Stripping of volatile organic compounds with CO₂

Marcelle van der Waals

Deltares

28-2-2013

Stripping of volatile organic compounds with CO₂

Focus on toluene and trichloroethylene

Marcelle van der Waals
Student nr.   3367460
Department of Hydrogeology
1 September-28 February

Supervisor Utrecht University: Prof. Dr. Ir. S.M. Hassanizadeh
Supervisor Deltares: D.A. Den Hamer, MSc

Abstract

Nowadays our urban landscape expands at an ever increasing rate. Brownfields are created mostly in urban areas. These brownfields may be highly polluted. Due to expensive remediation methods, alternative methods need to be developed. Ecogrout is a method where the soil will be approved by in situ strengthening and simultaneously remediation of the groundwater is achieved. With the Ecogrout reaction CO_2 is obtained, which can be used to strip dissolved contaminants. The stripping potential for trichloroethylene (TCE) and toluene with CO_2 from the Ecogrout process was evaluated by performing batch experiments. Within the batches a layer of gravel was present. The contaminants were dissolved in $NaHCO_3$ stock solutions. These $NaHCO_3$ stock solutions were mixed thoroughly with $CaCl_2$ to obtain the Ecogrout reaction. Different experiments were performed during this research. These experiments include pressure experiments, vapor pressure experiments and batch experiments. The development of setup and methods used for these research experiments was an important part of this master research. Resulting from the batch experiments stripping of TCE in the first 30 minutes increased proportionally with the CO_2 production. The equilibrium concentrations of gaseous contaminants for both concentrations $CaCl_2$ and $NaHCO_3$ used differed due to different ionic strengths. Also the results of TCE differed from the results obtained for toluene. Different interpretations were given to discuss the difference in results obtained from the experiments. Nevertheless due to the release of CO_2, the gaseous contaminant concentrations increased with reference to the volatilization rates. Concluding from this positive result it is recommended to perform more research. More research can be done by for example column and field experiments to obtain more advanced systems.

Table of contents

List of tables

List of figures

List of abbreviations

Atm	atmosphere
C	Celsius
DNAPL	Dense non-aqueous phase liquid
g	gram
GC	Gas Chromatograph
IAS	In situ Airsparging
K	Kelvin
L	litre
LNAPL	Light non-aqueous phase liquid
mg	milligram
min	minutes
ml	millilitre
mM	millimolar
ms	milliseconds
NAPL	non-aqueous phase liquid
RPM	rates per minute
s	seconds
sec	seconds
VOC	volatile organic compound
μl	microlitre

Chemical

$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
CO_2	Carbon dioxide
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate
HgCl	Mercury chloride
H_2O	Dihydrogen monoxide (Water)
N_2	Nitrogen
NaCl	Natriumchloride (salt)
$NaHCO_3$	Sodium bicarbonate
O_2	Oxygen
PCE	perchloroethylene
TCE	trichloroethylene

Notation

Latin symbols

C cumulative dilution factor, [-]

C_g^i gas phase mass concentration, [ML^{-3}]

C_w^i aqueous phase mass concentration, [ML^{-3}]

H_c^i Henry coefficient, [various dimensions]

I ionic strength, [mol L^{-3}]

c_i molarity, [mol L^{-3}]

M_{wt}^i molecular weight of chemical component i, [M mol^{-1}]

n_g number of moles in gas phase, [-]

P_g^i pressure gas phase, [ML^{-1}T^{-2}]

P_g^{atm} atmospheric pressure, [ML^{-1}T^{-2}]

R universal gas constant, [J mol^{-1}K^{-1}]

T absolute temperature, [K]

V_g volume gas phase, [L^3]

V_p volume pure phase, [L^3]

V_w volume aqueous phase, [L^3]

z_i charge number ion i, [-]

Greek symbols

ρ density, [ML^{-3}]

Indices and qualifiers

g gas phase

i chemical component

p pure phase

w water phase

1 Introduction

Nowadays our urban landscape expands at an ever increasing rate. Abandoned sites are increasing mostly in urban areas. These abandoned sites are called brownfields. Brownfields may be highly polluted. Re-using these sites by remediating them takes the pressure off natural environments. However, current remediation technologies are often very expensive and alternative methods need to be developed.

With the Ecogrout method the soil will be approved by in situ strengthening. Simultaneously, remediation of the groundwater is achieved. With the Ecogrout method different goals can be pursued and therefore the total costs are lower compared with other methods. The reaction for the Ecogrout process is:

$$CaCl_{2\ (aq)} + 2NaHCO_{3\ (aq)} \rightarrow 2NaCl_{(aq)} + CO_{2\ (g)} + CaCO_{3\ (s)} + H_2O_{\ (l)}$$
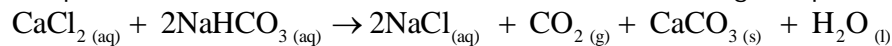
The products formed, include gaseous CO_2 and solid $CaCO_3$. The gaseous CO_2 will escape to the atmosphere and can potentially being used to "strip" volatile organic contaminants. With stripping is meant the compound goes from a dissolved/aqueous phase into the gas phase due to for example injection of gas. This gas phase with the contaminant bubbles upwards to the unsaturated zone.

Nelson et al. (2009) introduced CO_2 into the soil with pumps injecting CO_2-supersaturated water. Also Li (2009) and Doughty (2006) have done research at CO_2-supersaturated water injections. Concluded from these researches it was found that CO_2 has potential to strip residual volatile hydrocarbons. In these experiments however only the residual concentration was taken into account and different volatile hydrocarbons were used compared with the experiments that will be done in this research. The experiments that will be done in this research contain dissolved volatile organic contaminants. Nevertheless it is thought, using the research experiments obtained from literature, the CO_2 obtained at the Ecogrout reaction has the capability to strip volatile organic contaminants.

This research focuses on volatile organic compounds (VOCs) which are commonly detected in groundwater and cause a threat to groundwater. Two important groups of VOC pollutants in brownfields are chlorinated hydrocarbons and petroleum products. The main research objective is to investigate the potential for stripping of toluene (C_7H_8) and trichloroethylene (TCE, C_2HCl_3) with CO_2 generated from the Ecogrout reaction. The stripping potential is compared using two parameters; the velocity increase of phase transition (stripping velocity) and the absolute increase of maximum concentration.

In order to reach the research objective the following research question is defined:

To what extent can generated CO_2 from the Ecogrout reaction strip contaminants from volatile organic contaminated groundwater at brownfields?

The focus of this research project is on dissolved phases of TCE and toluene. The reason for this focus is the fact TCE and toluene have a low solubility and continue to dissolve in groundwater. Moreover, these contaminants are a threat to drinking water supplies and therefore need to be remediated.

The research objective is divided in sub questions:

1. *Does the pressure increase in the experiments have an influence on the amount of gaseous contaminant?*

The experimental determination of stripping of TCE and toluene with CO_2 generated from the Ecogrout reaction is based on batch experiments. These batch experiments

are closed systems. This means when the Ecogrout reaction starts CO_2 is formed and the pressure in the batch will increase due to the increase of gas. The influence of this pressure increase on the concentration measured is determined doing pressure experiments.

2. *Which contaminant, TCE or toluene, has a higher potential for stripping with CO_2?*

For stripping to occur the contaminant has to go from a dissolved phase into a gas phase. The vapor pressure is a measure of tendency of a substance to pass from a solid or liquid state to a gas state (Fetter 1993). A higher vapor pressure means the contaminant will go more likely into the gas state compared with a lower vapor pressure. Vapor pressure experiments are done to verify if ideal gas behavior may be assumed. The reason for doing these experiments is that CO_2 can much more liquefy than N_2 (main substance of air). The critical temperature of CO_2 is 304 K (NVON-commission 2004). For N_2 the critical temperature is 126 K (NVON-commission 2004). The experiments are done by determining the vapor pressure of TCE and toluene for CO_2 and air.

3. *Does the concentration of $CaCl_2$ and $NaHCO_3$ have an influence on the concentration of contaminant in the gas phase?*

Both $CaCl_2$ and $NaHCO_3$ are dissolved in water. The ratio of both solutions used in the batch experiments is always 1 $CaCl_2$:2 $NaHCO_3$. The CO_2 concentration is dependent on the concentrations of $CaCl_2$ and $NaHCO_3$ used. The batch experiments are done using two different concentrations of $CaCl_2$:$NaHCO_3$. This is done to obtain the stripping potential for different CO_2 concentrations.

The different experiments will be performed in a laboratory from Deltares. The development of laboratory setup and measuring methods going to be used for these research experiments are an important part of this master research.

In chapter 2 a brief literature review and theoretical background of performed research is presented. Chapter 3 describes the methodology used in this research. The results are presented and discussed in respectively chapter 4 and 5. A final conclusion of this research is given in chapter 6.

2 Background and Literature review

2.1 Brownfields

With the increase of urban areas also the brownfields are increasing. The project HOMBRE, 'Holistic Management of Brownfield Regeneration', seeks to bring about 'zero brownfields' (Grotenhuis 2012). With 'zero brownfields' is meant, the concept of 'zero waste'. HOMBRE is based on providing scientific and technical information to support four concepts (Grotenhuis 2012):

- Land-use life cycle: land is a finite resource and is in a cycle of use. It is important to prevent future brownfield generation. Land that is already abandoned needs to be re-used
- Intermediary land use: remediation is needed to bring land back into re-use. The land can be restored until it can be re-integrated into the land use cycle
- Combining technologies: the costs are lowered by sharing the land management costs with other services such as renewable energy and climate control
- Benefits and responsibilities: there are many benefits and responsibilities for many stakeholders. Benefits for the earth and people are for example better resource optimization and societal benefits

The project HOMBRE is developing practical, science based information to deliver the concept of a land cycle as a working system for planners and land managers (Figure 2.1).
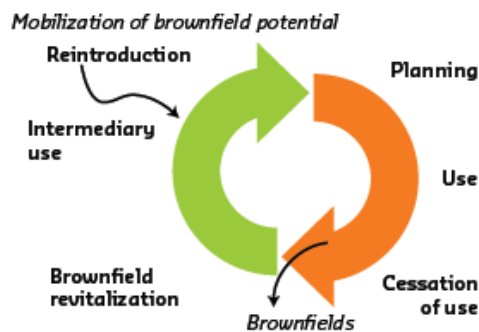
Figure 2.1 Land cycle HOMBRE (Grotenhuis 2012)

Ecogrout is part of this research project Hombre. It is integrated in the combining technologies concept. Experiments based on obtaining the effect of Ecogrout on contaminants are important. Not only because a lot of the brownfields of today are contaminated, but also because research is done whether a so called 'win-win' situation for the Ecogrout process can be obtained (in situ strengthening of the soil and simultaneously remediation of contaminants).

2.2 Volatile organic compounds

Soil and groundwater contamination with non-aqueous phase liquids (NAPLs) is usually caused by accidental releases of NAPLs in the subsurface through for example spills, disposal or leaking storage tanks. The NAPLs move under gravitational, viscous and capillary forces. VOCs can exist as light non-aqueous phase liquids (LNAPLs) or dense non-aqueous phase liquids (DNAPLs) (Semer, Adams and Reddy 1998). LNAPLs have a density less than water and therefore can float on top of the water table. A DNAPL has a density higher than water and may become trapped underneath the groundwater table as a pure phase (Figure 2.2).
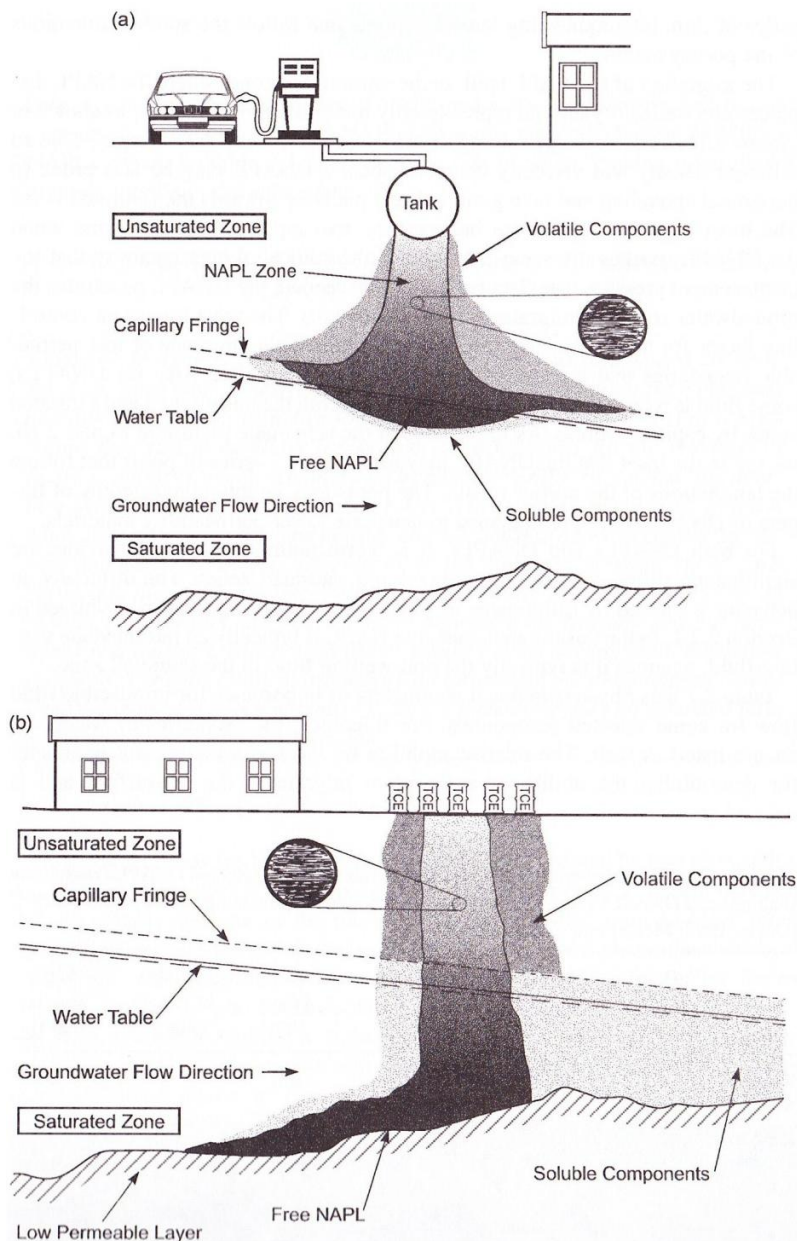
Figure 2.2 A LNAPL source zone (a) and DNAPL source zone (b) (Mayer and Hassanizadeh 2005)

Due to their low solubility NAPL source zones continue to dissolve into groundwater. Once in the groundwater, the dissolved contaminants are transported as plumes (Gvirtzman and Gorelick 1992) and can be a threat for drinking water supplies.

2.3 Methods of brownfield remediation

There are different methods for remediating the volatile organic contaminants in the groundwater. In situ remediation methods using the transition from dissolved phase to gas phase include air sparging, supersaturated water injection with CO_2 and potentially the Ecogrout process.

2.3.1   Air sparging

In situ air sparging (IAS) can remove volatile organic contaminants through volatilization or by the addition of oxygen to the groundwater to facilitate biodegradation (Tomlinson, et al. 2003). There must be contact between the injected air and groundwater for effective biodegradation and volatilization of the contaminant. During the process of air sparging, volatile organic contaminants are transferred from the contaminated water to the rising air bubbles (Gvirtzman and Gorelick 1992). The effectiveness of vapor stripping depends on the concentration gradient between the water and gas phase, the time available for mass exchange, the temperature and the interface area of the air bubbles. Within the boundary layer between the aqueous phase and gas phase a concentration gradient is developed.

Mass of the VOCs can be removed from the aqueous, sorbed and non-aqueous phases to the gas phase. When the contaminations are volatilized and reach the unsaturated zone, soil vapor extraction (SVE) is often used to remove these contaminated vapors.

In coarse sediment, air movement occurs primarily within pathways. The formation of these pathways is controlled by heterogeneities in the soil. Air will enter pores with the lowest entry pressure. This causes channels to preferentially form trough zones with larger pores and therefore higher permeability. According to Lundegard and LaBrecque (quoted in Tomlinson, et al. 2003) within a homogeneous medium, air distribution is generally characterized as parabolic in shape around the inlet. The observed air flow pattern will depend on the type of soils (Semer, Adams and Reddy 1998). Gravel has a higher permeability than sand and is therefore less restrictive towards air flow. The air is flowing easier in the form of bubbles. Therefore, the air entry pressure applied to create air movement is higher in sand compared with gravel. This is due to capillary pressures that must be overcome in the sand. When the air flow is dominated by channels the location and the density of these channels (number of channels per unit area of cross section) is important (Nelson, et al. 2009). Air channels will preferentially form where the pore sizes are largest due to smaller capillary pressures. Within a heterogeneous medium, the injected air will flow upwards due to buoyancy until it reaches a capillary barrier. The air will be trapped underneath this capillary barrier. The air pressure and capillary pressure underneath the capillary layer will continue to increase until the capillary pressure exceeds the entry pressure of the barrier and the air will break through the capillary barrier. Due to these lower permeability zones the air spreads laterally. This results in inefficient treatment of contaminants located above these higher capillary pressure layers (Figure 2.3).
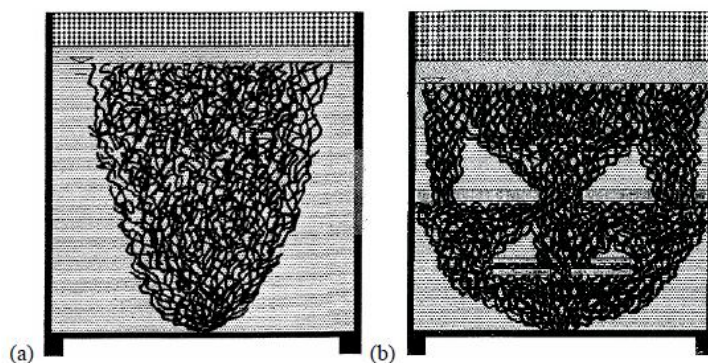
Figure 2.3 Drawing air channels at high air injection rate (a) uniform medium (b) stratified medium (Ji, et al. 1993)

2.3.2 Supersaturated water injection with CO_2

The technique of supersaturated water injection with CO_2 consists of dissolving high concentrations of CO_2 into water at elevated pressures (Nelson, et al. 2009). The water in the experiment of Nelson (2009) contained a concentration of 5 g/L CO_2. This is calculated with PHREEQC to a CO_2 pressure of about 3.35 atm (Appendix 10.1 1).

When the carbonated water leaves the well screen the water pressure drops and the water becomes supersaturated with CO_2. This supersaturated water wants to reach thermodynamic equilibrium. Therefore CO_2 bubble nucleation will begin as the water flows away from the well. The distance from the well CO_2 evolution occurs is dependent on many factors. These factors include the water injection rate, the water pressure and the hydraulic conductivity of the porous medium. The CO_2 bubbles rise due to buoyancy forces.

This supersaturated water injection system with CO_2 has advantages relative to air sparging systems (Nelson, et al. 2009):

1. The injected fluid is water and not gas. Therefore the supersaturated water has the capability to reach places that would not be able to reach with an IAS-system due to capillary forces
2. The supersaturated water has the capability to create a larger zone of influence compared with an IAS-system
3. Groundwater extraction wells can be used to control the hydraulics in the system
4. The supersaturated injection system has a more homogeneous in situ distribution of gas. Due to the presence of gas the permeability of the soil will decrease, which will cause the water to migrate into other areas with perhaps a lower initial hydraulic conductivity

In the field experiment of Nelson (2009) at Borden, pentane (C_5H_{12}) and hexane (C_6H_{14}) were chosen to be representative of volatile hydrocarbons. Soltrol 130 (mixture decane, undecane, dodecane and tridecane) was representative of non-volatile hydrocarbons. In this field experiment only the residual concentration was taken into account. It was concluded more pentane was removed compared with hexane, because of the higher vapor pressure of pentane.

2.3.3 Ecogrout process

In the Ecogrout process the ground is improved by in situ strengthening. The structure of the soils is kept intact using in situ methods. The process requires injecting materials in the soil at relatively low pressures (Van der Star 2012). The injected materials react in situ and produce a precipitate that increases strength and stiffness (Figure 2.4).

Figure 2.4 Cementation of column with Ecogrout process (Van der Star 2012)

To obtain the Ecogrout reaction in the batch experiments, dissolved $CaCl_2$ and $NaHCO_3$ are mixed to obtain solid $CaCO_3$. Other products are gaseous CO_2, H_2O and dissolved NaCl.

2.4 Research experiment hypotheses

Based on literature review it is expected that the escape of CO_2, generated in the Ecogrout process, will increase the volatilization of the contaminants. This hypothesis is tested by performing four experiments. The hypotheses of these experiments are described below.

1. *Pressure experiments*
   1. *Pressure experiments* will be done to evaluate the process of taking gas samples under pressure and return it to atmospheric pressure. It is expected the sampling method going to be used is an adequate method for taking gas samples under pressure.
   2. Other *pressure experiments* will be done because it is thought the pressure increase in the experiment has an influence on the concentration of contaminants in the gas phase (phase transition). Using Henry's law, when increasing the pressure (P_g^i), the concentration in the aqueous phase (c_w^i) has to increase also, Equation 2.1 (Mayer and Hassanizadeh 2005).

      Equation 2.1 Henry's law units of pressure x volume/mol

      $$H_m^i = \frac{P_g^i}{C_w^i}; [ML^{-1}T^{-2}L^3mol^{-1}]$$

      Therefore under higher pressures the concentration of contaminant in the gas phase will be lower.

2. *Vapor pressure* experiments will be done to evaluate the vapor pressure for CO_2. It is expected no difference in vapor pressures for CO_2 and air will be observed. This is expected because it is thought the vapor pressure is dependent on the amount of gas particles present. Therefore it is assumed ideal gas behavior may be used for calculations.

3. The *concentrations of $CaCl_2$ and $NaHCO_3$* will probably have an influence on the stripping potential. This is because these concentrations determine the total concentration of CO_2 produced and the production rate. The CO_2 production will be lower when lower concentrations of $CaCl_2$ and therefore $NaHCO_3$ are used. For a lower CO_2 production and rate, the stripping potential will probably be also lower. The different concentrations of $CaCl_2$ and $NaHCO_3$ used should not have an influence on the equilibrium concentration of TCE and toluene. This equilibrium concentration cannot differ because the system will be closed and therefore equilibrium will set in between the gas and aqueous phase. Without adding CO_2 the dissolved contaminant will volatilize to the same equilibrium concentration. This theoretical equilibrium concentration in the batches can be calculated using Henry's law (Equation 2.2, 2.3). The mass of contamination present ($V_w \times C_w^i$) at the initial condition will reach equilibrium between the liquid phase and gas phase (Figure 2.5).

Equation 2.2

$$V_w \times C_w^i = \left(C_w^i H_c^i V_g \right) + \left(C_w^i V_w \right)$$

$$C_g^i$$

Headspace

→ Liquid layer

Saturated
sediment

$$C_w^i$$
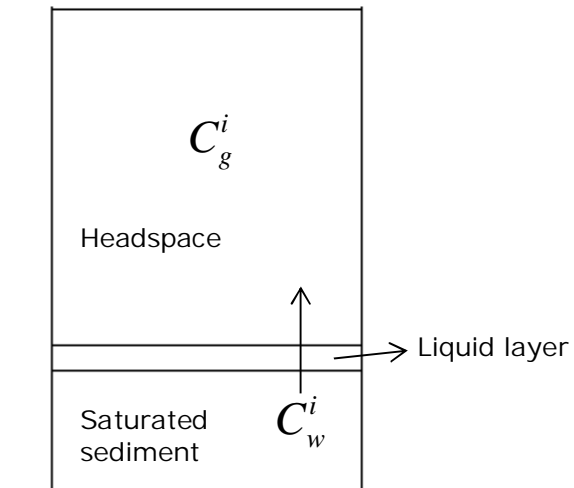
Figure 2.5 Equilibrium will reach between the liquid phase and gas phase

Using Henry's law (Equation 2.3) the gaseous concentration (C_g^i) is calculated from the aqueous phase concentration (C_w^i) (Mayer and Hassanizadeh 2005).

Equation 2.3

$$H_C^i = \frac{C_g^i}{C_w^i} ; [-]$$

3 Methodology

This research focused on TCE (>99.5%, Sigma Aldrich) and toluene (Merck). The properties of both contaminants are described below (Table 3.1). The parameter Henry's law constants, was assumed to be constant during the small differences in temperatures within the experiments.

Volatile organic contaminant	Density [g/cm^3 at 20-25 °C]	Molecular weight [g/mol]	Vapor pressure for air [mm Hg at 20 °C]	Vapor pressure for air [mm Hg at 25 °C]	Henry's law constant [-]	Solubility [mg/L at 25 °C]	10% solubility [mg/L at 25 °C]
TCE	1.46[1]	131.4[2]	60[3]	74[4]	0.422[5]	1100[6]	110
Toluene	0.86[7]	92[8]	22[9]	28[10]	0.272[11]	500[12]	50

Table 3.1 Properties TCE, toluene

For this research, lab experiments were performed. These lab experiments consisted of pressure experiments, vapor pressure experiments and batch experiments. All the experiments were done separately for TCE and toluene. A lot of problems were discovered developing the measuring methods and laboratory setup used in the experiments. All the changes made and problems defined in this research are described in Appendix 10.2.

3.1 Selection of septa

The batches used in all experiments were closed with viton septa because the contaminants will not diffuse through this septum. Butyl septa are also often used in experiments. Therefore the pressure in the batches closed with viton and butyl was compared (Figure 3.1).

---

[1] (Mayer and Hassanizadeh 2005)
[2] (Mayer and Hassanizadeh 2005)
[3] (Domenico and Schwartz 1990)
[4] (U.S. Department of Health and Human Services 1997)
[5] (United States Environmental Protection Agency 2007)
[6] (Fetter 1993)
[7] (Mayer and Hassanizadeh 2005)
[8] (Mayer and Hassanizadeh 2005)
[9] (U.S. Department of Health and Human Services 1997)
[10] (Fetter 1993)
[11] (United States Environmental Protection Agency 2007)
[12] (Fetter 1993)
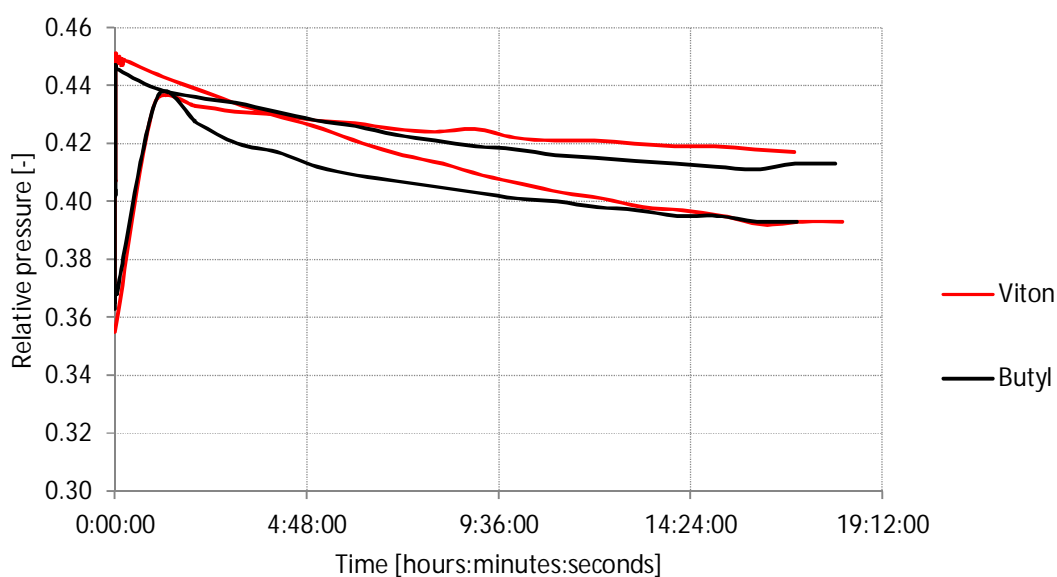
Figure 3.1 Difference in pressure between viton and butyl septa, 20.5°C (duplo experiment)
Note: y-axis starts at relative pressure 0.3

Relative pressure was the pressure amount [-] the pressure device (PressDaq PD-32, Appendix 10.3) measured. The time, used in the results of this research, was the duration time of the experiment. This means at time zero the experiment started.

Observed from Figure 3.1 no clear difference between butyl and viton septa was discovered. Until about five hours the viton and butyl septa showed a similar decrease in pressure (Figure 3.1). This decrease in pressure after five hours was assumed to be negligible for both septa. It was also assumed this pressure decrease was constant for all batches. Combined with the fact no diffusion of contaminants takes place trough viton, the viton septa were used in the experiments.

3.2 Gas sampling

Gas samples of 250 µl (Luer gas syringe, 250 µl) were collected from the batches in the experiments. Gas sampling was done by flushing the syringe three times. The fourth time 250 µl of gas was extracted after which ten seconds was waited for complete diffusion from the batch to the syringe. After ten seconds the syringe was "closed" to prevent diffusion of contaminant gas from the syringe to the surrounding air. A volume of 50 µl was pushed out of the syringe in the fume hood after which 200 µl was injected in the working vials (10 ml headspace vial, blue magnetic caps Alltech CH-20 MC BC) for measurement in the Gas chromatograph (GC) (Varian CP-3800+CTC analytics combipal (1), Appendix 10.3). This pushing out of gas in the fume hood was done to eliminate the dead volume of the needle (which cannot be closed) and to reduce the pressure in the syringe to atmospheric pressure. This sample collection method was evaluated in pressure experiments.

3.3 Measure gaseous contaminant concentrations

The GC gives an output in peak area [µv.min]. From the batches 200 µl of gas was injected in the working vials. Also an internal standard was added to obtain changes in peak area due to changes in for example temperature and pressure between experimental conditions. The internal standard for TCE was perchloroethylene (PCE) and for toluene it was TCE. These internal standards were chosen because of different retention times in the GC. With retention time is meant the time at which a

10

substance was attached to the column and a corresponding peak was given. The peak area of the internal standard should be around the same for all measurements. If changes were observed a factor for recalculating the peak area was obtained (Appendix 10.4).

The obtained peak areas from the GC were converted to gaseous contaminant concentrations using calibration lines. These calibration lines were made using Henry's law, Equation 2.3. The contaminant gas concentrations were plotted versus peak area to obtain a calibration line (trend line of general form, Equation 3.1, Appendix 10.5).

Equation 3.1

$$Peak\ area\ =\ slope \times gaseous\ concentration\ contaminant;\ [\mu v.min]$$

The gas contaminant concentrations obtained from the GC were calculated to number of moles to obtain qualitative results (Equation 3.2).

Equation 3.2

$$n = \frac{\dfrac{C_g^i}{1000}}{M_{wt}^i};\ [mol\ L^{-3}]$$

3.4 Experimental setup pressure experiments

Two kinds of pressure experiments were performed in this research. The first experiment evaluated the sampling method. The second experiment evaluated the effect of a pressure increase on the phase transition of contaminants in the gas phase when a liquid phase was present. In both experiments it was assumed the gas concentration of contaminant was evenly distributed in the headspace. For the experiments, 250 ml batches were used and capped with viton septa (20 mm standard aluminum seals). It was assumed all batch volumes were similar.

1. *Sampling method (pressure influence)*

A volume of 13 µl pure phase (V_p) was injected into the batch. The pure phase concentration [mol] put in the batch was calculated using Equation 3.3.

Equation 3.3

$$n = \frac{V_p \rho}{M_{wt}^i};\ [mol]$$

The amounts of pure TCE and toluene injected in the batches were respectively 1.44×10^{-4} and 1.22×10^{-4} mol.
For ten seconds the batch was shaken. After five minutes, to make sure the contaminant was fully volatilized, gas samples were collected. The gas samples were collected at different pressures. These different pressures were obtained in the batch by injecting a volume of air in the batch. Sampling was done for 0, 70, 190 and 250 ml of added air.
Due to higher partial pressures in the batch by injecting air, the gaseous contaminant concentration measured had to be corrected for dilution. This

correction was calculated assuming ideal gas behavior (Equation 3.4).

$$P_g^{atm} V_g = n_g RT$$

The universal gas constant (R) is 8.3145 J mol^{-1} K^{-1} (NVON-commission 2004). The parameter n_g was the number of moles present at atmospheric pressure (P_g^{atm}). This means the total amount of moles gas present in the batch; the amount of moles contaminant and air. The correction factor (C) due to higher partial pressures (P_g^*) was calculated in Equation 3.8 using Equation 3.4, 3.5, 3.6 and 3.7. The star (*) in the equations is used to represent a new situation.

$$n_g + n_{air\_added} = \frac{P_g^* V_g}{RT} = \frac{P_g^{atm} V_g^*}{RT}; \ [mol]$$

The number of air molecules added to the batch was derived from the pressure measured ($P_2 - P_1$), Equation 3.6.

$$n_{air\_added} = \frac{((P_2 - P_1)V_{batch})}{RT}; \ [mol]$$

By adding air to the batch the initial condition was changed; higher total amount of moles were present in the batch. This changed condition corrected for a higher partial pressure should be the same with reference to the initial condition (Equation 3.7).

$$\frac{n^{TCE}}{V_g^*} \times C = \frac{n^{TCE}}{V_g} \rightarrow$$

$$n^{TCE} V_g C = n^{TCE} V_g^* \rightarrow$$

$$n^{TCE}\left(\frac{n_g RT}{P_g^{atm}}\right)C = n^{TCE}\left(\frac{n_g + n_{air\_added}}{P_g^{atm}}\right)RT$$

$$C = \frac{n_g + n_{air\_added}}{n_g} = 1 + \frac{n_{air\_added}}{n_g} = 1 + \frac{\dfrac{((P_2 - P_1)V_{batch})}{RT}}{\dfrac{P_g^{atm} V_g}{RT}} = 1 + \frac{((P_2 - P_1)V_{batch})}{P_g^{atm} V_g}; \ [-]$$

Equation 3.9

$$n_{corrected} = n_{measured} \times C; \ [\text{mol}]$$

The measured amount of mol contaminant present in the gas phase ($n_{measured}$) corrected for a higher partial pressure (Equation 3.9) should be the same as the initial condition calculated (Equation 3.3). So, if $n_{measured}$ was not similar to n_g (Equation 3.4) a correction for sampling was obtained.

2. *Effect pressure increase on amount of gaseous contaminant (phase transition)*
   In this experiment a volume of 0.8 ml pure phase was injected into the batch. For ten seconds the batch was shaken and gas samples were collected after 110 minutes. It was assumed after 110 minutes equilibrium was reached between the liquid phase and gas phase. During the experiment, pure phase was present in the batch. This means the amount of moles of contaminant in the gas phase increased with the injection of air (increased partial pressure). Therefore no dilution took place in this experiment and no correction factor had to be obtained. Sampling was done for 0, 70, 190 and 250 ml of added air.

3.5 Experimental setup vapor pressure experiments

To obtain an answer on which contaminant, TCE or toluene has a higher potential for stripping with CO_2, vapor pressure experiments were done. These experiments were done using batches of 0.5 L. This volume was assumed to be similar for all batches used. The batches were flushed for two minutes with CO_2 or air. Flushing was done by closing the batch with a viton septum and a silicone septum for inserting the needle. Next, a needle connected to a gas tap (air or CO_2) was inserted through the septa to inject gas. Another needle was inserted through the septa to release gas and therefore overpressure in the batch.

After flushing, 1.5 ml pure phase of TCE or toluene was injected. Directly after injecting the pure phase, gas samples were collected. The gas samples were collected at 0, 5, 30, 120 and 240 minutes after the injection of pure phase. With the gaseous contaminant concentrations obtained (C_g^i), the average vapor pressure (P_g^i) was calculated using Equation 3.10 (Mayer and Hassanizadeh 2005).

Equation 3.10

$$C_g^i = \frac{P_g^i \times M_{wt}^i}{RT}; \ [\text{ML}^{-3}]$$

3.6 Experimental setup batch experiments

The batch experiments consisted of batches (volume dependent on batch used, $\pm$ 1 L) with sediment. These batches contained dissolved TCE and toluene of 10% of the maximum solubility (Table 3.1). This amount of dissolved TCE and toluene in groundwater represents the fact pure phase of NAPL is present in the soil and was therefore chosen to be a representative value for the experiments (Nipshagen and Praamstra 2007).

The sediment that was used in these experiments was gravel. This gravel had a specific grain size distribution with a median grain size of 8.411 mm (Figure 3.2).

Parameter	Value
d_{50} [mm]	8.411
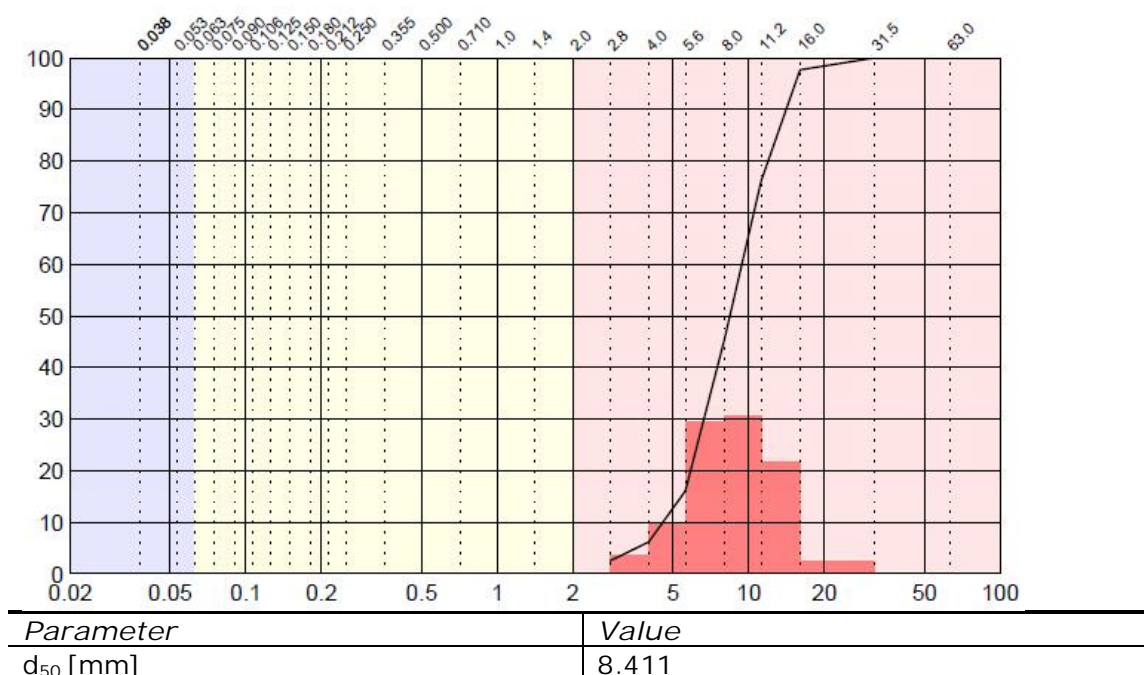
Figure 3.2 Grain size distribution. On the x-axis the diameter [mm], on the y-axis cumulative amount of particles [%]

The batches were closed with viton rubber and a silicone septum. Due to practical reasons the final measurement of the experiments was done after three hours. This experimental duration was obtained by trial and error, to obtain an equilibrium concentration between the liquid phase and headspace in the closed batch systems. The second practical reason was the fact the duration time of the experiment had to be short as possible to obtain more results and therefore a higher accuracy.

3.6.1 Preparation batch experiment

The experiments consisted of two identical batches next to each other. One batch contained the Ecogrout process attached to a pressure device. The other batch contained the Ecogrout process with contamination. The reason for performing the experiment in duplo was because the pressure device that was used might not be contaminated with substances such as TCE and toluene (Appendix 10.3).

The batches were prepared in the following sequence (more detailed in Appendix 10.6):

1. Stock solutions were made
2. The calculated amount of sediment was put in both batches
3. Stock solution $CaCl_2$ was added to both batches
4. Stock solution $NaHCO_3$ was added to the Ecogrout batch
5. The Ecogrout batch was connected to the pressure device
6. The batch was shaken for ten seconds, relative pressure was constantly measured
7. Stock solution $NaHCO_3$ + contamination was added to the contaminated batch and shaken for ten seconds

   The contaminants were dissolved in the $NaHCO_3$ stock solution, because the volume of $NaHCO_3$ was calculated to be larger than the pore volume. Due to this larger volume of $NaHCO_3$ the contamination could be evenly distributed along the pores. The $NaHCO_3$ stock solutions with contamination were made

in vacuum bags (Supelco analytical, screw cap valve 1 L, Appendix 10.3), to obtain no exchange between the aqueous contaminant concentration and the gas phase.

8. Contaminated batch: concentration of gaseous contaminant was measured at 0, 10, 30, 45, 60, 180 min
9. A calibration line was made
10. Concentration liquid phase contaminant was measured in the vacuum bag

The setup of the experiment can be seen in Figure 3.3.

In Figure 3.3 the setup of the experiments is presented. One batch was standing on the pressure device and contained the Ecogrout process. The batch next to the pressure device contained contaminants and was not connected to the pressure device.

Figure 3.3 Setup batch experiments

3.6.2 CO_2 degassing

A pressure device was attached to the Ecogrout batch to measure constantly the relative pressure in the batch. With this relative pressure the CO_2 production in the batch was calculated using Equation 3.11.

Equation 3.11

$$CO_2 \ production = \frac{P_{real}}{RT} - \frac{P_{atmosphere}}{RT}; [\text{mol L}^{-3}]$$

The parameters for calculating the CO_2 production were calculated using Equation 3.12 and 3.13 and were used in Equation 3.11 to obtain the CO_2 production. The parameter, P_{real}, in this equation was calculated using the pressure device. The pressure device measured a relative pressure [-]. This pressure was converted to a real pressure [Pa] using a calibration line. The calibration line was made by injecting different volumes of air in closed vials. After this the pressure in these vials was calculated using Equation 3.12.

Equation 3.12

$$P_{calculated} \ = \ \frac{volume\_bottle \ + \ added\_volume\_injected}{volume\_bottle} \times 101325; [\text{ML}^{-1}\text{T}^{-2}]$$

The calculated pressures were plotted versus the measured values from the pressure device and a trend line was added (Equation 3.13, Appendix 10.7).

Equation 3.13

$$P_{real} = measured\_pressure \times slope + intercept; [ML^{-1}T^{-2}]$$

3.6.3   Stock solutions

The highest concentrations used in this research were 478 mM $CaCl_2$ (Merck):750 mM $NaHCO_3$ (99%, Alfa Aesar). The lowest concentrations used were 319 mM $CaCl_2$:500 mM $NaHCO_3$. These concentration values were obtained by trial and error of the Ecogrout process in relation to batch volume. Goal was to obtain a measurable pressure increase in the batch and visually see $CaCO_3$ formation. Furthermore the pressure device was not able to measure a relative overpressure increase higher than 2 atm and the time interval had a minimum of 5 seconds. The experiment was done using dissolved $CaCl_2$ and $NaHCO_3$ with theoretical real concentrations of respectively 1014 mM and 1190 mM (Appendix 10.8). The reason for using dissolved phases instead of solid material is described below.

The $NaHCO_3$ stock solutions had a concentration close to the maximum solubility of $NaHCO_3$. The highest concentration $CaCl_2$:$NaHCO_3$ used in the batch experiments was limited to this maximum solubility of $NaHCO_3$. Both the concentrations of $CaCl_2$ and $NaHCO_3$ were limited to the volume ratio of 37% $CaCl_2$:63% $NaHCO_3$. It was thought using solid material of $NaHCO_3$ and $CaCl_2$ the concentration of $NaHCO_3$ in the experiment was not limited anymore (Figure 3.4, Appendix 10.9).
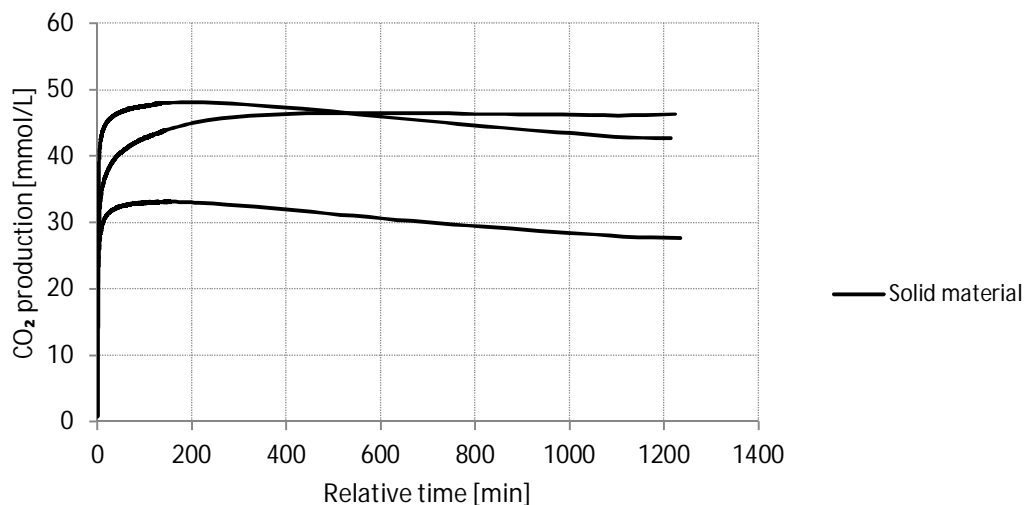
Figure 3.4 Experiment solid material 478 mM $CaCl_2$:750 mM $NaHCO_3$, 20.8°C. The experiment was performed in triplo.

Observed from Figure 3.4 a large variance within the triplo experiment was obtained. This means the reproducibility of the experiment using solid material was low. During the experiment it was observed the reaction was highly dependent on the shaking process of 10 seconds. A difference in intensity of shaking had an influence on the CO_2 produced. It was therefore decided to perform the experiment using dissolved phases of $CaCl_2$ and $NaHCO_3$.

However in the case of using dissolved phases the CO_2 production was limited due to the maximum solubility of $NaHCO_3$. It was not known from the research experiments performed whether the Ecogrout reaction was limited by the concentrations 478 mM $CaCl_2$:750 mM $NaHCO_3$ used. Therefore an experiment was done using 957 mM $CaCl_2$:1500 mM $NaHCO_3$ for solid material (Figure 3.5, Appendix 10.9).

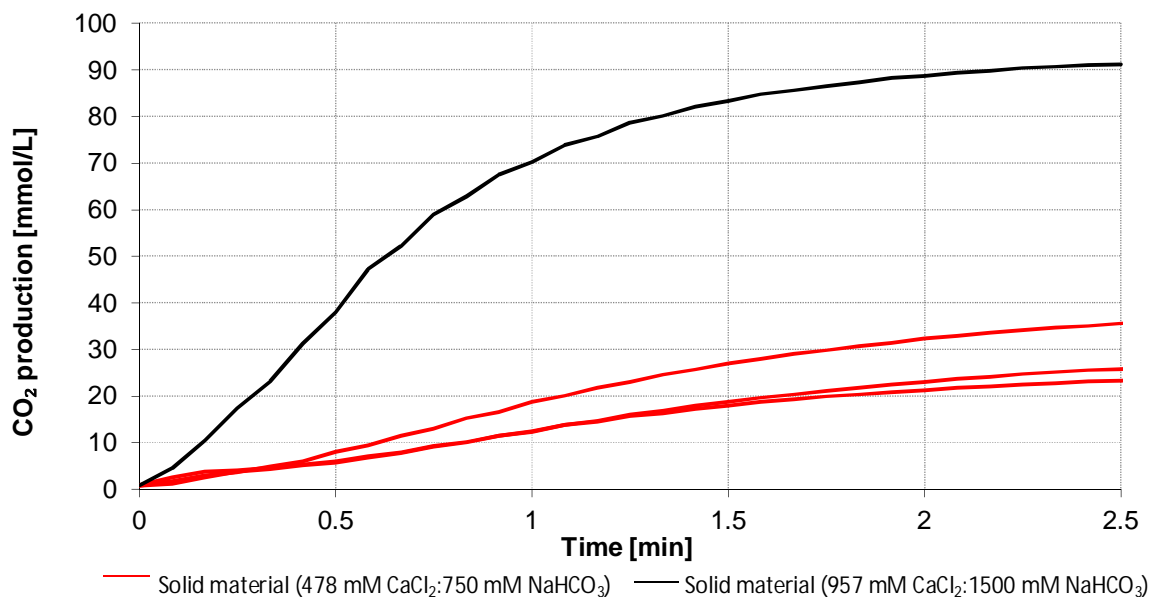Figure 3.5 CO_2 production solid material concentration ratio 957 mM $CaCl_2$:1500 mM $NaHCO_3$ and concentration ratio 478 mM $CaCl_2$:750 mM $NaHCO_3$, 20.2°C. The experiment was performed in triplo.

Conclusion of the experiment with a higher concentration of $CaCl_2$ and $NaHCO_3$ was the fact the Ecogrout process was not limited to the concentrations used in this research. However due to the lack of reproducibility using solid material it was chosen to perform the experiment using dissolved $NaHCO_3$ and $CaCl_2$.

Due to the fact the $NaHCO_3$ stock solution was close to the maximum solubility of $NaHCO_3$ not all solid material was dissolved properly. Therefore the suspension was stirred for one day and was filtrated through glass fiber. Then the concentration of the solution was measured using titration (Mettler Toledo, DI50 graphix, Appendix 10.3). The concentration could alter between different stock solutions due to changes in temperature in the lab. The volume of the stocks needed to make the concentrations of $CaCl_2$ and $NaHCO_3$ were dependent on the batch used and the real concentration measured for $CaCl_2$ and $NaHCO_3$. Therefore the volume was calculated for each batch separately (Appendix 10.8 and 10.10). The molarity measured for $CaCl_2$ was 1293 mM instead of the theoretical maximum concentration (Dionex ICS-3000, Appendix 10.3). This increase in molarity was probably due to higher temperatures. The volatilization rate i.e. reference experiment consisted of exclusively $NaHCO_3$ stock solutions.

The ionic strength for the stock solutions used can be calculated using the charge of the ions (z_i) present and molarity (c_i) (Equation 3.14) (Solomon 2001). This ionic strength was calculated at equilibrium concentrations.

Equation 3.14

$$I = \frac{1}{2}\sum c_i z_i^2 \, ; [\text{mol L}^{-3}]$$

3.6.4 Concentration liquid phase contaminant in vacuum bag

The concentration of the liquid contaminant phase in the vacuum bags was measured to compare the results for different vacuum bags (Varian CP-3800+CTC analytics combipal (2), Appendix 10.3). This liquid concentration was measured using a calibration line for TCE and toluene (Appendix 10.11). For these calibration lines stock solutions of 1000 mg/L TCE and 1000 mg/L toluene dissolved in methanol were made. Using the internal standard (1,2-Dibromoethane dissolved in acetone) a corrected value for the liquid contaminant concentration was given (Appendix 10.4). With this liquid contaminant concentration the actual contaminant concentration in the liquid phase (C_w^i) was calculated using Equation 3.15.

Equation 3.15

$$C_w^i = \left(\left(\frac{corrected\_concentration}{1000} \right) \times 8.035 \Big/ volume \right) \times 1000; \ [\text{mg/L}]$$

The value of 8.035 was the total volume [ml] of liquid phase in the working vial (22 ml headspace vial). Eight ml of this volume consisted of MilliQ water and stock solution in different ratios. The other 35 µl consisted of mercury chloride (HgCl) and 1,2-Dibromoethane dissolved in acetone. The parameter volume in the equation was the amount of liquid from the vacuum bag added to the vial. A correction factor was obtained by the difference between the liquid contaminant concentration measured (C_w^i) in the vacuum bag and the calculated liquid contaminant concentration that should be present in the bag. The liquid contaminant concentrations measured for all vacuum bags, were lower compared with the calculated concentrations based on literature values. When this was observed experiments were done measuring the maximum solubility of TCE and toluene dissolved in the NaHCO$_3$ stock solution. The maximum solubility for TCE and toluene measured in NaHCO$_3$ was 331.35 mg/L for TCE and 124.29 mg/L for toluene. The calculations done in this research were corrected for these lower maximum solubilities.

4   Results

The research objective was divided in three sub questions. To answer the sub questions, various experiments were performed. The results of these experiments are explained below.

4.1   The influence of pressure increase on gaseous contaminant

The Ecogrout process increased the pressure within the closed batch systems due to CO_2 production. Two experiments were performed evaluating the possible consequences of this pressure increase. The first experiment contained the evaluation of the sampling method used for taking gas samples under pressure. The second experiment was done to obtain the influence of pressure on the gas concentration if a liquid phase was present. The maximum change in headspace volume by taking gas samples was about $4.0 \times 10^{-3}\%$. This inaccuracy was assumed to be negligible.

4.1.1   Sampling method (pressure influence)

The results of the sampling method experiment are shown in Figure 4.1 and 4.2 for respectively TCE and toluene.
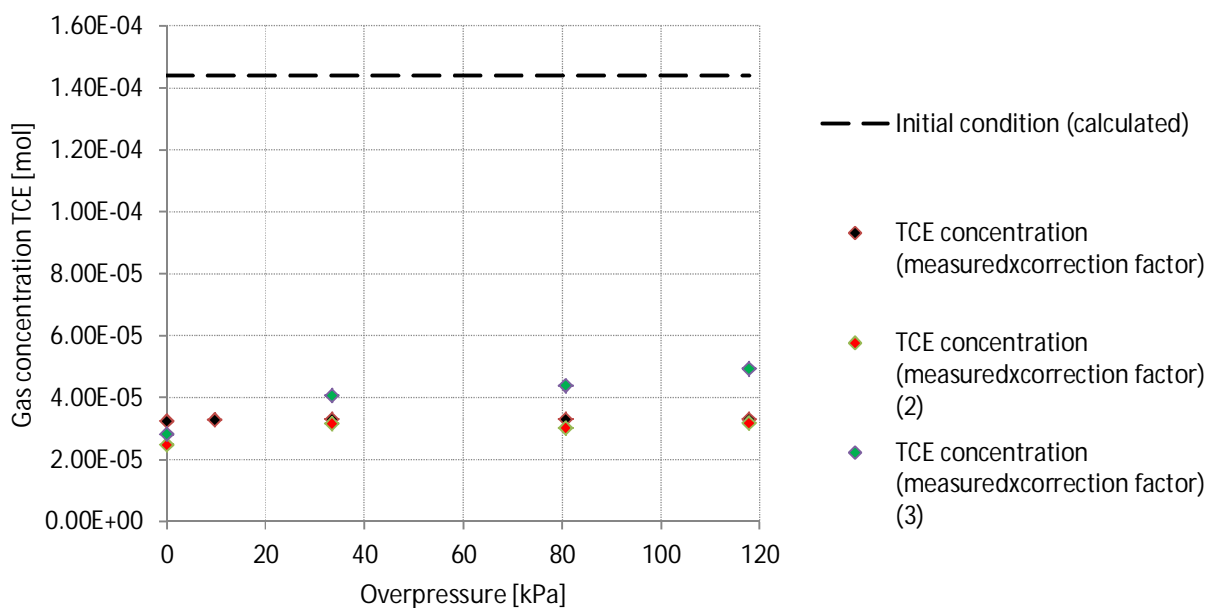
Figure 4.1 Pressure influence on sampling method TCE, 20.5°C. The test was performed in triplo.
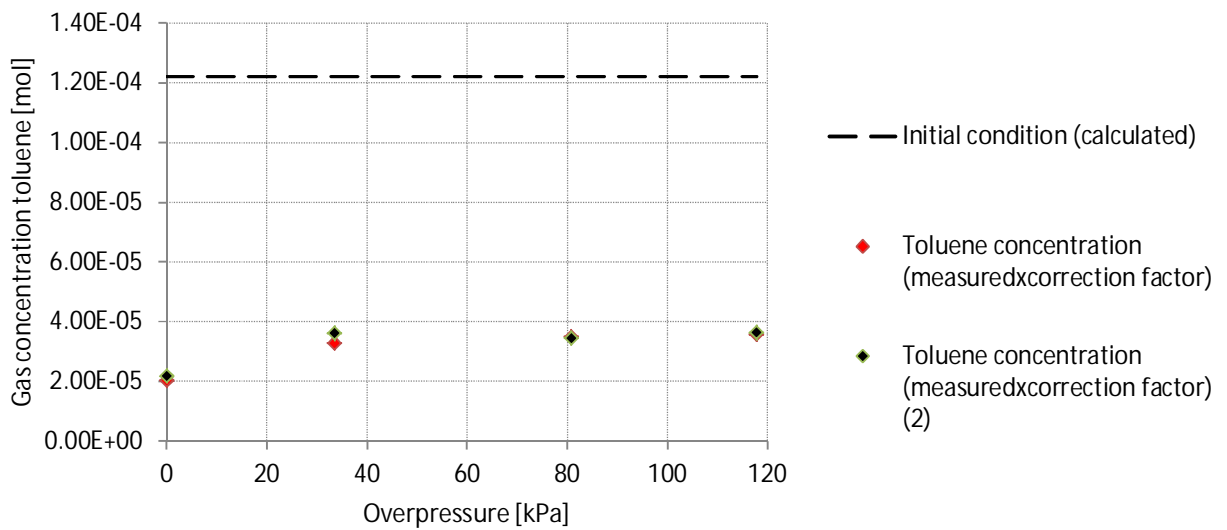
Figure 4.2 Pressure influence on sampling method toluene, 21°C. The test was performed in duplo.

The measurements (red, black, blue rhombs) shown in Figures 4.1 and 4.2 were measured gaseous contaminant concentrations corrected for dilution with air molecules according to Equation 3.9. The initial condition represents the calculated gaseous contaminant concentration of pure phase injected in the batch. It was observed from Figures 4.1 and 4.2 the initial condition of both gas contaminant concentrations present in the batch (black interrupted line) was not measured. The measurements for TCE gas were an average factor 4.35 ± 0.75 lower compared with the initial condition. For toluene gas this factor was 4.07 ± 1.09. This factor was in general constant and did not increase or decrease with increase of pressure from overpressure of more than 35 kPa. The results of the following experiments (influence pressure increase on phase transition contaminant, vapor pressure experiments and batch experiments) were multiplied by the correction factors of 4.35 for TCE and 4.07 for toluene.

4.1.2 The influence of pressure increase on the phase transition of TCE and toluene

Figures 4.3 and 4.4 show the results of the pressure influence on phase transition for TCE and toluene.
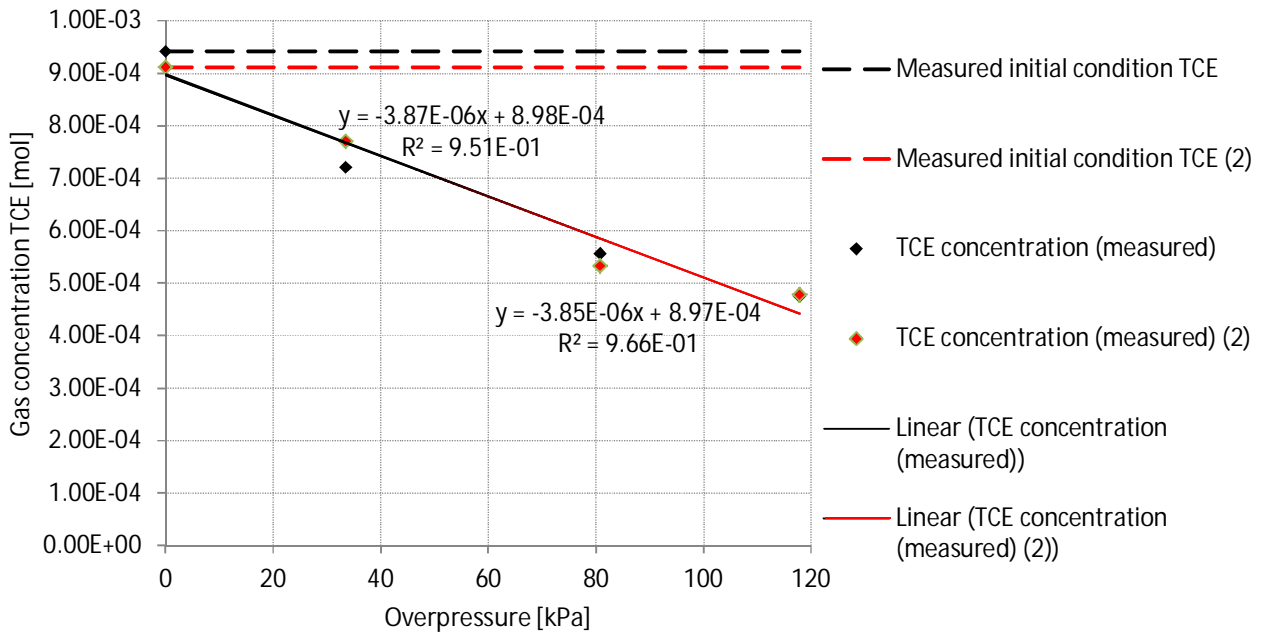
Figure 4.3 Pressure influence on phase transition, TCE, 20.6°C. The test was performed in duplo.
Note: the general trend line obtained for TCE is the same for the duplo experiment
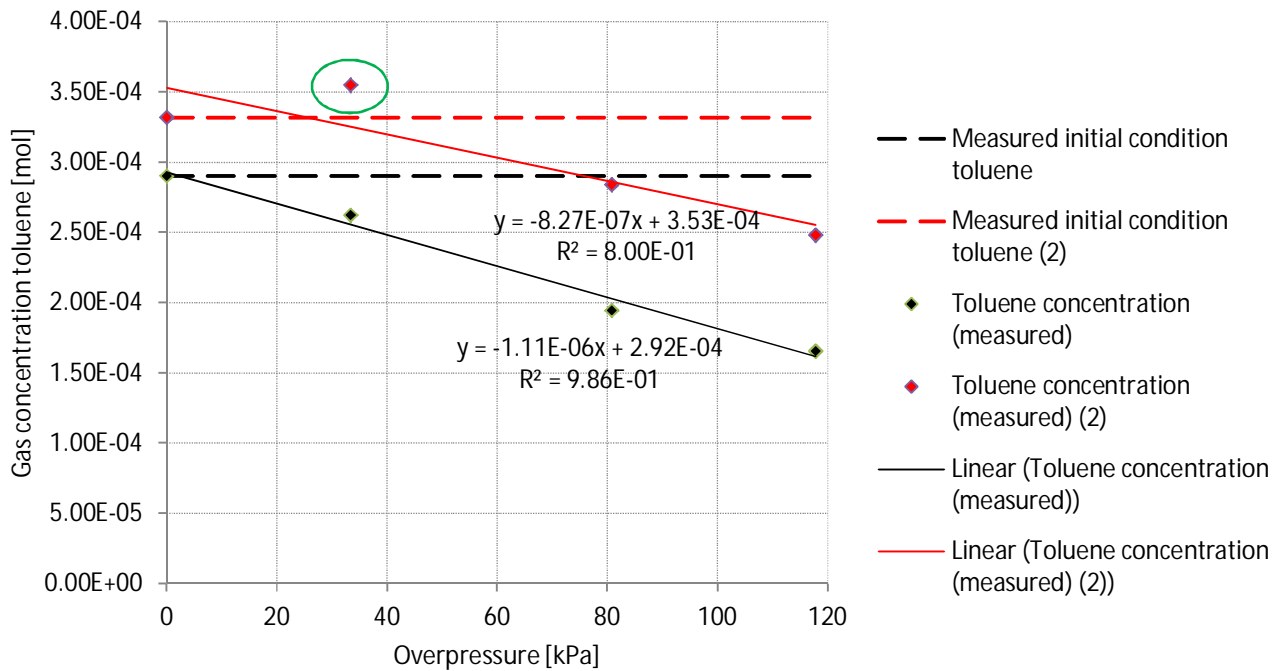

Figure 4.4 Pressure influence on phase transition, toluene, 20.7°C. The test was performed in duplo.

For both TCE and toluene an increase in pressure caused a decrease in gas concentration. The concentration of TCE decreased with factor 1.8 for a pressure increase with factor two. For toluene the trend lines were not similar. The results

obtained show a large variance between measurements. Therefore the relation between pressure and toluene gas concentration was calculated for both trend lines individually. For the first trend line (black measurements) the toluene gas concentration decreased with factor 1.6 with a pressure increase of factor two. For the second trend line (red measurements) this gas concentration decreased with a factor 1.3. The average decrease of toluene gas concentration was therefore 1.45. The pressure in the experiments increased in total with about 120 kPa. Therefore the contaminant gas concentrations were decreased with factor 2.1 (TCE) and 1.7 (toluene).

One measurement for toluene had a gas concentration above the measured initial gas concentration (green encircled in Figure 4.4). This measurement was probably affected by changing environmental conditions, sampling conditions or changes in GC conditions. The measurement above the initial gas concentration had an influence on the toluene trend line obtained. The trend line obtained is therefore an underestimation of the general trend obtained.

4.2   Stripping potential TCE and toluene with CO_2

The maximum inaccuracy obtained by taking gas samples was 2.5×10^{-3}% and was assumed to be negligible. In Figure 4.5 the uptake of organic contaminants (TCE and toluene) by air and CO_2 was obtained. It was assumed at the final measurement (240 minutes) equilibrium was reached between the headspace and liquid phase. Different results were obtained by performing the experiment. The first result contained a higher uptake of TCE in air and CO_2 compared with the uptake of toluene for both gasses. Secondly no clear difference between the uptake of a similar contaminant in air or CO_2 could be observed from the experiment. So it is assumed the ideal gas law may be used for calculations. The inaccuracy of TCE in air at equilibrium was at least 4.3×10^{-4} mol. The inaccuracy for toluene was at least 1.4×10^{-4} mol. The equilibrium gas concentrations measured for TCE and toluene in CO_2 were within these inaccuracies of the air measurements. Furthermore there were two peaks for the uptake of TCE in air observed (green encircled, Figure 4.5). It was first thought these higher measurements could be interpreted by the fact more gas was present (more flushing) in the batch and therefore more uptake of contaminants took place. However this interpretation contradicted the results obtained at the influence of pressure experiment on the phase transition of contaminants. So probably the two peaks obtained were affected by measurement errors and changing environmental conditions. At last a large variance between the duplo results of the experiments can be observed.

From the equilibrium gaseous contaminant concentrations, the average vapor pressure was determined using Equation 3.10 (Table 4.1).

Contaminant	Vapor pressure air [Pa]	Vapor pressure CO_2 [Pa]
TCE	6240	6019
Toluene	2389	2404

Table 4.1 Calculated vapor pressures for air and CO_2

The vapor pressure of TCE in CO_2 was about a factor 2.5 higher compared with toluene. This vapor pressure experiment at atmospheric pressure was assumed to be representative for the batch experiments with an overpressure of max. 120 kPa.
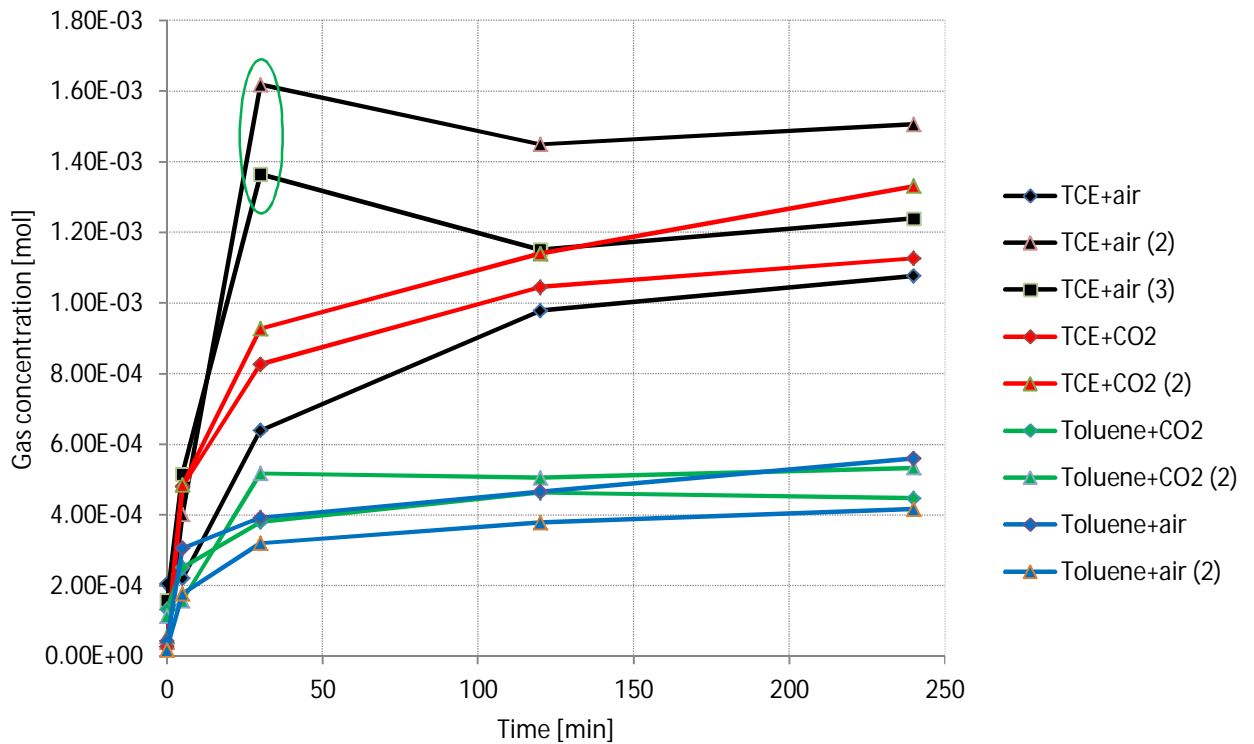
Figure 4.5 Uptake volatile organic contaminants by air and CO_2, different temperatures. The experiment was performed in duplo.

4.3 Influence concentration $CaCl_2$ and $NaHCO_3$ on gaseous contaminant

The CO_2 produced during the Ecogrout process was different for both concentrations of $CaCl_2$ and $NaHCO_3$ used in this research. Figure 4.6 shows the CO_2 production for the Ecogrout process (more detailed in Appendix 10.12).
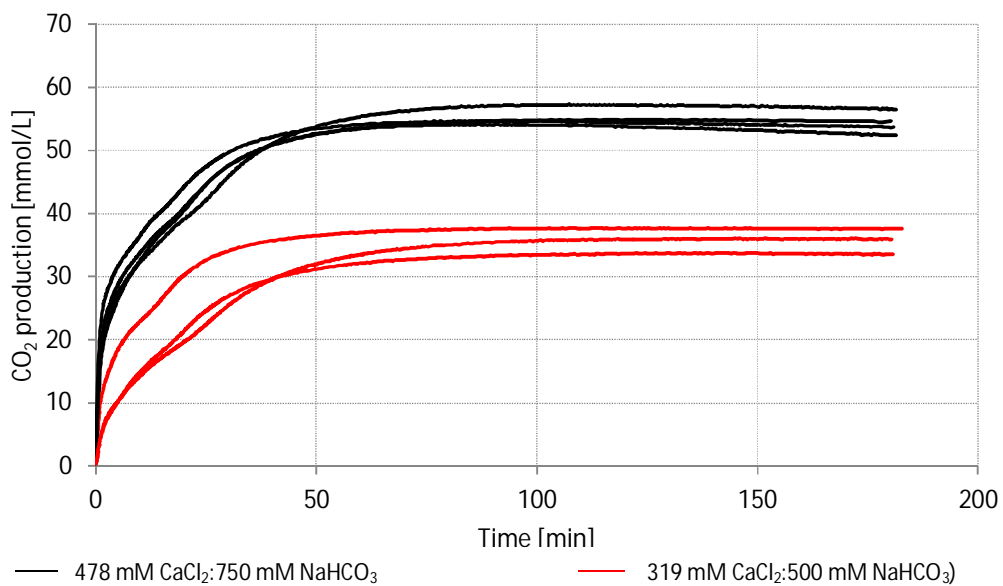
Figure 4.6 CO_2 production both concentrations $CaCl_2$:$NaHCO_3$ used, different temperatures

The batch system behaved the first minute as an open system and showed an infinite increase in CO_2 produced (Figure 4.6). Due to the fact the system was closed and the $CaCO_3$ precipitation was limited a decreasing release of CO_2 to the gas phase with time was observed.

Two parameters of the CO_2 production were important for evaluating the stripping potential. These parameters included the CO_2 production velocity and equilibrium concentration. The CO_2 production velocities were calculated from 1 to 30 minutes, to eliminate the open system situation. It was assumed after 180 minutes equilibrium was reached. Both parameters for the CO_2 production are shown in Table 4.2.

Concentration	Average CO_2 production velocity $\left[\dfrac{\text{mmol L}^{-1}}{\text{min}}\right]$	Average equilibrium CO_2 concentration [mmol/L]
319 mM $CaCl_2$:500 mM $NaHCO_3$	0.78±0.05	35.7±2.05
478 mM $CaCl_2$:750 mM $NaHCO_3$)	1.02±0.07	54.3±1.72

Table 4.2 Parameters CO_2 production

The ionic strengths (Equation 3.14) for the different concentrations of $CaCl_2$ and $NaHCO_3$ used were different. The highest concentrations $CaCl_2$:$NaHCO_3$ used had an ionic strength of 5.184 mol L^{-1}. For the lowest concentrations $CaCl_2$ and $NaHCO_3$ used the ionic strength was 2.907 mol L^{-1}. The ionic strength of the volatilization rate was 3.614 mol L^{-1}. So the stock solutions are saline (Dead sea ionic strength of 9.4 (Appelo and Postma 2005)) and in the same order of magnitude.

Due to precipitation of $CaCO_3$ in the Ecogrout process, the total headspace volume changes. It was assumed the liquid volume stayed constant and the volume of precipitates changed. For an average liquid volume of 173 ml and the highest CO_2 production applied (assuming ratio 1 CO_2:1 $CaCO_3$):

$$\left(\frac{54.3}{1000}\right)\times 0.173 = 9.39\times10^{-3} \text{ mol}$$

$$9.39\times10^{-3}\times100.1 = 0.939 \text{ g }^1$$

$$\frac{0.939}{2.7} = 0.348 \text{ ml}^2$$

Using the radius of the batches (9.5 cm) the precipitate level increased with:

$$\frac{0.348}{\pi r^2} \rightarrow \frac{0.348}{\pi \times 9.5^2} = 1.23\times10^{-3} \text{ cm}$$

So the precipitation of $CaCO_3$ decreased the headspace with 1.23×10^{-3} cm. It was assumed this decrease of headspace was negligible. Consequently also the increase in precipitate level of lower stock solution concentrations of $NaHCO_3$ and $CaCl_2$ was assumed to be negligible.

---

[1] (NVON-commission 2004), assuming the stable mineral calcite was formed in the Ecogrout process

[2] (NVON-commission 2004), assuming the stable mineral calcite was formed in the Ecogrout process

The gas concentrations of TCE and toluene were measured during the CO_2 production from Ecogrout. The inaccuracy obtained by taking gas samples was maximum 1.8×10^{-3}% and assumed to be negligible. The average measured gaseous contaminant concentrations for TCE and toluene are given in Figure 4.7 (more detailed in Appendix 10.13).
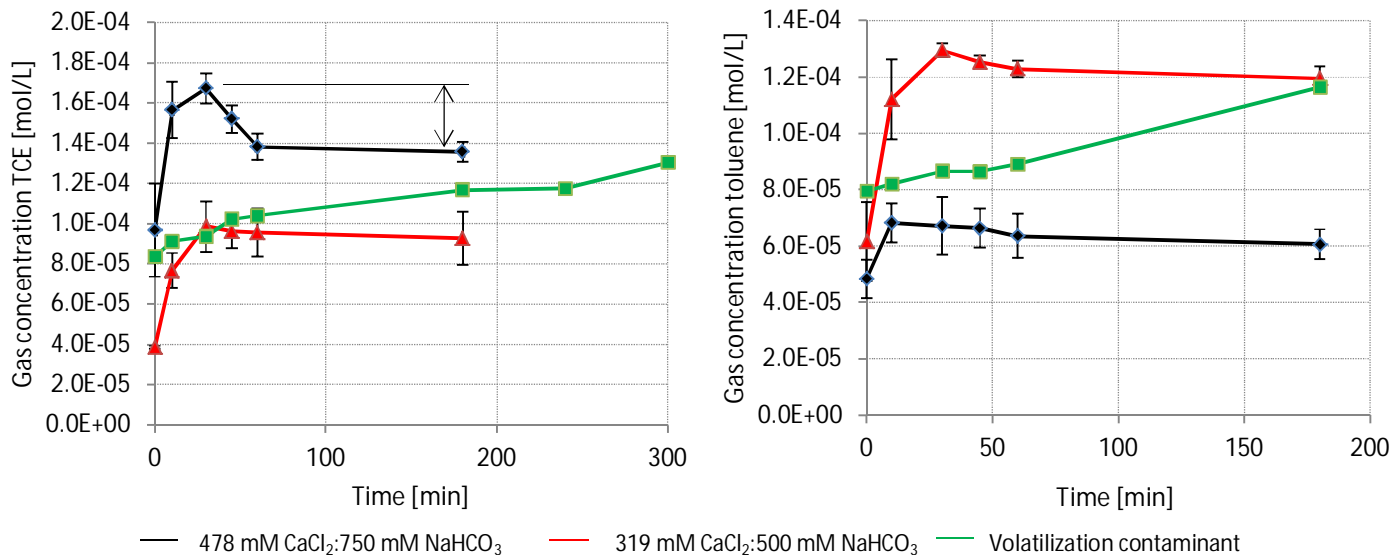

Figure 4.7 Stripping of TCE (left figure) and toluene (right figure)
Note: values are expressed as means ± standard deviation (n=3). For the volatilization graph values are expressed as means to obtain clear results

When the results obtained (Figure 4.6 and 4.7) were combined it was observed in general until about 30 minutes the stripping of TCE was proportional with the CO_2 production. After 30 minutes the CO_2 production was slightly increased while the stripping of contaminants was decreased. After about 60 minutes it was assumed the concentration of contaminants in the gas phase was in equilibrium with the liquid phase. However equilibrium of the CO_2 production was reached at about 70 minutes.

Different results were obtained for TCE and toluene in the batch experiments (Figure 4.7). For a higher CO_2 production, gaseous TCE had a higher peak concentration with reference to the equilibrium concentration (Table 4.2 and 4.3) compared with toluene. An example of the peak concentration with reference to the equilibrium concentration is shown with an arrow in Figure 4.7. It was assumed equilibrium was reached at the final time of the experiment (180 minutes). Also a higher stripping velocity and higher equilibrium concentration compared with a lower CO_2 production were observed (Table 4.2 and 4.3). The results obtained for TCE were contradictive with the results obtained for toluene. The maximum concentration with reference to the equilibrium concentration, stripping velocity and equilibrium concentration for lower CO_2 production rates were higher compared with higher production rates (Table 4.2, 4.3). Furthermore a difference between the first point measurements i.e. initial condition for both concentrations in $CaCl_2$ and $NaHCO_3$ was observed (sequence of red, green, black for TCE; sequence of red, green, black for toluene in Figure 4.7). The initial condition of TCE for higher CO_2 productions was higher compared with lower CO_2 productions. This difference was reversed for toluene. However for both contaminants almost a constant deviation for both CO_2 concentrations was measured. For TCE the lowest concentration $CaCl_2$:$NaHCO_3$ used

was an average factor 5.81×10^{-5} lower. For toluene the initial condition deviated from the rest, but when this concentration was left out the low concentration of $CaCl_2$:$NaHCO_3$ used was an average factor 5.67×10^{-5} higher than higher CO_2 production rates.

In Table 4.3 the parameter values are given for high CO_2 production rates for both TCE and toluene.

Parameter	TCE	toluene
Average equilibrium concentration [mol/L]	$1.36 \times 10^{-4} \pm 4.90 \times 10^{-6}$	$6.06 \times 10^{-5} \pm 5.35 \times 10^{-6}$
Average maximum concentration [mol/L]	$1.67 \times 10^{-4} \pm 7.35 \times 10^{-6}$	$6.71 \times 10^{-5} \pm 1.04 \times 10^{-5}$
Average maximum concentration with reference to equilibrium [mol/L]	$3.15 \times 10^{-5} \pm 6.57 \times 10^{-6}$	$6.58 \times 10^{-6} \pm 5.40 \times 10^{-6}$
Average stripping velocity $\left[\dfrac{mol}{min\,L} \right]$	$2.35 \times 10^{-6} \pm 7.60 \times 10^{-7}$	$6.29 \times 10^{-7} \pm 2.57 \times 10^{-7}$

Table 4.3 Parameter values for high CO_2 production rates (478 mM $CaCl_2$:750 mM $NaHCO_3$)
Note: different molecular weights (Table 3.1)

The stripping velocity was obtained by calculating the increase of gaseous contaminant until the peak concentration at 30 minutes. Because the average velocity was taken over the first 30 minutes, the stripping velocity was an underestimation. In Table 4.4 the parameter values are given for low CO_2 production rates.

Parameter	TCE	toluene
Average equilibrium concentration [mol/L]	$9.28 \times 10^{-5} \pm 1.31 \times 10^{-5}$	$1.20 \times 10^{-4} \pm 4.22 \times 10^{-6}$
Average maximum concentration [mol/L]	$9.86 \times 10^{-5} \pm 1.25 \times 10^{-5}$	$1.30 \times 10^{-4} \pm 2.30 \times 10^{-6}$
Average maximum concentration with reference to equilibrium [mol/L]	$5.84 \times 10^{-6} \pm 2.94 \times 10^{-6}$	$1.00 \times 10^{-5} \pm 1.92 \times 10^{-6}$
Average stripping velocity $\left[\dfrac{mol}{min\,L} \right]$	$2.01 \times 10^{-6} \pm 4.42 \times 10^{-7}$	$2.27 \times 10^{-6} \pm 3.96 \times 10^{-7}$

Table 4.4 Parameter values for low CO_2 production rates (319 mM $CaCl_2$:500 mM $NaHCO_3$)
Note: different molecular weights (Table 3.1)

It was also observed the average volatilization of both contaminants (without the Ecogrout process) increased linear with time and was still increasing at the final time of the experiment (Figure 4.7). The average volatilization was obtained by dissolved

contaminants within $NaHCO_3$ stock solutions. The initial volatilization concentration of TCE was higher than the stripping with low CO_2 productions and was almost similar to the stripping with high CO_2 concentrations. The entire graph of the volatilization for TCE was higher compared with stripping for low CO_2 concentrations. For toluene the initial volatilization concentration measured was higher than the stripping with high CO_2 concentrations. This was the case for the entire volatilization graph. In Table 4.5 the parameters average velocity and average concentration at 30 minutes are given for the volatilization graph. Also this velocity was calculated from zero to 30 minutes.

Parameter	TCE	toluene
Average concentration at 30 minutes [mol/L]	$9.37 \times 10^{-5} \pm 1.53 \times 10^{-5}$	$8.66 \times 10^{-5} \pm 2.84 \times 10^{-5}$
Average volatilization velocity $\left[\dfrac{mol}{min\ L} \right]$	$3.37 \times 10^{-7} \pm 1.46 \times 10^{-7}$	$2.36 \times 10^{-7} \pm 2.42 \times 10^{-7}$

Table 4.5 Parameters volatilization graph
Note: different molecular weights (Table 3.1)

In Table 4.6 the difference in parameters due to stripping is given (stripping–volatilization). A negative value represents a decrease in parameter.

CO_2 production	Parameter	TCE	toluene
Low	Average concentration at 30 minutes [mol/L]	$4.92 \times 10^{-6} \pm 1.97 \times 10^{-5}$	$4.34 \times 10^{-5} \pm 2.85 \times 10^{-5}$
	Average velocity $\left[\dfrac{mol}{min\ L} \right]$	$1.67 \times 10^{-6} \pm 4.66 \times 10^{-7}$	$2.03 \times 10^{-6} \pm 4.64 \times 10^{-7}$
High	Average concentration at 30 minutes [mol/L]	$7.33 \times 10^{-5} \pm 1.70 \times 10^{-5}$	$-1.95 \times 10^{-5} \pm 3.02 \times 10^{-5}$
	Average velocity $\left[\dfrac{mol}{min\ L} \right]$	$2.01 \times 10^{-6} \pm 7.74 \times 10^{-7}$	$3.93 \times 10^{-7} \pm 3.54 \times 10^{-7}$

Table 4.6 Difference parameters due to stripping
Note: different molecular weights (Table 3.1)

It can be observed from Table 4.6, using CO_2 TCE was stripped with a higher velocity from solution versus in absence of CO_2 (volatilization rate). For toluene using low CO_2 production rates the stripping velocity was lower compared with the volatilization rate. This result is in contradiction with higher CO_2 production rates.

For evaluating the stripping potential the average velocity of phase transition and the average concentration at 30 minutes were important parameters. The difference for both parameters between stripping and volatilization was plotted

versus the CO_2 produced during Ecogrout to obtain an extrapolation for different CO_2 concentrations (Figure 4.8 and 4.9).

Figure 4.8 Difference stripping velocity-volatilization rate (stripping potential) versus CO_2 production
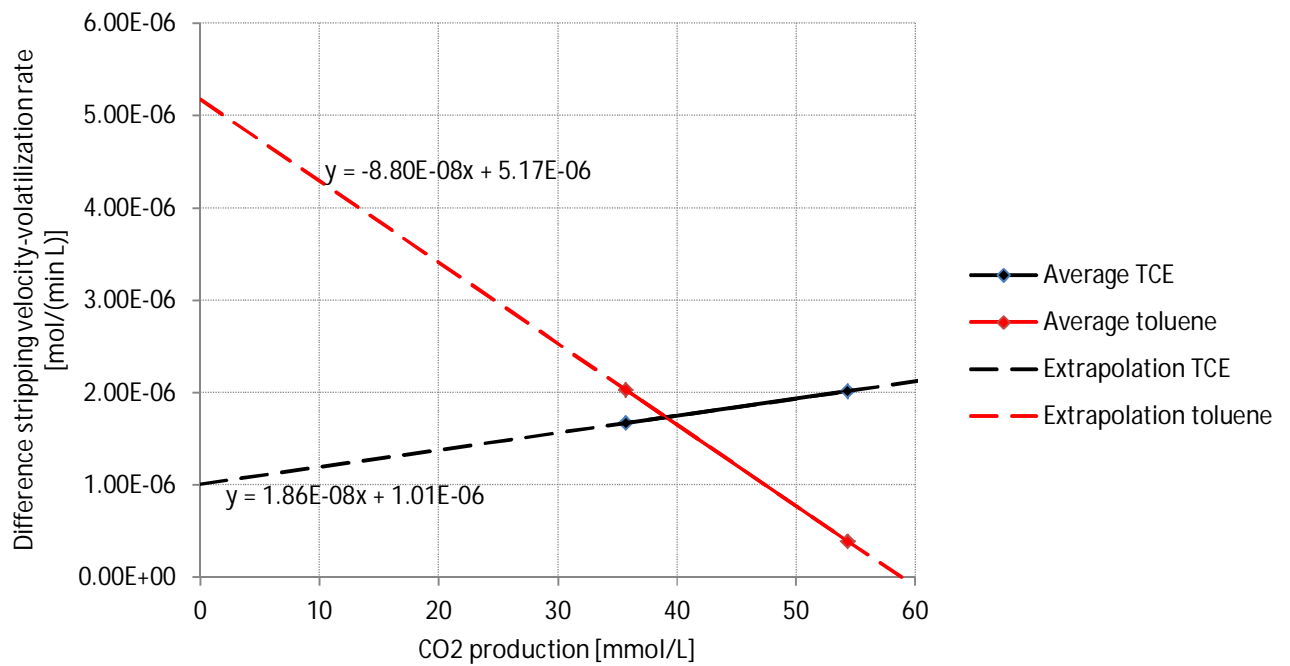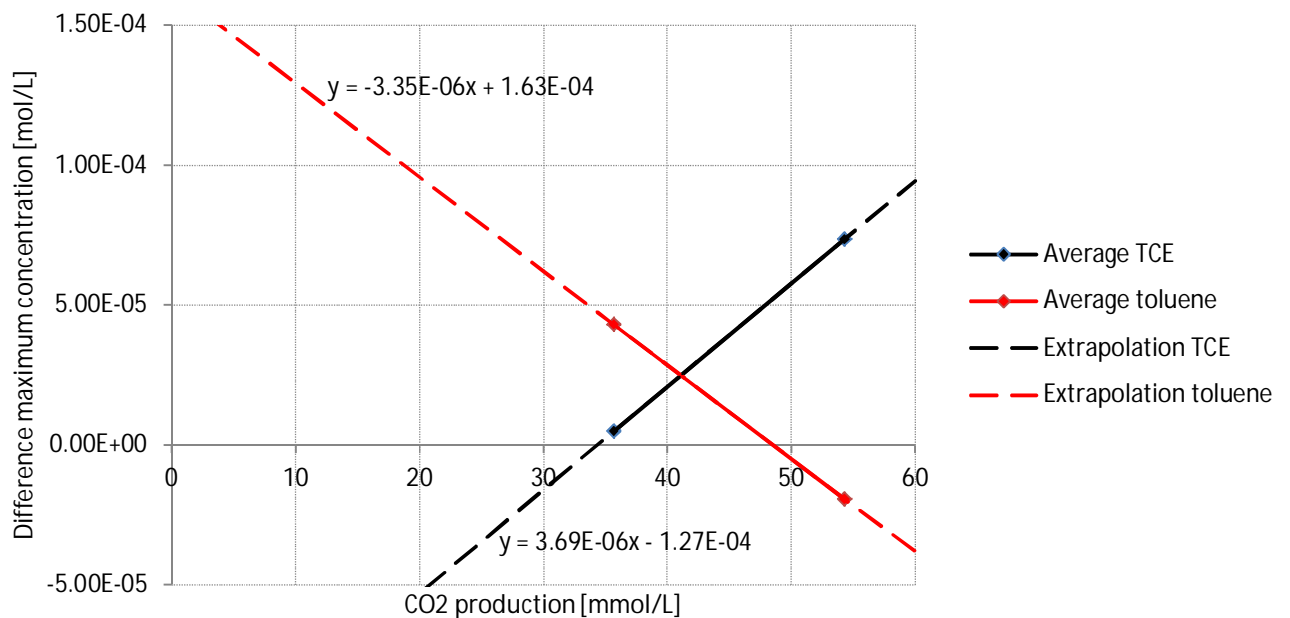Note: different molecular weights (Table 3.1)

Figure 4.9 Difference maximum concentration-volatilization rate (stripping potential) versus CO_2 production
Note: different molecular weights (Table 3.1)

The results obtained for both stripping parameters were different for TCE and toluene and are discussed in the next section (Figure 4.8, 4.9).

5 Discussion

The influence of pressure increase on phase transition and the difference in vapor pressure experiments for both TCE and toluene will not be discussed.

5.1 The influence of pressure increase on gaseous contaminant
For the sampling method a constant deviation between measured and calculated gaseous contaminant concentrations was observed, independent of pressure. The measured gas contaminant concentrations were constantly lower than calculated concentrations. Probably the contaminants were partly lost by opening the syringe to eliminate the dead volume of the needle. This is the only step in the experiment that sample volume could be lost.

5.2 Influence concentration $CaCl_2$:$NaHCO_3$ on gaseous contaminant

5.2.1 General discussion points
Testing the stripping potential in batch experiments could have had an influence on the results. TCE and toluene could attach to the glass surface of the batches and therefore have lower gas concentrations. It is also possible the contaminants attach to the gravel surface because these surfaces are erratic. The contribution of these effects is not taken into account for further interpretations.

5.2.2 Stripping of TCE and toluene
First the stripping potential of TCE and toluene will be discussed. Subsequently, the difference in results for TCE and toluene will be discussed.

The stripping velocity decreases during the initial 30 minutes. This could be related to decreasing CO_2 production and a decrease in concentration of the contaminant in the liquid phase.

The gaseous contaminant concentrations decreased after 30 minutes. This can be caused by two effects. Due to stripping CO_2 gas was bubbling upward to the headspace. Contaminants diffused into these gaseous CO_2 bubbles. Due to this stripping and the use of a closed system eventually a higher concentration of contaminants was present in the gas phase compared to the equilibrium concentration. Consequently gaseous contaminant concentrations were diffused back into the aqueous solution to reach equilibrium. This back diffusion of contaminants into the aqueous solution was higher compared with the concentration of contaminants stripped by the slightly increasing CO_2 production. Therefore the net gaseous contaminant concentration was decreasing. The second effect which influences the decrease in gaseous contaminant concentrations is the change in chemical composition of the solution during the stripping process (Equation 5.1).

Equation 5.1

$$CaCl_{2\,(aq)} + 2NaHCO_{3\,(aq)} \rightarrow 2NaCl_{(aq)} + CO_{2(g)} + CaCO_{3\,(s)} + H_2O_{(l)}$$

The observed lower maximum dissolution concentration for TCE and toluene in dissolved $NaHCO_3$ in the experiments is due to a higher ionic strength compared with water (assuming demi water has ionic strength of approximately zero). Volatile organic compounds can dissolve less well in water which contains ions (Peng and Wan 1998). The solubility of the contaminants will decrease if the water contains more ions, i.e. has a high ionic strength. This is known as the "salting-out" effect. The stock solutions used in the batch experiments consisted of the maximum

solubility of $NaHCO_3$ and contained therefore many ions (ionic strengths of 5.184, 2.907, and 3.614). The chemical composition changed during the Ecogrout process from an aqueous solution containing many ions into a solution with fewer ions present. This decrease in ions was caused by the precipitation of $CaCO_3$. Due to the decrease in ion content the solubility of $CaCO_3$ decreased (Mucci 1983). This effect was due to a decrease of ion activity coefficients of the calcium and carbonate ions with increasing ion content. Therefore more CO_2 was produced than was expected from the initial solution. The ionic strength has not only an influence on the solubility of VOCs but probably also affects the Henry coefficients. Bakierowska (2004) observed decreasing Henry coefficients with increasing ionic strength for sodium chloride solutions. This is assumed to occur linear for the stock solutions used in this research. Consequently due to the effects on both solubility and Henry coefficients, for lower ionic strengths the equilibrium gaseous contaminant concentration is expected to be higher compared with higher ionic strengths. It is not known to what extent the Henry coefficient and solubility differ with different ionic strengths. In the experiments the gaseous contaminant concentrations were higher due to stripping compared with the equilibrium concentration for water, dependent on ionic strength. Therefore the gaseous contaminants were dissolved back into the solution with fewer ions (water) due to a change in chemical composition. Probably both effects, back diffusion due to stripping and a change in chemical composition influenced the decrease in gaseous contaminant concentrations after 30 minutes.

Observed from the results a difference in gaseous contaminant concentrations can be observed for different concentrations of $CaCl_2$ and $NaHCO_3$ used. This difference is assumed to be significant. The difference in gas concentrations measured results from solutions with different ionic strength. The results for different ionic strength solutions used differed almost a constant factor throughout the experiment. These deviations were almost similar for TCE and toluene.

Both the gas concentrations for the high and low concentrations of $CaCl_2$:$NaHCO_3$ used were calculated with the calibration line for the volatilization rate (without adding $CaCl_2$). This calibration line had an ionic strength in between the high and low concentrations of $CaCl_2$:$NaHCO_3$ used. However the ionic strengths were in the higher region of the graph. Therefore the contribution of the difference between these high ionic strengths is expected to be small. Nevertheless the measured gaseous contaminant concentrations with low CO_2 productions are an underestimation. The concentrations for high CO_2 productions are due to a higher ionic strength, compared with the calibration line, an overestimation. The contribution of these small differences in concentrations by the use of no comparable calibration lines is not taken into account for further interpretations.

The average equilibrium concentration of TCE expected to be in the gas phase with an average liquid volume and headspace volume is:

$$0.17282 \times 110 = (0.422 \times C_w^i \times 0.83585) + (C_w^i \times 0.17282)$$

$$C_g^i = 15.26 \text{ mg/L} \rightarrow 1.16 \times 10^{-4} \text{ mol/L}$$

For toluene this expected concentration is:

$$0.17282 \times 50 = \left(0.272 \times C_w^i \times 0.83585\right) + \left(C_w^i \times 0.17282\right)$$

$$C_g^i = 5.87 \text{ mg/L} \rightarrow 6.38 \times 10^{-5} \text{ mol/L}$$

These theoretical concentrations are calculated for contaminants dissolved in demi water. Compared with the experiments the equilibrium concentration should be higher than both stripping potentials and the volatilization rate, because of lower ionic strengths. This is however not the case for both TCE and toluene and can be due to changes in environmental conditions or measurement errors. The difference in

calculated concentration and measured concentration can also be explained by the attachment of contaminants to the glass surface of the batch and sediment.

When the results of TCE and toluene are compared a difference in gaseous contaminant concentrations is observed. The gaseous concentrations of TCE for stripping with different CO_2 productions were switched compared with the expectation in relation with ionic strength. These reversed results are probably due to differences in liquid concentrations in the vacuum bags. The liquid concentration in the vacuum bags for TCE for high CO_2 productions was not measured. Therefore the correction factor for different liquid concentrations in the vacuum bags for high CO_2 productions was calculated to be the average of a test bag and the volatilization rate bag. This concentration was 25.73 ± 7.84 mg/L. The concentration for the low CO_2 productions was measured with one bag and was lower than expected (high correction factor). Due to the high standard deviation for the high CO_2 concentrations and high correction factor for the low CO_2 concentrations, the stripping graphs can be reversed. For further interpretations the results for high and low CO_2 productions for TCE are reversed. This assumption is done to obtain relatively accurate results.

The volatilization concentration at the final time of the experiment was still increasing and had not reached the equilibrium concentration. Due to no active stripping with CO_2 the volatilization rate was linear increased with time. Eventually equilibrium had to be set in. It was expected beforehand that the volatilization concentration would reach the same equilibrium concentration as the experiments with the Ecogrout reaction due to a closed system. This expectation is rejected due to the difference in ionic strength. Considering this difference, the equilibrium concentration of the volatilization rate should be higher compared with the high CO_2 production. This is in line with the results for both contaminants. However the concentration should be lower than the concentrations for low CO_2 productions. This is in contradiction with the results obtained. It is not known why the volatilization rate was able to have at least a similar concentration with low CO_2 productions at the final time of the experiment.

The maximum TCE concentration with reference to the equilibrium concentration was higher for a higher CO_2 production. This is in line with the expectation; due to more stripping more contaminant is present in the gas phase. This was however not observed for toluene. Also almost no increase between both CO_2 productions for the peak concentration of toluene could be observed. This difference can be explained by two reasons. Firstly there is the possibility a thin layer of pure phase was present during the experiment. This thin layer covers the gas liquid interface (Kierzkowska-Pawlak and Zarzycki 2000). In experiments done by Kierzkowska-Pawlak and Zarzycki it was observed the CO_2 solubility increases with increasing toluene fraction in the emulsion. The pure phase toluene layer has a higher CO_2 absorption capacity than the water phase. For higher concentrations of $CaCl_2:NaHCO_3$ used, more CO_2 was produced and therefore more toluene was diffused into the gas bubbles. However when these gas bubbles reached the pure phase toluene layer the CO_2 with toluene was absorbed on the pure phase. The maximum concentration with reference to the equilibrium concentration can therefore be lower for higher CO_2 productions. Another possible explanation can be the fact toluene is less volatile compared with TCE. Therefore the diffusion of toluene into the CO_2 bubbles was less compared with TCE for a similar time of mass exchange. Consequently the peak concentration of stripping for toluene was lower compared with TCE. The maximum concentration for high CO_2 productions for toluene was a factor 2.5 lower compared with TCE. This factor is in line with the factor difference in vapor pressures. It is not known whether the low peak concentrations results from CO_2 absorption or a difference in volatility. This is

because it was not known beforehand whether the more volatile contaminant also relatively would have a higher stripping potential. Due to a higher volatilization rate the more volatile component may have a lower stripping potential than the less volatile compound. Since it is not known which effect influences the toluene gaseous peak concentration, a general conclusion for stripping of VOCs is difficult to obtain.

According to Nelson et al. (2009) the compound with a higher vapor pressure has a higher absolute concentration stripped contaminant. This is in line with the results from this research experiment. From the results obtained it was observed the stripping velocity was higher for more volatile compounds (TCE). Also for higher CO_2 productions the increase of maximum concentration with reference to the equilibrium concentration was higher for TCE. In general was observed the difference in stripping velocity with reference to the volatilization velocity was higher for TCE. The stripping velocity for less volatile contaminants can however differ from toluene, due to the possible influence of a pure phase layer. The absolute difference in maximum concentration with reference to the volatilization concentration is not possible to discuss due to the reversed stripping potentials of TCE. For toluene this absolute difference is also difficult to discuss due to the possible influence of a pure phase layer.

5.3   Up scaling to field conditions

From the results of the batch experiments it is thought stripping of TCE and toluene with CO_2 obtained at the Ecogrout process in the field will occur. However in the batch experiments the system was closed therefore the pressure increased and the CO_2 production decreased with time. The pressure increase will be an important parameter in the soil. Not only because of heterogeneities in the soil but also because of the hydrostatic pressure. For the occurrence of the Ecogrout process in the field, the hydrostatic pressure needs to be exceeded. The 478 mM $CaCl_2$: 750 mM $NaHCO_3$ concentration ratio used has the potential to create a partial pressure of CO_2 of about 11 atm (Appendix 10.1 2). Therefore the potential of CO_2 production for this Ecogrout reaction reaches to 100 meter depth. So the potential of the release of CO_2 in the field will be dependent on the depth of injection. This injection of $CaCl_2$ and $NaHCO_3$ will increase the ionic strength of the groundwater. Freshwater has an ionic strength of less than 0.02 (Appelo and Postma 2005). The increase of ionic strength due to the Ecogrout injection will contribute to a lowering of stripping potentials.

Another important parameter contributing in the field is groundwater flow. This flow will probably have consequences on the concentration of contaminants stripped. Due to the groundwater flow a larger zone of influence for stripping can be reached compared with no flow. Also due to the movement of the dissolved contaminants the stripping will be higher due to a constantly high contaminant concentration near the injection point. However in the batch experiments the contact surface between the liquid phase and gas phase was large (one centimetre liquid above the sediment layer). This contact surface in the soil will be smaller due to the unsaturated zone and therefore the stripping potential will be lower. Nevertheless the stripping potential in the soil will be probably much higher compared with the batch experiments.

The gaseous contaminant concentrations in the soil will probably show a linear increase with time (first 10 minutes in closed batch systems) due to open system conditions. However the possibility of stripping of toluene in the field will be smaller. This is because of the possibility of CO_2 absorption when a pure phase layer is present. Therefore for toluene first the presence of a pure phase layer has to be determined, before the process of stripping can be evaluated.

To obtain the most optimal condition for stripping in the field a higher CO_2 production has to be obtained. Though with a higher CO_2 production the Ecogrout

process is going faster and therefore more and faster $CaCO_3$ is formed. This causes faster well clogging and therefore a smaller stripping area can be obtained. The most optimal condition for the increase in tensile strength and simultaneously remediation of the soil has to be obtained.

In the experiments done for this research only gravel with a median grain size of 8.411 mm is used. In field situations different sediments will occur. Sands have a smaller median grain size. Therefore the CO_2 bubbles that will arise are smaller. Gas channels must be developed within sands to allow for CO_2 movement; this is not the case for gravel where injected gas travels in bubble form free of preferential pathways (Semer, Adams and Reddy 1998). The surface of the gas bubbles in sand is large compared with its volume. Therefore more diffusion of contaminants can take place compared with gas bubbles in gravel. However it is not known to what extent the volume of the bubbles in sand is limited. Consequently it is not known whether the potential for stripping of contaminants in sand is the same compared with gravel. More research has to be done to obtain the effects of bubble size and volume on the stripping potential. It is however difficult to perform batch experiments with sand due to compaction.

6 Conclusion

It is concluded the Ecogrout process can be used to remediate volatile organic contaminated groundwater at brownfields. Both TCE and toluene have potential for stripping with CO_2 from the Ecogrout reaction. The parameter stripping velocity is increasing with increasing CO_2 production. The increase of stripping velocity compared with the volatilization rate was higher for more volatile compounds but may have been influenced by a pure phase layer for toluene.

The conclusions of the sub questions are described separately.

1. *Does the pressure increase in the experiments have influence on the amount of gaseous contaminant?*

It was concluded the pressure increase had no influence on the sampling method of TCE or toluene from the headspace. However, the measured concentrations were a constant factor lower than the initial condition. These constant deviation factors for TCE and toluene were used to correct the results for the other experiments.

The contaminant gas concentrations also had a reversed proportional relation with pressure. This conclusion is in accordance with literature.

2. *Which contaminant, TCE or toluene, has a higher potential for stripping with CO_2?*

It is concluded ideal gas behavior may be assumed for the research experiments. TCE was more volatile in air and CO_2 compared with toluene. The fact TCE was more volatile in air is in line with the expectation beforehand.

3. *Does the concentration of $CaCl_2$ and $NaHCO_3$ have an influence on the concentration of contaminant in the gas phase?*

It is concluded higher concentrations of $CaCl_2$ and $NaHCO_3$ used causes higher contaminant concentrations in the headspace. For the higher concentrations used of $CaCl_2$ and $NaHCO_3$ on average more CO_2 was produced than lower concentrations of $CaCl_2:NaHCO_3$. Until 30 minutes the increase in gaseous TCE contaminant concentration was proportional with the CO_2 increase. Toluene deviated from this proportional relation due to differing peak concentrations. After 30 minutes the gaseous contaminant concentrations were decreasing, while the CO_2 production was slightly increasing. This decrease of stripping can be due to two effects. These effects include the back diffusion of contaminants into the liquid phase due to stripping and the change in chemical composition of the liquid phase.

Almost no increase of maximum toluene gas concentration for high CO_2 productions could be observed. This difference of toluene compared with TCE can be due to the fact CO_2 was absorbed to the emulsion present (Kierzkowska-Pawlak and Zarzycki 2000). This low peak concentration compared with TCE can also be explained by the fact toluene is less volatile compared with TCE.

7 Recommendations

The first batch experiments for the stripping process of VOCs with CO_2 from Ecogrout are positive but more research has to be done to obtain more efficient results for field conditions.

It is recommended to perform column experiments. In these column experiments not only the groundwater flow can be simulated but also the injection of Ecogrout products into the saturated zone can be monitored. Within the column an unsaturated zone above the saturated zone can be obtained to obtain more advanced gas flow in the sediment. Not only the stripping potential has to be evaluated but also more attention has to be paid to the increase in tensile strength of the soil to obtain the most optimal condition for both processes. In the first place the Ecogrout process has to increase the strength of the soil. The second goal concerns the possibility of simultaneously remediation of the soil.

After column experiments, field experiments can be done to obtain representative results for stripping of different volatile organic contaminants. Within these field experiments it is important the increase in strength of the soil is researched in comparison with the stripping potential.

Due to the correction factor obtained for the sampling method it is recommended to change the sampling method. To decrease this factor it is possible to perform the experiment with an expanding headspace volume. This could be done by using a balloon for example. Then probably no concentration of contaminants will be lost during the sampling.

The final recommendation is to perform more research at the influence of ionic strength on the stripping potential. The contribution of ionic strength on the solubility and Henry coefficients is important to know for further experiments.

8 Acknowledgements

9   References

Appelo, C.A.J., and D. Postma. *Geochemistry, Groundwater and Pollution.* California: Balkema, 2005.

Avogadro. *Avogadro.* November 19, 2001. http://avogadro.chem.iastate.edu/MSDS/CaCl2-2H2O.htm (accessed November 7, 2012).

Bakierowska, A., and J. Trzeszczynski. "Dependence of the Water/Gas Partition Coefficient of Volatile Organic Compounds on the Ionic Strength of Sodium Chloride Solution." *Journal of solution chemistry*, 2004: 329-338.

Domenico, P.A., and F.W. Schwartz. "Physical and Chemical Hydrogeology." 431. John Wiley & Sons, Inc., 1990.

Doughty, Cynthia. "NAPL Recovery Using CO2-Supersaturated Water Injection: Distribution of the CO2 Gas Phase." Master thesis University of Waterloo, Waterloo, Ontario, Canada, 2006.

Fetter, C.W. *Contaminant Hydrogeology second edition.* Waveland Press, Inc., 1993.

Grotenhuis, Tim. "In Depth Analysis and Feasibility of the Technology Trains." Project Deltares, Utrecht, 2012.

Gvirtzman, H., and S.M. Gorelick. "The concept of in-situ vapor stripping for removing VOCs from groundwater." *Transport in porous media 8*, 1992: 71-92.

Hinshaw, J.V. *Chromatography online.* December 2005. http://www.chromatographyonline.com/lcgc/data/articlestandard/lcgc/172006/321506/article.pdf (accessed February 24, 2013).

Ji, W., A. Dahmani, D. Ahlfeld, J.D. Lin, and E. Hill III. "Laboratory Study of Air Sparging: Air Flow Visualization." *Ground Water Monitoring and Remediation*, 1993: 115-126.

Kierzkowska-Pawlak, H., and R. Zarzycki. "Calorimetric studies of CO2 absorption into Toluene/Water emulsions." *Chem. papers*, 2000: 437-441.

Li, Meichun. "Recovery of Non-Aqueous Phase Liquids from Contaminated Soil by CO2-Supersaturated Water Injection." Master thesis University of Waterloo, Waterloo, Ontario, Canada, 2009.

Masterton, W.L., C.N. Hurley, and E.J. Neth. *Chemistry: Principles and reactions.* Belmont: Brooks/Cole, 2012, 2009.

Mayer, A.S., and S.M. Hassanizadeh. *Soil and Groundwater Contamination: Nonaqueous Phase Liquid.* Washington DC: American Geophysical Union, 2005.

Mucci, A. "The solubility of calcite and aragonite in sea water at various salinities, temperatures, and one atmosphere total pressure." *American Journal of Science*, 1983: 780-799.

Nelson, L., J. Barker, T. Li, N. Thomson, M. Ioannidis, and J. Chatzis. "A field trial to assess the performance of CO2-supersaturated water injection for residual volatile LNAPL recovery." *Journal of contaminant hydrology 109*, 2009: 82-90.

Nipshagen, A., and T. Praamstra. *VOCL vluchtige chloorkoolwaterstoffen (VOCL) in bodem.* Gouda: Quantes, 2007.

NVON-commission. In *Binas Informatieboek voor natuurwetenschappen en wiskunde*. Wolters Noordhoff, 2004.

Peng, J., and A. Wan. "Effect of ionic strength on Henry's constants of volatile organic compounds." *Chemosphere*, 1998: 2731-2740.

ScienceLab.com, Inc. *ScienceLab.com.* June 9, 2012. http://www.sciencelab.com/msds.php?msdsId=9927258 (accessed November 7, 2012).

Semer, R., J.A. Adams, and K.R. Reddy. "An experimental investigation of air flow patterns in saturated soils during air sparging." *Geotechnical and Geological Engineering 16*, 1998: 59-75.

Solomon, T. "The Definition and Unit of Ionic Strength." *Journal of chemical eduaction*, 2001: 1691-1692.

Tomlinson, D.W., N.R. Thomson, R.L. Johnson, and J.D. Redman. "Air distribution in the Borden aquifer during in situ air sparging." *Journal of contaminant hydrology 67*, 2003: 113-132.

U.S. Department of Health and Human Services. *Agency for Toxic Substances and Disease Regisrty.* September 1997. http://www.atsdr.cdc.gov/toxprofiles/tp19-c3.pdf (accessed September 11, 2012).

United States Environmental Protection Agency. *United States Environmental Protection Agency.* July 16, 2007. http://www.epa.gov/superfund/health/conmedia/soil/pdfs/part_5.pdf (accessed November 7, 2012).

Van der Star, Wouter. *Ecogrout Feasibility of in situ calcium carbonate precipitation.* Draft version Deltares, Deltares, 2012.

10 Appendices

10.1 PHREEQC calculation

1
Solution 1

EQUILIBRIUM_PHASES 1

CO2(g) 0.525

SELECTED_OUTPUT
        -file D:\Marcelle\CaCl2+NaHCO3_EcoGrout.txt
        -totals Ca C Na Cl
        -equilibrium_phases CO2(g) Calcite
        -alkalinity
        -saturation_indices Calcite CO2(g)
    -gas CO2(g)
END

CO_2 pressure is then: $10^{0.525} = 3.35$ atm

2
Solution 1

EQUILIBRIUM_PHASES 1

CO2(g) 1.042

SELECTED_OUTPUT
        -file D:\Marcelle\CaCl2+NaHCO3_EcoGrout.txt
        -totals Ca C Na Cl
        -equilibrium_phases CO2(g) Calcite
        -alkalinity
        -saturation_indices Calcite CO2(g)
    -gas CO2(g)
END

CO_2 pressure is then: $10^{1.042} = 11.02$ atm

10.2 Problems solved during the research

- Use of viton septa instead of butyl because toluene diffuses trough butyl
- Switched of silicone working vial caps to blue magnetic caps Alltech CH-20 MC BC
- The stock solutions were made in vacuum bags instead of batches. So no gas exchange took place between the headspace and liquid phase
- Changed use of syringes; gas tight with a push valve because of loss contamination
- The pressure device could not be used obtaining pressure in contaminated batches because of contamination of the device and channels. Therefore the batch experiments consisted of two identical batches next to each other
- The internal standard of 1,2-Dibromoethane dissolved in methanol or acetone used in the batch experiments acted as a cosolvent and dissolved the contamination. Therefore PCE and TCE were used as internal standard
- The Ecogrout experiment was done in batches of 1 L instead of smaller batches used before, because these batches can withstand a pressure of maximum 2 atm and the overpressure can't be released because of loss of the contaminant phase
- Change of GC use. Therefore own method prepared in GC
- Autosampler connected to GC, because no one used the autosampler at this GC before. So own method prepared in autosampler
- Syringe in GC bended a lot by taking samples. The syringe was therefore unravelled and it appeared the elastic tapes in the autosampler were stretched out. They were renewed
- After the measurements of differences of TCE concentrations for different $CaCl_2$, $NaHCO_3$ concentrations used it was found out how liquid concentration measurements could be done. Because already vacuum bags used, the concentrations of the higher concentration vacuum bags were assumed to be the average of other vacuum bags measured

10.3 Used apparatus

Dionex ICS-3000
The concentration calcium ions was measured using cation chromatography. The column used was CS 12A.

Mettler Toledo, DI50 graphix
The HCO_3^- concentration was measured using a titrant of 0.1 mol/L hydrochloric acid (HCl). The apparatus titrated until it reached pH 4.5. The used volume must be entered, to precisely calculate the concentration of HCO_3^- (g/L). The calculated concentration (g/L) could be converted to a concentration in mM using the molecular weight.

PressDaq PD-32
Made at Wageningen University. The number is 26PCDFA6G.

It was obtained from the Wageningen University; the pressure device had a silicone membrane. This membrane could absorb the contaminations used in this experiment. The silicone membrane can absorb TCE and toluene to about 200%. This means the membrane can swell to about twice its original size. This will affect the measurements.
　　　　To prevent contamination of the pressure device the experiment was done using two identical batches. One batch was attached to the pressure device (without contamination) and from the other batch gas samples were taken (with contamination).

Supelco analytical, screw cap valve, 1 L
Supel™ Inert gas sampling bags nr 30221-4

Varian CP-3800+CTC analytics combipal (1)
The internal standard for TCE was gaseous PCE, because it has a retention time different from TCE. The internal standard for toluene was gaseous TCE because PCE has the same retention time as toluene. The retention times obtained with this GC and used method were 16.8 minutes for TCE, 19.2 minutes for toluene and 19.22 minutes for PCE. The retention time is the time the contaminant is attached to the column within the GC and therefore visible as a peak on the computer.
The GC used is a GC FID (flame ionization detector). A FID is sensitive to molecules that are ionized in a hydrogen/air flame (Hinshaw 2005).
Properties method GC:
Column　　　initial 50°C, 3 minutes
　　　　　　　10°C/min to 250°C, 25 minutes
　　　　　　　Constant flow 2.0 ml/min

Autosampler
Syringe　　　　　　1 ml
Sample volume　　　900 µl
AGI speed　　　　　250 rpm
AGI on time　　　　5 sec
AGI off time　　　　2 sec
Injection speed　　　250 µl/s
Pre inj Del　　　　　0 ms
Post inj Del　　　　10 sec
Syringe flushing　　　2 min

GC runtime   30 min
Fill speed   100 µl/s
Pull up del   10 sec
Injection to   front

Varian CP-3800+CTC analytics combipal (2)
The retention times [min] for liquid sampling were 12.2 acetone, 17.38 internal standard, 15.53 TCE and 17.2 toluene
Properties method GC:
Column   initial 40°C, 3 minutes
               10°C/min to 70°C, 6 minutes
               15°C/min to 250°C, 9 minutes
               Constant flow 1.4 ml/min

Autosampler
Syringe   1 ml
Sample volume   500 µl
AGI speed   500 rpm
AGI on time   5 sec
AGI off time   2 sec
Injection speed   250 µl/s
Pre inj Del   500 ms
Post inj Del   500 sec
Syringe flushing   2 min
GC runtime   30 min
Fill speed   500 µl/s
Pull up del   500 ms
Injection to   front
Incubation time   20 min
Incub. Temperature   80 °C
Syringe temperature   80 °C

10.4 Calculation correction concentration

Calibration line:

Calibration nr.	Contaminant area [µv.min]		Concentration [µg/L]	Internal standard [µv.min]
0	Contaminant area	$\dfrac{Contaminant\_area}{Internal\_standard\_area}$	Concentration	Internal standard
1	Contaminant area	$\dfrac{Contaminant\_area}{Internal\_standard\_area}$	Concentration	Internal standard
2	Contaminant area	$\dfrac{Contaminant\_area}{Internal\_standard\_area}$	Concentration	Internal standard
3	Contaminant area	$\dfrac{Contaminant\_area}{Internal\_standard\_area}$	Concentration	Internal standard
4	Contaminant area	$\dfrac{Contaminant\_area}{Internal\_standard\_area}$	Concentration	Internal standard
5	Contaminant area	$\dfrac{Contaminant\_area}{Internal\_standard\_area}$	Concentration	Internal standard

Corrected concentration:

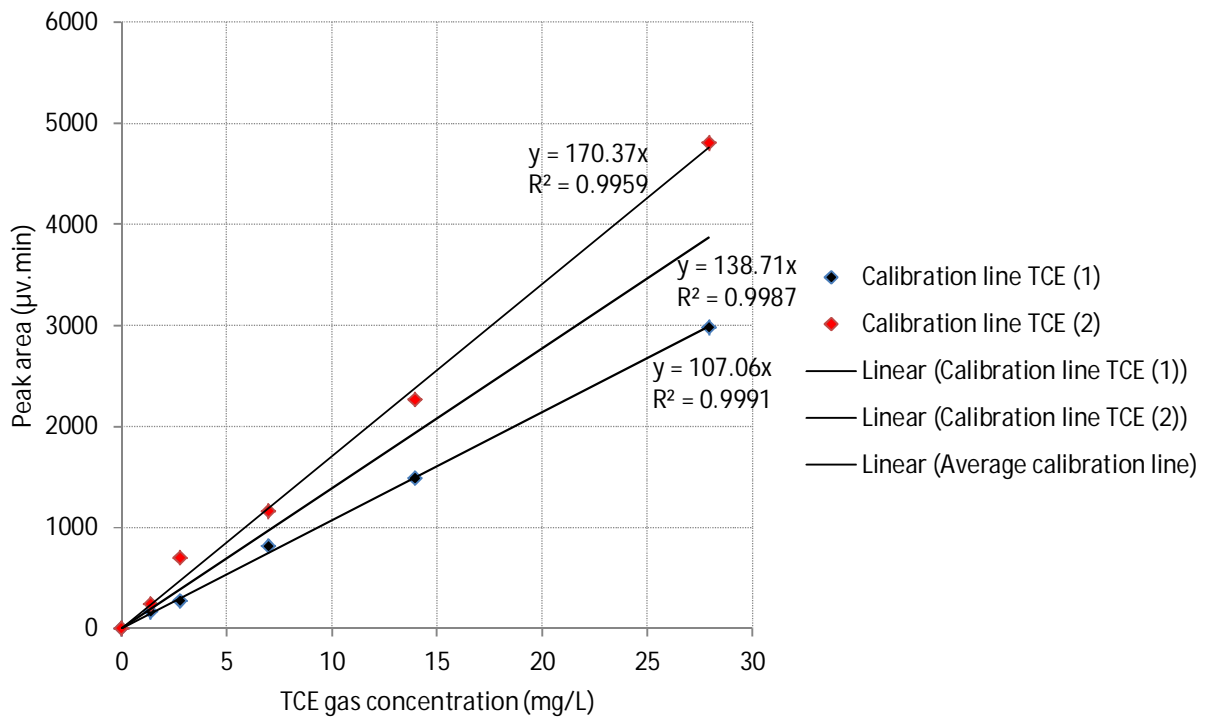|			
$\dfrac{\dfrac{Contaminant\_area}{Internal\_standard\_area}}{slope\_shaded\_area}$	$\dfrac{Contaminant\_area}{Internal\_standard\_area}$	Measured contaminant area [µv.min]	Measured internal standard [µv.min]

10.5 Calibration lines
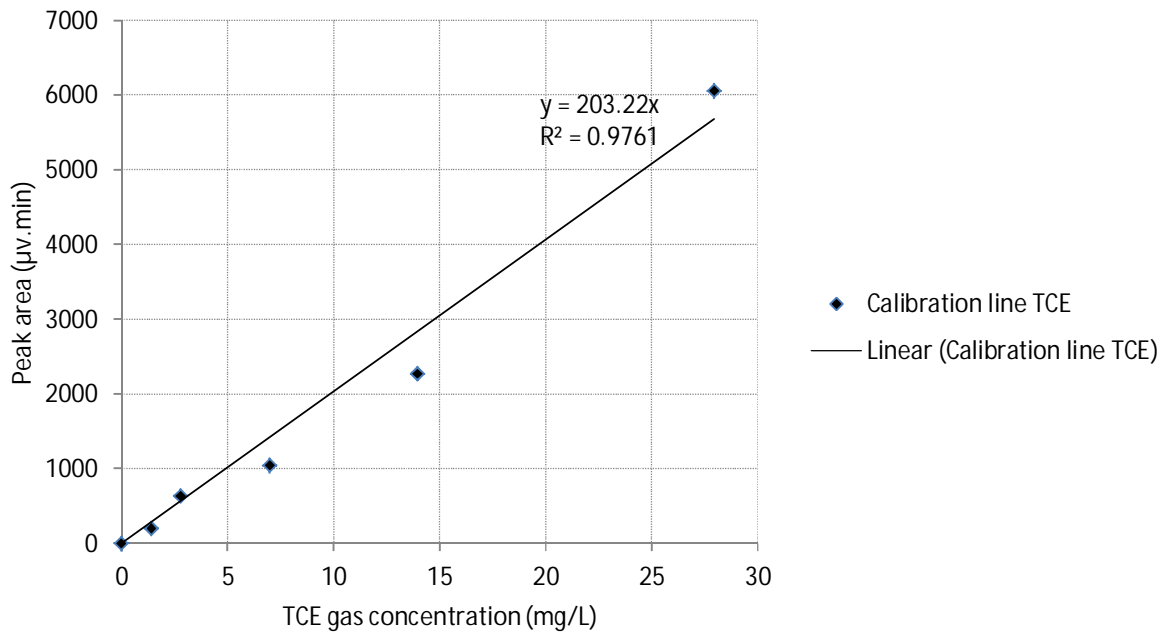

Figure 10.1 TCE calibration line
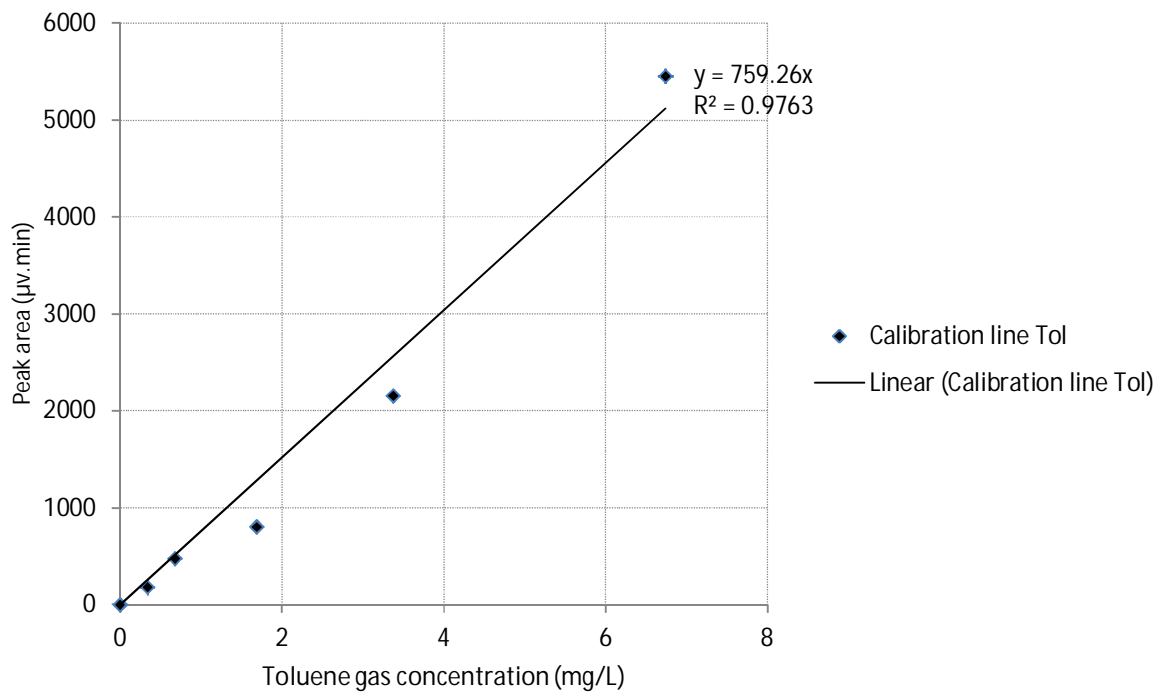

Figure 10.2 TCE calibration line (2)
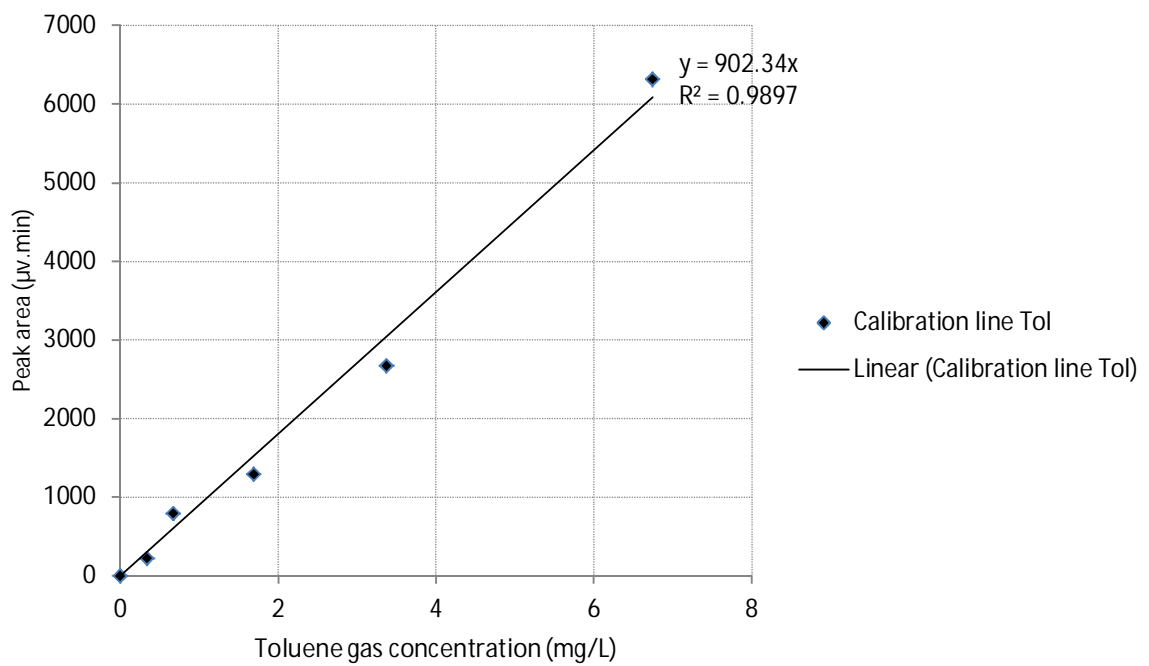
Figure 10.3 Toluene calibration line

Figure 10.4 Toluene calibration line (2)

10.6 Experimental setup

1. Stock solutions were made

A stock solution of $NaHCO_3$ and contamination was made. This was done by making stock solutions of maximum solubility of TCE and toluene. From this maximum solubility stock a volume was injected into a vacuum bag and diluted with maximum dissolved $NaHCO_3$ without contamination. This vacuum bag was shaken for about four hours. This time of shaken could not be longer because three experiments were done with one bag (total time of 1.5 days) and diffusion of contamination would take place through the bags after two days.

In this research study the contamination amount was 10% of the maximum solubility in the batches (Table 3.1). The percentage contamination dissolved in the vacuum bag was higher because of dilution with $CaCl_2$ and demi water in the batches (demi water was only used for the 319 mM $CaCl_2$:500 mM $NaHCO_3$ concentration ratio). For the 478 mM $CaCl_2$:750 mM $NaHCO_3$ concentration ratio the percentage was about 15.4. For the lower concentration ratio it was about 22.3%.

2. The calculated amount of sediment was put in both batches

The calculated amount of sediment from the calculation sheet was weighted and put in the batch (Mettler Toledo, model No. PG 4002-S). After this the batch was filled with demi water till a lens of water could be seen at the top of the batch. The weight of the sediment + demi water was measured. Then the volume of the sediment was determined (Equation 10.1).

Equation 10.1

$$Total\_solids\_volume \ = \ total\_volume\_batch - \left(weight\_water + sediment - weight\_sediment\right)$$

3. Stock solution $CaCl_2$ was added to both batches

The amount of $CaCl_2$ was weighted and put in the Ecogrout and contaminated batch.

4. Stock solution $NaHCO_3$ was added to the Ecogrout batch

5. The Ecogrout batch was connected to the pressure device

6. The batch was shaken for ten seconds, relative pressure was constantly measured

The batch was shaken for ten seconds to distribute the liquids and contamination evenly throughout the sediment layer.

7. Stock solution $NaHCO_3$ + contamination was added to the contaminated batch and shaken for ten seconds

The $NaHCO_3$ stock solution with contamination was added to the contaminated batch. The volume of $NaHCO_3$ with contamination was obtained from the vacuum bag with a syringe (BD Plastipak, 50 ml). The volume of $NaHCO_3$ with contamination was then added to the batch.

8. Contaminated batch: concentration of gaseous contaminant was measured at 0, 10, 30, 45, 60, 180 min

First the working vials were capped and an internal standard was injected. After injecting the internal standard gaseous contaminant concentrations were measured at different times. From the batch 250 µl of gas was extracted into the syringe. The

syringe was locked and taken out of the batch. After this the syringe was unlocked and 50 µl was flushed out. A volume of 200 µl was injected in the working vial. For the GC it was important to inject under atmospheric pressure to measure no fluctuations within results.

9. *A calibration line was made*

A 110 ml batch was used to make a saturated solution for TCE and toluene. This was done by adding 10 ml of maximum $NaHCO_3$ stock solution and 2 ml of pure phase. Assumed was the fact the concentration of contaminant in the headspace was in equilibrium with the liquid phase. The concentration of contaminant in the headspace was calculated using Henry's law (Equation 2.3). Samples were collected from the headspace (see section 3.2 Gas sampling). These samples were diluted and with the dilution factor and the assumption of equilibrium concentration of contaminant in the gas phase the concentration was calculated. These concentration values were plotted versus the measured peak area from the GC. The trend line obtained from this graph (Equation 3.1) was the calibration line. With this calibration line measurements of peak area [µv.min] were converted to concentration values [mg/L].

10. *Concentration liquid phase contaminant was measured in the vacuum bag*

10.6.1 Organic material

The amount of organic material attached to the sediment was measured (TOC-5050A shimadzu) to be sure no contamination was adsorbed to the organic material. The concentration of carbon was lower than 10 mg/L and was negligible. This value was within measurement errors.

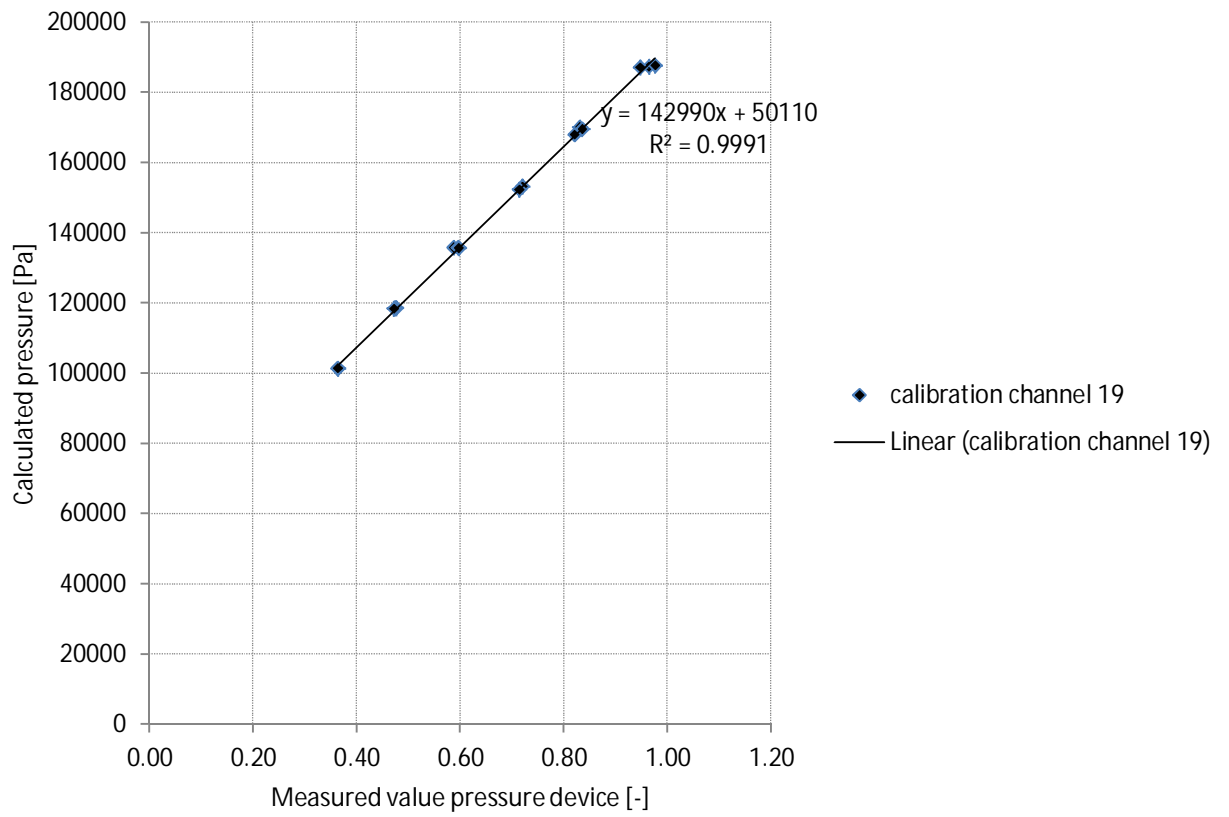## 10.7 Calibration line pressure device

Figure 10.5 Calibration line pressure device

10.8 Stock solutions

	NaHCO$_3$	CaCl$_2$
	formula	formula
Molecular weight [g/mol]	84.01[15]	147.02[16]
Density [g/ml]	2.16[17]	1.85[18]
Max. dissolution [g/L]	100	740
Mol/L	$\dfrac{Max\_dissolution}{Molecular\_weight}$	1.014 (Easy factor to work with in experiment)
g/L	$\left(mol/L\right) \times Molecular\_weight$	
ml/L	$\dfrac{g/L}{density}$	
Demi water added to 1 L [ml]	$1000 - ml/L$	
Powder [g]	$Liter\_stock\_solution \times g/L$	
Demi water total [g]	$Liter\_stock\_solution \times Demi\_water\_added$	$Demi\_water\_total\_NaHCO_3 + 100$
Volume powder [ml]	$\dfrac{powder}{density}$	
Theoretical real concentration [g/L]	$\dfrac{powder}{\left(demi\_water\_total + volume\_powder\right)} \times 1000$	
Theoretical real concentration [mol/L]	$\dfrac{real\_concentration[g/L]}{molecular\_weight}$	
Theoretical real concentration [mmol/L]	$real\_concentration[mole/L] \times 1000$	
Density solution [g/ml]	$\dfrac{\left(powder + demi\_water\_total\right)}{\left(demi\_water\_total + \dfrac{powder}{density}\right)}$	

---

[15] (ScienceLab.com, Inc. 2012)
[16] (Avogadro 2001)
[17] (ScienceLab.com, Inc. 2012)
[18] (Avogadro 2001)

10.9 Calculation solid material concentration ratio

	Formula
Batch number	No.
Total amount liquid phase needed [ml]	Calculated for concentration ratio in liquid phase
CaCl$_2$ needed [ml]	Calculated for concentration ratio in liquid phase
NaHCO$_3$ needed [ml]	Calculated for concentration ratio in liquid phase
CaCl$_2$ calculated [g]	$\left(\dfrac{CaCl_2\_needed}{1000} \right) \times real\_concentration\_CaCl_2$
NaHCO$_3$ calculated [g]	$\left(\dfrac{NaHCO_3\_needed}{1000} \right) \times real\_concentration\_NaHCO_3$
CaCl$_2$ calculated [ml]	$\dfrac{CaCl_2\_calculated}{density\_CaCl_2}$
Demi water calculated [ml]	$Total\_amount\_liquid\_phase\_needed - CaCl_2\_calculated - NaHCO_3\_calculated$

10.10 Calculation sheet

	Formula	
CaCl$_2$ solution [mM]	Ca^{2+}	$$\frac{\left(Volume\_CaCl_2 \cdot 2H_2O \times real\_concentration\_CaCl_2 \cdot 2H_2O(mM)\right)}{total\_sample\_volume - total\_solids\_volume}$$
	Cl$^-$	$$\frac{\left(Volume\_CaCl_2 \cdot 2H_2O \times real\_concentration\_CaCl_2 \cdot 2H_2O(mM)\right)}{total\_sample\_volume - total\_solids\_volume} \times 2$$
NaHCO$_3$ solution [mM]	CO$_3{}^{2-}$	$$\frac{\left(Volume\_CaCl_2 \cdot 2H_2O \times real\_concentration\_NaHCO_3(mM)\right)}{total\_sample\_volume - total\_solids\_volume}$$
	Na$^+$	$$\frac{\left(Volume\_CaCl_2 \cdot 2H_2O \times real\_concentration\_NaHCO_3(mM)\right)}{total\_sample\_volume - total\_solids\_volume}$$
CaCl$_2$·2H$_2$O reactive fluid	Weight (g)	$volume\_CaCl_2 \cdot 2H_2O \times density\_solution$
	Volume (ml)	$0.37 \times \left(total\_sample\_volume - total\_solids\_volume\right) \times 1$ [19]
NaHCO$_3$ reactive fluid	Weight (g)	$volume\_NaHCO_3 \times density\_solution$
	Volume (ml)	$0.63 \times \left(total\_sample\_volume - total\_solids\_volume\right) \times 1 + A$ [20]
Demi water	Weight (g)	$\left(total\_sample\_volume - total\_solids\_volume\right) - \left(volume\_NaHCO_3 + volume\_CaCl_2\right)$
	Volume (ml)	$\left(total\_sample\_volume - total\_solids\_volume\right) - \left(volume\_NaHCO_3 + volume\_CaCl_2\right)$
Total fluids	Weight (g)	$Weight\_NaHCO_3 + weight\_CaCl_2 + weight\_demi\_water$
	Volume (ml)	$Volume\_NaHCO_3 + volume\_CaCl_2 + volume\_demi\_water$
ml pore space/ml added solids	$$\frac{0.4 \times total\_volume}{0.6 \times total\_volume}$$ [21]	
Pore volume [ml]	$total\_solids\_volume \times ml\_porespace / ml\_added\_solids$	
Total solids	Weight (g)	$volume\_total\_solids \times gravel\_volweight$
	Volume (ml)	$(1 - 0.4) \times total\_sample\_volume \times 0.8$ [22]
Factor solids	$$\frac{total\_solids\_weight}{total\_solids\_volume}$$	
Total		

[19] 0.37 was obtained by trial and error obtaining volume ratio 478 mM CaCl$_2$: 750 mM NaHCO$_3$. One was obtained from the highest ratio. If the ratio was 319 mM CaCl$_2$: 500 mM NaHCO$_3$ the formula was divided by 6 and this was multiplied by 4 to obtain the right concentration ratio

[20] 0.63 was obtained by one minus percent CaCl$_2$·2H$_2$O. A was a variable that was obtained by the fact the stock solutions alter due to temperature differences and this variable took this difference into account

[21] The numbers 0.4 and 0.6 represented the porosity and sediment amount respectively

[22] 0.8 was obtained by the fact a layer of liquid was present above the sediment. This 0.8 represented the sediment volume of total sample volume

sample volume [ml]	$total\_volume\_batch - headspace$
Headspace	$total\_volume\_batch \times 0.72$ [23]

[23] 0.72 was the percentage of headspace calculated for the batches using the volume of liquids and volume of solids

10.11 Calibration line liquid phase

1. 25 µl of HgCl (1 g/L) was added in a working vial (22 ml headspace vial) with a pipette (Gibson 20-200 µl, P200N)
2. The calculated amount of MilliQ was added to the working vial (Table 10.1) with a pipette (Gibson 1000-5000 µl, P5000)
3. The vial was capped
4. The calculated amount of stock solution of TCE or toluene dissolved in methanol was injected
5. 10 µl of internal standard (1,2 Dibromoethane, $C_2H_4Br_2$, dissolved in methanol) was injected

Working vial	MilliQ [ml]	stock solution [µl]	Concentration liquid phase in vial [µg/L]
1	8.000	0	0
2	7.995	5	625
3	7.990	10	1250
4	7.985	15	1875
5	7.980	20	2500
6	7.975	25	3125

Table 10.1 Calibration line liquid phase

It is observed from Figures 10.6 and 10.7 the variance between the liquid phase calibration lines was low. Due to the internal standard connected to one calibration line it was decided to use the calibration line first made.
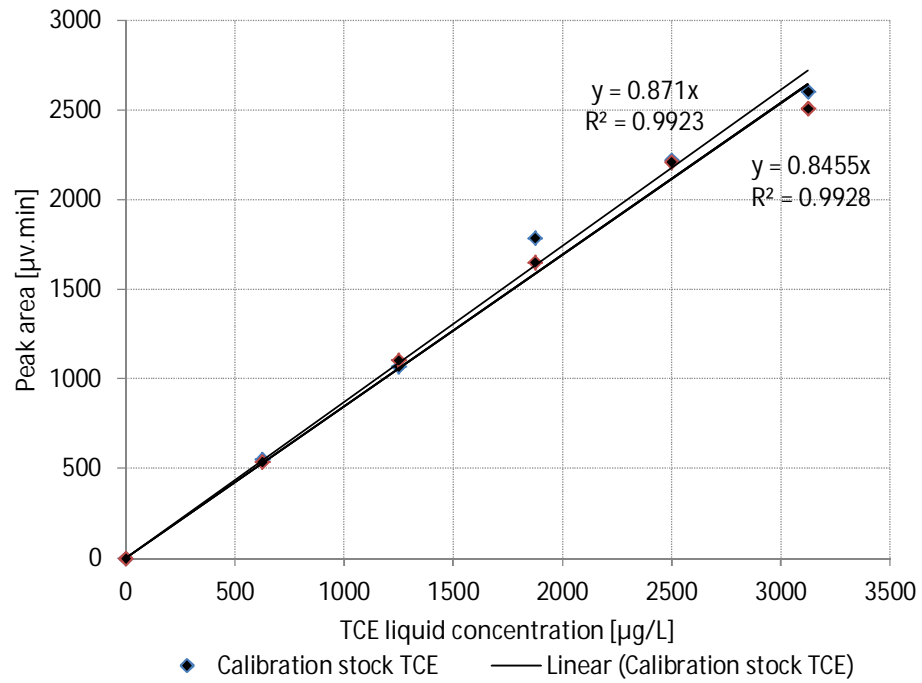
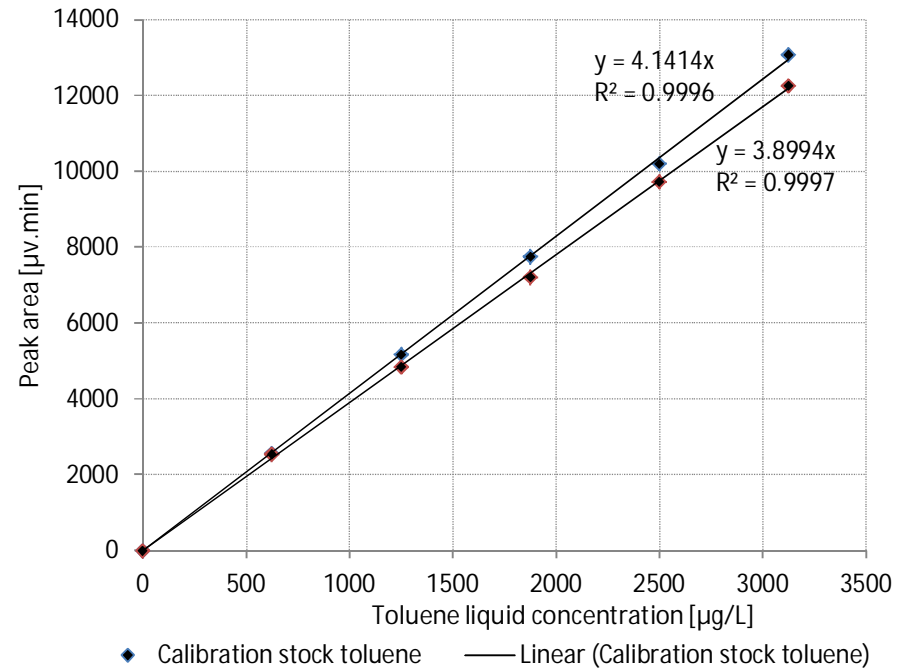Figure 10.7 Calibration line liquid phase, TCE

Figure 10.6 Calibration line liquid phase, toluene

10.12 CO_2 production Ecogrout

In Figure 10.8 the CO_2 production obtained at the Ecogrout process can be seen. A few batches in the experiments have leaked (dashed lines in Figure 10.8). This means gas from the batch was escaped. The measured CO_2 production measured in the batch was then lower compared with other batches (Figure 10.8). To obtain accurate calculations, it was decided to not take into account the leaking batches for further calculations.
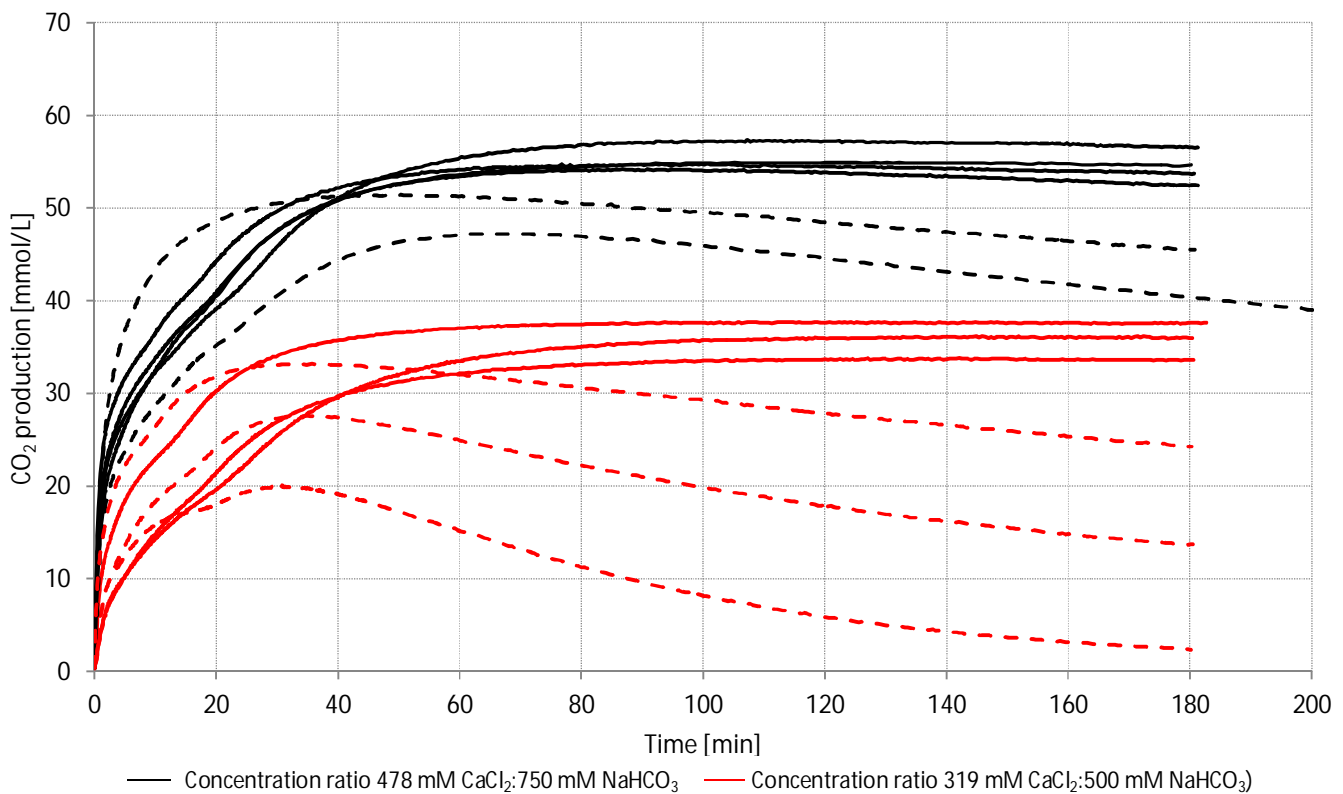
Figure 10.8 CO_2 production Ecogrout

10.13 Gaseous contaminant concentrations

In Figures 10.9-10.12 the gaseous contaminant concentrations are given. There were differences observed between the measurements with internal standard and the measurements without internal standard. The use of an internal standard in general was more accurate, because corrections were made for pressure and temperature differences. However it can be seen in Figures 10.9-10.12 the use of an internal standard for TCE was less accurate compared with the results obtained without the internal standard. This could be due to the fact the experiment with TCE was done first and the sampling was therefore not as accurate as the sampling for toluene. Another argument for the difference in use of internal standard could be the use of different internal standards. Gaseous PCE was used as internal standard for TCE. PCE is less volatile than TCE but could have an influence on the measurements in the GC. Based on the results of the measurements with and without an internal standard it was decided to use the internal standard only for toluene. The results for TCE were obtained without an internal standard. With these results further calculations were done. The measurement of toluene volatilization (3) was left out in the calculations because of a measurement error. Probably something went wrong with the column in the GC.
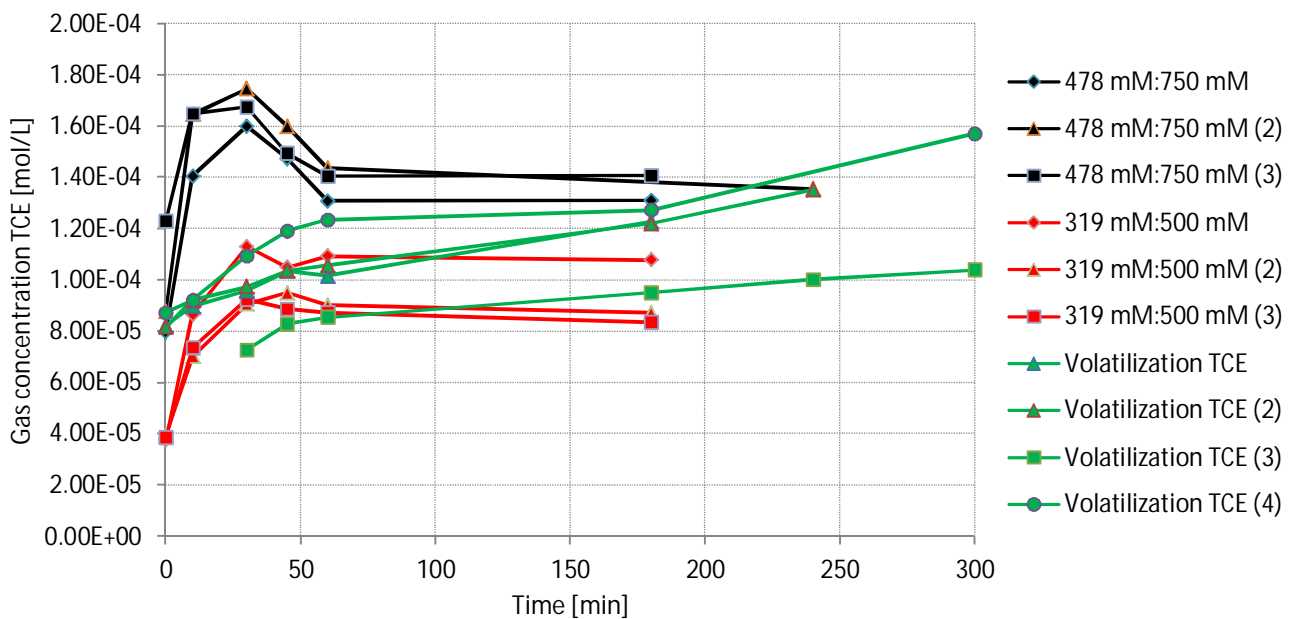

Figure 10.9 Stripping TCE (without internal standard)
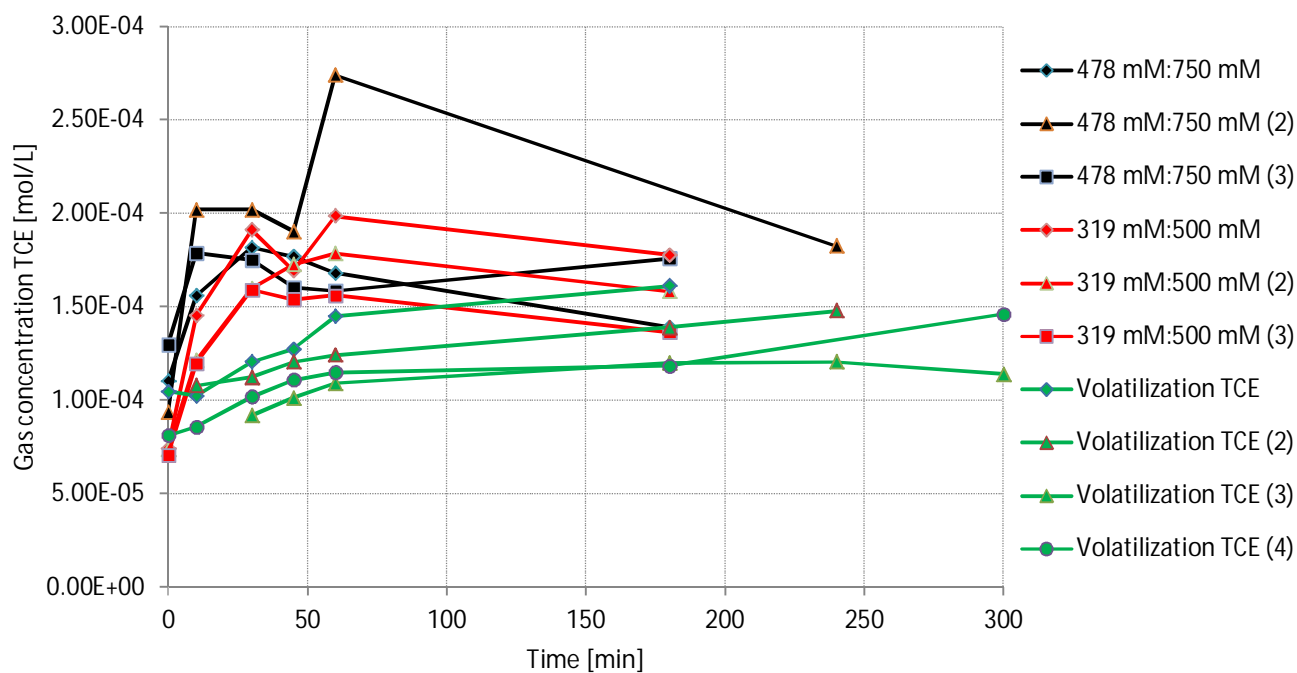
58

Figure 10.10 Stripping TCE (with internal standard)
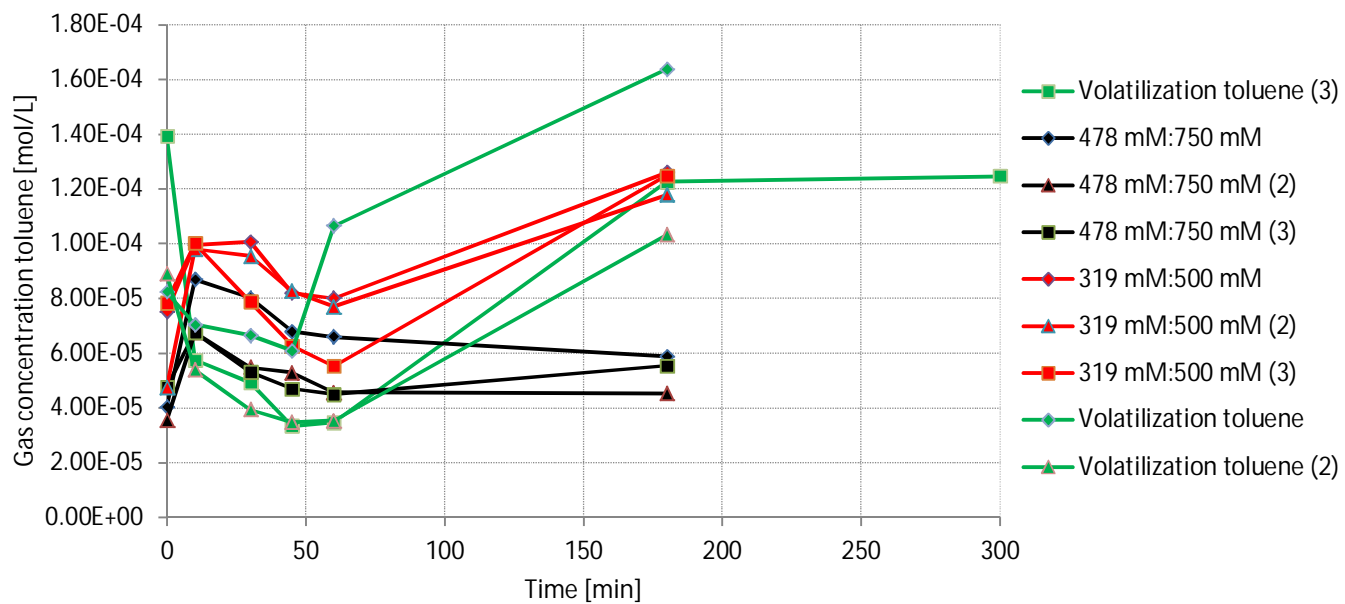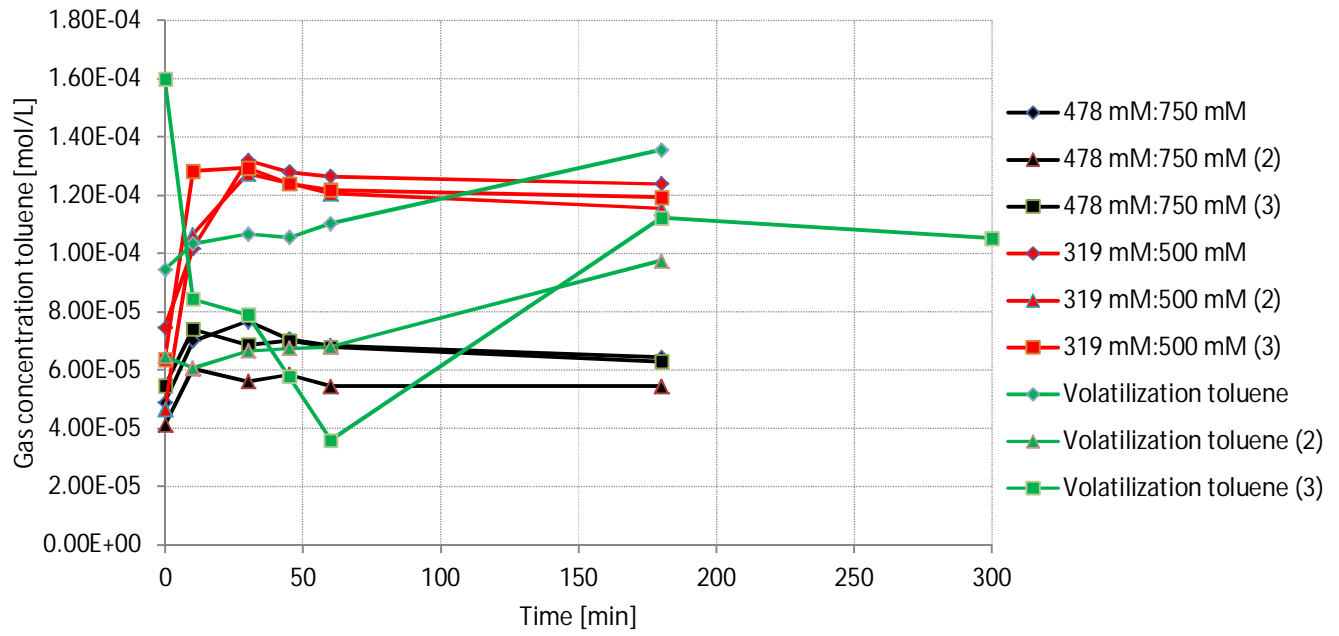

Figure 10.11 Stripping toluene (without internal standard)

Figure 10.12 Stripping toluene (with internal standard)

10.14 Statement of originality

Statement of originality of the MSc thesis

I declare that:

1. this is an original report, which is entirely my own work,

2. where I have made use of the ideas of other writers, I have acknowledged the source in all instances,

3. where I have used any diagram or visuals I have acknowledged the source in all instances,

4. this report has not and will not be submitted elsewhere for academic assessment in any other academic course.

Student data:

Name: Marcelle o.d. waals

Registration number: 3367460

Date: 28-02-'13

Signature: