

# MASTER THESIS

45 ECTS

## The Carbon sequestration capacity of the Sand Motor

---

<b>Author</b>	Annemieke Wijnakker
<b>Student number/email:</b>	4187253 a.w.p.wijnakker@students.uu.nl
<b>Master:</b>	Sustainable Development
<b>Track:</b>	Global Change and Ecosystems
<b>Supervisors:</b>	Prof. dr. Jasper Griffioen (Universiteit Utrecht, TNO) Iris R. Pit MSc (Universiteit Utrecht)
<b>Date:</b>	13-08-2015
<b>Word count:</b>	16300

# CONTENT

<b>Abstract</b> .....	4
<b>1. Introduction</b> .....	5
<b>1.1 Background</b> .....	5
<b>1.2 Problem definition</b> .....	10
<b>1.3 Aim</b> .....	10
<b>1.4 Research question</b> .....	10
<b>2. Chemical processes</b> .....	11
<b>3. The Sand Motor</b> .....	14
<b>4. Methods</b> .....	15
<b>4.1 Samples</b> .....	15
<b>4.2 Experiments</b> .....	18
<b>4.3 Modelling</b> .....	20
<b>5. Results</b> .....	23
<b>5.1 Fieldwork</b> .....	23
<b>5.2 Experiments</b> .....	25
<b>5.3 Modelling calcite dissolution in the Sand Motor (PMWIN)</b> .....	34
<b>5.4 Sand Motor CO<sub>2</sub> sequestration capacity estimate</b> .....	35
<b>6. Discussion</b> .....	37
<b>6.1 Calcite dissolution in the experiments and phreeqc results</b> .....	37
<b>6.2 Dissolved inorganic carbon isotopes from fieldwork and experiments</b> .....	39
<b>6.3 Calcite dissolution and rainwater infiltration at the Sand Motor</b> .....	39
<b>6.4 Modelling C sequestration</b> .....	41
<b>6.5 Sequestration estimate</b> .....	41
<b>7. Conclusion</b> .....	43
<b>8. Recommendations</b> .....	45
<b>9. Acknowledgements</b> .....	46
<b>10. References</b> .....	47
<b>11. Appendices</b> .....	51
Appendix A. Rainwater imitation .....	51
Appendix B. Flow calibrations .....	52
Appendix C. Preliminary Sand Motor data .....	53
Appendix D. Examples of phreeqc input files.....	55
Appendix E. Calcite weathering module for PHT3D in PMWIN. ....	57

*This thesis is dedicated to my father Wil, who loved to walk the Sand Motor.*

*His enthusiasm was the motivation to choose this research, his encouragement gave the strength to finish my thesis.*



**Universiteit Utrecht**

## ABSTRACT

The Sand Motor is an innovative mega nourishment at the Dutch Coast. It is intended to protect the hinterland from floods in the next twenty years by slowly depositing sand upon the beach through wave and wind action. Since the traditional nourishment techniques entail that a vulnerable beach is nourished with a reoccurrence time of (approximately) four years, a mega nourishment is thought to be less damaging for local ecosystems. Motivated by an initiative of the Dutch government to reduce CO<sub>2</sub> emissions, stakeholders involved in the construction of the Sand Motor wished to know if the Sand Motor captures CO<sub>2</sub>. Carbon can be sequestered through calcium carbonate dissolution in barren sandy calcareous soils. Although Ca-carbonate dissolution is well researched in the laboratory, this is not the case for sandy soils in natural settings. This research aims to estimate the C sequestration capacity of the Sand Motor with fieldwork, laboratory experiments and a groundwater model. Groundwater and soil samples were collected at the Sand Motor to characterise the intensity of Ca-carbonate weathering. Laboratory experiments were done to establish Ca-carbonate dissolution rates. The unsaturated zone was mimicked with an experiment that was flushed with CO<sub>2</sub> pressures (PCO<sub>2</sub>) varying between 0.0004 atm and 0.005 atm and soil with calcite concentrations of 0.6 % (low) and 3.3 % (average) content. The saturated zone experiment was executed with atmospheric pressures at two different temperatures: at 4°C and room temperature (~20°C) with 3.3 % calcite content. Groundwater fluxes and calcite dissolution were modelled with PHT3D and Modflow (Processing Modflow was used as interface). Fieldwork indicated that calcite is the most abundant Ca-carbonate and confirmed that calcite dissolution occurs at the Sand Motor predominately at the higher grounds, where rain water infiltration happens. The Ca an alkalinity reaction products of the experiments showed that there is significant inhibition of the calcite dissolution rate in respect to literature values, which can be attributed to the presence of foreign ions. An experiment with average calcite (3.3 % calcite, 50 g) at room temperature reached saturation in 2 days, while experiments with less calcite and the cooled experiment needed more time (probably 3-5 days). Analyses of the C isotopes in the alkalinity from experiments and the Sand Motor, revealed that the C captured is inorganic. This justifies the assumption that the alkalinity produced can be seen as CO<sub>2</sub> capturing. The model did not represent calcite weathering on the Sand Motor accurately yet and needs further research. The alkalinity concentrations are translated to CO<sub>2</sub> amounts captured and scaled up to the volume of the Sand Motor to arrive at an estimation of 4.2\*10<sup>5</sup> kg CO<sub>2</sub> captured a year and 8.3 Mkg CO<sub>2</sub> in twenty years. After inspection of the groundwater fluxes modelled for the Sand Motor, it can be viewed as a hydrologically isolated system from which all groundwater will be lost to the North Sea in twenty years. The CO<sub>2</sub> sequestered by the Sand Motor can, as a consequence, be regarded as captured since the North Sea is an effective CO<sub>2</sub> sink.

## **1. INTRODUCTION**

The origin of the Sand Motor, the stakeholders in this research and the state of the art will be discussed in this chapter. It will be concluded with the problem definition, aim and research questions.

### **1.1 BACKGROUND**

#### **1.1.1 Building with Nature**

Royal Boskalis Westminster and Van Oord initiated the “Building with Nature (BwN) innovation programme” in 2008 (De Vriend & van Koningsveld, 2012). They envisioned a more integral approach for engineering that enhances ecosystems, recreation and involves the local residents in the process of fulfilling their assignments. Ecosystems, for example, can be enhanced if the local natural processes are seen as asset rather than an obstruction in the design face of the engineering project. To put their BwN visions into action, a consortium under the name “Ecoshape” was realised (De Vriend & van Koningsveld, 2012). Government agencies (both European and Dutch authorities), applied research institutes and other private parties benefit from shared knowledge and expertise under this umbrella (Ecoshape, 2014). An example of a BwN project is the pilot project called “the Sand Motor”. This mega-nourishment at the Dutch coast is intended to enforce the coast for a period of 20 years through the natural processes of wave and wind action that are inherent to the local ecosystem (De Vriend & van Koningsveld, 2012).

#### **1.1.2 The origin and history of the Sand Motor in context of Dutch coastal protection**

In the Netherlands 60 % of the inhabitants live below sea level and approximately 65% of the gross national product is accomplished in the coastal zones (Zeenivea, 2014; Stive et al., 2013). Therefore, it is crucial that the dunes that protect the Netherlands from flooding, are not eroding and can withstand future sea level rise (Centre for Climate Adaptation. 2014). To prevent coastal erosion, Rijkswaterstaat (RWS, a Dutch government agency) deposits approximately  $12 * 10^6 \text{ m}^3$  sand a year along the Dutch coast to maintain them to their 1990 conditions. They renew their plans for coastal protection once every 4 years and decide which locations are vulnerable and should, therefore be nourished. On a yearly basis, the council reviews the state of the beaches so that interim adjustments can be made to the plans that will strengthen the more vulnerable beaches (Rijkswaterstaat, 2014). This strategy will be referred to as traditional nourishment in this paper, it means that every 4-5 years the ecosystems of eroding coastal areas can be disturbed with sand nourishments.

Ecoshape developed a new coastal maintenance strategy to lessen the damage to these coastal habitats (De Zandmotor, 2014). A mega-nourishment, called the Sand Motor, was realised in 2011 at the Dutch coast between Kijkduin and Ter Heijde (De Zandmotor, 2014). With almost twice the amount of sand that the Dutch government usually distributes over all beaches on a yearly basis, the distinct shape of  $21.5 * 10^6 \text{ m}^3$  sand was formed (Figure 3). The sand of the Sand Motor will gradually be deposited along the coast through tidal motions, currents and wind action (De Zandmotor, 2014a; Stive et al., 2013). Estimations are that the Sand Motor will be able to protect the adjacent 10 km of coastline for at least 20 years from erosion. This is a benefit for the local ecosystems since they are left undisturbed in this timespan, as the sand will be deposited naturally, while they are normally disturbed once every five years (De Zandmotor, 2014; Centre for Climate Adaptation. 2014; Stive et al., 2013). This form of soft engineering is,

thereby, thought to be more cost effective and more efficient than the traditional nourishments, (De Zandmotor, 2014; Stive et al., 2013). Since the Sand Motor is a pilot project, it is closely monitored by scientists from multiple universities, private companies and Dutch government agencies (Nature Coast, 2014; De Zandmotor, 2014).

**1.1.3 The CO<sub>2</sub> board**

Some of the stakeholders involved in the build of the Sand Motor also joined a “CO<sub>2</sub> board”, hosted by Ecoshape (participants listed in Table 1). The goal of the CO<sub>2</sub> board is to design a tool that indicates where CO<sub>2</sub> emissions can be lessened in coastal enforcement projects. They can achieve financial benefits if they can proof CO<sub>2</sub> reduction to the Dutch government. The Dutch government initiated a “Green deal” with private parties in the Dutch civil engineering sector in 2013 in order to stimulate CO<sub>2</sub> emission reductions. They provided a framework called the “CO<sub>2</sub>-performance ladder” against which a company’s CO<sub>2</sub> emission is ranked. Initially, a company has to indicate the net CO<sub>2</sub> emissions of their practices which will put them on a certain rank at the CO<sub>2</sub> performance ladder. If they can proof CO<sub>2</sub> emissions reduction in a successive project, they will move up the ladder, and are consequently rewarded with tax reductions and a higher chance to be selected to execute projects for the Dutch government (CO<sub>2</sub>-Prestatieladder, 2014).

The tool envisioned by the CO<sub>2</sub> board will assess the CO<sub>2</sub> emission of the equipment deployed, the execution and the nourishment itself (Figure 1). This can be presented to the Dutch government to rank their engineering projects at the CO<sub>2</sub> performance ladder. The CO<sub>2</sub> board splitted up the entire engineering process into five stages in the CO<sub>2</sub> footprinting tool. These five stages were called “buttons” and they will be individually investigated for CO<sub>2</sub> emissions (Figure 1; Ecoshape, 2014a). Button four of the CO<sub>2</sub> footprinting tool is called “the sand pit”, this is the part in which the net CO<sub>2</sub> sequestration of a nourishment is investigated. The CO<sub>2</sub> board wishes to know the difference between a traditional and the mega-nourishment (the Sand Motor) in carbon (C) sequestration capacity to indicate the emissions in button four. If such a difference were to be found, engineers could select the nourishment type with the highest net C sequestration capacity in an early designing stage (Ecoshape, 2014a).

**Table 1: Stakeholders involved in the CO<sub>2</sub> board**

Name	Sector	Core business
Van Oord	Private	Dredging contractor
Boskalis	Private	Dredging contractor
Royal Haskoning DHV	Private	Engineering consultants
Arcadis	Private	Engineering consultants
Witteveen en Bos	Private	Engineering consultants
Deltares	Private	Applied research institute
Rijkswaterstaat	Public	Government agency
Wetlands international	NGO	Nature conservation

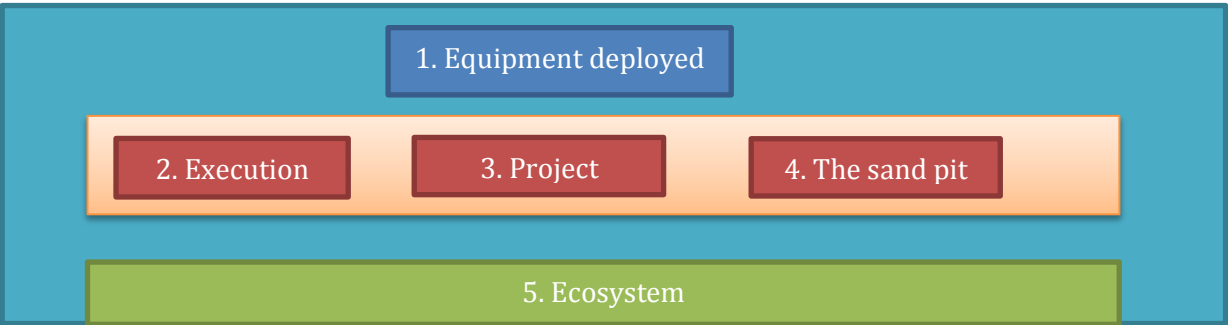


Figure 1. The five buttons of the CO<sub>2</sub> footprinting tool, adopted from Ecoshape (2014a).

#### **1.1.4 Social relevance**

Subsidising the “CO<sub>2</sub>-performance ladder” shows the engagement of the Dutch government in mitigating anthropogenic global warming (Duurzaam GWW, 2014). From an environmental ethics perspective, this approach can still be seen as anthropogenic since the cause of the problem ( fossil fuel emission) is not completely eliminated but it is only lessened (Curry, 2011). However, a complete elimination of fossil fuels is not a realistic expectation on the short term for the dredging industry while coastal protection is a necessity in the Netherlands. Therefore, every attempt to cut back emissions and increase the knowledge on C sinks should be welcomed. The Sand Motor is thought to be a sustainable nourishment technique, although this hypotheses still needs to be scientifically confirmed in the next  $\pm$  17 years. If significant differences are discovered between traditional nourishments and the Sand Motor, the nourishment technique that sequesters the most CO<sub>2</sub> can be selected. Reduced net CO<sub>2</sub> emissions of coastal enforcing projects will result in financial benefits (CO<sub>2</sub>- performance ladder) for the stakeholders which can be a positive incentive to further invest in sustainable practices.

The Sand Motor concerns a technique that protects Dutch assets and inhabitants. Due to the foreseen advantages of a mega-nourishment over the traditional techniques, this pilot project has gained worldwide interest from coastal countries. Increased scientific knowledge on CO<sub>2</sub> sequestration of the Sand Motor, could further enhance the attractiveness for worldwide deployment of mega-nourishments that is thought to inflict less damage to ecosystems than traditional nourishment techniques. Furthermore, Beaumont et al. (2014) advocates the importance to inform policy makers on the value of their coastal ecosystems as C stocks to stimulate coastal defence management that improves CO<sub>2</sub> sequestration. This research could provide information for policy makers on the value of the Sand Motor as a C sink.

#### **1.1.5 State-of-the-art**

The continuously rising anthropogenic CO<sub>2</sub> levels in the atmosphere result in an interest to identify CO<sub>2</sub> sinks in the biosphere. Knowledge on these C sinks could contribute to mitigating global warming and increase the understanding (and modelling) of the C cycle (IPCC, 2014). The C sinks are often associated with terrestrial vegetation although half (55% ) of the biological C is in fact captured by marine living organisms (Nellemen et al., 2009). CO<sub>2</sub> that is stored by marine and coastal habitats is called 'blue carbon'. Unfortunately, blue carbon ecosystems are thought to degrade in the coming two decades, while estimations reveal that restoring current degraded marine ecosystems could lead to the 10% atmospheric CO<sub>2</sub> reduction that is proposed to keep the CO<sub>2</sub> levels in the atmosphere below 450 ppm (Nellemen et al., 2009). Everard et al. (2010) demonstrated that the importance of blue carbon is underestimated by policy makers. For example, sand dunes were deemed “neglected ecosystems of significant and often under-appreciated societal value” in their paper. Blue carbon research has often been focussed on ecosystems with vegetation present (such as mangrove forest or algae) since C capturing through photosynthesis in plants is one of the main mechanisms that is thought of in this context. Sand dunes and beaches are often scarcely vegetated and are therefore not a main topic in C capturing research, although some research has been done at the coast of the United Kingdom (UK; Jones et al., 2008; Beaumont et al., 2014; Everard et al., 2010) .

The blue carbon stored in sand dunes and salt marshes at the coast of UK has been estimated by Beaumont et al. (2014). They found a 0.3-4.4 % C content in the soil of sand dunes and 4.3-5.5% C content in the soil of salt marshes. With these values UK C stocks were estimated (with 2000 as

baseline year) as  $3 * 10^3$  ton C in sand dunes and  $5 * 10^3$  ton C in salt marshes (Beaumont et al., 2014). The estimations were based on a C accumulation rate of  $582 \text{ kg C ha}^{-1}\text{yr}^{-1}$  in dry dune and  $730 \text{ kg C ha}^{-1}\text{yr}^{-1}$  in wet dune habitats, as established through field research of Jones et al. (2008). Beaumont et al. (2014), consequently, concluded that these coastal habitats have a significant impact in terms of  $\text{CO}_2$  sequestration and storage if they are kept unharmed. Everard et al. (2010) do not share this opinion: they concluded that there are relatively few coastal habitats where  $\text{CO}_2$  sequestration rates can be deemed high. However, Beaumont et al. (2014) calculated that the soil C stock of mobile/semi-fixed dunes (a category that fits the Sand Motor) is negligible which is associated to the lack of vegetation. There are multiple mechanisms that can result into C storage in sand dunes and salt marshes. Two main partakers (relevant for beaches and sand dunes) will be discussed subsequently: 1) calcium carbonates and 2) vegetation. Both calcium carbonate weathering and the photosynthesis/root respiration of vegetation can result in either C capturing or C release. They can interact in areas where soils containing calcium carbonates and vegetation are present.

### **Calcium carbonate weathering**

Calcium carbonate weathering will be the main focus of this research, since the Sand Motor does not have significant vegetation at the moment. Calcium carbonate dissolution or weathering is a possibility at lime rich beaches in the Netherlands (Eisma, 1968).  $\text{CO}_2$  can be sequestered by calcium carbonates in a dissolution reaction (reaction 1 in chapter 2; Appelo & Postma, 2005). Nonetheless, the reaction can also be reversed leading to  $\text{CO}_2$  degassing into the atmosphere. Calcium carbonates can consist of aragonite, dolomite and magnesium-calcites, but the most common form is calcite ( $\text{CaCO}_3$ ). Calcite dissolution is enhanced in the presence of dissolved  $\text{CO}_2$ . The gas pressure of  $\text{CO}_2$  in groundwater ( $P_{\text{CO}_2}$ ) is almost two orders of magnitude higher than that of atmospheric  $\text{CO}_2$  (0.03 vol %), caused by the infiltration of in rainwater dissolved  $\text{CO}_2$  (Hanson et al., 2000, Appelo & Postma, 2005). Even in sandy soils (with low vegetation density), the  $\text{CO}_2$  pressure is nearly an order of magnitude higher than the atmospheric pressure. Therefore, the residence time of C in soil is short (10-100 years) and the drop of  $\text{CO}_2$  concentrations in the top layer indicates that most of it escapes to the atmosphere (Lee 1997; Appelo & Postma, 2005). Groundwater distributes dissolved carbon. It is estimated that globally the amount of dissolved carbonate moving down with infiltrating groundwater is exceeded by the  $\text{CO}_2$  release back into the atmosphere from exfiltrating groundwater (flux in; 0.2 and flux out; 77Gt C/yr, Kessler & Harvey, 2001). The pH's at the Sand Motor are relatively high, the pH is between 7.3 and 8.8 in the pore water from unsaturated zone which is consistent with calcite weathering (I.R. Pit, personal communication, December 2014). It could be hypothesised that the high pH values of the Sand Motor indicate that it is indeed a calcium carbonate rich soil, which would be optimal for calcium carbonate weathering. The mobility of dunes plays a role in  $\text{CO}_2$  sequestration since fixed dunes store more C than mobile dunes (Beaumont et al., 2014). This could indicate low C sequestration values for the Sand Motor since it is mobile. A seasonal variation in calcite weathering is anticipated since  $\text{CO}_2$  dissolves better with lower temperatures. Therefore, the reaction products of calcite weathering are expected to increase with decreasing temperatures as well as increasing  $\text{PCO}_2$  (Van der Perk, 2013).



## **Organic carbon fluxes**

There is little vegetation present at the Sand Motor at the moment but this could change in the future. Beaumont et al. (2014) demonstrated that C stocks in coastal habitats correlate positively with vegetation densities. Studies on terrestrial vegetation show that the CO<sub>2</sub> that plants fixate in their photosynthesis process is distributed in the soil vertically with their roots as soil organic carbon (SOC). The absolute amount of SOC is dependent on climate, but how deep and how much CO<sub>2</sub> is distributed vertically depends primarily on vegetation type (Jobbagy & Jackson, 2000, 2004). Ecosystems with low decomposition rates can store the C in the soil through vegetation litter. Because the C limitation is reached early in these ecosystems, SOC concentrations are high (Bosatta & Berendse, 1984; Kooijman & Besse, 2002). Along these lines sea grass can be responsible for carbonated sand in the sparse vegetated fore dunes (Cardona & García, 2008). Spiteri et al. (2008) discovered that at the wedge of groundwater and salt water, the (marine derived) dissolved organic carbon (DOC) degrades, which can lead to CO<sub>2</sub> emissions. There can be seasonal fluctuations in soil CO<sub>2</sub> pressure due to vegetation. The fluctuations are caused by the winter stop of biological CO<sub>2</sub> sequestration and, consequently, groundwater degassing into the atmosphere (in unsaturated sand). While in the summer, when biological CO<sub>2</sub> production is high, C is sequestered in the deeper soil layers from where it cannot easily diffuse back into the atmosphere (Reardon et al., 1997).

Calcite precipitates when vegetation uses the dissolved carbonates in the sand for photosynthesis instead of atmospheric CO<sub>2</sub> (Appelo & Postma, 2005). CO<sub>2</sub> can furthermore be released from the soil by heterotrophic (microbes, soil fauna) and autotrophic (root) respiration, the oxidation of (dissolved) organic carbon and decomposing soil organic matter (SOM) (Hanson et al., 2000; Keller & Bacon, 1998; Appelo & Postma, 2005; Schlesinger, 1977). This could indicate that the presence of SOM in the soil, that was used to build the Sand Motor, can have a significant impact on the CO<sub>2</sub> sequestration rates.

## **Knowledge gap and expectation for the Sand Motor**

Calcite dissolution kinetics have been studied extensively in laboratory settings since it is an abundant mineral (Morse and Arvidson., 2002). Understanding its reaction is a key to many natural phenomena such as degradation of monuments (build with calcium carbonates) and the accumulation of carbonates in marine sediments. However, an accurate translation from laboratory results to that of specific ecosystems has not yet been made. One of the reasons is that there are voids in the comprehension of the inhibition of foreign ions on the calcite dissolution rate. Therefore, laboratory results can potentially be used as a benchmark for field conditions, but they will not be directly applicable to natural conditions (Morse and Arvidson., 2002). Field studies on calcite dissolution are often aimed at aquifers or carbonate rocks. Carbon stocks and CO<sub>2</sub> sequestering on the tidal plains, the beach and at the fore dunes have been little investigated (Jones et al., 2008; Beaumont et al., 2014). Most of the above cited information is from papers that investigate nitrogen (N) content in coastal soils and that mention C content briefly, sometimes even estimated as 50 % of the SOM, to calculate the N:C ratio (Cardona & García, 2008; Kooijman & Besse, 2002; Jones et al., 2008).

Summarizing the mechanisms addressed above, I expect that calcite weathering occurs at the Sand Motor at the higher parts in the centre where rainwater infiltrates. I anticipate that higher C sequestration will be achieved in winter time due to the colder conditions. Proving C sequestration at the Sand Motor will, therefore, entail knowledge on calcite dissolution kinetics

unique to its sand and the groundwater fluxes. The groundwater of the Sand Motor will be sampled to prove C sequestration. Therefore, this research will be a combination of fieldwork, laboratory research and modelling, resulting in a C sequestration estimate of the Sand Motor.

### **1.2 PROBLEM DEFINITION**

The Sand Motor is an unique mega nourishment that is thought to capture C through calcite dissolution. How much C will be captured depends on the local conditions that can influence calcite dissolution rate.

### **1.3 AIM**

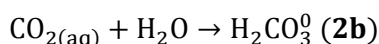
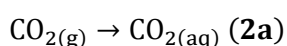
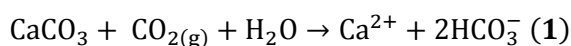
The capacity of the Sand Motor to store C through calcite dissolution will be researched. The influence on calcite dissolution rate of seasonal differences in temperatures, the variation of CO<sub>2</sub> pressure and calcite concentrations will be analysed. The saturated and unsaturated zone will be investigated separately and the groundwater fluxes will be studied to determine whether the Sand Motor sequesters C. This research will combine the results of fieldwork, laboratory experiments and modelling to derive the C sequestration capacity of the Sand Motor.

### **1.4 RESEARCH QUESTION**

1. What is the C sequestration capacity of the Sand Motor?
  - a. What is the Ca-carbonate content of the Sand Motor?
  - b. What is the net CO<sub>2</sub> sequestration rate of the Sand Motor?
  - c. Is the CO<sub>2</sub> sequestration capacity of the Sand Motor positively associated with Ca-carbonate concentrations?
  - d. What is the effect of low temperatures (4°C) at the Sand Motor on the Ca-carbonate dissolution rate?
  - e. Does the Sand Motor increase C sequestration in comparison to traditional nourishments?
  - f. Will the development of the calcite concentration at the Sand Motor influence the C sequestering within the twenty year life span of the Sand Motor?

## 2. CHEMICAL PROCESSES

This research focusses on the dissolution of calcium carbonates such as; aragonite, dolomite and calcite. In the Netherlands the beaches north of Bergen are calcium carbonate poor (less than 0.5 %), however, south of Bergen calcite concentration on beaches can reach up to 12% (Eisma, 1968). Even higher concentrations (up to 25% calcite) can be found in the adjacent dunes due to lag deposits. Sand samples of the Sand Motor contain 0-7.8 % calcite (appendix C). Just two of the 39 locations in appendix C do not exceed the 0.5 % calcite threshold and can, therefore, be called Ca-calcium poor (Eisma, 1968). On average the sand samples contain 4% calcite, which indicates that the Sand Motor is Ca-calcium rich. Calcite weathers when it is in contact with dissolved CO<sub>2</sub> (reaction 1), it results in calcium and the production of alkalinity (HCO<sub>3</sub><sup>-</sup>; Abanades & Alvarez, 2003; Juvekar & Sharma, 1973; Appelo & Postma, 2005). Reaction 1 is a simplification of several chemical reactions, which are listed in Table 2.1. Calcite dissolution is controlled by the availability of water and CO<sub>2</sub> (Kaufmann & Dreybrodt, 2007). Water is needed for calcite weathering since the dry reaction needs temperatures above 823 K (Abanades & Alvarez, 2003; Juvekar & Sharma, 1973). Considering CO<sub>2</sub> dissolves in water (reaction 2a,b), rainwater is a direct source for CO<sub>2</sub> input into soils (Appelo & Postma, 2005).



Plummer et al. (1978) investigated the dissolution kinetics of pure calcite in deionised water with temperatures between 5-60 °C and PO<sub>2</sub>: 0-1 atm. They demonstrated that reactions 3f, 3g and 3h from Table 2.1 can occur simultaneously. They indicated three pH regions with different mechanism that influence kinetics. In the first region (pH 0-3.5) the reaction is transport controlled and, consequently, the stirring rate of an laboratory experiment can influence the calcite dissolution rate. In the second region (pH 3.5-5.5) there is a transition from transport controlled to surface controlled kinetics, which is the dominant mechanism in the third region (pH > 5.5). In the third region the calcite dissolution reaches equilibrium, the pH at which the equilibrium is reached, depends on the PCO<sub>2</sub> (Plummer et al., 1978; Morse and Arvidson, 2002). The carbonate species of dissolved CO<sub>2</sub> also depend on pH. From pH 3-6.3 H<sub>2</sub>CO<sub>3</sub><sup>0</sup> is most abundant, followed by 2HCO<sub>3</sub><sup>-</sup> from pH 6.3-10.3. A pH higher than 10.3 results in CO<sub>3</sub><sup>2-</sup> as the most abundant carbonate species (Appelo & Postma, 2005). The distribution of carbonate species is the main reason that the reaction in Table 2.1 depend on pH. Temperature also has an significant effect on calcite dissolution. CO<sub>2</sub> dissolves better with lower temperatures while calcite dissolution happens faster with increasing temperatures (Plummer et al., 1978; Van der Perk, 2013). Figure 2 depicts the temperature dependency of the calcite dissolution rate and dissolved CO<sub>2</sub> with a PCO<sub>2</sub>= 0.004 atm. The dissolved CO<sub>2</sub> in Figure 2 was calculated in PHREEQC with demi water, which results in a pH below 5 and, consequently, H<sub>2</sub>CO<sub>3</sub><sup>0</sup> is the most abundant carbonate species. The log of the calcite dissolution rate increases a little. However, it not much on the calcite dissolution log scale of -3 to -8 that has been measured in experiments by Plummer et al. (1978).

It is possible that there is dolomite or magnesium-rich calcite (Mg-calcite) present on the Sand Motor. Dolomite can be identified since it weathers slower than calcite (Engesgaard & Kipp, 1992). Mg-calcite, on the other hand, weathers alongside with calcite. Therefore, Mg produced with a time lag relative to Ca indicates the presence of dolomite, while Mg produced simultaneously with Ca will most probably be a result of Mg-calcite dissolution (Appelo & Postma, 2005).

**Table 2.1 Reactions associated with calcite dissolution. All reactions with a (\*) are dependent on pH ( Table adapted from Kaufmann & Dreybrodt, 2007; Appelo & Postma, 2005 ).**

(3a)	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	Water dissociation into hydrogen- ad hydroxyl-ions
(3b)	$\text{CO}_{2,\text{atm}} \rightleftharpoons \text{CO}_2$	$\text{CO}_2$ dissolution in water
(3c)	$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3^0 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	Carbon conversion into hydrogen and bicarbonate*
(3d)	$\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$	Carbon conversion into bicarbonate*
(3e)	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	Bicarbonate dissociation into hydrogen and carbonate ions
(3f)	$\text{CaCO}_3 + \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^-$	Dissolution of calcite*
(3g)	$\text{CaCO}_3 + \text{H}_2\text{CO}_3^0 \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^-$	Dissolution of calcite*
	$\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O}$	Dissolution of calcite*
(3h)	$\rightleftharpoons \text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^-$	Dissolution of calcite*
(3i)	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	Dissolution of calcite*

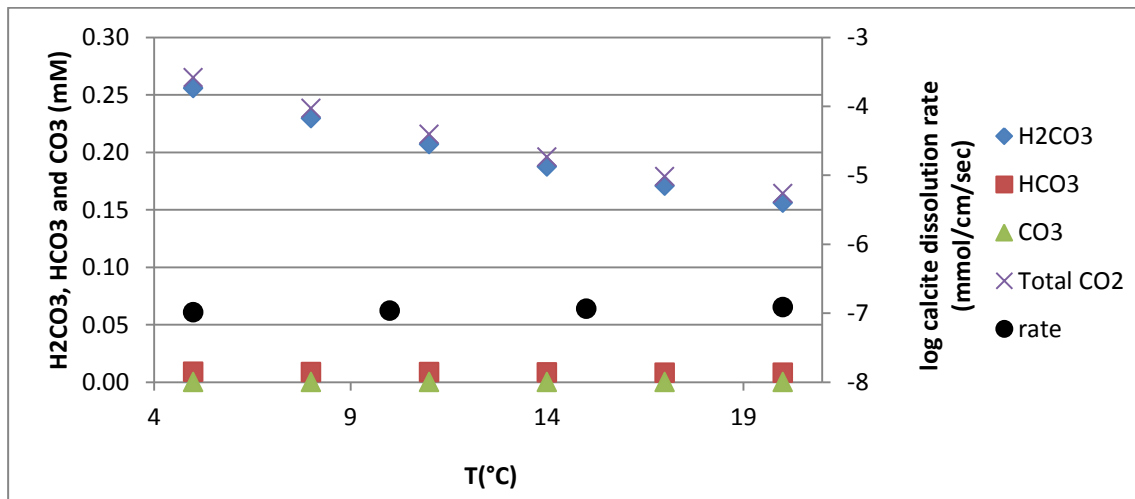


Figure 2. The dissolution of  $\text{CO}_2$  in demi water and the log of the calcite dissolution rate (black dot) dependent on temperature ( $\text{PCO}_2 = 0.004 \text{ atm}$ ).

### Carbon isotopes

When CO<sub>2</sub> dissolves into water, it produces four main carbon species; CO<sub>2(aq)</sub>, H<sub>2</sub>CO<sub>3</sub><sup>0</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, which will be indicated as dissolved inorganic carbon (DIC; Clark and Fritz, 1997). The <sup>13</sup>C / <sup>12</sup>C (δ<sup>13</sup>C) isotope ratio of C atoms in DIC vary significantly between organic sources and inorganic and, consequently, can indicate the sources of the C. For example, δ<sup>13</sup>C found in dissolved inorganic CO<sub>2</sub> is -8‰ while dissolved organic CO<sub>2</sub> δ<sup>13</sup>C = -24. Table 2.2 gives an overview of relevant δ<sup>13</sup>C values, the variation in DIC isotopes of seawater is dependent on location, season and depth (Mook and Tan, 1991). There is a difference in δ<sup>13</sup>C value of the DIC, between systems that are in open contact with CO<sub>2</sub> and systems that have a constant PCO<sub>2</sub>. The unsaturated zone at the San Motor is an open CO<sub>2</sub> system while the saturated zone is a system with constant PCO<sub>2</sub>, the latter will be referred to as a closed CO<sub>2</sub> system. In the closed CO<sub>2</sub> system I expect a 50/50 contribution of C isotopes from dissolved (inorganic) CO<sub>2</sub> and marine calcite. Two molecules HCO<sub>3</sub><sup>-</sup> are created in the calcite dissolution reaction (reaction 1). One of the HCO<sub>3</sub><sup>-</sup> molecules will get a C atom from the CO<sub>2</sub> molecule while the other HCO<sub>3</sub><sup>-</sup> receives the C from the calcite molecule. This means that a δ<sup>13</sup>C between -3 and -4 ‰ (since 0.5\*[-8+ 0 or 2] = -3 or -4) is expected for CO<sub>2</sub> sequestration in a closed system (Appelo & Postma, 2005). In the open CO<sub>2</sub> system, the carbonate species in the solution are important to establish the δ<sup>13</sup>C. In this case the CO<sub>2</sub> isotopes will be more abundant than any of the marine calcite isotopes since the gas exchange with water is quick and there is an unlimited supply of CO<sub>2</sub>. CO<sub>2</sub> dissolved in water has three different isotope signatures for dissolved CO<sub>2(aq)</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> (Table 2.2). Therefore, the ratio of the carbonate species in the sample will determine the final δ<sup>13</sup>C value of an open CO<sub>2</sub> experiment.

**Table 2.2. An overview of δ<sup>13</sup>C values relevant for this research.**

	δ <sup>13</sup> C (‰)	Reference
Dissolved inorganic CO <sub>2</sub>	-8	Appelo & Postma, 2005
HCO <sub>3</sub> <sup>-</sup> (inorganic origin)	2	Appelo & Postma, 2005
CO <sub>3</sub> <sup>2-</sup> (inorganic origin)	1	Appelo & Postma, 2005
Dissolved organic CO <sub>2</sub>	-24	Appelo & Postma, 2005
HCO <sub>3</sub> <sup>-</sup> (organic origin)	-14	Appelo & Postma, 2005
CO <sub>3</sub> <sup>2-</sup> (organic origin)	-15	Appelo & Postma, 2005
Average atmospheric CO <sub>2</sub>	-7	Mook 1986
Average oceanic DIC	1.5	Mook 1986
Calcite of marine origin	between 0 and 2	Mook 1986
DIC seawater	between 0 and 2	Mook and Tan, 1991

### 3. THE SAND MOTOR

The fieldwork described in this paper has been conducted at the Sand Motor. This mega-nourishment was realised in 2011 at the Dutch coast between Kijkduin and Ter Heijde for coastal defence purposes (De Zandmotor, 2014). The sand used for the construction was excavated in a sand pit located 10 km from the shoreline (De Zandmotor, 2014). A distinct shape ( Figure 3) of  $21.5 \times 10^6 \text{ m}^3$  sand was formed, which is almost twice the amount of sand that the Dutch government usually distributes over all beaches on a yearly basis (De Zandmotor, 2014). The mega-nourishment will gradually deposit the sand at the coast through tidal motions, currents and wind action during the next 20 years (De Zandmotor, 2014a; Stive et al., 2013). This will strengthen the coastline and protect the hinterland from flooding. An advantage is that the local ecosystems are left undisturbed for twenty years while traditional nourishment techniques disturb the ecosystems approximately once every five years.

The Sand Motor is a pilot project. Therefore, it is closely monitored by scientists from several universities, applied research institutes, private companies and Dutch government agencies (Nature Coast, 2014; De Zandmotor, 2014). Its geochemical composition is currently being analysed by the PhD student Iris Pit and an overview of the preliminary data (that are of significance for this research) sampled at the locations depicted in Figure 3 are listed in appendix C (I.R. Pit, personal communication, February 2015). The average pH found is around 8, average calcite content is 4% (0-7.8%), average alkalinity is 3.3 mM (1.5-9 mM) and the  $\text{PCO}_2$  in the soil ranges from 0.0003-0.0126 atm (all above atmospheric  $\text{CO}_2$  pressures). The groundwater of the Sand Motor consists of a fresh layer of rainwater on top of seawater. The Sand Motor can be regarded as an isolated system, since all the rainwater that infiltrates will, eventually, end up in the North Sea after a certain period (personal contact Sebastian Huizer, May 2015).



Figure 3. The distinct shape of the mega nourishment the Sand Motor. The sampling grid of 250 x 250m that was used for the results described in appendix C and the fieldwork in this research (section 4.1).

## 4. METHODS

The research questions will be answered with laboratory experiments, fieldwork and modelling. Two different experimental setups have been used to mimic an open CO<sub>2</sub> system (bioreactor, section 4.2.2) and a closed CO<sub>2</sub> system (closed CO<sub>2</sub> experiments, section 4.2.3). The recipe for the rainwater imitation that was used in the experiment is in section 4.2.1. PHREEQC calculations have been made to interpret the results of the experiments (section 4.3.1). Fieldwork at the Sand Motor has been done to collect sand samples for the experiments and to investigate the calcite dissolution at the Sand Motor with groundwater samples (section 4.1). The calcite dissolution in groundwater fluxes have been modelled with Modflow and PHT3D in purpose of a C sequestration estimation (section 4.3.2).

### 4.1 SAMPLES

#### 4.1.1 Field work

##### *Sand samples*

At the Sand Motor, locations A10, C8 and B7 (Figure 3) were sampled in January 2015 and location D8 was sampled in April 2015. Location A10 was selected to explore conditions at the beach, location C8 was chosen for its central position at the Sand Motor, location B7 for its proximity to the lake and location D8 because of its low calcite concentration. The surface at the locations A10 and C8 was densely covered with shells, location B7 was wet in comparison to the other two locations (Figure 4.1.1a,b). It bordered a section near the lake that was closed by authorities due to quicksand. The soil at locations A10 and C8 was frozen at approximately 3 cm depth and at location B7 at 1-2 cm depth. The frozen soil made it more difficult to obtain samples. Location D8 was at the tidal plains and the soil was not frozen on this field trip. The centre of a grid point, and 4 points at 1m distance from the centre, were sampled. At each of these five points, two sand samples were collected and put into a bucket. The sand was stored in a plastic bag and subsequently mixed by hand. Six bags of sand (~1 kg) were retrieved at locations A10, C8 and B7. At location D8 three bags of approximately 1 kg were collected. Since a layer of sand was removed when a bag was filled, the next bag of sand was sampled at increased depth. Therefore, the first bag of each location contained more shells than the other bags and, as a consequence, the first bag is not used in experiments. Some of the sand in bag number 3 of location D8 was in contact with sea foam before sampling.

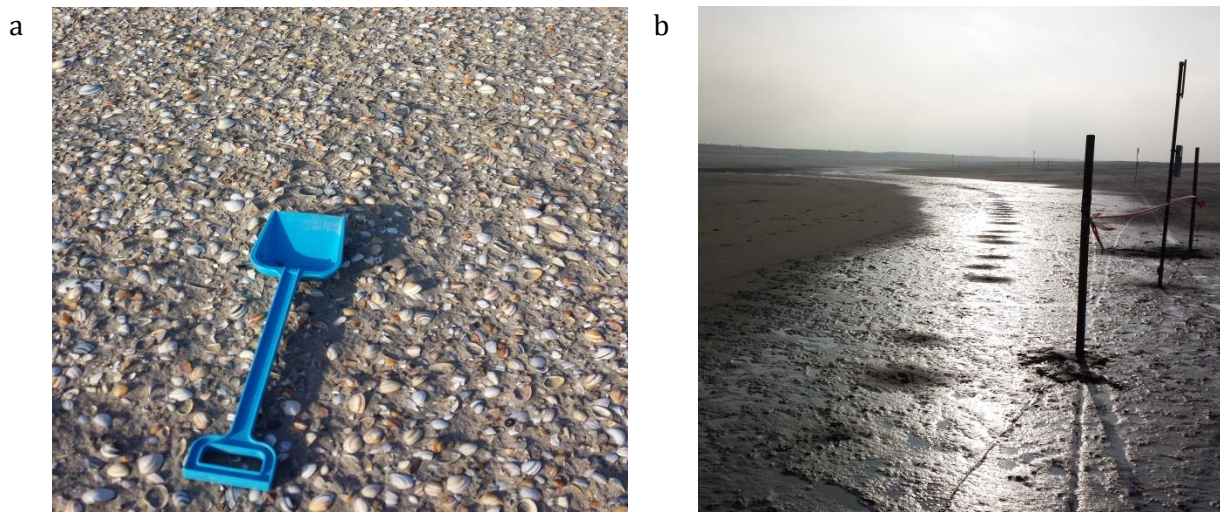


Figure 4.1.1. a) Location C8 and b) location B7 sampled at 23-1-2015

### Groundwater samples

At the Sand Motor, locations B7, D8, C8, B8, A8, C10 and C13 (Figure 3) were sampled in February 2015. At each location a hole was augered with a Edelman hand drill until the saturated zone was reached. A piezometer, with a filter sock at the end, was installed into the hole. Groundwater was extracted with a peristaltic pump using a polyethylene tube. When the groundwater became clear, a minimum of 1litre was extracted after which the samples were taken. Temperature and pH were measured immediately in the field and 5 bottles (specifications in Table 4.1.1) were filled with groundwater for further lab analysis after filtration through a 0.45 µm filter.

**Table 4.1.1. Specification of the groundwater sampling done at the Sand Motor and in experiments. Sample bottles intended for isotope analysis were filled completely to avoid interaction with remaining CO<sub>2</sub>. Acid was added to the sample intended for the ICP-MS/OES at the same day. All bottles were filtered through a 0.45µm filter.**

Number of samples	Volume samples field work	Volume samples experiment bioreactor	Volume samples experiment bottles	Type of bottle	Intended for	Particulars
1	2ml	2ml	2ml	glass	IC	filled up to $\frac{3}{4}$ of the bottle
2	2ml	2ml	2ml	glass	isotope analyses	no air in bottle
1	15-30ml	10/5ml	5ml	glass	alkalinity	
1	60ml	10/5ml	5ml	PE vial	ICP-MS/OES	600 µL HNO <sub>3</sub> added
1	-	-	5ml	glass	pH	
1	-	-	10ml	glass	Ca test	



#### **4.1.2 Laboratory protocol for the samples**

##### *Sand samples*

The samples were stored in a cooled storage room (4-5 °C). To prepare the sand for an experiment, a bag of sand ( $\geq 1$  kg) was put in an aluminium tray and dried in the oven for at least 24 hours at 105 °C. The sand was sieved with a 2 mm sieve, to remove large shells, and subsequently put in a preserving glass jar. When starting an experiment, the required amount of sand was taken from the jar. A sand sample for an experiment was obtained by means of a sandsplitter and, subsequently, weighed to get the required amount. Generally, samples were put into the bioreactor immediately after weighing, otherwise they were kept in a plastic container with lid.

##### *Groundwater samples*

All the samples were stored in a fridge at 4-5 °C prior to the lab analyses. Alkalinity was measured at the sampling day or at least the following day. Alkalinity was manually established with the GRAN method at room temperature (Sarazin and Prevot, 1999). The bottles of alkalinity samples taken during the bottle experiments were filled completely to avoid further interaction with the CO<sub>2</sub>. Samples destined for ICP-OES and ICP-MS were acidified with suprapur HNO<sub>3</sub> (10 µl per ml sample) and stored in a refrigerator (4-5 °C) until the analyses. The IC samples were analysed once a month and the ICP samples after the experimental phase. The isotope samples were measured using an IR-MS to determine dissolved inorganic carbon <sup>13</sup>C/<sup>12</sup>C ratio (DIC, δ<sup>13</sup>C). To prepare for the IR-MS, glass tubes with 3 drops of phosphoric acid were filled with helium and sealed with a lid. Each tube was subsequently injected with 0.7 ml sample. The groundwater samples from fieldwork were analysed with the IR-MS two days after. The samples obtained during experiments were analysed the day after or at the least two weeks after an experiment. The data of samples that contained an noticeable air bubble when preparing for the IR-MS, were excluded from further interpretation.

## 4.2 EXPERIMENTS

In this section the rainwater imitation will be discussed, followed by the experimental setups of the open CO<sub>2</sub> system (bioreactor) and a closed CO<sub>2</sub> system (bottle experiments). Table 4.2 is an overview of all experiments and their settings. The experiments will be identified with their (code in column 2) in the result and discussion chapters (Chapter 5 and 6).

**Table 4.2. Specifications of calcite dissolution experiments.**

Date	Code	Location sand	Calcite (%)	Sand (g)	PCO <sub>2</sub> (atm)	T (°C)	Type
5-3-2015	1lP	C8N4	3.3	50	0.0004	20	Bioreactor
11-3-2015	2hP	C8N4	3.3	50	0.0050	20	Bioreactor
18-3-2015	3	C8N4	3.3	50	0.0040	20	Bioreactor
19-3-2015	4lPlc	C8N4	3.3	5	0.0004	20	Bioreactor
25-3-2015	5lP	C8N4	3.3	50	0.0004	20	Bottle
26-3-2015	6lP	C8N4	3.3	50	0.0004	4	Bottle
7-4-2015	7	C8N4	3.3	50	0.0040	20	Bioreactor
9-4-2015	8lc	D8N1	0.6	50	0.0040	20	Bioreactor
13-4-2015	9lc	D8N1	0.6	5	0.0040	20	Bioreactor
14-4-2015	10	blank	blank	blank	0.0004	20	Bioreactor
16-4-2015	11	blank	blank	blank	0.0040	20	Bioreactor

### 4.2.1 Rainwater imitation

For the experimental setup, data on the composition of rainwater of monitoring station De Zilk was used to imitate rainwater (RIVM, 2014). De Zilk was chosen for the proximity to the North Sea. The elements in the RIVM (2014) dataset that were below detection levels of the equipment, were deemed insignificant and were not used in the rainwater stock. Calcium and magnesium were left out on purpose to ensure that all detected Ca and Mg are reaction products. The average values over the year 2012 of the elements that are selected from the dataset and their standard deviation are in Table 4.2.1. Sodiumchloride, ammoniumsulfate and ammoniumnitrate were mixed with demi water to create an imitated rainwater stock, furthermore, all experiments reported in this paper were done with a single stock. Table 4.2.1).

**Table 4.2.1 Recipe for rainwater. The stock in the last column is 1000 times the concentration needed for 1 L of imitated rainwater, adding up to 500 ml.**

Measurements at the Zilk			Laboratory rainwater stock	
Elements	Average 2012 (µmol/L)	Standard deviation (µmol/L)	Chemicals	mg/l
NH <sub>4</sub>	49	36	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	2.64
NO <sub>3</sub>	35	17	NH <sub>4</sub> NO <sub>3</sub>	2.80
Na	120	82	NaCl	6.43
Cl	139	97		
SO <sub>4</sub>	19	6		

#### 4.2.2 Bioreactor experiment (open CO<sub>2</sub> system)

For this experiment an Applikon 2L jacketed bioreactor was used. Continuous pH measurements were conducted with a Metrohm Synthrode 368mm and Tinet 2.4 software, the pH measurements were saved with a time interval of 10, 20 or 60 seconds. A Bronkhortst HI-TEC mass airflow controller was used to add and mix CO<sub>2</sub> and compressed air (CA) and the solution was stirred using an Applikon Stirrer Controller p100. The pH electrode was calibrated before an experiment with a pH 7 and pH 4 buffer. Subsequently, the bioreactor was filled with 1.5 litre demi water (WDI) and 1.5 ml rainwater stock was added. Next the bioreactor was put on its frame and closed with the lid (Figure 4.2.2, the experimental setup). The solution was stirred with 400 rounds per minute (rpm) and the continuous pH measurements were started. The sand was added after the pH of the solution was settled and, subsequently, the required mixture of gasses was switched on to achieve a certain PCO<sub>2</sub> (Flow calibrations in Appendix B). The bioreactor was sampled at regular time intervals (commonly with an hour interval), the type and number of samples can be found in Table 4.1.1. The variables in this experiment were: PCO<sub>2</sub>, and calcite concentration. Sand from location C08 (3.3 % calcite) and D08 (0.6 % calcite ) were used in the experiments. Experiments were done with atmospheric PCO<sub>2</sub> (0.0004 atm), ten times atmospheric pressures (0.004 atm) and a CO<sub>2</sub> pressure of PCO<sub>2</sub> = 0.005 atm.



*Figure 4.2.2. The experimental setup with the bioreactor for open CO<sub>2</sub> system experiments.*

### **4.2.3 Bottle experiment (closed CO<sub>2</sub> system)**

The variable in this experiment was mainly the temperature. The experiment was conducted at room temperature (~20°C) and repeated in the cooling cupboard (4- 5 °C). Calcite content and PCO<sub>2</sub> were kept unchanged during both experiments (PCO<sub>2</sub> = 0.0004 atm and 50g of sand from location C08). For each experiment three glass bottles were filled with 1 litre demi water (WDI) and 1 ml of rainwater stock. Sand was added and the bottles were closed with a cap containing a septum. The three bottles, with identical treatments, were placed on a shaker at 174 rpm. The bottles were sampled at (approximately) 1, 5 and 13 hours after the shaker was turned through the septum to avoid additional atmospheric CO<sub>2</sub> from entering the bottles. The three bottles were removed from the shaker, subsequently sampled, to be put back on the shaker. The type and number of the samples are found in Table 4.1.1 (lab procedures in section 4.1.2.). The pH was measured immediately after sampling (the pH electrode was calibrated each day with subsequently pH 10 and 7). The shaker with the three bottles was put into a cooling cupboard (4-5 °C) for the cooled experiment. The sampling took place inside the cupboard to avoid increasing temperatures, since it took 20-30 minutes to sample the three bottles.

## **4.3 MODELLING**

### **4.3.1 PHREEQC**

PHREEQC interactive v 2.18.3 was used to verify if the experiments have reached calcite saturation (PHREEQC interactive, 2011). An adapted PHREEQC database was used (personal contact Jasper Griffioen, March 2015) in which ammonia chemistry is thermodynamically decoupled from nitrate/ nitrite/nitrogen chemistry. Two different approaches were attempted. First of all, the reaction was modelled with the rainwater, calcite concentrations and temperature of an experiment to see if PHREEQC generates similar concentrations of alkalinity and Ca. The open CO<sub>2</sub> systems were modelled with a constant PCO<sub>2</sub> while the closed systems were modelled with a initial PCO<sub>2</sub> (an example of calculation of an open and closed CO<sub>2</sub> system can be found in appendix D). Secondly, the Ca, Mg and alkalinity concentrations that resulted from the experiment were used to establish the saturation index of a particular experiment (example in appendix D).

### 4.3.2 Processing Modflow

Processing Modflow v 8.0.42 (PMWIN) was used to insert chemical reactions with PHT3D into a Modflow model (PMWIN, 2015; Modflow, 2015; PHT3D, 2015). Modflow models groundwater fluxes while PHT3D models the reactive multicomponent transport. This means that the model imitates the saturated zone of the Sand Motor and is closed in respect to CO<sub>2</sub>. An existing Modflow model of the Sand Motor and its surroundings was used to provide the groundwater flux and rainwater input (personal contact Sebastian Huizer, May 2015). This 3D Modflow model has a scenario that describes the morphological changes of the Sand Motor area and the impact on the groundwater from the built till twenty years later. The density-driven groundwater flow of the model built by Sebastian Huizer could not be converted to PMWIN and is, consequently, not incorporated. The groundwater flow of the 4<sup>th</sup> year after the built in the scenario has been used since it represents the Sand Motor in its present state (2015). An attempt to reduce the grid of the model to exclusively the Sand Motor (the blue box in Figure 4.3.2b,c) resulted in significant changes in the groundwater flow (personal contact Sebastian Huizer, May 2015). Therefore, the dunes and hinterland of the Sand Motor are also included to model the chemical processes in the groundwater flow of the Sand Motor accurately. The thin blue line in Figure 4.3.2a indicates a transect in the 3D model that was chosen to obtain a 2D cross section. This transect in the model coincides with fieldwork sampling at the transect from A8 to D8 (Figure 3). The blue box in Figure 4.3.2b indicates this transect. At the right the dune ridge is visible, rivers or streams are indicated in blue and the yellow cells are drains.

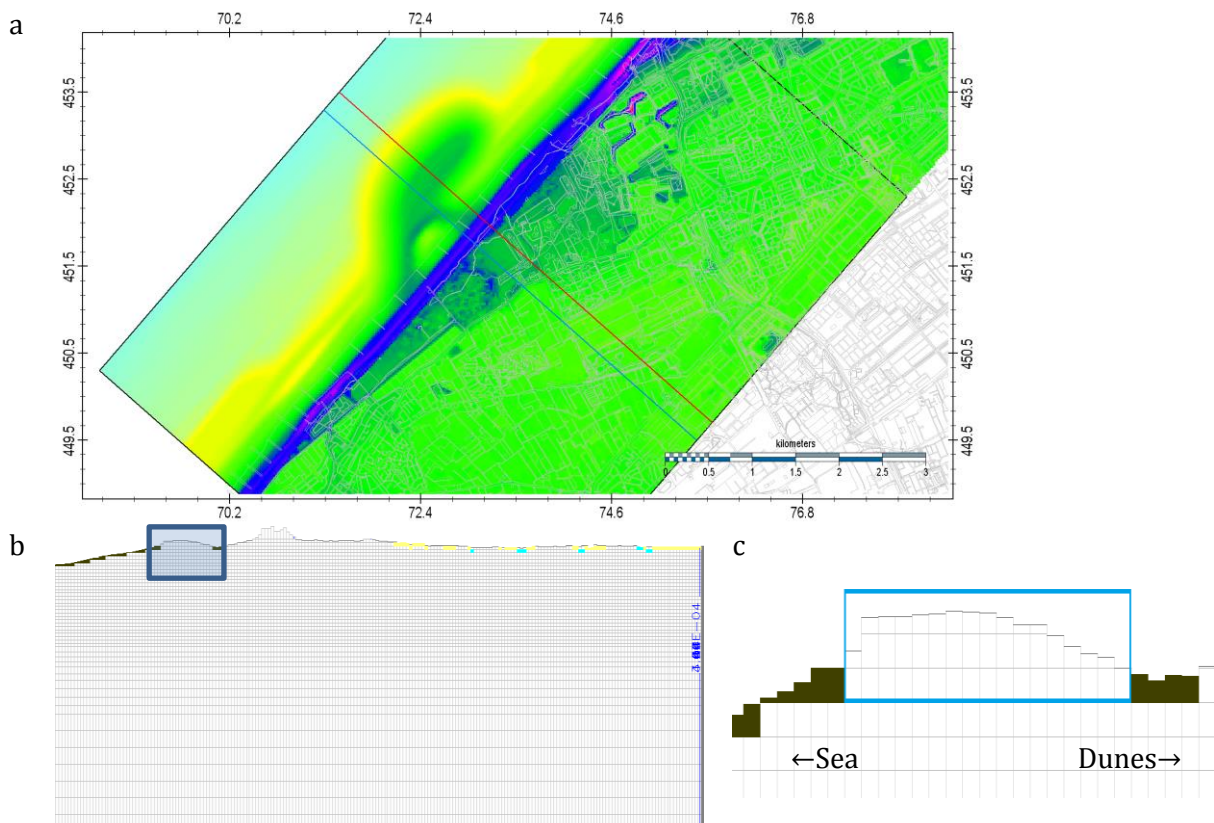


Figure 4.3.2. a) The thin blue line indicates the position of the transect that is taken for the 2D flow model (personal contact Sebastian Huizer, May 2015). b) The 2D transect used for the modelling of chemical reactions, in the middle the dunes are visible, the blue box indicates the Sand Motor. The blue and yellow cells at the right top of the model grid indicate rivers or streams and drains, respectively. c) The Sand Motor enlarged, the dark cells are inactive cells that represent the sea (left) and lake (right).

PHT3D was used to model calcite dissolution into the groundwater flow. A module was created to model calcite dissolution (Appendix E), additional setting for PHT3D are listed in Table 4.3.2. The recharge contained the elements that were deemed significant for rainwater imitation (Table 4.2.1) Calcium was enabled in the module with initial and recharge concentration set to zero to ensure that any Ca reported is the result of calcite dissolution. A time period of six months was chosen since the model had difficulties with converging the solutions parameters over long(er) time spans. The temperature was set to 20 °C, which is summer time at the Sand Motor. The Sand Motor has a range of PCO<sub>2</sub> in the soil (personal contact Iris Pit, July 2015), unfortunately, the PCO<sub>2</sub> cannot be changed per grid cell in PHT3D.

**Table 4.3.2. Settings used for PHT3D**

Variable		Reference
Calcite content in a cell	0.00165 mol/L	
Effective porosity	0.38	Olsthoorn, 1977
The longitudinal dispersivity	0.0067m	Engesgaard & Kipp, 1992
Advection	TVD scheme	
Solver	GCG	

#### *Water budget*

The water budget of the Sand Motor is needed for the C sequestration estimate. It is defined as the groundwater that enters or leaves the blue box in Figure 4.3.2c. The groundwater is discharged directly into the sea if it flows through the sides of the blue box, since the Sand Motor is surrounded by seawater and the lagoon (left and right). The rainwater that flows through the bottom of the box Figure 4.3.2c is stored temporarily in deeper layers of the Sand Motor, resulting in a fresh rainwater lens on top of saline water. The fresh water will be added to the sea during storms (personal contact Sebastian Huizer, May 2015). If any fresh water would remain, it would eventually be added to the sea since the entire Sand Motor will be deposited on to the beach in twenty years. Consequently, the Sand Motor can be considered to be an isolated system, of which all groundwater eventually will be deposited into the North Sea.

## 5. RESULTS

In this chapter the results of fieldwork will be discussed, followed by the results of the open CO<sub>2</sub> experiment (resembling the unsaturated zone of the Sand Motor) and the closed CO<sub>2</sub> experiment (the saturated zone at the Sand Motor). The PHREEQC results will be discussed alongside the results of the experiments. Subsequently, the results of the calcite dissolution modelled within the Sand Motor groundwater fluxes (with PMWIN) will be discussed. To conclude, an estimate of the Sand Motor C sequestration will be made based on previous discussed results.

### 5.1 FIELDWORK

In Figure 5.1 the Mg, Ca, pH, alkalinity and the DIC isotope ( $\delta^{13}\text{C}$ ) are plotted against Cl concentrations. Decreasing Cl at the sample locations, that are indicated with the black box in Figure 5.1, indicates freshening (the codes correspond with the sample locations in Figure 3). Overall, Mg and Ca content increase linear with Cl concentrations and are, therefore, an indication of freshening. The Mg, Ca, Na<sup>1</sup> and Cl concentrations in the sample from the lagoon ("Sea" in Figure 5.1) are in agreement with the average concentrations found in the sea (Goldberg, 1963). This is as expected since the lagoon is in open contact with the North Sea. Similar concentrations are found at the intertidal plains (locations C13 and D8), however, the declining concentrations found in the lake indicate freshening at that location. Locations that border de lake (A8, B7 and B8) show the most freshening. C10 and C8 are two locations at the centre of the Sand Motor where rainwater infiltration is expected and, therefore, these are the sites at which I expected calcite dissolution (personal contact Sebastian Huizer, May 2015). The Cl, Mg and Ca at location C8 indicate freshening similar to that of the locations that border de lake, however, location C10 is more saline. Nevertheless, there is still more rainwater infiltration at location C10 than at the lake.

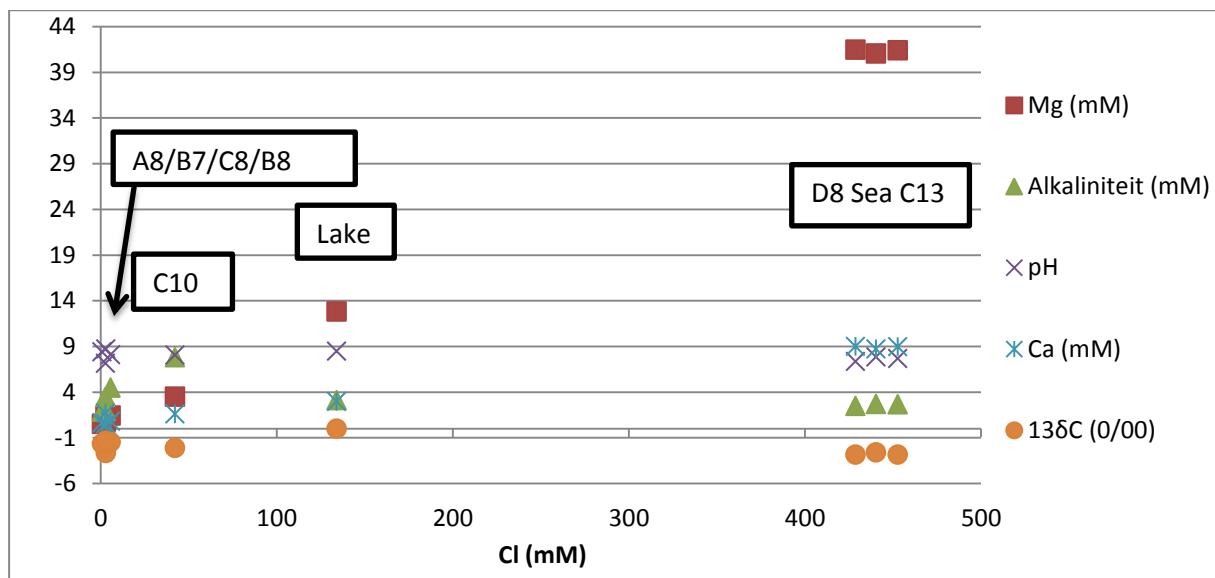


Figure 5.1. The Mg, alkalinity, pH, Ca and DIC isotopes ( $\delta^{13}\text{C}$ ), found in ground and surface water at

<sup>1</sup> The Na concentrations match Cl concentrations at the locations and are, consequently, not displayed in Figure 5.1.

*the Sand Motor. at a scale of increasing Cl. The codes in the black boxes correspond with sample locations in Figure 3.*

The seawater alkalinity is 2.3 mMol (Goldberg, 1963), which matches the concentrations found at C13, D8 and “Sea”. B8, C8 and “Lake” exceed 2.3 mM, and are therefore also possible locations for calcite dissolution. B7 and A8 do not exceed seawater alkalinity values and, consequently, there is no indication for calcite dissolution. C10 stands out with the highest alkalinity value (7.8 mM) which indicates, combined with the freshening at that location, that there is calcite dissolution due to rainwater infiltration (reaction 1). The DIC isotopes of Sea, D8 and C13 sample are on average  $\delta^{13}\text{C} = -2.7\text{‰}$  (standard deviation 0.1) which is not as anticipated since I expect  $\delta^{13}\text{C}$  values between 0 and 2‰ at sites with seawater infiltration (Mook 1986). The “Lake” sample is an open  $\text{CO}_2$  system with freshening and, therefore, the  $\delta^{13}\text{C} = 0\text{‰}$  is as expected (Chapter 2). At the locations that border the lake and in the centre of the Sand Motor I expect  $\delta^{13}\text{C}$  value between -3‰ and -4‰ for marine calcite dissolution in fresh water (Chapter 2). The  $\delta^{13}\text{C} = -3\text{‰}$  is approached by locations B7 ( $\delta^{13}\text{C} = -2.7\text{‰}$ ) and C10 ( $\delta^{13}\text{C} = -2.9\text{‰}$ ) and exceeded by locations B8 ( $\delta^{13}\text{C} = -1.5\text{‰}$ ), C8 ( $\delta^{13}\text{C} = -1.4\text{‰}$ ), and A8 ( $\delta^{13}\text{C} = -1.7\text{‰}$ ).

The calcite saturation index calculated with PHREEQC indicate that samples of locations; B7, B8, C10, C13, Sea and Lake sample are supersaturated for calcite. Locations D8 and A8 are saturated and C8 is the only location which is slightly unsaturated (SI = -0.5). The average pH on the Sand Motor is 7.96 (standard deviation 0.4) and the average temperature of 6.5 °C. Since the solubility of  $\text{CO}_2$  increases with decreasing temperature, calcite dissolution is expected to be enhanced at lower temperatures such as 6 °C (Chapter 2). The solubility of  $\text{CO}_2$  at 6 °C is comparable to the solubility at 4°C of the cooled experiment (section 5.2.1) it is, however, significantly enhanced compared to the  $\text{CO}_2$  solubility of the experiments at room temperature (Figure 2). Consequently, alkalinity concentrations from fieldwork are expected exceed those in the experiments at room temperature that are discussed in the next section.



## 5.2 EXPERIMENTS

In this chapter the bioreactor experiments will be discussed in the first section. These experiments will be referred to as the “open CO<sub>2</sub> experiments” since they are an open system with respect to CO<sub>2</sub> and are designed to imitate the conditions of the unsaturated zone at the Sand Motor. Secondly, the bottle experiments will be described which will be referred to as “closed CO<sub>2</sub> experiments” since they imitate the saturated zone in the Sand Motor. The PHREEQC results will be discussed alongside the results from the experiments for comparison. Lastly, the measurement errors will be discussed. The experiments have been given a number that corresponds with the specifications in Table 4.2. Experiment indicated solely with a number are executed with the standard initial settings of: PCO<sub>2</sub> = 0.004 atm and 50 grams of sand containing 3.3 % calcite. Experiments that deviate from these initial settings have additional letters that indicate; lower calcite content (lc), higher PCO<sub>2</sub> (hP) or lower PCO<sub>2</sub> (lP) (Table 4.2).

Before the results of the experiments are discussed, I need to establish if the experiments have reached calcite saturation. Since reaction 1 applies to a chemical reaction in equilibrium, the concentrations reported by PHREEQC can only be compared to the results of an experiment that has reached calcite saturation. The saturation index of all experiments, calculated with PHREEQC, is plotted in Figure 5.2. The input for Figure 5.2 was the pH and the amount of Ca and alkalinity of an experiments. The dotted lines are the borders of what I define as calcite saturation (SI = ±0.2). The experiments with the standard amount of calcite all reached saturation in 26 hours (2hP, 3, 7 and 5lP), except for the cooled experiment 6lP. The experiments with lower calcite concentrations (lc), and the cooled experiment 6lP, need more time to reach calcite saturation. If I extrapolate the unsaturated experiments, 1-3 days extra are anticipated, indicating that all experiments will at least reach saturation within a week.

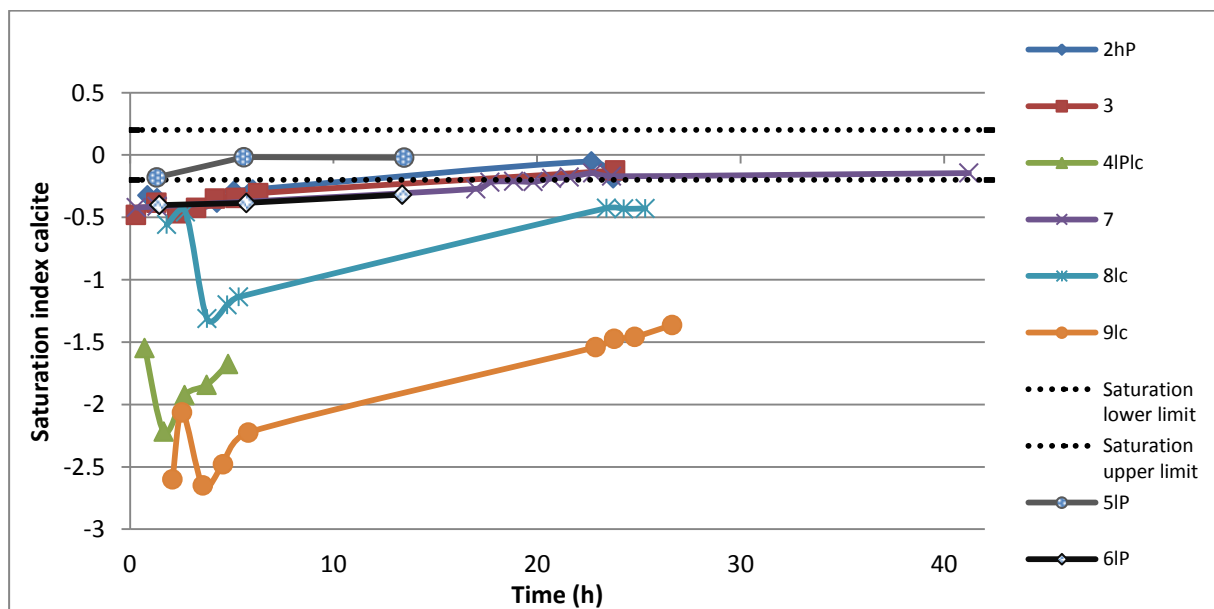


Figure 5.2. The saturation index of calcite plotted per sample moment of a certain experiment. The dotted black lines indicate the upper and lower limit of calcite saturation (SI ±0.2). Experiments 5lP and 6lP are closed CO<sub>2</sub> experiments, the other codes correspond to open CO<sub>2</sub> experiments (specifications of all experiment in Table 4.2).

### 5.2.1 Open CO<sub>2</sub> system experiments

The open CO<sub>2</sub> experiments were repeated several times while changing PCO<sub>2</sub> and calcite content (Table 4.2). In Figure 5.2.1, the alkalinity, pH, Ca, Mg and DIC isotopes are plotted of experiments 3 and 7 (that have similar initial conditions, Table 4.2). Experiments 3 and 7 combined create a dataset that covers 40 hours, the longest in this research. Figure 5.2.1 is not easy to interpret because of the limited resolution due to the many variable. However, it creates a meaningful overview of a single experimental setup. Subsequently, all the results will be discussed per variable. The pH of the rainwater solution is 5, it increases to 9 when the sand is added (50g sand, 3.3% calcite) and decreases when the CO<sub>2</sub> is added. The pH is 8.42 when the experiment has reached calcite saturation. The alkalinity, Mg, Ca and δ<sup>13</sup>C (of the DIC) increase in the first six hours and remain constant after calcite saturation is reached.

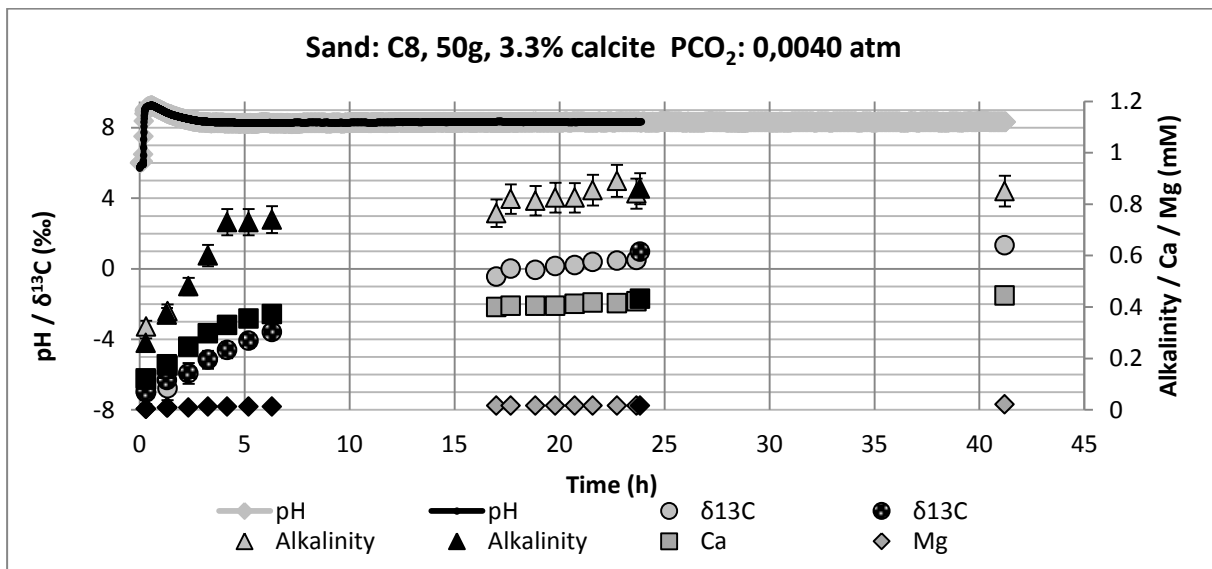


Figure 5.2.1.1 The pH, alkalinity (mM), Ca (mM), Mg (mM) and DIC ( $\delta^{13}\text{C}$ , ‰) of an open CO<sub>2</sub> experiment with a PCO<sub>2</sub> of 10 times atmospheric pressure. The black (experiment 3) and grey (experiment 7) colours in the graph indicate two different experimenting dates with similar setup.

### Description per variable

The pH in Figure 5.2.1.2a of experiment with the standard calcite concentration, all start around pH 5 (solely rainwater), increases when the sand is added and declines (due to CO<sub>2</sub> flushing) to stabilise around 8.16 (standard deviation 0.19) when calcite saturation is reached (Figure 5.2). Experiments 4lPlc, 8lc and 9lc, with low calcite concentrations, appear to eventually also approach the pH 8, but 24 hours are not sufficient for calcite saturation. There is no significant difference between the pH of two experiments with low and higher PCO<sub>2</sub> at calcite saturations (1lP and 2hP, Figure 5.2.1.2a). The pH of experiments with low PCO<sub>2</sub> resemble the PHREEQC pH better than the experiments with standard or higher PCO<sub>2</sub> (Figure 5.2.1.2b).

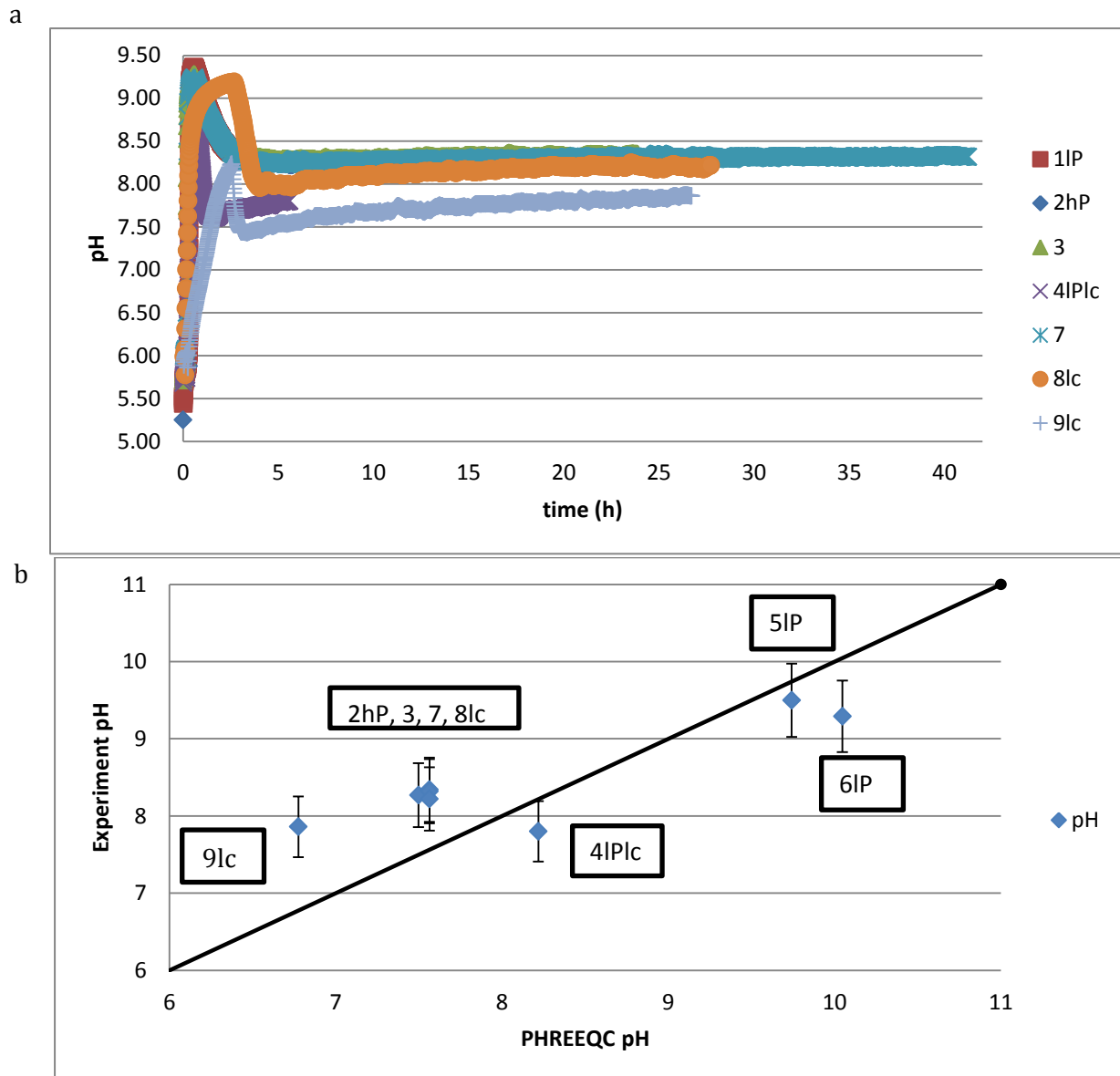


Figure 5.2.1.2. a) pH from the open CO<sub>2</sub> experiments. b) The comparison of the PH measured in the experiments and modelled with PHREEQC.

The alkalinity is on average 0.89 mM (Figure 5.2.1.3.a, standard deviation 0.2) an Ca 0.43 mM (Figure 5.2.1.3.ab, standard deviation 0.1) when calcite saturation is reached (experiments 2, 3 and 7). As expected, the experiments with lower calcite concentrations do not reach these alkalinity and Ca concentration since they are not yet saturated (experiments 4, 8 and 9). There is no significant difference in the amounts of alkalinity an Ca produced between experiment with difference in  $PCO_2$  such as experiment 2hP and 3. Consequently, the alkalinity and Ca is dependent on the initial calcite concentration and not on the  $PCO_2$  in these experiments. The alkalinity and Ca concentrations reached in experiment 8 (that has 10 times the calcite content of experiment 9, Table 4.2 ) and 9, show that ten times the amount of sand results in approximately doubling the concentration. According to the reaction stoichiometry of reaction 1, the Ca concentration (Figure 5.2.1.3b) should equal to half the alkalinity of an sample. The alkalinity/Ca ratio in indeed on average 2.04 when calcite saturation is reached (standard deviation 0.2). All alkalinity and Ca values are lower than those calculated by PHREEQC except for experiment 9lc that matches PHREEQC calculations well (Figure 5.2.1.4).

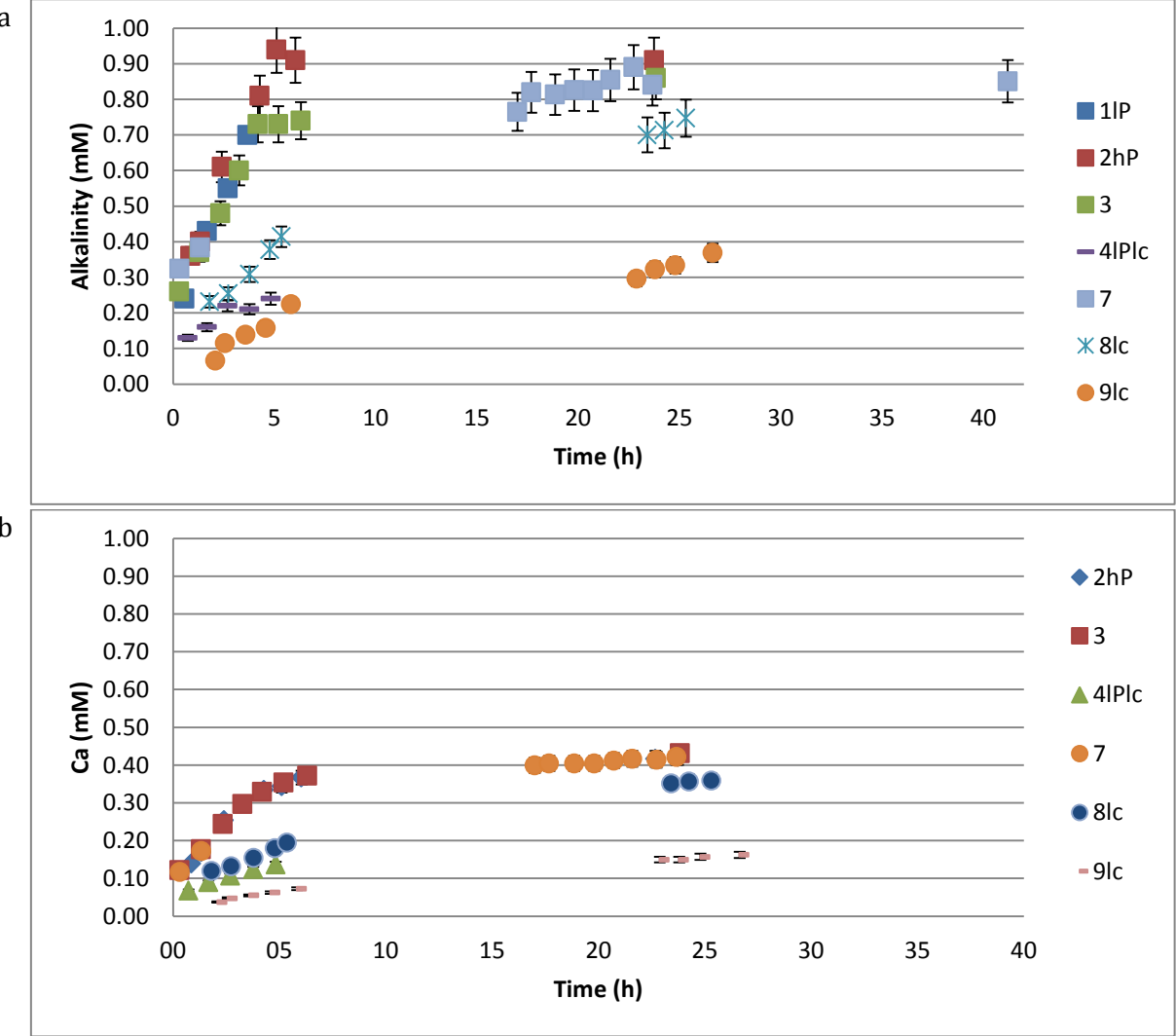


Figure 5.2.1.3. The a) alkalinity and b) Ca from the open  $CO_2$  experiments..

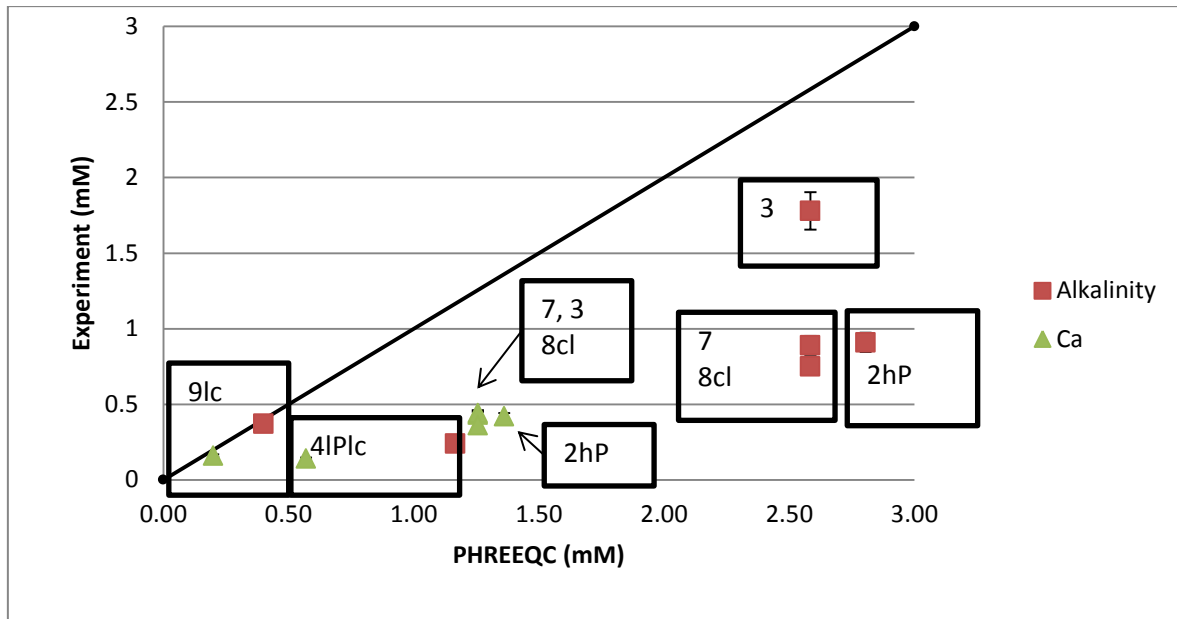
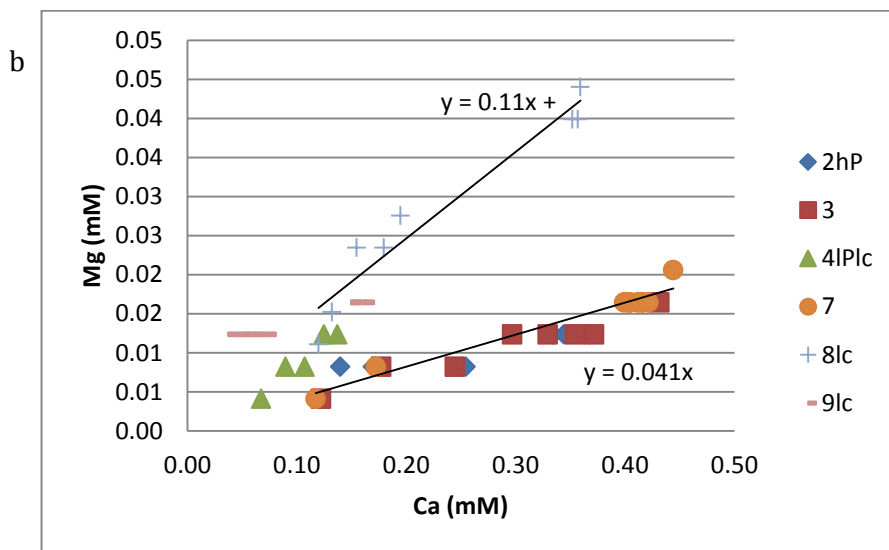
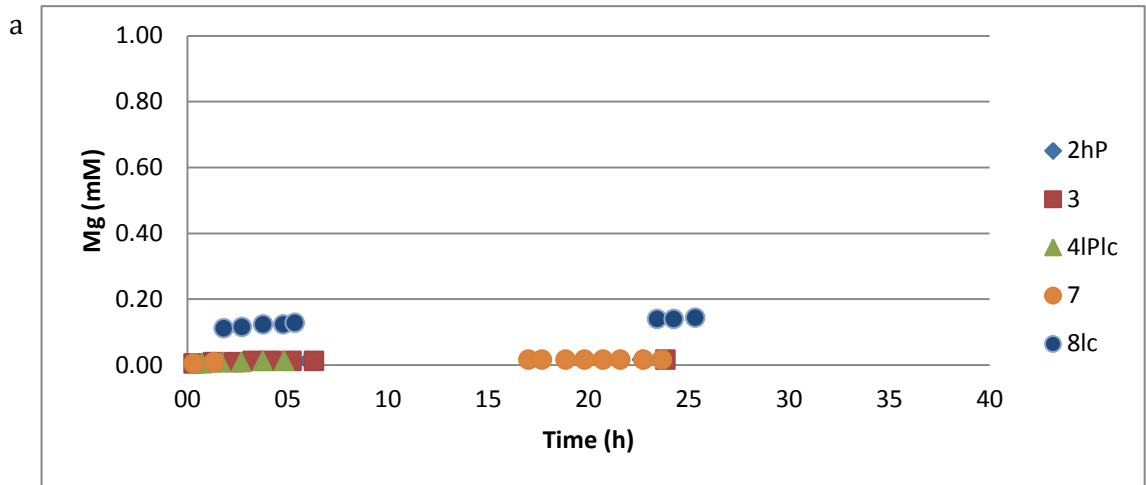


Figure 5.2.1.4. The comparison of the Ca, alkalinity found in the open CO<sub>2</sub> experiments and calculated with PHREEQC.

Although the amounts are much lower than Ca, some Mg is produced (Figure 5.2.1.5a). This indicates that there might be some magnesium in calcite present ( $\text{Ca}_{1-x}\text{Mg}_x\text{CO}_3$ ) in the sand samples. Since the Mg is produced alongside it is not dolomite, this would be produced with a time lag with respect to the Ca production (Appelo & Postma, 2005). The sand sample used in experiment 8lc stands out for its relative abundance in Mg. There is  $\pm 4\%$  Mg in respect to Ca found in the majority of the experiments (experiments 2, 3, 7 and 9, Table 5.2.1.1). This is high since it exceeds the 1% found on average along the Dutch coast (Appelo & Postma, 2005). The Mg percentage found in experiments 4lPlc and 8lc stand out since they are even higher, the Mg percentage is  $\pm 11\%$  (Table 5.2.1.1).

Isotope analyses of the DIC was done to understand the origin of the C in the alkalinity. The DIC values start around  $-8\text{‰}$ , which is in agreement with the average  $\delta^{13}\text{C}$  of dissolved inorganic CO<sub>2</sub> (Chapter 2). There is an increase in the  $\delta^{13}\text{C}$  in the first five hours and around 24 hours after the experiments is started, the values settle around  $\delta^{13}\text{C} = 1\text{‰}$  (saturated experiments). The  $\delta^{13}\text{C}$  value is dependent on the carbonate species present in the solution in an open CO<sub>2</sub> experiment (Chapter 2). Table 5.2.1.2 gives the distribution between carbonate species calculated with PHREEQC per experiment, the dominant species is  $\text{HCO}_3^-$  (as expected with a pH  $\sim 8$ , Chapter 2). With the ratios of the carbonate species known, a  $\delta^{13}\text{C}$  can be calculated for each experiment (Chapter 2). The  $\delta^{13}\text{C}$  of the experiments that have reached calcite saturation match well with the  $\delta^{13}\text{C}$  calculated with PHREEQC, which are indeed  $\delta^{13}\text{C} = 1\text{‰}$  (Table 5.2.1.2).



**Table 5.2.1.1.**  
**The Mg percentage**  
**in respect to Ca**  
**from Figure**  
**5.2.1.5b.  $Ca = x * Mg$ ,**  
**thus  $x * 100 = \%Mg$ .**

Experiment code	%Mg
2hP	3
3	4
4lPlc	12
7	4
8lc	11
9lc	4

Figure 5.2.1.5. a) Mg produced in the open CO<sub>2</sub> experiments. b) Mg concentrations plotted against the Ca concentrations found in the same sample. Table 5.2.1.1 gives the derived percentage Mg with respect to Ca.

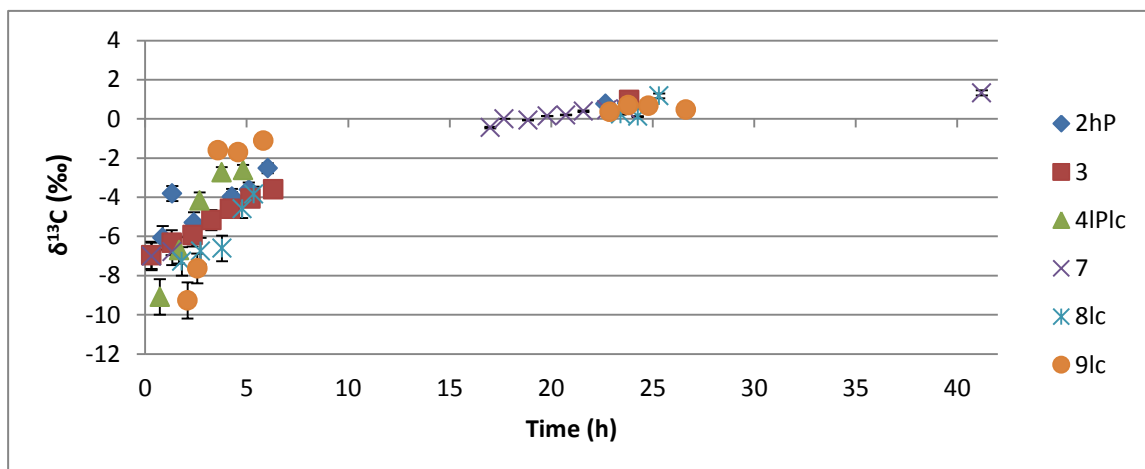


Figure 5.2.1.6. The isotope ratio <sup>13</sup>C / <sup>12</sup>C ( $\delta^{13}C$ ) of DIC of samples from the open CO<sub>2</sub> experiments.

**Table 5.2.1.2 The distribution of carbonate species calculated with PHREEQC per open CO<sub>2</sub> experiments. The last two columns indicates the  $\delta^{13}\text{C}$  value expected with the percentages carbonate species from PHREEQC and the actual isotopes measured.**

Experiment code	Calcite saturation	CO <sub>3</sub> <sup>-</sup>	CO <sub>2</sub>	HCO <sub>3</sub> <sup>-</sup>	$\delta^{13}\text{C}$ PHREEQC	max $\delta^{13}\text{C}$ experiment
2hP	Yes	0	7	93	1	0.8
3	Yes	0	6	94	1	1.0
4lPlc	No	1	1	98	2	-2.6
7	Yes	0	6	94	1	1.3
8lc	No	0	6	94	1	1.2
9lc	No	0	28	72	-1	0.5

### 5.2.2 Closed CO<sub>2</sub> system experiments

The closed CO<sub>2</sub> experiment was done with at room temperature (experiment 5lP, T~20°C) and cooled (experiment 6lP, T~4°C, Table 4.2). The results of the three bottles with similar treatments were averaged per experiment (Figure 5.2.2a,b). The pH, DIC isotopes and Mg concentrations do not differ significantly between the two experimental setups (Figure 5.2.2a,b). The difference between the two experiments is that there is a decrease in alkalinity and Ca around 13 hours in the cooled experiment, while these variables still increase in the experiment at room temperature (Figure 5.2.2a). I would expect a slower increase in alkalinity and Ca concentrations in the cooled experiment (due to the lower calcite dissolution rate for the cooled experiment, Chapter 2), nevertheless, a decline was not anticipated. The pH is on average 9.4 (standard deviation 0.08) which is higher than the average pH of the open CO<sub>2</sub> experiments. All other variables in closed CO<sub>2</sub> experiment at room temperature are significant lower than the values in the open CO<sub>2</sub> experiment. The average values found in the closed CO<sub>2</sub> experiment are: Ca = 0.16 mM, Mg = 0.01 mM,  $\delta^{13}\text{C}$  = -5.9‰ and alkalinity = 0.36 mM. While the average values of the open CO<sub>2</sub> experiment at equilibrium are: Ca = 0.44 mM, Mg = 0.2 mM,  $\delta^{13}\text{C}$  = 1.3‰, alkalinity = 0.91 mM. This is as expected since the closed CO<sub>2</sub> experiment have a limited amount of dissolved CO<sub>2</sub> for calcite dissolution while the open CO<sub>2</sub> experiment have a limitless CO<sub>2</sub> source. The alkalinity and Ca of the closed CO<sub>2</sub> experiment are in agreements with the calculations made with PHREEQC (Figure 5.2.2c). The  $\delta^{13}\text{C}$  between -7 and -5‰ of the closed CO<sub>2</sub> experiment in Figure 5.2.2b is unexpected, since it is lower than the  $\delta^{13}\text{C}$  = -4‰ anticipated for calcite dissolution in a closed CO<sub>2</sub> system (Chapter 2).

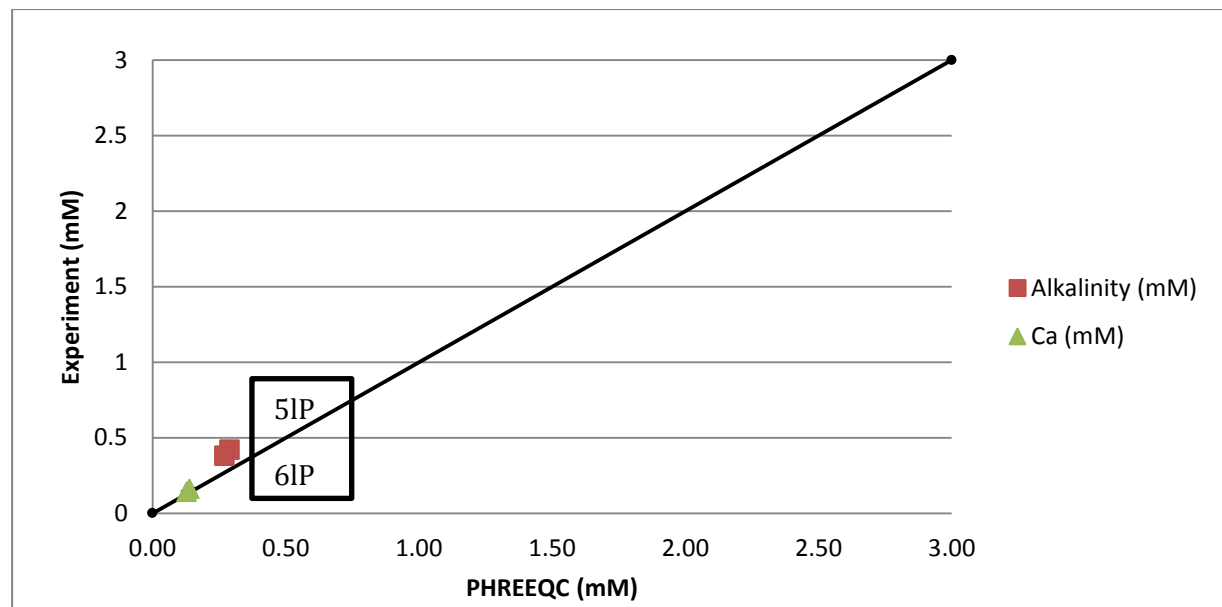
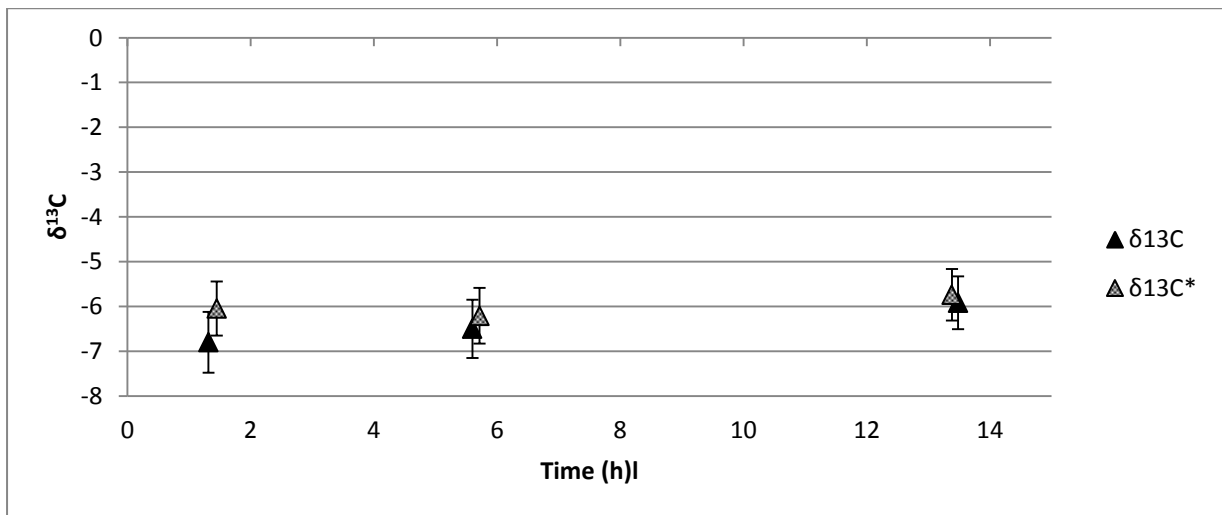
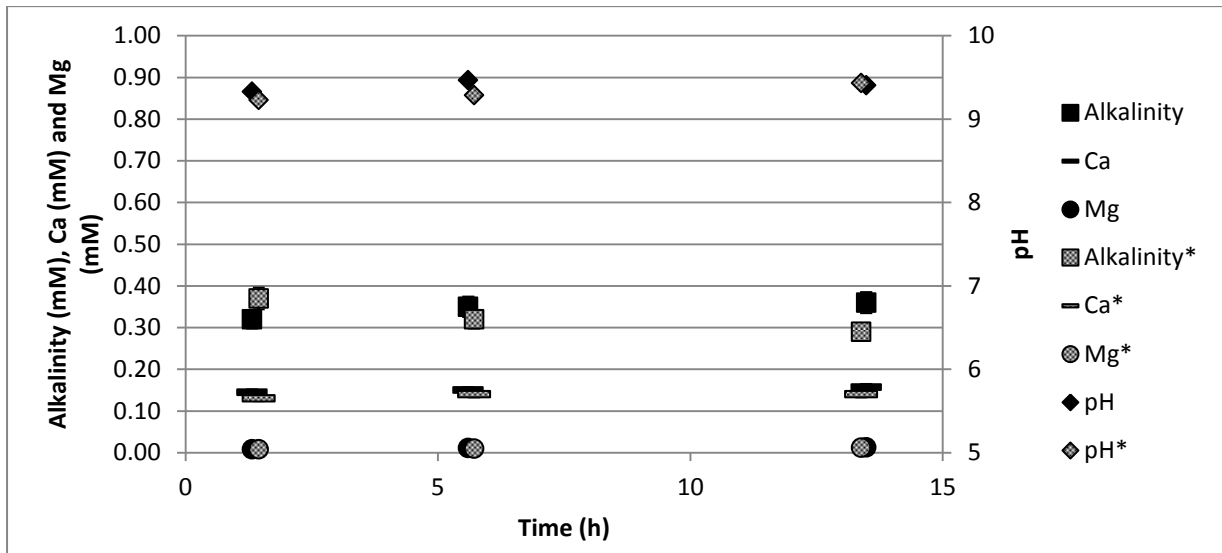


Figure 5.2.2. The a) alkalinity, Ca, Mg, pH and b)  $\delta^{13}\text{C}$  of the closed  $\text{CO}_2$  experiments. The (\*) indicates the cooled experiment. c) The comparison of the Ca, alkalinity found in the closed  $\text{CO}_2$  experiments and calculated with PHREEQC.



### 5.2.3 Blanks and measurement errors

The Alkalinity, Mg and Ca values of the demi water used for the experiments, were zero as expected. There  $\delta^{13}\text{C}$  of the demi water flushed with atmospheric  $\text{PCO}_2$  pressures ranged from -4 to -17 ‰ and the  $\delta^{13}\text{C}$  of demi water flushed with 10 times atmospheric  $\text{PCO}_2$  ranged from -15 to -30 ‰. This is a large variation in  $\delta^{13}\text{C}$  values and they are much lower than anticipated, since the expectation were  $\delta^{13}\text{C} = 2\text{‰}$  in both cases ( pH was above 5.5, which indicates  $\text{HCO}_3^-$ , Table 2.2). Table 5.2.1 displays all errors that are used in the Figures in the previous sections. They are calculated from duplo's (% difference errors) or uncertainties of the IC, ICP-OES and IR-MS measurements reported by analysts (instrument error/ precision).

**Table 5.2.1. Instrument errors reported by the analysts and percentage difference errors based on duplos. % Difference =  $\text{ABS}[100 * (x_1 - x_2) / (0.5 * (x_1 + x_2))]$ .**

Variable/ instrument	Instrument error/precision	% difference errors
Alkalinity	-	7%
Ca, Mg, Na (ICP-OES)	5% error	-
DIC (IR-MS)	-	10%
Cl (IC)	5% error	5%

### 5.3 MODELLING CALCITE DISSOLUTION IN THE SAND MOTOR (PMWIN)

In order to assess the transport of reaction products through the Sand Motor and indicate CO<sub>2</sub> sequestration, calcite dissolution in the Sand Motor was modelled with Processing Modflow. Figure 5.3.2.1 shows the Ca concentration increase caused by calcite dissolution in the first six months of 2015 (scenario year 4). The rainwater tracer in Figure 5.3.2.1f shows rainwater infiltration in the dune ridges and in a part of the hinterland but no rainwater infiltrated in the Sand Motor (indicated with the blue box). This is not as expected since at least a little rain water should be retained in 6 months in the Sand Motor. Since the model has spatial scale of 1 m and the model is run for 6 months, it is possible that it is not noticeable in the grid (recharge is 1.64 mm/day). Although there is no significant rainwater input in the rest of the grid, a uniform increase in Ca can be seen throughout the whole cross section (Figure 5.3.2.1a-e). This is a consequence of the fact that in every time step PCO<sub>2</sub> is brought into equilibrium with calcite, as if it were an open CO<sub>2</sub> system. The result is that the calcite weathering is not modelled as a process of rainwater and that the model does not represent the saturated zone (a closed CO<sub>2</sub> system).

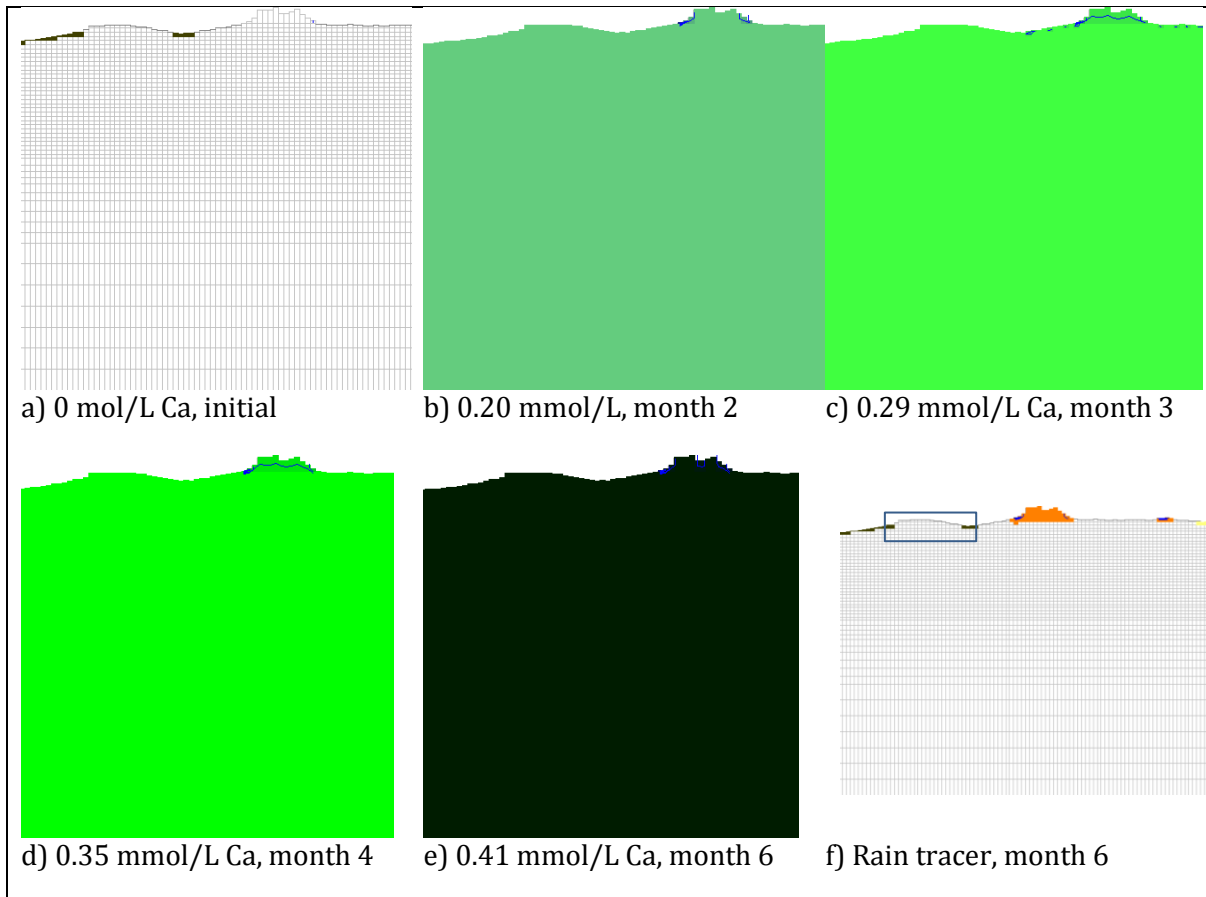


Figure 5.3.2.1. Results of six months calcite weathering at the Sand Motor in scenario year 4 (2015). a-e) The Ca increase each month and f) a tracer that indicates rainwater infiltration.

#### **5.4 SAND MOTOR CO<sub>2</sub> SEQUESTRATION CAPACITY ESTIMATE**

For this research I am interested in CO<sub>2</sub> sequestration since the Sand Motor was built in 2011. At the moment there is no significant vegetation present at the Sand Motor. Therefore, all organic C stored in the Sand Motor should not contribute to the CO<sub>2</sub> sequestration capacity of the Sand Motor in this research, since it was captured before the construction. Consequently, the approach to report the %C of the beach without discrimination between (in)organic C of Jones et al. (2008) and Beaumont et al. (2014), is not suitable for this research. Rather than measuring the %C in the Sand Motor and try to discriminate with isotopes between (in)organic C, it is more appropriate to estimate the amount of alkalinity produced by calcite weathering since the construction of the Sand Motor. With the amount of alkalinity produced and the net flux of water through the Sand Motor, I can answer the question whether CO<sub>2</sub> is captured or not. The net rainwater storage of the Sand Motor has to be known, to be able to estimate CO<sub>2</sub> sequestration.

The net groundwater storage of the Sand Motor, modelled with MODFLOW, is negative in general. In scenario year 4 (2015) the net storage is  $\pm -0.01 \text{ m}^3$  a day, other scenario years and other locations result in higher losses. The net storage of two transects at the Sand Motor varies from -4.5 to  $-0.01 \text{ m}^3$  a day in scenario year 1-5 (personal contact Sebastian Huizer, July 2015). The groundwater feeds the sequestered CO<sub>2</sub> (alkalinity) to the North Sea directly or after a period of retention. Since the fresh water lens of the Sand Motor is not in contact with the groundwater storage in the adjacent dunes, the Sand Motor can be viewed as a secluded sweet rainwater bubble surrounded by seawater (Chapter 3). This means that even if there is rainwater retained in reality, it will eventually be flushed out by yearly storms into the North Sea or end up in the North Sea since the entire Sand Motor is predicted to be deposited on to the beach in a period of twenty years. Therefore, I have to regard the Sand Motor as a facilitator that enables calcite dissolution (since it passes alkalinity on to the North Sea), rather than as a storage facility for alkalinity. Bozec et al. (2006) indentifies the North Sea as an CO<sub>2</sub> sink. The North Sea has effective mixing in its water columns due to physical drivers (such as exporting water to the North Atlantic Ocean). This effective mixing enables DIC enriched water transport to lower layers and, as a consequence, disables CO<sub>2</sub> degassing (Bozec et al., 2006). Consequently, the North Sea can be seen a sink for the alkalinity produced in the Sand Motor. Therefore, I can assume that over a period of approximately 20 years all the CO<sub>2</sub> that has been captured in the Sand Motor (though calcite dissolution), will be stored in the North Sea in the form of DIC.

The alkalinity, that is produced with 50 grams of C8 sand (3.3% calcite) in the open and closed CO<sub>2</sub> experiment, can be scaled up to the volume of the Sand Motor to estimate the production of the Sand Motor over a period of 20 years (4% is the average calcite concentrations found at the Sand Motor, appendix C). I base the estimation on sand of location C8 because it was used in most experiments, it was sampled for groundwater and because the location lies on the transect chosen for modelling. In the experiments that mimic the saturated zone 0.36 mM alkalinity is produced (12 hours) and in the experiments that mimic the unsaturated zone there is on average 0.85 mM (24 hours) alkalinity produced. The sampling depth of the groundwater was 3 m at C8, this means that the unsaturated zone ranges from the top of the Sand Motor to 3 m depth. The sweet water bubble has a height of 0.5m at the transect depicted in blue in Figure 4.3.2.1. (personal contact Sebastian Huizer, July 2015) and the surface of the Sand Motor is approximately  $128 \cdot 10^4 \text{ m}^2$  (De Zandmotor, 2014). Since the groundwater sampling depth was zero at the edges of the Sand Motor and increases to 3.25m depth in the middle, I assume that half of the area is actually flooded with seawater and not suitable for calcite weathering. If we

calculate with an average of 135 days of rain a year ( $> 1\text{mm}$ ) on the Sand Motor, I arrive at  $1.89 \cdot 10^7$  mole alkalinity produced a year (sand  $\pm 1600 \text{ kg/m}^3$ ; Laine & Sandvik, 2001; KNMI, 2015). This means that  $\pm 9.43 \cdot 10^6$  mole  $\text{CO}_2$  is sequestered and that  $\pm 9.43 \cdot 10^6$  mole calcite is consumed a year. It comes down to an estimated annual sequestration rate of  $\pm 4.2 \cdot 10^5 \text{ kg CO}_2$ ,  $\pm 177 \text{ g C/m}^2$  or  $\pm 0.08 \text{ kg/ m}^2 \cdot \text{yr CO}_2$ . With this estimation I can scale up to the twenty year life extend of the Sand Motor. If I assume that of the  $21.5 \cdot 10^6 \text{ m}^3$  sand that was deposited initially 3.3% is calcite, then there is  $0.71 \cdot 10^6 \text{ m}^3$  calcite that can react potentially (Stive et al., 2013). To deplete this bulk of calcite, 2000 years are needed. This exceeds the life time of the Sand Motor significantly even if I take into account that the Sand Motor will gradually loose sand. I estimate that in the 20 years that the Sand Motor exists, approximately 1 % of the total initial available calcite will be consumed. This results in  $\pm 1.9 \cdot 10^8$  mole or 8.3 Mkg  $\text{CO}_2$  captured in twenty years.

## 6. DISCUSSION

In this chapter the PHREEQC and the kinetics of calcite dissolution in the experiments will be discussed, followed by a consideration of the C isotopes of both fieldwork and the experiments. Subsequently, fieldwork, and the PMWIN model results are discussed to conclude with an discussion on the C sequestration estimate.

### 6.1 CALCITE DISSOLUTION IN THE EXPERIMENTS AND PHREEQC RESULTS

#### *Calcite dissolution kinetics in an open CO<sub>2</sub> system*

The concentrations of alkalinity and Ca found in the open system experiments (unsaturated zone) were lower than calculated with PHREEQC. Also calcite saturation was reached in 2-5 days while pure calcite in distilled water reaches calcite saturation within  $\pm$  8 hours (Appelo & Postma, 2005). The main reason for three of the experiment (experiments 4, 8 and 9) is that they did not reach saturation while PHREEQC calculates concentrations at equilibrium. The difference between the PHREEQC and laboratory results of the experiments that did achieve saturation, can be caused by several factors that influence reaction rate of calcite dissolution (kinetics). First, PHREEQC assumes pure calcite, while the sand samples from the Sand Motor are 4% calcite (on average). Therefore, foreign ions in the other  $\sim$ 96 % of the sand sample can dissolve and suppress calcite weathering, since foreign ions influence the dissolution rate (Plummer et al. 1978; Appelo & Postma, 2005). Morse and Arvidson (2002) deem the limited number of reaction inhibitors that are researched the greatest weakness to translate experimental results to natural systems since the influence of foreign ions can be profound. For example, metal ions can severely suppress calcite dissolution even if present in submicromolar concentrations (Dromgoole and Walter, 1990; Salem et al., 1994). Magnesium, strontium, barium, sulphate, phosphate, silicate, nitrate and organic matter may lower the calcite dissolution rate (Morse and Arvidson, 2002). In general, the restraint of these ions on calcite dissolution rates increases while approaching calcite saturation. Manganese and phosphate are more successful in calcite dissolution inhibition than (for example) sulphate (Griffioen, 1992). Anyhow, phosphate, nitrate, sulphate and (trace) amounts of metals were present in both experiment and field samples of groundwater. This indicates that the discrepancy between PHREEQC Ca and alkalinity concentrations (based on pure calcite dissolution) and the concentrations found in the experiments can be, partly, explained by the calcite dissolution inhibition of foreign ions present in the sand samples. This needs further research to be confirmed.

A second factor that can contribute to the difference between PHREEQC predictions and concentrations found in the open system experiment, is the degree of understanding of the calcite dissolution rate near equilibrium. Numerous studies indicate that as the saturation increases, three separate stages in kinetics can be identified (Chapter 2). The first stage is when the solution is in undersaturation for calcite. In this stage a diffusion controlled kinetics is applicable (Morse and Arvidson, 2002). Therefore, the stirring rate can have a significant impact on the calcite dissolution during undersaturation in an experiment (Plummer et al., 1978). The stirring rate used in my open CO<sub>2</sub> experiments was 400 rpm while Plummer et al. (1978) used rates of 800-2300 rpm. However, above a pH of 5.5 the influence of the stirring rate becomes negligible and the surface-controlled calcite dissolution kinetics is dominant (Plummer et al., 1978). Since the pH is above 5.5. in all the experiments (as well in the fieldwork), the stirring rate will not have lowered the calcite dissolution rate significantly. When the appropriate pH is reached for a given PCO<sub>2</sub>, the dissolution rates decreases significantly and calcite saturation is

reached (Plummer et al., 1978; Morse and Arvidson, 2002). However, the results of the open CO<sub>2</sub> experiment do not show this calcite dissolution rate dependency on PCO<sub>2</sub>. Plummer et al. (1978) experimented with a PCO<sub>2</sub> range of 0 to 1.0 atm while the PCO<sub>2</sub> used in the open CO<sub>2</sub> experiments was 0.0004, 0.004 or 0.005 atm. The calcite dissolution rate should increase linearly with PCO<sub>2</sub>, however, the increase between 0.0004 and 0.005 atm is negligible since it does not exceed the measurement uncertainties of Plummer et al. (1978). This notion is strengthened by the fact that the open experiments (with the high calcite concentrations) all had a similar pH around 8 after a few minutes (Figure 5.2.1.2.a) while Plummer et al. (1978) demonstrated that higher PCO<sub>2</sub> corresponds with higher dissolution rates but also with a lower pH at calcite saturation. This indicates that the range in PCO<sub>2</sub> in the open CO<sub>2</sub> experiments was too narrow to be able to detect a significant change in the calcite dissolution rate.

#### *Calcite dissolution kinetics in a closed CO<sub>2</sub> system*

The results of PHREEQC and the alkalinity and Ca concentrations of the closed CO<sub>2</sub> experiment match better than it did for the open CO<sub>2</sub> experiment. The alkalinity of the closed CO<sub>2</sub> experiment was slightly higher than calculated with PHREEQC, this could be caused by foreign ion inhibition as discussed in the previous section. As expected, the calcite dissolution rate is slower with lower temperature. The alkalinity and Ca produced in the closed CO<sub>2</sub> experiment at room temperature is as expected, because of the limited CO<sub>2</sub> access, lower than found in the open CO<sub>2</sub> experiment. The cooled closed CO<sub>2</sub> experiment had even lower alkalinity and Ca concentrations than the similar experiment at room temperature, surprisingly they started to decline while almost reaching calcite saturation (Figure 5.2.2.). I would have expected higher values in the cooled experiment since CO<sub>2</sub> dissolves better in colder solutions (Chapter 2; Van der Perk, 2013). It is, however, debatable if such a positive influence on the reaction products can be detected in the cooled closed CO<sub>2</sub> experiment, since the bottle was closed before putting it in the cooled environment. It will probably only slow down the dissolution rate without the benefits of an increased PCO<sub>2</sub> (Chapter 2). Furthermore, temperature dependency of calcite dissolution in near equilibrium and the effect of temperature on inhibition, is not well researched (Morse and Arvidson, 2002).

#### *Mg-calcites in the experiments*

The experimentally observed Mg percentage in calcite was between 3% and 12% in the open CO<sub>2</sub> experiments. Mg-calcites are classified into low (<5%) and high (5-30%) Mg-calcites, thereby, categorizing the experimental results in both low and high Mg-calcites. Since the uptake of Mg in shells is temperature dependent, a typical Mg percentage is 1% at the Dutch coast, while in subtropical areas average Mg percentages in Mg-calcites are between 10 and 15% (Appelo & Postma, 2005). As a consequence, the Mg-calcite percentage is high in respect to average Dutch conditions. Some of the sand samples from the Sand Motor even fall in the high calcite range and match subtropical Mg-calcite percentages, this is probably due to allochthonous origin such as the Dover Strait (Griffioen et al., 2015). In distilled water, Mg-calcites have a congruent dissolution at first whereby both Ca and Mg are produced. However, the Ca concentrations should start to decline while Mg still increases (due to the precipitation of Mg-calcites with a lower Mg percentage) after approximately 80 hours resulting in an incongruent dissolution (Plummer and Mackenzie, 1974). Since none of the experiments exceeded 40 hours, it is not surprising that the decline in Ca is not captured in the results.

## **6.2 DISSOLVED INORGANIC CARBON ISOTOPES FROM FIELDWORK AND EXPERIMENTS**

The DIC  $\delta^{13}\text{C}$  isotopes found in fieldwork and in the closed  $\text{CO}_2$  experiment do not fit predicted values well (except for the lake sample in fieldwork). The fieldwork samples should lie between  $\delta^{13}\text{C} = -3$  and  $-4$  ‰ at the sites with calcite dissolution (at the [borders] of the lake and in the centre of the Sand Motor) and between  $\delta^{13}\text{C} = 0$  and  $2$ ‰ for the locations with seawater intrusion (Appelo & Postma, 2005). Instead all the  $\delta^{13}\text{C}$  found are in between  $\delta^{13}\text{C} = -3$  and  $0$  ‰ with the  $\delta^{13}\text{C}$  value of the location at the tidal plains closer to that predicted for marine calcite dissolution in fresh water. The closed  $\text{CO}_2$  experiments resulted in  $\delta^{13}\text{C} \sim -6$ ‰ while a  $\delta^{13}\text{C}$  is expected of at least  $-4$  ‰ as for the saturated zone. These values are even lower than  $\delta^{13}\text{C}$  found at the Sand Motor. An explanation could be that there is still a lot of  $\text{CO}_{2(\text{aq})}$  present with a  $\delta^{13}\text{C}$  of  $-8$  ‰ which cannot be the case since a pH around 8 (which is found in the experiments and fieldwork) indicates that  $\text{HCO}_3^-$  is the main species present (Appelo & Postma, 2005). The differences between the anticipated  $\delta^{13}\text{C}$  and the  $\delta^{13}\text{C}$  is most likely caused by measurement errors. The  $\delta^{13}\text{C}$  isotopes of the open  $\text{CO}_2$  experiment better fit the expectations. They increase from  $\delta^{13}\text{C} = -8$  ‰ (consistent with dissolved  $\text{CO}_2$ ) up to  $\delta^{13}\text{C} = 0-2$  ‰, which is consistent with dissolved  $\text{CO}_3^{2-}$  and/or  $\text{HCO}_3^-$  (Appelo & Postma, 2005). Although not all the  $\delta^{13}\text{C}$  values of the alkalinity measured in the field and the experiments fit the theory, it can still be concluded that the C in the alkalinity is of inorganic origin since organic dissolved  $\text{CO}_2$  has a  $\delta^{13}\text{C}$  of  $-24$  ‰. This would have resulted in significantly lower  $\delta^{13}\text{C}$  than reported in this research.

## **6.3 CALCITE DISSOLUTION AND RAINWATER INFILTRATION AT THE SAND MOTOR**

The challenge with the field study lies in identifying calcite dissolution due to rainwater infiltration as little or no carbonate processes are expected for the seawater environment. The concentrations of Mg and Ca that are used as calcite dissolution indicators in the experiment, do not indicate this mechanism in the field since the Mg and Ca (and Na) concentrations increase linearly with Cl concentrations (Figure 5.1). As a consequence, Mg and Ca (that are abundant in seawater) are just an indication of the presence of saline water with seawater origin at the Sand Motor. The two variables that do vary independently of the Cl are alkalinity and  $\delta^{13}\text{C}$  values and these will be discussed as indicators of calcite dissolution. The ion concentrations found in groundwater samples at the intertidal plains (Sea, D8 and C13) compare well with average seawater values found in literature (Goldberg, 1963). The groundwater sampled at the sites that are close to the lake (B7/B8/A8) do not differ significantly with one another at any of the variables. Compared to the samples taken at the tidal plains, they have slightly higher alkalinity and  $\delta^{13}\text{C}$  values, implying some calcite dissolution did happen. There are three groundwater samples that stand out: C8, Lake and C10. Location C8 and C10 lie at the centre of the Sand Motor and are, therefore, the prime locations where rainwater infiltration (and thus calcite weathering) was anticipated. The alkalinity at location C10 is significantly higher than the alkalinity at the other locations that were sampled, which indicates calcite weathering at C10.

The  $\delta^{13}\text{C}$  of C10 does not differ much from the sites at the tidal plains. I would expect similar conditions in location A8 because of its position at the Sand Motor. Instead the concentrations found at A8 are similar to those surrounding the lake. There is some calcite dissolution at the lake sites and A8 yet C10 is the only location sampled that succeeds to capture a significant amount of C. The lake sample has similar alkalinity values to that of the samples at its border, but its  $\delta^{13}\text{C}$  value is significantly higher than of the other samples. The  $\delta^{13}\text{C} = 0$ ‰ is in the range of values found in the open  $\text{CO}_2$  experiments. Apart from the Sea sample, this is the only sample that is taken from an open  $\text{CO}_2$  system. The  $\delta^{13}\text{C} = -2.6$ ‰ of the Sea sample verifies that this is

not a trade that can solely be contributed to the fact that it is an open CO<sub>2</sub> system. Its Cl, Na, Mg and Ca concentrations show that it is freshening compared to the samples at the tidal plane, but still contains more saline water than the rest of the groundwater samples. The low alkalinity value compared to C10 could, partly, be explained with degassing at warmer temperature (Appelo & Postma, 2005). Nevertheless, the lake was not thought of as a prime site for calcite dissolution at the start of this research. The  $\delta^{13}\text{C}$ , the freshening and the supersaturation for calcite, hint that the lake might be a suitable site for calcite dissolution with its open access to CO<sub>2</sub> and rainwater retention.

The alkalinity found in the open and closed CO<sub>2</sub> experiments do not exceed 1 mM while the alkalinity found at the Sand Motor ranges from 1.8-7.8 mM. The experiments (except for the cooled one that did not reach saturation) are done at room temperatures, while the Sand Motor was sampled in the winter. These high alkalinity concentrations found at the Sand Motor can be a cause of the seasonal variation in DIC. There are several factors that contribute to seasonal variation in DIC (alkalinity) at the Sand Motor. Seasonal variation can occur because of degassing soil when the biological CO<sub>2</sub> production stops in the winter. This is not a mechanism anticipated for the Sand Motor since there is no significant vegetation present (Bolin et al, 1979). The DIC content in the North Sea is increased in the winter compared to summer values due to biological production (Bozec et al., 2006). As a consequence, alkalinity in the samples taken at the tidal plains will be higher compared to samples taken in the summer. The same can be true for the samples taken at the centre of the Sand Motor since the lower temperatures in the winter enhance the solubility of CO<sub>2</sub> and, as a consequence, calcite dissolution.

I will discuss the effect of several ions on calcite dissolution kinetics, as I did for the experiments, that are relevant for the conditions at the Sand Motor. Calcium and magnesium are inhibitors for the calcite dissolution rate (Appelo & Postma, 2005; Sjöberg, 1978). The precipitation rate of calcite is negligible with Mg concentrations found in seawater (Berner, 1975). The suppressing influence of phosphate and sulphate on the calcite dissolution rate is enhanced with increasing Mg and Ca concentrations. These four are identified as the main controlling ions on the calcite dissolution rate in seawater (Sjöberg, 1978). Morse (1974) singled out phosphate as a restraint on calcite dissolution, which is present in Sand Motor soil. However, when seawater (that is supersaturated with calcite) mixes with fresh water (with a higher PCO<sub>2</sub> and also saturated with calcite), the mixture can dissolve additional calcite (Mischungskorrosion; Dreybrodt, 1981; Appelo & Postma, 2005). In the salt/fresh water interface zone on the Sand Motor, Ca and Na cation exchange will take place. This results either in Na adsorption when (for example) salt water flushes the Sand Motor during storms, or Ca adsorption when it is exchanged for Na from infiltrated rainwater (Appelo & Postma, 2005). The two mechanisms that occur during fresh and salt water mixing; cation exchange between Ca, Na and Mg as well as the Mg inhibition on calcite precipitation, could contribute to the higher alkalinity concentrations found at the Sand Motor in comparison to the experiments. Morse and Arvidson (2002) postulate that there is still a knowledge gap between laboratory results of calcite dissolution kinetics and the natural conditions.



#### **6.4 MODELLING C SEQUESTRATION**

The PMWIN model should represent the saturated zone of the Sand Motor (section 5.3.2). Therefore, it should at least be an accurate representation of the fresh water infiltration into the Sand Motor, since this is the main source of carbonate input needed for calcite weathering. The fresh water in the saturated zone was established to be 0.5 m (personal contact Sebastian Huizer, July 2015). To be able to detect changes in rainwater infiltration in this area, a vertical discretization with (for example) 0.1 m spacing would be needed. The current vertical discretization is 1m, this results in 3-5 layers in the part of the model that represents the Sand Motor (Figure 4.3.2.2). The model should accurately show the infiltration of rainwater in the Sand Motor to produce relevant results, but no rainwater infiltration can be detected (Figure 5.3.2.1). This is probably a consequence of the coarse grid spacing.

Although, there is no rainwater at the Sand Motor according to the current model, calcite weathering is detected in the model in the form of an uniform Ca increase (Figure 5.3.2.1). After six month calcite dissolution in the model, there is still no equilibrium reached. This is not to realistic since calcite saturation is reached in a couple of hours with PHREEQC calculations, and excepted within a week for all experiments. Furthermore, for the model to be a representation of the field conditions, I should at least be able to model  $PCO_2$  differences. The model does not accurately represent the fresh water, calcite weathering due to rainwater infiltration and differences in the soil  $PCO_2$  of the Sand Motor. These are all factors that should at least be modelled well to be able to claim that the results are applicable to the Sand Motor. Consequently the results of the model are not used for the sequestration estimate (Section 5.4). The attempt did, however, indicate that PMWIN can be used to model calcite dissolution in the Sand Motor in further research (see Chapter 8 for recommendations).

#### **6.5 SEQUESTRATION ESTIMATE**

In the sequestration estimation a number of assumption have been made based on the experiments and fieldwork. To prevent overestimations, the premises taken were sooner chosen to be the less optimistic option. A basic assumption in the estimation is that there is no significant vegetation present throughout the entire life span of the Sand Motor. However, some vegetation could possibly grow around the lagoon and also algae from the lagoon/ lake can be deposited on/into the soil. This could enhance the calcite dissolution because organic matter and root respiration can be an additional source of  $CO_2$  to react with. On the other hand, organic matter can decay and degas  $CO_2$  back into the atmosphere (Appelo & Postma, 2005). As discussed for the fieldwork, freshening of the Sand Motor can enhance calcite dissolution (Dreybrodt,1981; Appelo & Postma, 2005). The groundwater samples from the fieldwork reveal that there is significantly more alkalinity present at the Sand Motor than in the experiments, which is related to freshening. Location C10 stands out with a sevenfold of the maximum alkalinity produced in the experiments. Furthermore, I expect that the alkalinity in the experiments will eventually reach concentrations calculated with PHREEQC. Since the C sequestration estimate is based on the alkalinity from the experiments, the positive influence of freshening on alkalinity concentrations is not included. Calculations based on PHREEQC alkalinity would also result in a higher C sequestration rate. This indicates that the C sequestration at the Sand Motor might be higher than calculated in this research.

The dissolution of other calcium carbonate minerals at the Sand Motor can also influence calcite weathering. The experiments in this research did not indicate that there was dolomite present, however, dolomite dissolution happens after calcite dissolution, which might be the reason that it was not measured. Consequently, there is a possibility of dolomite at the Sand Motor. If the Sand Motor should contain some dolomite, this would result in groundwater that is supersaturated for calcite. Some of the dissolution of calcite will be replaced with dolomite dissolution, with a slower dissolution rate. Since the slower rate is not significant on the life span of the Sand Motor, this indicates that dolomite (if found at the Sand Motor) will not have a negative effect on the C sequestration (Appelo & Postma, 2005). The groundwater model of the Sand Motor shows that during storm the whole Sand Motor gets flooded and that, consequently, all alkalinity will be flushed out (and can be thought of as stored into the sea). This is based on the current vertical discretisation of 1m that is too coarse to detect rainwater infiltration (Section 6.4). Nevertheless, groundwater samples taken after a storm, do prove that fresh water is still present in the Sand Motor (personal contact Iris Pit, July 2015). Eventually, the entire Sand Motor is thought to be redeposited on to the coastline, or dispersed into the North Sea, in a period of twenty years. Therefore, it can still be assumed that all alkalinity produced will, eventually, be stored in the North Sea. Since the alkalinity used for the calculations is taken from the experiments at room temperatures, the increased dissolved CO<sub>2</sub> in winter time, can have a positive effect on the C sequestration estimation. The C sequestration estimations are based on experiments at 20°C, a temperature common for the Dutch coast in summer time. In the estimations the increase in alkalinity during winter time, that would increase the amounts of C sequestered on a yearly basis, was not taken into account. Several mechanisms are discussed that can either enhance or decrease the C sequestered on a yearly basis. Therefore, the C sequestration estimation should be thought of as an educated guess.

The Sand Motor has proven to be significantly different from traditional nourishments. The main reason is the fact that it can be thought of as an isolated system that is hydrologically separated from the dunes. Therefore, all the C sequestered will eventually be stored in the North Sea. Calcite dissolution can also occur at a beach with traditional nourishment. However, traditional nourishment just adds sand onto an existing beach, which will only adjust the height of both the saturated and unsaturated zone, while the Sand Motor provides a location for calcite weathering that previously did not exist. The southern North Sea has an annual uptake of 1.9 kg/ m<sup>2</sup> CO<sub>2</sub> while the Sand Motor sequesters ± 0.08 kg/ m<sup>2</sup>\*yr CO<sub>2</sub> which indicates a decline in CO<sub>2</sub> sequestration at the location of the Sand Motor (Bozec et al., 2006). However, the estimates of Bozec et al. (2006) are made on measurements in water columns of 30 m depth and not at intertidal planes (the location of the Sand Motor). Furthermore, there are regions with net annual uptake and release in the southern North Sea, indicating that local conditions should be investigated to conclude if there is indeed a net reduction of CO<sub>2</sub>. Compared to traditional nourishments a mega nourishment is preferable to a traditional one, since it will sequester additional C to that already captured by the beach.

## 7. CONCLUSION

This research aimed to estimate CO<sub>2</sub> capturing through Ca-carbonate dissolution at the Sand Motor. The translation between the kinetics of theoretical (pure) calcite dissolution and conditions specific for the Sand Motor was researched with laboratory experiments and fieldwork. An (existing) groundwater model of the Sand Motor was used to model the calcite reaction and the transport in order to be able to estimate net annual CO<sub>2</sub> sequestration rates. Unfortunately, the results from the model were not representing the conditions at the Sand Motor accurately. Consequently, the model needs further investigation and alteration of its initial conditions to correctly represent calcite weathering at the Sand Motor. Fieldwork confirmed that calcite dissolution occurs at the Sand Motor, predominately at the higher grounds, where rain water infiltration happens. The soil of the Sand Motor can be categorised as calcium carbonate rich, with calcite as the main contributor and some high-Mg calcites. Fieldwork indicated, furthermore, an enhancement of calcite dissolution due to the cation exchange of Ca, Mg and Na related to the freshening of the Sand Motor. This indicates that the Sand Motor is a good facilitator for calcite weathering. The Experiments revealed the differences between literature calcite dissolution rates and the rates specific for Sand Motor soil. Experiments with low calcite content (0.6 %) or low temperatures (4°C) revealed that equilibrium can probably be reached within 3-5 days, while experiments with average calcite content (3.3 %) at room temperature reached calcite saturation within ±2 days. The experiments showed, furthermore, that a significant inhibition of the calcite dissolution rate is to be expected at the Sand Motor in respect to literature values, which can be attributed to the presence of foreign ions such as phosphates. The range in PCO<sub>2</sub> (0.0004 to 0.005 atm) in this research was not wide enough to detect a significant increase in the calcite dissolution rate. As expected, the open CO<sub>2</sub> experiment resulted in higher alkalinity and Ca concentrations than the closed CO<sub>2</sub> experiment. This research cannot be conclusive on the positive effect of lower temperatures (4°C) on CO<sub>2</sub> solubility and, therefore, calcite dissolution. It can only conclude that lower temperatures slow down the calcite dissolution rate. However, the dissolution rate is overall fast enough to reach equilibrium within 2-5 days, which confirms that calcite dissolution at the Sand Motor will be fast enough to sequester CO<sub>2</sub> dissolved in rainwater.

Analyses of the C isotopes in the alkalinity from experiments and the Sand Motor revealed that the C captured is indeed inorganic. This proves that CO<sub>2</sub> is captured by the calcite dissolution reaction in the form of alkalinity and justifies the use of alkalinity for C sequestration calculations. The C sequestration rate reported in this research is based on the alkalinity concentrations found in the experiments. The alkalinity concentrations were translated to CO<sub>2</sub> amounts captured (± 0.08 kg/ m<sup>2</sup>\*yr CO<sub>2</sub>) and scaled up to the volume of the Sand Motor to arrive at an estimation of 4.2\*10<sup>5</sup> kg CO<sub>2</sub> captured a year and 8.3 Mkg CO<sub>2</sub> in twenty years. Inspection of the Sand Motor groundwater model, defined it as a hydrologically isolated system from which all groundwater will be lost to the North Sea in a period of twenty years. The CO<sub>2</sub> sequestered by the Sand Motor can, as a consequence, be regarded as captured since the North Sea is an effective CO<sub>2</sub> sink. Calculations revealed that the calcite at the Sand Motor cannot be depleted in the twenty year life span of the Sand Motor. The Sand Motor sequesters less CO<sub>2</sub> (± 0.08 kg m<sup>2</sup>\*yr ) than the southern North Sea does (1.9 kg/ m<sup>2</sup> CO<sub>2</sub>). However, this is based on water columns of ± 30 m depth and not the intertidal plains. The local net CO<sub>2</sub> uptake of the North Sea needs to be investigated to indicate whether the construction of the Sand Motor decreased the CO<sub>2</sub> uptake of the location.

This research indicates the Sand Motor as a facilitator that enables calcite dissolution and that passes alkalinity on to the North Sea rather than as a storage facility for alkalinity. Since the Sand Motor creates an additional location for calcite dissolution, it stands out in respect to traditional nourishments. Traditional nourishment only add sand to a location where calcite dissolution already is taking place, while the construction of the Sand Motor provides an additional location for Ca-carbonate weathering. Additional fieldwork to establish calcite dissolution both vertically and horizontally will be helpful for further modelling attempts and more accurate quantification. Furthermore, experiments with a longer time span and more variation in temperature,  $\text{PCO}_2$  and calcite concentration are needed to fully understand calcite dissolution kinetics that are specific for the Sand Motor. Lastly, to put the C sequestration rate of the Sand Motor into context, the local net  $\text{CO}_2$  uptake of the North Sea needs to be researched.

## 8. RECOMMENDATIONS

Additional field sampling of groundwater should ideally be done both in the horizontal as in a vertical direction. The presently exploited horizontal sampling grid can identify the locations that have the most abundant calcite weathering while the vertical grid can determine a calcite dissolution front. A dissolution front can be determined with declining  $PCO_2$  and alkalinity in the saturated zone (Appelo & Postma, 2005). The open  $CO_2$  experiment could be repeated with lower temperatures and with significantly higher  $PCO_2$  to determine the seasonal difference in calcite dissolution rate. The closed-system  $CO_2$  experiments should also be repeated with different  $PCO_2$  since the saturated zone in the Sand Motor showed the most variation in  $PCO_2$ . Furthermore, if the experiment was to be repeated with low temperatures, the bottle should not be closed before cooling: the artificial rainwater should be flushed with the appropriate  $PCO_2$  in a cooled setting, to enable more  $CO_2$  to dissolve, before it is put in the closed bottle. This experiment need also to be repeated with several calcite concentrations. The experiments that are cooled and that contain less calcite need more than two days to get to equilibrium. An open  $CO_2$  experiment in saturated with calcite (from a Sand Motor sand sample) could be injected with saline water, to investigate the role of freshening on calcite dissolution kinetics at the intertidal plains of the Sand Motor.

The model needs extensive further attention. A certain  $PCO_2$  as input in PHREEQC translates in specific alkalinity concentrations than can be put into the model grid. This enables to simulate different  $PCO_2$  in the layers of the model. Furthermore, the vertical layer thickness of the model needs to be adjusted to be able to detect rainwater infiltration on a smaller vertical resolution than 1 m. Adjusting the converging parameters is needed to model the calcite dissolution in twenty years. Also the density-driven groundwater flow should be reintroduced in the model to investigate the fresh water lens and the effect of freshening on calcite dissolution in the Sand Motor. The C sequestration estimations should be adjusted to the new results to enhance the best guess made in this research.

## **9. ACKNOWLEDGEMENTS**

I would like to thank Jasper Griffioen and Iris Pit from Utrecht University for their assistance during fieldwork, their guidance in the laboratory and their patience with my lack of geochemistry knowledge during numerous meetings. I thank the CO<sub>2</sub> board for the opportunity of this research. I also want to thank Thilo Behrends from Utrecht University for the usage of his experimental setup and Bas van der Grift from Deltares for guiding me through the initial stage of the experiments. Sebastian Huizer from Utrecht University was kind enough to share his groundwater model of the Sand Motor and provided me with crucial information and feedback for the C sequestration estimates. Finally I want to thank Rémon Saaltink, Amir Raoof, Thom Claessen, Dineke van de Meent-Olieman, Arnold van Dijk from Utrecht University, Andre Cinjee and Rob van Galen from Deltares, Henning Prommer and Francisco Negrao for their indispensable help and advice.

## 10. REFERENCES

- Abanades, J., & Alvarez, D. (2003). Conversion limits in the reaction of CO<sub>2</sub> with calcium carbonate. *Energy & Fuels*, 17(2), 308-315. doi:10.1021/ef020152a.
- Appelo, C. A. J., & Postma, D. (2005). *Geochemistry, groundwater and pollution*. CRC Press.
- Beaumont, N. J., Jones, L., Garbutt, A., Hansom, J. D., & Toberman, M. (2014). The value of carbon sequestration and storage in coastal habitats. *Estuarine Coastal and Shelf Science*, 137, 32-40. doi:10.1016/j.ecss.2013.11.022.
- Berner, R. A. (1975). The role of magnesium in the crystal growth of calcite and aragonite from sea water. *Geochimica et Cosmochimica Acta*, 39(4), 489-504.
- Bolin, B., Degens, E. T., Duvigneaud, P., & Kempe, S. (1979). The global biogeochemical carbon cycle. *The global carbon cycle*, 13, 1-56.
- Bosatta, E., & Berendse, F. (1984). Energy or nutrient regulation of decomposition: implications for the mineralization-immobilization response to perturbations. *Soil Biology and Biochemistry*, 16(1), 63-67.
- Bozec, Y., Thomas, H., Schiettecatte, L. S., Borges, A. V., Elkalay, K., & De Baar, H. J. (2006). Assessment of the processes controlling the seasonal variations of dissolved inorganic carbon in the North Sea. *Limnology and Oceanography*, 51(6), 2746-2762.
- Cardona, L., & García, M. (2008). Beach-cast seagrass material fertilizes the foredune vegetation of Mediterranean coastal dunes. *Acta Oecologica*, 34(1), 97-103.
- Centre for Climate Adaptation. (2014). Vulnerabilities - The Dutch coast. Retrieved from: <http://www.climateadaptation.eu/netherlands/coastal-erosion/>, viewed 22-11-2014
- Clark, I. D., & Fritz, P. (1997). *Environmental isotopes in hydrogeology*. CRC press.
- CO<sub>2</sub>-prestatieladder. (2014). Wat is de ladder? Retrieved from <http://www.co2-prestatieladder.nl/Wat-is-de-ladder>, viewed 21-11-2014
- Curry, P. (2011). *Light Green or Shallow (Anthropocentric) Ethics*. Ecological ethics: An introduction. Cambridge, UK: Polity Press.
- De Vriend, H.J. & Van Koningsveld, M. (2012) Building with Nature: Thinking, acting and interacting differently. EcoShape, Building with Nature, Dordrecht, the Netherlands. Retrieved from [http://www.google.nl/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0CCMQFjAA&url=http%3A%2F%2Fwww.ecoshape.nl%2Ffiles%2Fpaginas%2FEFCOSH\\_BwN\\_WEB.pdf&ei=YFN4VNxeJ4H7PK\\_rgagG&usg=AFQjCNH9\\_NQ7k2J8RQE77s0YxcowSaO\\_yQ&sig2=cqFW4igu5iBiwUdAshJjcQ&bvm=bv.80642063,d.ZWU](http://www.google.nl/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&uact=8&ved=0CCMQFjAA&url=http%3A%2F%2Fwww.ecoshape.nl%2Ffiles%2Fpaginas%2FEFCOSH_BwN_WEB.pdf&ei=YFN4VNxeJ4H7PK_rgagG&usg=AFQjCNH9_NQ7k2J8RQE77s0YxcowSaO_yQ&sig2=cqFW4igu5iBiwUdAshJjcQ&bvm=bv.80642063,d.ZWU)
- De Zandmotor. (2014). De zandmotor. Retrieved from: <http://www.dezandmotor.nl/>, viewed 20-2-2015.
- De Zandmotor. (2014a). Hoe bruikbaar is de zandmotor? Retrieved from <http://www.dezandmotor.nl/nl-NL/downloads/>, viewed 13-11-2014
- Dreybrodt, W. (1981). Mixing corrosion in CaCO<sub>3</sub>/1bCO<sub>2</sub>/1bH<sub>2</sub>O systems and its role in the karstification of calcium carbonate stone areas. *Chemical Geology*, 32(1), 221-236.
- Dromgoole, E. L., & Walter, L. M. (1990). Inhibition of calcite growth rates by Mn<sup>2+</sup> in CaCl<sub>2</sub> solutions at 10, 25, and 50 C. *Geochimica et Cosmochimica Acta*, 54(11), 2991-3000.
- Duurzaam GWW. (2014). Green Deal 2013. Retrieved from <http://duurzaamgww.nl/index.php/actueel/greendeal/?lang=en>, viewed 21-11-2014
- EcoShape. (2014). About EcoShape. Retrieved from [http://www.ecoshape.nl/en\\_GB/about-ecoshape.html](http://www.ecoshape.nl/en_GB/about-ecoshape.html), viewed 21-11-2014

- Ecoshape. (2014a). Pressing the CO<sub>2</sub> buttons: Towards ecosystem-based CO<sub>2</sub> footprinting for maritime engineering projects. Retrieved from [http://www.ecoshape.nl/nl\\_NL/Nieuws.html/newsitem/20](http://www.ecoshape.nl/nl_NL/Nieuws.html/newsitem/20), viewed 22-11-2014
- Eisma, D. (1968). Composition, origin and distribution of Dutch coastal sands between Hoek van Holland and the island of Vlieland. *Netherlands Journal of Sea Research*, 4(2), 123-267.
- Engesgaard, P., & Kipp, K. L. (1992). A geochemical transport model for redox-controlled. movement of mineral fronts in groundwater flow systems: A case of nitrate removal by oxidation of pyrite. *Water resources research*, 28(10), 2829-2843.
- Everard, M., Jones, L., & Watts, B. (2010). Have we neglected the societal importance of sand dunes? An ecosystem services perspective. *Aquatic Conservation: Marine and Freshwater Ecosystems*, 20(4), 476-487.
- Goldberg, E. D. (1963). *Chemistry-the oceans as a chemical system*. In Hill, M. N., *Composition of Seawater, Comparative and Descriptive Oceanography of the Sea*. Interscience, N.Y.
- Griffioen, J. (1992). *Cation-exchange and carbonate chemistry in aquifers following groundwater flow*. PhD thesis, Free University, Amsterdam.
- Griffioen, J., Gerard Klaver, G., & Westerhoff, W. (2015). *The mineralogy of suspended matter, aquatic and Cenozoic sediments in the Rhine–Meuse Scheldt delta area, the Netherlands: An overview and review*. Neth. J. Geosci., to be accepted after revision.
- IPCC. (2014). *Fifth Assessment Report (AR5)*. Retrieved from <http://www.ipcc.ch/report/ar5/>, viewed 22-11-2014
- Jobbágy, E. G., & Jackson, R. B. (2000). The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecological applications*, 10(2), 423-436.
- Jobbágy, E. G., & Jackson, R. B. (2004). The uplift of soil nutrients by plants: biogeochemical consequences across scales. *Ecology*, 85(9), 2380-2389.
- Jones, M. L. M., Sowerby, A., Williams, D. L., & Jones, R. E. (2008). Factors controlling soil development in sand dunes: evidence from a coastal dune soil chronosequence. *Plant and Soil*, 307(1-2), 219-234.
- Juvekar, V., & Sharma, M. (1973). Absorption of Co<sub>2</sub> in a suspension of calcium carbonate. *Chemical Engineering Science*, 28(3), 825-837. doi:10.1016/0009-2509(77)80017-1.
- Kaufmann, G., & Dreybrodt, W. (2007). Calcite dissolution kinetics in the system CaCO<sub>3</sub>-H<sub>2</sub>O-CO<sub>2</sub> at high undersaturation. *Geochimica et Cosmochimica Acta*, 71(6), 1398-1410.
- Keller, C. K., & Bacon, D. H. (1998). Soil respiration and georespiration distinguished by transport analyses of vadose CO<sub>2</sub>, <sup>13</sup>CO<sub>2</sub>, and <sup>14</sup>CO<sub>2</sub>. *Global biogeochemical cycles*, 12(2), 361-372.
- Kessler, T. J., & Harvey, C. F. (2001). The global flux of carbon dioxide into groundwater. *Geophysical research letters*, 28(2), 279-282.
- KNMI. (2015). Nader verklaard, Regendagen. Retrieved from <http://www.knmi.nl/cms/content/101549/regendagen>, viewed 21-7-2015.
- Kooijman, A. M., & Besse, M. (2002). The higher availability of N and P in lime-poor than in lime-rich coastal dunes in the Netherlands. *Journal of Ecology*, 90(2), 394-403.
- Laine, L., & Sandvik, A. (2001, November). Derivation of mechanical properties for sand. In *Proceedings of the 4th Asia-Pacific Conference on Shock and impact loads on structures, CI-Premier PTE LTD, Singapore* (Vol. 361, p. 368). ANSYS Inc.
- Modflow. (2015). MODFLOW: USGS three-dimensional finite-difference ground-water model. Retrieved from <http://water.usgs.gov/ogw/modflow/MODFLOW.html>, viewed 12-8-2015.
- Mook, W. G. (1986). <sup>13</sup>C in atmospheric CO<sub>2</sub>. *Netherlands Journal of Sea Research*, 20(2), 211-223.



- Mook, W. G., & Tan, F. C. (1991). Stable carbon isotopes in rivers and estuaries. *Biogeochemistry of major world rivers*, 42, 245-264.
- Morse, J. W. (1974). Dissolution kinetics of calcium carbonate in sea water; V, Effects of natural inhibitors and the position of the chemical lysocline. *American Journal of Science*, 274(6), 638-647.
- Morse, J. W., & Arvidson, R. S. (2002). The dissolution kinetics of major sedimentary carbonate minerals. *Earth-Science Reviews*, 58(1), 51-84.
- Nature Coast. (2014). *Nature Coast*. Retrieved from <http://www.naturecoast.nl/home>, viewed 20-2-2015.
- Nellemen, C., Corcoran, E., Duarte, C.M., Valdés, L., De Young, C., Fonseca, L., Grimsditch, G. (Eds.), 2009. Blue Carbon: the Role of Healthy Oceans in Binding Carbon. A Rapid Response Assessment. United Nations Environment Program.
- Olsthoorn, Th. N., 1977. In Nederlandse zandformaties zijn het doorstroomde en het totale porievolume aan elkaar gelijk. *H2O* (10) 1977 nummer 5. p118-122
- PHREEQC interactive. (August 16, 2011). Phreeqci-A Graphical User Interface for the Geochemical Computer Program PHREEQC. Retrieved from [http://wwwbrr.cr.usgs.gov/projects/GWC\\_coupled/phreeqci/](http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqci/), viewed 12-8-2015
- PHT3D. (2015). A reactive multicomponent transport model for saturated porous media. Retrieved from <http://www.pht3d.org/>, viewed 12-8-2015.
- Plummer, L. N., & Mackenzie, F. T. (1974). Predicting mineral solubility from rate data; application to the dissolution of magnesian calcites. *American Journal of Science*, 274(1), 61-83.
- Plummer, L. N., Wigley, T. M. L., & Parkhurst, D. L. (1978). The kinetics of calcite dissolution in CO<sub>2</sub>-water systems at 5 degrees to 60 degrees C and 0.0 to 1.0 atm CO<sub>2</sub>. *American Journal of Science*, 278(2), 179-216.
- PMWIN.(2015). Processing Modflow 8.043. Retrieved from <http://www.simcore.com/>, viewed 12-8-2015.
- Rijkswaterstaat (RWS). (2014). Retrieved from [http://www.rijkswaterstaat.nl/water/veiligheid/bescherming\\_tegen\\_het\\_water/veiligheidsmaatregelen/kustlijnzorg/planning\\_en\\_aanpak/index.aspx#v3](http://www.rijkswaterstaat.nl/water/veiligheid/bescherming_tegen_het_water/veiligheidsmaatregelen/kustlijnzorg/planning_en_aanpak/index.aspx#v3), viewed 13-11-2014
- RIVM. (2014). Chemische samenstelling van neerslag vanaf 1992. Retrieved from: <http://www.lml.rivm.nl/gevalideerd/>, viewed 20-2-2015.
- Salem, M. R., Mangood, A. H., & Hamdona, S. K. (1994). Dissolution of calcite crystals in the presence of some metal ions. *Journal of materials science*,29(24), 6463-6467.
- Sarazin, G., Michard, G., & Prevot, F. (1999). A rapid and accurate spectroscopic method for alkalinity measurements in sea water samples. *Water Research*, 33(1), 290-294.
- Schlesinger, W. H. (1977). Carbon balance in terrestrial detritus. *Annual review of ecology and systematics*, 51-81.
- Sjöberg, E.L., 1978. Kinetics and mechanism of calcite dissolution in aqueous solutions at low temperatures. *Stockholm contributions in geology*, 32, 92 pp.
- Spiteri, C., Slomp, C. P., Charette, M. A., Tuncay, K., & Meile, C. (2008). Flow and nutrient dynamics in a subterranean estuary (Waquoit Bay, MA, USA): field data and reactive transport modeling. *Geochimica et Cosmochimica Acta*, 72(14), 3398-3412.
- Stive, M. J. F., de Schipper, M. A., Luijendijk, A. P., Aarninkhof, S. G. J., van Gelder-Maas, C., de Vries, J. S. M. v. T., et al. (2013). A new alternative to saving our beaches from sea-level rise: The sand engine. *Journal of Coastal Research*, 29(5), 1001-1008. doi:10.2112/JCOASTRES-D-13-00070.1.

Van der Perk, M. (2013). *Soil and water contamination*. CRC Press.  
Zeenivea. (2014). Laag en (toch) droog. Retrieved from  
<http://www.zeeniveau.nl/laagdroog.html>, viewed 13-11-2014

## 11. APPENDICES

### APPENDIX A. RAINWATER IMITATION

**Table B. The rainwater stock that is described in section 4.2.1 . The green section summarizes the rainwater data gathered at weather station the Zilk (RIVM, 2014).**

RIVM 2012 de Zilk	NH4	NO3	SO4	Cl	Na	K	Mg	Ca
min	11,0	10,0	7,3	17,5	16,9	1,2	2,1	1,4
max	269,0	134,8	47,1	566,7	482,0	23,7	54,3	24,0
average	49,3	34,5	19,2	138,5	119,6	5,2	13,7	7,5
stand.dev	36,1	17,2	6,6	97,4	82,1	3,2	9,1	4,0
Recipe	(NH4)2SO4	NH4NO3	NaCl					
500ml stock (g)	1,32	1,40	3,21					

## APPENDIX B. FLOW CALIBRATIONS

Flow calibrations for the bioreactor experiments (section 4.2.2)

**Table C.1. CA and CO<sub>2</sub> flow calibration**

CO <sub>2</sub>		CA	2-Lucht	
7,5 ml/min	ml/min	1000 mL/min	ml/min	
%		%		
100	8,6	100	overflow	
90	7,6	90	overflow	
80	6,5	80	overflow	
70	5,45	70	910	
60	4,8	60	730	
50	4	50	620	
40	3,2	40	460	
30	2,3	30	270	
20	1,2	20	190	
10	0,2	10	100	

**Table C.2. Used CA and CO<sub>2</sub> flows in bioreactor experiment**

CA %	CO <sub>2</sub> %	tot V (ml)	CO <sub>2</sub> (atm)	SI CO <sub>2</sub>	Date used
70	37	703,182	0,0050	-2,29	11-3-2015
70	30	702,58	0,0042	-2,37	18-3-2015
100	0	1000	0,0004	-3,39	05-3-2015/ 19-3-2015

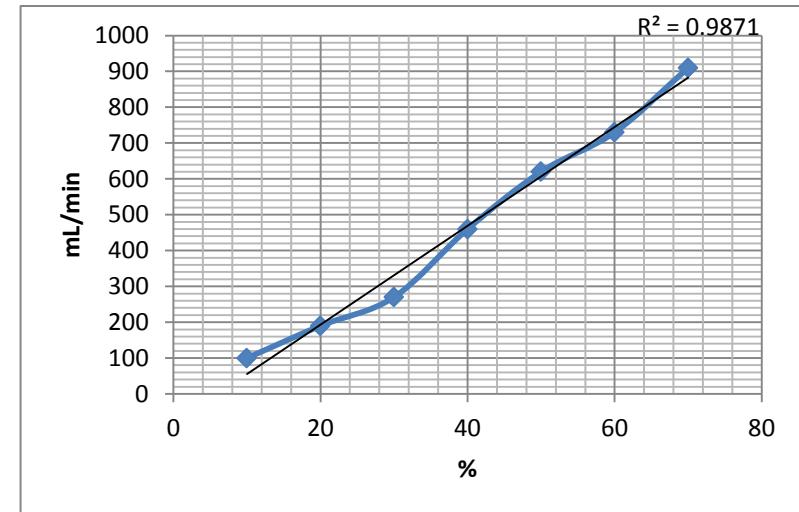


Figure B.1. The calibration of the flow of compressed air

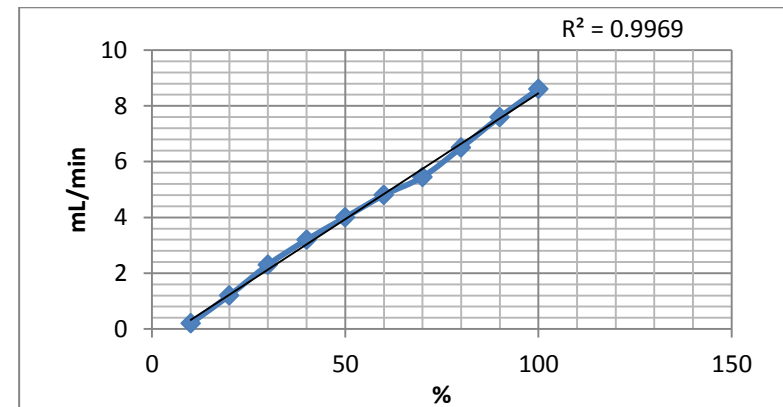


Figure B.2. The calibration of the flow of CO<sub>2</sub>

APPENDIX C. PRELIMINARY SAND MOTOR DATA

Table D. Priliminary data on Ca, CaCO<sub>3</sub>, soil moistur, pH. Alkalinity and PCO<sub>2</sub> from the Sand Motor (personal contact Iris Pit, May 2015).

Data Iris					Groundwater at 50 cm depth			
Sample name	X	Y	Ca	CaCO <sub>3</sub> tot	Soil moisture	pH	Alkalinity	PCO <sub>2</sub>
	UTM	UTM	g/kg	%	%	-	mmol/L	atm
A01	580351	5765807	11.4	0.0	0.22	7.94	3.56	0.0026
A02	580520	5765996	9.3	2.5	0.16	8.17	3.00	0.0013
A03	580679	5766188	11.6	4.0	0.34	8.21	4.18	0.0016
A04	580839	5766374	19.8	4.4	0.35	8.34	4.84	0.0014
A05	581002	5766568	12.7	4.5	0.17	8.37	2.13	0.0006
A06	581164	5766756	14.2	4.3	0.48	8.66	2.41	0.0003
A07	581325	5766950	16.8	3.7		8.21	1.78	0.0007
A08	581485	5767140	15.0	3.5	0.14	8.5	1.47	0.0003
A09	581645	5767332	8.8	2.4	0.14	8.52	2.05	0.0004
A10	581809	5767522	22.7	5.8	0.15	8.75	4.51	0.0005
A11	581969	5767712	17.9	5.7	0.16	8.47	2.55	0.0005
A12	582131	5767902	27.2	6.2	0.17	8.47	2.62	0.0006
A13	582292	5768094	35.9	6.1	0.17	8.67	8.99	0.0012
A14	582454	5768285	24.4	4.7	0.17	8.17	2.04	0.0009
A15	582615	5768475	8.1	4.4	0.21	7.68	2.09	0.0028
A16	582776	5768670	5.5	4.8	0.15	8.24	4.20	0.0015
A17	582930	5768862	5.5	1.8	0.16	8.35	5.72	0.0016
B03	580483	5766348	0.0		0.57	7.63	3.27	0.0048
B04	580660	5766546	4.1	1.2	0.56	7.93	2.87	0.0021
B05	580831	5766747	18.3	5.2	0.16	8.77	6.77	0.0007
B06	580991	5766937	15.8	3.0	0.19	8.42	1.82	0.0004
B07	581154	5767130	17.9	2.1	0.31	7.84	3.98	0.0036
B08	581315	5767322	13.8	3.4	0.13	8.33	1.89	0.0006
B09	581477	5767510	24.8	5.0	0.49	7.76	5.12	0.0056
B10	581641	5767701	0.0			8.5	3.21	0.0006
B11	581803	5767889	0.0					
B12	581963	5768080	13.2	3.2		7.27	3.73	0.0126
B13	582124	5768271	14.0	3.2		7.42	3.83	0.0092
B14	582268	5768449	9.9	2.7		7.4	4.04	0.0101
B15	582453	5768644	7.8	3.7	0.57	7.61	2.84	0.0044
C06	580813	5767119	13.7	4.9	0.57	7.64	2.64	0.0038
C07	580976	5767309	23.7	6.1	0.17	8.49	2.33	0.0005
C08	581138	5767499	11.0	3.3	0.14	8.37	1.87	0.0005
C09	581297	5767690	29.1	5.7	0.14	8.4	1.65	0.0004
C10	581461	5767881	27.6	6.0	0.14	8.63	5.54	0.0008
C11	581620	5768072	30.6	7.8	0.16	8.53	4.61	0.0009

Data Iris					Groundwater at 50 cm depth			
Sample name	X	Y	Ca	CaCO <sub>3</sub> tot	Soil moisture	pH	Alkalinity	PCO <sub>2</sub>
	UTM	UTM	g/kg	%	%	-	mmol/L	atm
C12	581781	5768266	19.0	5.6	0.22	7.81	2.22	0.0022
C13	581965	5768448	3.6	4.1	0.55	7.69	2.40	0.0031
D08	580963	5767675	3.3	0.6	0.57	7.66	2.74	0.0038
D09	581123	5767866	11.6	4.8	0.20	7.71	1.65	0.0020
D10	581288	5768062	12.8	3.9	0.34	7.76	2.55	0.0028
D11	581453	5768256	7.0	1.2	0.57	7.72	2.90	0.0035
Average				4.0				

## APPENDIX D. EXAMPLES OF PHREEQC INPUT FILES

### Example of an PHREEQC input file for an open CO<sub>2</sub> system

```
#Experimental date: 19-3-2015.
#Bioreactor experiment
#C08/5g sand/Patmosphere

TITLE Modeling experiment 1. Bioreactor experiment.
SOLUTION 1
  temp      20
  pH        7
  pe        4
  redox     pe
  units     mmol/kgw
  density   1
  Amm       75 umol/kgw
  N(5)      35 umol/kgw
  Na        130 umol/kgw
  Cl        130 umol/kgw
  S(6)      20 umol/kgw
  -water    1 # kg
EQUILIBRIUM_PHASES 1
  O2(g) -0.68      # P_O2 = 0.21 atm (log 0.21 = -0.68)
  CO2(g) -3.4      # P_CO2 0.0004 atm (log 0.0004 = -3.4)
SAVE solution 1
END

TITLE Calculating equilibrium in bioreactor flushed with CO2
USE solution 1
EQUILIBRIUM_PHASES 2
  Calcite  0      0.0011
  CO2(g)   -3.4  # P_CO2 0.0004 atm (atmosphere, log 0.0004 = -3.4)
END
```

### Example of an PHREEQC input file for a closed CO<sub>2</sub> system

```
#Experimental date: 26-3-2015.
#Bottle experiment in cooled storage room at 4 degrees Celsius
#C08/50g sand/Patmosphere

TITLE Modeling experiment 2. Bottle experiment
SOLUTION 1
  temp      4
  pH        7
  pe        4
  redox     pe
  units     mmol/kgw
  density   1
  Amm       75 umol/kgw
  N(5)      35 umol/kgw
  Na        130 umol/kgw
  Cl        130 umol/kgw
  S(6)      20 umol/kgw
  -water    1.0 # kg
EQUILIBRIUM_PHASES 1
  O2(g) -0.68      # P_O2 = 0.21 atm (log 0.21 = -0.68)
  CO2(g) -3.4      # P_CO2 0.0004 atm (log 0.0004 = -3.4)
SAVE solution 1
END

TITLE Calculating equilibrium in bottles
USE solution 1
EQUILIBRIUM_PHASES 2
  Calcite  0      0.0165
END
```

**Example of an PHREEQC input file for saturation index calculation, with the Ca, Mg and alkalinity measured in an experiment.**

TITLE Experiment 18-03-2015 Bioreactor

SOLUTION\_S  
-pe 4  
-temp 20  
-units mmol/kgw  
-density 1  
-water 1 # kg

pH	Cl	S(6)	Alkalinity	Ca	Mg	Na	N(5)	Amm
9.14	0.13	0.02	0.26	0.12	0.004	0.13	0.035	0.075
8.85	0.13	0.02	0.37	0.18	0.008	0.13	0.035	0.075
8.5	0.13	0.02	0.48	0.24	0.008	0.13	0.035	0.075
8.35	0.13	0.02	0.6	0.30	0.012	0.13	0.035	0.075
8.3	0.13	0.02	0.73	0.33	0.012	0.13	0.035	0.075
8.28	0.13	0.02	0.73	0.35	0.012	0.13	0.035	0.075
8.29	0.13	0.02	0.74	0.37	0.012	0.13	0.035	0.075
8.35	0.13	0.02	0.86	0.43	0.016	0.13	0.035	0.075

SELECTED\_OUT  
-file 15-03-18.prn  
-reset false  
-ph true  
-alkalinity true  
-totals Ca Mg  
-saturation\_indices CO2(g) Calcite Dolomite



## APPENDIX E. CALCITE WEATHERING MODULE FOR PHT3D IN PMWIN.

# Adjustments to example 13 to fit calcite weathering research Annemieke Wijnakker 13-5-2015

# Rainwater elements and Ca / Mg that can be produced in reactions.

9

pH

pe

Amm

Ca

Cl

Mg

N(5)

Na

S(6)

#[Minerals\_equilibrium]

#Format:

#Line 1: Number of Minerals\_equilibrium

#FOR i=0 to Number of Minerals\_equilibrium -1

# Line 2+i: Name of the Mineral\_equilibrium

# Line 3+i: Chemical equation

#NEXT i

#Maybe use Dolomite and Quartz later on. First start with only calcite

1

Calcite

$\text{CaCO}_3 = \text{CO}_3^{-2} + \text{Ca}^{+2}$

#Dolomite

$\text{CaMg}(\text{CO}_3)_2 = \text{Ca}^{+2} + \text{Mg}^{+2} + 2 \text{CO}_3^{-2}$

#Quartz

$\text{SiO}_2 + 2 \text{H}_2\text{O} = \text{H}_4\text{SiO}_4$

#[GAS\_EQUILIBRIUM]

#[Gas\_equilibrium]

#Format:

#Line 1: Number of Gases (equilibrium)

#FOR i=0 to Number of Gases (equilibrium) -1

# Line 2+i: Name of the Gas

#Next i

#CO2 used for calcite weathering

2

CO2(g)

O2(g)