

The groundwater composition in limestone and marlstone quarries in the Slite industrial area

Grundvattnets sammansättning i kalkstens-
och mägerstensbrott i Slite industriområde

Frida Pettersson

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Abstract

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Limestone and marlstone quarrying is of great importance to Gotland, but there are also negative aspects to these activities. Effects of quarrying can be the drawdown of groundwater level and intrusion of relict saltwater or seawater into the quarry and in the surrounding area. Cementa AB in Slite intends to submit an application to the Environmental Court for the continued expansion of quarrying activities and groundwater extraction in two quarries, the Western quarry and File Hajdar quarry.

The aim of this Master thesis is to classify the type of groundwater (freshwater, saltwater or a mixture) flowing into the limestone quarries in Slite and to determine the sources of the groundwater discharging to the quarries by studying changes in groundwater chemistry. In addition, the aim is to point out any fluctuations and tendencies in historic groundwater data and to examine the potential impact of limestone quarrying in Slite on the composition of groundwater. To classify the water samples as a mixture between freshwater and saltwater, Piper diagrams and mixing ratios have been used.

Freshwater was only found discharging from the upper bench in the Western quarry and in File Hajdar (File Hajdar is located above the mean sea level). Water samples from the rest of the sampling points were considered contaminated by seawater or a mixture of seawater and freshwater. The origin of seawater influence in the deeper bench is probably the Baltic Sea or a relict saltwater with a similar groundwater composition. One sample point in the deeper bench had a larger contribution of seawater than the other two sampling points in the deeper bench but no conclusions could be drawn about the exact relative contribution. One sampling point in the Western quarry was a landfill for waste products, alkalis and chloride from the cement manufacturing process. This sampling point was highly contaminated by potassium, sodium and chloride from the waste products and any contamination caused by seawater influence could not be ascertained. Fluctuations and tendencies in groundwater chemistry predominantly concerned Bogevisken and Tingstäde träsk and were probably not caused by limestone quarrying in Slite. The alkalinity and pH have slightly increased in the Drinking water wells 23v281 over the last 12 years but no conclusions could be made concerning the reason. This study has demonstrated that the limestone quarrying in Slite has a small impact on the groundwater composition in the area.

Keywords: Limestone quarry, groundwater, chemistry, seawater intrusion, Piper diagram.

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Referat

Grundvattnets sammansättning i kalkstens- och mörgelstensbrotten i Slite industriområde

Frida Pettersson

Kalksten och mörgelstens brytning är av stor betydelse för Gotland men stenbrytningen och dess industri har också negativa aspekter. Effekter av kalkstensbrytning kan vara sänkning av grundvattennivån och saltvatteninträngning av relict saltvatten eller havsvatten i stenbrottet och i det omgivande området. Cementa AB i Slite har för avsikt att lämna in en ansökan till Miljödomstolen för fortsatt brytning av kalksten och mörgelsten samt grundvattenuttag i två stenbrott, Västra brottet och File Hajdar brottet.

Syftet med detta examensarbete är att klassificera vilken typ av grundvatten (sötvatten, saltvatten eller en blandning) som infiltreras i kalkstensbrotten i Slite och att undersöka grundvattnets ursprung genom att studera förändringar i grundvattnets kemi. Dessutom är syftet att undersöka eventuella variationer och tendenser i äldre grundvattendata och att undersöka de eventuella konsekvenserna av kalkstensbrytning i Slite med avseende på grundvattnets sammansättning. För klassificeringen av vattenprover har Piper-diagram använts.

Sötvatten återfanns endast i den övre pallen (avsatsen) i Västra brottet och i File Hajdar brottet (File Hajdar är beläget ovanför havsnivån). Vattenprover från resten av provtagningspunkterna klassificerades att vara förorenade av havsvatten eller en blandning av havsvatten och sötvatten. Det inträngande havsvattnets ursprung i den djupa pallen är troligen från Östersjön eller relict saltvatten med liknande sammansättning. En provplats hade en högre halt av inträngande havsvatten än de andra två men inga slutsatser kunde dras angående exakt andel havsvatten. En provtagningspunkt i Västra brottet är en deponi för restprodukter, alkalier och klorid från cementprocessen. Denna provtagningspunkt är starkt förorenad av kalium, natrium och klorid från restprodukterna vilket gör att slutsatser angående eventuell förorening orsakad av havsvattensinträngning inte kan dras. De variationer och tendenser som främst berör Bogeviden och Tingstäde träsk är troligen inte orsakade av kalkstensbrytningen i Slite. Alkaliniteten och pH-värdet har en svag ökning i dricksvattenbrunnarna 23v281 över de senaste 12 åren men inga slutsatser kan dras angående orsak. Studien visar att kalkstensbrytningen i Slite har en liten påverkan på grundvattnets sammansättning i området.

Nyckelord: Kalkstensbrott, grundvatten, kemi, havsvatteninträngning, Piper-diagram.

Preface

This Master thesis was performed as the final part of the Master of Science in Aquatic and Environmental Engineering programme at Uppsala University and comprises 30 ECTS points. This project was developed by Cementa AB in Slite (part of the international group HeidelbergCement) in cooperation with the engineering consultant company Golder Associates in Stockholm. Supervisors at Cementa AB and Golder Associates AB were Environmental manager Kerstin Nyberg and Project manager and senior hydrologist Peter Vikström, respectively. Associate professor Roger Herbert was the subject reviewer and Professor Allan Rodhe was the examiner, both at the Department of Earth Sciences at Uppsala University.

First I would like to thank both my supervisors, Kerstin Nyberg and Peter Vikström, for their dedicated supervision and rewarding discussions that were a great help during this project. A big thank you is offered to my subject reviewer Roger Herbert for support, advice and rapid response concerning my questions and thoughts for this master thesis. I would also like to thank the personnel at Cementa AB and Cementa Research AB in Slite for their warm welcome and help.

Additionally, I would like to thank Anders Carlstedt at SGU in Uppsala for the informative discussion of the project area and Jonas Aaw from Gotland municipality for providing me with data.

Finally I would like to thank my family and friends for their great support during this project!

Uppsala, January 2009-01-12

Frida Pettersson

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POPULÄRVETENSKAPLIG SAMMANFATTNING

Att säkerställa en god tillgång och kvalitet på dricksvatten anses vara en av huvudfrågorna på Gotland. Gotlands berggrund består huvudsakligen av kalksten och mägersten. Både kalksten och mägersten, där mägersten innehåller mer lera, är kalkhaltiga och löses upp av surt vatten. Vatten sipprar ner i sprickzoner och löser upp kalkstenen så sprickorna blir större. Områden med stora och utvecklade spricksystem kallas karst. I dessa sprickor flödar vattnet snabbt och på ett sätt som är svårberäknligt. Detta gör grundvattnet känsligt för föroreningar och grundvattensänkningar då påverkningsområdet och omfattningen är svåra att bestämma.

Den kalkhaltiga berggrunden bildades för ca 400 miljoner år sedan under Silurtiden. Då var Östersjön ett grunt tropiskt hav och låg nära ekvatorn. Marina organismer dog, föll till botten och sedimenterades. Av tid och vikt har dessa bottensediment utvecklats till kalksten och mägersten. Kalkstenen och mägerstenen ligger i breda stråk i nordöstlig-sydvästlig riktning över Gotland. De lagrade sedimenten har en svag lutning åt sydöst vilket gör att de äldsta kalkstenslagren som kommer i dagen ligger i nordväst och de yngsta i sydöst. Över den kalkhaltiga berggrunden ligger ett tunt eller osammanhängande jordlager av vittringsjord eller lerig morän alternativt svallsediment. Svallsedimentet bildades efter senaste istiden. Gotland trycktes ner av isens tyngd och steg först över vattenytan i Littorinahavet för ca 6 500 år sedan. Att delar av Gotland legat under havsytan i det salta Littorinahavet gör att det finns akviferer i berggrunden med relik saltvatten inkapslat.

Kalkstensbrytning har en lång historia på Gotland. De medeltida husen och kyrkorna samt gamla kalkbrotten på ön är bevis på detta. Nu bryts den största mängden kalksten och mägersten för att producera cement samt till stål- och pappersindustrin vilket sker på norra Gotland. Kalkstens- och mägerstensbrytningen är mycket viktig för Gotland men det finns även negativa aspekter av stenbrytningen och industrin kring denna. De ofta djupa brotten kan skapa en grundvattenavsänkning i det omgivande området. Den låga grundvattennivån i brotten gör att grundvattnet söker sig dit och grundvatten nivån i det omgivande området sjunker. Denna förändring i grundvattennivå kan även orsaka saltvatteninträngning i kustområden eller områden med relik saltvattenakviferer. Det tyngre saltvattnet tvingas uppåt och kan ibland läcka in i dricksvattenbrunnar och förorena dricksvattnet.

Cementa AB i Slite avser att ansöka till Miljödomstolen om utökad täktverksamhet och grundvattenuttag i två kalkstensbrott, Västra brottet och File Hajdar brottet belägna i Slites omgivning. Konsultföretaget Golder Associates AB är anlitate av Cementa AB att undersöka hur grundvatten och ytwater fungerar i området samt skriva en miljökonsekvensbeskrivning (MKB).

Syftet med detta examensarbete är att klassificera vilken typ av grundvatten som flödar in i kalkstensbrotten och att avgöra grundvattnets ursprung genom att undersöka förändringar i grundvattnets sammansättning. I tillägg har även syftet varit att påvisa eventuella fluktuationer och tendenser i historiska och nutida grundvattendata för att avgöra cementindustrins eventuella påverkan på grundvattnets sammansättning i Slite och dess omgivning. Detta examensarbete är en tolkning av grundvattenflödet i kalkstensbrotten som är av vikt för Cementa AB:s ansökan till Miljödomstolen. För att klassificera de olika grundvattentyperna; sötvatten, havsvatten (relik eller nutida) eller

en blandning, har Piper-diagram och blandningsförhållanden använts. Denna metod har använts för att identifiera saltvatteninträngning i kalkstensbrotten orsakat av kalkstensbrytningen i Slite.

Det behandlade området, Österby 1:229, ligger på norra Gotland i Othem socken. Fastigheten ägs av Cementa AB och inom området finns de två kalkstensbrotten, Västra brottet och File Hajdar, som ansökan avser. Det finns även ett tredje brott, Östra brottet, som är avslutat och idag används som lagerplats för krossad kalksten, mörkelsten och bränslet kol. Västra brottet, File Hajdar och Östra brottet har bottendjup på -50, +20 respektive -24 meter över havet. Västra och Östra brottet ligger i Slite samhälle medan File Hajdar ligger ca 5 km väster om Västra brottet.

Fyra olika provtagningsprogram från området har studerats och jämförts för att finna fluktuationer och trender för att undersöka eventuell påverkan av kalkstensbrytningen i Slite. Dessa provtagningsprogram har även använts för att klassificera de olika grundvattentyperna. Som en del av detta examensarbete har ett nytt provtagningsprogram utvecklats och utförts för att lokalisera grundvattnets ursprung. Flera olika parametrar har studerats i de olika provtagningsprogrammen, bl a alkalinitet, baskatjoner, kväve (som ammonium), pH, sulfat och konduktivitet. Provtagningsplatserna är bland andra insjön Tingstäde träsk väster om File Hajdar, Bogeviden som praktiskt taget är avsnörd från Östersjön, Gotlands Kommuns dricksvattenbrunnar som ligger strax öster om File Hajdar samt ett flertal provpunkter i kalkstensbrotten.

Sötvatten återfanns endast i den övre pallen (avsatsen) i Västra brottet och i File Hajdar brottet (File Hajdar är beläget ovanför havsnivån). Vattenprover från resten av provtagningspunkterna klassificerades att vara förorenade av havsvatten eller en blandning av havsvatten och sötvatten. Det inträngande havsvattnets ursprung i den djupa pallen är troligen från Östersjön eller relict saltvatten med liknande sammansättning. En provplats i den djupare pallen i Västra brottet hade en högre halt av inträngande havsvatten än de andra två men inga slutsatser kunde dras angående exakt andel havsvatten. En provtagningspunkt i Västra brottet är en deponi för restprodukter, alkalier och klorid, från cementprocessen. Denna provtagningspunkt är starkt förorenad av kalium, natrium och klorid från restprodukterna vilket gör att slutsatser angående eventuell förorening orsakad av havsvattensinträngning inte kan dras.

De tendenser i grundvattendata som visuellt påvisats är att Bogeviden har med tiden fått ökad konduktivitet, ammoniumhalt och minskat pH-värde, alkalinitet, kloridhalt och natriumhalt, medan sulfathalten, magnesiumhalten och kaliumhalten har fluktuerat. Tingstäde träsk har fått minskad alkalinitet, sulfathalt, kalciumhalt, nitrat- och nitrithalt, medan ammoniumhalten har fluktuerat. Dricksvattenbrunnarna 23v281 har fått ökat pH-värde och alkalinitet. De variationer och tendenser som främst berör Bogeviden och Tingstäde träsk är troligen inte orsakade av kalkstensbrytningen i Slite. Alkaliniteten och pH-värdet har en svag ökning i dricksvattenbrunnarna 23v281 över de senaste 12 åren men inga slutsatser kan dras angående orsak. Studien visar att kalkstensbrytningen i Slite har en liten påverkan på grundvattnets sammansättning.

TABLE OF CONTENTS

1. INTRODUCTION	1
1.1. GROUNDWATER ON GOTLAND.....	1
1.2. LIMESTONE QUARRYING ON GOTLAND.....	1
1.3. EFFECTS OF QUARRYING	2
1.4. CEMENTA AB AND FUTURE PLANS.....	3
1.5. AIM.....	3
2. BACKGROUND	4
2.1. GROUNDWATER IN CARBONATE AQUIFERS.....	4
2.1.1. <i>Groundwater flow</i>	4
2.1.2. <i>Groundwater chemistry</i>	5
<i>Carbonate equilibrium reactions</i>	6
<i>Ion exchange</i>	8
2.1.2.1. Chemical parameters	8
<i>Conductivity</i>	9
<i>pH</i>	9
<i>Alkalinity</i>	9
<i>Chloride (Cl⁻) and sulphate (SO₄²⁻)</i>	9
<i>Nitrogen as nitrate (NO₃⁻), nitrite (NO₂⁻) and ammonium (NH₄⁺)</i>	10
<i>Calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺) and sodium (Na⁺)</i>	10
2.2. STUDY AREA.....	11
2.2.1. <i>Geology</i>	13
2.2.2. <i>Soil</i>	14
2.2.3. <i>Hydrology</i>	15
2.2.3.1. <i>Climate</i>	15
2.2.3.2. <i>Groundwater levels</i>	16
2.2.4. <i>Cementa AB in Slite</i>	17
2.2.5. <i>The process description of cement production in Slite</i>	18
2.2.6. <i>Golder Associates AB's present work</i>	20
2.2.7. <i>Protected areas in the study area and its surroundings</i>	22
3. METHOD	23
3.1. SAMPLING PROGRAMMES.....	23
3.1.1. <i>Previous sampling by SGU</i>	23
3.1.2. <i>National water survey, SLU</i>	25
3.1.3. <i>Gotland Municipality: Drinking water wells</i>	25
3.1.4. <i>New sampling programme</i>	25
3.1.4.1. <i>Analyses</i>	28
3.2. PIPER DIAGRAM.....	28
3.3. CALCULATIONS OF MIXING RATIOS.....	30
4. RESULTS	31
4.1. CONDUCTIVITY.....	31
4.2. PH.....	34
4.3. ALKALINITY (HCO ₃ ⁻).....	36
4.4. CHLORIDE (CL ⁻) AND SULPHATE (SO ₄ ²⁻).....	38
4.5. NITROGEN AS NITRATE (NO ₃ ⁻), NITRITE (NO ₂ ⁻) AND AMMONIUM (NH ₄ ⁺).....	41
4.6. CALCIUM (CA ²⁺), MAGNESIUM (MG ²⁺), POTASSIUM (K ⁺) AND SODIUM (NA ⁺).....	43

5. DISCUSSION.....	51
5.1. PIPER DIAGRAM	51
5.2. FRESHWATER.....	51
5.3. GROUNDWATER AFFECTED BY SEAWATER.....	52
5.4. GROUNDWATER AFFECTED BY THE LANDFILL IN THE WESTERN QUARRY.....	55
5.5. CALCITE PRECIPITATION AND CHARGE BALANCE ERROR	57
5.6. FLUCTUATIONS AND TENDENCIES.....	59
6. CONCLUSIONS.....	61
REFERENSES.....	63
APPENDIX 1 NATURE RESERVES AND NATURA 2000.....	66
APPENDIX 2 ANALYZING METHODS	67
APPENDIX 3 DATA.....	68

1. INTRODUCTION

1.1. GROUNDWATER ON GOTLAND

Securing a sustainable water supply with good quality drinking water is considered the major environmental issue on Gotland (Holpers, 2007). The bedrock on Gotland consists predominantly of limestone and marlstone but also sandstone. The dissolution of calcium, Ca^{2+} , and magnesium, Mg^{2+} minerals in the limestone generates permeable fracture zones which can develop to larger fracture zones/channels called karst. Since large areas of Gotland have a thin or absent soil cover, especially along the coast (SGU, 2008, internet), precipitation rapidly percolates to the groundwater table along fractures, with little filtration through soil. The carbonate bedrock on Gotland therefore results in groundwater resources that are vulnerable to anthropogenic impact and groundwater flow in fracture zones that is difficult to predict. Limestone quarrying on Gotland is an activity that can potentially lead to widespread effects on groundwater resources by affecting groundwater availability and quality.

1.2. LIMESTONE QUARRYING ON GOTLAND

The limestone is a readily accessible building material on Gotland; quarrying for limestone on Gotland has a long history. The many medieval churches and houses as well as old inactive quarries are evidence of the importance of limestone quarrying. Limestone was not only used as a building material but was also used to produce burned lime (*bränd kalk*, Swedish) for the plastering and painting of houses and churches. To produce burned lime, the limestone was crushed and burned in lime burners to eliminate the carbonate dioxide in order to generate calcium oxide. When mixing calcium oxide with water an exothermic reaction takes place; when mixed with sand, water and gravel, it hardens to solid mass, mortar (*bruk*, Swedish). The quarrying was small-scale (only satisfying household demands) in the 12th century while the bigger lime burners built in the 1650's demanded larger quarries (Länsstyrelsen Gotland, 2006).

In year 1824, Joseph Aspdin of Leeds took out a patent for Portland cement. The limestone was now mixed with clay, crushed and burned (Gillberg et al, 1999). The essential ingredients and process for manufacturing cement is approximately the same today. The cement industry has been active on Gotland since the 1880's and the first cement factory was founded in 1885 in Visby (Länsstyrelsen Gotland, 2006). The cement industry has through the centuries been concentrated to fewer companies and bigger quarries. The number and size of quarries during the last three centuries can be seen in Figure 1. The limestone industry has played a major part in the industrial history of Slite and the whole of Gotland and is part of the identity of Gotland.

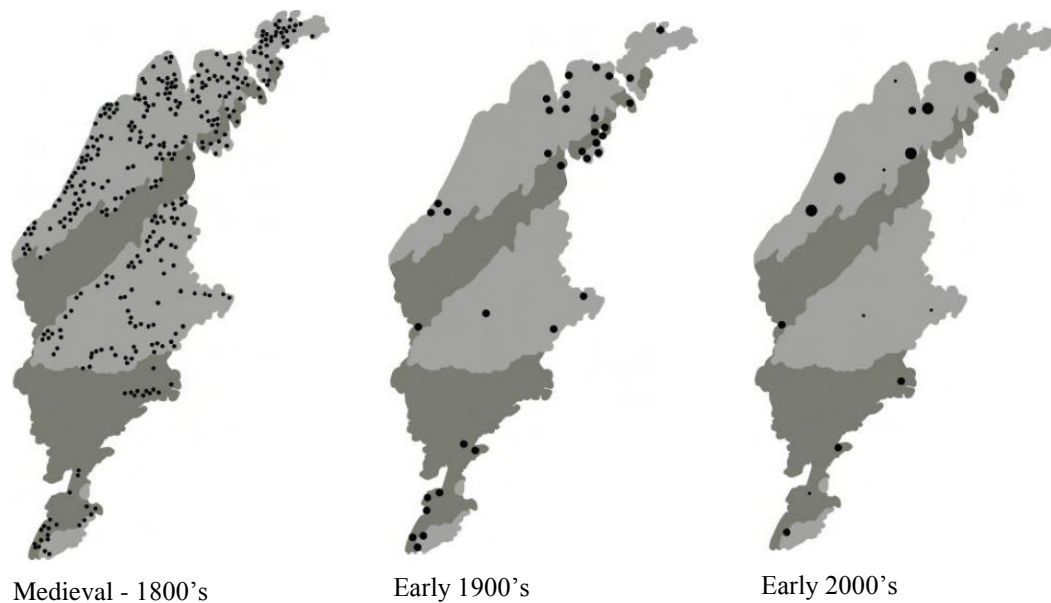


Figure 1 Limestone quarries on Gotland (quarries displayed as black dots). The shaded zones on the map indicate areas of different bedrock: limestone in light gray and marlstone in dark gray (base material to the county museum's exhibition "What would Gotland be without limestone?", Sara Eliasson).

1.3. EFFECTS OF QUARRYING

The main effects on the environment due to the cement production are the use of natural resources, the combustion of fossil fuels and waste fuels, and emissions to the air in the form of SO_2 , NO_x , CO_2 and limestone dust. Additional effects on the surrounding area include noise, vibrations and stone dust from blasting and traffic.

Other effects can be a decline in the groundwater level and saltwater influence into the quarry and in the surrounding area. If quarrying requires the removal of rock below the groundwater table, the removal of rock will result in groundwater flowing into the open pit. In order for quarrying to continue, this water must be continuously pumped from the quarry. This groundwater extraction often results in the drawdown of the groundwater table in the surrounding area outside the quarry. This may also affect surface water in the area. The area of influence is dependant of the depth and volume of quarry and the characteristics of groundwater flow and geology.

Quarries in the coastal area can also have a problem with saltwater intrusion. If quarrying is done below the mean sea level, groundwater pumping and the resultant decrease in piezometric pressure can lead to the seepage of seawater into the quarry and its area of influence. Another reason for saltwater influence can be the occurrence of deep relict saltwater aquifers. The origin of the relict saltwater is the Littorina Sea. About 6500 years ago, Gotland was covered by the post-glacial Littorina Sea. As Gotland arose from the Littorina Sea, salty seawater became entrapped in the rock aquifer. With time, the infiltration of fresh precipitation has depressed the saltwater deeper in the bedrock and below sea level. The current interface between fresh and salt water can be found at between -15 to -30 meters below mean sea level (Tullström, 1955). With pumping, the decreased piezometric pressure allows the heavier and deeper relict saltwater to flow upwards to the quarry and its area of influence. This can contaminate groundwater aquifers in the area. Because of the vulnerable and

complicated hydrogeology on Gotland, the effect of quarrying on the groundwater table and groundwater composition in the surroundings is difficult to foresee.

1.4. CEMENTA AB AND FUTURE PLANS

Cemeta AB is a cement producing company in Slite (Figure 2) and part of the international group HeidelbergCement. The company intends to submit an application to the Environmental Court for the continued expansion of quarrying activities and groundwater extraction. The application refers to two active limestone and marlstone quarries, the Western quarry and File Hajdar quarry in Slite and owned by Cemeta AB. For the production of cement Cemeta AB intends to excavate 3.8 million tonnes of limestone and marlstone per year. The total amount of groundwater extraction in the application is not yet set but the amount of groundwater extracted previously is 2 million m³/year (Nyberg, pers. comm.). The company also has a third quarry, the Eastern quarry, which is no longer active and is used for storage of crushed limestone, marlstone and coal. The application for continued expansion of the two quarries will apply for 20 years after the current quarrying permit expires (year 2011). This is the first time the company applies for groundwater extraction in the area.

The engineering consultant company Golder Associates AB in Stockholm has been commissioned by Cemeta AB to prepare the technical documents and the Environmental Impact Assessment (EIA) as part of the application to the Environmental Court for continued expansion of quarrying activity and groundwater extraction.

1.5. AIM

The aim of this Master thesis is to classify the type of groundwater (freshwater, saltwater or a mixture) flowing into the limestone quarries in Slite (Figure 2 and 4) and to determine the sources of the groundwater discharging to the quarries by studying changes in groundwater chemistry. In addition, the aim is to point out any fluctuations and tendencies in historic and current groundwater data and to examine the potential impact of limestone quarrying in Slite on the composition of groundwater. This Master thesis provides an interpretation of existing groundwater flow patterns, which is necessary for Cemeta AB's application to the Environmental Court.

To classify the water samples as a mixture between freshwater and saltwater, Piper diagrams and mixing ratios have been used. This method was used to identify saltwater influence in the studied area due to limestone quarrying.

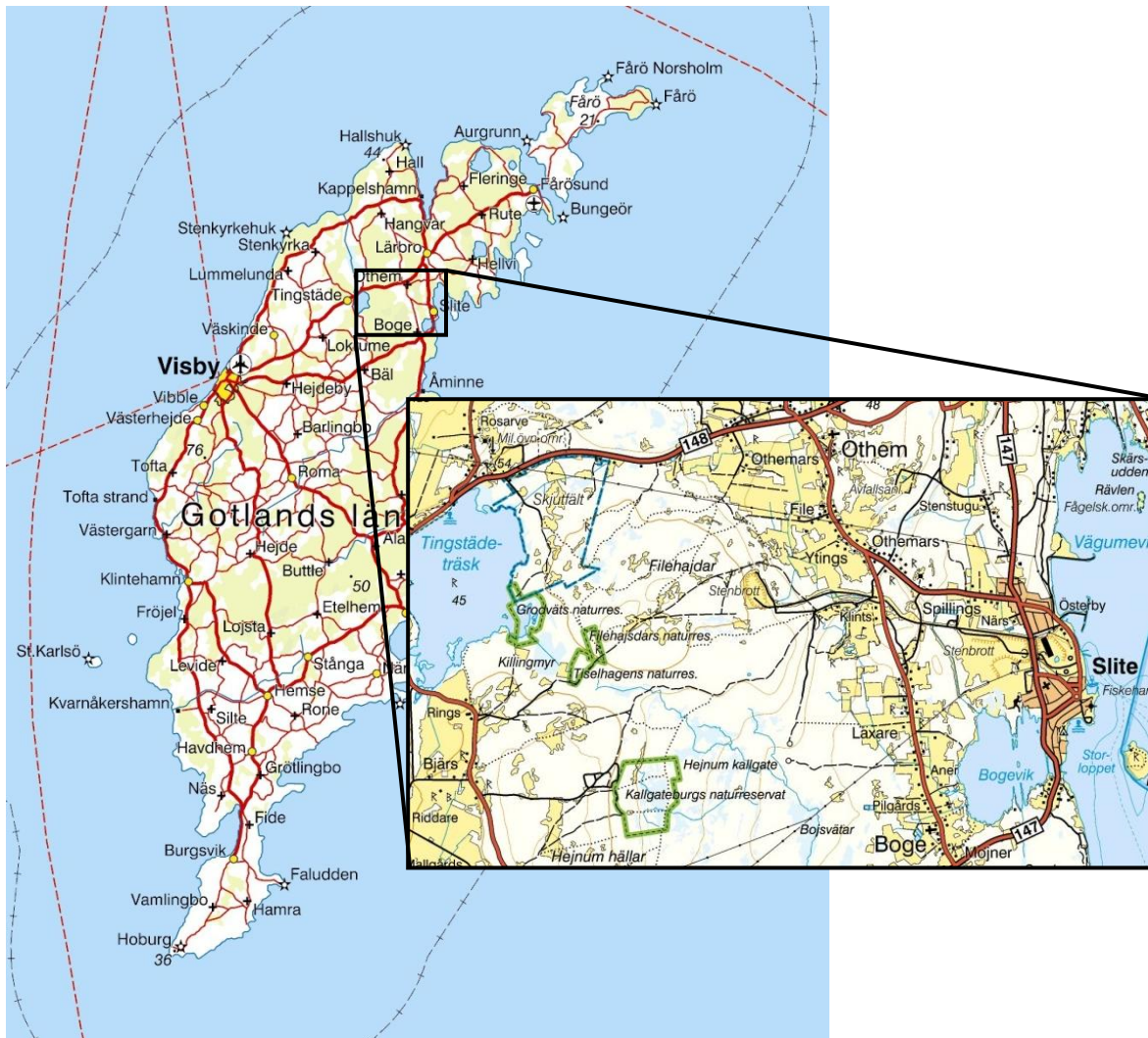


Figure 2 Map of Gotland and the studied area (black rectangle) (© Lantmäteriverket Gävle. Medgivande I 2008/1902).

2. BACKGROUND

2.1. GROUNDWATER IN CARBONATE AQUIFERS

2.1.1. Groundwater flow

Two different types of water flow apply to a limestone aquifer; matrix flow and conduit flow. In matrix flow, the water flows through the pores or fine fractures in a way that resembles Darcy flow through soil. Conduit flow occurs when the water is transported in larger fractures with a greater velocity than matrix flow; this flow can sometimes be characterised as turbulent flow. An investigation made by Atkinson (1975) is described by Appelo and Postma (2005). Atkinson (1975) examined Mendip Hills, a carbonate aquifer in England, South of Bristol and Bath. Mendip Hills is an area of limestone hills and karst, which are quarried at several sites. Karst is a carbonate aquifer which has weathered over time and formed wide fracture zones and underground caves. The weathering of carbonate aquifers is discussed in section 2.1.2. Atkinson (1975) concluded from a hydrograph analysis along with other parameters that conduit flow accounts for between 60 and 80% of the transfer of water in the aquifer, but accounts for only 3% of all the stored groundwater when the aquifer is fully recharged.

Because of conduit flow, groundwater in carbonate aquifers is quickly recharged by precipitation. Deeper down in the bedrock, the fractures are finer as they have not dissolved to the same extent as the areas where groundwater flow is more rapid. The finer fractures lead to a lower groundwater velocity and groundwater pumping can result in a slower drawdown in these areas.

Both flows discussed above occur simultaneously and an exchange of water takes place between matrix flow and conduit flow. In Figure 3, matrix flow (2) and conduit flow (3-6) can be seen.

2.1.2. Groundwater chemistry

The chemical composition of groundwater is very dependent on the flow path. Appelo and Postma (2005) describe an investigation made by Gunn (1981) in New Zealand karst where Gunn examined the correlation between water flow and calcium, Ca^{2+} , and magnesium, Mg^{2+} , concentrations in groundwater (Figure 3). Water with little contact time and little surface contact with the carbonate bedrock has a lower calcium and magnesium concentration (1 and 2 in Figure 3) than water which has been transported through the fracture zones for a longer time (3, 4, 5 and 6 in Figure 3). The longer contact time and larger surface contact gives an increased dissolution of carbonate rock and the groundwater has a higher ratio of calcium and magnesium ions.

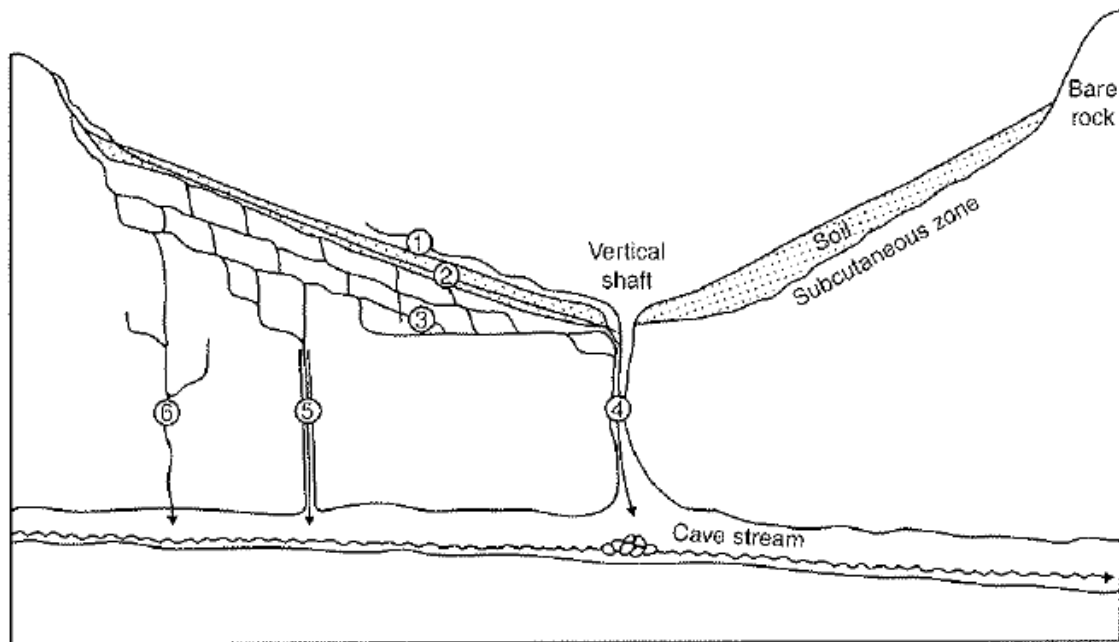


Figure 3 Different types of water flow a New Zealand karst (Appelo & Postma, 2005). 1) Overland flow, 2) Through flow, 3) Subcutaneous flow, 4) Shaft flow, 5) Unsaturated flow and 6) Unsaturated seepage.

Variability in the chemical composition of the groundwater also depends on the type of water flow. Shuster and White (1972) describe how conduit flow exhibits a larger variation while matrix flow has a more stable water composition through the different seasons. Conduit flow has a higher velocity and there is therefore less time for the groundwater composition to reach equilibrium with the surrounding bedrock. Matrix flow is slower and the geochemical processes have more time to stabilise. The

combined effect of groundwater velocity, aquifer composition, and reaction kinetics provides the final groundwater composition.

The major geochemical processes affecting groundwater composition in carbonates aquifers are carbonate reactions (e.g. dissolution or precipitation of primarily calcium carbonate) and ion exchange. These processes will be described below.

Carbonate equilibrium reactions

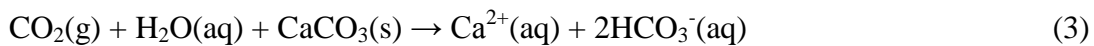
The system treated in this master thesis mostly concerns calcium carbonate (calcite) which follows the solubility equilibrium according to Equation 1 (Appelo & Postma, 2005). Solubility equilibrium is a chemical equilibrium which regulates the relationship between a solid and the concentration of dissolved solute in a liquid phase.



where K_{calcite} is the solubility product for the reaction. The activity of calcite, $\text{CaCO}_3(\text{s})$, can be set to its activity in the standard state, which has the value of 1 (ideal). The activities of dissolved calcium and carbonate are therefore defined by their relationship with the solubility product K_{calcite} , which is then defined by Equation 2. For dilute solutions, the solute activity can be assumed to be the same as the solute concentration.

$$K_{\text{calcite}} = [\text{Ca}^{2+}(\text{aq})] [\text{CO}_3^{2-}(\text{aq})] = 10^{-8.48} \quad (2)$$

However, the carbonate system in a groundwater aquifer is far more complex. Calcite also reacts with water and carbon dioxide. In the sursurface, carbon dioxide is a by-product of aerobic respiration (i.e. the oxidation of organic matter). Water (H_2O) reacts with carbon dioxide (CO_2) and forms carbonic acid (H_2CO_3). The acid contributes hydrogen ions (H^+) which react with carbonate ions (CO_3^{2-}) and form bicarbonate (HCO_3^-). Equation 3 shows the chemical reaction for carbon dioxide, water and calcite (Appelo & Postma, 2005).



Equation 3 is fundamental in comprehending the process of calcite dissolution and precipitation. If the carbon dioxide partial pressure increases, calcite will dissolve, while precipitation occurs if the carbon dioxide partial pressure decreases. This relation displays the connection between the biological carbon cycle and the chemical reactions of carbonate minerals.

Appelo & Postma (2005) describe how calcite dissolves differently depending on the type of system (open or a closed) for CO_2 gas. In the subsurface, CO_2 gas is supplied by root respiration in both systems, but an open system for CO_2 refers to an unlimited supply of CO_2 gas. If there is CaCO_3 present over the groundwater table in the unsaturated zone, it will react and dissolve with CO_2 -charged water (Appelo & Postma, 2005). The CO_2 used in the dissolution with CaCO_3 is continuously provided by root respiration, which gives an unlimited system with respect to CO_2 gas (i.e. an open system). The calcium concentration for an open system in a carbonate aquifer can be calculated for a given CO_2 partial pressure (P_{CO_2}) according to Equation 4 (Appelo & Postma, 2005).

$$m_{Ca^{2+}} = \sqrt[3]{\frac{10^{-6.0}[P_{CO_2}]}{4}} \quad (4)$$

When $CaCO_3$ is not present over the groundwater table but is present below the water table, calcite dissolution can only take place in the saturated zone under the groundwater table. The CO_2 present in the groundwater is at least partially consumed by calcite dissolution but is not continuously resupplied because of its slow dissolution in water (Appelo & Postma, 2005); this is thus a closed system with respect to the exchange of CO_2 gas. Equation 4 cannot be used but Appelo & Postma (2005) assume that the present CO_2 is consumed by the dissolution reaction (Equation 3).

According to Equation 3, the total amount of CO_2 (and associated carbonate species) consumed in the dissolution reaction is equal to the concentration of Ca^{2+} (Equation 5).

$$m_{Ca^{2+}} = (\sum CO_2)_{root} \quad (5)$$

where $\sum CO_2$ is the total dissolved inorganic carbon concentration. Appelo & Postma (2005) have assumed that the pH is <8.3, which makes the presence of CO_3^{2-} insignificant.

These calculations can be done by hand or, more conveniently, performed using PHREEQC, a hydrogeochemical transport model developed by Parkhurst and Appelo (1999), to illustrate possible concentrations of dominating parameters in a carbonate system. Table 1 illustrates results from PHREEQC calculations of alkalinity (as HCO_3^-), pH and Ca^{2+} concentrations in a carbonate system, both open and closed systems concerning CO_2 gas (Appelo & Postma, 2005). The initial values of $[P_{CO_2}]$ were chosen from $10^{-1.5}$ standard atmosphere (atm) in a productive soil to $10^{-3.5}$ atm in desert sand (Appelo & Postma, 2005).

Table 1 Calculated concentrations of important components in a carbonate system, both open and closed system with regard to CO_2 gas, using PHREEQC (Appelo & Postma, 2005).

		Open system (constant $[P_{CO_2}]$)		Closed system (known initial $[P_{CO_2}]$)	
		Initial	Final	Initial	Final
$[P_{CO_2}]$ (atm)	Initial	$10^{-1.5}$	$10^{-3.5}$	$10^{-1.5}$	$10^{-3.5}$
	Final	$10^{-1.5}$	$10^{-3.5}$	$10^{-2.5}$	$10^{-6.4}$
Alkalinity (mg/l)		0.35	0.07	0.16	0.005
Ca^{2+} (mg/l)		0.12	0.02	0.05	0.0047
pH		6.98	8.29	7.62	10.06

The Ion Activity Product (IAP) of calcite is defined as the product of calcium and carbonate activities in a water sample. A water sample is oversaturated if the IAP exceeds $K_{calcite}$. It should be noted that if the water has a constant but small oversaturation, then the minerals precipitate slowly and are not in equilibrium with the surrounding groundwater.

With the same reasoning, a water sample is undersaturated with respect to calcite if the IAP for calcite is below $K_{calcite}$. The Ca^{2+} and CO_3^{2-} concentrations in the water sample are probably not high enough for calcite to precipitate.

The degree of over- and undersaturation for a water sample for different minerals is determined with the so-called Saturation Index, SI (Equation 6).

$$SI = \log \left(\frac{IAP}{K_{calcite}} \right) \quad (6)$$

A positive value for SI indicates oversaturation and a negative value can be interpreted as undersaturation.

Ion exchange

Clay minerals and organic matter possess negative surface charges, and cation sorption can occur in bedrock and aquifers that contain these materials. There are three different types of sorption: adsorption, where the ions bind to the surface of the media, absorption, where the media assimilate the ion, and ion exchange where an exchange occurs between ions on the surface of a solid material and the dissolved ions in solution. For ion exchange, equilibrium occurs between the dissolved ions in the water and the sorbed ions on the solid material. If the composition of groundwater changes, for example when the interface between freshwater and saltwater alters, ion exchange will occur until ions in the groundwater and on the aquifer surfaces reach a new equilibrium.

On the freshwater side of the freshwater – saltwater interface, the water composition is dominated by the ions Ca^{2+} and HCO_3^- because of equilibrium with calcite, where cation exchange is controlled by the adsorption of Ca^{2+} . The seawater composition is dominated by Na^+ and Cl^- ions and the ion exchange between sediment and the seawater is (mostly) regulated by Na^+ ions. Appelo and Postma (2005) describe the cation exchange when seawater infiltrates a freshwater aquifer on the coastline (Equation 7).



where X is the exchange site on the media (bedrock/soil). Na^+ binds to the solid material while Ca^{2+} is desorbed. The dominating Cl^- ion will not react and the seawater composition (partly) alters from a NaCl-type to a CaCl_2 -type of water. Inversely, Appelo and Postma (2005) describe the process where freshwater with the dominating Ca^{2+} and HCO_3^- flushes out a saltwater aquifer (Equation 8).



The sediment now binds Ca^{2+} ions while Na^+ is desorbed; this results in a NaHCO_3 -type of water. In this way the water composition can indicate if there is an influence of seawater in a freshwater aquifer or freshwater flushing a saltwater aquifer. Section 3.2 describes how the water composition can indicate which processes govern the composition of the aquifer.

2.1.2.1. Chemical parameters

The chemical parameters analyzed in this Master thesis are described in the following sections.

Conductivity

The conductivity of water reflects content of dissolved chemical substances in the groundwater, which is dependent on the geological conditions of weathering and other sources that may affect the concentrations of dissolved compounds. Conductivities greater than 250 mS/m are not desirable for drinking water (Socialstyrelsen, 2003).

pH

The pH is a measure of acidity of a solution, i.e. the activity of dissolved hydrogen ions. A low value of pH, a larger activity of dissolved hydrogen ions, can give corrosion of water pipes which can lead to increased concentration of metals in the water. Gotland, with its carbonate bedrock, has naturally high pH values. Water with a pH value within 6.5-10.5 is fit for drinking (Socialstyrelsen, 2003).

Alkalinity

Alkalinity is a measure of the buffering capacity of water to withstand acidification and is predominantly represented by the hydrogen carbonate ion, HCO_3^- , because of the above-neutral pH. In limestone bedrock, the alkalinity is naturally high.

Chloride (Cl^-) and sulphate (SO_4^{2-})

There is a risk of saltwater influence in drinking water wells in coastal areas and in areas previously located beneath the ocean surface (SGU, 2008-11-21). The highest surface on Gotland is located beneath the highest coastline on the mainland, which means that the island was covered by the ocean during the latest glaciation (Gotland was covered with ice up to 15 000 years ago). The reason for saltwater influence in coastal areas can be either a relict saltwater aquifer originating from the ice age and the Littorina Sea transgression, or groundwater extraction and a change in piezometric pressure which forces the heavier saltwater to penetrate into the drinking water wells. Other reasons for a high chloride concentration in groundwater are road salt, sewage discharge, or seepage from landfills. Concentrations greater than 100 mg/l can lead to technical problems in water pipes, and concentrations greater than 300 mg/l are not desirable for aesthetic reasons (Socialstyrelsen, 2003). A taste difference can be noticed at a chloride concentration of 300 mg/l.

Precipitation and dry fallout have historically been a source of sulphate to groundwater, but high sulphate concentrations are also caused by weathering of sedimentary bedrocks, sulphide mineralizing or in areas with gyttja clay (*gyttjeleror*, Swedish). Sulphate can accelerate corrosion. A taste difference can be noted at 250 mg/l. Concentrations greater than 100 mg/l can lead to technical problems in water pipes and concentrations greater than 250 mg/l are not desirable for aesthetic reasons (Socialstyrelsen, 2003).

Nitrogen as nitrate (NO₃-), nitrite (NO₂-) and ammonium (NH₄⁺)

The nitrogen cycle involves four key processes; nitrogen fixation, decomposition, nitrification and denitrification. Nitrogen gas, dissolved in air or water, is fixed by certain algae and bacteria. The decomposition of organic matter releases ammonium ions (NH₄⁺) which are oxidized by bacteria (“nitrification”) to nitrite (NO₂⁻) and nitrate (NO₃⁻). Nitrate is then reduced by denitrification to nitrogen gas and nitrous oxide gas, and the nitrogen cycle is complete.

Groundwater has naturally low concentration of nitrogen compounds and vegetation growth is often limited by the availability of nitrogen. Nitrate is the nitrogen compound that most commonly occurs in groundwater, and high concentrations are foremost caused by agriculture or sewage effluents. Nitrate is mobile in soil and water because the ion is not adsorbed to the soil particles. In the quarry areas, a part of the nitrate is expected to originate from ammonium nitrate – based explosives used in the blasting activities. Water with a nitrate-nitrogen concentration of 50 mg/l is unfit as drinking water. Concentrations greater than 20 mg/l can lead to technical problems (Socialstyrelsen, 2003).

A high concentration of nitrite can indicate influence of agriculture and sewage effluents but can also form under anoxic conditions. Water with a nitrite-nitrogen concentration of 0.5 mg/l is unfit as drinking water. Concentrations greater than 0.1 mg/l can lead to technical problems (Socialstyrelsen, 2003).

Ammonium nitrogen can indicate an agricultural or sewage influence on the groundwater or surface water. Concentrations greater than 0.5 mg/l can lead to technical problems and concentrations greater than 1.5 mg/l are hazardous for health (Socialstyrelsen, 2003).

Calcium (Ca²⁺), magnesium (Mg²⁺), potassium (K⁺) and sodium (Na⁺)

There is a risk for hard water and the precipitation of calcite if the concentration of calcium is too high. The relative high concentration of calcium is due to the carbonate bedrock on Gotland. Concentrations greater than 100 mg/l can lead to technical problems in water pipes (Socialstyrelsen, 2003).

Carbonate bedrock also gives naturally high concentrations of magnesium ions. Concentrations greater than 30 mg/l are not desirable for aesthetic reasons (Socialstyrelsen, 2003).

Potassium exists naturally in groundwater but can imply an influence of contamination. Concentrations greater than 12 mg/l can lead to technical problems (Eklund, 2005).

A high concentration of sodium can indicate the influence of relict saltwater and seawater influence. The use of a water softener, when there is an ion exchange with sodium ions, can also result in a high sodium concentrations in drinking water. Concentrations greater than 100 mg/l can lead to technical problems in water pipes and concentrations greater than 200 mg/l are not desirable for aesthetic reasons (Socialstyrelsen, 2003). A taste difference can be noted at 200 mg/l.

2.2. STUDY AREA

The area studied, Österby 1:229, is located in the Othem parish on northern Gotland. The property where the limestone quarries Western quarry, Eastern quarry and File Hajdar quarry can be found is owned by Cementa AB. The property Österby 1:229 extends from the lake Tingstäde träsk to the harbour of Slite community at the eastern shore (Figure 4). The property is located within the catchment Sjuströmmar with an area of 46 km². The area of the catchment is determined by the government agency SMHI, the Swedish Meteorological and Hydrological Institute. The catchment Sjuströmmar includes three streams: Aner stream and Spilling stream that flow into Boge Viken and Närsbäcken which discharges into the Spillings pond.

Two of the three limestone quarries are active today: the Western quarry and File Hajdar quarry, which have a bottom level at -50 meters and +20 meters, respectively, above mean sea level (m asl). The Eastern quarry, where the quarrying is completed, is drained and is today used for the storage of limestone, marlstone and coal. The bottom level in the Eastern quarry is -24 m asl. Both the Western quarry and Eastern quarry are located in the Slite community. The quarry File Hajdar is located 5 km west of the Western quarry.

- LEGEND**
- Outer protection zone
 - Inner protection zone
 - Drinking water zone
 - Wells
 - Observation wells
 - Quarry wall
 - Stream
 - Road
 - Property Osterby 1:229
 - Border area
 - Water
 - Nature reserve
 - Natura 2000
 - Nature interest
 - Geological interest

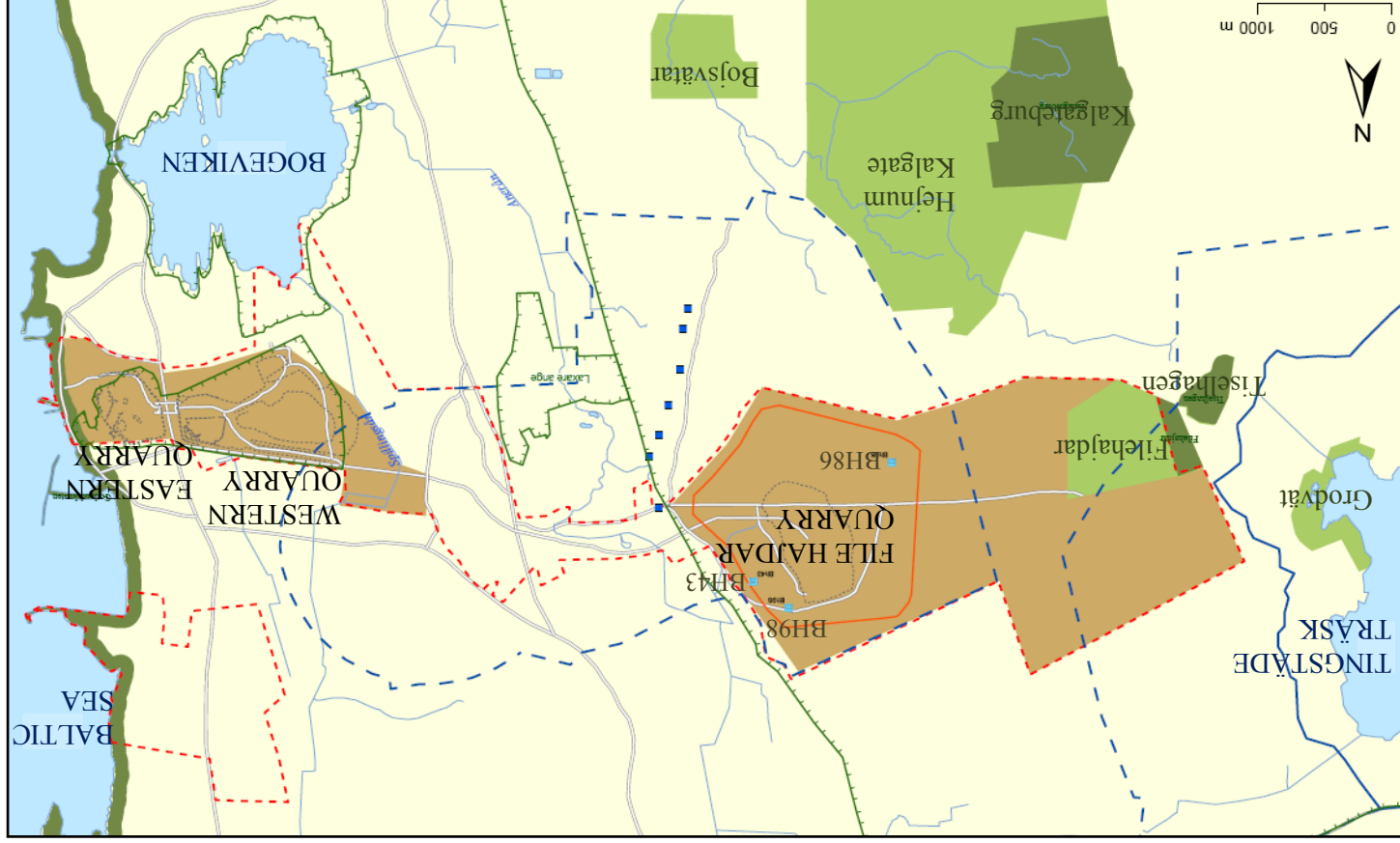


Figure 4 Study area, Osterby 1:229, marked with red broken line (map from Golder Associates AB, 2008).

2.2.1. Geology

The Gotlandic bedrock consists of limestone, marlstone and sandstone and the geographic distribution of these rocks is illustrated in Figure 5. Both limestone and marlstone are carbonate bedrocks and consist of calcite but marlstone has higher clay content. Sandstone consists of sand and quartz. The bedrock originates from the Silurian period about 400 million years ago when the Baltic Sea was a shallow tropical sea located near the Equator (Karlqvist, Fogdestam & Engqvist, 1982). The carbonate-dominated bottom sediments, consisting of deposited marine organisms, have sedimented and with time and compression transformed to limestone. Figure 5 shows the location of limestone, with varying clay content, crystal size, layering and strength, which is located in a line from Visby towards the northern part of Gotland and in a zone across the middle part of Gotland. In between these parts of limestone, mostly carbonate clays, marl and marlstone, can be found. Sandstone is found in an area along the western coast on the south of Gotland. The strike of the sedimentary limestone is dominantly northeast-southwest and the limestone dips to the southeast (0.15° - 0.3°) (Länsstyrelsen Gotland, 2006). The direction of the dip exposes the oldest limestone layers in the northwest and the younger in the southeast direction.

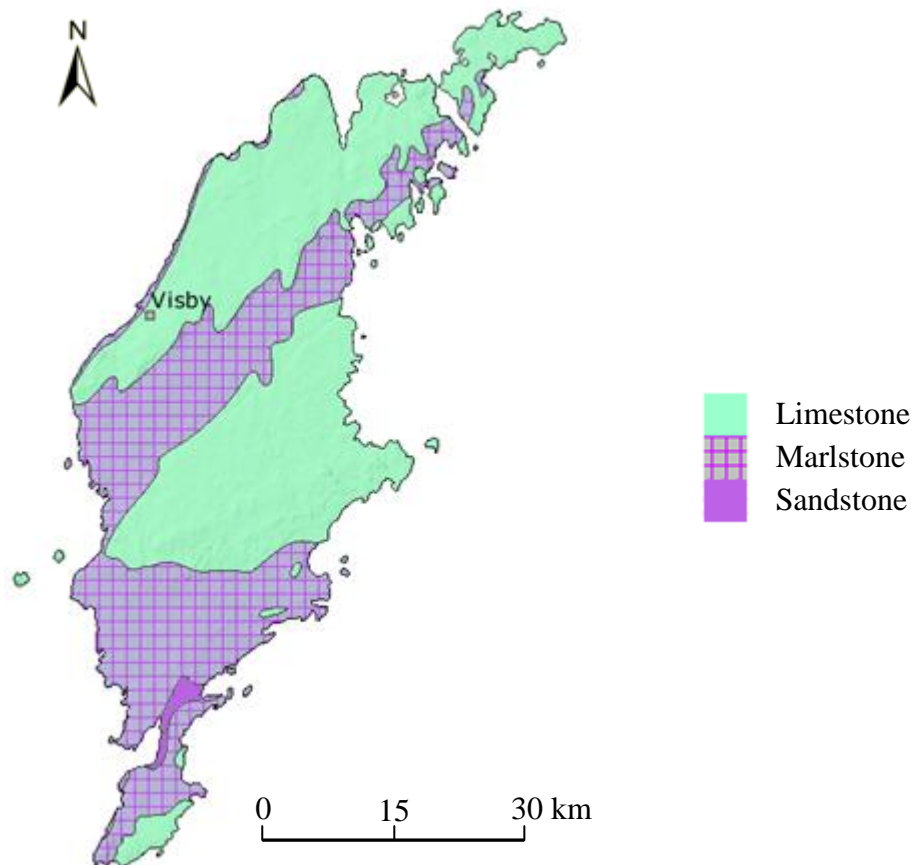


Figure 5 Bedrock of Gotland (SGU, www.sgu.se).

The upper part of the bedrock on northern Gotland mostly consists of limestone with relatively low clay content (compared to the rest of Gotland). The clay content increases with depth and towards the south to gradually convert to marlstone. The thickness of the limestone with low clay content in the north varies between 15-60 meters (Länsstyrelsen Gotland, 2006). Because of the high calcite concentration, this limestone dissolves more easily than the limestone with higher clay content and marlstone.

The bedrock in the area studied appertains to the stratigraphic segment named *Slite layers* and consists mostly of layered limestone that overlies marlstone bedrock. In the south-eastern part of the area, reef limestone is visible and the slope of the sedimentary limestone in the north-western parts of the quarry area indicates a major reef limestone body close to the present surface. The tectonic movement in the area seems to have been very small and only resulted in fissures.

2.2.2. Soil

The north of Gotland is dominated by flat limestone land areas. The limestone flat land areas are characterized of a thin or lack of soil cover. The thickness of the soil cover amounts to 0.5 meters on an average (Länsstyrelsen Gotland, 2006) and is dominated by weathered soil or clayey till but can also consist of wave-washed deposits (*svallsediment*, Swedish). The quarry property is dominated by sedimentary bedrock but also clay till (*moränlera*, Swedish) which can be viewed in the soil map in Figure 6. Clay till was formed during the last glaciation when the inland ice caught and processed loose parts of the sedimentary bedrock which was deposited when the ice melted. Clay till is a soil cover with a thickness of one to a few meters (Länsstyrelsen Gotland, 2006). Areas with washed deposit of gravel and sand can also be found on the property. The washed deposit was formed after the last glaciation when Gotland arose from the Littorina Sea, because of isostatic rebound, and the sediments were exposed to intense wave-wash and breaker action. Areas which have been located below the sea level can contain relict saltwater aquifers which can result in a high chloride concentration in the groundwater. Smaller areas of clay and silt particles can also be found on the property. These particles were transported with the melt water from the inland ice or were released by wave-washes and deposited in low-lying areas.

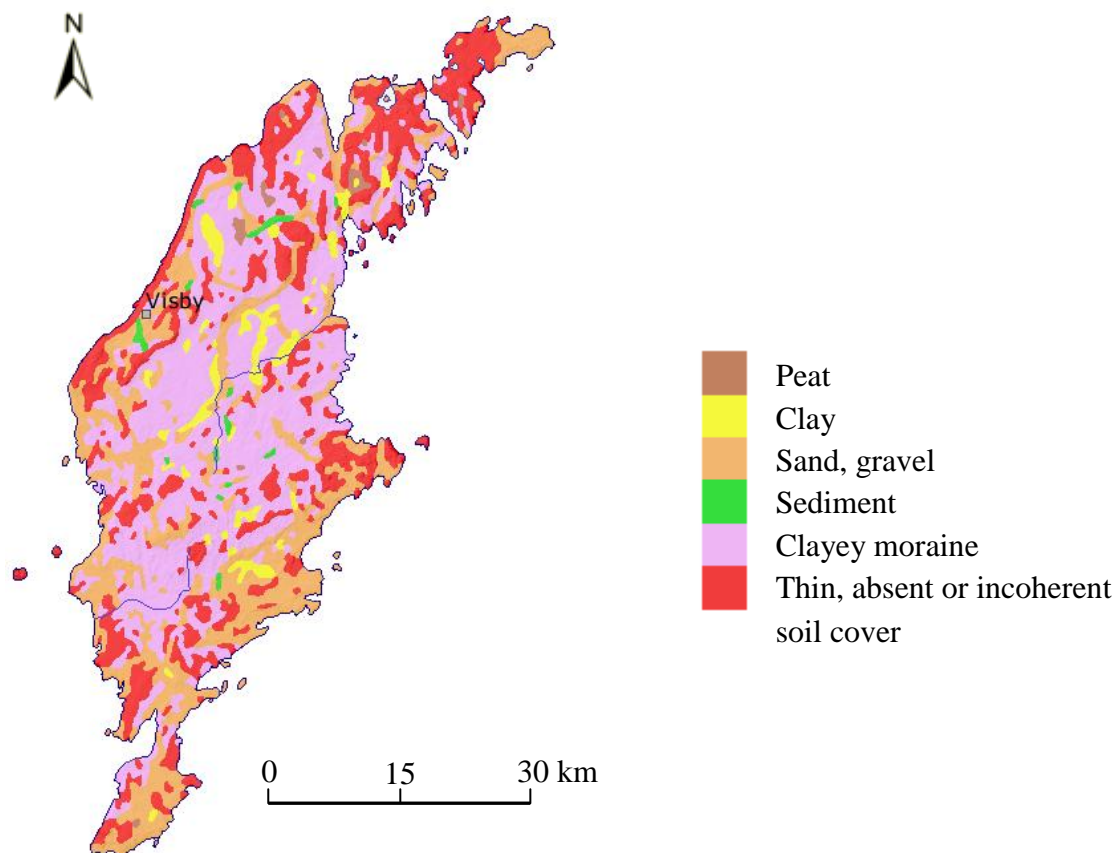


Figure 6 Soil map of the different soil types on Gotland (SGU, www.sgu.se).

2.2.3. Hydrology

2.2.3.1. Climate

The coastal climate on Gotland is mostly affected by the Baltic Sea which gives Gotland its cold and late springs and mild and lingering autumns (Eklund, 2005).

The yearly precipitation (P) in the area is 630 mm (calculated as an average of 1997-2007 from SMHI's station Hejnum). In Figure 7, two years with heavy precipitation can be viewed: 1999 (697 mm) and 2001 (756 mm), while 1997 (520 mm) and 2006 (511 mm) showed less precipitation.

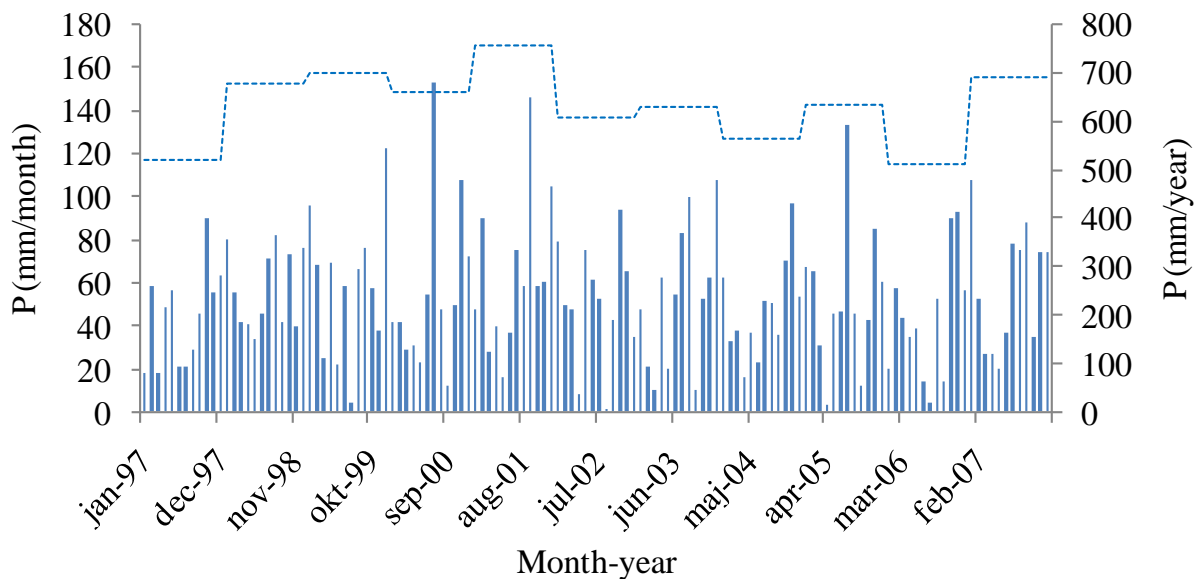


Figure 7 Monthly (bars = mm/month) and yearly (broken line = mm/year) precipitation (P) in mm from SMHI's station in Hejnum, 8.6 km west of Slite community.

The potential evapotranspiration (PET) from year 2001 at Visby airport was 675 mm (SMHI) and is plotted with precipitation (annual P 756 mm) in Hejnum the same year in Figure 8. Karlqvist, Fogdestam & Engqvist (1982) estimate the actual evapotranspiration (AET) to 450 mm/year. The potential evapotranspiration is the amount of water that evaporates from a free water surface. Actual evapotranspiration is the actual amount of water that evaporates from a soil surface and transpires from vegetation. Vegetation type, root depth, soil and topography are parameters taken into consideration when actual evapotranspiration is calculated.

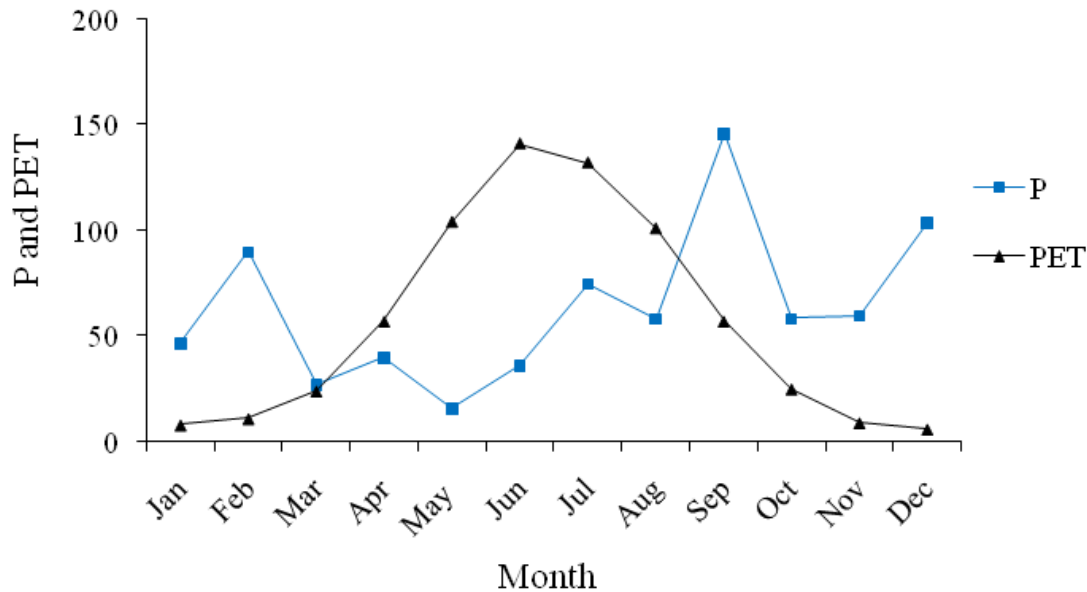


Figure 8 Precipitation (P) and potential evapotranspiration (PET) both in mm from 2001 from SMHI:s station in Hejnum, 8.6 km west of Slite community, and Visby airport respectively, 35.1 km west of Slite community.

As can be noted in Figure 8, most of the precipitation occurs during September-February while the potential evapotranspiration peaks during summer. This shows that the major groundwater recharge occurs during the winter months. The groundwater recharge is dependent on bedrock and soil characteristics.

2.2.3.2. Groundwater levels

The groundwater levels on the property Österby 1:229 vary and seem to slightly decrease in both in mean maximum and mean minimum level (Figure 9). The locations of observation wells BH43, BH86 and BH98 are marked in Figure 4, showing very large normal variations. From the groundwater level variations, it can be read that the levels react to precipitation by a rapid increase in groundwater level, while a decline in groundwater level during periods of low percolation occurs more slowly. The major increases in BH 86 occur during the winter months and the major decreases during the summer months with the lowest value usually in late July and August. This behaviour is characteristic for limestone bedrock on Gotland with fracture zones (Lindblom & Ryegård, 2005). The infiltration of precipitation/groundwater recharge mostly occurs through fracture zones which have a higher vertical hydraulic conductivity than horizontal hydraulic conductivity which is shown in the slower decline in the groundwater level (Figure 9).

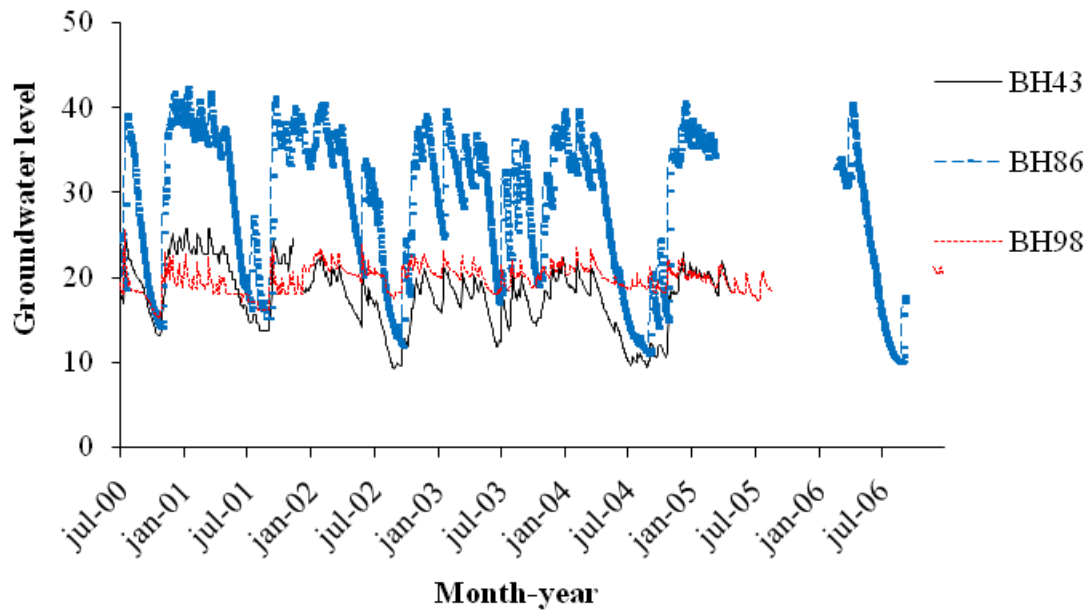


Figure 9 Groundwater level in meters in observation wells 43, 86 and 98, with bottom level at level at +29.56, +49.20 and +31.85 m asl and groundwater intake from +3.36, -10.80 and -8.15 m asl respectively. The observation wells are marked in Figure 4 (data from Cementa AB).

2.2.4. Cementa AB in Slite

Cementa AB is the largest of three major limestone mining industries in northern Gotland, where Nordkalk AB and Svenska mineral AB are the other two.

The company Slite Cement Kalkaktiebolag was established in Slite and construction on the cement factory started in 1917. The production of cement started two years later on the 4th of April and has continued uninterrupted since. The location was chosen because of Slite's access to limestone and marlstone as well as the harbour. The ownership of the company has changed during the years. The company is today part of the international group HeidelbergCement which is one of the leading producers of cement in the world. HeidelbergCement has two other cement factories in Sweden, in Skövde and Degerhamn, together with 16 terminals scattered along the Swedish coastline.

Today, the cement factory in Slite is one of the largest in northern Europe. It has a capacity of 7 000 tonnes cement per day, which is 2.5 million tonnes per year. The actual production in 2007 was 1.7 million tonnes, i.e. 4 700 tonnes per day. For the production of cement during 2007, 1.6 million tonnes of limestone and 1.2 million tonnes marlstone were excavated. The cement factory in Slite has 210 employees (Cementa AB, 2007).

2.2.5. The process description of cement production in Slite

The process of the production of cement in Slite can be viewed in Figure 10.

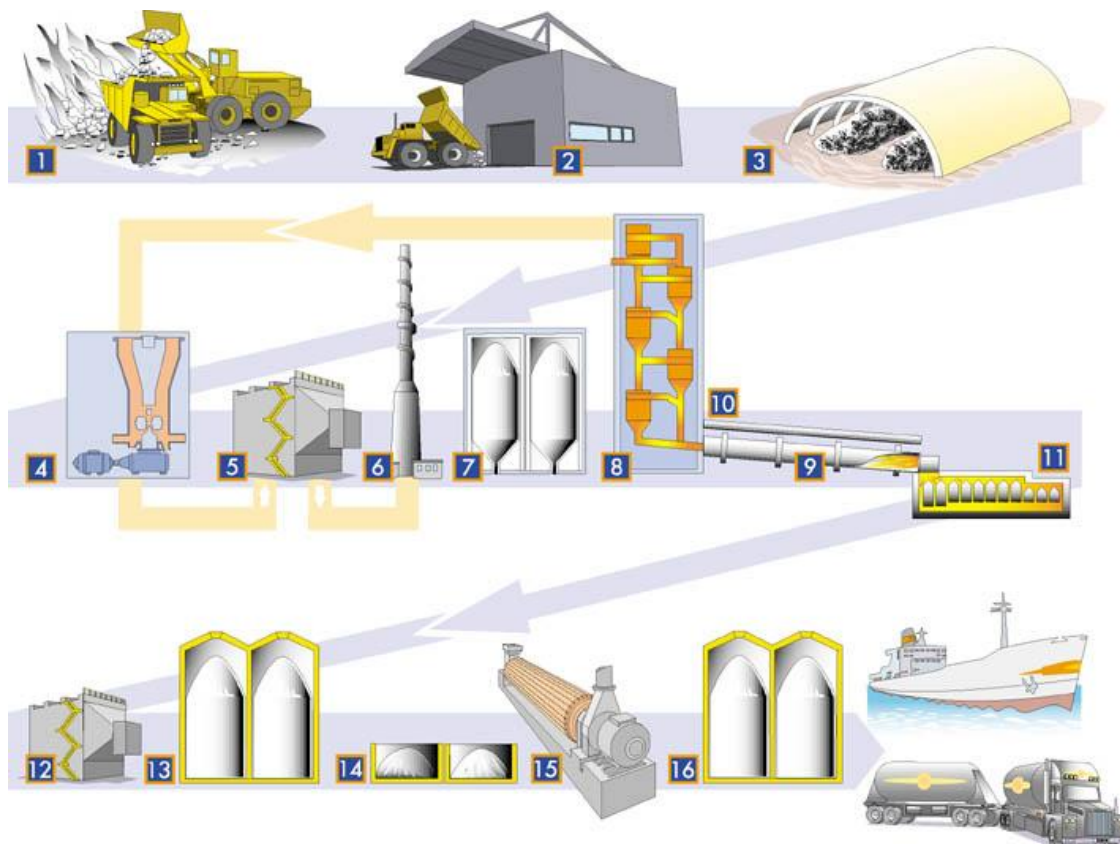


Figure 10 Flow chart of the cement production. Description of the different steps in the process can be found on the next page (Cemeta AB's presentation material, 2008).

- (1) Limestone and marlstone (with higher clay content) is quarried from Cementa AB's active quarries, Western quarry and File Hajdar quarry.
- (2) The quarried stone is crushed to a maximum size of 80 mm.
- (3) The crushed stone is stored and mixed to achieve the optimal mix of limestone and marlstone.
- (4) The mixed stone is ground in a raw mill to a fine powder.
- (5) An electrostatic precipitator removes the dust from the flue gases released by the kiln.
- (6) The flue gases are washed from sulphur with the help of ground limestone and water, in a wet scrubber. The waste that results from the wet scrubber, gypsum, is returned to the process.
- (7) Intermediate storage of ground limestone.
- (8) Precalcination occurs in the cyclone tower; calcium carbonate breaks down to calcium oxide and carbon dioxide.
- (9) The limestone powder is heated in the kiln, a 80 m long (slightly tilted) cylindrical rotating steel pipe, to a temperature of 1450 °C and is converted to clinker (marbles). The kiln is heated with coal and alternative fuels such as rubber tires, plastic pellets and anaerobically digested sludge.
- (10) A by-pass filter removes alkalis (K, Na), which has a negative effect on the durability of cement if the alkali content is too high. The by-pass filter also removes chloride. A high chloride concentration in the cement can result in corrosion of the reinforcement bars used when casting concrete. Most of the removed alkalis and chloride are returned to the process as long as the concentrations are below the restricted limits. The waste product, alkalis and chloride, are stored on a landfill in the Western quarry.
- (11) The clinker is air-cooled.
- (12) The gas from the cooler is cleaned from dust in an electrostatic precipitator.
- (13) Clinker is stored in silos.
- (14) Gypsum and additives are stored before grinding with clinker.
- (15) Clinker, gypsum and possibly limestone is ground together to result in finished cement.
- (16) Cement is stored and 99% of the cement produced is exported by ships partly (43%) to the foreign market, the Baltic states, Norway, Denmark, Florida and Africa, partly (56%) to one of the terminals on the mainland (to the Swedish market). The remaining 1% is transported by trucks to the Gotlandic market (Cementa AB, 2007).

2.2.6. Golder Associates AB's present work

The engineering consultant company Golder Associates investigated the geological structure in the quarries File Hajdar and Western Quarry in February 1991, to identify fracture zones and aquifers in the area and to describe the groundwater flow. Hydrogeological tests (resistivity measurements and double packer tests) in File Hajdar were also performed (Golder Associates AB, 1991). A groundwater and surface water model was developed and based on the dominating hydrogeological structures defined during this investigation of boreholes.

The hydrogeological investigations performed by Golder Associates AB describe 5 sub-horizontal aquifers separated by less permeable aquitards (Figure 11). Vertical flow occurs in vertical fracture zones. Larger visible vertical fractures can be found in the quarries. The aquifers can be found both in the limestone and underlying marlstone bedrock. The sub-horizontal aquifers were identified by laterally extrapolating the visible sub-horizontal aquifers observed in the Western quarry. The spaces and levels between the extrapolated aquifers correspond with the resistivity measurements in the boreholes in File Hajdar (Golder Associates AB, 1991).

A major vertical fracture zone intersects the area in a north-south direction, just east of File Hajdar. SGU, through Anders Carlstedt, interpreted the vertical fracture zone from geophysical measurements from the air.

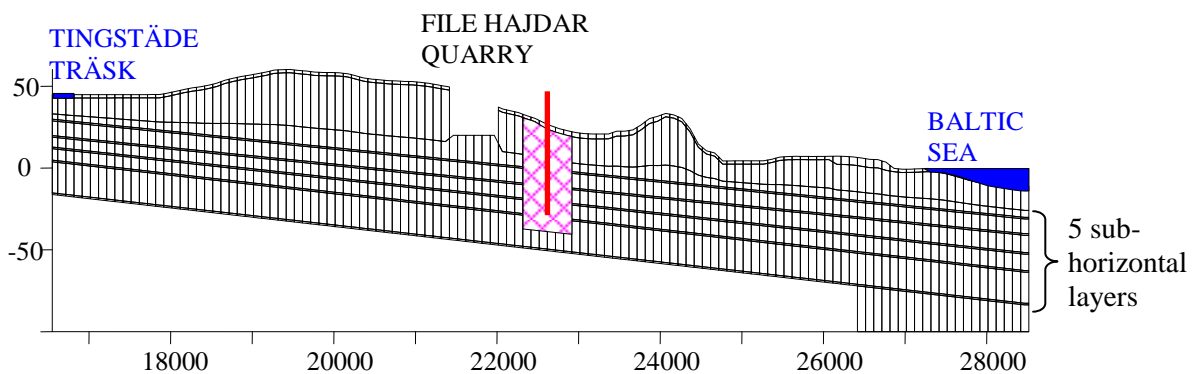


Figure 11 Cross section of the studied area from the groundwater and surface water model (conceptual diagram). Height in meter above mean sea level on y-axis, coordinate system in meters on x-axis. The 5 sub-horizontal layers, File Hajdar quarry, drinking water wells (vertical line in red) and fracture zone (checked pink area) are marked in the figure (Holmén, 2007). The X-axis goes from Tingstäde träsk in the west to the Baltic Sea in the east (cf. Figure 4).

The interpretation of the geological structure is of utmost importance to the hydrogeological model as discussed above, but also to reach some sort of understanding regarding the groundwater composition in the area. In Figure 11, the sub-horizontal aquifers, fracture zones and quarry are marked that represent the current situation. File Hajdar is active and quarrying will change the size of the quarry.

One part of the application to the Environmental Court for the continued expansion of quarrying activities and groundwater extraction is a groundwater and surface water model developed by Johan Holmén (Golder Associates AB). A more thorough description of the model and computer code can be found in the rapport by Holmén (2007). It is a conceptual

model i.e. a simplification of the system, where parameters such as geology, hydrology, and climate are taken into consideration. From the conceptual model, a formal model is developed, which is a mathematical description of the conceptual model. The formal model is a three-dimensional, transient model based on different formulations of Darcy’s law and the continuity equation. The formal model is used for simulations of different scenarios of the system for different time spans.

The formal model is numerically calculated with the computer code GEOAN (Holmén, 2007) and is based on a finite difference numerical model.

The result of the simulations are given as piezometric head, groundwater flow, velocity and transport in three dimensions as well as surface water flow and velocity (Holmén, 2007).

Figure 12 illustrates the drawdown which can occur in the surroundings of a quarry. The groundwater level and potentials were calculated in GEOAN and are projected results for year 2021. The Groundwater level (dark blue) dominantly follows the topography of the area while the groundwater potential for first layer (purple) and fourth layer (turquoise) are higher than the topography in the quarry but lower than in the other areas. When the groundwater potentials are higher than the actual surface, the groundwater is artesian.

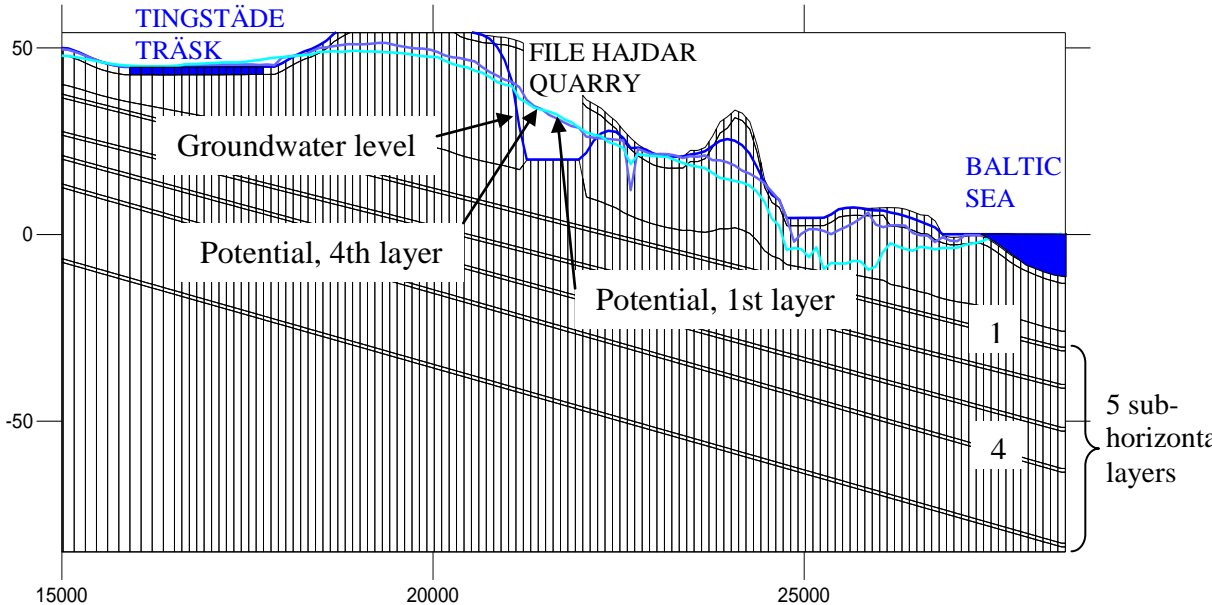


Figure 12 Calculated groundwater level and potentials around a quarry (preliminary results for year 2021) (Holmén, 2007). Height in meter above mean sea level on y-axis, coordinate system in meters on x-axis. Groundwater level in dark blue, groundwater potential for first layer in purple and fourth layer in turquoise. The X-axis goes from Tingstäde träsk in the west to the Baltic Sea in the east (cf. Figure 4).

2.2.7. Protected areas in the study area and its surroundings

The study area and its surroundings host several protected areas. The areas are protected concerning different interests; mineral extraction, nature reserve and Natura 2000.

The property Österby 1:229 is protected for mineral extraction by the area protection law Geological Reform. This means that the Swedish government considers the mineral extraction on the property Österby 1:229 to be in the country's interest.

The property is located near several areas which provide natural services. The nature reserves and Natura 2000 areas are marked in Figure 4 and a full description of the areas can be found in Appendix 1. The information on the nature reserves and Natura 2000 areas was provided by Naturvårdsverket (www.naturvardsverket.se, 2008-11-15).

The property Österby 1:229 is adjacent to the nature reserve Tiselhagen (0.126 km²) and Natura 2000 area Filehajdar (0.643 km²) in the southwest. The Natura 2000 area Grodvät (0.240 km²) is located within a distance of 500 m southwest of the property. Nature reserve Kallgateburg (1.155 km²) and Natura 2000 area Hejnum Kallgate (9.53 km²) is located at a distance of 1330 m respectively 500 m south of the property Österby 1:229. At a distance of 2250 m south of the property, the Natura 2000 area Bojsvätar (0.454 km²) is located.

Even though the nature reserve Tiselhagen and Natura 2000 area Filehajdar are adjacent to the property, the areas will probably not be affected by the expansion of the quarry File Hajdar because of the actual distance to the quarry, the slope of the aquifers and the fact that the protected areas are located upstream (topographically) of the quarry File Hajdar.

The nature reserve Kallgateburg and Natura 2000 area Hejnum Kallgate can be affected in the future if they end up inside the drawdown area of pumping in the quarry File Hajdar. The Natura 2000 area Bojsvätar will probably not be affected since the distance is too large.

3. METHOD

To examine the potential impact of limestone quarrying in Slite and to search for long-term trends, four different sampling programmes from the area were studied and compared. The results from the sampling programmes were also used for classification of groundwater types. As part of this Master thesis, a new sampling programme were planned and carried out to locate sources of groundwater discharging to the quarries. A number of parameters from each sampling programme were studied, including alkalinity, base cations, nitrogen (as ammonium), pH, sulphate and conductivity.

3.1. SAMPLING PROGRAMMES

3.1.1. Previous sampling by SGU

A hydrogeological investigation was made in the beginning of the 1950's by Helge Tullström from the Geological Survey of Sweden (SGU). The results were summarised in the report *Hydrogeologiska förhållanden inom Slite Köping på Gotland (Hydrogeological conditions within Slite Köping on Gotland; Tullström, 1955)*. It was an investigation of the area (Figure 23) before the development of the drinking water supply in Slite. The groundwater components analyzed in the investigation and used in this Master thesis are: pH, HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , Ca^{2+} , Mg^{2+} and $\text{Na}^+ + \text{K}^+$.

In the hydrogeological investigation Tullström summarized that the dominating bedrock in Slite Köping (municipality) was Slite-marlstone. It was superposed by limestone on the hills and in the eastern area of File Hajdar. Tullström regarded the marlstone to be about 43 m thick and the superposed on a harder limestone of unknown depth. Today we know from boreholes that the marlstone continues deeper with increasing clay content. Tullström found thicker Quaternary deposit aquifers in the valleys of File Hajdar and Ytlings but considered them not sufficiently investigated. Figure 13 shows a contour map of the freshwater - saltwater interface. Tullström concluded the origin of salt groundwater to be from recent seawater influence and relict seawater from the Littorina Sea.

Tullström considered the wells in the area to be artesian or half-artesian. A pumping test of wells 20 and 27 was performed in 1951 to investigate the drawdown of water table and the yield. Results showed that the two wells were artesian and the area of influence reached to the church in Othem (Figure 13).

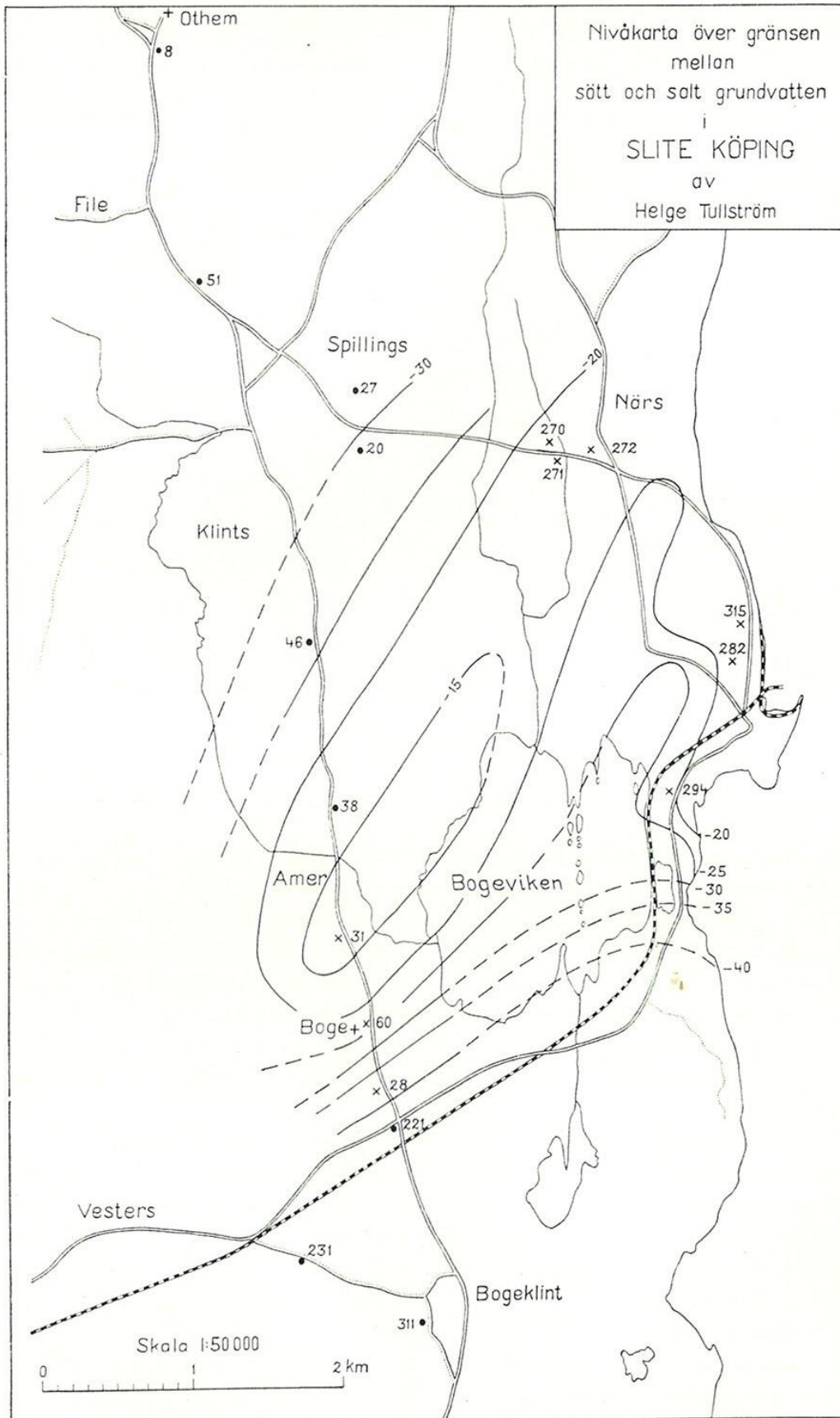


Figure 13 Contour map of the fresh water – saltwater interface in the Slite area, probably in m asl. Dot and cross-marked wells refer to the water analyses and chlorine analyses in appendix 3 (Tullström, 1955).

3.1.2. National water survey, SLU

The National water survey (Riksinventering) is a control programme where Naturvårdsverket, through SLU, investigates any long-term changes in lakes and streams in Sweden. The control programme started in 1972 and the sampling takes place every fifth year. Location of the sampling that concerns this investigation is Tingstäde träsk, a lake and drinking water reservoirs west of File Hajdar and Bogevisken, a bay south of Slite community. The data used were results from the following sampling dates: 1990-02-20, 1995-11-06, 2000-11-08 and 2005-11-10. The surface water components and parameters used are conductivity, pH, alkalinity (as HCO_3^-), Cl^- , SO_4^{2-} , NO_3^- , $\text{NH}_4^+\text{-N}$, Ca^{2+} , Mg^{2+} , Na^+ and K^+ .

3.1.3. Gotland Municipality: Drinking water wells

There are seven drinking water wells that provide Slite municipality with drinking water (Figure 4). All seven drinking water wells produce approximately 240 000 m^3 water/year and are added together in the Slite water supply facilities to one mixed sampling point: 23v281. The production is sufficient today but the Gotland municipality (Gotlands Kommun) is looking to increase the production of drinking water in the area. The groundwater wells which produce groundwater to 23v281 are between 39-57 m deep. The chemical parameters analyzed and used in the investigation were: conductivity, pH, alkalinity (as HCO_3^-), Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ and K^+ . Groundwater samples from the time period 1995-2007 have been used.

3.1.4. New sampling programme

A new sampling programme was planned and carried out with the aim to determine the sources of water contributing to groundwater discharging to the Western quarry. The chemical parameters analyzed in the investigation were: conductivity, pH, alkalinity (as HCO_3^-), Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ and Na^+ . A total of 26 samples were collected on three occasions in this programme. Sampling locations were selected so as to try to locate the origin of groundwater inflow into the quarries.

The groundwater and surface water which seeps into File Hajdar quarry is pumped to the Aner stream which flows into Bogevisken. The sampling point "File Hajdar" was 3 m upstream from the pump station in the File Hajdar quarry.

The groundwater and surface water which seeped into the Western quarry from bench 1 and 2 are gathered in two streams: the northern stream and the southern stream. A "bench" in the quarry is a level area created during the excavation of the quarry (Figure 14). Bench 1 is located -13 m m asl, and lies above Bench 2 that is located at -34 m m asl. Bench 1 was sampled at two sampling points in the quarry wall: "Bench 1 N" and "Bench 1 NW". Bench 2 was also sampled in two sampling points in the quarry wall: "Bench 2 N" and "Bench 2 NW". The reason for sampling the quarry walls was to determine the composition of the groundwater seeping into the Western quarry. Both streams were also sampled: "Stream N" and "Stream S". Both streams later meet in a small pond from where the water is pumped to the more eastern pond. The water in the eastern pond is then pumped to a sedimentation pond in the Eastern quarry, where most suspended substances are allowed to settle to the bottom. The western and eastern ponds together with the sedimentation pond were sampled: "Pump W", "Pump E" and "Sedimentation pond". The water was then pumped from the sedimentation pond to the harbour. The "Harbour" was a sampling point to have a reference

sample for seawater. The northern quarry wall in the Eastern quarry was also sampled: “Bench 2 N”. The sampling in the quarry walls was performed along the northern and northwestern parts because of the strike and dip of the sedimentary limestone, where the groundwater theoretically flows. The landfill in the Western quarry, where the alkali and chloride waste products are stored was also sampled. The sample point, “Landfill”, was located downstream of the landfill. All sample points are marked in Figure 15.

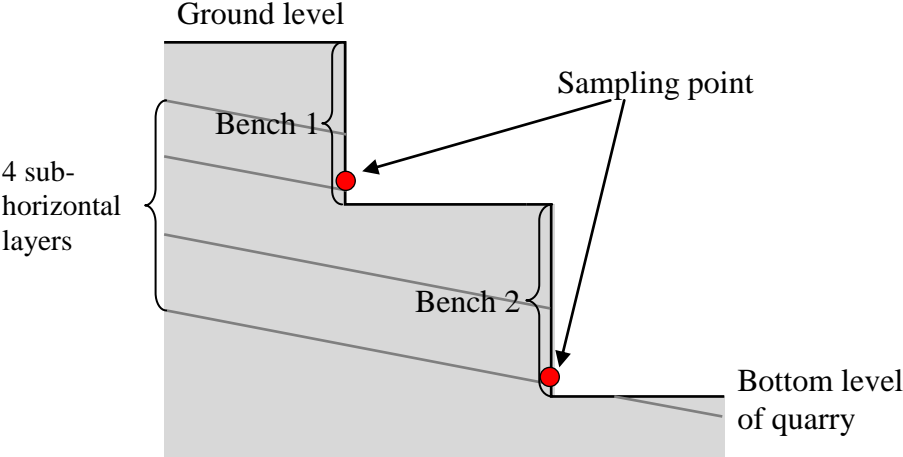


Figure 14 Conceptual figure of bench 1 and 2 in the Western Quarry. Sampling points marked as red dot in figure.

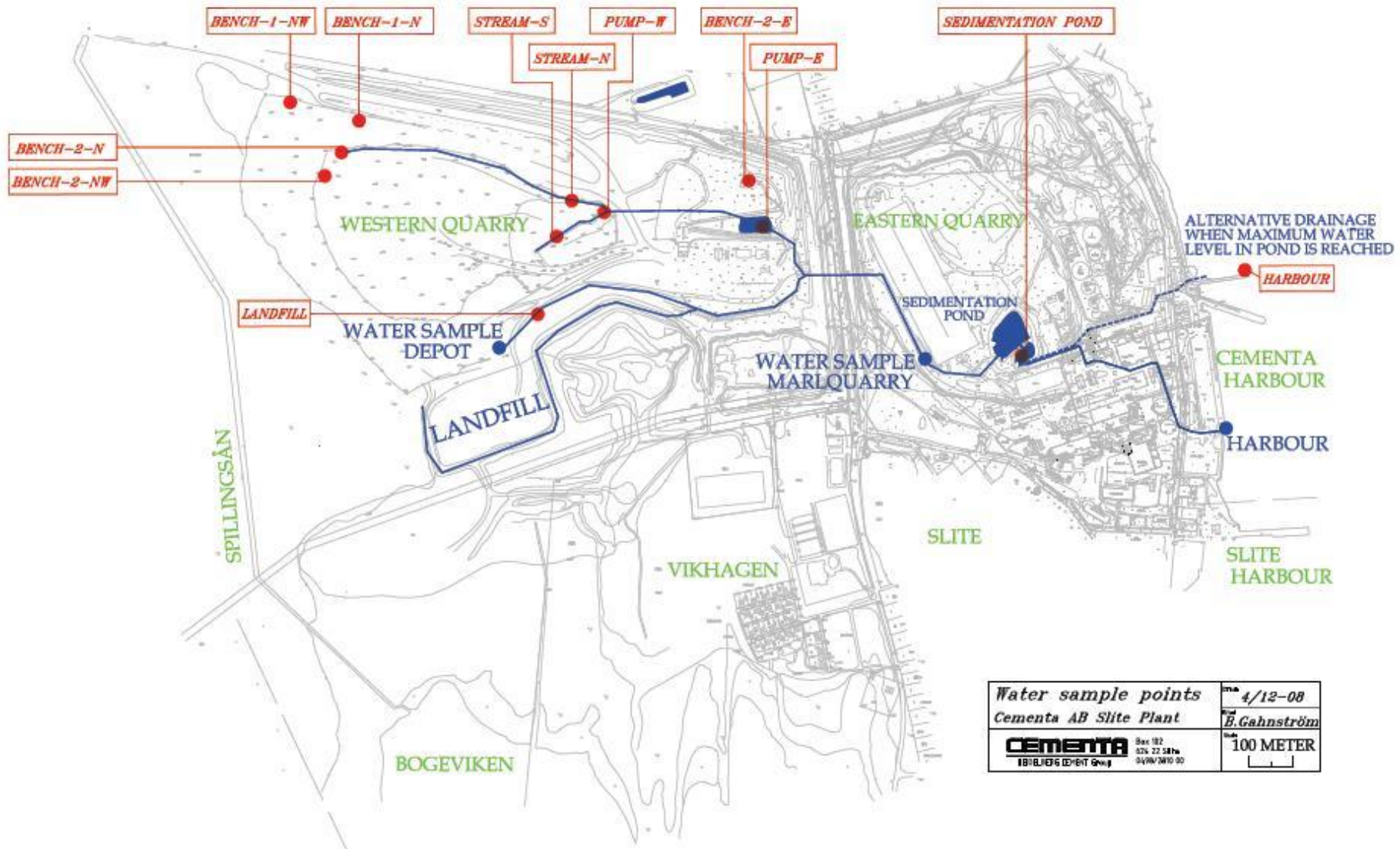


Figure 15 Sampling points in Eastern and Western quarry (Cemeta AB).

3.1.4.1. Analyses

The water samples discussed in section 3.1.4 were analyzed by the accredited laboratory Eurofins in Lidköping. The parameters analyzed were: conductivity, pH, alkalinity (as HCO_3^-), Cl^- , SO_4^{2-} , NO_3^- , NH_4^+ -N Ca^{2+} , Mg^{2+} , K^+ and Na^+ . Methods and measurement error for the different analyses can be found in Appendix 2.

3.2. PIPER DIAGRAM

Using major ions as natural tracers has been a common method (at reasonable price) to examine the different flow paths in an aquifer (Back, 1966). Separating the test results into different water types with similar chemical characteristics, water types can be correlated with sampling location. The spatial variability in the different water types can give an insight into the system's heterogeneity and how various parts of the system are interconnected (Güler et al., 2002) by, for example, fracture zones with higher permeability. The spatial variation can also give a certain understanding of physical and chemical processes that regulate the water chemistry in the system. This classification of water types is an important tool in the analysis of the hydrogeological system.

In order to classify the water samples, Piper diagrams were used to study the mixing behaviour of freshwater and saltwater in the Slite area. Saline groundwater is primarily derived from saltwater influence in the studied area due to limestone quarrying.

The Piper diagram is a graphical method that classifies different water types by calculating the ratio of anions and cations in a water sample. The parameters in a Piper diagram are the anions chloride (Cl^-), sulphate (SO_4^{2-}), hydrogen carbonate (HCO_3^-) and carbonate (CO_3^{2-}), and the cations calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+) and sodium (Na^+). The relative concentration of the reactive ions is calculated with Equations 11-16 (Rao, 1998).

$$\text{Ca}^{2+} \% = \text{Ca}^{2+} * 100 / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+) \quad (11)$$

$$\text{Mg}^{2+} \% = \text{Mg}^{2+} * 100 / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+) \quad (12)$$

$$(\text{Na}^+ + \text{K}^+) \% = (\text{Na}^+ + \text{K}^+) * 100 / (\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+) \quad (13)$$

$$\text{Cl}^- \% = \text{Cl}^- * 100 / (\text{Cl}^- + \text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-}) \quad (14)$$

$$\text{SO}_4^{2-} \% = \text{SO}_4^{2-} * 100 / (\text{Cl}^- + \text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-}) \quad (15)$$

$$(\text{HCO}_3^- + \text{CO}_3^{2-}) \% = (\text{HCO}_3^- + \text{CO}_3^{2-}) * 100 / (\text{Cl}^- + \text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-}) \quad (16)$$

where Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-} are ion concentrations in eq/l.

The result of the calculations is plotted in two triangles, one for anions and one for cations. The total solution of the two triangles is projected in a diamond shaped diagram (Figure 16).

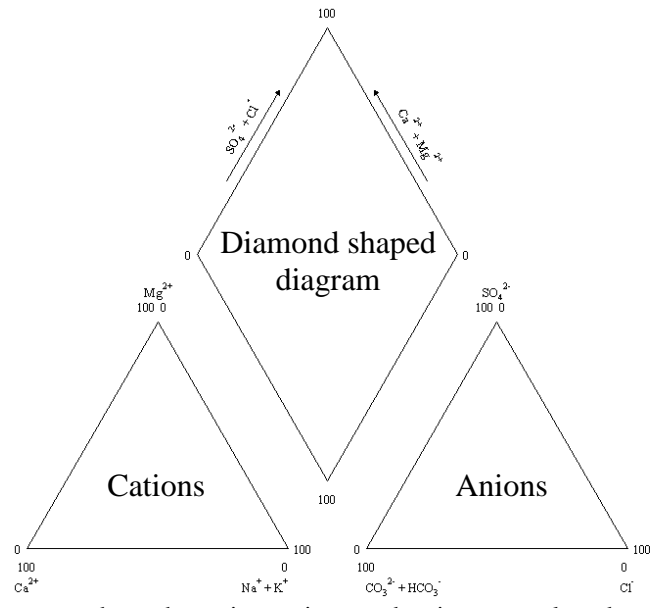


Figure 16 Piper diagrams where the ratios cations and anions are plotted and then projected in the diamond shaped diagram.

The different classification zones for various water types can be seen in Figure 17. The result plotted in the cation triangle, B_s , and the result plotted in the anion triangle, B_s , are projected in the diamond shaped diagram, B_s . Depending on positioning of the results, the water type of the water sample can be read in the diamond shaped diagram. If a sample, B_m , is plotted on an imaginary line between two other samples, freshwater and seawater, the diagram indicates the sample, B_m , to be a mixture of freshwater and seawater.

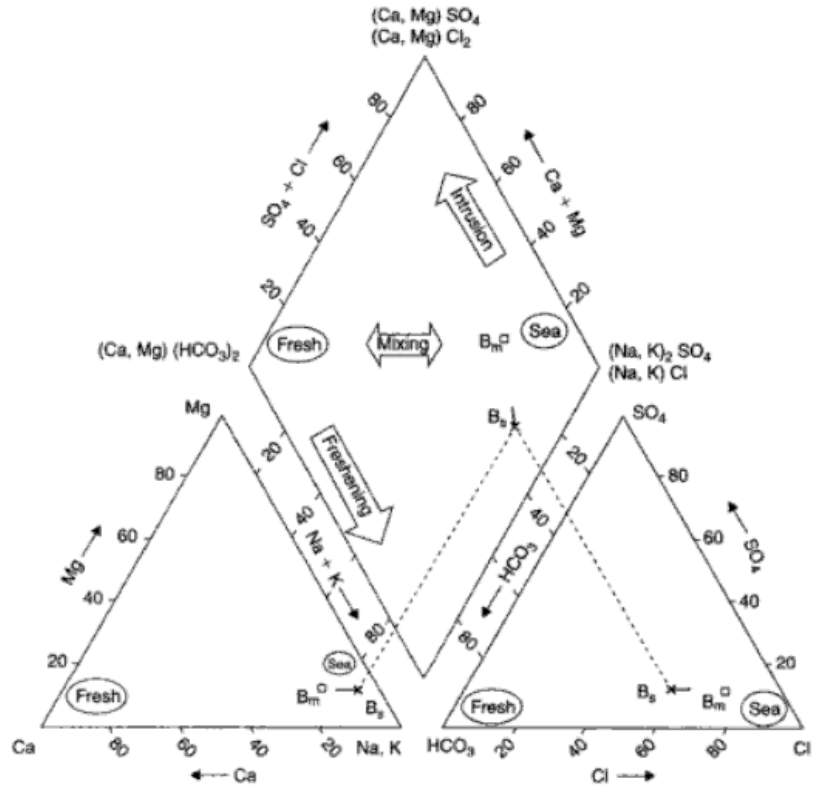


Figure 17 Classification zones for fresh- and seawater (Appelo & Postma, 2005).

3.3. CALCULATIONS OF MIXING RATIOS

The groundwater composition of samples from a number of wells and other sampling points in the Slite area is the result of mixing between relatively young groundwater and seawater or older saline groundwater from the Littorina transgression. The calculations of relative mass balance have been made by combining two end-members at various mixing ratios. An end-member is a possible source of water contributing to the system. The resulting mixing line is then compared with available groundwater samples. The intersection in the graph implies the relative mixing of the two different water types that result in the third water type (Figure 18). Two assumptions have been made in these calculations: 1) there are only two end-members contributing to the water sample and 2) there is no precipitation in the water. A possible mixture is calculated from Equation 17 and plotted in Figure 18.

$$[\text{Concentration in end-member 1}] * \text{Mixing ratio} + [\text{Concentration in end-member 2}] * (1 - \text{Mixing ratio}) = \text{Concentration in mixed sample} \quad (17)$$

The actual concentration of the water sample in the mixed sample for the two different water flows is plotted as a straight line in the graph (Figure 18).

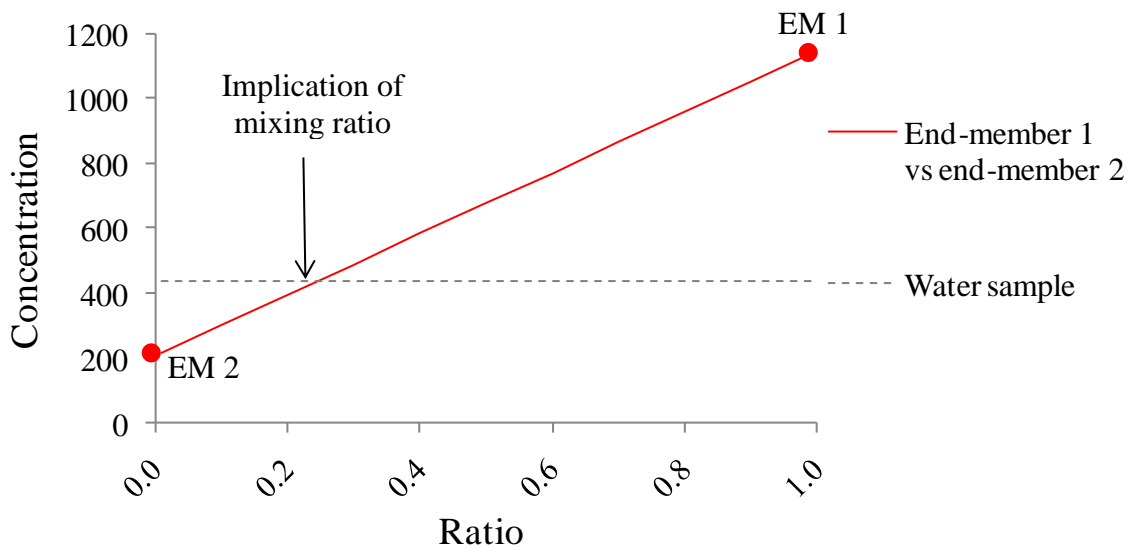


Figure 18 Mixing ratios between two end-members (EM 1 and EM 2) and actual value of water sample are plotted and the intersection implies the relative mixing ratio.

The graph implicates the mixing ratio of the actual value in the resulting sample, i.e. the mixed water sample consists of 29% of end-member 1 and 71% of end-member 2. This procedure has been applied to possible combinations of mixed water flows.

4. RESULTS

All data used in this Master thesis can be found in Appendix 3. Water quality data are compared with Swedish guideline values for drinking water (Socialstyrelsen, 2003). Guidelines are based on health, technical and aesthetic criteria. For some compounds, water is not fit for drinking because of technical reasons (e.g. corrosive to water pipes) or aesthetic reasons (e.g. smell, colour).

4.1. CONDUCTIVITY

Conductivity results from sampling in Bogevisken, Tingstäde träsk and Drinking water wells can be seen in Figure 19 and Figure 20 (except Bogevisken). Sample points are marked in Figure 4. The conductivity in Bogevisken is naturally high because of the connection to the Baltic Sea. The other sampling points, Tingstäde träsk and Drinking water wells, can more easily be viewed in Figure 20.

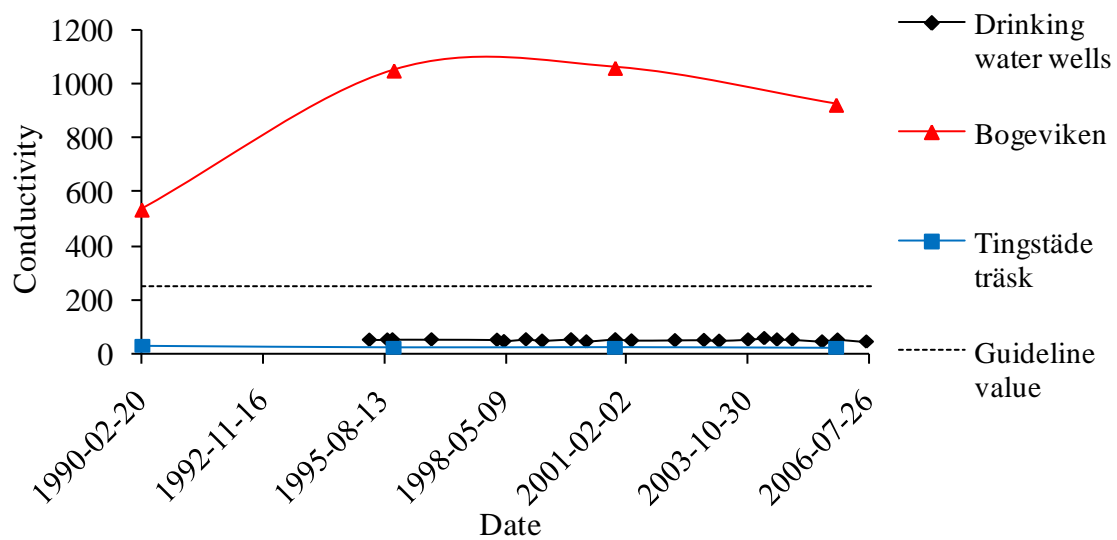


Figure 19 Conductivity (mS/m) from the studied area. Drinking water guideline of 250 mS/m marked as dotted line.

The conductivity in Tingstäde träsk and Drinking water wells were low, indicating acceptable drinking water quality.

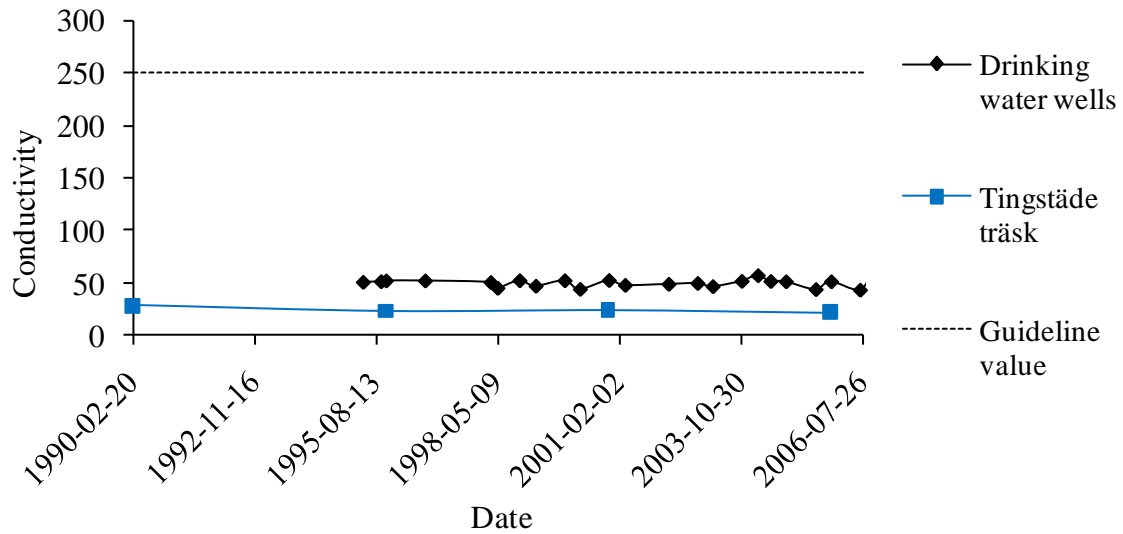


Figure 20 Conductivity (mS/m) from the studied area without results from Bogevisken. Drinking water guideline of 250 mS/m marked as dotted line.

The conductivity results of the sampling in the quarries and water bodies can be seen in Table 2. A large variation of conductivity was found. Bench 1 and File Hajdar quarry showed values similar to the Drinking water wells and Tingstäde träsk, i.e. freshwater/groundwater. The Landfill showed the highest conductivity and Bench 2 E showed also a high conductivity. The Harbour showed naturally high conductivity.

Table 2 Conductivity results from new sampling programme. Values marked with * are sampled on the 18th of September 2008. Samples marked with **, *** and **** are median values sampled during the period 1995-2007, 1990-2005 and 1951-1953 respectively. Units in mS/m.

Sampling point	Conductivity	
Median Drinking water wells**		52.3
Median Bogevisken***		891.8
Median Tingstäde träsk***		24.8
Median Tullström****		-
Sampling point	11/9, 18/9* 2008	24/10 2008
Bench 1 N	58*	65
Bench 1 NW	62*	60
Bench 2 E	730*	790
Bench 2 N	160*	160
Bench 2 NW	150*	260
Landfill	1500	1400
File Hajdar	65	74
Harbour	1100*	1200
Pump E	290	360
Pump W	390	330
Sed. Pond	370	360
Stream N	190	200
Stream S	450	310

4.2. pH

Results from sampling in Bogevisken, Tingstäde träsk and Drinking water wells can be seen in Figure 21. Sample points are marked in Figure 4. The pH value in all sampled points was stable and naturally high because of the connection to the Baltic Sea and well within technical and drinking water quality limits.

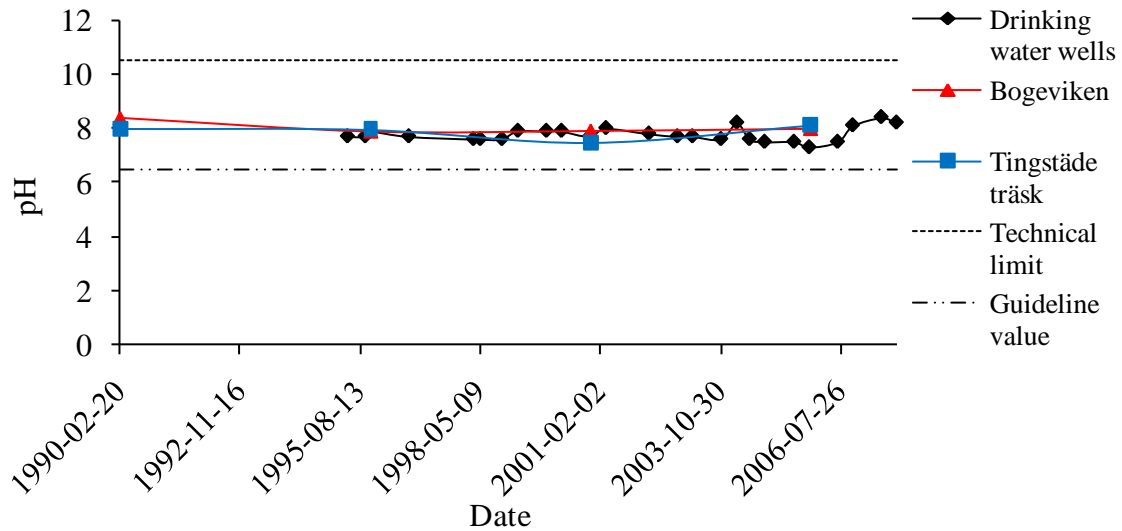


Figure 21 pH from the studied area. Technical pH limit at 10.5, marked as dotted line, and drinking water quality limit at 6.5 marked as broken line.

The pH value in the drinking water wells from the investigation made by Tullström in 1955 was stable in every well sampled and well within today's technical and drinking water quality limits.

The median value of pH for water samples from Drinking water wells, Bogevisken, Tingstäde träsk and Tullström's investigation can be viewed in Table 3. The results of the sampling in the quarries and water bodies from the most recent control programme can be seen in Table 3. All sampled points showed high pH where the Landfill showed the highest value of pH.

Table 3 pH results from new sampling programme. Values marked with * are sampled on the 18th of September 2008. Samples marked with **, *** and **** are median values sampled during the period 1995-2007, 1990-2005 and 1951-1953 respectively.

Sampling point	pH	
Median Drinking water wells**		7.7
Median Bogevisken***		8.1
Median Tingstäde träsk***		8.0
Median Tullström****		7.5
Sampling point	11/9, 18/9*	24/10
	2008	2008
Bench 1 N	7.9*	8.2
Bench 1 NW	7.8*	8.3
Bench 2 E	8.1*	8.3
Bench 2 N	8.4*	8.5
Bench 2 NW	8.2*	8.4
Landfill	12.3	12.3
File Hajdar	8.4	8.3
Harbour	8.2*	8.1
Pump E	8.4	8.2
Pump W	8.3	8.2
Sed. Pond	8.5	8.6
Stream N	8.4	8.4
Stream S	8.5	8.3

4.3. ALKALINITY (HCO_3^-)

Alkalinity results from sampling in Bogevisken, Tingstäde träsk and the Drinking water wells can be seen in Figure 22. Sample points are marked in Figure 4. The alkalinity in the area is high and stable.

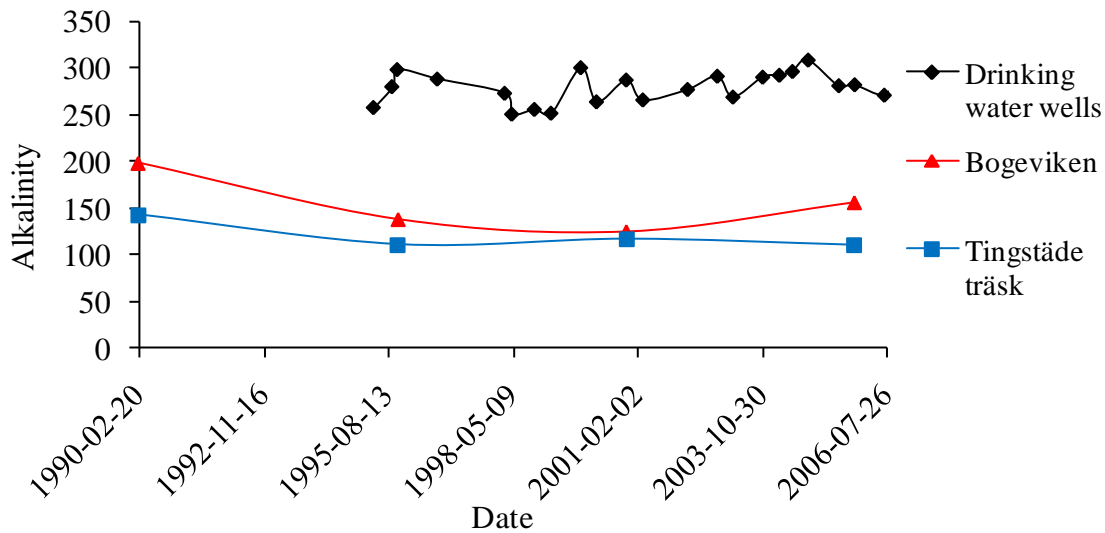


Figure 22 Alkalinity (mg HCO_3^- /l) from the studied area.

The alkalinity is naturally high in the drinking water wells from the investigation made by Tullström in 1955 and has values in the same range as the Drinking water wells 23v281 from the Gotland municipality which can be viewed in Figure 22.

The results of the sampling in the quarries and water bodies from the most recent control programme can be seen in Table 4. The alkalinity was naturally high and had values in the area of the Drinking water wells from the Gotland municipality and the investigation made by Tullström in 1955. The alkalinity in the Landfill, which contains alkali waste products, was considerably higher while the Harbour had a lower value of alkalinity than the other.

Table 4 Alkalinity results from new sampling programme. Values marked with * are sampled on the 18th of September 2008. Samples marked with **, *** and **** are median values sampled during the period 1995-2007, 1990-2005 and 1951-1953 respectively. Units in mg HCO₃⁻/l.

Sampling point	Alkalinity	
Median Drinking water wells**		280.5
Median Bogevisken***		154.3
Median Tingstäde träsk***		119.8
Median Tullström****		302.3
Sampling point	11/9, 18/9* 2008	24/10 2008
Bench 1 N	280*	260
Bench 1 NW	320*	240
Bench 2 N	260*	270
Bench 2 NW	260*	240
Bench 2 E	210*	180
Landfill	1500	1400
File Hajdar	240	260
Harbour	63*	96
Pump E	210	200
Pump W	140	150
Sed. Pond	130	120
Stream N	210	230
Stream S	120	140

4.4. CHLORIDE (Cl⁻) AND SULPHATE (SO₄²⁻)

Chloride and sulphate results from sampling in Bogevisken, Tingstäde träsk and the Drinking water well can be seen in Figures 23 and 24, respectively. Figures 25 and 26 illustrate the same results with the samples from Bogevisken removed. Sample points are marked in Figure 4. The chloride and sulphate concentrations in Bogevisken were naturally high because of the connection to the Baltic Sea.

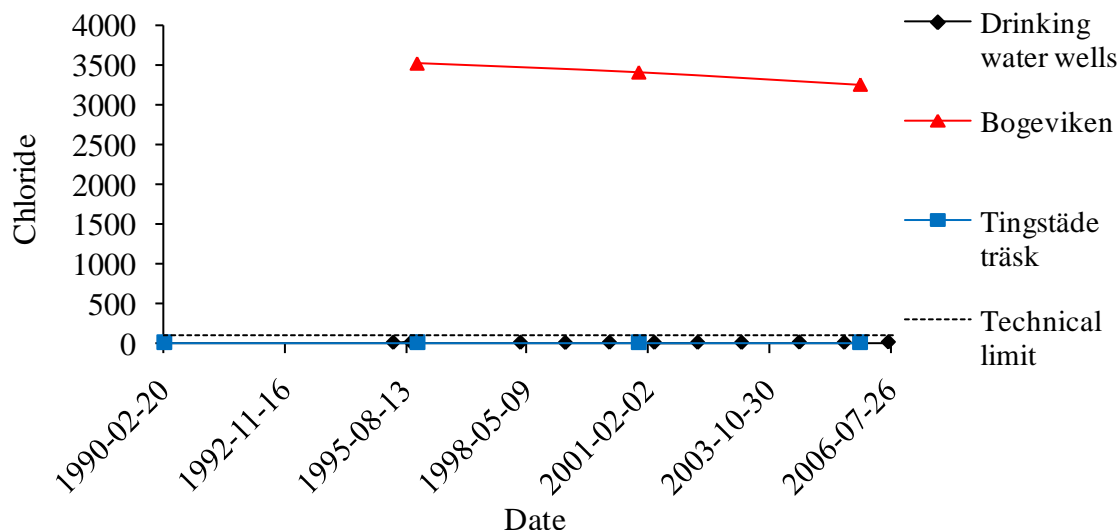


Figure 23 Chloride concentrations (mg/l) from the studied area. Technical limit of 100 mg/l marked as dotted line.

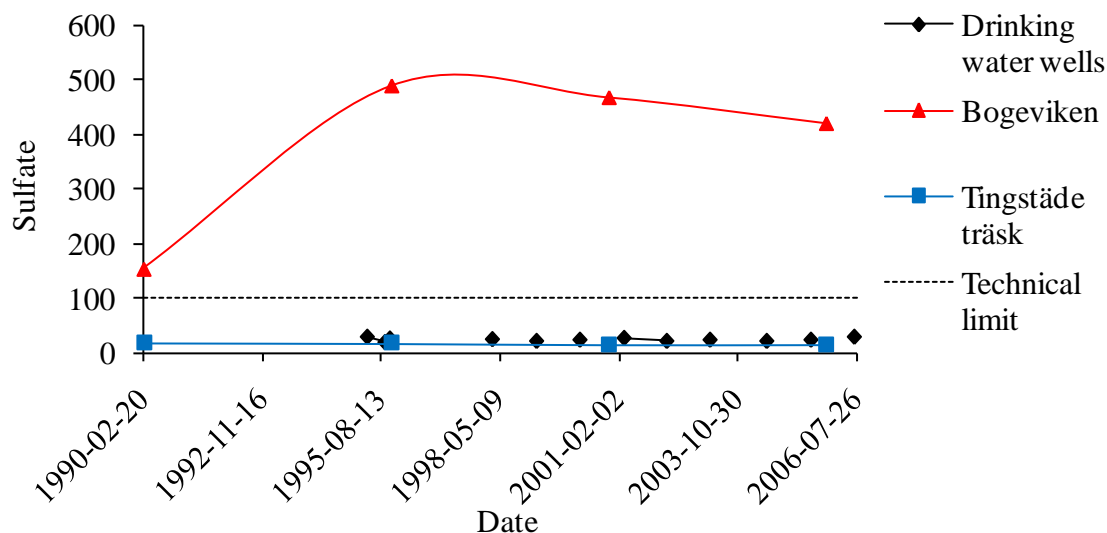


Figure 24 Sulphate concentrations (mg/l) from the studied area. Technical limit of 100 mg/l marked as dotted line.

The chloride and sulphate concentrations in Tingstäde träsk and drinking water wells were low and well under the technical limit. The low chloride concentration can be interpreted as freshwater/groundwater/surface water and unaffected by seawater.

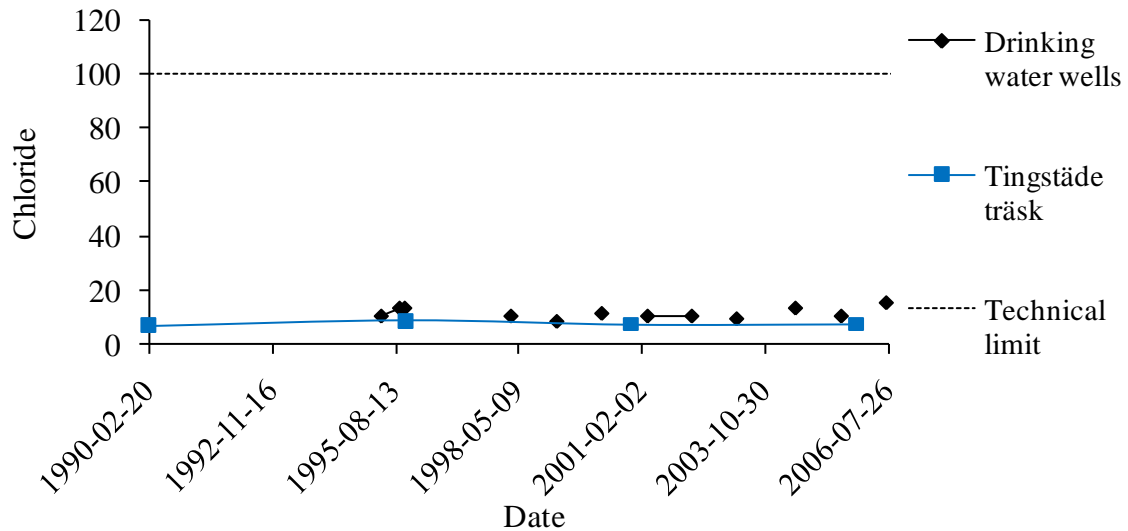


Figure 25 Chloride concentrations (mg/l) from the studied area. Technical limit of 100 mg/l marked as dotted line.

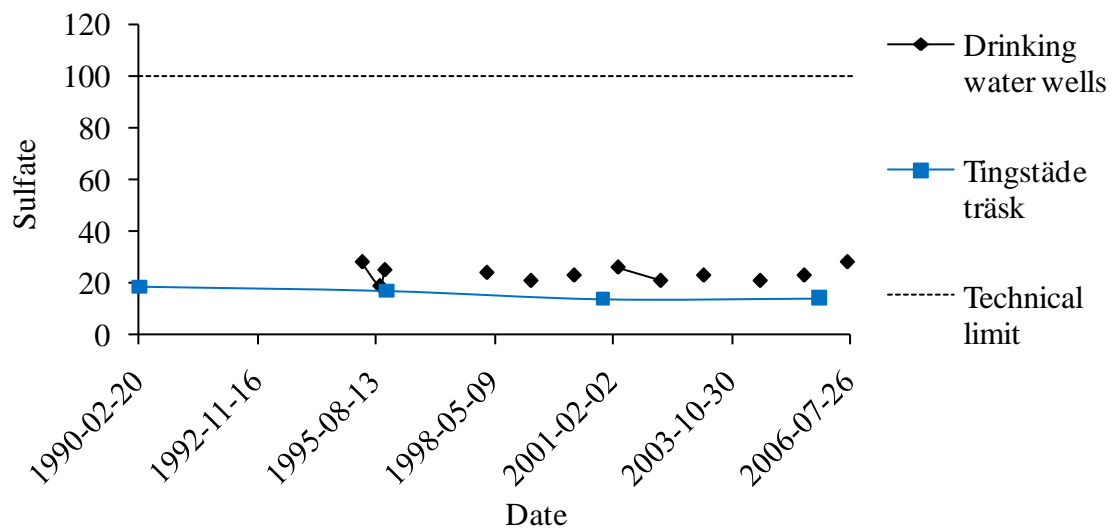


Figure 26 Sulphate concentrations (mg/l) from the studied area without results from Bogevisken. Technical limit of 100 mg/l marked as dotted line.

A large variation of chloride concentration was found in the drinking water wells from the investigation made by Tullström in 1955. Wells 8 and 311 located in Othem, north of Slite respectively in Bogeclint, south of Slite municipality (Figure 13) showed values similar to the Drinking water wells and Tingstäde träsk, i.e. freshwater/groundwater. Wells 51, 46, 38 and 231 had chloride concentrations under the technical remark while wells 27, 20 and 221 showed larger values than the technical limit. Well 20 had the largest chloride concentration and are located in Spillings (close to well 27 which also had a large chloride concentration). Well 221 was located 1 km south of Bogevisken.

A quite large variation of sulphate concentration was found in the drinking water wells from the investigation made by Tullström in 1955. Well 8 located in Othem, north of Slite, showed a very low sulphate concentration. Wells 20 and 27, both located in Spillings, resulted in slightly higher values while wells 46, 311, 231, 51, 221, 38 showed larger values of sulphate concentration. Wells 46, 231 and 311 had values similar to Drinking water wells from Slite municipality. All wells sampled showed sulphate concentrations below today's technical limit of 100 mg/l.

The chloride and sulphate results of the sampling in the quarries and water bodies from the most recent control programme can be seen in Table 5. A large variation of chloride concentration was found. Bench 1 and File Hajdar quarry showed values similar to the Drinking water wells and Tingstäde träsk, i.e. freshwater/groundwater. Bench 2 E and Landfill showed considerably higher chloride concentrations and the Sedimentation pond, Stream S, Pump E and Pump W had high chloride concentrations.

A large variation of sulphate concentration was found. The Landfill showed the highest sulphate concentration. All sampled points showed high sulphate concentrations and higher than the technical limit except Bench 1 and Bench 2.

Table 5 Chloride and sulphate results from new sampling programme. Values marked with * are sampled on the 18th of September 2008. Samples marked with **, *** and **** are median values sampled during the period 1995-2007, 1990-2005 and 1951-1953 respectively. Units in mg/l.

Sampling point	Cl⁻		SO₄²⁻	
Median Drinking water wells**	12		24.1	
Median Bogevisken***	3392		382.5	
Median Tingstäde träsk***	7.5		15.8	
Median Tullström****	101.8		35.1	
Sampling point	11/9, 18/9*	24/10	11/9, 18/9*	24/10
	2008	2008	2008	2008
Bench 1 N	16*	24	77*	110
Bench 1 NW	15*	21	89*	70
Bench 2 E	2300*	2500	490*	520
Bench 2 N	430*	380	45*	52
Bench 2 NW	370*	780	48*	49
Landfill	2100	2000	1500	1400
File Hajdar	13	12	150	180
Harbour	4000*	3900	520*	570
Pump E	930	1100	210	250
Pump W	1100	830	400	370
Sed. Pond	1000	1000	390	400
Stream N	540	490	160	150
Stream S	1100	750	510	430

4.5. NITROGEN AS NITRATE (NO₃⁻), NITRITE (NO₂⁻) AND AMMONIUM (NH₄⁺)

Nitrate and nitrite results from sampling in Bogevisken, Tingstäde träsk and Drinking water wells can be seen in Figure 27. Sample points are marked in Figure 4. The nitrite and nitrate concentrations in all sampled points are low.

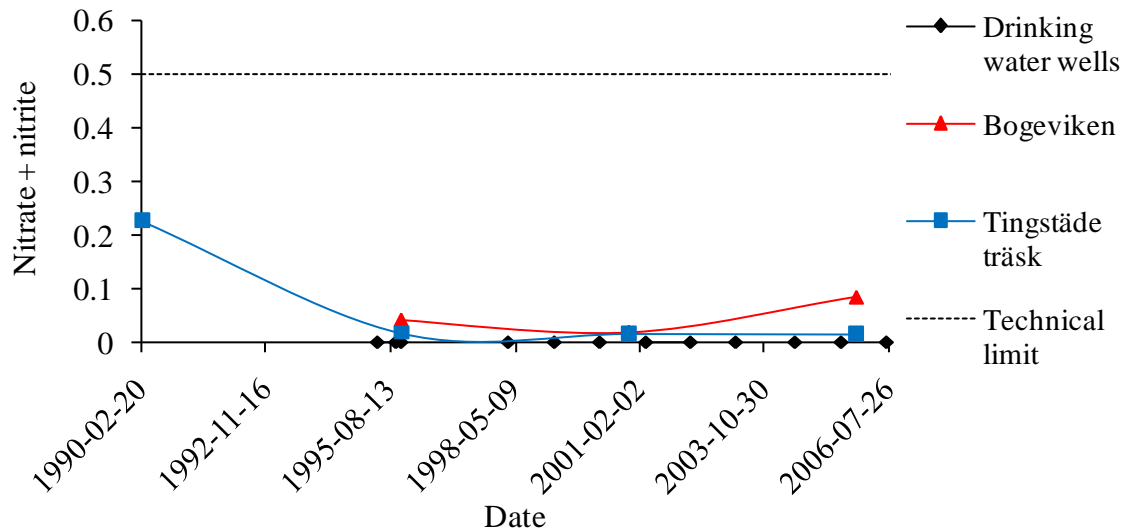


Figure 27 Sum of nitrate and nitrite concentration (mg/l) from the studied area. Technical limit of 0.5 mg/l marked as dotted line.

Results for ammonium concentration from sampling in Bogevisken, Tingstäde träsk and Drinking water wells can be seen in Figure 28. Sample points are marked in Figure 4. The ammonium concentration in the area is low and relative stable. The value of ammonium is higher in the two surface water recipients than the Drinking water wells.

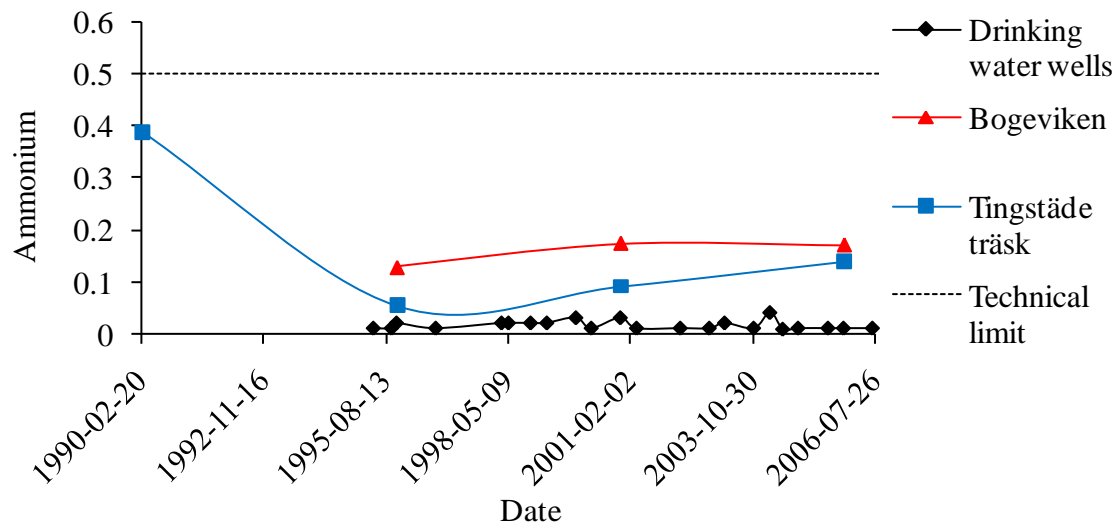


Figure 28 Ammonium concentrations (mg/l) from the studied area. Technical limit of 0.5 mg/l marked as dotted line.

Tullström (1955) only analyzed the water samples for nitrate which resulted in a quite large variation of nitrate concentrations in the drinking water wells. Wells 8, 20, 27, 51

and 311 showed a nitrate concentration lower than what could be analyzed for. Well 38, 46 and 231, located west of Bogevisken (Figure 13), contained very high nitrate concentrations.

The nitrate and ammonium results of the sampling in the quarries and water bodies from the most recent control programme can be seen in Table 6. All sampled points showed low nitrate concentrations where File Hajdar showed the largest value of nitrate concentration.

The ammonium concentration was low and had values in the area of the Drinking water wells from the Gotland municipality and National water survey. The ammonium nitrogen in File Hajdar quarry was considerably higher than the other and almost hazardous for health if consumed.

Table 6 Nitrate and ammonium results from new sampling programme. Values marked with * are sampled on the 18th of September 2008. Samples marked with **, *** and **** are median values sampled during the period 1995-2007, 1990-2005 and 1951-1953 respectively. Units in mg/l.

Sampling point	NO₃⁻		NH₄⁺	
Median Drinking water wells**	<1		-	
Median Bogevisken***	0.05		-	
Median Tingstäde träsk****	-		-	
Median Tullström****	6.1		-	
Sampling point	11/9, 18/9* 2008	24/10 2008	11/9, 18/9* 2008	24/10 2008
Bench 1 N	<0.1*	<0.1	0.05*	0.21
Bench 1 NW	<0.1*	0.11	0.38*	0.066
Bench 2 E	0.16*	0.14	<0.01*	0.074
Bench 2 N	0.11*	<0.1	0.15*	0.17
Bench 2 NW	<0.1*	0.29	0.27*	0.18
Landfill	0.15	0.11	0.16	0.15
File Hajdar	2.4	3.5	0.23	1.2
Harbour	<0.1*	<0.1	0.029*	0.037
Pump E	<0.1	<0.1	0.07	0.11
Pump W	0.47	1.0	0.07	0.1
Sed. Pond	1.4	1.7	0.093	0.25
Stream N	0.31	0.19	0.1	0.16
Stream S	0.67	1.2	0.07	0.14

4.6. CALCIUM (Ca²⁺), MAGNESIUM (Mg²⁺), POTASSIUM (K⁺) AND SODIUM (Na⁺)

Calcium and magnesium results from sampling in Bogeviken, Tingstäde träsk and Drinking water wells can be seen in Figures 29 and 30, respectively. Sample points are marked in Figure 4. The calcium concentration in the area is quite high and relatively stable. The value of calcium is generally higher than the technical limit in surface water Bogeviken. The other sampling points have a relative stable variation of calcium concentration. The magnesium concentration in Bogeviken is naturally high because of the connection to the Baltic Sea. The magnesium results from sampling points Tingstäde träsk and Drinking water wells can more easily be viewed in Figure 31.

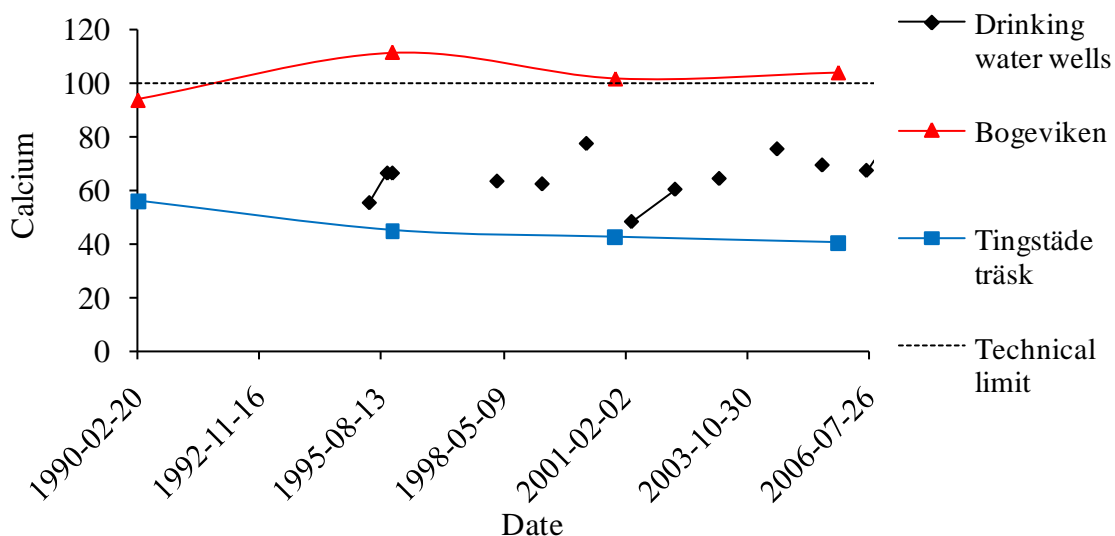


Figure 29 Calcium concentrations (mg/l) from the studied area. Technical limit of 100 mg/l marked as dotted line.

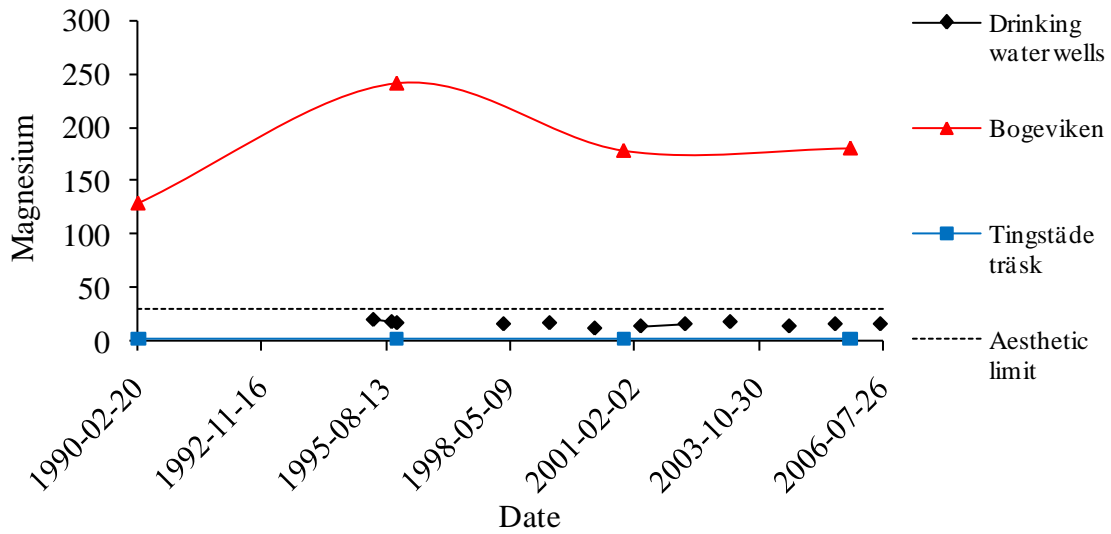


Figure 30 Magnesium concentrations (mg/l) from the studied area. Aesthetic limit of 30 mg/l marked as dotted line.

The magnesium concentration in Tingstäde träsk and Drinking water wells were quite low and well under the aesthetic limit. The low magnesium concentration can be interpreted as freshwater/groundwater/surface water and unaffected by seawater.

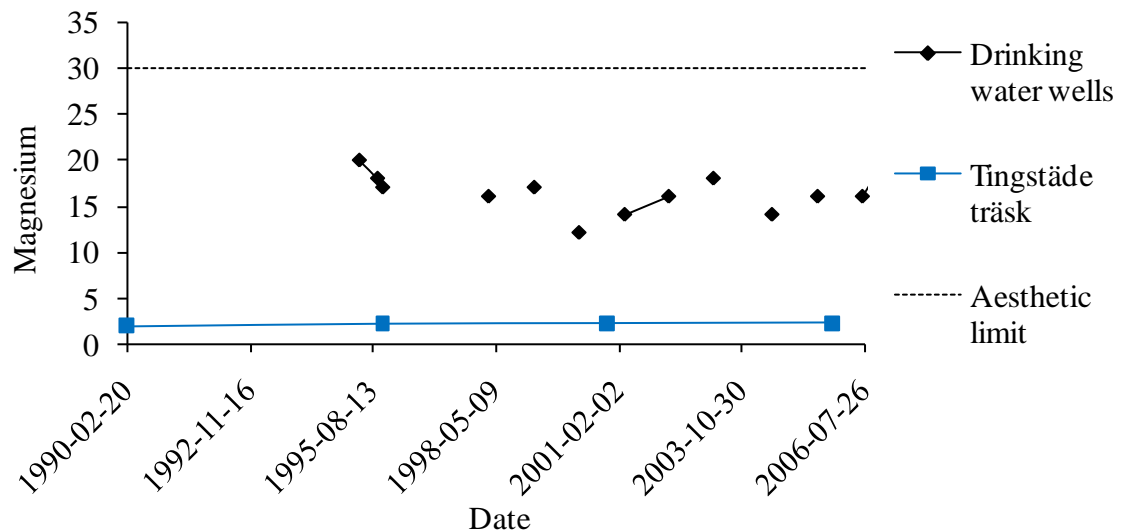


Figure 31 Magnesium concentrations (mg/l) from the studied area without results from Bogevisken. Aesthetic limit of 30 mg/l marked as dotted line.

Potassium results from sampling in Bogevisken, Tingstäde träsk and Drinking water wells can be seen in Figures 32 and 33 (except Bogevisken). Sample points are marked in Figure 4. The potassium concentrations in the area are low and stable except for results from sampling in Bogevisken which show high potassium concentrations.

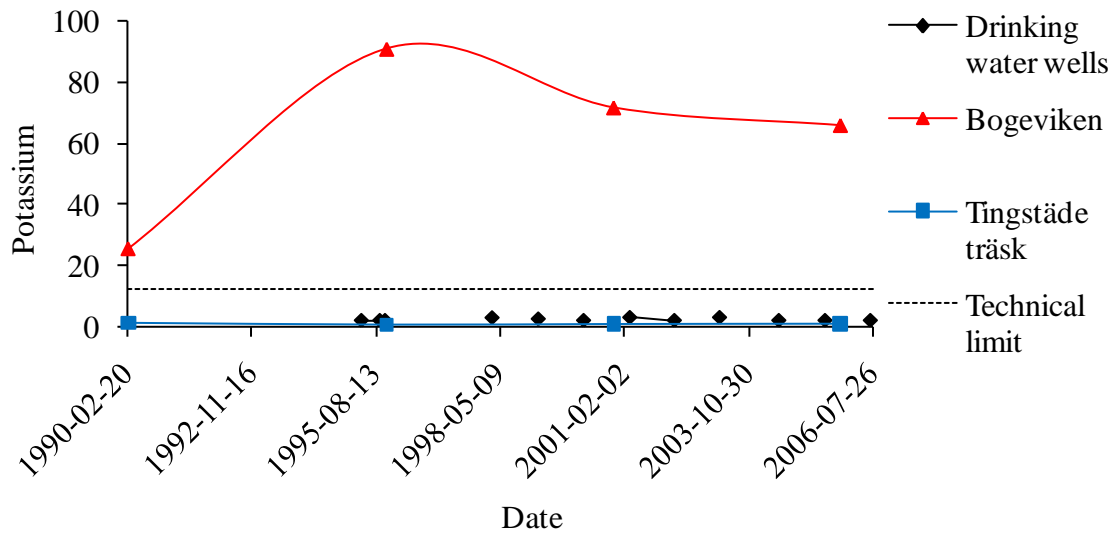


Figure 32 Potassium concentrations (mg/l) from the studied area. Technical limit of 12 mg/l marked as dotted line.

The potassium concentration in Drinking water wells and Tingstäde träsk were quite low and well under the technical limit.

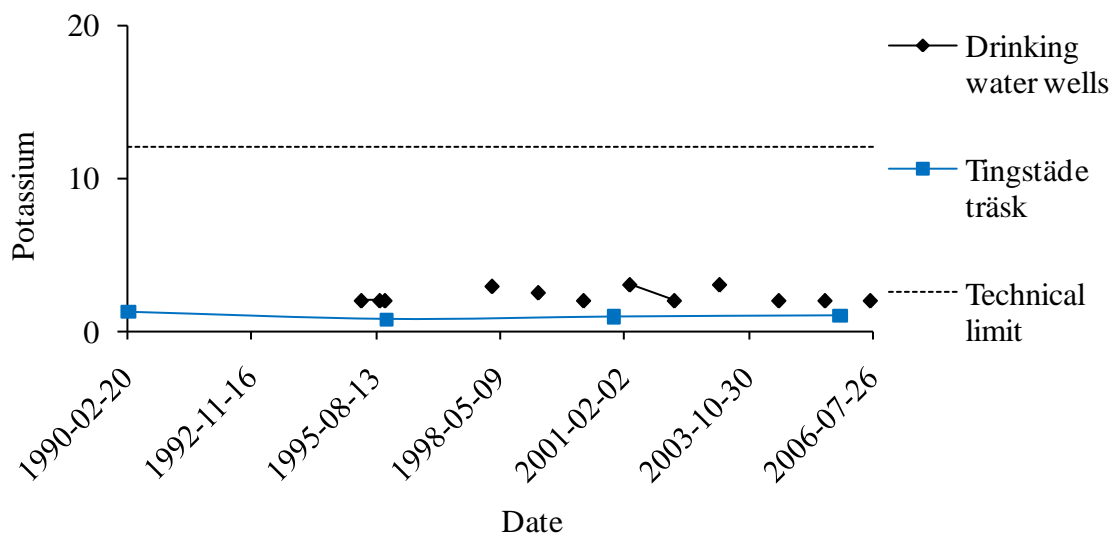


Figure 33 Potassium concentrations (mg/l) from the studied area without results from Bogevisken. Technical limit of 12 mg/l marked as dotted line.

Sodium results from sampling in Bogevisken, Tingstäde träsk and Drinking water wells can be seen in Figure 34 and Figure 35 (except Bogevisken). Sample points are marked in Figure 4. The sodium concentration in Bogevisken was naturally high because of the connection with the Baltic Sea. The other sampling points Tingstäde träsk and Drinking water wells can more easily be viewed in Figure 35.

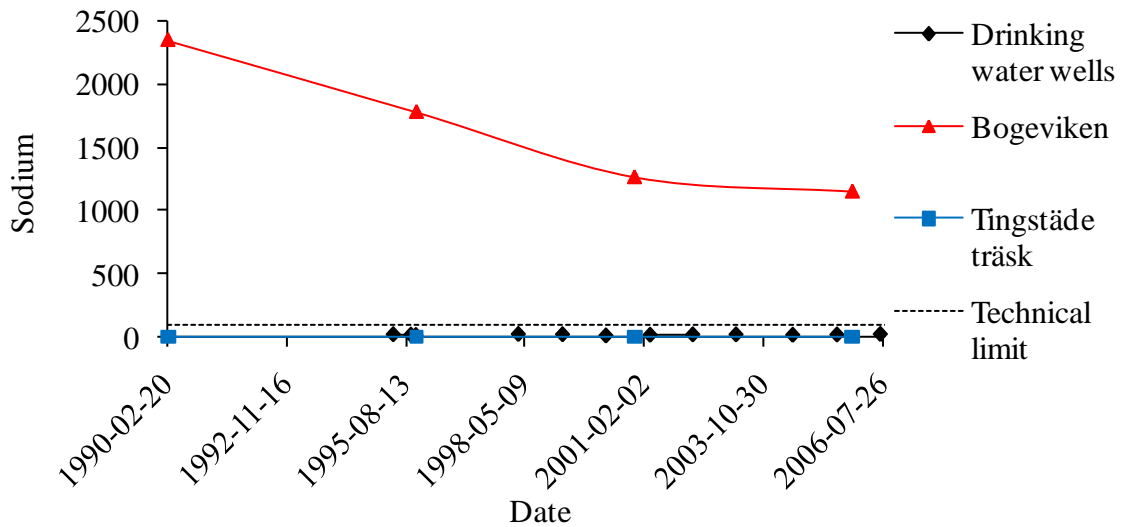


Figure 34 Sodium concentrations (mg/l) from the studied area. Technical limit of 100 mg/l marked as dotted line.

The sodium concentrations in Tingstäde träsk and Drinking water wells were very low and well under the technical remark. The low sodium concentrations can be interpreted as freshwater/groundwater/surface water and unaffected by seawater.

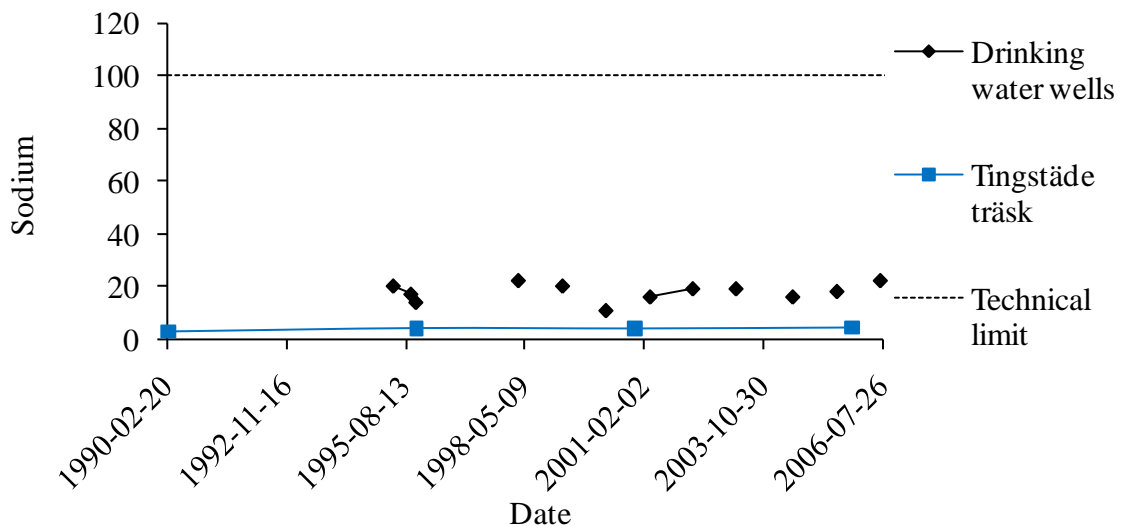


Figure 35 Sodium concentrations (mg/l) from the studied area without results from Bogevisken. Technical limit of 100 mg/l marked as dotted line.

The calcium concentrations in the drinking water wells from the investigation made by Tullström in 1955 are naturally high and have predominantly values that are similar to concentrations in the Drinking water wells from the Gotland municipality, except for wells 38, 221, 231 and 311 which were located in the surroundings west and south-west of Bogevisken (Figure 13). The calcium concentration in the noted wells is relatively similar to the values in Bogevisken except for Well 38 which showed twice the value as in Bogevisken.

A large variation of magnesium concentration was found in the drinking water wells from the investigation made by Tullström in 1955. Well 8 located in Othem, north of Slite, showed a similar value as Tingstäde träsk, while well 39, west of Bogevisken and well 311 in Bogevisken, south of Slite community, resulted in a slightly higher magnesium concentration (Figure 13). Wells 51, 46 as well as 8, 38, 231 and 311 had magnesium concentrations under the aesthetic limit while wells 20 and 221 showed larger values than the technical limit. Well 27 had the largest concentration but the value consider both the magnesium and calcium concentration and no conclusion can be drawn from the result of well 27.

The analysis for potassium in the drinking water wells from the investigation made by Tullström in 1955 were combined with sodium and no conclusion can be drawn from this, but the results can be taken into consideration whilst making a final conclusion. The potassium and sodium concentrations result in values below the technical limit of 12 mg/l.

The calcium and magnesium results of the sampling in the quarries and water bodies from the most recent control programme can be seen in Table 7. The calcium concentration was naturally high and has values that are similar to the concentrations in the Drinking water wells from the Gotland municipality, except for Bench 2 E and Pump E which were located near each other. The calcium concentration was also high in File Hajdar quarry.

A large variation of magnesium concentration was found. The Harbour showed a high magnesium concentration comparable to Bogevisken. Bench 2 E also showed a high magnesium concentration. The Sedimentation pond, Stream N and S, Pump E and W, all showed higher magnesium concentrations than the aesthetic limit. The water sample from the Landfill resulted in a low magnesium concentration.

Table 7 Calcium and magnesium results from new sampling programme. Values marked with * are sampled on the 18th of September 2008. Samples marked with **, *** and **** are median values sampled during the period 1995-2007, 1990-2005 and 1951-1953 respectively. Units in mg/l.

Sampling point	Ca²⁺		Mg²⁺	
Median Drinking water wells**	65.3		16.7	
Median Bogevisken***	102.5		181.5	
Median Tingstäde träsk****	45.8		2.2	
Median Tullström*****	87.2		17.1	
Sampling point	11/9, 18/9* 2008	24/10 2008	11/9, 18/9* 2008	24/10 2008
Bench 1 N	82*	110	16*	13
Bench 1 NW	97*	89	9.7*	16
Bench 2 E	150*	170	28*	28
Bench 2 N	57*	57	25*	39
Bench 2 NW	51*	73	150*	87
Landfill	3.3	64	<0.5	<0.5
File Hajdar	110	140	12	16
Harbour	75*	95	210*	230
Pump E	130	170	59	83
Pump W	96	120	49	58
Sed. Pond	76	84	48	61
Stream N	79	90	32	45
Stream S	81	99	45	43

The potassium and sodium results of the sampling in the quarries and water bodies can be seen in Table 8. All sampled points showed low potassium concentrations except the Landfill that showed very high potassium concentrations.

A large variation of sodium concentration was found. Bench 1 and File Hajdar quarry showed values similar to the Drinking water wells and Tingstäde träsk, i.e. freshwater/groundwater. Bench 2 E and the Harbour showed considerably high sodium concentrations. Bench 2, Sedimentation pond, Stream N and S, Pump E and W, all had high sodium concentrations.

Table 8 Potassium and sodium results from new sampling programme. Values marked with * are sampled on the 18th of September 2008. Samples marked with **, *** and **** are median values sampled during the period 1995-2007, 1990-2005 and 1951-1953 respectively. Units in mg/l.

Sampling point	K⁺		Na⁺	
Median Drinking water wells**	2.2		18.5	
Median Bogevisken***	63.5		1634	
Median Tingstäde träsk***	0.9		3.9	
Median Tullström K ⁺ + Na ⁺ ****	1.8		1.8	
Sampling point	11/9, 18/9* 2008	24/10 2008	11/9, 18/9* 2008	24/10 2008
Bench 1 N	3.9*	4	18*	19
Bench 1 NW	3.7*	4.1	10*	20
Bench 2 E	150*	160	1000*	1100
Bench 2 N	9.4*	8.7	210*	230
Bench 2 NW	9*	11	190*	390
Landfill	3300	3100	360	440
File Hajdar	5.7	4.3	8	10
Harbour	97*	88	1900*	2000
Pump E	36	38	310	440
Pump W	340	200	460	360
Sed. Pond	360	340	400	380
Stream N	30	24	220	250
Stream S	490	260	440	330

5. DISCUSSION

5.1. PIPER DIAGRAM

The results from Drinking water wells 23v281, National water survey Bogeviken and Tingstäde träsk, Helge Tullström's investigation and the new sampling programme are plotted in a Piper diagram to classify the different water samples (Figure 36) and then discussed in terms of the mixing of water of different compositions.

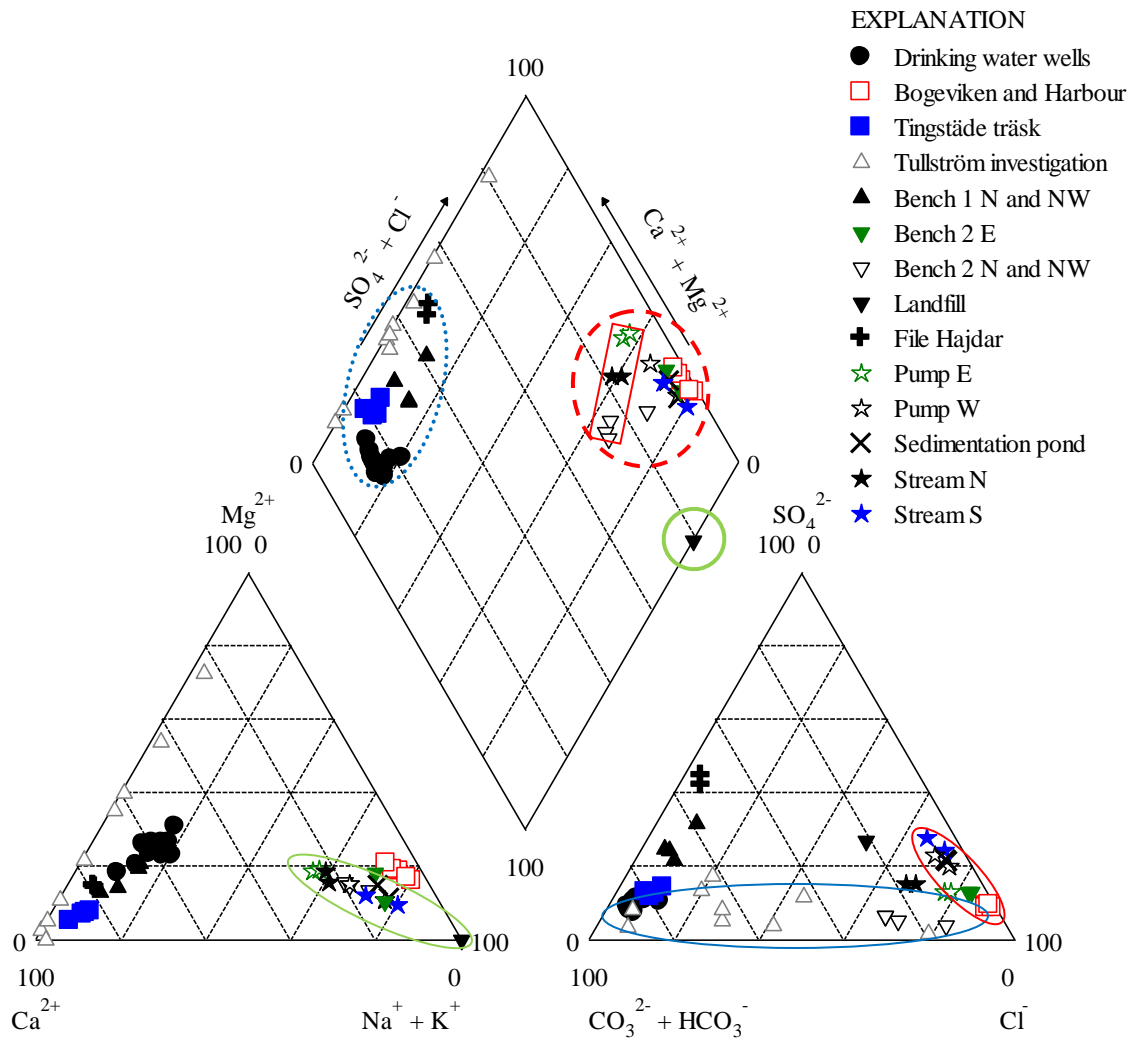


Figure 36 Piper diagram of water samples from the studied area. Sampling points for drinking water wells, Helge Tullström's investigation and the new sampling programme are marked in Figure 4, 13 and 15, respectively.

5.2. FRESHWATER

Freshwater is water predominantly unaffected by chemical processes and contains low concentrations of dissolved ionic compounds, and is dominated by calcium and bicarbonate ions in carbonate aquifers. Using the water type classification from Appelo & Postma (2005), water samples classified as freshwater (blue dotted ellipse in Figure 36) are derived from the following sampling locations: Drinking water wells, Tingstäde träsk, Helge Tullström's wells, Bench 1 N and NW in the Western quarry and File

Hajdar. The results from Helge Tullström's investigation are scattered along the sulphate and chloride part of the diagram in the diamond-shaped area. In the anion triangle, the samples from Tullström's investigation are plotted on the bicarbonate - chloride axis (blue ellipse) which indicates that the variability in the diamond-shaped diagram is predominantly caused by the increase in the relative proportion of the chloride concentration, relative to the bicarbonate concentration. The increase in chloride and calcium concentrations indicates saltwater influence according to section 2.1.2. The dominating process when saltwater mixes with freshwater is ion exchange between calcium and sodium. Although water samples from File Hajdar quarry plot close to some of Tullström's wells in the diamond-shaped area, samples from File Hajdar showed slightly higher values of sulphate, which can be seen in the anion triangle. A reason for relatively high sulphate concentrations can be weathering of bedrock containing sulphur which in this case probably is the dissolution of pyrite (FeS_2). There is pyrite in the bedrock in the study area (Nyberg, pers. comm.) but the amount and locations have not been investigated in this Master thesis.

Much of the groundwater on Gotland is considered to be young, i.e. the composition of the groundwater is dominated by recently infiltrated precipitation which, through fractures in the bedrock, is transported down to relatively deep aquifers (Kulander & Rodhe, 1997).

5.3. GROUNDWATER AFFECTED BY SEAWATER

The Harbour, Bogevisken, Bench 2 E, N and NW in the Western quarry, Stream S, Pump E and W in the Western quarry and Sedimentation pond in the Eastern quarry show similar values and can be classified as seawater or a water type that has been strongly impacted by seawater (or relict seawater; red dashed circle in Figure 36). The following observations can be made:

- Bench 2 N and NW lie along an imaginary mixing line between Bogevisken/Harbour and Drinking water wells, indicating seawater mixing with freshwater.
- Bench 2 N and NW seems to be an end-member to Stream N and Pump E in the Western quarry (red rectangle in Figure 36). Although Pump E could, using a literal interpretation of the Piper diagram, be the other end-member to Stream N, this is not likely since Pump E is simply drainage water that is being pumped to the Eastern quarry and Sedimentation pond. More likely, Stream N and Pump E lie along a mixing line between Bench 2 N and NW and an unidentified, unsampled end-member. If there is another end-member, it should have a higher calcium and/or magnesium concentration.
- In the anion triangle, Bench 2 E, Pump E and W in the Western quarry, and Sedimentation pond in the Eastern quarry (red ellipse in Figure 36) seem to be a mixing of water from Stream S and seawater from the Harbour and/or Bogevisken.

To support the theory of a seawater influence on Bench 2 E, N and NW in the Western quarry, mixing ratio diagrams were used. Stream S, Pump E and W in the Western quarry and Sedimentation pond are also affected by seawater but these surface water samples are likely a further evolution of groundwater observed at Bench 2 E, N and NW.

The chloride, calcium and potassium concentrations in Bench 2 E, N and NW were compared to mixing of Baltic seawater (Harbour) and Drinking water wells 23v281 at different mixing ratios. The mixing ratios should be in the same range for all three ions at the same sampling point. If not, there are two possibilities for the different ratios: 1) there is another end-member contributing to the recipients sampled, or 2) there is a chemical reaction changing the groundwater composition, for example precipitation of calcite or gypsum.

The analysis of the chloride content in the Bench 2 N and NW in the Western quarry resulted in a contribution of 9.4% and 19.7% for Bench 2 N and NW, respectively, from a saline water source of similar composition to Harbour (Figure 37). Bench 2 E has a different composition and consists of 64.0% water from a saline source (Figure 37).

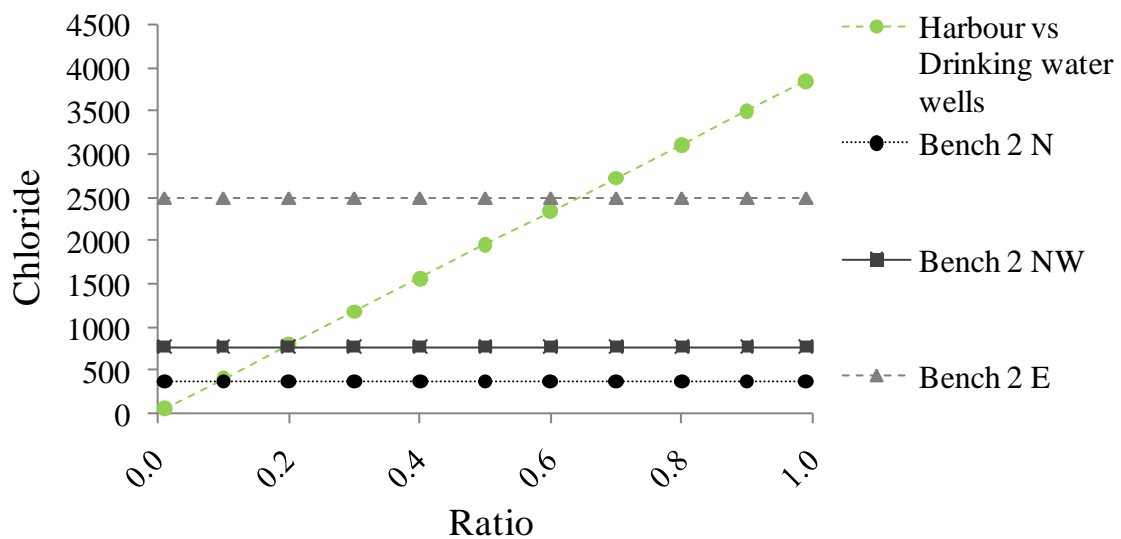


Figure 37 Mixing ratios between water from the Drinking water wells and a saline source with a composition similar to the Harbour samples. The actual measured value in Bench 2 E, N and NW are plotted. The intersection implies the relative mixing ratio that applies for a particular sample.

The analysis of the calcium content in the Bench 2 E, N and NW in the Western quarry resulted in different mixing ratios. Based on calcium content alone, Bench 2 N appears to only consist of groundwater from the Drinking water wells while Bench 2 E only consists of water from a saline source (Figure 38). Bench 2 NW consists of 21.4% of water from a saline source (Figure 38).

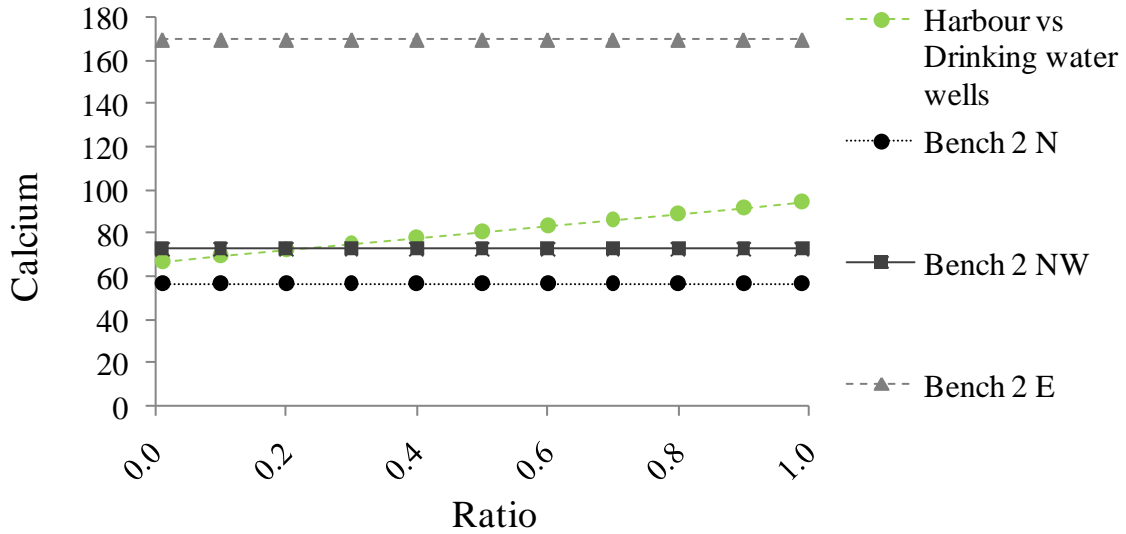


Figure 38 Mixing ratios between water from the Drinking water wells and a saline source with a composition similar to the Harbour samples. The actual measured value in Bench 2 E, N and NW are plotted. The intersection implies the relative mixing ratio that applies for a particular sample.

The analysis of the potassium content in the Bench 2 E, N and NW in the Western quarry resulted in mixing ratios that were somewhat similar to the calcium results. Based on potassium content alone, Bench 2 E only consists of water from a saline source (Figure 39). The other two sampling points resulted in a contribution of 0.4% and 7.9% for Bench 2 N and NW, respectively, from a saline water source of similar composition to Harbour (Figure 39).

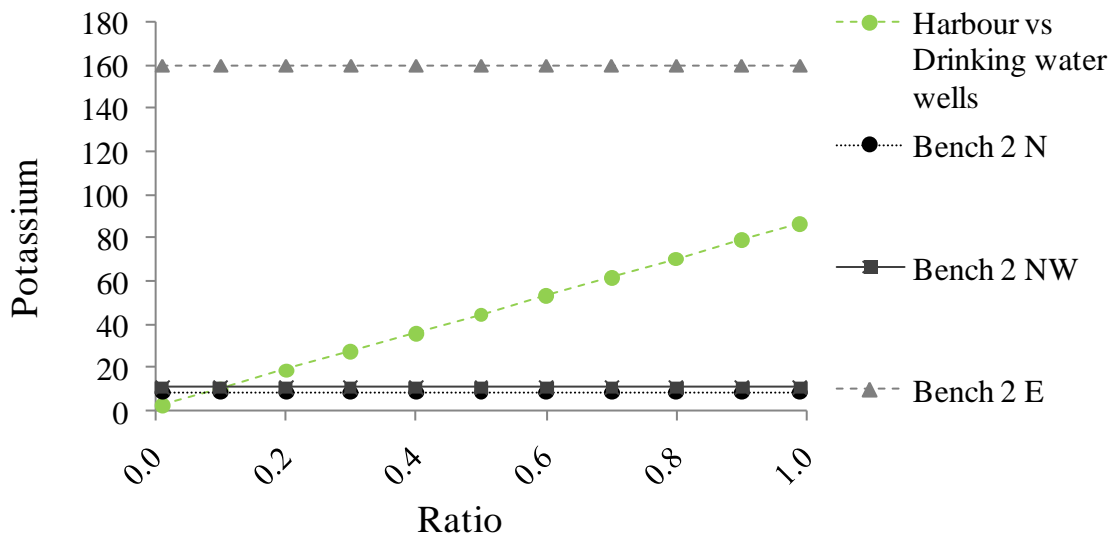


Figure 39 Mixing ratios between water from the Drinking water wells and a saline source with a composition similar to the Harbour samples. The actual measured value in Bench 2 E, N and NW are plotted. The intersection implies the relative mixing ratio that applies for a particular sample.

The mixing ratios are quite different for the combinations that result in the three sampling points Bench 2 E, N and NW. There could be another end-member contributing to Bench 2. The Drinking water wells are located west of Bench 2 in the Western quarry and the Harbour in the east. Considering the strike and dip of the sub-horizontal aquifers, water from Bench 2 could be the result of the mixing of another

groundwater (i.e. end-member) that originates from the north and a saline water. Another reason of the different results of the mixing ratios with respect to calcium content, could be precipitation of calcite.

5.4. GROUNDWATER AFFECTED BY THE LANDFILL IN THE WESTERN QUARRY

Water samples from the Landfill contain high concentration of potassium, sodium, and chloride, making the sample stand out in the Piper diagram (green circle in Figure 36). In the cation triangle, potassium and sodium concentrations in Bench 2 E, N and NW in the Western quarry, Pump E and W in the Western quarry, Sedimentation pond and Stream S (green ellipse in Figure 36) might be explained by contamination from the landfill. Since the water sample from the landfill also has high chloride content, the origin of the saltwater contamination in the sampling points Bench 2 E, N and NW in the Western quarry, Pump E and W in the Western quarry, Sedimentation pond and Stream S might be either seawater influence or seepage from the landfill. Mixing ratio diagrams have been used to investigate the influence of landfill leakage on the sampling points closest to the Landfill. As noted previously, Bench 2 N is a likely end-member to Pump W, Stream N and S.

Analyzing the chloride content in Pump W, Stream N and S in the Western quarry resulted in the following mixing ratios. Pump W and Stream S consists of 27.8% and 22.8%, respectively, of water from the Landfill (Figure 40). Stream N has a different composition and consists of 6.8% of water from the Landfill (Figure 40).

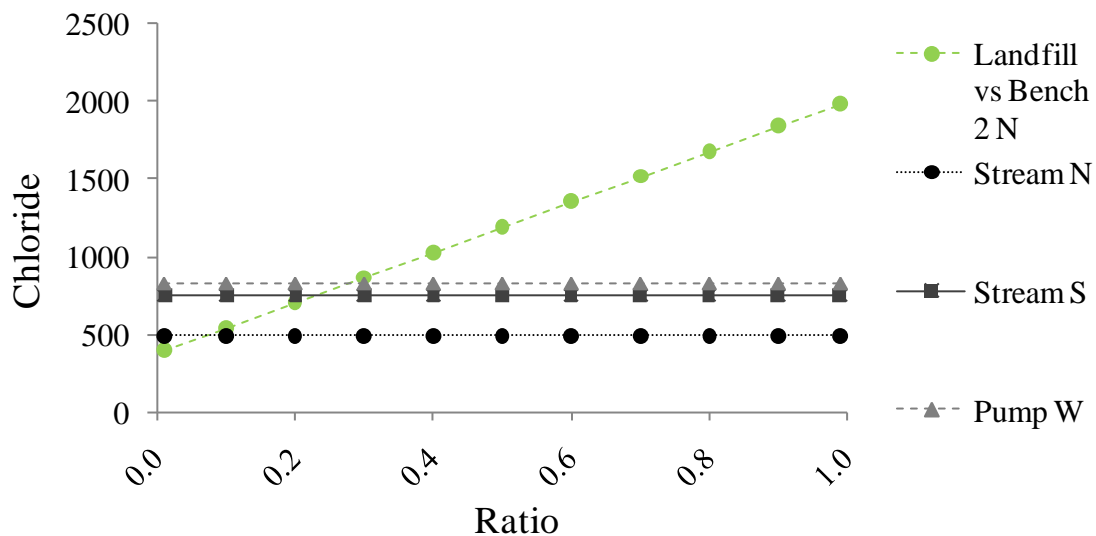


Figure 40 Mixing ratios between water from the Landfill and Bench 2 N. The actual measured value in Pump W, Stream N and S are plotted. The intersection implies the relative mixing ratio that applies for a particular sample.

Pump W, Stream N and S in the Western quarry have higher calcium concentration than both Bench 2 N and the Landfill which indicates that there is another end-member or the dissolution of calcite contributing to the high calcium content (Figure 41).

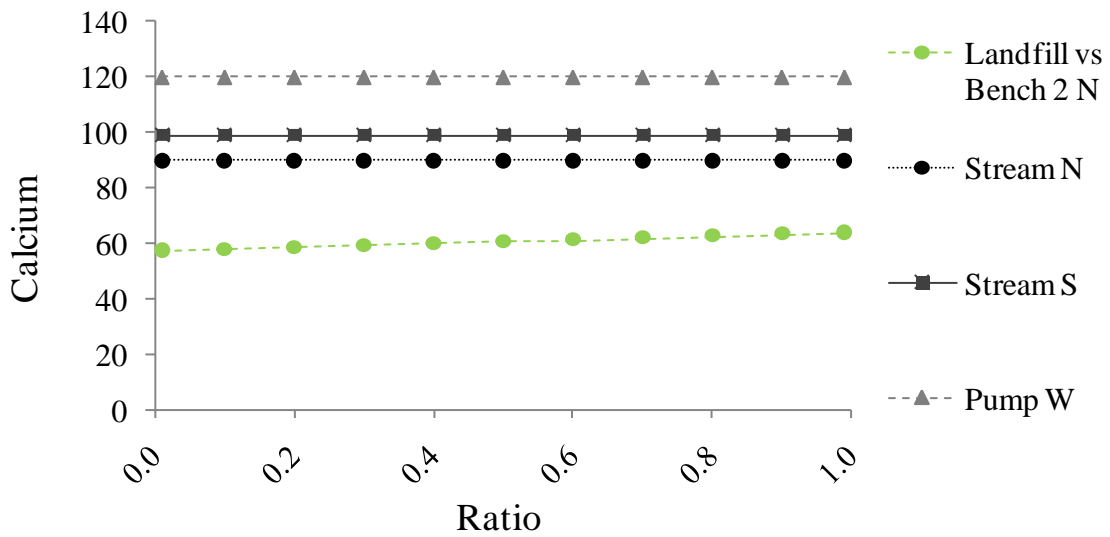


Figure 41 Mixing ratios between water from the Landfill and Bench 2 N. The actual measured value in Pump W, Stream N and S are plotted. The intersection implies the relative mixing ratio that applies for a particular sample.

Analyzing the potassium content in the Pump W, Stream N and S in the Western quarry resulted in the following mixing ratios. Pump W and Stream S consists of 6.2% and 8.1%, respectively, of water from the Landfill (Figure 42). Stream N has a different composition and consists of 0.5% of water from the Landfill (Figure 42).

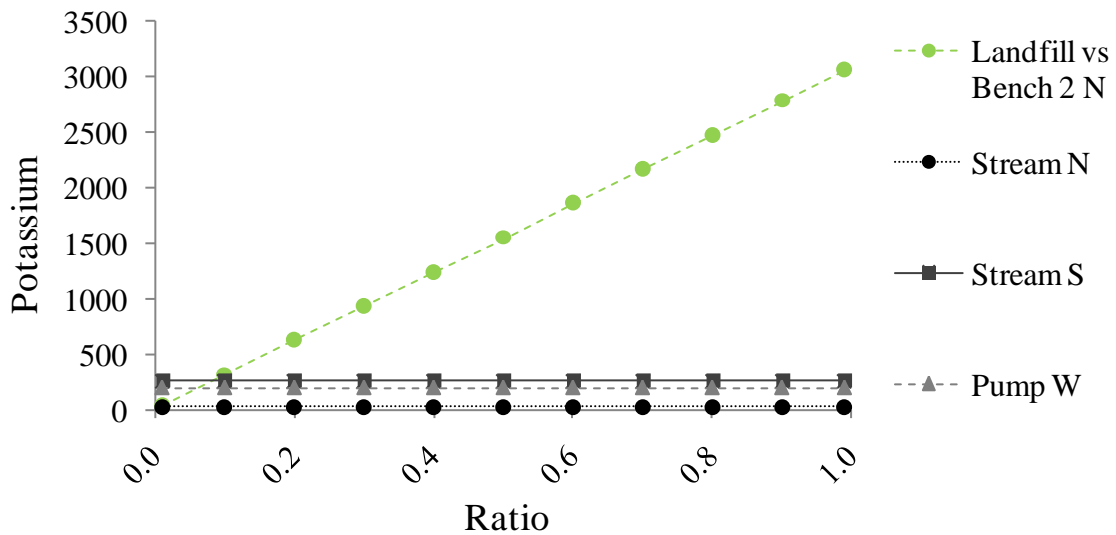


Figure 42 Mixing ratios between water from the Landfill and Bench 2 N. The actual measured value in Pump W, Stream N and S are plotted. The intersection implies the relative mixing ratio that applies for a particular sample.

The water in Stream N is almost exclusively from Bench 2 N. The mixing ratios from Bench 2 N and the Landfill are quite different for the two sampling points Pump W and Stream S. There could be another end-member contributing to Pump W and Stream S. The mixing ratio model used only consider the existance of two end-members but there could be several sources to the sampling points. Another reason for the high calcium content in the sampling point (Figure 41) could be cation exchange between potassium

and calcium. The potassium content decrease which contributes to an increase of calcium.

5.5. CALCITE PRECIPITATION AND CHARGE BALANCE ERROR

Saturation indices (SI) for calcite and the partial pressure of CO₂(g) were calculated using PHREEQC (Table 9). The SI for calcite shows that the water samples are predominantly oversaturated with respect to calcite, except for water in the wells in Tullström's investigation. However, the charge balance error for samples from Tullström's investigation (see below) is large such that no conclusions should be drawn from the results of the investigation. The calculated partial pressure of CO₂(g) shows that the water has a higher partial pressure than CO₂ in air (ca. 10^{-3.5} atm) and is a closed system with respect to exchange for CO₂ gas. The reason for the low partial pressure of CO₂(g) in the Landfill is the high pH. When there is an equilibrium in the carbonate system, a high pH results in high CO₃²⁻ which gives a low CO₂(g) concentration.

The charge balance error between anions and cations in the results from the water sampling programs Drinking water wells 23v281, National water survey, Tullström's investigation and the new sampling program have been calculated using PHREEQC (Table 9). An error within ±5% indicates that the water sample has been sampled and analyzed correctly. The percent error should be taken into consideration while interpreting the results from the water samples. Incorrect sampling can affect the pH-value but is usually insignificant. Water samples with high chloride content (e.g. seawater) can introduce analytical interferences when analyzing by ICP-MS (Inductively coupled plasma mass spectrometry) and can give a high percent error.

Bogeviken sampled 1990-02-20 was not analyzed for chloride which gives the large percent error (Table 9). The water samples from the wells in Tullström's investigation have quite large percent error which should be taken into consideration.

Table 9 Percent error and saturation indices (SI) for calcite and CO₂(g) partial pressure (P_{CO2}) calculated in PHREEQC. Unit for CO₂(g) in atm.

Date	Sampling point	pH	Error (%)	SI Calcite	log P _{CO2}
1995-04-24	23v281	7.7	2.2	0.2	-2.4
1995-09-19	23v281	7.7	2.0	0.3	-2.4
1995-10-31	23v281	7.9	-3.9	0.5	-2.5
1998-03-09	23v281	7.6	2.3	0.2	-2.3
1999-03-15	23v281	7.9	6.4	0.4	-2.6
2000-03-13	23v281	7.9	2.4	0.5	-2.6
2001-03-19	23v281	8.0	-9.4	0.4	-2.7
2002-03-12	23v281	7.8	-0.7	0.3	-2.5
2003-03-10	23v281	7.7	4.2	0.2	-2.4
2004-06-28	23v281	7.6	-0.1	0.3	-2.2
2005-07-04	23v281	7.5	2.1	0.1	-2.2
2006-07-03	23v281	7.5	2.0	0.1	-2.2
2007-07-02	23v281	8.4	-0.7	1.0	-3.1

Date	Sampling point	pH	Error (%)	SI Calcite	log P _{CO2}
1990-02-20	Bogeviken	8.4	91.2	0.7	-3.3
1995-11-06	Bogeviken	7.9	-3.2	0.0	-3.0
2000-11-08	Bogeviken	7.9	-17.4	0.0	-3.0
2005-11-10	Bogeviken	8.0	-18.3	0.2	-3.0
1990-02-20	Tingstäde träsk	8.0	3.6	0.3	-2.9
1995-11-06	Tingstäde träsk	8.0	4.7	0.1	-3.0
2000-11-08	Tingstäde träsk	7.5	1.6	-0.4	-2.5
2005-11-10	Tingstäde träsk	8.1	2.1	0.1	-3.1
1953-05-19	Well 8	7.3	-1.2	-0.3	-1.7
1951-02-20	Well 20	7.8	-49.5	-0.7	-1.8
1951-02-20	Well 27	8.1	-41.9	-0.4	-1.7
1953-05-19	Well 38	7.0	-3.0	0.2	-1.5
1953-05-19	Well 46	7.4	-17.0	-0.3	-1.6
1953-09-05	Well 51	7.7	-54.2	-1.2	-1.6
1953-09-05	Well 221	7.3	-20.2	-0.3	-1.6
1953-05-19	Well 231	7.3	-11.9	-0.2	-1.6
1953-05-19	Well 311	7.4	-2.1	-0.2	-1.6
2008-09-18	Bench 1 N	7.9	-2.9	0.5	-2.6
2008-09-18	Bench 1 NW	7.8	-10.6	0.6	-2.4
2008-09-18	Bench 2 E	8.1	-8.1	0.6	-3.0
2008-09-18	Bench 2 N	8.4	-9.0	0.8	-3.1
2008-09-18	Bench 2 NW	8.2	-9.2	0.5	-2.9
2008-09-11	Landfill	12.3	-7.1	0.9	-8.9
2008-09-11	File Hajdar	8.4	-3.5	1.0	-3.1
2008-09-18	Harbour	8.2	-8.2	-0.2	-3.6
2008-09-11	Pump E	8.4	-14.4	0.9	-3.2
2008-09-11	Pump W	8.3	-5.4	0.5	-3.3
2008-09-11	Sed. Pond	8.5	-5.8	0.6	-3.6
2008-09-11	Stream N	8.4	-13.5	0.8	-3.2
2008-09-11	Stream S	8.5	-5.2	0.5	-3.6
2008-10-24	Bench 1 N	8.2	1.9	0.9	-2.9
2008-10-24	Bench 1 NW	8.3	0.8	1.0	-3.0
2008-10-24	Bench 2 E	8.3	-11.3	0.7	-3.2
2008-10-24	Bench 2 N	8.5	-2.8	0.9	-3.2
2008-10-24	Bench 2 NW	8.4	-5.7	0.8	-3.2
2008-10-24	Landfill	12.3	-3.4	2.1	-9.0
2008-10-24	File Hajdar	8.3	3.3	1.1	-3.0
2008-10-24	Harbour	8.1	-4.6	0.0	-3.3
2008-10-24	Pump E	8.2	-5.7	0.8	-3.1
2008-10-24	Pump W	8.2	-3.3	0.5	-3.2
2008-10-24	Sed. Pond	8.6	-5.8	0.6	-3.7
2008-10-24	Stream N	8.4	-2.7	0.9	-3.2
2008-10-24	Stream S	8.3	-5.0	0.5	-3.3

5.6. FLUCTUATIONS AND TENDENCIES

Results from sampling in the National water survey and Drinking water wells were visually analyzed for fluctuations and tendencies in the data for the time periods 1990-2005 and 1995-2007, respectively. The data were not statistically analyzed because of the low frequency of sampling. Following temporal fluctuations and tendencies have been recognised:

Increase in concentration or level = (+), decrease in concentration or level = (-), fluctuation for example first a large increase and later a smaller decrease = (++-):

- Conductivity: Bogevisken (+)
- pH: Bogevisken (-), Drinking water wells 23v281 (+)
- Alkalinity: Bogevisken (-), Tingstäde träsk (-), Drinking water wells 23v281 (+)
- Chloride: Bogevisken (-)
- Sulphate: Bogevisken (++-), Tingstäde träsk (-)
- Nitrate and nitrite: Tingstäde träsk (-)
- Ammonium: Bogevisken (+), Tingstäde träsk (--+)
- Calcium: Tingstäde träsk (-)
- Magnesium: Bogevisken (+-)
- Potassium: Bogevisken (++-)
- Sodium: Bogevisken (--)

The fluctuations and tendencies predominantly concern Bogevisken and Tingstäde träsk and are probably not caused by limestone quarrying in Slite. There are only four sampling occasions over a time period of 15 years in the National water survey which make any conclusions concerning trends hard to make. The alkalinity and pH have slightly increased in the Drinking water wells 23v281 over the last 12 years but no conclusions can be made concerning reason. Theoretically, an explanation of the slight increase in alkalinity and pH can be the decrease in groundwater withdrawal during the last 10 years by the Gotland municipality in the Drinking water wells. The groundwater stays in the bedrock for a longer time which gives more time for calcite to dissolve. This results in an increase in alkalinity and pH.

Continued sampling in the Drinking water wells is needed to follow up any changes in drinking water quality caused by the extended quarrying in File Hajdar quarry but also in the Western quarry. The groundwater level in the surroundings of the Western quarry will probably not be significantly lowered since there will only be a horizontal expansion of the quarry. File Hajdar quarry will be expanded both horizontally and vertically, but not below mean sea level. The groundwater level in the surroundings of the File Hajdar quarry can decrease. Since the quality of water trickling into File Hajdar is relatively good, a possibility can be to return the water to the system downstream to minimize any affect on the surroundings due to decline in groundwater level. Saltwater intrusion in the File Hajdar quarry will probably not be an issue, and if so the origin is most likely relict saltwater from the Littorina Sea. If the origin of the saltwater seepage into the Western quarry is the Baltic Sea, the chloride content in the water flowing in the quarry will most likely not change. If the saltwater seepage into the Western quarry is caused by flushing of a relict saltwater aquifer, the chloride concentration in the water in the Western quarry will almost certainly decrease with time. Continued sampling in the Western quarry and File Hajdar quarry is necessary to follow up changes in water composition, and the analysis of oxygen and hydrogen isotopes could give an indication of the age of the water trickling into the quarries.

6. CONCLUSIONS

Using the water type classification from Appelo & Postma (2005), water samples from the following sampling locations are classified as freshwater:

- Bench 1 N and NW in the Western quarry
- File Hajdar quarry

Since the groundwater in Gotland is considered young groundwater, the groundwater in Bench 1 N and NW in the Western quarry and File Hajdar quarry could be considered young groundwater.

Water samples classified as impacted by seawater are from the sampling locations:

- Bench 2 E, N and NW in the Western quarry
- Pump E and W in the Western quarry
- Sedimentation pond in the Eastern quarry
- Stream S in the Western quarry

The origin of seawater influence in Bench 2 E, N and NW is probably the Baltic Sea or a relict saltwater with a similar groundwater composition. Bench 2 E has a larger mixing ratio of seawater than Bench 2 N and NW but no conclusions could be drawn about the exact relative amount.

Water samples from the Landfill in the Western quarry contain high concentrations of both potassium and sodium but also chloride; this result stands out in the Piper diagram. The high concentration of alkalis, potassium and sodium are a result of the waste products from the by-pass filter from the cement process. The waste products also contain chloride which explains the high chloride concentration. Because of the high chloride concentration caused by the waste products, it is difficult to draw any conclusions with regard to high chloride concentrations caused by saltwater influence of relict saltwater or seawater.

The temporal fluctuations and tendencies primarily concern Boge Viken and Tingstäde träsk and are probably not caused by limestone quarrying in Slite. The alkalinity and pH have slightly increased in the Drinking water wells 23v281 over the last 12 years but no conclusions can be made concerning reason.

The expansion of the Western quarry will probably not affect the surroundings significantly. The continued quarrying in File Hajdar can result in a decline in groundwater level in the surroundings but the water trickling into the quarry is of relatively good quality and can be returned to the system downstream. Continued sampling is needed in the Drinking water wells, Western quarry and File Hajdar quarry to follow up any changes in water composition and to indicate the origin of saltwater seepage into the Western quarry.

Faced with the up-coming application to the Environmental Court, Cementa AB wants to obtain a better understanding regarding the groundwater and surface water interactions in the area and the quality of the inflowing groundwater to the quarries. The results from this Master thesis will be used to create a better understanding of the area.

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PERSONAL COMMUNICATION

Nyberg, Kerstin, Environmental manager, Cementa AB in Slite, 2008-12-08.

APPENDIX 1: NATURE RESERVES AND NATURA 2000

Name	Code	Type	Area	General description	Quality
Bojsvätar	SE0340118	Lacks specific area protection (100%)	0.454 km ²	Open fen area	Peat land- and forest area with characteristic flora
Filehajdar	SE0340111	Lacks specific area protection (5%), Nature reserve (95%)	0.643 km ²	Wooded limestone pavements	Rich area for lichen <i>Evernia divaricata</i>
Grodvät	SE0340141	Lacks specific area protection (100%)	0.240 km ²	Spring fen characterized wetland area	The area has probably Sweden's richest population of <i>Eurphrasia salisburgensis</i> ssp <i>schoenicola</i> (brun ögontröst) and has a rich spring fen flora
Hejnum Kallgate	SE0340147	Lacks specific area protection (100%)	9.53 km ²	Mosaic of calcareous clay wetland and coniferous swamp forest	Biggest wetland on the island of Gotland. Calcareous-rich wetland with intact hydrology
Kallgateburg	SE0340103	Nature reserve (100%)	1.155 km ²	Open alkaline fen with rich flora	Spring fen flora, rich in species
Tiselhagen	SE0340066	Lacks specific area protection (3%), Nature reserve (97%)	0.126 km ²	Forest area dominated by old pine forest and swamp woods	Forest area with rich flora and rich birdlife

APPENDIX 2: ANALYZING METHODS

Parameter	Unit	Measurement error	Method/Standard
Conductivity	mS/m	± 10 %	SS EN 27888
pH		± 3 %	SS 028122-2. Titro.
Alkalinity	as mg HCO ₃ /l	± 10 %	SS-EN ISO 9963-2
Chloride, Cl ⁻	mg/l	± 15 %	Konelab
Sulphate, SO ₄ ²⁻	mg/l	± 15 %	Konelab
Nitrate-nitrogen, NO ₃ ⁻	mg/l	± 20 %	Konelab
Ammonium-nitrogen, NH ₄ ⁺	mg/l	± 15 %	Konelab
Calcium, Ca ²⁺	mg/l	± 15 %	ICP-AES
Magnesium, Mg ²⁺	mg/l	± 20 %	ICP-AES
Potassium, K ⁺	mg/l	± 20 %	ICP-AES
Sodium, Na ⁺	mg/l	± 20 %	ICP-AES

All analyzes was performed at the laboratory Eurofins in Lidköping.

APPENDIX 3: DATA

Previous sampling by SGU

Date	Sample type	Sampling point	pH	Alkalinity (mg HCO ₃ /l)	Chloride Cl ⁻ (mg/l)	Sulphate SO ₄ ²⁻ (mg/l)	Nitrate nitrogen (mg/l)	Calcium Ca ²⁺ (mg/l)	Magnesium Mg ²⁺ (mg/l)	Potassium Sodium K ⁺ , Na ⁺ (mg/l)
1953-05-19	Helge Tullström	Well 8	7.3	254	12	8	<2	89	1.4	0.05
1951-02-20	Helge Tullström	Well 20	7.8	211	486	13	<2	52	39	6
1951-02-20	Helge Tullström	Well 27	8.1	262	115	14	<2	64	0	2.45
1953-05-19	Helge Tullström	Well 38	7.0	422	79	92	6.2	198	6.8	0.4
1953-05-19	Helge Tullström	Well 46	7.4	350	87	22	7.5	74	30	1.4
1953-09-05	Helge Tullström	Well 51	7.7	298	51	48	<2	11	20	2.6
1953-09-05	Helge Tullström	Well 221	7.3	296	174	63	2	96	32	1.9
1953-05-19	Helge Tullström	Well 231	7.3	332	80	33	8.7	104	17.5	1
1953-05-19	Helge Tullström	Well 311	7.4	296	12	23	<2	97	7.3	0.1

Source of data: (Tullström, 1955).

The water samples which result can be found in the Table above was analyzed at two different laboratories. Wells 20, 27, 51 and 221 were analyzed at Lk.V = The Agricultural Chemical Control Station, Visby. Wells 8, 38 and 46 were analyzed at Y.G. = Y. Gamers Water Laboratory, Norrköping.

National water survey, SLU

Date	Sample type	Sampling point	Conductivity (mS/m)	pH	Alkalinity (mg HCO ₃ ⁻ /l)	Chloride Cl ⁻ (mg/l)	Sulphate SO ₄ ²⁻ (mg/l)	Nitrate nitrogen (mg/l)	Calcium Ca ²⁺ (mg/l)	Magnesium Mg ²⁺ (mg/l)	Potassium K ⁺ (mg/l)	Sodium Na ⁺ (mg/l)
1990-02-20	National water survey SLU	Bogeviken	534	8.4	198		153		94	128	25	2345
1995-11-06	National water survey SLU	Bogeviken	1050	7.9	138	3523	489	0.04	111	240	91	1778
2000-11-08	National water survey SLU	Bogeviken	1060	7.9	125	3406	468	0.02	101	178	72	1263
2005-11-10	National water survey SLU	Bogeviken	923	8.0	156	3246	420	0.09	104	180	66	1150
1990-02-20	National water survey SLU	Tingstäde träsk	28.8	8.0	143	6.8	18		56	2.0	1.0	3.1
1995-11-06	National water survey SLU	Tingstäde träsk	23.7	8.0	110	8.6	17		45	2.2	0.8	4.2
2000-11-08	National water survey SLU	Tingstäde träsk	24.4	7.5	116	7.3	14		42	2.2	0.9	4.0
2005-11-10	National water survey SLU	Tingstäde träsk	22.1	8.1	110	7.4	14		40	2.3	1.0	4.3

Source of data: (Institutionen for Water and Environment, SLU) ([www.info1.ma.slu.se/ri/www_ri_acgi\\$Project?ID=Intro](http://www.info1.ma.slu.se/ri/www_ri_acgi$Project?ID=Intro), 2008-10-28)

Gotland Municipality: Drinking water wells

Date	Sampling point	Sample point description	Conductivity (mS/m)	pH	Alkalinity (mg HCO ₃ ⁻ /l)	Chloride Cl ⁻ (mg/l)	Sulphate SO ₄ ²⁻ (mg/l)	Nitrate nitrogen (mg/l)	Nitrite nitrogen (mg/l)	Ammonium nitrogen (mg/l)	Calcium Ca ²⁺ (mg/l)	Magnesium Mg ²⁺ (mg/l)	Potassium K ⁺ (mg/l)	Sodium Na ⁺ (mg/l)
1995-04-24	23v281	Drinking water	50.9	7.7	258	10	28	<1	0.004	<0.01	55	20	2	20
1995-09-19	23v281	Drinking water	51.5	7.7	280	13	19	<1	<0.001	<0.01	66	18	2	17
1995-10-31	23v281	Drinking water	52.2	7.9	298	13	25	<1	<0.001	0.02	66	17	2	14
1996-09-16	23v281	Drinking water	52.2	7.7	288				<0.001	<0.01				
1998-03-09	23v281	Drinking water	50.7	7.6	273	10	24	<0.2	<0.002	<0.02	63	16	2.9	22
1998-05-05	23v281	Drinking water	45.2	7.6	251				<0.002	<0.02				
1998-11-02	23v281	Drinking water	52.4	7.6	256				<0.002	<0.02				
1999-03-15	23v281	Drinking water	47.2	7.9	252	8	21	<0.2	<0.002	<0.02	62	17	2.5	20
1999-11-08	23v281	Drinking water	52.4	7.9	300				0.001	0.03				
2000-03-13	23v281	Drinking water	44.2	7.9	264	11	23	<1.0	<0.001	<0.01	77	12	2	11
2000-11-06	23v281	Drinking water	52.6	7.7	287				0.001	0.03				
2001-03-19	23v281	Drinking water	48.0	8.0	266	10	26	<1.0	<0.001	<0.01	48	14	3	16

Date	Sampling point	Sample point description	Conductivity (mS/m)	pH	Alkalinity (mg HCO ₃ ⁻ /l)	Chloride Cl ⁻ (mg/l)	Sulphate SO ₄ ²⁻ (mg/l)	Nitrate nitrogen (mg/l)	Nitrite nitrogen (mg/l)	Ammonium nitrogen (mg/l)	Calcium Ca ²⁺ (mg/l)	Magnesium Mg ²⁺ (mg/l)	Potassium K ⁺ (mg/l)	Sodium Na ⁺ (mg/l)
2002-03-12	23v281	Drinking water	49.0	7.8	277	10	21	<1.0	0.002	<0.01	60	16	2	19
2002-11-05	23v281	Drinking water	49.8	7.7	291				<0.001	<0.01				
2003-03-10	23v281	Drinking water	46.8	7.7	269	9	23	<1.0	<0.001	0.02	64	18	3	19
2003-11-03	23v281	Drinking water	51.8	7.6	290				<0.001	0.01				
2004-03-15	23v281	Drinking water	57.2	8.2	292				<0.001	0.04				
2004-06-28	23v281	Drinking water	51.7	7.6	296	13	21	<1.0	<0.001	0.008	75	14	2	16
2004-11-01	23v281	Drinking water	51.4	7.5	308				0.001	<0.01				
2005-07-04	23v281	Drinking water	44.0	7.5	281	10	23	<0.1	<0.001	<0.01	69	16	2	18
2005-11-08	23v281	Drinking water	51.4	7.3	282				0.001	<0.01				
2006-07-03	23v281	Drinking water	43.4	7.5	271	15	28	<1.0	<0.001	<0.01	67	16	2	22
2006-11-06	23v281	Drinking water	58.0	8.1	288						73	18		
2007-07-02	23v281	Drinking water	54.0	8.4	292	24	31				68	17	2.3	27
2007-11-06	23v281	Drinking water	61.0	8.2	303						67	22		

Source of data: Jonas Aaw, Gotland Commune.

New control programme

Date	Sampling point	Conductivity (mS/m)	pH	Alkalinity (mg HCO ₃ ⁻ /l)	Chloride Cl ⁻ (mg/l)	Sulphate SO ₄ ²⁻ (mg/l)	Nitrate nitrogen (mg/l)	Ammonium nitrogen (mg/l)	Calcium Ca ²⁺ (mg/l)	Magnesium Mg ²⁺ (mg/l)	Potassium K ⁺ (mg/l)	Sodium Na ⁺ (mg/l)
2008-09-18	Bench 1 N	58	7.9	280	16	77	<0.1	0.05	82	16	3.9	18
2008-09-18	Bench 1 NW	62	7.8	320	15	89	<0.1	0.38	97	9.7	3.7	10
2008-09-18	Bench 2 E	730	8.1	210	2300	490	0.16	<0.01	150	150	150	1000
2008-09-18	Bench 2 N	160	8.4	260	430	45	0.11	0.15	57	28	9.4	210
2008-09-18	Bench 2 NW	150	8.2	260	370	48	<0.1	0.27	51	25	9	190
2008-09-11	Landfill	1500	12.3	1500	2100	1500	0.15	0.16	3.3	<0.5	3300	360
2008-09-11	File Hajdar	65	8.4	240	13	150	2.4	0.23	110	12	5.7	8
2008-09-18	Harbour	1100	8.2	63	4000	520	<0.1	0.03	75	210	97	1900
2008-09-11	Pump E	290	8.4	210	930	210	<0.1	0.07	130	59	36	310
2008-09-11	Pump W	390	8.3	140	1100	400	0.47	0.07	96	49	340	460
2008-09-11	Sed. Pond	370	8.5	130	1000	390	1.4	0.09	76	48	360	400
2008-09-11	Stream N	190	8.4	210	540	160	0.31	0.1	79	32	30	220
2008-09-11	Stream S	450	8.5	120	1100	510	0.67	0.07	81	45	490	440

Date	Sampling point	Conductivity (mS/m)	pH	Alkalinity (mg HCO ₃ ⁻ /l)	Chloride Cl ⁻ (mg/l)	Sulphate SO ₄ ²⁻ (mg/l)	Nitrate nitrogen (mg/l)	Nitrite nitrogen (mg/l)	Ammonium nitrogen (mg/l)	Calcium Ca ²⁺ (mg/l)	Magnesium Mg ²⁺ (mg/l)	Potassium K ⁺ (mg/l)	Sodium Na ⁺ (mg/l)
2008-10-24	Bench 1 N	65	8.2	260	24	110	<0.1	0.005	0.21	110	13	4	19
2008-10-24	Bench 1 NW	60	8.3	280	21	70	0.11	0.004	0.07	89	16	4.1	20
2008-10-24	Bench 2 E	790	8.3	180	2500	520	0.14	<0.002	0.07	170	87	160	1100
2008-10-24	Bench 2 N	160	8.5	270	380	52	<0.1	0.013	0.17	57	28	8.7	230
2008-10-24	Bench 2 NW	260	8.4	240	780	49	0.29	0.031	0.18	73	39	11	390
2008-10-24	Landfill	1400	12.3	1400	2000	1400	0.11	0.35	0.15	64	<0.5	3100	440
2008-10-24	File Hajdar	74	8.3	260	12	180	3.5	0.037	1.2	140	16	4.3	10
2008-10-24	Harbour	1200	8.1	96	3900	570	<0.1	0.002	0.04	95	230	88	2000
2008-10-24	Pump E	360	8.2	200	1100	250	<0.1	0.003	0.11	170	83	38	440
2008-10-24	Pump W	330	8.2	150	830	370	1	0.011	0.1	120	58	200	360
2008-10-24	Sed. Pond	360	8.6	120	1000	400	1.7	0.03	0.25	84	61	340	380
2008-10-24	Stream N	200	8.4	230	490	150	0.19	0.004	0.16	90	45	24	250
2008-10-24	Stream S	310	8.3	140	750	430	1.2	0.018	0.14	99	43	260	330

Source of data: Cementa AB