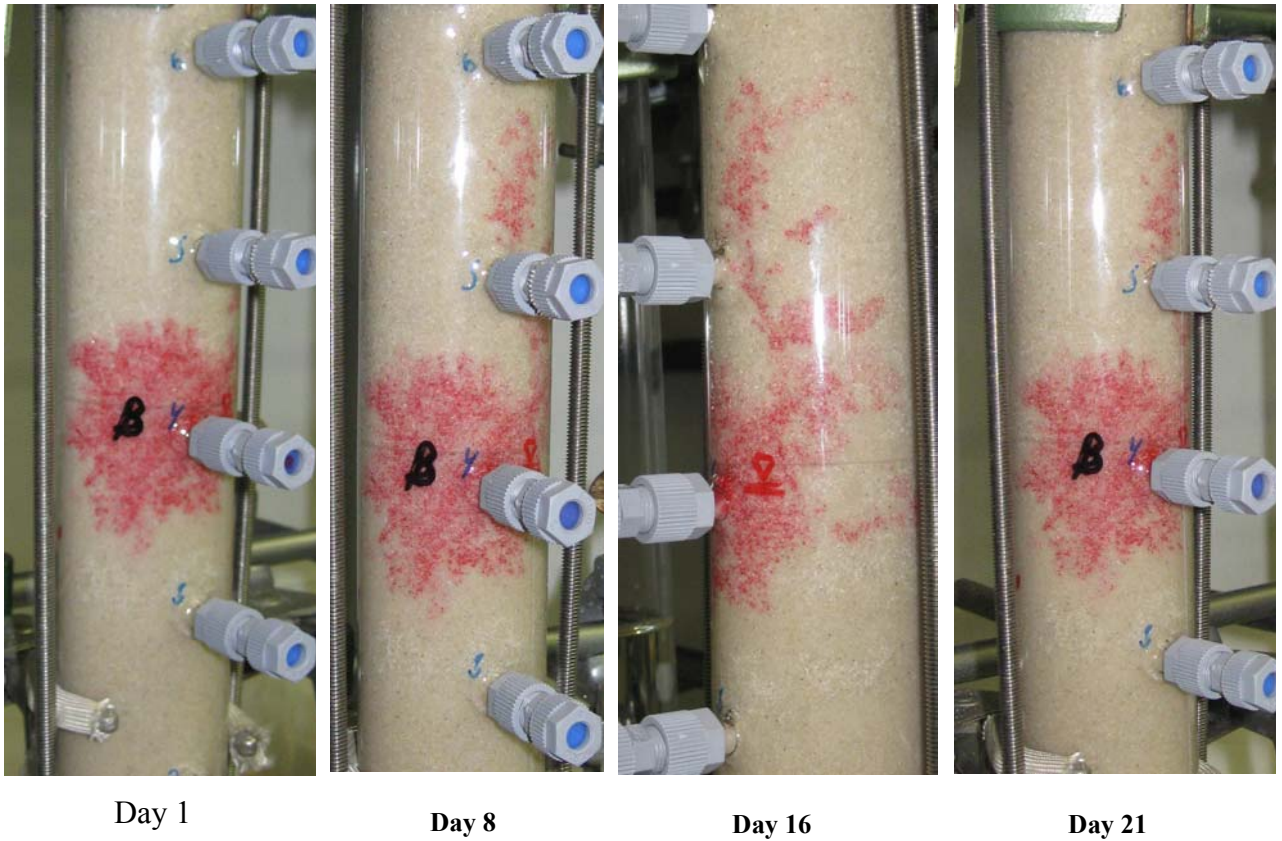


Fig. 17: Pictures of the sterile column for the dynamic-water-level setup.

The first picture of the sterile column shows noticeably different lens of toluene as compared to the live column even though the volume injected was same and sand filling in the columns were done in exactly same way. Also, it can be seen that in this column that spreading of toluene in the unsaturated zone has occurred a week faster than the live column. Detailed results of the measurements from the liquid phase and gas phase are shown below.

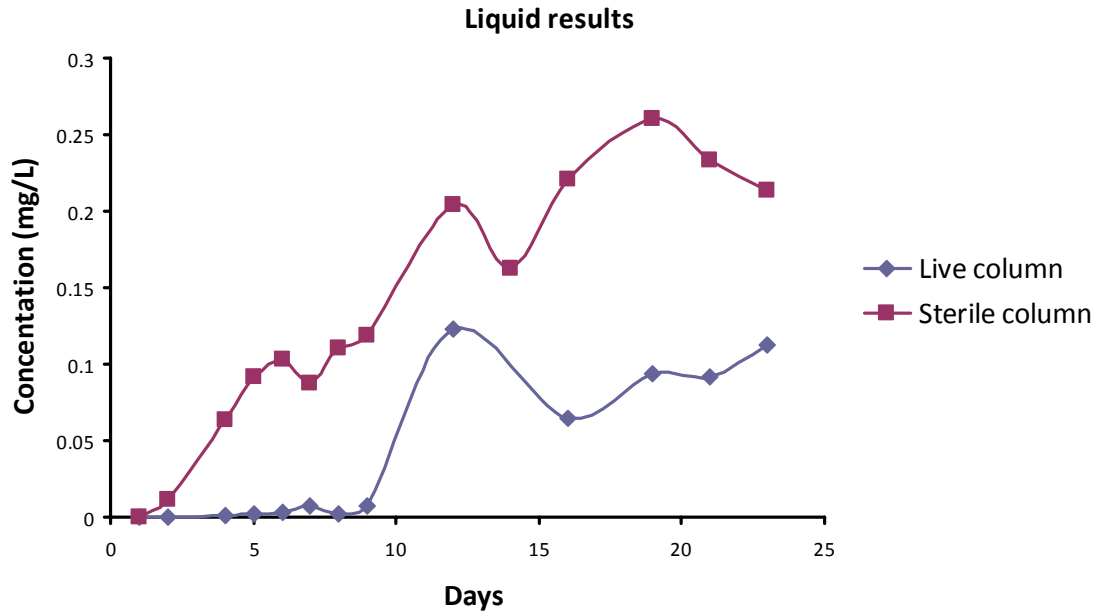


Fig. 18: Concentration in liquid phase of samples from port 1 in dynamic-water-level setup.

Fig. 18 shows that the concentration of toluene in liquid from port 1 slowly increased over time in both live and sterile columns of the dynamic-water-level setup. It was seen that from the 16th day onwards the trend of increase in concentration slowed down relatively compared to the first week. It can be expected that toluene will slowly dissolve out from the pure phase of the lens. Over a longer period of time the concentration will slowly increase to much higher values than seen now as the solubility limit of toluene is 500mg/L. In case of live column concentration can be expected to be much lower than the sterilized one. The difference between concentration in the live column and sterile column shows that microbes are actively degrading dissolved toluene coming out from the lens.

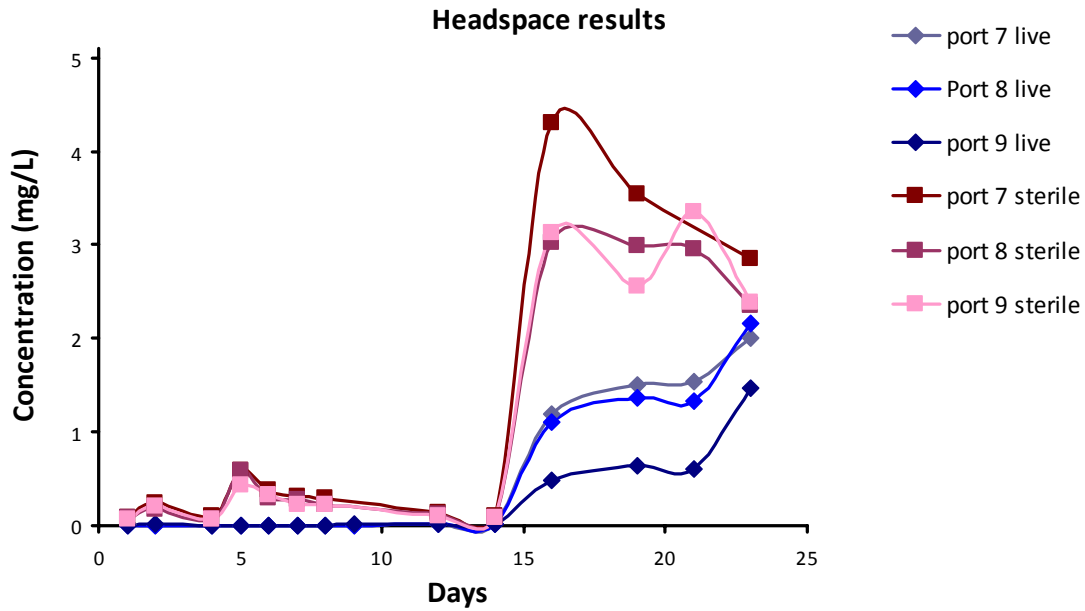
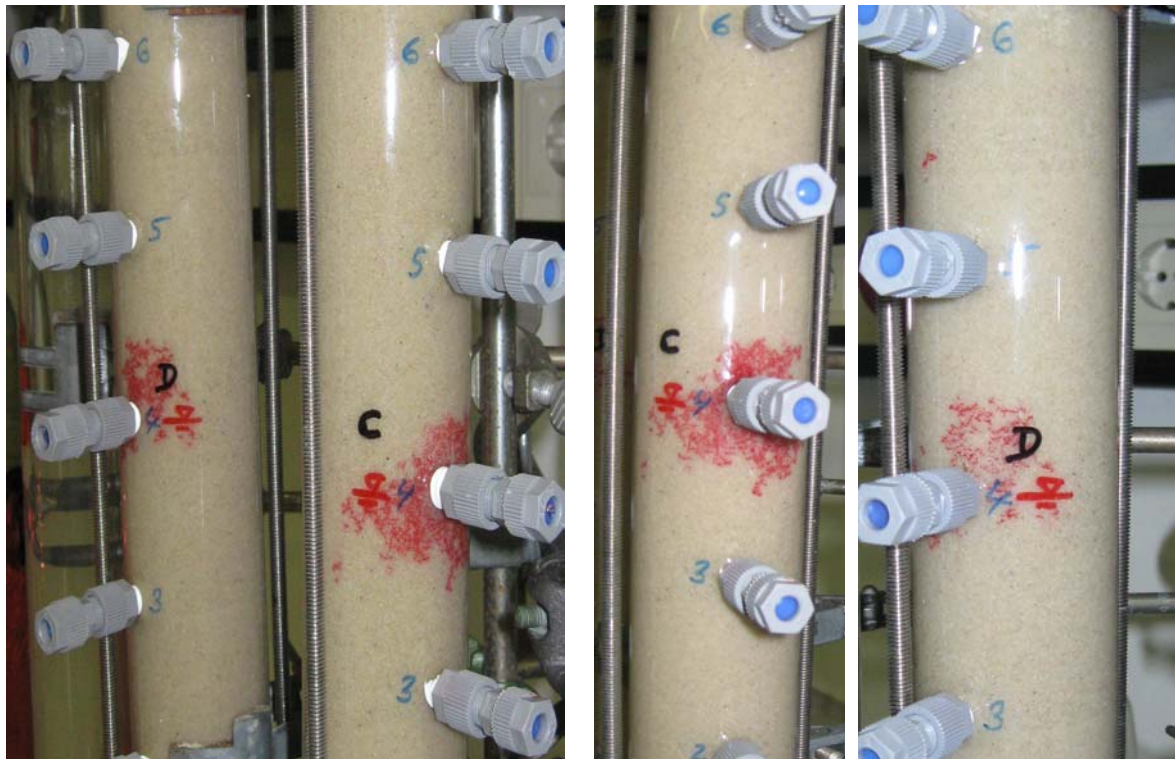


Fig. 19: Concentration in the gas phase for the dynamic-water-level setup.

Concentration of toluene has also increased slowly over time in the unsaturated zone and the headspace of the column (Fig. 19). The concentrations in the live column have remained relatively lower than the sterile one throughout the measurement phase. It can be seen clearly for the sterile column that there isn't much difference in concentration between the ports 7, 8, 9 whereas for the live column port 9 is showing relatively lower concentrations. Note that port 7 and 8 lie on the unsaturated zone of the column whereas port 9 is in the headspace of the column (Fig. 3). This means they are representative of the pore air and air above the column respectively. Hence, it can be concluded that toluene is being constantly degraded also in the unsaturated zone of the live column.

4.4.2 Static-water-level setup



Column C (live) & D (sterile)
Day 1

Column C
Day 21

Column D
Day 21

Fig. 20: Pictures of the live and sterile column for the static-water-level setup.

It can be seen in Fig. 20 that the size and shape of the lens is quite different for the sterile setup although the volume of toluene injected was the same. It could be because after the setups were ready it was kept for 2 days before injection of toluene which meant that for the dynamic setup water level was being fluctuated. This could have led to higher water content in the pores present in the unsaturated zone of the dynamic setup. Throughout the experiment the lens has remained constant for the static water level setup. Unlike the previous setup there is no movement of toluene seen in the unsaturated part of the column.

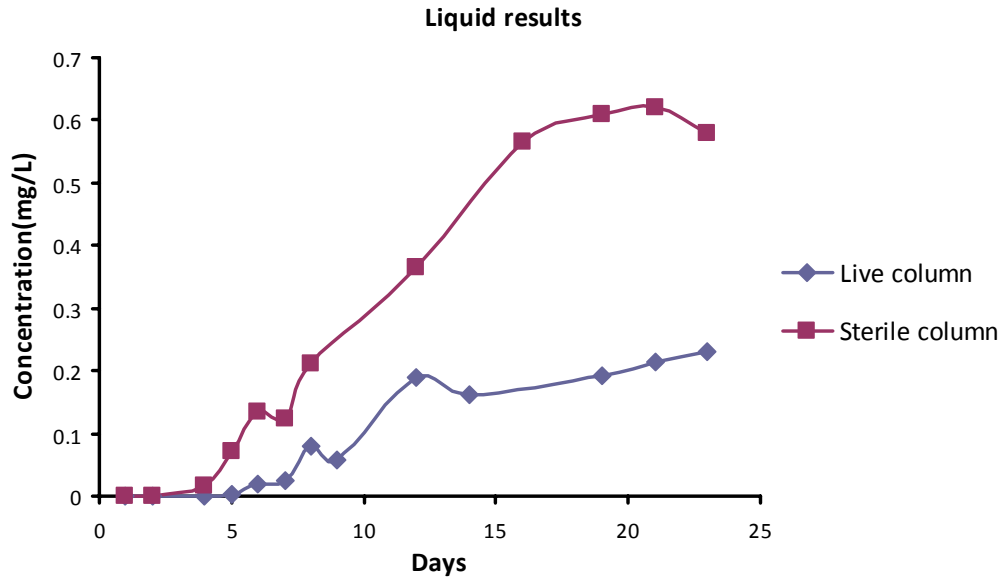


Fig. 21: Concentration in liquid phase of samples from port 1 for static-water-level setup.

In this case also there is a distinct difference between the concentrations of toluene in liquid samples from sterile and live columns. Note that a direct comparison between the concentrations of the two setups cannot be made as there are different volumes of groundwater involved.

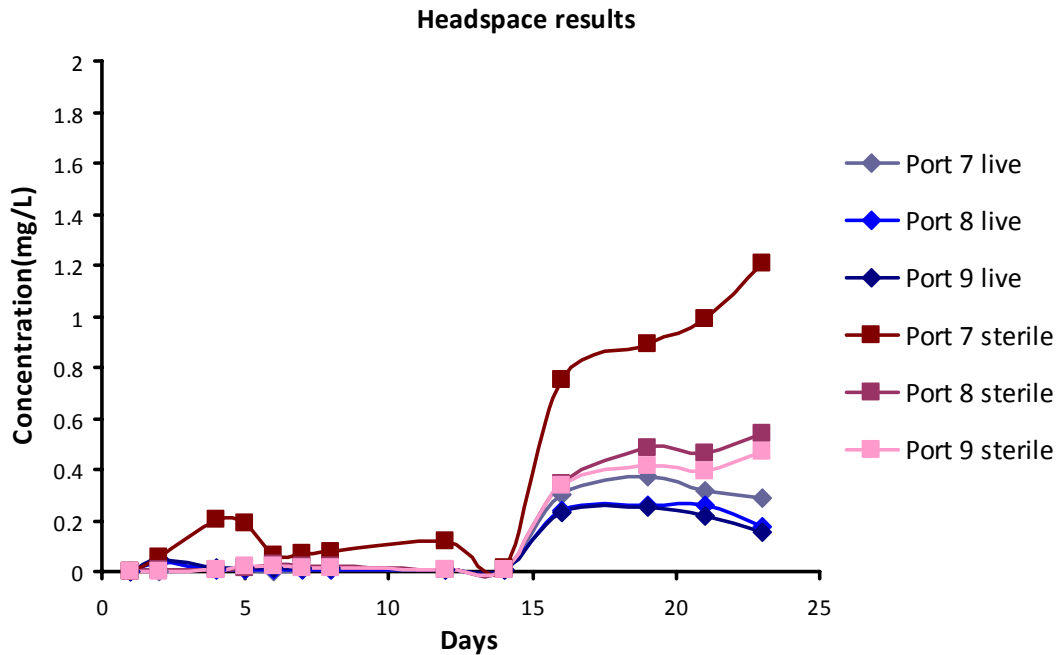


Fig. 22: Concentration in the gas phase for the static-water-level setup.

Despite the fact that both live and sterile columns in the static water level setup were filled with same sand and in a similar way, they showed different water level. It was noticed during the experiment that water level in the sterile column was slightly higher than the live one. This can also be seen in the result of the gas phase samples from port 7 of the sterile column which showed higher values. This was also the port where even drops of liquid came out while taking out air samples. More particularly, it can be seen that the difference between the live and sterile concentrations isn't significant.

4.4.3 Oxygen measurement

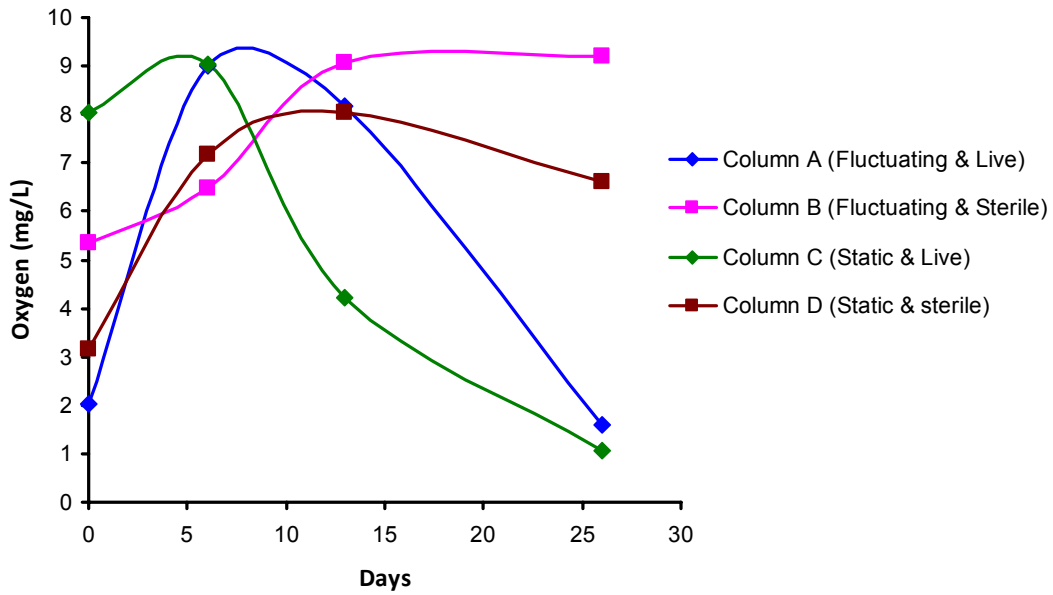


Fig. 23: Dissolved oxygen concentration for the column setups.

Given in Fig. 23 are weekly dissolved oxygen concentrations measured in samples from port 1 for all the columns during the experiment. The first measurement was done right after toluene injection. The graph distinctly shows that there is oxygen consumption in the live columns for both setups. Also, until the end of the experiment, oxygen content has remained higher in both live and sterile columns of the dynamic setup which is expected due to the water level fluctuations. Note that half saturation constant for oxygen (i.e. the amount of oxygen needed to degrade BTEX present into half) is 0.1mg/L in water for BTEX degradation (Bordon *et. al* 1986). Hence, until the end of the experiment oxygen is not limiting.

5. Conclusion and recommendation

Biodegradation of toluene (a LNAPL) under different environmental conditions such as changing soil temperature and fluctuating water table conditions were investigated. For this, batch and column experiments were run. The goal of batch experiments was to look at the effect of diurnal as well as seasonal change of soil temperature at arid and semi-arid polluted sites. There were two types of batch experiments: first type with three sets of constant temperatures and second type with three sets of fluctuating temperatures. The first type was aimed at seasonal effect thus winter (10°C), spring and/or autumn (21°C), and summer (30°C) were chosen. The second type was for diurnal effects of change in temperature at different seasons hence winter (21°C-10°C), summer (21°C-30°C) and weather extremes (10°C-30°C) were chosen.

Results of the first type of batch experiments showed a double increase in degradation times (21-49-102 hours) while going from summer to spring/autumn and then to winter. It also showed a similar trend in the lag phase. For summer case there was no lag phase seen and while going from spring/autumn to winter it doubled (0-16-49 hours). Similarly, degradation rates calculated showed half amount decrease while decreasing the temperature by 10°C (0.248 - 0.120- 0.054 hr⁻¹). The second type of batch experiments showed that microbes were able to overcome the effect of diurnal change of temperature and continued degrading toluene. It took them more time than what it would take if the temperatures were constant. For winter and summer cases degradation time and rate were more close to the lower temperature between the two limits. However, for the extreme case degradation time was different than expected and the degradation rate was more close to the upper temperature.

The aim of the column experiment was to investigate the effect of water table dynamics on biodegradation in a semi-arid coastal region. For this two sets were designed firstly with static water table and secondly with dynamic water table conditions. Each set was comprised of a pair of sterile and live columns. In the dynamic water level setup, water level was changed by 2.5 cm above and below the mean level where toluene lens was created. This was done to represent semi-diurnal tidal fluctuations. In case of the static water level setup water level was kept at a fixed height right at the place of the toluene lens.

Results showed that concentration of toluene slowly increased over time in liquid and gaseous phase for columns of both setups. A significant difference between liquid concentrations in live and sterile columns of the setups suggested biodegradation going on in the saturated zone. Also, it was observed that even though gaseous concentrations in ports directly above the lens in the unsaturated zone were high, relatively lower concentrations in the headspace above were seen. This seems due to the bio-degradation of toluene in the unsaturated zone.

During the designing phase of the experiment it was not realized that the difference between the dynamic water level case and static water level would lead to different volumes of groundwater in the columns. Hence, a direct comparison between the two setups couldn't be done to quantify the exact amount of biodegradation rates. Nevertheless, weekly oxygen measurements of all columns indicated that there was oxygen consumed in the live columns. This supported the fact that microbes were degrading toluene by consuming oxygen.

It was realized during this research that there is room of improvement in method of storing and analyzing gas samples in the current laboratory. Hence this is strongly recommended for any further research. Also, the difference between the design of the setup of the dynamic water level and static water level could be improved such that quantification of degradation rates can be done. Further, it would be interesting to quantify the fate and transport of the introduced LNAPL in the column setup using a numerical tool for better understanding of the remediation processes in arid and semi arid environments

References

- Alvarez, J. J. P., Illman, W. A., (2006). Bioremediation and Natural Attenuation, process fundamentals and mathematical models. John Wiley and Sons, Inc., Publication.
- Atlas, R.M. (1994). Microbial hydrocarbon degradation-bioremediation of oil spills. J. Chem. Tech. Biotechnol. 52:149–156.
- Corseuil, H., W. Weber., (1994). Potential biomass limitations on rates of degradation of monoaromatic hydrocarbons by indigenous microbes in subsurface soils. Water Resesearch. 28:1415–1423.
- Dobson, R., Schroth H. M., Zeyer J., (2007). Effect of water-table fluctuation on dissolution and biodegradation of a multi-component light nonaqueous-phase liquid. Journal of Contamination Hydrogeology 94: 235-248.
- Deeb , R. A., Cohen, L.A., (1999). Temperature effects and substrate interactions during the aerobic biotransformation of BTEX mixtures by Toluene-enriched consortia and *Rhodococcus rhodochrous*. Biotechnology and Bioengineering, volume 62 (5), pp 526-536.
- Gentry, T. J., C. Rensing, and I. L. Pepper (2004). New approaches for bioaugmentation as a remediation technology. Crit. Rev. Environ. Sci. Technology. 34(5):447-494.
- JRB Associates, Inc. (1984). Summary report: Remedial Response at Hazardous Waste Sites. Prepared for Municipal Environmental Research Laboratory, Cincinnati, OH. PB 85-124899.
- Ju, M., Devanny, J.S., and Paspalof, 1993. Effects of pulverization on soil
- Lee, C. H., Lee J. Y., Cheon J. Y., Lee K.K. (2001). Attenuation of petroleum hydrocarbons in smear zones. Journal of Environmental Engineering, Volume 127, Issue 7, pp 639-647.
- Mayer, A., Hassanizadeh, S. M., (2005). Soil and groundwater contamination: Nonaqueous phase liquids- Principles and observations. Water Resources Monograph, vol. 17. American Geophysical Union, Washington, D.C.
- National Research Council. (1993). In situ Bioremediation: When Does It Work? National Academy Press, Washington, DC.
- Nielsen, D.M. (2006). Environmental site characterization and groundwater monitoring. Taylor and Francis group Publication.

Oostrom, M., Hofstee, C., Wietsma, T.W., (2006). Behavior of a viscous LNAPL under fluctuating water table conditions. *Soil and Sediment Contamination*, 15:543-564.

Parr, J. F., Sikora, L. J., and Burge, W.D. (1983). . Factors affecting the degradation and inactivation of waste constituents in soils. In *Land Treatment of Hazardous Wastes*. Parr, J.F., Marsh, P.B., and Kla, J.M., Eds. Noyes Data Corp., Park Ridge, NJ. pp. 20–49, 321–337.

Perk M., (2006). Soil and groundwater contamination from molecular to catchment scale. Taylor and Francis Group Publication.

Pinder, G., F. and Celia, M. A., (2006). *Subsurface Hydrology*. John Wiley and Sons, Inc., Publication.

Rainwater, K., Mayfield, M. P., Heintz, C., Claborn, B. J., (1993). Enhanced in situ biodegradation of diesel fuel by cyclic vertical water table movement: Preliminary Studies. *Water Environment Research* 65(6), 717-725.

Roberts, E.R. (1998). *Remediation of Petroleum Contaminated Soils*. Lewis Publishers.

Robinson C., Brovelli A., Barry D. A., Li L., (2009). Tidal influence on BTEX biodegradation in sandy coastal aquifers. *Advances in water Resources* 32:16-28.

Sims, R. and Bass, J. (1984). Review of In-Place Treatment Techniques for Contaminated Surface Soils. Volume 1: Technical Evaluation. EPA Report No. EPA-540/2-84-003a. Sims, R.C., Doucette, W.J., McLean, J.E., Grenney, W.J.,

Sinke, A., J. C., Dury, O., Zobrist, J., (1998). Effects of a fluctuating water table: column study on redox dynamics and fate of some organic pollutants. *Journal of Contaminant Hydrology* 33: 231-246

U.S. E.P.A., (2001). Citizen's guide series. www.epa.gov/superfund/sites.

Zhou, E. and Crawford, R.L. (1995). Effects of oxygen, nitrogen, and temperature on gasoline biodegradation in soil. *Biodegradation*. 6:127–140.

Appendix A: Calculations for the experiments

Mass balance for Toluene in the batch system with sand and groundwater

At equilibrium:

Mass in soil + Mass in water + Mass in air = Mass added (from the stock solution)

$$C_s.V_s + C_w.V_w + C_a.V_a = C.V$$

Here:

$$C_s = s. \rho_b \quad ; \quad s = K_d. C_w$$

$$S_o, C_s = K_d. C_w. \rho_b$$

$$C_a = K_H. C_w$$

So,

$$K_d.C_w.V_s.\rho_b + C_w. (V_w+V) + K_H$$

$$.V_a = C.V$$

$$C_w \{K_d.V_s.\rho_b + (V_w+V) + K_H$$

$$.V_a\} = C.V$$

$$C_w \{0.0115 + 0.01504 + 0.0203412\}$$

$$= 0.0196$$

$$C_w = 0.41807 \text{ mg/L}$$

$$C_a = C_w. K_H = 0.0840 \text{ mg/L}$$

Cs	Conc. in soil		
Vs	Volume of soil	10g / 2.65 (g/ml) 3.773 ml	3.773 * 10 ⁻³ L
Cw	Conc. in water		
Vw	Volume of water	15 ml	0.015 L
Ca	Conc. in air		
Va	Volume of air	120-3.773- 15.00004(ml)	0.1012 27 L
C	Conc. of stock		490 mg/L
V	Volume of stock	40 µL	40*10 ⁻⁶ L
s	Adsorbed mass of solute/mass of dry soil		
ρb	Dry bulk density		2.65 kg/L
foc	Fraction of organic carbon	1 % for sand	0.01
Koc	Organic carbon partitioning coefficient	Log Koc = 2.06 for Toluene	114.81 5 L/kg
Kd	Distribution coefficient	Kd = foc. Koc	1.148 L/kg
KH	Henry' coefficient (dimensionless air-water)		0.201

Mass balance for Toluene in the batch system with only groundwater

At equilibrium:

Mass in water + Mass in air = Mass added (from the stock solution)

$$C_w \cdot V_w + C_a \cdot V_a = C \cdot V$$

Here:

$$C_a = K_H \cdot C_w$$

So,

$$C_w \cdot (V_w + V) + K_H \cdot V_a \cdot C_w = C \cdot V$$

$$C_w \cdot V_a = C \cdot V - K_H \cdot V_a \cdot C_w$$

$$C_w \cdot \{ (V_w + V) + K_H \cdot V_a \} = C \cdot V$$

$$C_w \cdot \{ 0.01504 + 0.021 \} =$$

$$0.0196$$

$$C_w \cdot \{ 0.0360 \} = 0.0196$$

$$[mg/L]$$

$$C_w = 0.5444 \text{ mg/L}$$

$$C_a = C_w \cdot K_H = 0.1094 \text{ mg/L}$$

$$C_a = 0.1094 \text{ mg/L}$$

C_w	Conc. in water		
V_w	Volume of water	15 ml	0.015 L
C_a	Conc. in air		
V_a	Volume of air	120- 15.00004(ml)	0.1049 L
C	Conc. of stock		490 mg/L
V	Volume of stock	40 μ L	$40 \cdot 10^{-6}$ L
K_H	Henry' coefficient (dimensionless air-water)		0.201

Basic calculation for the column experiment

1. The amount of sand needed in the column:

Column description:

Column length = 50 cm

Outside diameter = 5cm

10 ports on the sides, 1 ports on top and one down.

Internal diameter = 4.5 cm

Volume of the column (V) = $\pi r^2 h = 3180.86 \text{ cm}^3$

2. How much Toluene should be added (e.g. 1 cm height of the pure phase)

Average grain size = 0.4 mm

Area of the column (A) = πr^2

Height to be covered (h_1) = 1cm

Total Volume for the spill (V_s) = $A * h_1 = 15.89 \text{ cm}^3$

Volume of Toluene = $n * V_s = 6.04 \text{ cm}^3$

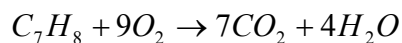
3. From the Toluene present how much smears as residual phase?

The amount of smeared volume depends on soil pore size distribution, soil wettability, LNAPL viscosity and LNAPL density.

For porosity 0.38: Residual saturation in saturated zone = 0.10 and 0.07 in unsaturated zone.

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6. How much Oxygen needed to degrade Toluene present?



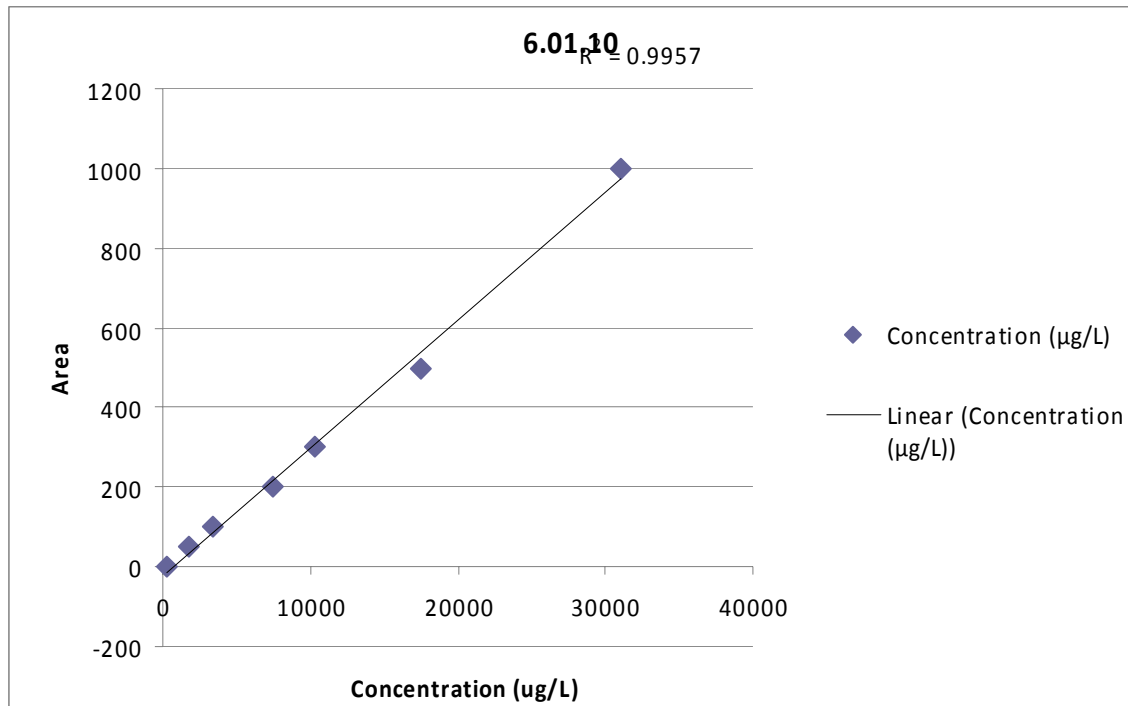
1 Molecule of Toluene requires 9 molecule of Oxygen, so to get a mass ratio of Oxygen

to Toluene: $\frac{32 * 9}{92.14} = 3.12$

Appendix B: Calibration curves

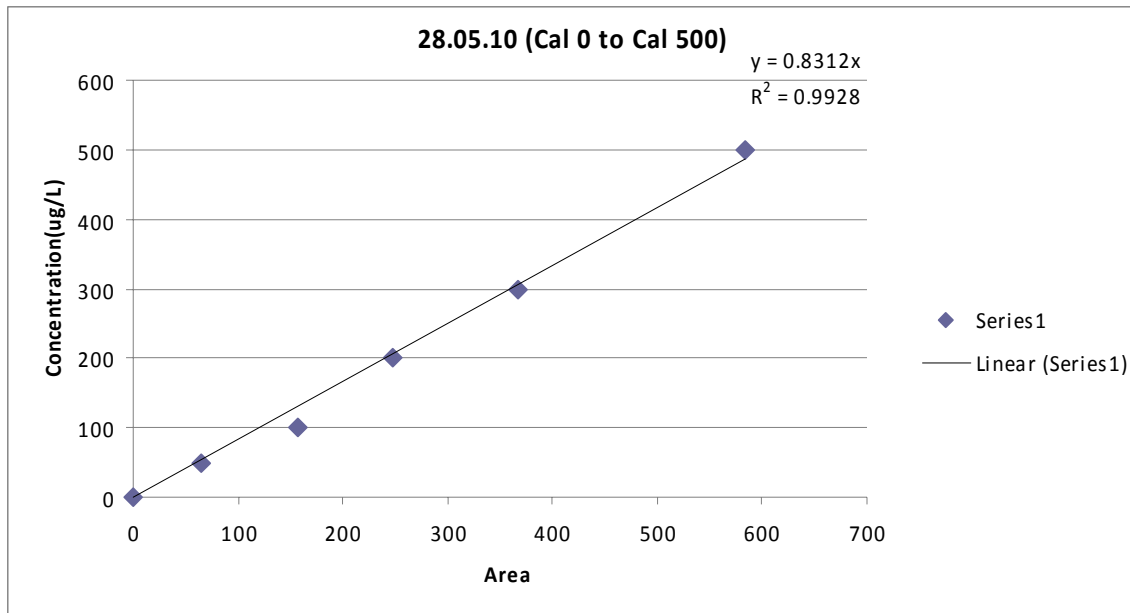
Type I: Example of batch experiment calibration curve:

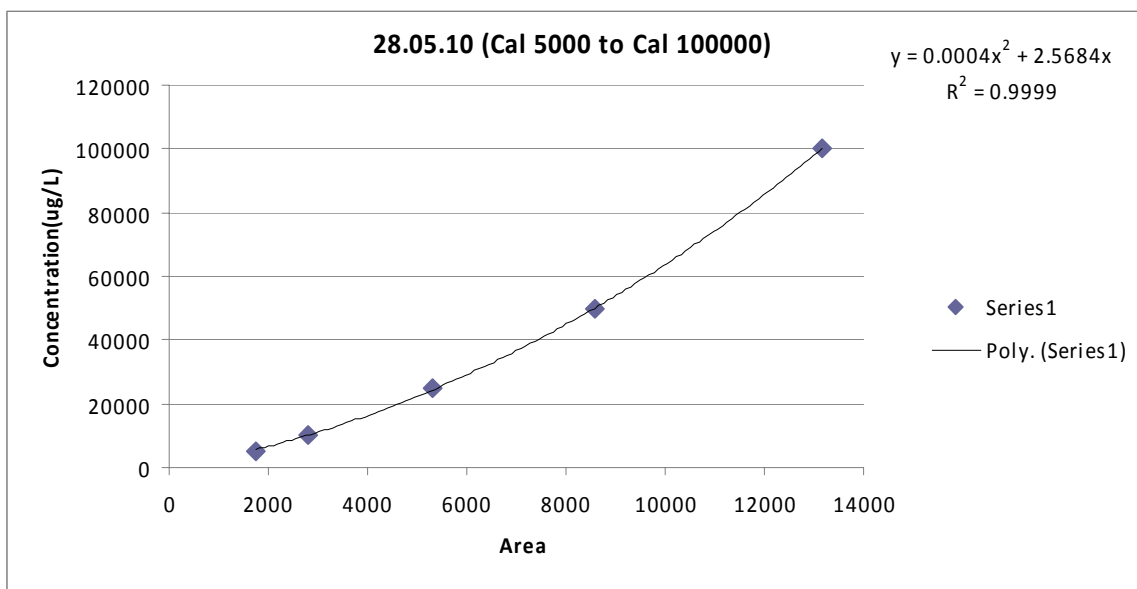
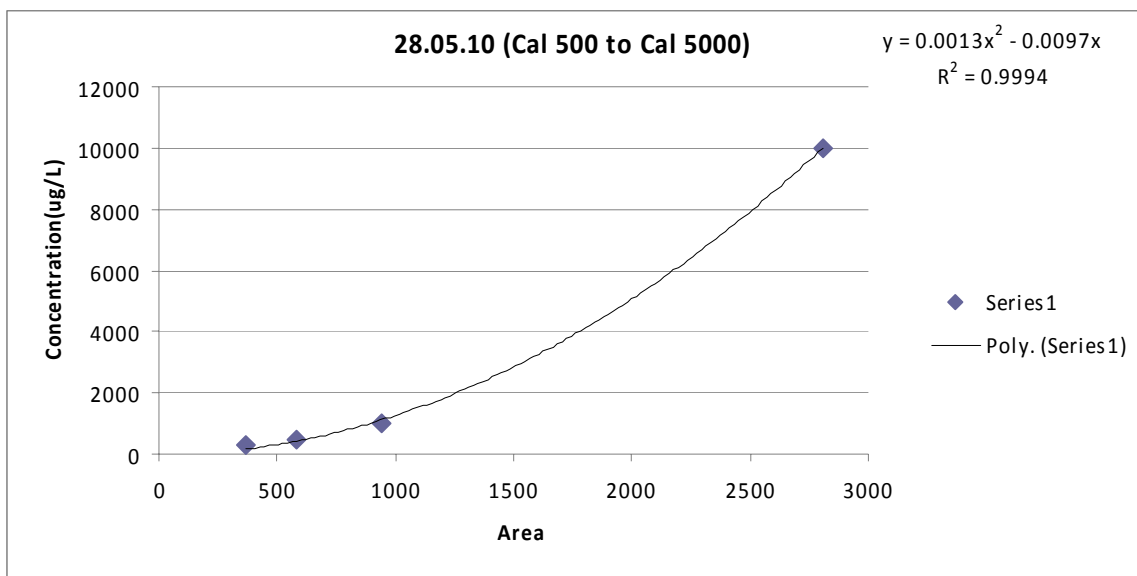
Name	Area	Concentration ($\mu\text{g/L}$)	Slope
Cal 0	261.3	0	31.14591
Cal 1	1785.4	50	
Cal 2	3380.6	100	
Cal 3	7464.3	200	
Cal 4	10249	300	
Cal 5	17510.3	500	
Cal 6	31087	1000	



Type II: Example of column experiment calibration curve:

Name	Area	Concentration ($\mu\text{g/L}$)	
Cal 0	0	0	0.8312
Cal 1	65.7	50	
Cal 2	157.6	100	
Cal 3	247.5	200	
Cal 4	366.5	300	
Cal 5	584.5	500	
Cal 6	942	1000	
Cal 7	903	2000	
Cal 8	1731	5000	
Cal 9	2806	10000	
Cal 10	5325.2	25000	
Cal 11	8584.3	50000	
Cal 12	13181.4	100000	
Cal 0 to Cal 500	$y = 0,3625 x$		0.8312
Cal 500 to Cal 5000	$y = 0,0013x^2 - 0,0097x$		0,0013-0,0097
Cal 5000 to Cal 100000	$y = 0,0004 x^2 + 2,5684x$		0,0004+2,5684





Appendix C: Experiment results

1. Constant temperature Batches (10C) : Headspace results

Name	Time (Hours)	Area	Conc (µg/L)	C/Co	Average Conc (µg/L)	Average Concentration (µg/L) (C/Co)	Standar Error	Standar deviation
Air								
Sandy soil (Sa)	0	8006.8	64.43740216	1	86.30014967	1	0	32.82782102
	2	11150.4	89.73657505	1.03982	83.14647154	0.931340717	0.065672406	7.138956087
	6	9826.9	79.08526594	0.9164	80.67793241	0.880090366	0.006538045	12.53856871
	28	8003.9	64.41406344	0.7464	68.47741514	0.86055312	0.110196595	15.57922601
	49	8654.7	69.65159421	0.80709	69.38521088	0.823803276	0.087090791	5.034782256
	54				35.33125687	0.409399717		
	71	12497	100.5737891	1.1654	7.094568601	0.139992526	0.090142653	5.506869514
	76	22457.4	180.733441	2.09424	1.924237255	0.034333423	0.017425957	0.734097517
	102	3890.4	31.30929577	0.3628	0.230972853	0.003056302	3.50353E-05	0.134300011
	120	704.9	5.672918617	0.06573	0.109450551	0.0016004	0.021379243	3.212148827
Sandy soil (Sb)	0	13440	108.1628972	1				
	2	7439.3	59.87025602	0.55352				
	6	11672.3	93.93673993	0.86847				
	28	9013.7	72.54076683	0.67066				
	49	7980.1	64.22252498	0.59376				
	71	397.7	3.200623825	0.02959				
	76	174.6	1.405151923	0.01299				
	102	40.5	0.325937302	0.00301				

	120	16.4	0.131984488	0.00122				
Sandy soil (Sc)	0	5453	43.88484213	1				
	2	12404.9	99.83258357	1.20068				
	6	8575.2	69.01179136	0.8554				
	28	5271.9	42.42737929	0.96679				
	49	9230	74.28151346	1.07057				
	71	1365.4	10.98851338	0.25039				
	76	303.6	2.443322588	0.05568				
	102	16.9	0.136008405	0.0031				
	120	10.8	0.086916614	0.00198				

Sterlized sandy soil (SSa)	0			1	69.63147462		1	
	2	7067.6	56.8788759	0.83223	68.34516239	0.992479893	0.046659054	13.66547186
	6	6394.1	51.45865929	0.95232	54.03477115		1 0.100704103	3.71605801
	28	4491.6	36.14765394	0.73569	49.13417639	0.915750584	0.092421927	2.026450588
	49	4744.3	38.18134175	0.91649	41.66042065		1 0.074883724	5.403457179
	102	5587.6	44.96808067	1.07435	41.85598303		1 0.095933193	6.954838887
	120	6887.7	55.43107045	0.96512	57.43457888	1.00636447	0.021121592	8.062373131
Sterlized sandy soil (SSb)	0			1				
	2	8038.2	64.69010417	0.94652				
	6	7034.3	56.610883	1.04768				

	28	4847.7	39.01348784	0.79402
	49	4835.4	38.91449948	0.93409
	102	6539.5	52.62881444	1.25738
	120	7385.6	59.4380873	1.03488
Sterlized sandy soil (SSc)	0	8652.2	69.63147462	1
	2	10371.3	83.4665071	1.19869
	6	6137.8	49.39599928	0.70939
	28	8976.5	72.24138739	1.03748
	49	5950.1	47.88542072	1.14942
	102	4814.2	38.74388538	0.92565
	120	8817.4	70.9609769	1.01909

Liquid results:

Name	Time (Hrs)	Area	Concentration ($\mu\text{g/L}$)	C/Co	Avg. Concentration ($\mu\text{g/L}$)	Average (C/Co)	Standar Error	Standar deviation
Sandy soil (Sa)	0	12299	394.8832935	1	401.4363205	1	0	9.26738
	2	11842.6	380.2296846	0.962891292	379.616442	0.954614915	0.013097277	0.867256
	5	11081.6	355.7963009	0.901016343	358.86733	0.913037045	0.01938458	4.343091
	28	11327.8	348.0902456	0.881501576	351.9129143	0.87671264	0.027587158	5.40607

	49	10825.2	332.6459265	0.842390478	335.5759222	0.849098148	0.013561152	4.14364
	54		253.2114383	0.893189879	257.4134429	0.641231074	0.066531046	5.942532
	72		16.26347757	0.905696029	15.17814378	0.329355696	0.027177441	2.362781
	75		5.624385362	0.851727629	5.249045251	0.293404649	0.003994919	0.817119
	80		3.186952671	0.825812669	2.974273223	0.280651302	0.001253332	0.463005
	96		3.217593987	0.128847692	3.002869709	0.048381374	0.004036678	0.467457
	102	5556.6	170.7479174	0.432400966	1.270637869	0.003735123	0.000878881	0.262916
	120	587.4	18.05012538	0.045710025	1.773054536	0.005661947	0.01360423	9.489156
Sandy soil (Sb)	0	12707.2	407.9893476	1				
	2	11804.4	379.0031994	0.928953664				
	5	11272.9	361.9383591	0.887126983				
	28	11576.6	355.735583	0.871923703				
	49	11015.9	338.5059178	0.829693029				
	54		261.6154475	0.300280578				
	72		16.80325735	0.007900099				
	75		5.81105697	0.009350402				
	80		3.292726642	0.009605631				
	96		3.324384934	0.013092116				
	102	35.3	1.084728338	0.002658717				
	120	14.9	0.457859837	0.001122235				
Sandy soil (Sc)	0	9428.5	302.7203132	1				
	2	9164.5	294.2440802	0.971999788				
	5	8966.2	287.8772734	0.95096781				
	28	9448	290.3261569	0.959057401				
	49	8622	264.9441284	0.875210935				
	54		194.1136715	0.730222765				

72		12.46769642	0.074470961
75		4.311693421	0.019135915
80		2.443140357	0.006535607
96		2.466630206	0.003204314
102	47.4	1.4565474	0.004811528
120	100.5	3.088249235	0.010201658

second set	Time (hrs)	Area	Concentration (ug/L)	decrease in conc	average decrease
Sandy soil (SA)	0	29463.5	730.761	0	0
	54	26316.5	652.7083291	0.106810121	0.358768926
	72	26470.2	661.8473358	0.094303971	0.95881447
	75	24892.9	622.4093337	0.148272371	0.985756841
	80	24135.5	603.4716917	0.174187331	0.991929381
	96	3538.5	94.15686857	0.871152308	0.991851785
	Sandy soil (SB)	0	33573.6	832.7007147	0
54		10081.5	250.0438516	0.699719422	
72		263.1	6.57841777	0.992099901	
75		311.4	7.786086254	0.990649598	
80		319.9	7.998615904	0.990394369	
96		409.7	10.90181406	0.986907884	
Sandy soil (SC)		0	28258.5	700.8742925	0
	54	20635	511.7943637	0.269777235	
	72	2087.5	52.19478181	0.925529039	
	75	536.4	13.41187112	0.980864085	
	80	183.2	4.580639055	0.993464393	

96	84.4	2.245821593	0.996795686
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Sterlized sandy soil (SSa)	0	6910.9	221.8878732	1	246.0467426	1	0	32.47884
	2	7116.9	228.5019035	1.029807984	257.5019648	1.070284982	0.051684315	2.145437
	5	6846.8	219.8298182	0.990724797	236.8197422	1.010256282	0.027774653	10.80665
	28	6729.6	206.7928562	0.931970068	232.0447993	0.992780918	0.034527255	5.566861
	49	6946	213.4425789	0.96193891	236.8835686	1.01145968	0.027252124	1.099466
	102	4179.6	128.4342935	0.578825204	213.307372	0.889352495	0.012203519	43.89607
	120	6158.1	189.2313195	0.852824072	211.8538975	0.908657974	0.021204779	28.94547
Sterlized sandy soil (SSb)	0	6492.3	208.4479068	1				
	2	7211.4	231.5360096	1.11076198				
	5	6370.8	204.5469132	0.981285523				
	28	6985.8	214.6655871	1.029828461				
	49	6895.4	211.8876992	1.016501928				
	102	5931.5	182.2681625	0.874406298				
	120	6569	201.8578032	0.968384889				
Sterlized sandy soil (SSc)	0	8415.8	270.2056119	1				
	2	9732.1	312.4679812	1.156408185				
	5	8910.3	286.0824953	1.058758526				
	28	8938.7	274.6759546	1.016544226				
	49	9285.1	285.3204275	1.0559382				
	102	7951.7	244.3465815	0.904298692				
	120	7955.8	244.4725698	0.90476496				

1. Batches (21C) : Headspace results

Name	Time (Hours)	Area	Concentration (µg/L)	C/Co	Average Con (µg/L)	Average C/Co	Standar Error	SD
Air								
Sandy soil (Sa)	0	712.7	6.215985494	1	3.432005461	1	0	2.609634
	2	15600.8	136.0661519	1.06167252	128.1620733	1	0.050355406	11.17806
	5	18213	158.8490863	1.23943911	125.5881419	0.85015533	0.105969999	23.52356
	8	8998.6	78.48346718	0.6123767	89.31892331	0.696921648	0.048318964	18.51527
	16	11410.8	100.8231026	0.78668439	96.3190734	0.751541161	0.041617651	9.23842
	25	9774.9	85.25415547	0.66520581	82.42831107	0.643156817	0.082411215	8.89619
	30	4385.4	38.24832718	0.29843718	44.53888357	0.424905832	0.040075957	8.89619
	38	141.3	1.248493042	0.00974152	1.543901987	0.012046481	0.00193641	0.30431
	42	92.2	0.814657172	0.00635646	0.826732712	0.006450681	0.000267382	0.066652
	49	3540.3	30.87758305	0.24092606	0.271246175	0.002116431	0.000377839	17.67068
Sandy soil (Sb)	0	348.4	3.038654898	1				
	2	13788.3	120.2579946	0.93832748				
	5	14399.8	125.5913398	0.97994154				
	8	7259.4	63.31461357	0.49401989				
	16	10391.3	91.81504418	0.71639793				
	25	10310.3	89.92377611	0.70164108				
	30	5827.9	50.82943996	0.39660282				
	38	210.1	1.856393404	0.01448473				
	42	101.7	0.898596903	0.00701141				
	49	37.9	0.33055402	0.00257919				

Sandy soil (Sc)	0	119.4	1.04137599	1
	2	22811.5	198.9560167	1.55237826
	5	10585.5	92.3239995	0.72036912
	8	11483.3	100.1543794	0.7814666
	16	15332.2	135.4716561	1.0570339
	25	8267.5	72.10700164	0.56262356
	30	8518.1	74.29267017	0.5796775
	38	172.8	1.526819516	0.01191319
	42	86.8	0.766944062	0.00598417
49	24.3	0.21193833	0.00165367	

Sterilized sandy soil (SSa)	0	199.4	1.739115346	1	1.002564238	1	0	1.041641
	2	12459.1	108.6650552	0.9135979	118.9418838	0.944965072	0.074278424	15.30235
	5	16195.5	141.2529719	1.15033845	122.7925329	1	0.123551152	26.107
	8	22678.8	197.7986415	1.63202234	121.1984891	1	0.03695822	7.758341
	25	13823.9	120.5684887	0.97573353	123.5670235	1	0.145601523	4.240569
	30	17157.9	149.6467763	1.17040744	127.858702	0.914796279	0.085724657	24.5874
	52	21247.1	185.3117236	1.418516	130.6377397	1	0.210456848	7.178007
	0	30.5	0.26601313	1				
Sterilized sandy soil (SSb)	2	14815.7	129.2187123	1.0864021				
	5	11962.3	104.3320938	0.84966155				
	8	10133.8	88.38438866	0.72925322				
	25	14511.5	126.5655584	1.02426647				
	30	13171.1	114.8749355	0.89845223				

	52	12426	108.3763656	0.82959462
Sterilized sandy soil (SSc)	0	81	0.706461099	1
	2	11385.8	99.30400959	0.83489521
	5	7701.5	67.17049569	0.54702427
	8	8875.8	77.41243727	0.63872444
	25	8007.9	69.84283743	0.5652223
	30	13650.3	119.0543943	0.93114033
	52	11262.1	98.22513011	0.75188939

Liquid results:

Name	Time (Hrs)	Area	Concentration (µg/L)	C/Co	Avg. Con (µg/L)	Average (C/Co)	Standard Error	SD
first set								
Sandy soil (Sa)	0	14710.2	422.6814077	1	391.2206612	1	0	0.1849
	2	12418.2	356.8233102	0.844189746	352.5649463	0.859679619	0.025936673	6.0222
	5	13490.5	387.6346705	0.917084744	343.3835076	0.854056522	0.022141002	15.381
	8	14989	344.3099289	0.814584987	322.6897738	0.734714091	0.029495392	30.576
	10		322.553365	0.753292088	298.5452835	0.763112262	0.007653597	0.1411
	16		336.0870232	0.946315474	298.5639085	0.795130841	0.0647048	0.147
	25	12166.4	279.4724344	0.661189324	268.6370889	0.635743314	0.02856276	15.323
	30	10300.2	236.6042518	0.559769717	240.6115149	0.480659658	0.071667461	9.122
	38		11.94319794	0.052322109	16.18206118	0.050076863	0.017147283	2.2293
	42		8.653858743	0.037911801	8.782133584	0.02095454	0.009139277	0.9889
	49		367.8789554	1.611645636	3.231657066	0.001667282	0.005926362	0.9993

	54	1191.8	28.67609068	0.067843274	0.635214628	0.001667282	0.022058952	16.19
Sandy soil (Sb)	0	11434.6	328.5606467	1				
	2	10408.9	299.088286	0.910298568				
	5	9627.4	276.6327436	0.84195337				
	8	10823.4	248.6225956	0.756702296				
	10		250.7286581	0.757853484				
	16		261.2487033	0.865424528				
	25	8042.2	184.7360938	0.562258736				
	30	11210.7	257.5192021	0.783779813				
	38		17.75842807	0.088985602				
	42		9.545525317	0.047831616				
	49		3.938257325	0.01973419				
	54	20.1	0.483629319	0.001471964				
Sandy soil (Sc)	0	14701.1	422.4199292	1				
	2	12121.8	348.3065824	0.824550544				
	5	12733.5	365.8831086	0.866159675				
	8	13106.6	301.0696187	0.712725887				
	10		322.3538275	0.778191213				
	16		335.8791136	0.724837155				
	25	11223	257.8017434	0.610297303				
	30	10649.1	244.6187781	0.579089103				
	38		14.60569429	0.030180345				
	42		8.147016691	0.016834515				
	49		2.525056807	0.005217628				
	54	32.7	0.786799937	0.001862601				

second set	Time	Area	Concentration(ug/L)	decrease in conc	avg decrease in conc	avg conc
Sandy soil (Sa)	0	8352.5	297.5136468	0	0	361.7454866
	16	7904.1	281.5417678	0.053684526	0.204869159	298.4065142
Sandy soil (Sb)	0	8528.3	303.7755922	0		
	16	7380.6	262.8948484	0.134575472		
Sandy soil (Sc)	0	13586.5	483.9472208	0		
	16	9848	350.7829265	0.275162845		

third set	Time	Area	Concentration(ug/L)	decrease in conc	avg decrease in conc	avg conc
Sandy soil (Sa)	0	9310.2	228.2629303	0	0	200.813125
	10	7013.3	171.9486594	0.246707912	0.236887738	153.0235927
Sandy soil (Sb)	0	8139.7	199.5651837	0		
	10	6168.7	151.2411697	0.242146516		
Sandy soil (Sc)	0	7121.9	174.6112611	0		
	10	5542.2	135.8809491	0.221808787		

first set	Time (Hrs)	Area	Concentration (µg/L)	C/Co	Avg. Concentration (µg/L)	Average (C/Co)	Standard Error	SD
Sterlized sandy soil (SSa)	0	12825	368.5122604	1	380.5776248	1	0	17.063
	2	11385.1	327.1383186	0.887727096	325.5622642	0.856434533	0.02555027	2.2289
	5	10848.1	311.7082146	0.84585575	308.6796616	0.899189842	0.050676324	4.283
	8	12341.5	283.4946286	0.769294971	269.4215431	0.800499489	0.053199123	19.902
	25	11842.2	272.0252879	0.738171608	266.7844906	0.76200505	0.034800745	7.4116
	30	12114.4	278.2779507	0.755138921	267.8985764	0.71772345	0.029863991	14.679
	54	11217.1	269.8964397	0.732394736	262.7791485	0.791916729	0.0581658	10.065
Sterlized sandy soil (SSb)	0	13664.8	392.6429892	1				
	2	11275.4	323.9862099	0.825141971				
	5	10637.3	305.6511086	0.778445349				
	8	11116.2	255.3484577	0.6503324				
	25	11385.9	261.5436934	0.666110692				
	30	11210.7	257.5192021	0.655860945				
	54	10625.5	255.6618573	0.65113058				
Sterlized sandy soil (SSc)	0	7426.9	213.4037978	1				
	2	12517	359.6622194	1.685359975				
	5	7074.3	203.2722249	0.952523933				
	8	7726.7	177.4887936	0.831704006				
	25	7300.6	167.7009185	0.785838491				

30	6320.2	145.1803064	0.680307979
54	7551.6	181.7002571	0.851438723

3. Batches (30C) : Headspace results

Name	Time (Hours)	Area	Concentration (µg/L)	C/Co	Average Con (µg/L)	Average (C/Co)	Standard Error	Standard Deviation
Air								
Sandy soil (Sa)	0	13213.2	96.03251399	1	95.46876547	1	0	1.023371583
	2	18159.2	131.9796588	1.135264563	116.2545394	0.932367719	0.068772063	3.550671419
	4	11473	83.3848752	0.868298368	93.79399385	0.976386299	0.172446847	14.72071677
	6	15494.5	112.6128257	1.093199532	103.0121423	0.953400234	0.046900372	1.337733059
	13	11255.9	99.45444322	1.035633028	62.90796821	0.661717101	0.134518218	10.95618869
	18	3282.7	29.00515292	0.302034714	11.05412617	0.11529008	0.093502069	1.120235306
	21	71.6	0.632640494	0.006587774	0.293936319	0.00306938	0.001761115	0.017493914
	24	13133.8	95.45544094	0.993990858	0.236798397	0.048926358	0.071559202	6.192220925
	28	8324.5	60.50182111	0.630013925	0.357848324	0.028546286	0.006963813	3.305100262
Sandy soil (Sb)	0	12973.1	94.28748579	1				
	2	14568.3	105.8812758	0.910771109				
	4	18923.4	137.5338052	1.458664467				
	6	13643.2	99.15772068	0.962582842				
	13	7996.5	70.65516353	0.749358867				
	18	324.9	2.870738777	0.030446657				
	21	15.5	0.136954297	0.001452518				
	24	1017.9	8.993921211	0.095388281				
	28	569.5	5.031965939	0.053368333				
Sandy soil (Sc)	0	13220.6	96.08629662	1				

2	15259.2	110.9026835	0.953964328
4	14337.4	104.2031125	1.08447423
6	13382.9	97.26588044	0.944217626
13	6242.9	55.16077289	0.574075335
18	145.6	1.286486814	0.013388869
21	12.7	0.112214166	0.001167848
24	26.8	0.236798397	0.002464435
28	40.5	0.357848324	0.003724239

Sterlized sandy soil (SSa)

0	20158.7	146.5118699	1	122.4017483	1	0	14.01716065
2	23937.4	173.9751688	1.187447603	128.6480431	1.06752914	0.060467688	3.843091746
4	19133.8	139.0629761	0.949158428	113.935103	1.036345694	0.103034316	22.17179357
6	18955	137.7634716	0.940288808	111.9670707	1.006276674	0.101368385	14.95331427
24	12308.6	89.45795127	0.610585008	118.0460823	1.021725116	0.154277138	1.122400692
30	21135.6	153.6119035	1.048460466	109.017021	1.015818424	0.047884245	10.93158659

Sterlized sandy soil (SSb)

0	17431.2	126.6886112	1
2	17326.9	125.9305669	0.994016476
4	13363.5	97.12488275	0.766642572
6	15221.9	110.63159	0.873256001
24	18099.6	131.5464906	1.038345036
30	16063.3	116.74682	0.92152577

Sterilized sandy soil (SSc)	0	12934.2	94.0047636	1
	2	18074.7	131.3655194	1.021123339
	4	14532	105.6174502	1.123532959
	6	15589.4	113.3025515	1.205285213
	24	18318	133.1338049	1.416245303
	30	13936.2	101.287222	1.077469036

Liquid results:

Name	Time (Hours)	Area	Concentration (µg/L)	C/Co	Average Concentration (µg/L)	Average (C/Co)	Standard Error	SD
Air								
Sandy soil (Sa)	0	10293.1	287.5589983	1	287.415588	1	0	18.96409
	2	9534.6	266.3687349	0.926309858	247.7216756	0.860204898	0.03967685	0.962044
	4	9358.7	261.4546053	0.90922074	232.7436841	0.809466418	0.050021897	29.72933
	6	8721	268.2519928	0.932858976	179.8179347	0.607383558	0.030648765	3.893272
	13	6979.9	180.4634136	0.566072166	133.6185253	0.495366261	0.035490492	0.981746
	18	1336.5	34.55484351	0.108390586	1.171361846	0.038818508	0.034786045	19.27396
	21	23.8	0.847749152	0.002659194	0.64709144	0.002139405	0.000273209	0.181288
	24	132	4.060229681	0.014119641	1.065810291	0.007169101	0.003477863	1.734239
28	67.1	2.063950088	0.007177484	1.198588004	0.004238272	0.001724738	0.847989	
Sandy soil (Sb)	0	10964.2	306.3075623	1				
	2	9485.9	265.0081999	0.865170281				

	4	8400.5	234.6853101	0.766175371
	6	8542	262.7460753	0.85778514
	13	5141.2	132.9243258	0.465419918
	18	41.2	1.161494779	0.004066846
	21	13.9	0.495114001	0.001733587
	24	39.1	1.202689246	0.003926411
	28	12	0.369111789	0.001205036
Sandy soil (Sc)	0	9606.6	268.3802036	1
	2	7580.9	211.7880921	0.789134553
	4	7233.8	202.091137	0.753003144
	6	274.9	8.455735904	0.031506556
	13	5194.9	134.3127247	0.454606699
	18	41.9	1.181228913	0.003998092
	21	16.8	0.598411166	0.002025435
	24	30.2	0.928931336	0.003461251
	28	37.8	1.162702136	0.004332295

Sandy soil (Sa)	0	11308.3	318.7993059	290.5245198
Sandy soil (Sb)	0	10130.7	285.6008532	
Sandy soil (Sc)	0	10480	295.4481864	

Sterlized sandy soil (SSa)	0	11522.3	321.899238	1	302.252963	1	0	17.36354
	2	11577.9	323.4525387	1.004825425	280.4164222	0.925498833	0.046559236	38.40849
	4	11362.5	317.4348951	0.986131241	277.6902303	0.904787105	0.122156809	56.20744
	6	9119.9	280.5218839	0.871458676	261.9740165	0.866557649	0.002906716	16.50318
	24	9069.1	278.9593106	0.866604445	246.7163705	0.814516985	0.026295827	28.29509
	28	8805.8	270.8603828	0.841444623	249.8681751	0.826102002	0.010002217	19.17184
Sterlized sandy soil (SSb)	0	10343.4	288.9642327	1				
	2	9599.4	268.1790567	0.928070074				
	4	8517.2	237.9455655	0.823442968				
	6	8092.3	248.913611	0.86139938				
	24	7348.1	226.0225282	0.782181677				
	28	7584.2	233.2848026	0.807313765				
Sterlized sandy soil (SSc)	0	10591.5	295.8954183	1				
	2	8935	249.6176711	0.843601001				
	4	5999.9	167.6195931	0.566482557				
	6	8338.5	256.4865545	0.86681489				
	24	7645.4	235.1672728	0.794764833				
	28	7980	245.4593398	0.829547619				

4. Variable temperature Batches (21-10C) : Liquid results

Name	Time (Hrs)	Area	Concentration (µg/L)	C/Co	Avg. Concentration (µg/L)	Average (C/Co)	Standard Error	SD
Sandy soil (Sa)	0	28307	755.3258554	1	733.5068724	1	0	93.09748
	10	24035.1	641.3372122	0.849086798	599.6738148	0.824128373	0.050052881	38.46273
	24	28173.1	689.9357598	0.913427966	663.2070581	0.886759583	0.043241811	34.10783
	34	20764.1	508.4955191	0.673213442	467.6761587	0.639319782	0.023014284	51.35162
	48	26943.2	716.7863608	0.948976334	285.6615735	0.392733602	0.020549668	71.63078
	58	21650.7	572.1554221	0.757494819	31.95906644	0.043051811	0.009323644	15.07811
	72	25139.9	664.3632814	0.879571746	9.571731809	0.01382386	0.004578267	2.896402
	82	19764.6	522.3121218	0.691505683	6.301434152	0.008949942	0.001818463	0.70448
	96	23959.4	633.1666237	0.838269496	1.378149679	0.001729195	0.001411124	1.664964
	106	17461.5	461.4489094	0.610926935	0.095135932	0.000125817	4.62994E-05	0.063534
Sandy soil (Sb)	0	23664.1	631.4376859	1				
	10	21193.7	565.5191147	0.89560558				
	24	25990.2	636.4783564	1.007982847				
	34	16742.9	410.0196795	0.649343061				
	48	8833.8	235.0109621	0.372183934				
	58	805.9	21.29723541	0.033728167				
	72	439.7	11.61979701	0.018402128				
	82	257.3	6.799576462	0.010768405				
	96	7.6	0.200842523	0.000318072				
	106	1.9	0.050210631	7.9518E-05				

Sandy soil (Sc)

0	30496.8	813.7570758	1
10	22192.3	592.1651175	0.727692742
24	28580.2	699.9052998	0.8600912
34	19784.8	484.5132776	0.595402844
48	12641.6	336.3121849	0.413283269
58	1612.8	42.62089747	0.052375455
72	284.7	7.52366661	0.009245593
82	219.6	5.803291842	0.007131479
96	96.7	2.555456836	0.003140319
106	5.3	0.140061233	0.000172117

Sterlized sandy soil (SSa)

0	28814.9	768.8783336	1	732.6387737	1	0	39.74648
10	22625.2	603.7163438	0.785190995	601.6359312	0.82213457	0.018488787	19.60318
24	26619.4	651.8869405	0.847841475	628.0320426	0.857607795	0.006202877	26.31581
34	19679.2	481.9272215	0.626792563	459.9343166	0.627535788	0.006783018	30.40153
48	26226	697.7062524	0.907433884	710.116836	0.9426329	0.035199017	17.55122
58	20113.5	531.5323792	0.691308827	526.6416876	0.719755694	0.015366627	11.51038
72	23553.4	622.4374047	0.80953953	612.0543749	0.836817569	0.02342551	9.426482
82	19379.8	512.1431478	0.666091273	525.2393135	0.71846323	0.027003805	15.11961
96	24998.8	660.6344814	0.859218491	649.5722866	0.887236113	0.014151155	26.26721
106	19078.3	504.1755135	0.6557286	516.0921698	0.706168024	0.028273802	10.51577

Sterlized sandy soil
(SSb)

0	27691.7	738.9075843	1
10	23239.8	620.1159365	0.839233417
24	25823.9	632.4058079	0.855865904
34	19299.7	472.6335825	0.639638288
48	27159	722.5274197	0.977831917
58	20240.9	534.8991341	0.723905324
72	22857	604.0338873	0.817468788
82	20501.5	541.7859185	0.733225548
96	25296.4	668.4990517	0.904712668
106	19831.1	524.0694939	0.709249039

Sterlized sandy soil
(SSc)

0	25863.7	690.1304033	1
10	21776.7	581.0755133	0.841979299
24	24492.6	599.8033795	0.869116006
34	17364.5	425.2421459	0.616176514
48	18866	501.9036894	0.727259206
58	19430.9	513.4935495	0.744052931
72	23071.1	609.6918325	0.883444389
82	19744.8	521.7888742	0.756072869
96	23445.4	619.5833268	0.897777179
106	19678.3	520.0315021	0.753526434

5. Variable temperature Batches (21-30C) : Liquid results

Name	Time (Hrs)	Area	Concentration (µg/L)	C/Co	Avg. Concentration (µg/L)	Average (C/Co)	Standard Error	SD
Sandy soil (Sd)	0	78.9	525.3569289	1	551.3251422	1	0	30.30173605
	10	71.3	474.7522058	0.903675539	457.4400636	0.830285421	0.045623384	11.77070491
	24	74.9	498.7228641	0.949302915	385.5280885	0.683519069	0.088755758	12.24153311
	34	81.9	545.3324776	1.038022814	49.93887157	0.086484388	0.055884633	47.08281965
	48	72.8	484.7399801	0.922686946	8.323145262	0.014662092	0.00242219	2.354140982
	58	49.2	327.5989975	0.623574144	20.64140025	0.035860264	0.019948392	16.94981507
	72	22.7	151.148318	0.287705957	15.64751309	0.027573237	0.004317423	4.237453768
Sandy soil (Se)	0	81.7	544.0007743	1				
	10	61	406.1694888	0.746634027				
	24	56.6	376.8720175	0.692778458				
	34	2.5	16.64629052	0.030599755				
	48	1	6.65851621	0.012239902				
	58	1.3	8.656071073	0.015911873				
	72	1.9	12.6511808	0.023255814				

Sandy soil (Sf)	0	87.8	584.6177232	1
	10	73.8	491.3984963	0.840546697
	24	59.2	394.1841596	0.674259681
	34	12.5	83.23145262	0.142369021
	48	1.5	9.987774315	0.017084282
	58	4.9	32.62672943	0.055808656
	72	2.8	18.64384539	0.031890661

Sterlized sandy soil (SSd)	0	72.2	480.7448703	1	463.4327282	1	0	16.6861938
	10	72	479.4131671	0.997229917	435.6889107	0.93913399	0.029419138	37.98468058
	24	70.8	471.4229477	0.980609418	442.3474269	0.954238465	0.01820622	25.35778852
	34	49.5	329.5965524	0.685595568	351.3477053	0.758449575	0.068234899	54.62148234
	48	56.1	373.5427594	0.77700831	422.3718782	0.914189232	0.069723682	42.37104992
	58	60	399.5109726	0.831024931	359.1159742	0.773508928	0.033710518	39.95849492
	72	54.1	360.2257269	0.749307479	398.1792693	0.861988123	0.067791625	40.10063402
Sterlized sandy soil (SSe)	0	67.2	447.4522893	1				
	10	61.7	410.8304501	0.918154762				
	24	64.7	430.8059988	0.962797619				

34	46.7	310.952707	0.694940476
48	67.5	449.4498442	1.004464286
58	48	319.6087781	0.714285714
72	66.1	440.1279215	0.983630952

Sterlized sandy soil
(SSf)

0	69.4	462.101025	1
10	62.6	416.8231147	0.902017291
24	63.8	424.8133342	0.919308357
34	62.1	413.4938566	0.89481268
48	66.7	444.1230312	0.961095101
58	53.8	358.2281721	0.775216138
72	59.2	394.1841596	0.853025937

6. Variable temperature Batches (10-30C) : Liquid results

Name	Time (Hrs)	Area	Concentration (µg/L)	C/Co	Avg. Concentration (µg/L)	Average (C/Co)	Standard Error	SD
Sandy soil (Sa)	0	29990.9	798.3733823	1	780.4879416	1	0	18.14177573
	10	27354.4	728.1883788	0.912090001	710.6960344	0.910811238	0.017670444	21.32009438
	24	3988.3	106.1706238	0.132983672	316.2877268	0.317173406	0.09740113	65.39489816
	34	32	0.851856671	0.00106699	286.2145243	0.246801054	0.137202594	120.3333138
	48	8.1	0.21562622	0.000270082	0.365588488	0.000471231	0.000107133	0.137097837
	58	6.6	0.175695438	0.000220067	0.199653907	0.000255643	4.4597E-05	0.060878984
	72	41.8	1.112737776	0.001393756	0.694795597	0.000884673	0.000255439	0.362655139
	76	77.5	2.044624511	0.002560988	0.385180876	0.001183744	0.000715406	0.993740432
	82	51.7	1.363962416	0.001708427	0.546112611	0.001043099	0.000354839	0.498012319
	96	66.9	1.764972642	0.002210711	0.780914652	0.001413581	0.000420967	0.593461897
Sandy soil (Sb)	0	28628.3	762.1002604	1				
	10	26932.3	716.9518569	0.940757921				
	24	10144.3	270.0465509	0.354345176				
	34	7555.3	201.1260221	0.263910187				
	48	18.2	0.484493482	0.000635735				
	58	5.8	0.154399022	0.000202597				
	72	19.1	0.50845195	0.000667172				
	76	4.6	0.121358358	0.000159242				

	82	26.7	0.704406122	0.000924296				
	96	36.1	0.952399288	0.001249703				
Sandy soil (Sc)	0	29337.9	780.9901821		1			
	10	25805.2	686.9478677	0.879585792				
	24	13618.4	362.5289027	0.46419137				
	34	13948	371.3030265	0.475425985				
	48	14.9	0.396645762	0.000507875				
	58	10.1	0.268867262	0.000344265				
	72	17.4	0.463197065	0.000593089				
	76	24.6	0.649003393	0.000831001				
	82	14.7	0.387819101	0.000496574				
	96	23.1	0.609430015	0.00078033				

Sterlized sandy soil (SSa)	0	31430.6	836.6989463		1	803.6983738		1	0	35.56845543
	10	27148.8	716.2464763	0.856038459		688.002517	0.856186978	0.004545221		27.21601662
	24	14851.3	395.349343	0.472510865		438.8987406	0.547891413	0.038541018		37.74156497
	34	24202.7	644.2884828	0.770036207		635.5294441	0.791429916	0.013185466		9.971832658
	48	19152.2	509.8415417	0.609348851		495.6545787	0.616640674	0.00828105		26.31582359
	58	24538.4	653.2249917	0.780716881		655.9997373	0.817661346	0.028911033		12.8462107

72	20865.7	555.4558044	0.663865787	533.1327228	0.663585697	0.007962291	19.59428655
76	28823.6	760.4314716	0.908847172	751.3111271	0.935424838	0.013443748	19.02991576
82	26525.8	699.8103335	0.836394424	701.7890024	0.874970551	0.037521329	25.00583959
96	19268.1	508.335865	0.607549307	501.4483384	0.624673832	0.015586897	7.382735687

Sterlized sandy soil (SSb)

0	30366.5	808.37205	1
10	25995.3	685.8145489	0.848389735
24	17358.5	462.0923132	0.571633214
34	23952.3	637.6227044	0.788773813
48	19227	511.8327566	0.633164836
58	24220.7	644.7676522	0.797612501
72	19727.8	525.1643135	0.649656694
76	28961.3	764.0643076	0.945188923
82	25692.7	677.8312796	0.838513998
96	18711.6	493.6541419	0.610676905

Sterlized sandy soil (SSc)

0	28775.7	766.0241252	1
10	25090.6	661.9465258	0.864132739
24	17251.9	459.2545657	0.599530159
34	23466	624.677145	0.815479728
48	17478.6	465.2894378	0.607408334

58	25168.8	670.0065681	0.874654657
72	19487.9	518.7780506	0.677234611
76	27648.8	729.4376022	0.952238419
82	27583.9	727.7253941	0.950003231
96	19041.4	502.3550085	0.655795284

7. Column results : Dynamic water level setup

**LIVE
COLUMN
(Ca)**

Port 1 (Liquid)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0
28.05.10	2	22.1	18.36952	0.01836952
30.05.10	4	681.4	596.988168	0.59698817
31.05.10	5	941.7	1143.70407	1.14370407
1.06.10	6	1156.4	1727.22217	1.72722217
2.06.10	7	1678.8	3647.59591	3.64759591
3.06.10	8	956.2	1179.33883	1.17933883
4.06.10	9	1635.2	3460.18131	3.46018131
8.06.10	12	9579.5	61310.7159	61.3107159
9.06.10	14	19635.4	204651.135	204.651135
11.06.10	16	6299.5	32053.1159	32.0531159
14.06.10	19	8059.2	46679.5311	46.6795311
16.06.10	21	7978.3	45952.7741	45.9527741
18.06.10	23	9068	56181.7008	56.1817008

Port 7 (Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1	1.3	9.27979	0.00927979
28.05.10	2	2.2	2.739	0.002739
30.05.10	4	4.4	5.478	0.005478
31.05.10	5	2.6	3.237	0.003237
1.06.10	6	9.2	3.335	0.003335
2.06.10	7	8.6	3.1175	0.0031175
3.06.10	8	5.6	2.03	0.00203
4.06.10	9	8.8	3.19	0.00319
8.06.10	12	58.1	21.06125	0.02106125
9.06.10	14	59.7	21.64125	0.02164125
11.06.10	16	1562	1191.8244	1.1918244
14.06.10	19	2026.3	1501.26178	1.50126178
16.06.10	21	2072.8	1537.00261	1.53700261
18.06.10	23	2603.5	2006.17325	2.00617325

Port 8 (Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0
28.05.10	2	5.1	6.3495	0.0063495
30.05.10	4	4.3	5.3535	0.0053535

Port 9 (Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0
28.05.10	2	8.8	10.956	0.010956
30.05.10	4	5.2	6.474	0.006474

31.05.10	5	2.4	2.988	0.002988
1.06.10	6	3.8	1.3775	0.0013775
2.06.10	7	9.2	3.335	0.003335
3.06.10	8	6.4	2.32	0.00232
4.06.10	9	13.7	4.96625	0.00496625
8.06.10	12	51.3	17.87125	0.01787125
9.06.10	14	51.9	17.0375	0.0170375
11.06.10	16	1399.4	1103.84479	1.103844792
14.06.10	19	1834.4	1362.91339	1.362913392
16.06.10	21	1789.7	1332.80258	1.332802578
18.06.10	23	2758.8	2164.77493	2.164774928

31.05.10	5	4.2	5.229	0.005229
1.06.10	6	7.4	2.6825	0.0026825
2.06.10	7	13.1	4.74875	0.00474875
3.06.10	8	6.2	2.2475	0.0022475
4.06.10	9	32.6	11.8175	0.0118175
8.06.10	12	49.3	17.87125	0.01787125
9.06.10	14	47	17.0375	0.0170375
11.06.10	16	1295.7	481.912283	0.481912283
14.06.10	19	1567.5	636.957875	0.636957875
16.06.10	21	1514	598.264	0.598264
18.06.10	23	2246.1	1475.51747	1.475517467

STERILE COLUMN (Cb)

Port 1 (Liquid)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0
28.05.10	2	1771.6	5805.60406	5.80560406
30.05.10	4	6232.5	31545.1755	31.5451755
31.05.10	5	7985	46012.764	46.012764

Port 7 (Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1	13.3	94.93939	0.09493939
28.05.10	2	309.6	248.674699	0.2486747
30.05.10	4	122.8	98.6345382	0.09863454
31.05.10	5	722.2	580.080321	0.58008032

1.06.10	6	8603.5	51705.3143	51.7053143
2.06.10	7	7751.7	43945.0074	43.9450074
3.06.10	8	8970.1	55223.8824	55.2238824
4.06.10	9	9365	59134.356	59.134356
8.06.10	12	13069.5	101892.436	101.892436
9.06.10	14	11394.5	81199.4859	81.1994859
11.06.10	16	13727.2	110631.348	110.631348
14.06.10	19	15120.2	130282.901	130.282901
16.06.10	21	14163.7	116622.206	116.622206
18.06.10	23	13432.8	106676.85	106.67685

1.06.10	6	1031.3	373.84625	0.37384625
2.06.10	7	844.3	306.05875	0.30605875
3.06.10	8	787	285.2875	0.2852875
4.06.10	9		0	0
8.06.10	12	378.5	137.20625	0.13720625
9.06.10	14	284	102.95	0.10295
11.06.10	16	4330.5	4312.75445	4.31275445
14.06.10	19	3840.6	3537.23295	3.53723295
16.06.10	21	NA	#VALUE!	#VALUE!
18.06.10	23	3341.7	2846.12674	2.84612674

Port 8 (Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1	11.2	79.94896	0.07994896
28.05.10	2	221.6	177.991968	0.177991968
30.05.10	4	87.4	70.2008032	0.070200803
31.05.10	5	738.4	593.092369	0.593092369
1.06.10	6	825.7	299.31625	0.29931625
2.06.10	7	753	272.9625	0.2729625
3.06.10	8	634.5	230.00625	0.23000625
4.06.10	9	NA	#VALUE!	#VALUE!
8.06.10	12	314.9	114.15125	0.11415125
9.06.10	14	254.4	92.22	0.09222
11.06.10	16	3476.9	3023.57944	3.023579442
14.06.10	19	3455.2	2994.60517	2.994605168
16.06.10	21	3422.8	2951.69461	2.951694608
18.06.10	23	2936.7	2358.31234	2.358312338

Port 9(Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1	10.7	76.37981	0.07637981
28.05.10	2	259.4	208.353414	0.208353414
30.05.10	4	96.8	77.751004	0.077751004
31.05.10	5	529.9	425.62249	0.42562249
1.06.10	6	898.7	325.77875	0.32577875
2.06.10	7	604	218.95	0.21895
3.06.10	8	627.9	227.61375	0.22761375
4.06.10	9	NA	#VALUE!	#VALUE!
8.06.10	12	264.9	96.02625	0.09602625
9.06.10	14	235.3	85.29625	0.08529625
11.06.10	16	3560	3136.278	3.136278
14.06.10	19	3110.3	2559.37586	2.559375858
16.06.10	21	3710.8	3347.84437	3.347844368
18.06.10	23	2968.5	2394.24125	2.39424125

7. Column results : Static water level setup

LIVE
COLUMN
(Cc)

Port 1
(Liquid)

Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1	2.4	1.99488	0.00199488
28.05.10	2	50.9	42.30808	0.04230808
30.05.10	4	303.4	252.18608	0.25218608
31.05.10	5	1108	1585.2156	1.5852156
1.06.10	6	2611.9	9437.2126	9.4372126
2.06.10	7	3126.5	11940.1035	11.9401035
3.06.10	8	7228.6	39466.9994	39.4669994
4.06.10	9	5842	28656.1784	28.6561784
8.06.10	12	12537.9	95081.9169	95.0819169
9.06.10	14	11343	80598.8208	80.5988208
11.06.10	16	21269.4	235583.278	235.583278
14.06.10	19	12629.4	96238.0487	96.2380487
16.06.10	21	13438.1	106747.429	106.747429
18.06.10	23	14022.9	114673.106	114.673106

Port 7
(Headspace)

Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0
28.05.10	2	2.4	2.988	0.002988
30.05.10	4	4.5	5.6025	0.0056025
31.05.10	5	3.3	4.1085	0.0041085
1.06.10	6	5.7	2.06625	0.00206625
2.06.10	7	13.5	4.89375	0.00489375
3.06.10	8	19.5	7.06875	0.00706875
4.06.10	9	536.4	194.445	0.194445
8.06.10	12	16.4	5.945	0.005945
9.06.10	14	16.2	5.8725	0.0058725
11.06.10	16	370.5	302.328	0.302328
14.06.10	19	454.5	370.872	0.370872
16.06.10	21	384.4	313.6704	0.3136704
18.06.10	23	354.3	289.1088	0.2891088

Port 8
(Headspace)

Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0

Port 9(Headspace)

Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0

28.05.10	2	42.8	34.37751	0.03437751
30.05.10	4	8.7	6.98795181	0.00698795
31.05.10	5	9	7.22891566	0.00722892
1.06.10	6	26.3	9.53375	0.00953375
2.06.10	7	24.3	8.80875	0.00880875
3.06.10	8	23.2	8.41	0.00841
4.06.10	9	551.9	200.06375	0.20006375
8.06.10	12	15	5.4375	0.0054375
9.06.10	14	14.3	5.18375	0.00518375
11.06.10	16	289.3	236.0688	0.2360688
14.06.10	19	321.7	262.5072	0.2625072
16.06.10	21	319.6	260.7936	0.2607936
18.06.10	23	214.3	174.8688	0.1748688

28.05.10	2	65.5	52.6104418	0.05261044
30.05.10	4	13.5	10.8433735	0.01084337
31.05.10	5	15.2	12.2088353	0.01220884
1.06.10	6	41.5	15.04375	0.01504375
2.06.10	7	35	12.6875	0.0126875
3.06.10	8	31.7	11.49125	0.01149125
4.06.10	9	353	127.9625	0.1279625
8.06.10	12	14.6	5.2925	0.0052925
9.06.10	14	12.5	4.53125	0.00453125
11.06.10	16	280.8	229.1328	0.2291328
14.06.10	19	313.8	256.0608	0.2560608
16.06.10	21	267.7	218.4432	0.2184432
18.06.10	23	187.1	152.6736	0.1526736

**STERILE
COLUMN
(Cd)**

Port 1 (Liquid)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0
28.05.10	2	102.3	85.03176	0.08503176
30.05.10	4	2348.8	8239.4025	8.2394025
31.05.10	5	6728	35386.5888	35.3865888
1.06.10	6	10106.4	66813.0061	66.8130061

Port 7 (Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (ug/L)
27.05.10	1		0	0
28.05.10	2	44.8	55.776	0.055776
30.05.10	4	164.9	205.3005	0.2053005
31.05.10	5	154.6	192.477	0.192477
1.06.10	6	180.1	65.28625	0.06528625

2.06.10	7	9635.8	61888.0454	61.8880454
3.06.10	8	13396	106187.413	106.187413
4.06.10	9	9018.1	55692.5391	55.6925391
8.06.10	12	18373.3	182221.245	182.221245
9.06.10	14	10396.3	69935.0784	69.9350784
11.06.10	16	23557.5	282487.406	282.487406
14.06.10	19	24578	304757.369	304.757369
16.06.10	21	24818.1	310118.043	310.118043
18.06.10	23	23895.1	289762.496	289.762496

2.06.10	7	190.7	69.12875	0.06912875
3.06.10	8	217.4	78.8075	0.0788075
4.06.10	9	329.1	119.29875	0.11929875
8.06.10	12	32	11.6	0.0116
9.06.10	14	34.1	12.36125	0.01236125
11.06.10	16	922.8	753.0048	0.7530048
14.06.10	19	1093.7	892.4592	0.8924592
16.06.10	21	1209.4	986.8704	0.9868704
18.06.10	23	1475.3	1203.8448	1.2038448

Port 8 (Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0
28.05.10	2	2.9	3.6105	0.0036105
30.05.10	4	5.7	7.0965	0.0070965
31.05.10	5	13.7	17.0565	0.0170565
1.06.10	6	81.2	29.435	0.029435
2.06.10	7	58.1	21.06125	0.02106125
3.06.10	8	54	19.575	0.019575
4.06.10	9	94.2	34.1475	0.0341475
8.06.10	12	22.3	8.08375	0.00808375
9.06.10	14	18.8	6.815	0.006815
11.06.10	16	423.7	345.7392	0.3457392
14.06.10	19	592.1	483.1536	0.4831536
16.06.10	21	570.8	465.7728	0.4657728
18.06.10	23	658	536.928	0.536928

Port 9(Headspace)				
Date	Days	Area	Conc (ug/L)	Conc (mg/L)
27.05.10	1		0	0
28.05.10	2	2.5	3.1125	0.0031125
30.05.10	4	5.2	6.474	0.006474
31.05.10	5	18	22.41	0.02241
1.06.10	6	64.1	23.23625	0.02323625
2.06.10	7	46.1	16.71125	0.01671125
3.06.10	8	45.3	16.42125	0.01642125
4.06.10	9	70.5	25.55625	0.02555625
8.06.10	12	26.6	9.6425	0.0096425
9.06.10	14	18.3	6.63375	0.00663375
11.06.10	16	414.1	337.9056	0.3379056
14.06.10	19	510.9	416.8944	0.4168944
16.06.10	21	481.2	392.6592	0.3926592
18.06.10	23	578.5	472.056	0.472056