Bioresource Engineering

Remediation of TCE Contaminated Groundwater

BREE 495 Final Design Report

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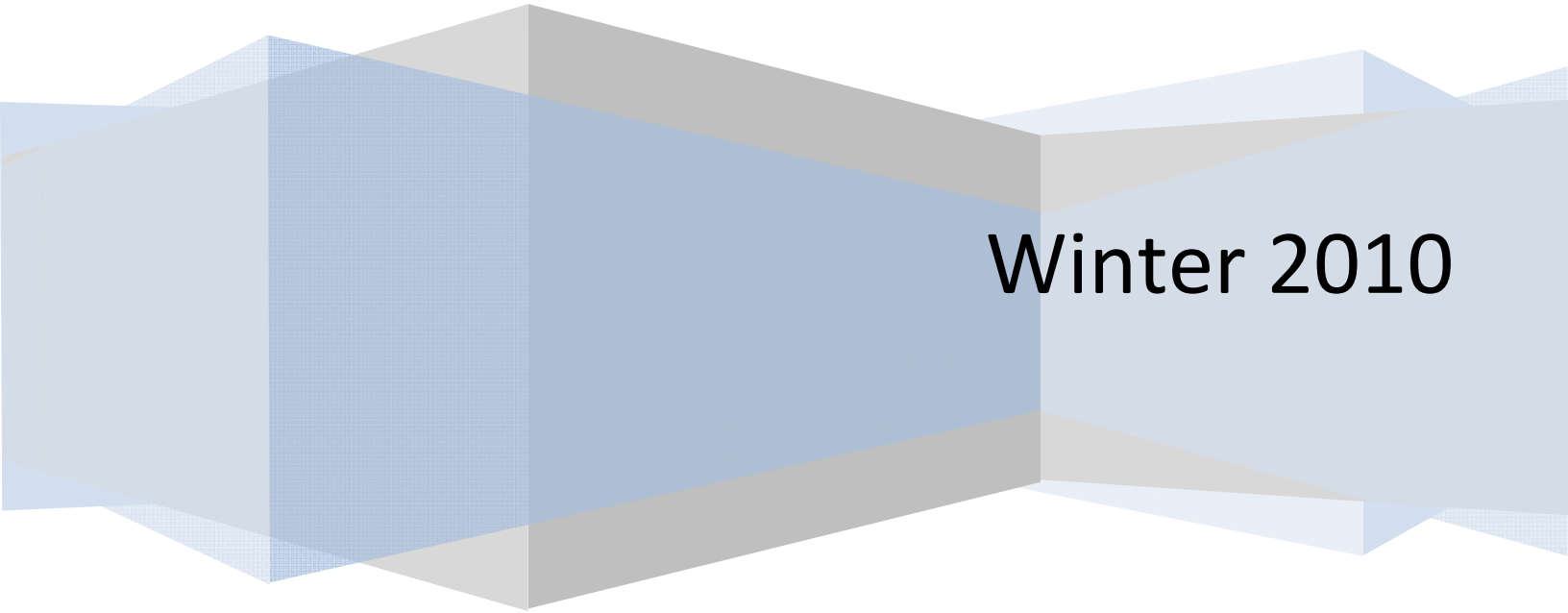

Winter 2010

McGill University, Macdonald Campus

Faculty of Agriculture and Environmental Sciences

Department of Bioresource Engineering

Design of a Biobarrier System for the Remediation of Trichloroethylene Contaminated Groundwater

Presented to Dr. V.Raghavan

Design 3 –BREE 495

April 14, 2010

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Opening letter

April 14, 2010

Dr. Vijaya Raghavan

Professor of McGill University

Macdonal Campus

21111 Lakeshore Rd,

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Dear Dr. Vijaya Raghavan,

We, the student engineers registered in the BREE 495 Design 3 course, have been working on a biobarrier system to remediate the trichloroethylene(TCE) contaminated aquifers in the town of Shannon and in the Valcartier Military Complex. We wish to present you this final report on behalf of our dedication to problem solving.

This report contains a background of the TCE contamination in Shannon, the objectives of this project, the planning process of this project, the final design and its specifications, the economical analysis and impact evaluations. There are three annexes attached with this report which will elaborate on the experiment designs and additional information. We hope that this report can increase your interest in the design of a biobarrier system and that you also enjoy reading it.

This is in the fulfillment of the report.

Sincerely,

Wilson Wong, Jr Engineer.

Julien Hanrahan, Jr Engineer.

Arnaldo Garcia, Jr Engineer.

Executive Summary

Since the year of 2000, the Town of Shannon discovered that their aquifers have been contaminated with trichloroethylene (TCE). It is known that this compound has been extensively used by Shannon's neighbour, Canadian Military Base Valcartier, as an industrial degreasing agent. After its usage, trainloads of TCE have been improperly disposed in lagoons for the past decades which, as a result, seeped into the aquifer system of the surrounding. Due to TCE's health damage attributes, it is believed that many residence of this town have developed various sorts of cancer because of this compound.

The report suggests the implementation of a peat biobarrier system for the remediation of TCE contaminated groundwater. Several hydrogeological findings (Boutin, et al., 2007) suggest that the implementation of a reactive barrier is possible. Also, C.M Kao et al (Kao & Lei, Using a Peat Biobarrier to Remediate PCE/TCE Contaminated Aquifers, 1999) have performed series of peat biobarrier experiments suggesting positive reinforcements for this technology.

The design of a biobarrier system involves rigorous steps. In order to achieve the design goal, the following objectives were established:

- Determine the suitability of a site for the implementation of a biobarrier
- Determine site characteristics which will affect the design (i.e. hydrogeological data)
- Design experimental protocol and perform testing
- Determine design specifications
- Elaborate a monitoring strategy
- Perform Cost analysis of system

A batch test and column test was laid out and performed for the purpose of determining specific design parameters of the biobarrier. A batch test evaluates the degradability of the contaminants. The column test has a similar purpose, but instead, the reactive media is subjected to dynamic flow conditions. A column has been design and constructed in order to achieve this purpose. The tests serve the following purposes: to screen and select the reactive medium, to determination of the half-life of the contaminant and to determine hydraulic properties of the medium.

After a series of experimental tests, design specifications and design considerations have been established. The dimension of the biobarrier has a height of 16 m, a thickness of 1.2 m and a length which may range 25 m to 500 m depending on the intentions of the client. The configuration of the barrier is continuous. It is suggested that the barrier should be oriented perpendicularly to groundwater flow. Backhoe excavation and clamshell excavation is recommended to be the construction method of the biobarrier. A monitoring system layout has been proposed in this project. It mainly consists of injections well, which is used to replenish biological activity in the biobarrier, and monitoring wells, which is used to evaluate the performance of the system. The cost of the project will vary depending of the design specifications. However, it is estimated that a biobarrier with a length of 25 m will have an initial cost of 292413,98$ CAD and an operation and maintenance cost of 51982,32$ CAD.

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A Biobarrier System for the Remediation of Trichloroethylene Contaminated Groundwater

1) Introduction

1.1) Trichloroethylene (TCE) Contamination

Trichloroethylene (TCE) is a chlorinated hydrocarbon that has been widely used as an industrial solvent and it is especially effective in removing organic compounds like grease from metals. . TCE, like other contaminates, persists in a liquid phase in the environment especially when it seeps into the soil layer and into groundwater. Within groundwater there is a slow dissolution of TCE resulting in a continuous spread of the contaminant throughout the aquifer, referred to as a plume. TCE has been documented as being toxic to humans, the degree of which depends on concentration and duration of exposure, through oral ingestion, inhalation or cutaneous exposure. This is especially dangerous in cases when plumes extend into populated areas since TCE can be volatilized into residential homes and water sources destined for human consumption. It should also be noted that some of TCE's degraded forms are also toxic, such as: cis-Dichloroethylene (cDCE), trans-Dichloroethylene (tDCE) and Vinyl Chloride (VC). Once TCE is degraded to Ethylene and Ethane can it be considered non-toxic.

1.2) History of the TCE Groundwater Contamination in Shannon, QC

For several decades, trichloroethylene (TCE) was used as a degreasing agent by CFB Valcartier and SNC Tec, a factory fabricating ammunition for the military. The TCE was disposed of improperly on several sites across the military base and, most notably, in SNC TEC's Lagoons A, C and Bleu. Consequently, large amounts of TCE infiltrated the sandy soil and contaminated the aquifer system

shared by the town of Shannon and CFB Valcartier. This resulted in a plume size of 5 km long and 650m wide with concentrations varying from 5 ppb to 13 500 ppb (Canadian Council of Ministers of the Environment, 2007) (Please also refer to figure 3 in the Annex C). Currently, the residents of Shannon are pumping clean water from a new aqueduct system. However, the TCE contamination still persists in the groundwater and if this problem is left untreated, the plume will likely spread and contaminate other areas.

2) Planning of the Project

2.1) Design Methodology

The design of a biobarrier involves in the following steps:

1. Preliminary assessment
2. Suitability of a site for biobarrier application
3. Determine the site characteristics related to the design of biobarrier
4. Perform laboratory scale testing (Batch Test and Column Test)
5. Determine design specifications
6. Elaborate a monitoring plan
7. Cost analysis

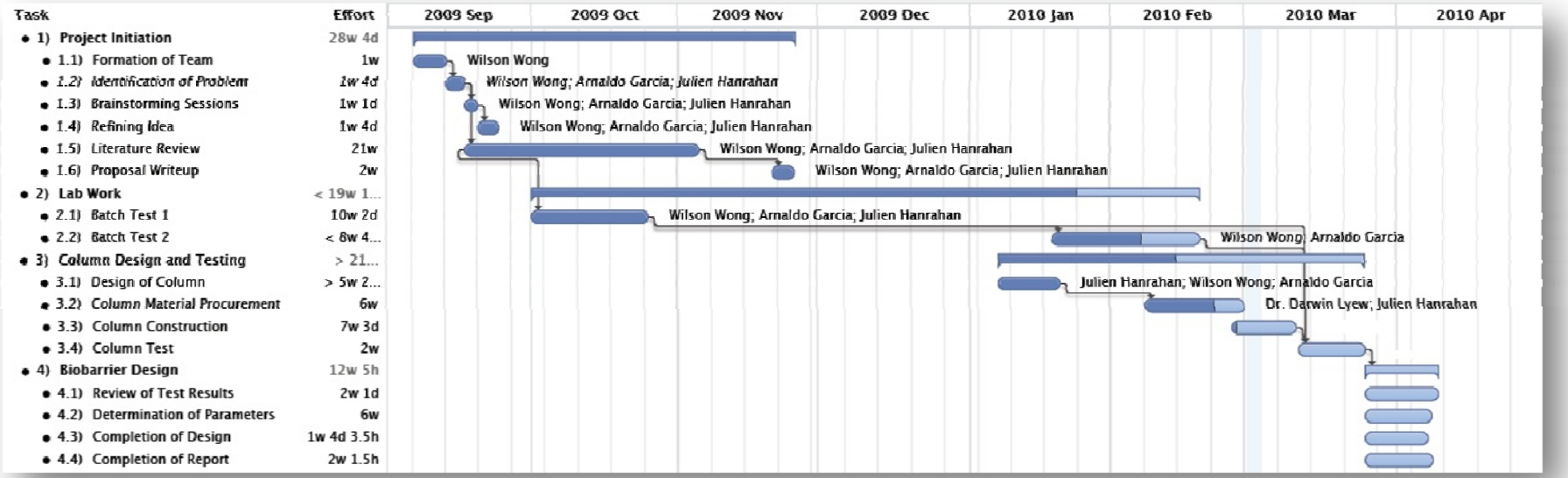
A detailed flow chart of the biobarrier design methodology is illustrated by figure 4 in Annex C. It is important to note that not all of the step in the flow chart will be assessed in this project. A detailed scope of the project will be described in the following section.

2.2) Deliverables and Schedule

In order to achieve the goal of this project, objectives must be established and managerial tools must were used in order to aid this process. This project will consists of gathering information, literature review, elaborating experimental protocols, determining design specifications, elaborating a monitoring plan and perform a cost analysis. The proposal of this project was handed in on December 1st, 2009. The proposal mainly includes the gathered information, the literature review and the experimental protocol layout. This final report will mainly focus on the design of the reactive biobarrier. Moreover, the experimental protocols and results will be included in the annex sections of the report.

A Gantt chart was generated in order to assist the organization of this project. A breakdown of the project's tasks were listed and assigned to different team members. The Gantt chart enabled the team to meet their objectives within the allocated amount of time. The following illustration is the Gantt chart of this project. A program called OmniPlan was used to generate the chart.

Gantt chart of the Project



* This Gantt chart was generated using a program called OmniPlan

3) Objectives and Scope

3.1) Scope

The objective of this design was to find a cost effective and sustainable method of reducing TCE concentrations in the contaminated groundwater, at the site of Shannon, QC, to levels that are considered safe for human consumption.

Therefore, the scope of work taken on by the design team was to develop a bio-remediation method to remove TCE from groundwater contaminated with TCE of a concentration of higher than 5μg/L. The design must foremost be cost effective, be in-situ, be low maintenance and low in energy inputs. The remediation method would only target areas that are at relatively low concentration, have low immediate risk to human health and be capable of operating on a long timeframe. The design limits itself to the designing the biochemical medium to be used within a given set of parameters. The design work would limit itself to the following:

- Investigating biochemical processes that could be used in remediating TCE contaminated soils through published academic research;
- Developing initial design that can be tested in the lab;
- Developing the lab protocols;
- Designing any apparatus required for the lab tests (column design);
- Conducting the laboratory tests and recording all results;
- Establishing the parameters under which the bioremediation method will operate in the field;
- Determine the lifecycle sustainability of the remediation system;

- Make recommendations as to the construction of the system insofar as what construction work methodologies could affect the performance of the system. However, the actual construction engineering and geotechnical considerations would need to be assessed and designed by engineers trained in the respective disciplines or would fall into the scope of another project altogether;
- Identify environmental concerns associated with the construction and implementation of the remediation system. This does not include any assessment of the environmental or health conditions associated with the TCE contamination but is limited to the environmental effects directly attributable to the implementation of the bioremediation system.

3.2) Proposed Design

Due to large spread of the contaminant, even at the source, any remediation solution will take a long time to bring concentrations back to safe levels. Many remediation methods exist on the market for groundwater and soils but generally these are generally high in cost, energy and maintenance requirements hence they are more suited to sites with contaminants in high concentrations that are not widespread. Due to the large extent of the plume in the area of Shannon and CFB Valcartier, these traditional solutions would not be suitable and fall out of the scope of work stated above. The chosen alternative was to utilize a passive bio-barrier system or a passive reactive zone within the aquifer that once put in place would require little or no maintenance and utilize the natural flow of ground water. Laboratory-scale and bench scale tests show that certain microorganisms can scavenge or degrade certain contaminants. In this case, TCE will undergo reductive dechlorination as will be explained in the following sections. Such microorganisms can be found directly within the soil where the contaminant is present but in such small quantities that the degradation of TCE is negligible. Our system uses the environment's natural TCE reductive abilities by providing nutrients and a substrate to maximize the

microorganisms ability to break down the TCE to non toxic forms within the barrier. To achieve this the bio-barrier will be composed of peat as a substrate with regular injections of molasses as a source of carbon for the microorganisms obtained from waste treatment sludge.

The following sections of the report will state the specifications of the bio-barrier and give parameters for its implementation dependent on the hydraulic and soil conditions as well as the contaminant concentrations and depth of contamination for the sites being targeted by the client for remediation. The annexes to this report also provide a full account of experiments conducted in developing this design as well as the design of any laboratory equipment created for that purpose.

4) The Design of a Biobarrier

4.1) Site Characteristics

The soil composition in the area of Shannon is composed of 3 categories of soils including, (1) permeable layer, (2) semi permeable layer, and (3) the impermeable layer. (Soil composition graph shown in Figure 1 of Annex C)

Permeable Layer

The permeable layer is relatively uniform and is composed primarily of medium to fine grain sand. The layer is located between 0 to 30 m depth from the soil surface.

Semi Permeable Layer

This layer is composed of clayey silt soil and its thickness ranges from 0.5 to 2 m. The clayey silt is a result of silt decantation from the ice age. This layer is located at a distance of 30 to 32 m below the surface. With a clay constituent, the clayey silt layer acts as a semi permeable layer between the permeable layer above.

Impermeable Layer

The impermeable layer consist of till and bedrock located at a depth of 32 to 35 m.

4.1.1) Soil Hydrological Properties

As mentioned previously, soil properties can be deduced from soil characterization or, can be determined from further field tests as what was the case for the project conducted by Université de Quebec in 2003.

For the design of the permeable barrier, the hydraulic conductivity of soils is an important characteristic of an aquifer as it controls the flow of groundwater. Soil characterization alone allows for estimations and predictions on hydraulic conductivity, however when dealing with a soil profile consisting of difference porosities and hydraulic gradients, additional field permeability tests are an asset as they allow for the comparisons of results between existing and newly collected data.

The project on characterization and modelling of TCE in Valcartier Quebec undertaken by Université de Québec involved permeability tests to be performed at well sites. In addition to the estimated values of soil hydrological conductivity obtained from the soil samples, the hydraulic characteristics obtained through the permeability tests provided a validation of estimation. An additional advantage to this is that the collected permeability test results were used as inputs in the soil modelling stage which further enhances the validity of the model. The results of hydraulic conductivity obtained from the tests are shown in the following table.

Depth from surface (m)	**Soil Type**	**Hydraulic Conductivity (10^{-4} m/s)**
0 – 30	Fine, medium grain Sandy	9.05
30 – 32	Clayey silt	4.78

Several interesting characteristics of the soil profile underlying in Shannon are the similar hydraulic conductivities for the fine, medium and coarse grain sandy soil. The sudden change in

hydraulic conductivity occurs at approximetely 30 meters and the result is a hydraulic gradient. Interestingly, by analysing the contamination distribution map shown in Figure 2 of Annex C, we clearly see that the highest levels of contamination (300 ppm) are located along the clayey silt layer profile. From hydrology principles, we can predict that the water infiltrating into the soil and moving along the plume will decrease in velocity as it enters the clayey silt layer. Adding to this, the TCE in the soil will be transported through the profile by infiltrating water as well as plume water flows. The time lag once water along with TCE reaches the clayey silt layer explains the accumulation of contamination at this location. Also interesting to note from the contamination distribution shown in Figure2 on Annex C is high concentration of TCE (300 ppm) in the layer overlying the bedrock (31 – 32 m). Since the bedrock is an impermeable layer, accumulation of TCE will occur resulting in high concentrations at the soil profile overlying the bedrock.

An important concern for our contaminated site is the ground water velocity. Targeting volumes of water that will pass through the reactive barrier is an important phase when designing the permeable barrier. Deciding on a location and configuration requires groundwater flow characteristics to be understood. In our particular case, the groundwater model done by Université of Québec found velocities ranging from 35 mm/day to 185 mm/day.

The above information and analysis is essential in obtaining accurate characteristics of groundwater flows as well as contamination distribution maps. When the characterization of a site has been accomplished, the experimental design of the permeable barrier can be carried through.

4.2) Design Specification Development

In order to determine design specifications a series of experiments was performed. The tests serve the following purposes:

- Screening and selection of the reactive medium
- Determination of the half-life of the contaminant
- Determine hydraulic properties of the medium

Two batch tests and one column test has been performed. The batch test is an initial screening tool for the evaluation of the degradability of the contaminants exposed to the reactive media. A batch test simply allows the determination of the reaction rate. The column testing is an experiment that is performed to determine the half-life of the degradation in a dynamic flow conditions. The column can be used as a simulation tool to mimic the movement of groundwater travelling through the reactive barrier. The developments of these experiments will be assessed in the Annexes attached with this report.

4.3) Product Description

4.3.1) Dimension of the biobarrier

The dimensions are the most important part in the design of a biobarrier. A barrier which is too thin will decrease its efficiency and a barrier too thick might cause extra expenses. Moreover, the dimensions of a PRB are highly dependent on the site characteristics and experimental results. Based on the distribution of the contaminant (Please refer to Figure 2 in Annex C), the biobarrier will have a height of 16 m. This height will ensure that all contaminant are exposed to the barrier. The length of the system is customizable depending on the customer and location of the barrier. The length may vary from 25 m to 500 m. Finally, the barrier will have a thickness of 1.2 m. Please refer to annex C Calculation 1) for a complete detail in determining the thickness of the barrier.

4.3.2) Configuration of the PRB

A funnel/gate system is undesired in this situation due to the biological nature of the biobarrier. According to experimental results, the maximum concentration that the media was tested at

approximately 1000 ppb while on the contaminated site, the concentrations may easily reach up to 10 times the tested concentration. There are strong concerns that a too large concentration (above 1000 ppb) of TCE might inhibit the growth of the biological activity in the barrier. Therefore, a continuous barrier system is recommended to be implemented in the area of Shannon/Valcartier military base.

4.3.3) Reactive Media

The reactive media of the barrier is the main component in this type of remediation technology. The choice of the media will highly affect the performance of the system. The choice of the media will be based on the following considerations:

- High reactivity (rapid degradation rate)
- Availability and Cost
- Hydraulic Performance
- Environmental compatibility
- Ease of construction

In response of the above criteria, a peat/activated sludge is chosen for the design of the biobarrier. Several batch tests have been performed in order to determine the reactivity of the chosen reactive media. These experiments have generated promising results for its application in biobarriers. Peat moss and activated sludge are both available and inexpensive in Quebec. Peat moss is a very porous material which will allow the groundwater to flow through easily. Another reason why this media was chosen is that this media has a very low environmental impact since peat moss and activated sludge are natural products. The construction method will be discussed in the following section.

The volume of peat used will depend on the length that the customer desires. It may range from 480 m^3 to 9600 m^3. The volume of activated sludge used is also dependant on the length of the

biobarrier. The amount is determined to be 1920 kg to 38400 kg. Please refer to the Calculation section in Annex C for addition information on calculations.

The biobarrier is design to host anaerobic bacteria for the biodegradation of TCE. In fact, under anaerobic conditions, TCE is transformed by sequential reductive dechlorination reactions by replacing the chlorine atom with a hydrogen atom at each step (Kao & Lei, Using a Peat Biobarrier to Remediate PCE/TCE Contaminated Aquifers, 1999). The metabolites of this pathway are DCE isomers and VC. The objective of the biobarrier is to biodegrade TCE to its non-toxic metabolite, ethylene.

4.3.4) Location and Orientation of the Barrier

All bioremediation activities will be done in-situ. The selection in the location of the barrier will depend on several criteria:

- The hydrological characteristics of the site: The barrier must be oriented perpendicular to the groundwater flow in order to fully capture the contaminant
- Geotechnical considerations: The location must allow the usage of heavy machineries. This barrier must also not disrupt underground utilities.
- Administrative considerations: It is very important in having the community's participation in the decision making process for determining the location of the barrier. An environmental impact assessment is highly recommended to by perform alongside of this project. This will facilitate administrative problems that may occur in this project.

The determination in the location of the barrier will depend on many criteria and the exact location is not part of the scope of this project.

4.3.5) Longevity Considerations

It is very difficult to determine the exact life expectancy of the system. It would require more experimental testing and evaluation for this estimation. The system cease to perform once the peat is saturated with contaminant or that once microbial activity disappears due to lack of nutrients. A more in depth site characterization, more column testing must be performed and more computerized geochemical model must be used in order to give an exact life span of this system. However in order to increase the system's efficiency, injections wells will be used for the injection of activated sludge and molasses. The injections wells will be described later on in the report. It is desired for the biobarrier to have a concentration of 3g/L of molasses in the reactive zone and a concentration of 4g/L of VSS.

4.4) Construction and Geotechnical Considerations

To be implemented the peat biobarrier system needs to be put in place directly into the ground layer through which the contaminated groundwater flows. As stated previously, the scope of this design only includes the parameters under which the peat biobarrier system can be expected to function and what results over what time frame may be achieved. This does not include the actual construction or geotechnical aspects of implementing the design since this will require site specific assessments and will be highly variable depending on the site(s) targeted. However, certain aspects of the construction can impact the proper functioning of the system. As such, once areas for remediation have been identified, proper geotechnical, hydrogeological and construction engineers/experts should be hired to address issues within their areas of professional expertise. The following are general considerations that would need to be assessed and designed for:

- Excavation methods must be employed to reach the depths to which the contaminant needs to be remediated;

- Depending on the depth and width of excavation the walls of the trench will need to be reinforced temporarily or work methodologies will need to be employed that allow for simultaneous excavation and filled with the bio-barrier thereby preventing the collapse of the earth walls;
- Any excavation technique or earth wall reinforcement cannot allow for compaction of the soil layers or create permanent impermeable zones in the soil. Disregard for this criteria will significantly reduce the effectiveness or even cause failure of the system since this is a passive remediation barrier and must utilize the natural groundwater flow.
- The soil excavated will be contaminated with TCE itself and will need to be disposed of according to environmental regulations or need to be remediated using soil remediation techniques outside of the scope of this project. Before soil is excavated, tests should be conducted to establish at what depths the TCE is found is present such that the soil that is contaminated below 5μg/L can be kept separate and be used as backfill to cap the surface of the biobarrier. Any excess soil will need to be removed or stored according to the requirements of the client and within the municipal and governmental environmental guidelines.
- Depending on the site and excavation technique required, there may be environmental impacts to consider. The mobilization of the equipment to the site may have deleterious effects on local ecosystems environments through the direct disturbance of vegetation and habitats and also the effect of increased erosion and sediment transport. Environmental assessments will need to be conducted specific to the sites in question.

4.4.1) Excavation Methods Recommended

Regardless of the type of PRB being installed on a site, the excavation method being used would be the same for most types of mediums. Based on other similar projects, two excavation methods come out as being the most suitable for the peat bio-remediation system. The peat bio-remediation system is

meant to be implemented as a passive reactive barrier that must extend long distances over variable terrain. The width of the barrier will also be dependent on the concentrations of TCE contaminant in the area targeted. The most common types of excavation methods are Clamshell and Backhoe and they are discussed in the following sub-section. It should be noted again that it is not part of this project to design the excavation work since this will vary considerably depending on the sites targeted hence specialists in excavation, geotechnical engineering and hydrogeology should be consulted. The following information is from paper by Molfetta, Sethi and Day compare the two techniques.

Clamshell Excavator:

This type of excavation technique uses a crane with a grab bucket or clamshell shovel that is lowered straight down to the trench and lifts the earth up and out. The clamshell excavator can be both mechanically and hydraulically powered and for more precise excavation demands the excavators can be equipped with sensors. A main concern is not having the trench walls collapse under their own weight and due to the surcharge of the excavator. Generally, guide walls can be used with the combination of bentonite or biopolymer slurry to reinforce the trench walls while excavation is occurring. It is also recommended to continuously backfill the trench with the medium by using panels or endstops between the part of the trench being excavated and the part being backfilled. These considerations allow for a faster installation time and prevent collapse of the trench.

Max. Power	240-400 kW
Base Machine Weight	42,000 – 300,000 kg
Lifting Capacity	20,000-30,000 kg
Bucket/Grab Weight	8,000-24,000 (kg)
Excavation Width	0.5-1.2 (m)
Excavation Length	2-4.2 (m)
Bucket/Grab Capacity	1-1.2 m^3
Digging Force	300-400 kN
Excavation Depth	0-70 m
Excavation Rate	300 m^2/day

(Di Molfetta, Et Al. 2006)

Backhoe Excavator:

This method of excavation could be used for the construction of a continuous barrier but has been used generally with cases involving a funnel and gate system since the soil must reinforced with bentonite or biopolymer slurry. With the use of the Backhoe, excavation is conducted in a downwards triangular shape due to the fact that the Backhoe bucket digs by curling the bucket back towards itself. This means that continuous backfill as excavation can be made more difficult since the deeper the excavation required the longer the length of the open trench at the surface. Quality of excavation will be highly dependent on the skill of the operator and supervision on the ground. Unlike the clamshell method, no guide wall is required but generally there is a higher cost and need associated with the slurry.

Max. Power	50-485 kW
Base Machine Weight	7,000-110,000 kg
Lifting Capacity	3,500-40,000 kg
Bucket/Grab Weight	300-3,000 kg
Excavation Width	0.4-3.0 m
Bucket/Grab Capacity	0.2-1 m^3
Digging Force	50-430 kN
Excavation Depth	0-30 m
Excavation Rate	400 m^2/day

(Di Molfetta, Et Al. 2006)

4.4.2) Final Notes on Excavation Methods

In choosing either backhoe or clamshell excavation it should be noted that the presence of rock or large boulders will cause significant difficulty in excavation and cause delays. The buckets of either method are not designed to remove or break up large rock or boulder since expensive damages will be incurred by the machinery. Sites should be assessed before excavation to determine the presence of rock and boulders and find alternative means of removing them or find other sites to excavate and install the barrier.

With both types of excavation methods, a flat surface is preferred to conduct excavation operations. This may mean choosing suitable sites or preparing the site before excavation using bulldozers or mechanical graders. This means there will be a large amount of disruptions to the vegetation so a rehabilitation plan will be necessary once excavation operations are finished.

Although bentonite is commonly used in such types of construction, it is not recommended for a Bio-Remediation PBR since it will negatively affect the reactivity of the medium and even cause it to fail (Day, 2004). For this reason alternative slurry, bio-polymer slurries, like guar gum (Day, 2004) must be used since it is biologically degradable and causes no deleterious effects to the environment and soil quality.

In either case, a rigorous quality management plan must be established before the excavation begins and there must be constant supervision of the quality of excavation and PBR installation. Similarly, a safety management plan must be established as there is a high risk of injury or death associated with excavation and operation of heavy machinery.

4.4.2) PRB Medium Mixing and Backfilling Considerations

The PRB will be made of a mixture of peat, waste water sludge and molasses that will need to be prepared and mixed to the desired quantities and portions before being put into the trench. This will require a decision as to have the mixture made on or off site. The choice will depend on the space available at the site and accessibility of mixing equipment to the site. Mixers that could be employed are the following (Day, 2004):

- Pugmills
- Belt scales
- Transit mixers
- Volumetric scales
- Mixing boxes

Each have pros and cons that should be assessed depending on the site and also on their availability. Special consideration has to be placed on the nature of the PBR medium which is organic and microbiological in nature. The microorganisms used are anaerobic so their transportation and mixing should have limited contact with air and light so closed containers would be preferred for transportation and mixing. The medium must also be prevented from drying. Constructors must place undue care to these criteria or the PRB will be rendered ineffective.

4.5) Monitoring Systems Proposal

The objective of monitoring is to verify that the groundwater quality downgradient of biobarrier is in compliance with target cleanup objectives. Monitoring will be accomplished through groundwater sampling and analysis of target contaminants within the biobarrier. In addition, the monitoring will help identify any breakthroughs or bypasses of contaminants.

A secondary objective of monitoring is to verify the performance of the biobarrier. Accessing its performance is essential as it may provide warnings to problems that may occur in the future. The biobarrier's performance is based on contaminant monitoring which provides details on the current operating condition. Performance field parameters include pH, conductivity and inorganic constituents.

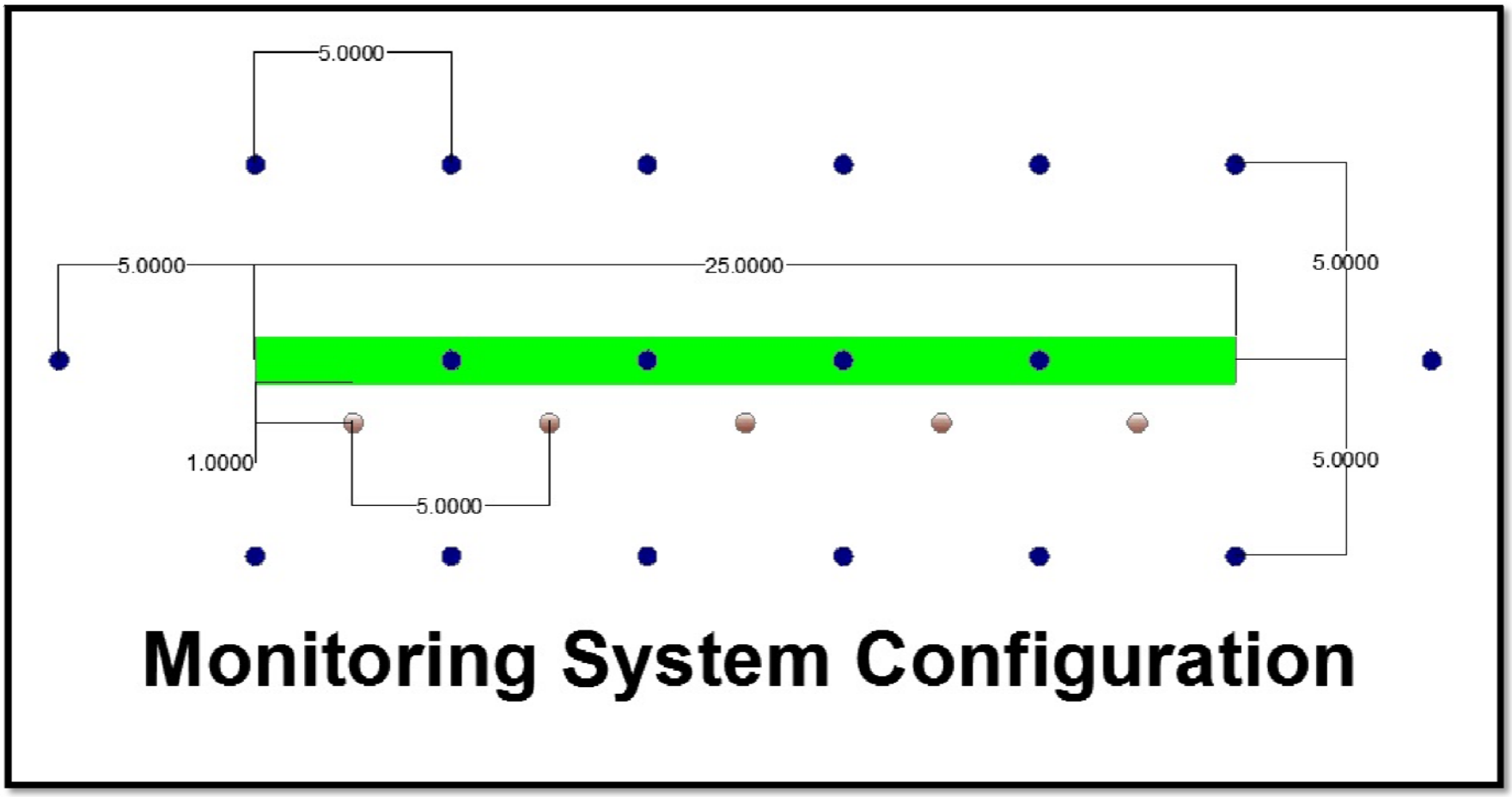
Along with the monitoring wells in the viscinity and within the biobarrier, there will also be injection wells which will be used to directly inject molasses nutrient in order to regenerate the reactive peat medium. Monitoring wells will be made of PVC piping and through these wells, groundwater samples will be collected. For monitoring wells in proximity to the biobarrier, groundwater sampling will be done using tubing and a peristaltic pump however for wells within the biobarrier, special precautions should be taken when extracting water. Ideally, water should be extracted at a rate between 100 – 500ml/min. Pumping water at a greater rate may cause disturbances to the medium.

Equally important are the wells positioned upgradient of the biobarrier. These wells will provide early warnings of changes in the plume characteristics or changes in influent concentrations over time.

Yet another important monitoring activity is the hydraulic performance strategy, which monitors the flow rates and direction of groundwater flow thereby allowing for the estimation of residence time available for the groundwater in the reactive cell. This may be done using velocity probes inserted into the monitoring wells well.

4.5.1) Monitoring System Layout (for a 25 m long bio-barrier)

AutoCad Drawing of the Monitoring System Configuration



The monitoring system configuration illustrated in the previous section is a suggested configuration. There are 18 monitoring wells and 5 injection wells. Monitoring wells at the front and back of the biobarrier are used to measure the concentration of TCE entering and leaving the biobarrier. Monitoring wells are also inserted in the middle of the reactive medium in order to assess the performance of the biobarrier. All of the wells are placed 5m apart. If the biobarrier is desired to be longer, an injection wells and a monitoring wells will be added at every 5 m.

4.6) Economical Evaluation

The interests in Biobarrier systems have been steadily increasing over the past decade due to its attractive and low operational and maintenance costs. In the case of the TCE contaminated groundwater in Shannon Quebec, the Biobarrier's passive remediation technology requires no energy or recurring operating labor. In addition, the only foreseeable operating costs are the monitoring of its groundwater through wells (quarterly) and the regeneration of its reactive media. These aspects of permeable reactive barriers are the major cost benefits that these systems have over alternatives such as pump and treat systems.

A key factor influencing the economics of permeable reactive barrier systems is the length of time that the system will be in operation. The decision to implement such a system should therefore reflect the operational and maintenance costs associated with periodic work required to keep the system running at its optimum level.

4.6.1) Capital Investment

The capital costs associated with the Biobarrier system include preconstruction, materials and construction costs. These funds cover the initial costs of acquiring and installing the Biobarrier system to the stage where it is ready for use. Capital investments can be divided into 2 categories; preconstruction costs and construction costs.

4.6.2) Preconstruction Costs

These costs include preliminary site assessment, soil and groundwater characterization, laboratory scale testing, modeling and proposal preparation. Since the Biobarrier system will most likely be a permanent structure that will be very difficult to upgrade, groundwater flow, contamination and soil characterization should be done by experts in order to design an effective Biobarrier that is most suitable for the location.

4.6.3) Construction Costs

Construction costs for permeable reactive barriers can vary significantly as they depend on the type of construction method and reactive media. Generally, the excavation and the reactive media are of greatest costs. Construction costs include site preparation, reactive media procurement, biobarrier construction and monitoring systems. The following table includes the mentioned activities along with their descriptions and costs.

Construction of Biobarrier						
ARTICLE	ACTIVITY	DESCRIPTION	QUANTITY	UNIT	UNIT PRICE	AMOUNT BILLED
2.1	Site Preparation	Arrangements for equipment, land clearance	20	hour	250.00	5,000.00
2.2	Reactive Media	Peat	480	m³	122.00	58,560.00
2.3	Biobarrier Construction	Mobilization				10,000.00
		Excavation	750	m²	200.00	150,000.00
		Restoration	250	m²	50.00	12,500.00
2.4	Monitoring System	PVC monitoring wells	18	well	1000.00	18,000.00
		PVC injection wells	5		1000.00	5,000.00
			Sub-Total			259,060.00
			PST (7.5%)			20,400.98
			GST (5%)			12,953.00
			Total			292,413.98

This table was generated by taking the case of remediating a contaminated zone at a depth of 30 m, over a length of 25 m. This would represent a small scale operation at the Shannon, Quebec site. The

cost of mobilization includes the rental and transportation costs for the clam shell excavator. Restoration of the site includes returning the area to grade and revegetating the area previously cleared on the work site and its surrounding.

4.6.4) Operation and Maintenance Costs

These costs include the groundwater sampling that will be taken from the monitoring wells at quarterly periods and the regeneration of nutrients which will be done on a yearly basis. The monitoring details are found in the Monitoring Plan section. The estimated costs for operation and maintenance activities are shown in the following table.

Biobarrier Operation and Maintenance Costs

ARTICLE	ACTIVITY	DESCRIPTION	QUANTITY	UNIT	UNIT PRICE	AMOUNT BILLED
3.1	Groundwater Sampling	Sampling from monitoring wells (quarterly)	18	well	500.00	9000 (quarterly)
3.2	Regeneration	Molasses Injection (yearly)	7180	gram	1.40	10,053.00
			Sub-Total			46,053.00
			PST (7.5%)			3,626.67
			GST (5%)			2302.65
			Total			51,982.32

The cost of groundwater sampling includes the sampling and the preparation of reports.

4.6.5) Cost Competitiveness

In order to emphasize the cost benefits of the peat biobarrier over alternatives such as pump and treat technologies, it is interesting to compare the capital and, operation and maintenance costs of the two technologies.

The following table includes the construction costs associated with a pump and treat system for the identical site considered for the peat biobarrier.

Construction of Pump and Treat System						
ARTICLE	ACTIVITY	DESCRIPTION	QUANTITY	UNIT	UNIT PRICE	AMOUNT BILLED
2.1	Site Preparation	Arrangements for equipment, land clearance	20	hour	250.00	5,000.00
2.2	Pump & Treat System Construction	Install 4 inch diameter well, pumps, catalytic oxidizer, piping	-	-	-	145,000.00
2.4	Monitoring System	PVC monitoring wells to monitor plume movement	18	well	1000.00	18,000.00
				Sub-Total		168,000.00
				TPS (7.50%)		13,230.00
				TVQ (5%)		8,400.00
				Total		189,630.00

Interestingly, the construction cost of the biobarrier ($292,413.98) is 43 % greater than that of the pump and treat system ($189,630.00). Although this is a significant difference in capital costs, the operation and maintenance costs for the biobarrier ($51,982.32) are 43% lower than that of the pump and treat system ($80,141.25). The details of the operation and maintenance costs of the pump and treat system are shown in the following table.

Pump & Treat Operation and Maintenance Costs						
ARTICLE	ACTIVITY	DESCRIPTION	QUANTITY	UNIT	UNIT PRICE	AMOUNT BILLED
3.1	Pump & Treat System Operation	Waste handling, energy, maintenance	-	-	-	35,000.00
3.2	Groundwater Monitoring	Sampling from monitoring wells (quarterly)	18	well	500	9,000.00 (quarterly)
				Sub-Total		71,000.00
				TPS (7.50%)		5,591.25
				TVQ (5%)		3550
				Total		80,141.25

4.6.6) Present Value (PV) Analysis

Present value analysis is typically used to determine the life cycle cost of a particular technology. More specifically, it is a representation of the amount of money that would be required to set aside today in order to cover the capital costs and the operation and maintenance costs that are to occur in

the present and future. The PV cost takes into account the interest rate and for this particular analysis, the interest rate is 4.5 %.

$$PV_{technology} = Capital\ Investment + PV_{annual\ O\&M\ costs\ over\ life}$$

$$PV_{annual\ O\&M\ costs} = \sum \frac{O\ \&\ M\ cost\ in\ Year\ t}{(1+r)^t}$$

The present value analysis summarized in the following two tables shows that the Peat Biobarrier system becomes a cost effective alternative to the Pump and Treat system only after year five. Following year five, the cumulative PV of annual costs for the Pump and Treat system are larger than the Biobarrier System. At the end of year 20, the cumulative PV of the Pump and Treat system is $1,232,102.29 and that of the Biobarrier is $968,596.70.

BioBarrier System			
Year	Annual Cost	PV of Annual Cost	Cumulative PV of Annual Cost
0	292,413.98	292,413.98	292,413.98
1	51,982.32	49,743.85	342,157.83
2	51,982.32	47,601.77	389,759.59
3	51,982.32	45,551.93	435,311.52
4	51,982.32	43,590.36	478,901.89
5	51,982.32	41,713.27	**520,615.16**
6	51,982.32	39,917.00	560,532.16
7	51,982.32	38,198.09	598,730.25
8	51,982.32	36,553.19	635,283.44
9	51,982.32	34,979.13	670,262.57
10	51,982.32	33,472.85	703,735.43
11	51,982.32	32,031.44	735,766.87
12	51,982.32	30,652.10	766,418.96
13	51,982.32	29,332.15	795,751.11
14	51,982.32	28,069.04	823,820.16
15	51,982.32	26,860.33	850,680.48
16	51,982.32	25,703.66	876,384.15
17	51,982.32	24,596.81	900,980.95
18	51,982.32	23,537.61	924,518.57
19	51,982.32	22,524.03	947,042.60
20	51,982.32	21,554.10	968,596.70

Pump and Treat System			
Year	Annual Cost	PV of Annual Cost	Cumulative PV of Annual Cost
0	189,630.00	189,630.00	189,630.00
1	80,141.25	76,690.19	266,320.19
2	80,141.25	73,387.74	339,707.93
3	80,141.25	70,227.51	409,935.44
4	80,141.25	67,203.35	477,138.79
5	80,141.25	64,309.43	**541,448.22**
6	80,141.25	61,540.12	602,988.35
7	80,141.25	58,890.07	661,878.42
8	80,141.25	56,354.14	718,232.55
9	80,141.25	53,927.40	772,159.96
10	80,141.25	51,605.17	823,765.13
11	80,141.25	49,382.94	873,148.06
12	80,141.25	47,256.40	920,404.46
13	80,141.25	45,221.43	965,625.90
14	80,141.25	43,274.10	1,008,900.00
15	80,141.25	41,410.62	1,050,310.62
16	80,141.25	39,627.39	1,089,938.01
17	80,141.25	37,920.95	1,127,858.96
18	80,141.25	36,287.99	1,164,146.94
19	80,141.25	34,725.35	1,198,872.29
20	80,141.25	33,230.00	1,232,102.29

5) Impact Analysis

Environmental considerations are essential in allowing us to outlines the environmental and health hazardous issues that arise from such a project. Once outlined, mitigation plans and potential alternatives can be suggested thereby reducing the negative impacts and worker injuries.

The main concerns we took into consideration are the disturbances to habitat that may be caused from the equipment on site as well as from the monitoring wells. The range of the area that will need to be cleared of vegetation varies largely from 500 – 10,000 m^2. This will depend on the needs of the client. In order to mitigate this impact, we recommend that a single gravel road be constructed for trucks to access the site. During construction, power stations will be placed in proximity to the excavation site. We also recommend that following the installation of the biobarrier, the excavation site be revegetated.

Another important consideration is the proper containment of the excavated soil that may contain harmful concentrations of TCE and its by products. The contaminated soil will be treated on site using an ex-situ method.

6) Conclusion

The contamination of TCE in the groundwater of Shannon,QC and CFB Valcartier is a real and tangible problem that has had a negative effect on the lives of residents for decades. Due to the extent and varying concentrations adds a degree of difficulty to removing the contaminant from the area given the standard remediation technologies. To solve this problem a PBR using our bio-remediation is the best alternative. It is made of natural products with little or no impact on the environment and it can operate over long time periods with little or no maintenance. With our stated PBR dimensions, determined from rigorous lab testing, we can guarantee that water contaminated with a TCE

concentration of 1000 ppb can be removed. As it was discussed, this is significantly cheaper than what could be achieved with the standard pump and treat system. Furthermore, the bio-barrier can be implemented using methods well known by excavators and constructors thereby adding a level of reliability to the system. This system is reliable and can be easily modified for different demands for different sites and targeted contaminant concentrations. For all these reasons our system is ready for field testing and future implementation.

Summary of the Final Design

Design Specifications	Final Design
Dimensions (height x thickness x length)	16 m x 1.2 m x (25 m to 500 m)
Configuration	Continuous Barrier
Reactive Media	Peat and Sludge
Nutrient Source	Molasses
Orientation of Barrier	Perpendicular to groundwater flow
Construction	Clamshell excavation or Backhoe excavation
Monitoring Wells (for 25 m long barrier)	18
Injection Wells (for 25 m long barrier)	5
Initial Cost (for 25 m long barrier)	292413,98$ CAD
O&M Cost (for 25 m long barrier)	51982.32$ CAD

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Annex A: Experimental Results

Annex A: Experimental Results

In order to assess the TCE ground water contamination problem at the area of Shannon, Quebec, a series of experiments were designed and performed in order to determine experimental results for the design the biobarrier system. This annex is divided into different subsections and each section will describe the experimental design that was necessary for this design. The sections are divided in the following fashion:

-Experiment 1) Standard Curves and Calibration of the Gas Chromatography

-Experiment 2) Batch Test 1

-Experiment 3) Batch Test 2

-Experiment 4) Column Test 1

Experiment 1) Standard Curves and Calibration of the Gas Chromatography (GC)

Standard curve is a research tool that uses a method of plotting assay data that is used to determine the concentration of a substance. In this experiment, the substances are trichloroethylene (TCE), cis-dichloroethylene (c-DCE), trans-dichloroethylene (t-DCE) and vinyl chloride (VC).

Materials and Methodology

In this experiment, trichloroethylene (TCE), trans-1,2-dichloroethylene (t-DCE) is obtained from SIGMA-ALDRICH and cis-1,2-dichloroethylene (c-DCE) and vinyl chloride (VC) were obtained from SUPELCO.

Concentration of Chemicals

Chemical	Concentration
TCE	99,5+% grade
t-DCE	200 µg/mL in 1 mL of Methanol
c-DCE	2000 µg/mL in 1 mL of Methanol
VC	200 µg/mL in 1 mL of Methanol

In order to calibrate the gas chromatography machine, a series of dilution was performed to all of the chemicals mentioned previously. Therefore, 20 mL of TCE was extracted from its bottle and stored in a 20 mL capped bottle with Teflon coated septa. The septa must be Teflon coated due to the high volatility of TCE. Four stock solutions were created. 0.137 mL of TCE was retrieved and diluted in 20 mL of Ethanol to create Stock solution 1. A similar process was used to create the other 3 stock solutions. Likewise, this process was repeated for the DCE isomers and VC. (Please refer to the following four tables for making the stock solutions)

The preparation of standard solutions is necessary in order to make standard curves. A standard curve can be yielded by plotting a linear function of the compound solution's concentration and area under the peaks generated from chromatograms. The standard solutions were diluted in distilled water instead of ethanol. For the case of TCE, each stock solution was used to yield 3 standard solutions each. For instance, Stock solution 2 of TCE was used to make 3 standard solutions with concentrations of 2 mg/L, 1 mg/L and 0.5 mg/L respectively in 10 mL of distilled water. These solutions were all capped with Teflon septa in a 20 mL vial. The following four tables illustrate the concentration of TCE, c-DCE, t-DCE and VC in the standard solutions. The C2 column shows the targeted dilution concentration.

Table A1.1

Concentration of Stock Solutions and Standards of TCE

TCE				
		Density of	1460	g/L

		TCE:		
	C1 (g/L)	**V1 (mL)**	**C2 (g/L)**	**V2 (mL)**
Stock 1	1460	**0.137**	10	20
Stock 2, made using Stock 1	10	**0.20**	0.1	20
Stock 3, made using Stock 2	0.1	**2.00**	0.01	20
Stock 4, made using Stock 3	0.01	**2.00**	0.001	20
Standards (ppm)	**C1 (mg/L)**	**V1 (mL)**	**C2 (mg/L)**	**V2 (mL)**
Use Stock 2				**H2O**
2	100	**0.20**	2	10
1	100	**0.10**	1	10
0.5	100	**0.05**	0.5	10
Use Stock 3				
0.2	10	**0.20**	0.2	10
0.1	10	**0.10**	0.1	10
0.05	10	**0.05**	0.05	10
Use Stock 4				
0.025	1	**0.25**	0.025	10
0.01	1	**0.10**	0.01	10
0.005	1	**0.05**	0.005	10

Table A1.2

Concentration of Stock Solutions and Standards of c-DCE

Cis-1,2-DCE	2000	ug/mL	mg/L	
MCL (EPA): 70 ug/L	in	1 mL		
	C1 (mg/L)	**V1 (mL)**	**C2 (mg/L)**	**V2 (mL)**
Stock 1 in EtOH	2000	**0.10**	10	20
Standards	**C1 (mg/L)**	**V1 (mL)**	**C2 (mg/L)**	**V2 (mL)**
(mg/L=ppm)	Stock 1			H2O
1.5	10	**1.50**	1.5	10
0.75	10	**0.75**	0.75	10
0.5	10	**0.50**	0.5	10
0.1	10	**0.10**	0.1	10
0.05	10	**0.05**	0.05	10
Total Volume of C-DCE used		2.90		

Table A1.3

Concentration of Stock Solutions and Standards of t-DCE

Trans-1,2-DCE	200	ug/mL	mg/L	
MCL (EPA): 100 ug/L	in	1 mL		
	C1 (mg/L)	**V1 (mL)**	**C2 (mg/L)**	**V2 (mL)**
Stock 1 in EtOH	200	**0.50**	5	20
Standards in H_2O	**C1 (mg/L)**	**V1 (mL)**	**C2 (mg/L)**	**V2 (mL)**
(mg/L=ppm)				H_2O
1	5	**2.00**	1	10
0.75	5	**1.50**	0.75	10
0.5	5	**1.00**	0.5	10
0.1	5	**0.20**	0.1	10
0.05	5	**0.10**	0.05	10
Total Volume Used		4.80		

Table A1.4

Concentration of Stock Solutions and Standards of VC

VC	200	ug/mL	mg/L	
MAC (HC), MCL (EPA): 2 ug/L	in	1 mL		
	C1 (mg/L)	**V1 (mL)**	**C2 (mg/L)**	**V2 (mL)**
Stock 1	200	**0.50**	5	20
Standards	**C1 (mg/L)**	**V1 (mL)**	**C2 (mg/L)**	**V2 (mL)**
(mg/L=ppm)	Stock 1			H_2O
1	5	**2.00**	1	10
0.5	5	**1.00**	0.5	10
0.1	5	**0.20**	0.1	10
0.05	5	**0.10**	0.05	10
0.01	5	**0.02**	0.01	10
Total Volume of VC used		3.32		

Calibration of the Gas Chromatography

The concentration of TCE, dichloroethylenes (DCEs) and VC will be determined using a Hewlett Packard 5890A gas chromatography machine equipped with a flame ionization detector. The sample will go through an 8ft 60/80 Carbopack B/1% SP-1000 column bought from SUPELCO (Bellefonte, PA). The gas chromatography machine has the following settings:

Table A1.5 Specifications of the GC

Initial Temperature (oven):	45°C
Final Temperature (oven):	220°C
Rate of Temperature increase of GC:	8°C/min
Cooling Time:	15 min
Duration of each run:	40 min
Helium flow rate:	250 kPa
H_2 (FID) flow rate:	250 kPa
Air (FID) flow rate:	250 kPa
Temperature of FID:	250°C
Temperature of Injection port:	200°C

A water-bath was used to heat every standard solution before the injection into the chromatography machine. The temperature of the water-bath is set to 85°C. The purpose of the water-bath is to push the TCE (or DCE/VC) solution into the headspace of the capped vials where a needle can be used to extract the compound in a gaseous state. The amount injected into the gas chromatography machine is 0.3 mL.

Results

Figure A1.1 Standard Curve of TCE

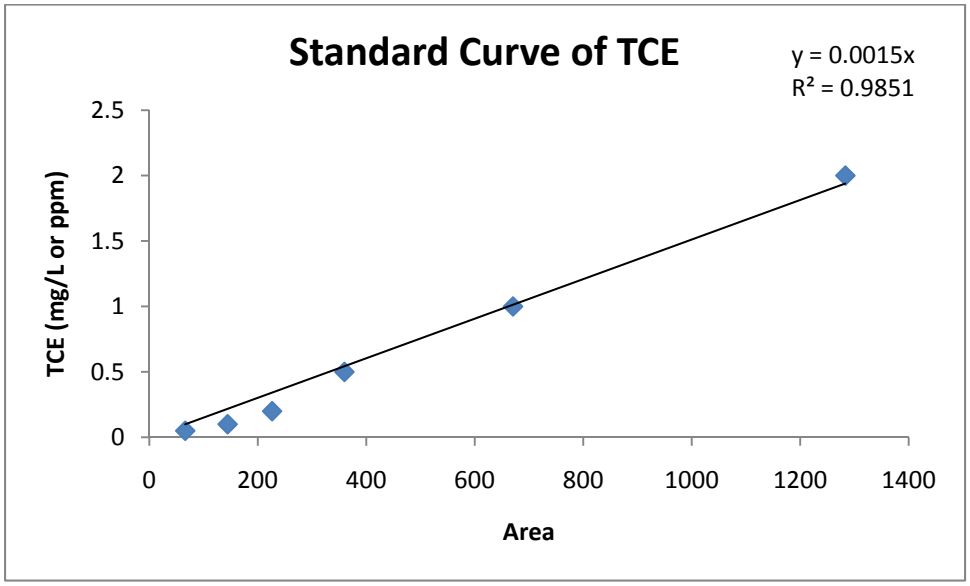


Figure A1.2 Standard Curve of c-DCE

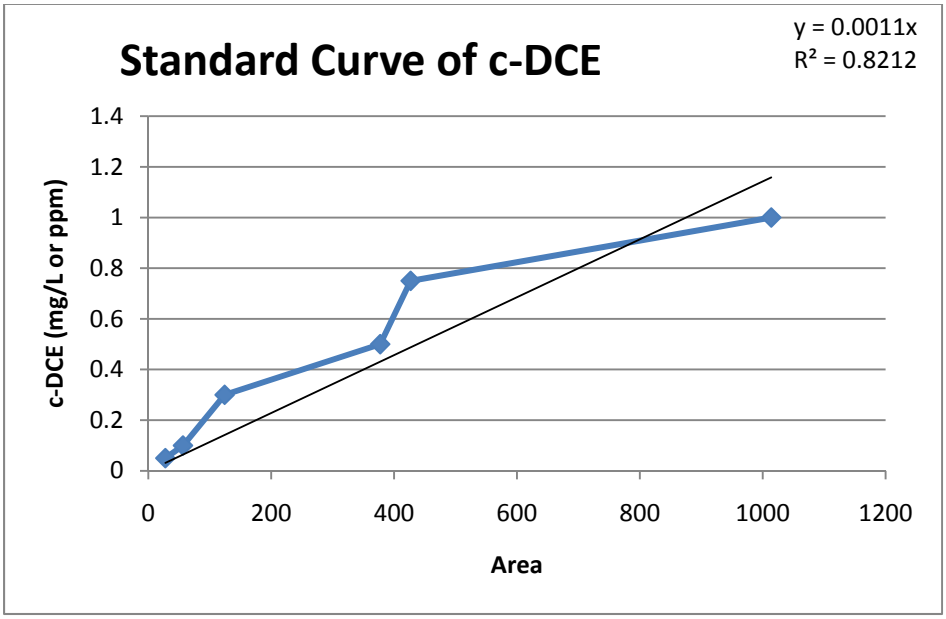


Figure A1.3 Standard Curve of t-DCE

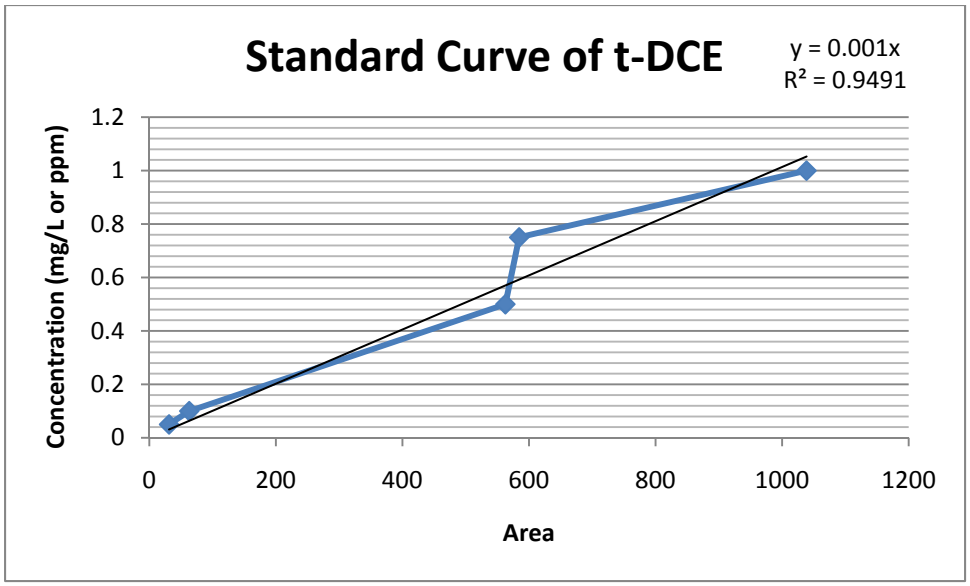
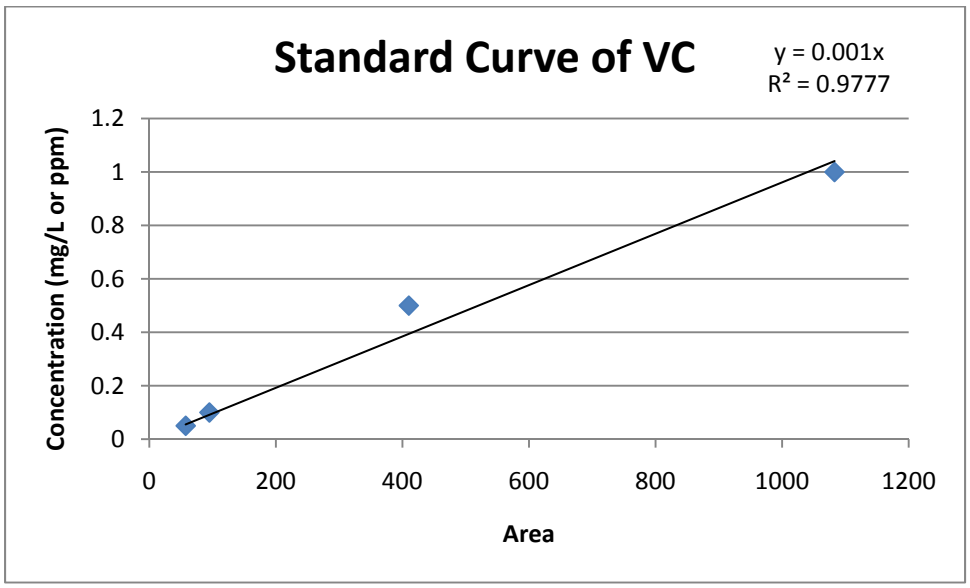


Figure A1.4 Standard Curve of VC



Discussion of Results

The following table illustrates the equation that will be used for the calculation in determining the concentration of the following compound: TCE, c-DCE and VC. According to different studies, it is fair to assume that c-DCE is the dominant compound within the DCE isomers (Kao & Lei, Using a Peat

Biobarrier to Remediate PCE/TCE Contaminated Aquifers, 1999). Therefore, this experiment will assume that the TCE will degrade to c-DCE only.

Table A1.6

Equations generated from results

Compound	equation
TCE	[conc mg/L] =0.0015(Area)
c-DCE	[conc mg/L] =0.001(Area)
VC	[conc mg/L] =0.001(Area)

Conclusion

It can be concluded that the GC using 8ft 60/80 Carbopack B/1% SP-1000 column is an effective method is measuring the concentration of the compounds in this experiment. It will be assumed that the main DCE isomer is c-DCE.

Experiment 2) Batch Test 1

Introduction

In order to assess the TCE ground water contamination problem at the area of Shannon, Quebec, a batch test was performed in order to determine the reactivity of the selected media. The main goal of a batch test is to determine the reaction rates or half-life of the contaminant in contact with the reactive media. In this case, the media of interest in a mixture of wetland sludge and peat moss. This test is usually the first experiment carried out for the design of a biobarrier system. It allows engineers to figure out if the consortium of microbes is able to biodegrade the targeted contaminant within a given period of time and within the maximum allowable concentration.

Under anaerobic conditions, TCE is transformed by sequential reductive dechlorination reactions by replacing the chlorine atom with a hydrogen atom at each step (Kao & Lei, Using a Peat Biobarrier to Remediate PCE/TCE Contaminated Aquifers, 1999). The metabolites of this pathway are DCE isomers

and VC. In fact, the degradation rate is inversely proportional to the number of chlorine atoms on the compound. This means that the degradation rate of VC is relative slow. This pathway yields very toxic metabolites. In terms of human health impact, DCE isomers affect the central nervous system causing nausea, fatigue, vertigo and drowsiness. The inhalation of large concentration (3000 ppm) causes the reduction of red blood cells and pathological liver changes (1,2-Dichloroethene: Health Information Summary, 2005). VC's health risk is very similar DCE isomers and moreover, it is a known carcinogen (Vinyl Chloride, 2006). This experiment will focus on the anaerobic pathway.

$$TCE \xrightarrow{k_1} DCE \xrightarrow{k_2} VC \xrightarrow{k_3} ethylene$$

where k is the reaction rate constant

In this experiment, the degradation goal of this experiment is to yield a TCE, c-DCE and VC concentration lower than the maximum allowable concentration in drinking water determined by federal agencies.

Table A2.1 The Maximum Contaminant Level of the Metabolites from TCE Degradation

Chemical	MCL (mg/L)	Reference
TCE	0.005	(Guidelines for Canadian Drinking Water Quality, 2008)
t-DCE	0.1	(National Primary Drinking Water Regulation, 2009)
c-DCE	0.07	(National Primary Drinking Water Regulation, 2009)
VC	0.002	(Guidelines for Canadian Drinking Water Quality, 2008)

*The Maximum Contaminant Level (MCL) is legal threshold limit of the amount of contaminant allowed in drinking water set by the Environmental Protection Agency (EPA)

The main goal of this experiment is to determine the reaction rate of TCE exposed to the reactive media. The reaction rate can be determined with the following equation:

$$C = C_0 e^{-kt}$$

Where C = concentration
C_0 = initial concentration

k = reaction rate constant

t = time

The equation can be modified into:

$$\ln\left(\frac{C}{C_0}\right) = -kt$$

The half-life of the contaminant can be expressed in the following fashion:

$$t_{0.5} = \frac{\ln(2)}{k}$$

The half-life represents the amount of time it takes to reduce the concentration of the contaminant to half of the initial value.

Material and Methodology

The biodegradation experiment is performed by setting up a batch test. Twenty bottles with a volume of 125 mL is filled with 50 mL (8 g) of media (peat moss purchased from Fanfard Inc. (St-Bonaventure, Quebec)). There are two types of bottle prepared: the controls and the microbial bottles. There are 4 control bottles prepared. The control bottles contain only 50 mL of the media peat moss and 40 mL the Liquid media. There will be 16 microbial bottles prepared. Each of these will contain 50 mL of peat moss, 10 mL of sludge and 40 mL of Liquid media. The sludge will be provided from a wetland project at McGill Macdonald Campus with the permission of Dr. Shiv O. Prasher. The sludge will be the microbial source of this experiment. However, the exact component of this sludge is unknown. The amount of organic material or volatile suspended solids (VSS) of the activated sludge was determined to be 37.7 g/L. Hence, every microcosm bottle will have approximately 1 g/L of VSS. The liquid media consists of TCE and the nutrients. The concentration of TCE in the media will be 0.2 mg/L. The reason for using 0.2 mg/L is because there is a chance that a high concentration of TCE will eliminate all microbial activity in the bottle which is not desired. Another reason is because this amount, 0.2 mg/L, is the average concentration in the aquifers of the town of Shannon (Canadian Council of Ministers of the

Environment, 2007). The amount and concentration of the nutrients is listed in table A2.2 . The anaerobic environment will force the bacteria to degrade TCE under the reductive dechlorination pathway. Lastly, each bottle will be capped with Teflon coated septa.

The purpose of using control samples is to analyze the adsorptive capacity of peat and biochar. When the TCE is forced into the headspace of the bottles, TCE may be still be trapped on the media. Therefore, it is important to assess this phenomenon.

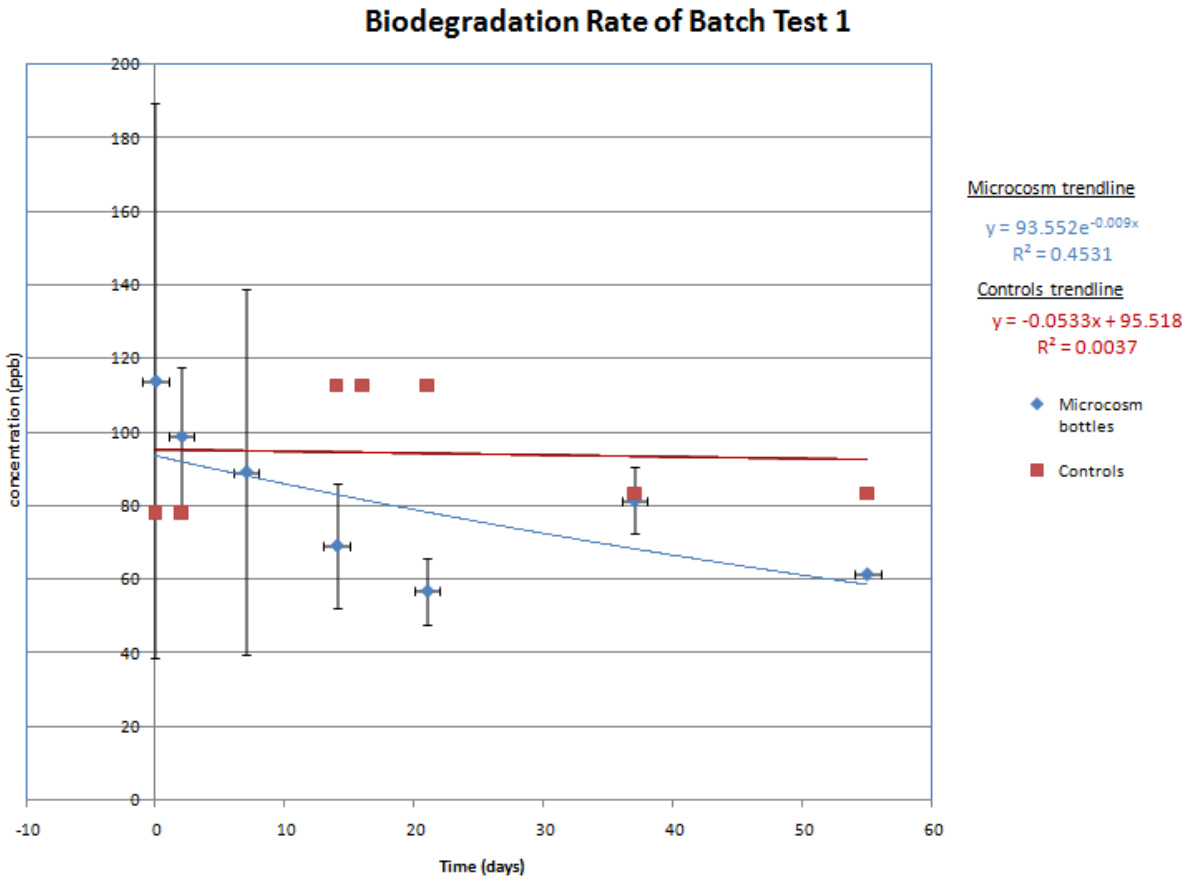
In order to trigger the growth of the organisms in the bottle, a source of nutrients must be added into each bottle. The following table lists the nutrients that will be added to each bottle. The concentration represents the exact concentration that is in the liquid media.

Table A2.2

List of the Nutrient Medium

Nutrients	Concentration (mg/L)	Reference
$NaNO_3$	92.1	(Lyew, Tartakovsky, F, & R, 2001)
K_2SO_4	188.4	
KH_2PO_4	539.1	
Na_2HPO_4	1610.6	
trace metal solution (TMS)	10 (in ml/L)	
Molasse	3000	
TMS constituents		
$MgSO_4 \cdot 7H_2O$	36.92	(Lyew, Tartakovsky, F, & R, 2001)
$CaCl_2 \cdot 2H_2O$	707.4	
$ZnSO_4 \cdot 7H_2O$	63.9	
$MnSO_4 \cdot 7H_2O$	16.3	
H_3BO_3	41.1	
$NaMoO_4 \cdot 2H_2O$	10.2	
$CoCl_2 \cdot 6H_2O$	9.7	
KI	22.2	
$FeSO_4 \cdot 5H_2O$	1000	

Results



Sample Calculations

-Half life of the contaminant

$$t_{0.5} = \frac{\ln 2}{k} = \frac{\ln 2}{0.009} = 77.02\ days$$

Discussion of results

The control bottles have an average concentration of 95.518 ppb. Assuming that every bottle contains 200 ppb, it can be said that the peat was able to sorbed approximately half of the TCE. There is a TCE decreasing trend in the microcosm bottles. However, there are no appearances of TCE metabolites (DCE and VC). The concentration of the TCE has a decreasing trend. It can be noticed that the degradation rate is very slow. This can be due to the lack of microbial activity in the activated sludge. A

lack in nutrients may also explain the slow degradation rate. The reaction rate constant (k) is determined to be 0.009. Hence, the half-life of TCE is determined to be 77.02 days. In comparison with other experiments, the half-life of TCE may range from 10 days to 30 days (Kao & Lei, Using a Peat Biobarrier to Remediate PCE/TCE Contaminated Aquifers, 1999).

Conclusion

It can be concluded that the reaction rate of TCE is very slow. It is determined that within the condition of the experiment, TCE has a half-life of 77.02 days. There are no signs of other desired metabolites.

In order to improve the outcome of the experiment, many suggestions can be made in order to improve the outcome of the experiment. The microcosm bottles may have been flushed or sparged with nitrogen before it is capped. This way, every bottle will immediately become anaerobic at the start of the experiment. In this experiment, aerobic bacteria may have been able to survive for a couple of days consuming the oxygen available in the headspace which may have inhibited the growth of anaerobic organisms. Also, in order to promote microbial activity in the bottles, the concentration of VSS and molasses will be doubled to 2 g/L of VSS and 6 g/L of molasses.

Experiment 3) Batch Test 2

Introduction

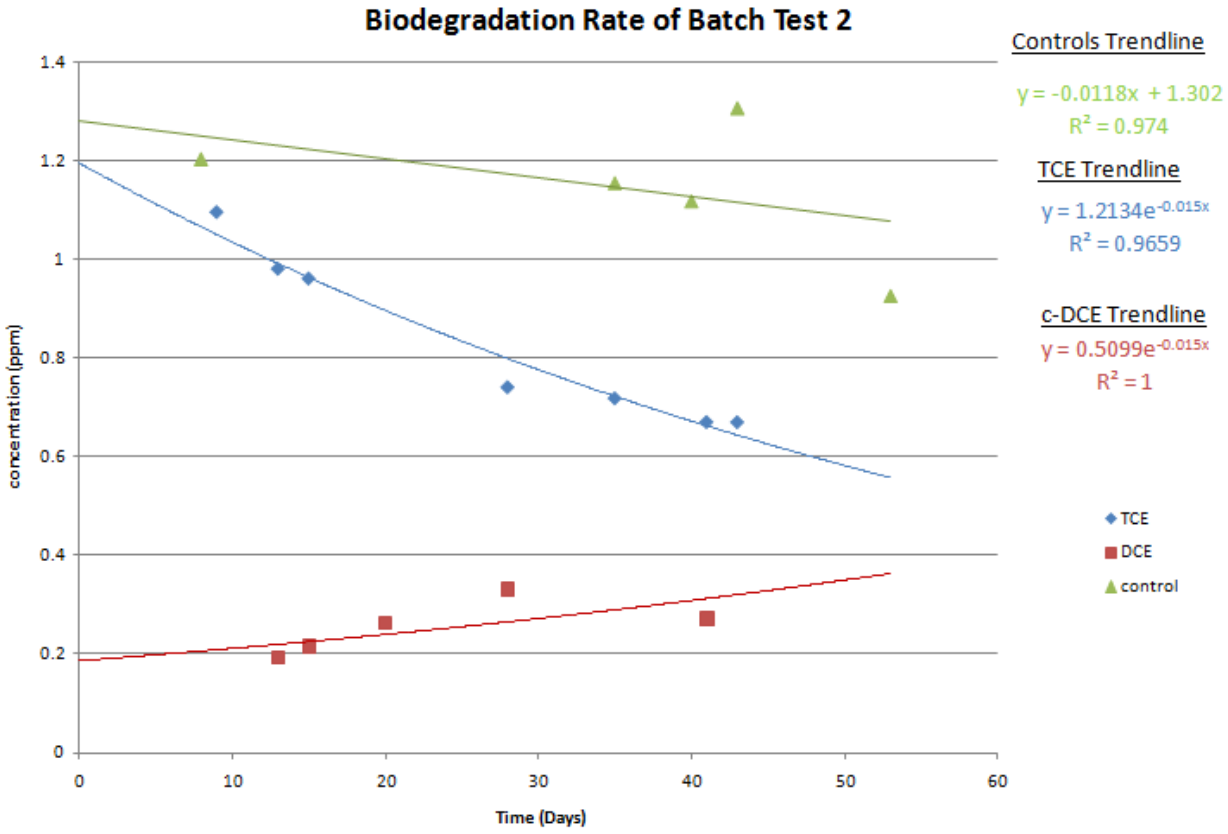
A second batch test was introduced due to the poor experiment results generated with the first experimental batch test. The experimental layout of the second batch test is very similar to the first test. However, certain modifications have been made in the methodology of the experiment which will be explained in the following section.

Materials and Methods

The material and methodology is very similar to Experiment 2) Batch Test 1. However, there are some additional features in this experiment in order to improve the results.

- Every microcosm bottles were sparged with N_2 gas for 5 minutes before it is capped.
- The concentration of the activated sludge is doubled
- The concentration of molasses is doubled

Results



Sample Calculations

-Half life of the TCE

$$t_{0.5} = \frac{\ln 2}{k} = \frac{\ln 2}{0.015} = 46.21\ days$$

-Half life of the DCE

$$t_{0.5} = \frac{\ln 2}{k} = \frac{\ln 2}{0.015} = 46.21\ days$$

Discussion of Results

In this experiment, there is the appearance of c-DCE which is a degradation by product. The control bottles yielded an average concentration of 1.302 ppm. The reaction rate constant (k) of TCE and c-DCE is both 0.015. This yielded a half-life of 46.21 days. This is a faster degradation rate compared to the experiment results in Batch Test 1). This is due to the increase in the concentration of organic matter (VSS) of the sludge and the increase of carbon source.

Conclusion

Hence, it can be concluded that the additional features of Batch Test 2) increased the degradation rate. The half-life of TCE decreased by approximately 40% compared to the first batch test. Also, there are signs of c-DCE is a desired by-product in the degradation pathway. This means that the given condition in this experiment favoured the growth of anaerobic bacteria which are degrading TCE in the desired path.

After the results of this experiment, a column testing of the reactive media will follow. Column testing can simulate the groundwater flow passing through a biobarrier. The column will use similar parameters of this experiment.

Experiment 4) Column Test 1

Introduction

A column test is an effective method in estimating the reaction rates of a biobarrier system. This experiment allows the determination of design parameters of a biobarrier under dynamic flow

conditions. Generally, the half-life determined from a column is usually more reliable than the half-life from a batch test (Gavaskar, 1999). The method in determining and evaluating the half-life and reaction rates is the method as in Experiment 2) Batch Test 1.

Materials and Methods

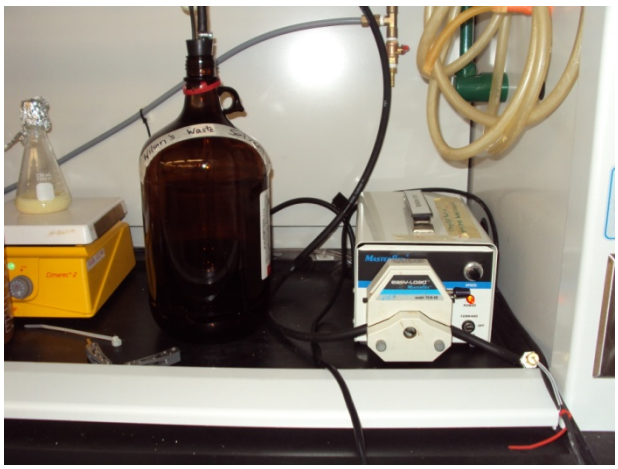
Experimental Design Specifications

Experimental Specifications	Unit
Volume of column	0.00904 m^3 = 9.04 L
Amount of water in column	4.5 L
Amount of Peat Used	9.04 L
Amount of Wetland Sludge	1 L
Concentration of TCE in liquid solution	0.5 mg/L
Flow rate of pump	1500 mL/day
Hydraulic Retention Time	3 days
Volume of Liquid media	4 L

First of all, the column is filled with a layer of peat/sludge and a layer (10 cm) of gravel at each end of the column. The layer of gravel is used to create a uniform flow throughout the column. A peristaltic pump will be used to pump the liquid media in the influent jug through the column. The liquid media in the influent jug consists of molasses, water, nutrients and contaminants. The concentration of the components is listed above and the nutrient solution has the same concentration as Batch Test 1). An effluent jug is used to capture the water. The following illustrates the experimental set-up:

 Layers of the column

 Saturated Column and Effluent Jug

 Influent jug and Peristaltic pump

While sampling the water from the column, a needle will be inserted into the sampling port. 10 mL of water sample will be retrieved and capped in a 20 mL bottle. Then, the solution is heated for 15mins and 0.3 mL will be retrieved for Gas Chromatography Analysis.

The data is gathered with the following table:

Concentration of Contaminants at Different Sampling Ports

		[Conc] µg/L or ppb		
Column Port	Residence Time (hrs)	TCE	DCE	VC
Influent	0			
Port A	34			
Port B	68			
Port C	124			
Effluent	170			

The residence time is the sampling time and it is determined using the following equation:

$$t = \frac{LAn}{Q}$$

Where t = residence time

L = distance between sampling ports

A = area of column

n = porosity

Q = flow rate

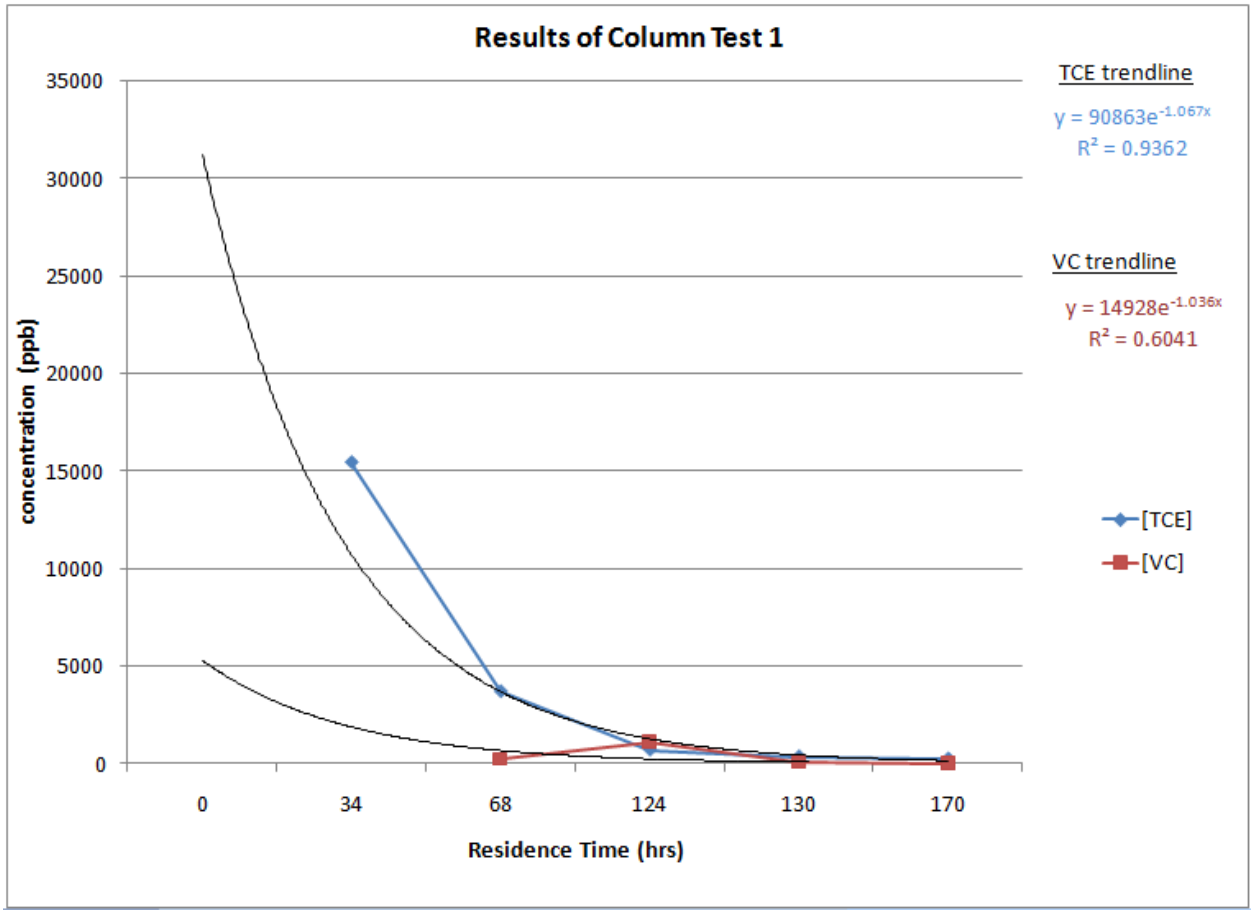
Results

Table

		[Conc] µg/L or ppb		
Column Port	Residence Time (hrs)	TCE	DCE	VC
Influent	0	500	0	0
Port A	34	15434.2446	0	0
Port B	68	3689.9256	0	251.0152
Port C	124	690.582	0	1102.453
Port C	130	350.031	0	72.9051
Effluent	170	241.112	0	19.6473

* 2 samples were taken on Port C

Figure



Sample Calculations

-Half life of the TCE

$$t_{0.5} = \frac{\ln 2}{k} = \frac{\ln 2}{1.067} = 0.650\ day$$

-Half life of the VC

$$t_{0.5} = \frac{\ln 2}{k} = \frac{\ln 2}{1.036} = 0.670\ day$$

Discussion of Results

It is noticeable that there is a decrease in concentration of the contaminants as it traveled through the reactive cell. There was an evident decrease in TCE concentration and an increase in VC concentration. It was impossible to determine the concentration of c-DCE that was generated in the

experiment. This is caused by the presence of ethanol which generated a peak on the chromatogram masking the peak of c-DCE. Solutions to this problem will be discussed in the conclusion.

The reaction rate constant (k) of TCE and VC is determined to be 1.067 and 1.036 respectively. As a result, the half-life of TCE in the column is 0.650 day and the half-life of c-DCE in the column is 0.670 day. These values are crucial for the determination of the thickness of a biobarrier.

Conclusion

In conclusion, the column experiment yielded a half-life of TCE of 0.650 day and a half-life of VC of 0.670 day. These values will play an important role in the determination of design specifications of a biobarrier.

In order to improve this experiment, several modifications in the experimental protocol could be changed in order to make the DCE peak appear on the chromatogram. The settings on the gas chromatography machine could have been modified (i.e. reduce temperature increase rate, reduce helium flow rate) allowing the peak of DCE to appear. In addition, TCE can be diluted in another compound instead of ethanol.

Normally, this experiment should have been repeated several times for the purpose of generating consistent results. However, due to the constraints of the project, this experiment was only performed once. There are many other tests that can be performed using the column which would aid in determining design specifications of the PRB. For instance, this column test can be tested in different temperature. This would allow the experimenter to evaluate the efficiency of the biobarrier in different temperatures.

Annex B: Column Design

Annex B: Column Design

Objective

After running batch tests for the peat, molasses and wetland sludge remediation design it was essential to be able to simulate conditions under water flow as would be seen under in situ conditions.

Problem Statement

An apparatus would need to be designed to test our PBR medium since none was available as prefabricated laboratory apparatus. A hydraulic column would need to be designed and constructed for that purpose.

Design Criteria

The following criteria needed to be considered in designing the column:

1. The design of the column needed to be able to represent the actual cross section of the peat bio-barrier as would be seen once constructed on site.
2. The hydraulic recharge rate of the column would need to simulate the actual flow rates of the target area to be remediated.
3. The design needed to be serviceable, meaning that it should allow for the users to have easy access to the inside to change the contents for different experiments. It needed to be easily transportable and able to fit into restrained areas as might be found in a lab.
4. Chemical resistivity needed to be considered. TCE will react with certain common building materials for a column of this type. Materials would need to be selected that would be chemically resistant to TCE.
5. Sampling ports would be required to take measurements of the TCE degradation at different heights in the column.

6. The design needed to be simple, in design, constructability, use and maintenance. It should allow for easy modifications to be made and parts to be swapped out when necessary.
7. It would be necessary for all the parts to be easily obtainable at relatively low cost and be constructible with available machinery at the MacDonald Campus machine shop.

Notes on Final Design Choices

Column:

The body of the column was chosen to be made out of an acrylic cylinder since this material would be readily available and easy to work with. As stated above, it had the TCE resistance required for the column test protocols. The cylinder dimension chosen was large enough to minimize the wall effect on the flow of contaminated water during the test and also be large enough to easily fill, empty and clean for experiments. The wall thickness was the thickest available from the manufacturer and was deemed sufficient to be able to machine and retain the water pressure required without cracking or breaking. The ends of the cylinder would be identically designed to have the flanges at either end made the acrylic sheets listed above with an opening the size of the cylinder interior and be glued directly to either end. The caps would be made of the same acrylic sheet used for the flanges and fit over top with a threaded hole placed in the middle to attach a standard fitting. A water tight seal would be ensured by using nuts and bolts at each corner with a Viton O-ring fitted around the outside perimeter of the column. Viton was chosen for the o-ring material since it would be chemically resistant to the TCE.

Sampling Ports:

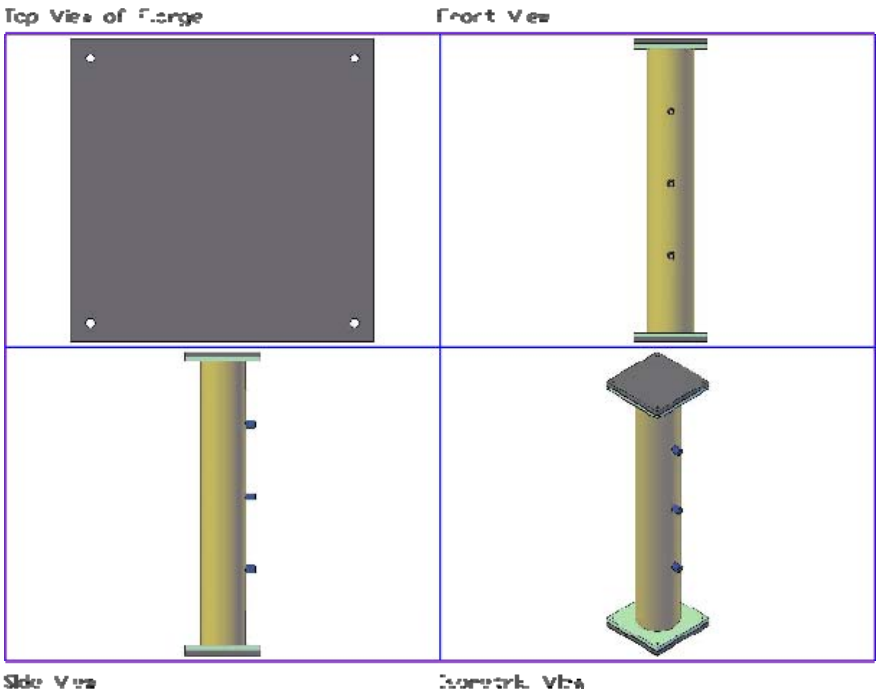
It was decided to choose to make the sampling ports with use of standard 13mm screw caps with septa attached. After consultation with the machine shop technicians the choice was made to purchase acrylic rods that would be machined to the required dimensions and the matching male screw

threads would also be machined directly onto the rod. The sampling port could then be glued directly into the side of the column at the desired heights.

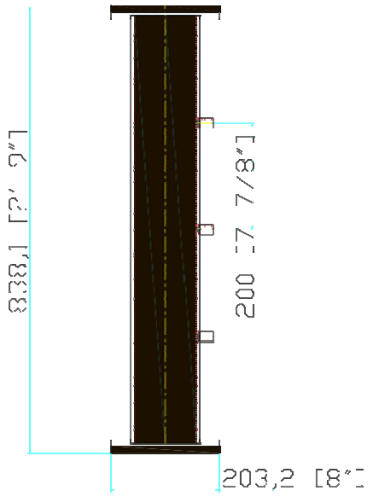
Fittings and Tubing

The materials used for the fittings and tubing needed to be resistant to TCE so Kynar and Teflon were chosen respectively. The dimensions were chosen based on lowest cost and compatibility to each other as well a possible flow rate requirements for the column test. Since these are standard sizes available from many manufacturers and distributors, for any other experiments larger or smaller sizes could be used and swapped out from the column design without need for major modifications beyond unscrewing the fitting from the cap.

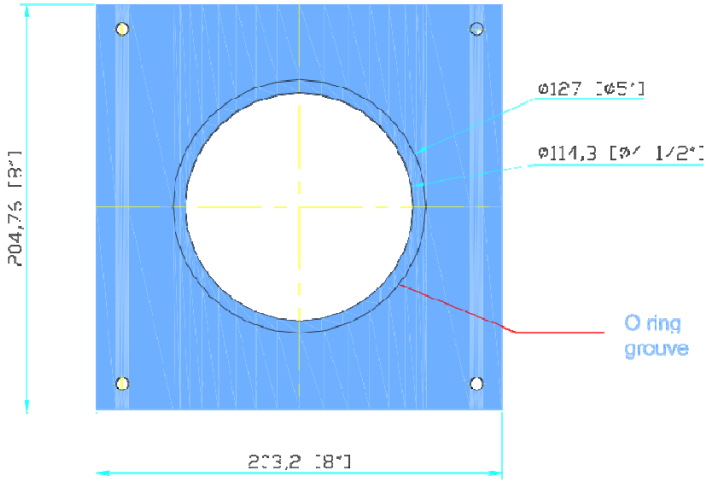
Column CAD Drawings:



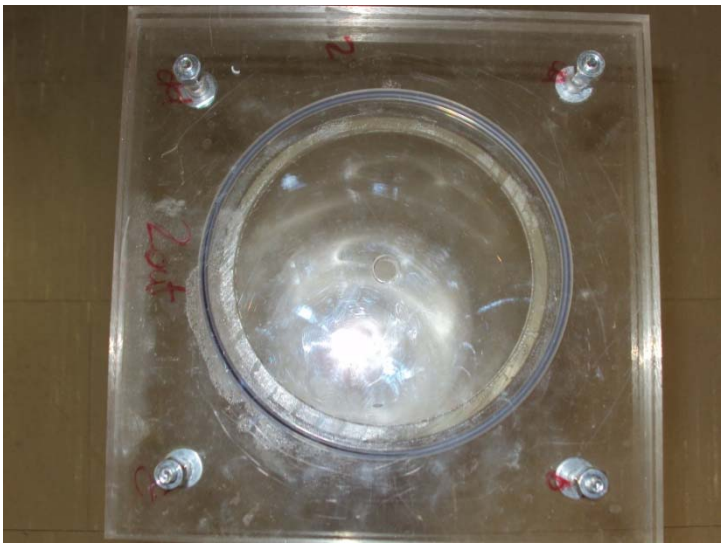
Column Cut Section



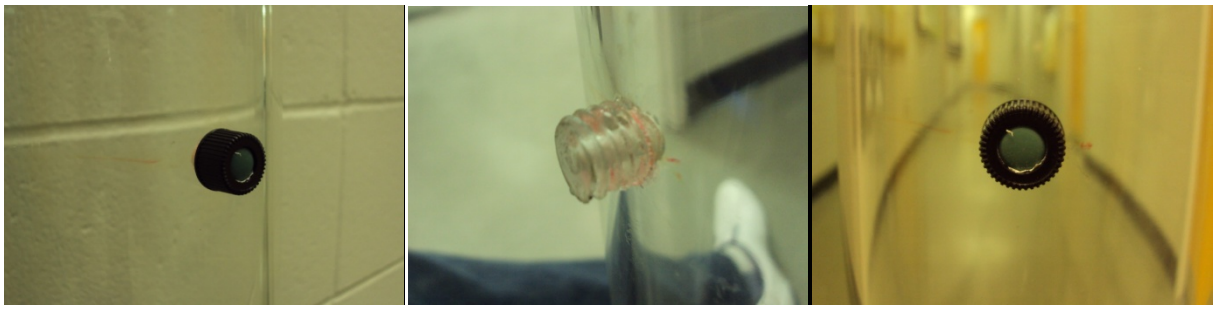
Top View of Column Lid



Pictures of Column



Side View and Top View of Experimental Column



Different views of the sampling port

Parts List

The following is a list of parts from manufacturers that were chosen to design and construct the column:

Column Section	Manufacturer	Type of Part and Dimensions
Column Body	Johnston Plastics	Acrylic Cylinder (Extruded): • 5 in OD • 4.5 in ID • 31.5 in long
Column End Caps	Johnston Plastics	Acrylic Sheets: • 4 sheets • 8 in by 8 in • ½ in thick
End Cap Fastners		Any Nut Bolt Washer assembly available. Must be capable of fastening 1in thick end caps.
O-ring End Cap Seals		Viton O-ring: • 5 1/8 in ID • 1/8 in Thickness • Round cross section
Sampling Ports	Johnston Plastics	Acrylic Rod (Extruded): • 3 rod sections • 1 in long • 9/16 in OD To be machined: • 13mm male thread • 1/8 in hole at center
Sampling Port Caps	Fisher Scientific	Screw Thread Caps with Bonded Septa 13-425: • 13mm thread • 7.5mm depth
End Fittings	Cole-Parmer	Kynar Elbow Fitting: • 1/8 – 27 in NPT • Size can vary depending on matching tube

		requirments
Tubing	Cole-Parmer	Teflon Tubing: • 1/8 in ID • 3/16 in OD • 25 ft/pack

Discussion - Initial Design Concepts:

Two possible concepts were seen as equivalent and possible: one was to have a single column with sampling ports and another option was to have several smaller columns linked with tubing where sampling ports would be placed at the entrance and exits to the columns. The multi column option, although feasible, was discarded as an option since it would require more time in terms of constructability, would require more parts, would take up excessive space in the lab and would be more difficult to set up and calibrate. One long column would require fewer fittings, tubing, take up less lab area and have more uniform flow characteristics.

The second aspect that needed to be considered was the chemical resistivity since TCE is known to be corrosive. To solve this problem chemical resistivity charts provided by lab equipment distributors, in this case Cole-Parmer, were consulted. A short list of materials was identified that would allow sufficient resistivity to the TCE concentrations used in the column test experiments. As for the material used for the body of the column, extra assurance was required so physical tests were conducted with a solution of 5ppm TCE. These test proved conclusive that acrylic would resist cracking due to TCE.

A difficult design choice to make was how to have sampling ports attached to the side of the column and to keep any option as simple as possible. Also, due to the non-uniform flow characteristics at the walls of the column, the samples would need to be taken as close to the inside of the column as possible, the sample volume could not originate directly at the wall. For this reason the most likely solution would be a needle inserted directly into the center of the column. The next step in the design

process was to determine how to allow for a needle to makes it way to the inside of the column, should it be fixed in place or be inserted at the time of sampling. Also, the ports would be under pressure so a water tight lock system would need to be included in the design to allow for the needle to be inserted. To meet the criteria that were established above and since this project was time intensive options were investigated from laboratory equipment and parts available on the market from major distributers like Cole-Parmer and Fisher Scientific. So among fittings available what seemed to be simplest option would be to use a septa as a sampling port, held in place with a screw cap, this idea came about from observing a similar concept on another lab apparatus. Certain manufacturers make screw caps and septa pre-packaged together making the concept even easier to implement. What would be necessary would be to find a fitting with the exact same screw thread such that it could be fitted to the side of the column and the screw cap could be attached to it.

Design Modifications Post Construction and Initial Testing

Once the body of the column was constructed it was tested to see leeking occurred before installing the sampling ports. With the column full of water only minor leaking was observed around the elbow fittings. This was considered acceptable since a tighter seal could be achieved using Teflon tape around the male screw threads.

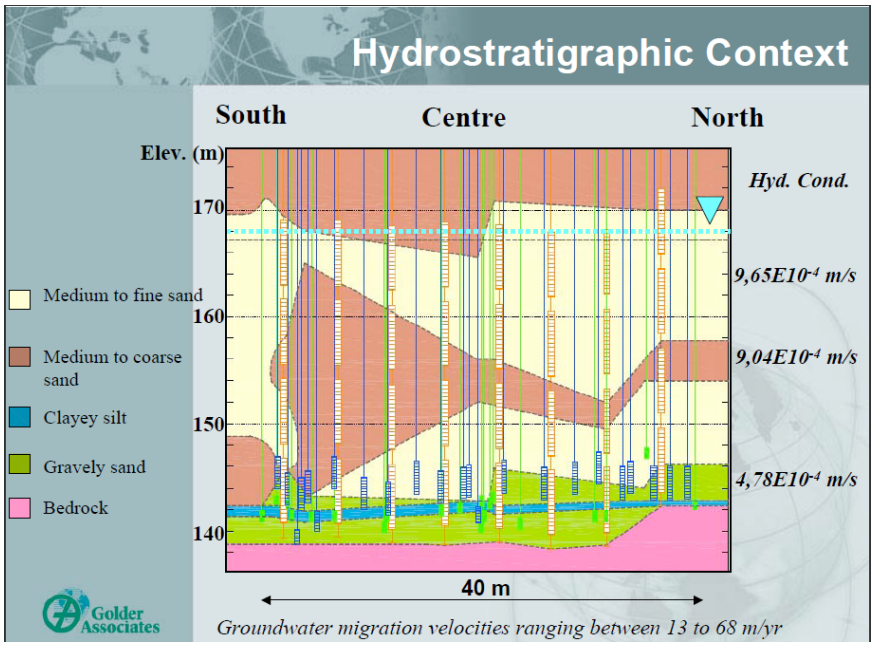
The sampling ports proved to be more problematic however since it was discovered that the proper sized die tool to make the male screw threads on the acrylic rods was unavailable at the shop and could not be obtained within the time frame required. The closest fit was a die tool that could make screw threads on the rod that would be slightly too deep to create a perfect seal between the male and female screw threads themselves. This was overcome by applying enough torque on the cap so that a seal was create on the inside of the cap against the male end and the septa. The one problem occurred when the sampling port was tested with a needle. The septa bonded to the cap proved to be too thin to

handle the water pressure since it did not re-seal when the needle was removed. Thicker septa were found and tested that were capable of creating the desired seal after a needle was inserted and removed repeatedly. Final notes on the sampling port design and potential for improvement are:

- Larger caps, wider and deeper, should have been sought, since they would handle higher pressures and be easier to work with;
- Screw caps with bonded septa available on the market proved to be too small and thin for the purposes of the design and should not be considered for future designs of this type;
- Male screw threads on the rod should have been made to the same specifications as the caps. This problem could have been avoided by verifying the available equipment and ordering the right part ahead of time.

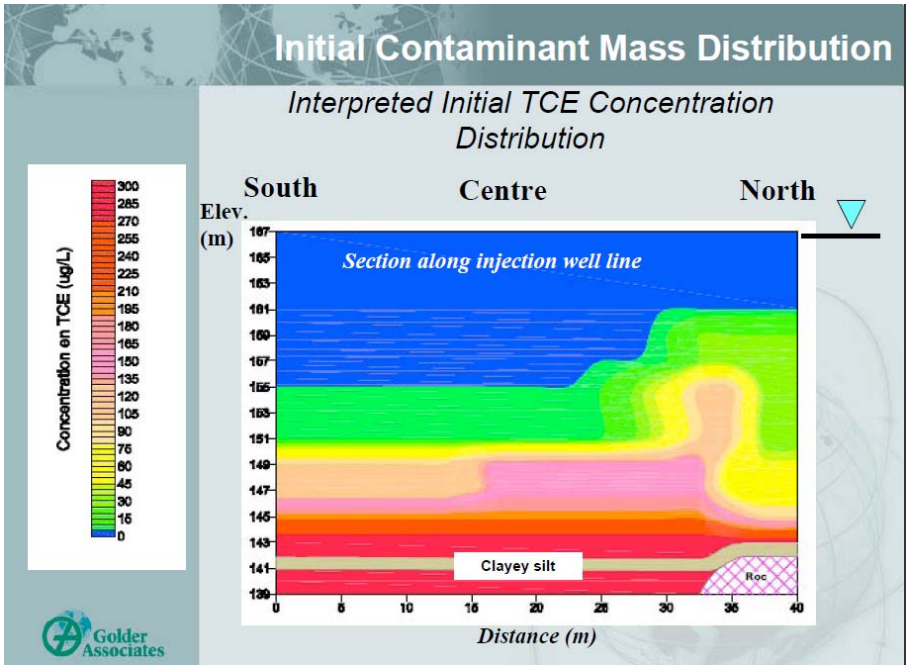
Annex C: Design Specifications

Figure 1)



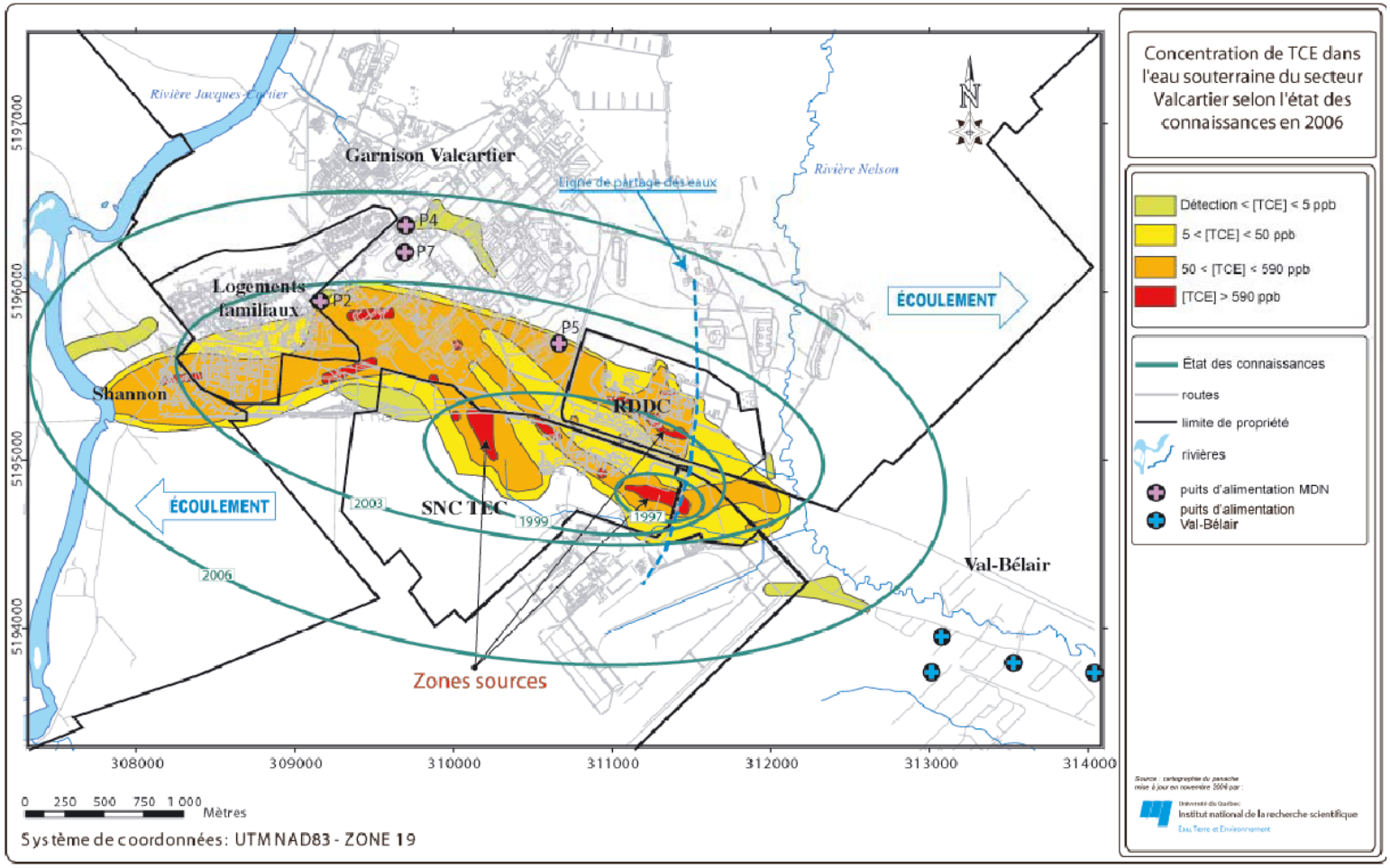
(Boutin, et al., 2007)

Figure 2)



(Boutin, et al., 2007)

Figure 3)



Ground water concentration of TCE in Valcartier in 2006 according to state of knowledge

(Environmental Protection and Contained-site Management at Valcartier Garrison, 2007)

Figure 4)

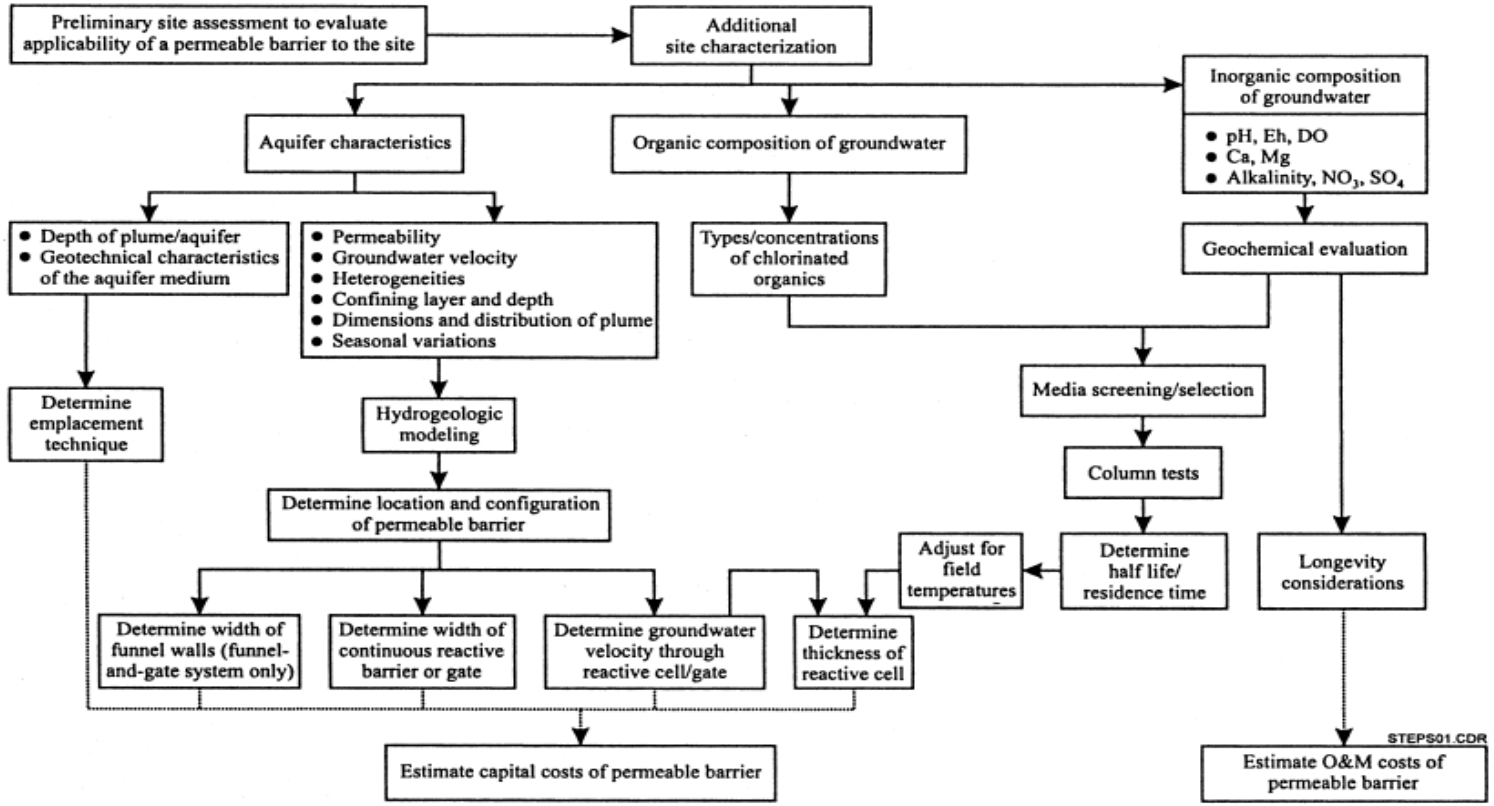


Fig. 2. Steps in the design of a permeable reactive barrier.

(Gavaskar, 1999)

Calculation 1) Determination of the Thickness of the Barrier

In order to determine the residence time of the contaminants in the biobarrier, the following table was generated:

Residence Time of Contaminant in Biobarrier

Contaminant	MEC	MAC	Half-Life (Hrs)	Half-life requirements	Residence Time (hrs)
TCE	1300	5	0.6496	9	5.8464
c-DCE	1300	7	1.8	9	16.2
VC	1300	2	0.6691	10	6.691
				Total	28.7374

*MEC = Maximum Expected Concentration in ppb
*MAC = Maximum Allowable Concentration in ppb

The maximum expected concentration is the amount of TCE that it expected to be in the biobarrier. This concentration is determined to be the concentration of TCE that was in the control bottles of Batch Test 2). The half-life of TCE and VC is determined with the experimental results of the Column Test 1). The half-life of c-DCE was estimated to be 3 times the half-life of TCE. According to Batch Test 2), the half-life of TCE and c-DCE is identical. However, due to uncertainties, a safety factor of 3 was used in the estimation of the half-life of c-DCE. The half-life requirement is the number of half-lifes that is required to reduce the MEC to MAC. The maximum allowable concentration is explained in Annex A Batch Test 1). By multiplying the half-life requirement with the actually half-life of the contaminants, the residence time is determined. The total residence time required for TCE to transform into ethylene is 28.7374 hours.

-Correction factor of the residence time

According to the Arrhenius equation, the reaction rate of any chemicals is greatly influenced by the temperature. The following equation illustrates their relationship:

$$k \, \alpha \, e^{-E/RT}$$

Where k = reaction rate
E = activation energy
R = the universal gas constant
T = temperature

In order to assess the decrease in the reaction rate in according to the temperature, a series of column tests must be performed at different temperatures. Due to the limitations of this project, these test were unable to be performed. Therefore, a safety factor of 2.5 was used based on a field observation of a reactive barrier site in New Jersey indicating that the degradation rate declines by a factor of 2 to 2.5 at temperatures of 8 to 10°C (Gavaskar, 1999).

Other factors may affect the performance of the biobarrier such as:

1) The barrier might encounter a much higher concentration than planned for over its useful lifetime. The adsorption capability of peat could have been tested. However, due to time constraints, the sorptive capacity of peat was not assessed in this experiment.

2) Some uncertainties in the hydrogeological information of the plume and groundwater. For example, the ground water velocity might change once it enters the reactive media.

Hence, a safety factor of 2 will be used to overcome these uncertainties.

Therefore, the final residence time of the contaminant is 145 hours. The thickness is determined by multiplying the fastest groundwater speed with the residence time of the barrier. According to a hydrogeological study of Shannon's contaminated sites, the range of groundwater migration velocity

was determined to be 13 to 68 m/yr. A velocity of 68 m/yr was used for the determination of the thickness of the barrier. The thickness of the biobarrier is calculated to be 1.2 m.

Calculation 2) Amount of Peat Calculation

Minimum amount of peat

The minimum amount of peat is calculated using the smallest length of biobarrier (length: 25m). This means that the total volume will be:

$$Volume\ of\ peat\ in\ biobarrier = 25m\ x\ 1.2m\ x\ 16m = 480\ m^3$$

Maximum amount of peat

The maximum amount of peat is calculated using the smallest length of biobarrier (length: 500m). This means that the total volume will be:

$$Volume\ of\ peat\ in\ biobarrier = 500m\ x\ 1.2m\ x\ 16m = 9600\ m^3$$

Calculation 3) Amount of Sludge Calculation

Assumptions:
-The concentration of volatile suspended solid (VSS) in sludge in 37.684 g/L
-The VSS is uniformly distributed within the sludge
-The required concentration of VSS in biobarrier is 4g/L

Minimum amount of sludge

The minimum amount of sludge used is calculated in the following fashion:

$$4\ \frac{g}{L} \cdot 1000\ \frac{L}{m^3} = 4000\ \frac{g}{m^3} \cdot 480m^3 = 1920\ kg$$

$$\frac{1920\ kg}{0.037684\ \frac{kg}{L}} = 50950.00\ L$$

Maximum amount of sludge

The maximum amount of sludge used is calculated in the following fashion:

$$4\ \frac{g}{L} \cdot 1000\ \frac{L}{m^3} = 4000\ \frac{g}{m^3} \cdot 9600 m^3 = 38400\ kg$$

$$\frac{38400\ kg}{0.037684\ \frac{kg}{L}} = 1019000.11\ L$$

Calculation 4) Amount of Molasses Calculation

Assumptions:
-the peat inside the biobarrier has a porosity of 0.5
-when the peat is saturated with water, the amount of water in biobarrier is 240000 L to 4800000L of water

Minimum amount of molasses

The minimum amount of sludge is calculated in the following fashion:

$$\frac{3\ g}{1\ L} = \frac{x}{240000 L} \rightarrow x = 720\ kg$$

Maximum amount of molasses

The minimum amount of sludge is calculated in the following fashion:

$$\frac{3\ g}{1\ L} = \frac{x}{4800000 L} \rightarrow x = 14400\ kg$$