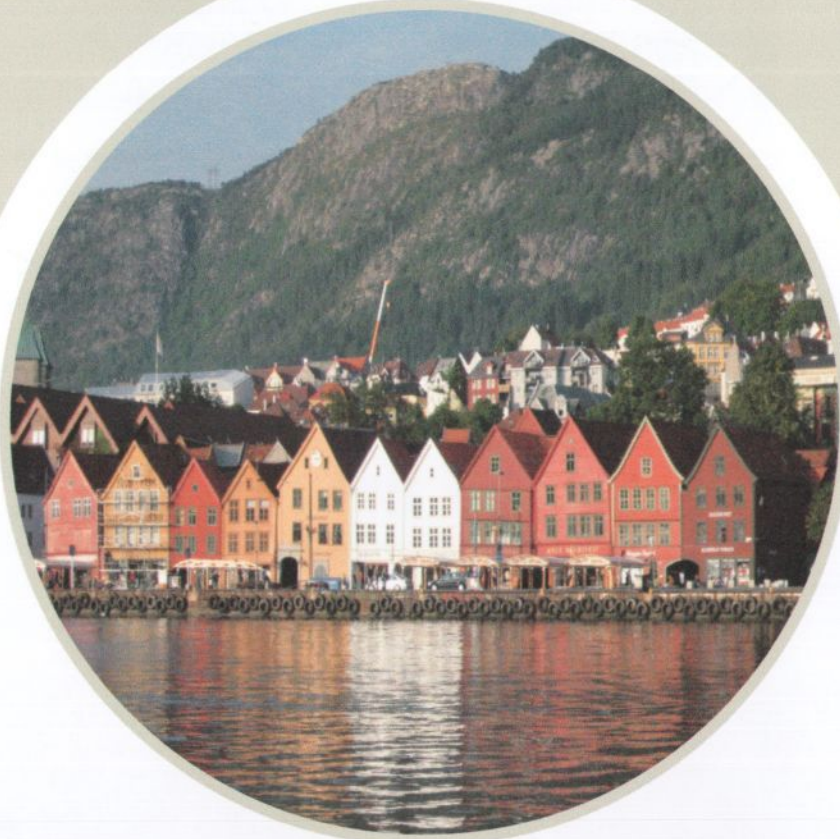




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Composition of soil and
groundwater in dipwells
MB24, 25, 26, 27 and FB1
at the quay front of
Bryggen, Bergen



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Title:
Composition of soil and groundwater in dipwells MB24, 25, 26, 27 and FB1 at the quay front of
Bryggen, Bergen

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Summary:

Four new dipwells and one multilevel piezometer were installed at the quay front in the Bryggen area in September 2007, as described in Dunlop (2008). Soil samples from the installation of dipwells MB24, 25 and FB1 have been analysed by Bioforsk, and water was sampled from all dipwells in May 2008 and analysed by Eurofins. The results are presented and commented on in this report, with special emphasis on sulphate reduction in the soil.

The analyses indicate different water flow patterns in different layers at the quay front: The soil surface is found at approximately 1 m asl, the ground water table is found at 0 m asl, and the deposits down to approximately -4 m asl are relatively porous with a good access of sulphate rich seawater. Between -4 and -7 m asl the deposits are more compact and their chemical signature indicates stagnant conditions. Beneath -7 m asl is found a layer of ooze and natural deposits which seem to have less stagnant conditions with a flow of fresh water.

Bioforsk has measured potential sulphate reduction rates in eight soil samples from different depths and found high rates for all samples except one. The reduction rates were measured by adding sulphate to the samples in the laboratory and measuring how fast it disappeared.

As for the preservation conditions, the layers above -2 m asl are modern and not of interest in an archaeological context. The layers between -2 and -4 m asl are organic in a poor to medium state of preservation, and prone to a substantial decay by sulphate reduction: The laboratory experiments show that up to 1/4-1% of the organic material in the soil may be oxidised per year, which in theory means that the material may be gone within a few centuries. Between -4 and -7 m asl the sulphate reduction is probably limited by the supply of sulphate, which cannot be estimated yet. The conditions beneath -7 m asl are also difficult to assess before we have an estimate of the water exchange rate, but sulphate reduction is probably not significant at this depth.


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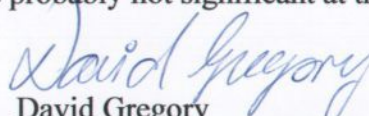

David Gregory
Control

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Appendix 1: Results from analysis of soil samples (Bioforsk, Thomas Hartnik)

Appendix 2: Results from analysis of sulphate reduction activity (Bioforsk, Roar Linjordet)

Appendix 3: Results from analysis of water samples (Eurofins)

Introduction

The buildings at the seaward facade of Bryggen are presently being restored. In this context it is important to assess the state of preservation and possible threats against the foundations and the cultural layers underneath the buildings. Especially the effect of seawater intrusion and sulphate reduction has been discussed (Matthiesen et al, 2008).

Four new dipwells and one multi level piezometer were installed in September 2008 in order to get a better overall picture of the quay front area (Figure 1). The National Museum of Denmark has been contracted by Riksantikvaren to evaluate the conditions of and threats to the cultural layers at these dipwells based on results from analyses of soil and water. The water samples are further discussed in Matthiesen (2008), where the results from a simultaneous sampling from all dipwells on Bryggen in May 2008 are compared.

Site and methods

The new and old dipwells on Bryggen are shown in Figure 1.

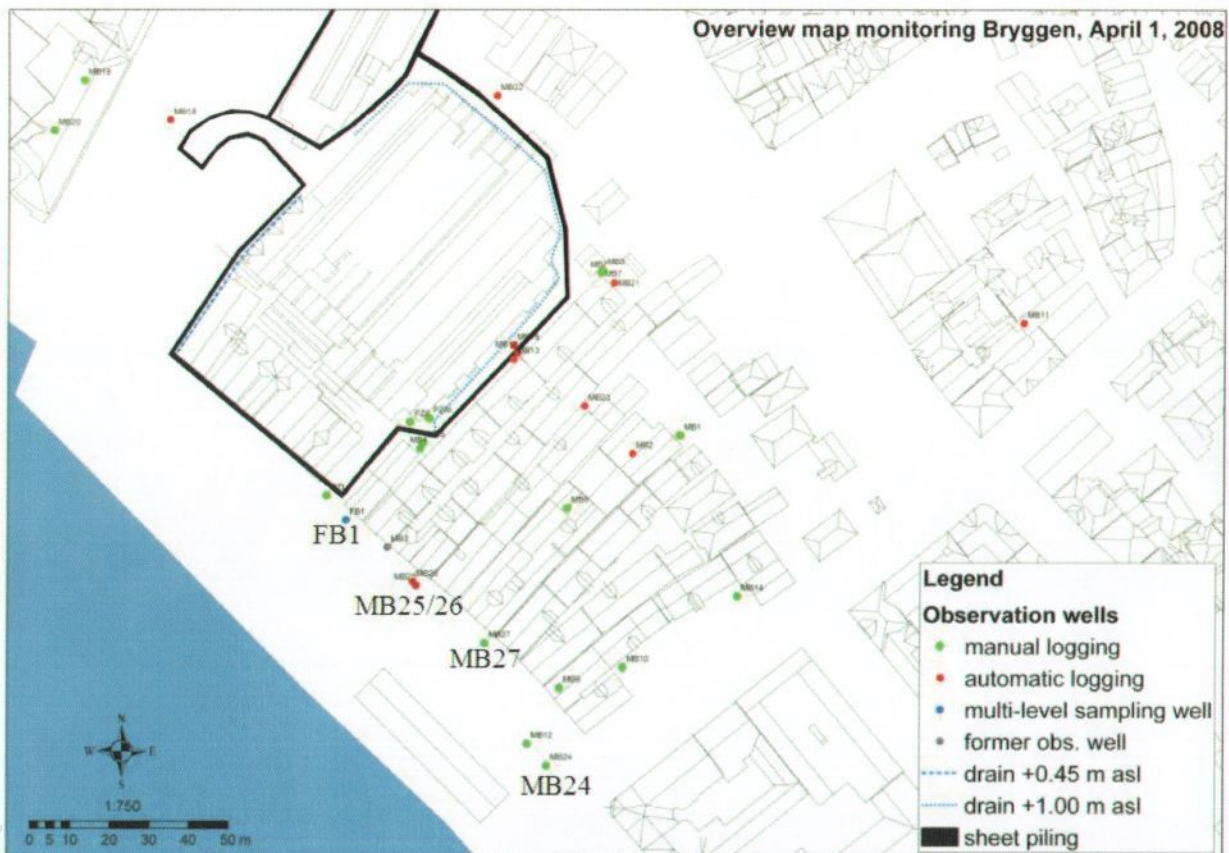


Figure 1: Map of Bryggen, showing the position of MB24-27 and FB1 at the quay front area. Other dipwells are marked as well. Map from Hans de Beer, NGU

In September 2007 the drilling work was made by Multiconsult avd. NOTEBY and archaeologist Rory Dunlop from the Norwegian Institute for Cultural Heritage Research (NIKU), with participation of Ove Bergensen from Bioforsk. The soil stratigraphy was described by Dunlop (Dunlop, 2008). Eight soil samples from MB24 and MB25 were sampled by Bioforsk during the drilling work and analysed for pH, water content, loss on ignition (LOI), water-soluble chloride, total sulphur, nitrogen and phosphorus, nitrate, ammonium, sulphate, acid volatile sulphide, iron(II) and (III), conductivity, and sulphate reduction activity. A further eight samples were taken by Dunlop during the installation of FB1, and sent to Bioforsk for analysis for the same parameters (except sulphate reduction activity). Four samples were taken from MB27, but they have not been analysed. Methods and results from Bioforsk are included as Appendix 1 and 2.

The position of the dipwells along with the level of their water intake is given in Table 1.

Dipwell	Y-COORD.	X-COORD.	Height of top (m asl)	Water intake – top (m asl)	Water intake – bottom (m asl)
MB24	297486.335	6701252.996	1.22	-2.46	-3.46
MB25	297453.172	6701298.498	1.00	-6.96	-7.96
MB26	297452.340	6701299.369	0.97	-3.86	-4.86
MB27	297470.672	6701283.982	0.93	-4.07	-5.07
FB1 multilevel	297435.437	6701315.099	1.00	-0.50/-2.00/-3.50/ -5.00/-6.50/-8.00	

Table 1: Position of dipwells (data from Multiconsult/NGU).

On the 20th-29th of May 2008 water was sampled from the dipwells by Multiconsult. The dipwells were emptied before the actual sampling, to ensure that fresh water from the cultural layers was sampled. The water samples were filtered in the field (0.45 µm Gelman high capacity in-line filter) and oxygen, temperature, pH and conductivity were measured in the field.

The samples were sent to the laboratory (Eurofins) and analysed for alkalinity, salt (sodium, chloride), nutrients (ammonium, nitrate, phosphate), redox active species (sulphate, nitrate, dissolved iron, dissolved manganese, sulphide, methane), and other major ions (calcium, magnesium, potassium), which gives a good description of the chemical conditions in the groundwater. The results are compiled in Appendix 3, and the original laboratory reports (ca 40 pages) are available on request.

Results

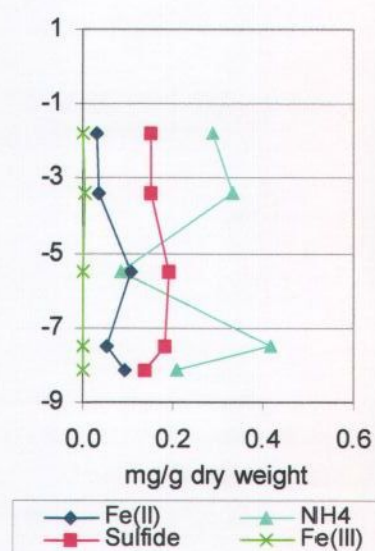
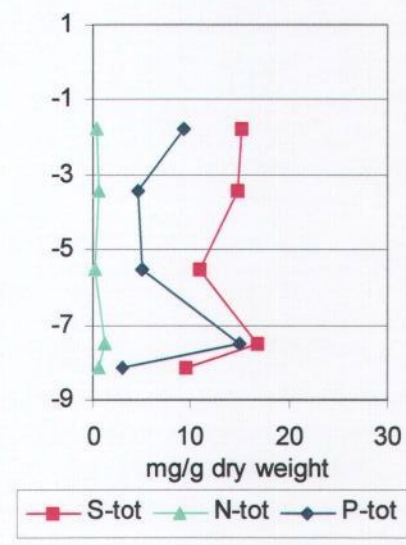
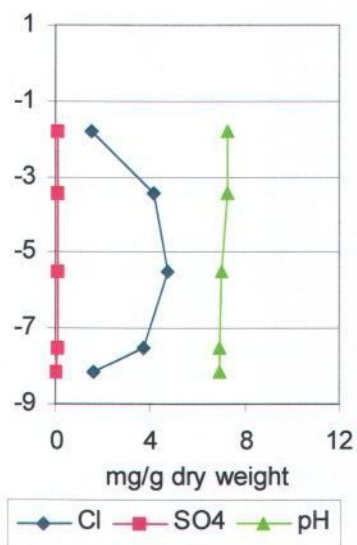
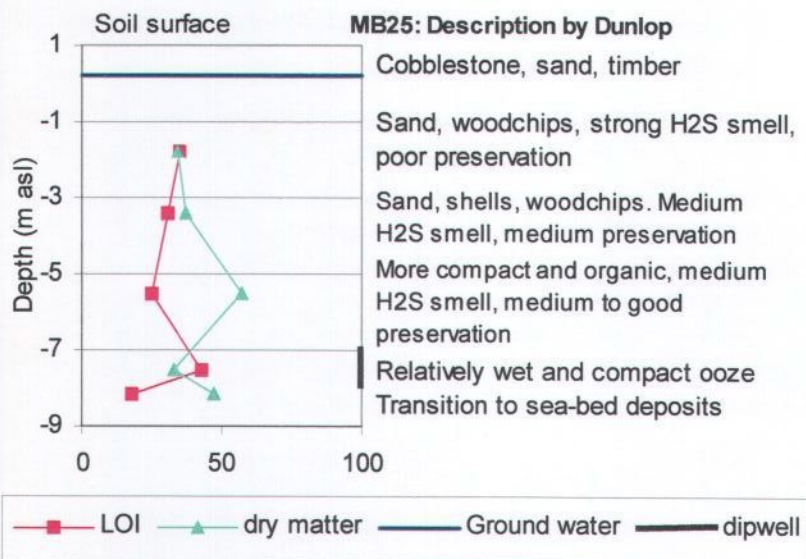
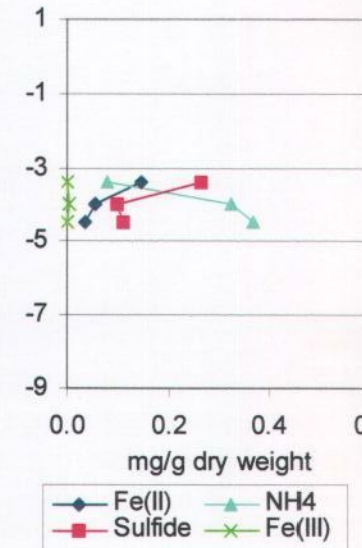
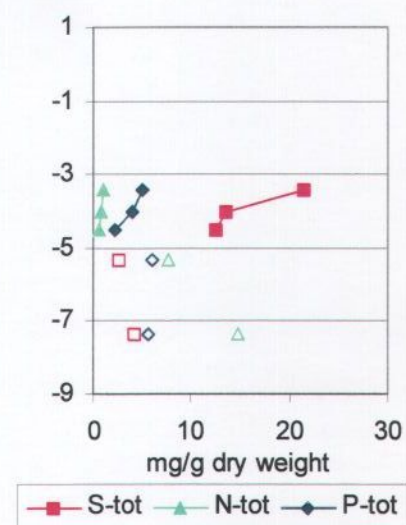
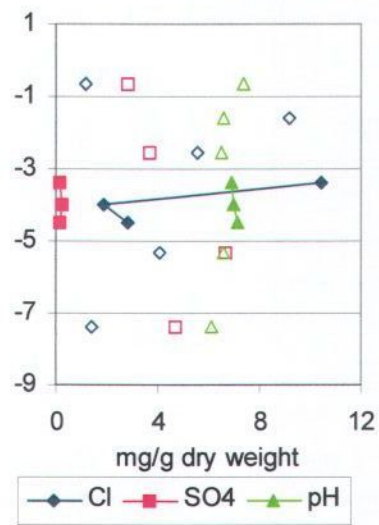
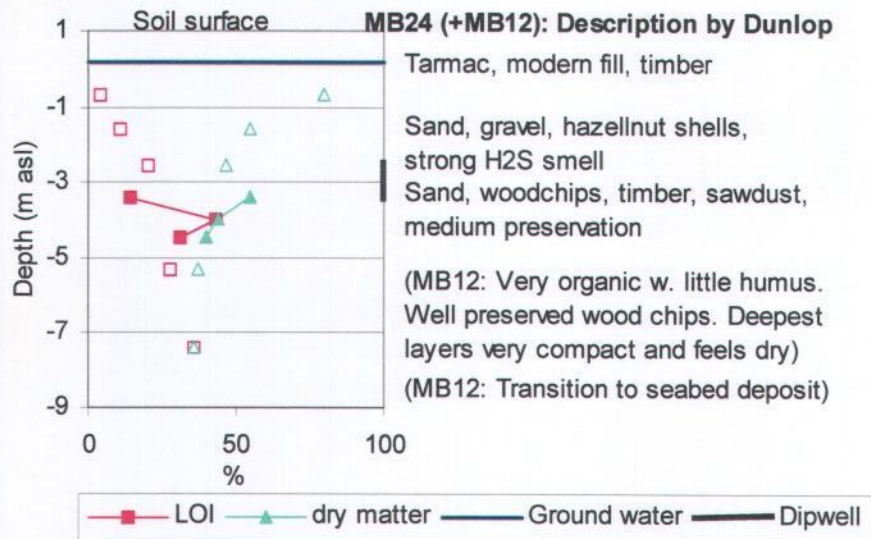
The results from the soil analyses from MB24, MB25 and FB1 are presented in Figure 2. The graphs of MB24 also include earlier results from MB12 (open symbols), which is situated next to

MB24 – the soil samples from MB12 were analysed by Eurofins in 2006 and are discussed in Matthiesen (2006). Results from measurements of sulphate reduction rates are presented in Figure 3. Results from the water samples from May 2008 are presented in Figure 4, where both new and old dipwells from the quay front are included.

A note about the units used: Dissolved species are given as “mmol/L” to allow an easy evaluation of the ion balance in the water and a good overview of their quantitative importance. Results from soil analysis are, on the other hand, normally presented as mg / g dry matter. Where it is necessary to make a direct comparison, the recalculation is made in the text.

The soil analyses presented in Figure 2 have been processed by Bioforsk and performed by AnalyCen, whereas earlier analyses of soil from Bryggen have been made by Eurofins. In principle this shouldn't influence the results, but there are some remarkable differences that should be noted: The results from water soluble SO_4 : This has earlier been analysed in MB10, 12, 13, 18, and 21, giving results between 0.6 and 9 mg SO_4 /g, which is similar to the results presented here for FB1. However, in MB24 and MB25 much lower levels of 0.02 to 0.2 mg/g are found. Of course this difference can be real (for instance due to local differences in the soil, or due to temporal variation in the sulphate content) but it could also be an artefact due to the sample handling: People from Bioforsk were present during drilling of MB24 and MB25 and they were able to keep the samples under anoxic conditions from the sampling until analysis. For FB1 samples were sent to the lab later, which has also been the case for all earlier drillings. It may be speculated if the higher sulphate levels found in FB1 and earlier drillings are due to an unwanted oxidation of sulphur species during handling and storage of the samples – this would give a production of sulphate and often also lower the pH of the samples.

The results for N-tot are also remarkably low for MB24 and MB25: Here the levels are 0.3-1 mg/g, giving estimated C/N ratios in the soil of 60-500. For comparison all earlier soil samples (and FB1) have had N-contents of 1-20 mg/g and the vast majority have had C/N ratios between 15 and 30. No explanation has been found yet, as storage of samples from FB1 would be expected to decrease, rather than increase, the N-content.



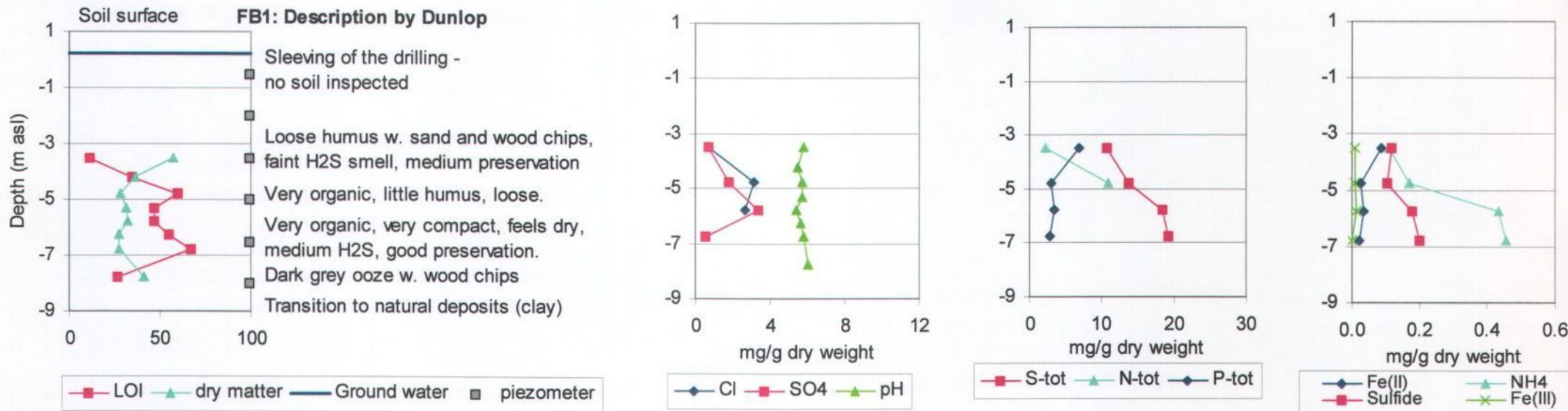


Figure 2: Description and soil analyses of drillings MB24, MB25 and FB1. Results from MB12 are included (with open symbols) in the graphs for MB24, as the two dipwells are situated next to each other. The nitrate content was measured as well, but was below the detection limit for all soil samples. Fe(II) and Fe(III) is the acid extractable fraction (0,5 M HCl) and sulphide is Acid volatile sulphide (6 M HCl). The soil surface is approximately 1 m asl for all the dipwells.

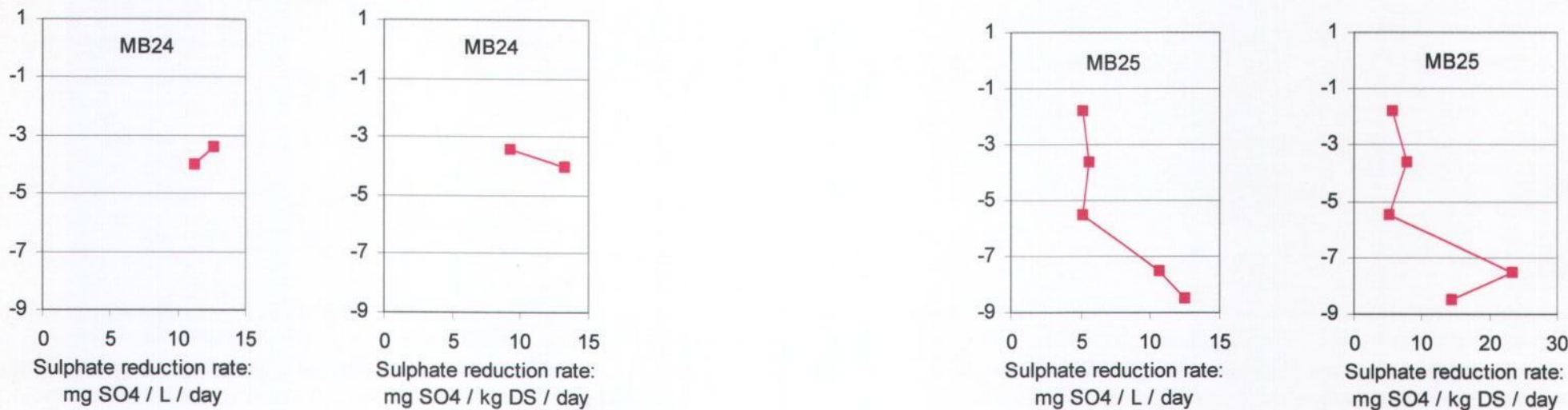


Figure 3: Results from measurements on sulphate reduction rates at Bioforsk (Appendix 2). Soil samples were incubated with seawater and the loss of sulphate measured after 32 days. Results are given both as the decrease in sulphate concentration in the water (mg/L), and recalculated in terms of the amount of dry matter in the soil (mg/kgDS).

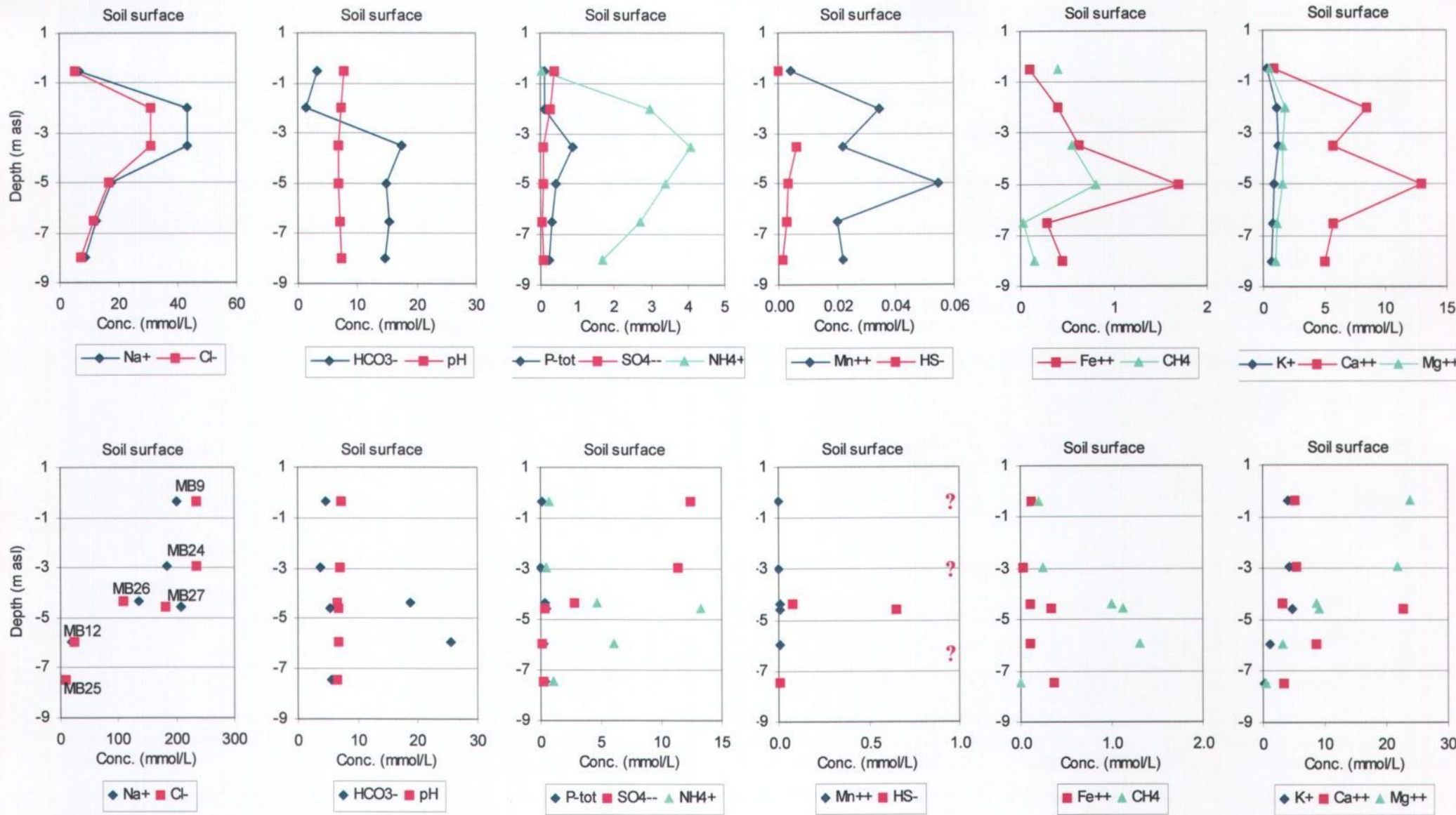


Figure 4: Results from analysis of water samples from 20th-29th of May, 2008. Upper row gives results from FB1 and lower row gives results for other dipwells at the quay front – here the middle of the filter is used as depth. Note different x-scales for some of the graphs. For HS⁻ the laboratory gave the results as “too high for analysis” for MB9, 12, and 24 (indicated by question marks in the graph). For FB1 the second piezometer (at -2 m asl) didn't give enough water to allow for HS⁻ and CH₄ analysis.

Discussion

Organic content, water table, and settling potential

Figure 2 (left) shows the organic content of the soil from drillings MB24, MB25, and FB1 along with a description of the different soil strata by Dunlop (2008). Generally, the upper 2-3 m consist of modern material (asphalt, cobblestone, sand, timber) that has not been analysed. The organic content is moderate down to approximately -4 m asl and the state of preservation is described as poor to medium (C2-C3). Beneath this depth the organic content of the soil is higher and the state of preservation is medium to good (C3-C4). A layer of ooze is found at -7 m asl (in two of the drillings) and natural sediment begin around -8 m asl. None of the deposits at the quay front have been classified as "excellent state of preservation" (C5).

MB24: is situated close to the harbour, next to a new 5 metre deep sewage pumping station. Down to approximately -3 m asl it is characterised by a sandy deposit with an un-definable or poor state of preservation and a strong smell of hydrogen sulphide. At -2.3 to -2.8 m asl a dark fatty substance is encountered, which Dunlop suggests comes from the sewage. Soil samples for chemical analysis have only been taken from -3.4 to -4.5 m asl, showing loss-on-ignition values of 14-43 %. These results may be compared with MB12 that is situated next to MB24.

MB12 is described in detail in Dunlop (2005) and Matthiesen (2006). Here the preservation conditions down to -1.75 m asl were described as "poor" and a strong rotten-egg stench was noted. A single soil sample from -2.55 m asl was analysed for oil, giving a content of 230 mg/kg, so oil pollution may be an alternative explanation for the "fatty substance" encountered in MB24. LOI values are 4-20% down to -3 m asl. Soil layers from beneath -3 m asl are described as very organic and with good state of preservation (LOI values 28-36%), and beneath -6 m asl the deposits are so compact that they feel dry. Transition to natural deposits at -8.25 m asl.

MB25: has a sandy deposit with timber down to approximately -3 m asl with an increasing content of organic matter towards the bottom (LOI of 35%). There is a strong H₂S smell in these upper layers. Between -3 and -7 m asl the soil is described as organic that gets more compact and better preserved with increasing depth (LOI of 25-31%). Between -7.15 a dark grey ooze (LOI 43%-18%) is found with a transition to natural seabed at -8.25 m asl

FB1: was only inspected from -3 m asl and downwards. Down to -4.55 m asl a layer of relatively loose humus with a LOI of 11-35% is found. Then follows a very organic layer, which gets more compact and "dry" with increasing depth and which has a high LOI of 47-67%. At -7.25 a dark grey ooze (LOI of 27%) is found with a transition to natural deposits at -8.40 m asl

MB26: no soil samples were taken for analysis, and it wasn't described archaeologically due to its proximity to MB25.

MB27: 4 soil samples were taken, but they haven't been analysed. The person responsible for the drilling describes the upper 2 m as cobblestone and sand, and beneath -1 m asl it is organic cultural deposits with a (very) strong H₂S odour.

At all the dipwells the ground water table is found approximately 1 m beneath the soil surface (around 0.2 m asl), which is 2-3 meters above the organic rich soil layers. The deposits at the quay front are thus not threatened by drainage, which leads to an increased oxygen access, decay of organic material, and settling of the soil surface other places on Bryggen. Approximately 0.5 mg/L oxygen was measured in water from all the dipwells (Appendix 3) but this is considered an artefact due to oxygen pollution during sampling as other species in the water indicate anoxic conditions under the water table. However, decay of the organic deposits at the quay front may take place due to other causes, which may eventually lead to settling.

Salt and seawater intrusion

Occasionally the quay front area of Bryggen is flooded, which gives a very visible input of seawater to the deposits. However, even without flooding there may be a subsurface input, and according to Hans de Beer (personal comment) seawater is intruding at the quay front whenever the waterlevel in the harbour is above 0.3 m asl, which occurs very frequently.

If seawater with a high salt content penetrates into the soil it will influence the composition of the soil pore water. The chloride content in dipwells MB9, MB24, MB26 and MB27 is indeed very high, 110-230 mmol/L (Figure 4), whereas the deeper dipwells MB12 and MB25 have much lower chloride content's (9-24 mmol/L). The same pattern is seen for the multilevel piezometer FB1, where the highest chloride contents are found between -2 and -4 m asl. For comparison the chloride content of pure seawater is 545 mmol/L at a salinity of 35 ‰. There is a good correlation between the chloride content measured in soil samples and in the dipwells (not shown).

This chloride distribution pattern may be explained by the soil strata found at the quay front: The upper layers consist of relatively loose and porous sandy deposits, where seawater can easily penetrate, either during flooding or through subsurface intrusion. The deeper layers are highly organic and compact, and it can be difficult for the seawater to be replenished. The concentration levels at FB1 are significantly lower than in the other drillings at the harbour front, but no explanation has yet been found.

The chloride data from all dipwells and soil samples from Bryggen are compiled in Figure 5.

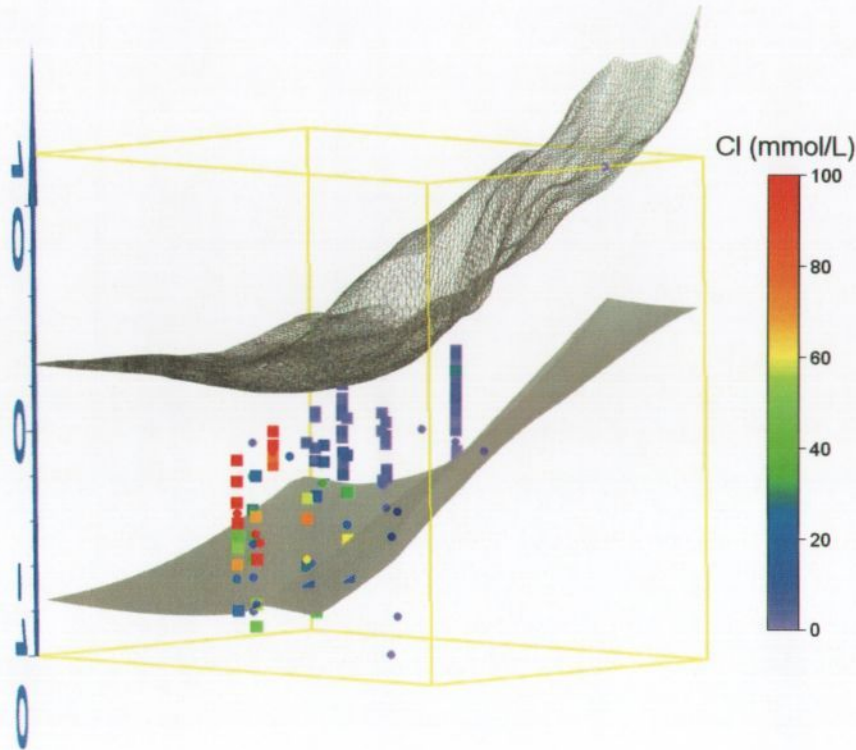


Figure 5: 3D picture of the chloride distribution in the deposits beneath Bryggen, seen from the south-east. Data from soil samples are shown as coloured squares, and data from dipwells are shown as circles. Results from soil samples have been recalculated to mmol/L using the water content of the soil. The terrain surface (black net) and the boundary to natural sediments (grey blanket) are also shown. Bounding box (yellow cube) is 345m x 174 m and z-scale is 10x exaggerated.

It is not easy to present 3D data on a 2-dimensional piece of paper. However, on the screen it is possible to rotate the picture, zoom in and out, add iso-surfaces and contour-lines, and thereby get an overview of the spatial distribution. This shows that the highest chloride contents are found near the quay-front, in the upper soil strata, and mainly in the south-eastern corner of Bryggen (near MB24). An interpolated map of the soil data projected onto a vertical profile is shown in Figure 6. Even if a single profile doesn't show the full variance it gives an idea of the distribution

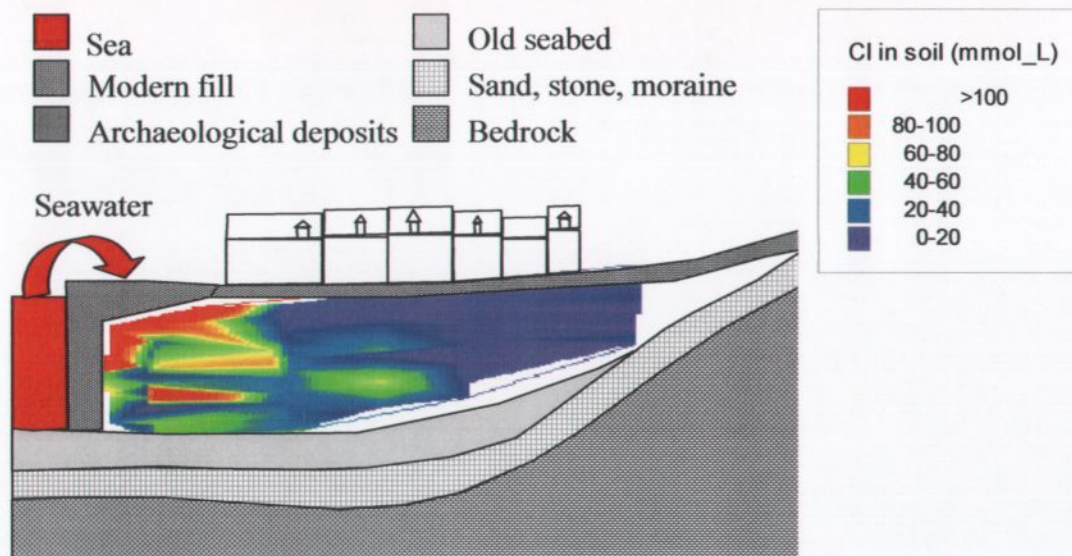


Figure 6: Draft profile of chloride concentrations measured in 136 soil samples taken beneath Bryggen 2001-2008. All data have been projected onto a single vertical profile. Figure updated from Matthiesen et al (2008).

Sulphate reduction

Sulphate reduction is the process where sulphate is used by bacteria to oxidise organic material:



presented here as a complete oxidation of organic matter (with the brutto formula CH_2O) all the way to bicarbonate/carbon dioxide. The process only gives a small energy output to the bacteria, and it is seldom considered problematic for the preservation of archaeological remains. However, the extent and effect of sulphate reduction on urban archaeological deposits have actually never been investigated in any detail.

Seawater contains both chloride and sulphate, at a fixed molar ratio of 0.052 $\text{SO}_4:\text{Cl}$ (28 mM SO_4 and 545 mM Cl at a salinity of 35 ‰). This means that whenever the quay front area is flooded with seawater, or there is a subsurface intrusion, sulphate enters the soil pore water along with the chloride. The ratio of $\text{SO}_4:\text{Cl}$ actually measured in water samples from the dipwells is given in Table 2:

Dipwell	MB9	MB12	MB24	MB25	MB26	MB27	FB1, 1.5	FB1, 3.0	FB1, 4.5	FB1, 6.0	FB1, 7.5	FB1, 9.0
$\text{SO}_4:\text{Cl}$	0.053	0.007	0.049	0.021	0.026	0.002	0.072	0.009	0.002	0.004	0.004	0.009

Table 2: Sulphate:chloride molar ratio measured in water from dipwells at the quay front

This shows, that MB9, MB24, and FB1(1.5) are close to the ratio found in seawater, MB 25 and MB26 has approximately half the expected sulphate content, and the rest of the dipwells have a much lower sulphate content than expected. There is a reasonable correspondence between the ratio found in water and in soil samples for MB24 and MB25 (not shown), whereas the sulphate content in soil samples from FB1 is remarkably high (c.f. comment in “Results”).

It is possible to calculate the “sulphate depletion” for the samples, which is defined as the amount of sulphate actually measured minus the amount that would be expected from the chloride content.

This is shown in Figure 7.

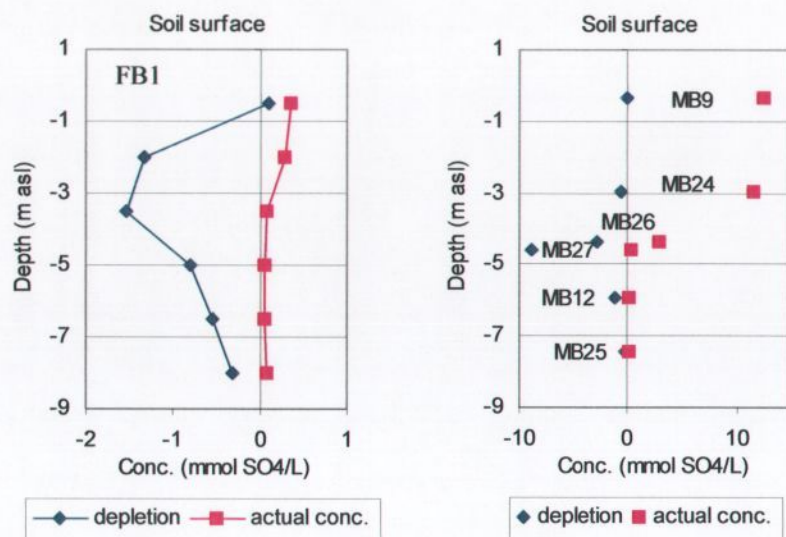


Figure 7: Sulphate depletion in water samples from May 2008, related to depth of the sample. The sulphate depletion is calculated as $[SO_4^{2-}] - 0.052 \cdot [Cl^-]$, where 0.052 is the $SO_4:Cl$ ratio normally found in seawater. The actual sulphate concentration in the water samples is included for comparison. Note different x-axis in the two graphs.

Figure 7 demonstrates that the highest sulphate depletion is found between -2 and -5 m asl.

A decrease in sulphate concentration in the soil can occur in four ways: by dilution, by precipitation of a solid sulphate species, by sorption of sulphate to positively charged soil particles, or by microbial sulphate reduction where sulphate is transformed into sulphide. As for dilution, the chloride would be diluted along with the sulphate giving no theoretical sulphate depletion. As for precipitation it has been checked that the water samples from the dipwells are not saturated regarding the normal sulphate minerals (gypsum, anhydrite, melanterite). As for sorption, there are normally only few anion exchange sites and sulphate sorption is normally of minor importance only (Christensen et al, 2001, page 688). This leaves us with the explanation that the sulphate is mainly removed by sulphate reduction.

Bioforsk have measured sulphate reduction rates in soil samples from MB24 and MB25 (Figure 3 and Appendix 2). Attempts to use radioactive $^{35}SO_4$ -tracers were not successful as the (short term) sulphate reduction rates were below the detection limit of this method. However, they also made some long term experiments, where they mixed a few grams of soil with a similar amount of seawater and followed the decrease in sulphate concentration over 32 days. This setup is considered similar to a situation where the quay front area is flooded, giving a fresh supply of sulphate to the soil.

The results showed sulphate reduction rates of 5-12 mg SO₄/L/day or 0.05-0.12 mM/day (Figure 3). Most literature values of sulphate reduction are significantly lower – for comparison Jakobsen & Cold (2007) measured rates up to 1½ mM/year (0.004 mM/day) in a sandy aquifer, and Andersen (2001) reported values of up to 5 mM/year (0.014 mM/day) in a seawater intrusion experiment in northern Sealand (page 135). However, the deposits on Bryggen are very organic, and for such sediments higher reduction rates have been found: For instance the author of this report calculated sulphate reduction rates of up to 0.28 mM/day in a fast accumulating organic sediment from the Baltic (Matthiesen et al, 1998) and Zaggia et al (2007) measured rates between 0.26 and 0.99 mM/day in sediments from the canals in Venice. The rates of 0.05-0.12 mM/day measured by Bioforsk for the deposits on Bryggen are thus not considered unrealistically high.

The rates can be put into perspective by comparing with the sulphate depletion in the pore water: MB27 was found to have a high sulphate depletion of -9 mmol/L (Figure 7), but at these rates such a depletion can arise in only 3-6 months.

When the sulphate reduction rates are compared to the amount of dry substance in the soil samples, the rates may be given as 5-24 mg SO₄/kg dry substance/day, which may oxidize 3-15 mg organic matter/kg/day (Appendix 2, Table 3). The soil contains up to 500 g organic matter/kg (Figure 2), and as stated in Appendix 2 (Table 3, last column) this means that in principle all the organic matter in the soil at the quay front could be oxidised in only 90-400 years! This has obviously not been the case until now (as there is still organic matter left in the soil), which can have several explanations:

- the conditions have changed and the high rates measured today are not representative of former conditions
- the experiments overestimate the sulphate reduction rates because of the experimental design where the soil is completely mixed with seawater to ensure a good physical contact. Bioforsk suggests that this may increase the reaction rate compared to undisturbed samples.
- there are not unlimited amounts of sulphate present in the soil, as it is only replenished when the quay front area is flooded or via subsurface intrusion.

The last explanation is probably valid for the deeper soil layers (approximately -4 m asl to -7 m asl): Here there is a low concentration of sulphate and high sulphate depletion, and further sulphate reduction may be limited by the supply of sulphate/seawater (as Dunlop describes the layers as compact). In the upper soil layers, on the other hand, there are high concentrations of sulphate and low sulphate depletion (Figure 7), and further sulphate reduction may be limited by the reactivity of the organic material rather than the supply of sulphate/seawater (as Dunlop describes these layers as sandy/“loose” and with “strong H₂S smell”). In these upper soil layers the high sulphate reduction rates measured by Bioforsk are considered realistic.

In an earlier paper we discussed the potential oxidation capacity of sulphate, using a very rough estimate of 675 g sulphate/m²/year or 7 mol/m²/year, which was then compared to the magnitude of

other preservation problems on Bryggen (Matthiesen et al, 2008). Now if we consider the measured sulphate reduction rate of 0.05-0.12 mM/day (18-44 mM/year) as representative for the -2 to -4 m asl zone and estimate the soil porosity to 50%, we end up with a sulphate reduction of 18-44 mol/m²/year just for this 2 m zone – i.e. significantly more than estimated in the 2007-paper.

Parts of the sulphide produced will normally precipitate in the soil, and the total extent of sulphate reduction over time can in principle be estimated from the amount of reduced sulphur species in the soil. At Bryggen the amount of “acid volatile sulphide” has been analysed giving relatively modest amounts (0.1-0.3 mg/g) compared to the total amount of sulphur in the samples (Figure 2).

However, the method applied for sulphide analysis mainly extracts amorphous sulphide compounds and does not include more refractive species like pyrite or sulphur so it might underestimate the amount of reduced species. In the study from Venice (Zaggia et al, 2007) finds that acid volatile sulphide only makes up 20% of the reduced sulphur species and estimates that only 10-25% of the sulphide produced actually precipitates (the rest escapes or is re-oxidised).

Looking at the total sulphur content instead, the samples from the quay front have a high content of 10-20 mg/g compared to other samples from Bryggen – in most other samples there is less than 10mg/g and only in MB9 (and a single samples from MB5) values of 20 mg/g have been found. It may be hypothesised, that a comprehensive sulphate reduction will lower the C/S ratio over time because of accumulation of reduced sulphur compounds in the soil. The C/S ratio of soil samples from MB24, MB25 and FB1 is between 3 and 22 (where the C content is estimated as LOI/2), which is very low indeed – the ratio in most other samples from Bryggen is between 20 and 200. This could indicate a substantial accumulated sulphate reduction at the quay front.

At this point we still can't give an exact extent or rate of the deterioration of organic material at the harbour front. If we shall get any closer to an estimate of the rate we need to have more knowledge about how much seawater enters the system, and how quickly the sulphate disappears (compared to chloride) under in situ conditions. This may be obtained by a detailed logging of the chloride/sulphate content in the dipwells at the quay front, for instance with sampling every one/two weeks for a period after a seawater intrusion event. A better estimate of the total extent of sulphate reduction would require more detailed analysis of sulphur speciation, especially the amount of pyrite, and even this could underestimate the total extent because of re-oxidation processes.

Other oxidants

Organic matter may be oxidized by several oxidants. Oxygen and sulphate have already been mentioned, but apart from them nitrate, manganese oxides, iron oxides, as well as fermentation/methane production should be considered.

The nitrate concentration is below the detection limit for all the soil and water samples from the quay front area, and nitrate reduction is not considered a big problem at the quay front. As for

manganese and iron reduction, the latter is quantitatively the most important in most natural systems. Relatively high concentrations of dissolved Fe^{2+} are found in some of the dipwells (especially FB1 at -5 m asl with 1.7 mmol/L), which indicates iron reduction (Figure 4). However, analysis of soil samples show that most of the extractable (amorphous) iron in the soil has already been reduced from Fe(III) to Fe(II) (Figure 2), which means that the iron reduction process can only continue at a low rate using more refractive Fe(III) compounds (if there are any present).

As for methane production, high concentrations of methane (approx 1 mmol/L) are found in water samples from the organic and compact soil strata from -4 to -7 m asl. This indicates that some methane production is taking place, but without knowledge of the water exchange in these soil layers we have no possibility to estimate the rate.

pH, nutrients and other species

The soil pH is important for the preservation of several different materials, e.g. bones and metals in the soil. Figure 2 shows the pH measured in soil samples, while Figure 4 shows the pH values measured in water samples. pH in the water samples is between 6.5 and 7.0 in the dipwells and between 6.9 and 7.9 in the piezometers (measured in the field by Multiconsult – the high values for the piezometers may be due to degassing of CO_2 during sampling). For the soil samples the pH is between 6.9 and 7.3 for MB24 and MB25 and between 5.5 and 6.1 for FB1 (measured by Bioforsk – the low values for FB1 may indicate an oxidation of the samples during storage). All values are in the neutral region, which is beneficial for the preservation of most materials.

As for the nutrients, only low contents of N are measured in soil samples from MB24 and MB25 (0.3 to 1.3 mg/g, giving an estimated C/N ratio of 60-500), and ammonium makes up a substantial part of it (0.1-0.4 mg/g). FB1 has a much higher N-content (2-11 mg/g, giving an estimated C/N ratio of 20-30), which is more similar to earlier results from Bryggen. Normally C/N ratios below 20 are considered “advantageous” for the microbial mineralization of organic matter, but at this stage it is not possible to discuss the nutrient contents in detail. In the water samples, MB27 shows the highest NH_4 content in any dipwell on Bryggen (13 mmol/L), whereas FB1 (4.5) has the highest P-content (0.87 mmol/L).

The concentration of Mg follows the pattern for Na and Cl, and may be used as an indicator for seawater intrusion (as it is present in seawater at a high concentration of 53 mmol/L).

The high concentrations of CH_4 , HCO_3^- , NH_4^+ , and Ca^{2+} found in dipwells MB12, MB26 and MB27 indicate relatively stagnant conditions as described in Matthiesen (2008).

Preservation conditions

The preservation conditions at the quay front varies down through the soil layers, and may be summarised as follows:

1 to 0 m asl: Modern soil material with limited archaeological interest. Above the groundwater level. Probably a good oxygen supply, but this hasn't been investigated. Timber, such as foundations, may be at risk of degradation by fungi.

0 to -2 m asl: Modern soil material with limited archaeological interest. Beneath the groundwater level, and probably limited oxygen supply. Porous soil with a high salt content, easy access of seawater, and strong H₂S smell. High sulphate reduction rate, which is probably limited by the reactivity of the organic material, rather than the access of sulphate. Timber, such as foundations, may be at risk of slow degradation by bacteria.

-2 to -4 m asl: Archaeological deposits in a poor to medium state of preservation. Porous soil with a high salt content, easy access of seawater, and strong H₂S smell. High sulphate reduction rate, which is probably limited by the reactivity of the organic material, rather than the access of sulphate. Timber, such as foundations, may be at risk of slow degradation by bacteria. Overall, the preservation conditions are considered bad, but further studies of the effect of sulphate reduction are necessary.

-4 to -7 m asl: Archaeological deposits in good state of preservation. Highly organic, compact soil with a limited access of seawater and moderate sulphide smell. High concentration of CH₄, HCO₃, NH₄, and Ca, which indicates stagnant conditions. The sulphate reduction rate is probably limited by the supply of sulphate. The presence of CH₄ shows that some methanogenesis takes place, but it is presently not possible to estimate the production rate. Overall, the preservation conditions are considered good.

-7 to -8 m asl: Archaeological deposits in good state of preservation. Wet grey ooze. Low concentrations of dissolved ions, which may indicate some water exchange, possibly by freshwater running through the natural deposits underneath. Difficult to assess the degradation rate without knowledge of the water exchange rate.

Conclusions and future work

It has been shown that

- Sulphate reduction may be quantitatively very important for decay at the quay front
- Sulphate reduction rates of up to 5-24 mg SO₄/kg dry substance/day have been measured in the laboratory – this corresponds in theory to an oxidation of all organic material in the soil within 90-400 years

- The actual rate and extent *in situ* will depend on the access of sulphate and the reactivity of the organic material
- In the upper soil layers (down to -4 m asl) at the quay front the sulphate reduction is probably limited by the reactivity of the organic material, as there is plenty of sulphate available
- In the compact soil layers between -4 m asl to -7 m asl there are stagnant conditions and the sulphate reduction is probably limited by the sulphate supply
- The deepest cultural layers (beneath -7 m asl) have a supply of fresh water possibly from the natural deposits underneath
- It cannot be recommended to use seawater to increase the water table or spray the foundations at other places on Bryggen, as this may increase the sulphate reduction

Further studies may include

- Mapping the extent of the porous soil layers by sampling of soil cores inside the quay front buildings
- Measurements of sulphate reduction rates in more soil samples to verify first results
- Frequent (weekly) measurements of the Cl and sulphate content in the dipwells/piezometers at the quay front to see how fast the sulphate disappears *in situ*
- Continuous logging of the conductivity in the dipwells at the quay front to better understand and quantify the seawater intrusion
- Numerical modelling of the geochemical data to verify the decay rates
- Measurement of the different sulphur pools (for instance pyrite) in soil samples from the quay front

References

Andersen, M.S. (2001). Geochemical processes at a seawater-freshwater interface. Technical University of Denmark .

Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.-J. & Heron, G. (2001). Biogeochemistry of landfill leachate plumes. *Applied Geochemistry* **16**, 659-718.

Dunlop, R. (2005). Archaeological investigation of archaeological strata in five dipwell boreholes in connection with monitoring project, Bryggen, Bergen, 2005. NIKU, Bergen Arkivrapport. 156132904eng1.

Dunlop, R. (2008). The Bryggen Monitoring Project, Part 7: report on the archaeological investigation of five dipwell boreholes, 2007. NIKU Bergens kontor Rapport arkeologiske utgravninger Bergen.

Jakobsen, R. & Cold, L. (2007). Geochemistry at the sulfate reduction-methanogenesis transition zone in an anoxic aquifer - a partial equilibrium interpretation using 2D reactive transport modelling. *Geochimica et Cosmochimica Acta* **71**, 1949-1966.

Matthiesen, H. (2006). Composition of soil and groundwater at MB12, 10, 14 and 13, Bryggen, Bergen. Copenhagen: National Museum of Denmark, Department of Conservation 12027-0004.

Matthiesen, H. (2008). Detailed chemical analysis of groundwater as a tool for monitoring urban archaeological deposits: results from Bryggen in Bergen. *Journal of Archaeological Science* **35**, 1378-1388.

Matthiesen, H., Dunlop, R., Jensen, J.A., de Beer, H. & Christensson, A. (2008). Monitoring of preservation conditions and evaluation of decay rates of urban deposits - results from the first five years of monitoring at Bryggen in Bergen. *Proceedings from the conference "Preserving Archaeological Remains in situ 3", Amsterdam December 2006*. Geoarchaeological and Bioarchaeological Studies 10, 163-174.

Matthiesen, H., Emeis, K.-C. & Jensen, B.T. (1998). Evidence for phosphate release from sediment in the Gotland Deep during oxic bottom water conditions. *Meyniana* **50**, 175-190.

Zaggia, L., Rosso, J. & Zonta, R. (2007). Sulphate reduction in the sediment of the Venice canals (Italy). *Marine Pollution Bulletin* **55**, 415-424.

Appendix 1

Results from soil analysis. Received as Excell spreadsheet from Bioforsk by email 26.02.2008

Borehull og lag nr	Dybde m	Beskrivelse av lag
MB 24 691-1	4,6	Tegel,sand,treverk,nøtter sterk sulfidlukt
MB 24 691-2	5,20	Treverk,sand , sulfidlukt bedre bevart
MB 24 691-3	5,7	Treverk,sand , sulfidlukt, bedre bevart
MB 25 692-1	2,8	Tegel, sand treverk lys
MB 25 692-2	4,6	Svart fettaktig , Sulfid og gass forekomster
MB 25 692-3	6-7	litt sulfid, bark org lag
MB 25 692-4	8-9	Lite sulfid, halm, mose org lag godt bevart
MB 25 692-5	9-10	Nær sjøbunn øverts, lik laget på 8-9 m
FB 1-1	4.5	
FB 1-2	5.2	
FB 1-3	5.7	
FB 1-4	6.2	
FB 1-5	6.7	
FB 1-6	7.2	
FB 1-7	7.7	
FB 1-8	8.7	

Prøve	Dybde meter	Organisk og vann	Surhet og salinitet	Redoksforhold *	Bevaring sforhold
MB 24 691-1	4,6	Middels org. og vanninnh.	nøytral og høy	Sulfatreduserende - metanogene	Bra
MB 24 691-2	5,20	Høyt org. og vanninnh.	nøytral og middels	Sulfatreduserende	Bra
MB 24 691-3	5,7	Høyt org. og vanninnh.	nøytral og middels	Sulfatreduserende	Bra
MB 25 692-1	2,8	Høyt org. og vanninnh.	nøytral og lav	Sulfatreduserende - metanogene	Bra
MB 25 692-2	4,6		nøytral og høy	Sulfatreduserende	Bra
MB 25 692-3	6-7	Middels org. middels vanninnh.	nøytral og høy	Sulfatreduserende - metanogene	Bra
MB 25 692-4	8-9	Høyt org. og vanninnh.	nøytral og middels	Sulfatreduserende - metanogene	Bra
MB 25 692-5	9-10	Middels org. høyt vanninnh.	nøytral og middels	Sulfatreduserende - metanogene	Bra
FB 1-1	4.5	Lavt org. middels vanninnh.	Middels sur og lav	Sulfatreduserende	Bra
FB 1-2	5.2	Høyt org. og vanninnh.	Middels sur og lav		
FB 1-3	5.7	Høyt org. og vanninnh.	Middels sur og lav	Sulfatreduserende	Bra
FB 1-4	6.2	Høyt org. og vanninnh.	Middels sur og lav		
FB 1-5	6.7	Høyt org. og vanninnh.	Middels sur og lav	Sulfatreduserende	Bra
FB 1-6	7.2	Høyt org. og vanninnh.	Middels sur og lav		
FB 1-7	7.7	Høyt org. og vanninnh.	Middels sur og lav	Sulfatreduserende	Bra
FB 1-8	8.7	Høyt org. og vanninnh.	Middels sur og lav		

Borehull og lag nr	Dybde meter	Glødetap %	TS %	Vann innh %	pH	Ledn.evne mScm -1	Redox forhold Eo (V)
MB 24 691-1	4,6	14	55	45	6.9	12	-0.11
MB 24 691-2	5,20	43	44	56	7.0	6	-0.10
MB 24 691-3	5,7	31	40	60	7.1	6	-0.10
MB 25 692-1	2,8	35	34	66	7.3	2	-0.10
MB 25 692-2	4,6	31	37	63	7.3	11	-0.15
MB 25 692-3	6-7	25	57	43	7.0	15	-0.12
MB 25 692-4	8-9	43	33	67	6.9	7	-0.11
MB 25 692-5	9-10	18	47	53	6.9	5	-0.11
FB 1-1	4.5	11	57	43	5.8	1.40	
FB 1-2	5.2	35	36	64	5.5	2.50	
FB 1-3	5.7	60	28	72	5.7	2.00	
FB 1-4	6.2	47	31	69	5.7	1.80	
FB 1-5	6.7	47	32	68	5.5	2.90	
FB 1-6	7.2	55	28	72	5.6	2.30	
FB 1-7	7.7	67	28	72	5.8	1.40	
FB 1-8	8.7	27	41	59	6.1	2.50	

Anvendte metoder:

Ledningsevne: Prøven (10 g) tilsættes 25 mL vand og rystes i en time. Efter sedimentation måles ledningsevne i vandfase. Ledningsevnen ganges med en faktor 3.6 for at estimere ledningsevne i porevæsken.

pH: Måles i samme opsløsning som ledningsevnen.

Nitrat og ammonium: Prøven (15 g) ekstraheres med 2 M KCl (70 mL) og analyseres ved hjælp av en TRAACS-800 autoanalysator som bruker en fargereaksjon til bestemmelse av nitrat- og ammoniumkonsentrasjon. Analysen ble gjennomført ved AnalyCen.

Sulfat: Jordprøven (15 g) ble ekstrahert med vann (70 mL) og ekstrahert sulfat analysert ved hjelp av ionekromatografi. Analysen ble gjennomført ved AnalyCen.

Sulfid: Bestemmes som syreflygtig sulfid ved ekstraktion med 6M HCl i 1 time i nitrogenatmosfære.

Fe(II) og Fe (III): ekstraheres med 0.5 M HCl i 24 timer under oxygenfrie forhold. Fe(II) måles spektrofotometrisk. Herefter reduceres ekstraheret Fe(III) med hydroxylamin og total-jern bestemmes spektrofotometrisk. Fe(III) beregnes som forskjellen på Fe-tot og Fe(II)

Tot-N: bestemmes ved Kjeldahl metoden

Tot-P og tot-S: bestemmes ved ICP-AES (ved AnalyCen)

Chlorid: Ekstraheres med vand og måles med ion chromatografi

Borehull og lag nr		Dybde meter	Nitrat - N (mg/kg TS)	Ammonium (mg/kg TS)	Sulfat (mg/kg TS)	Sulfid (mg/kg TS)	Jern (II) (mg/kg TS)	Jern (III) (mg/kg TS)
MB 24	691-1	4,6	<1,6	78	137	264	145	<0,1
MB 24	691-2	5,20	<2,1	323	253	97	57	4.5
MB 24	691-3	5,7	<2,3	366	167	112	34	1.3
MB 25	692-1	2,8	<2,6	290	77	151	32	<0,1
MB 25	692-2	4,6	<2,4	335	43	152	36	2.8
MB 25	692-3	6-7	<1,6	83	84	191	105	0.0
MB 25	692-4	8-9	<2,8	416	86	182	52	1.1
MB 25	692-5	9-10	<2,0	210	16	138	93	<0,1
FB 1-1		4.5	<0,2	108	728	119	88	10.2
FB 1-3		5.7	<0,2	169	1776	104	25	7.8
FB 1-5		6.7	<0,2	436	3381	180	36	11.1
FB 1-7		7.7	<0,2	457	516	198	23	4

Borehull og lag nr		Dybde meter	Tot - N (mg/kg TS)	Total S (mg/kg TS)	Total P (mg/kg TS)	Klorid (mg/kg TS)
MB 24	691-1	4,6	1100	21400	5000	10400
MB 24	691-2	5,20	730	13600	4100	1900
MB 24	691-3	5,7	600	12600	2200	2800
MB 25	692-1	2,8	350	15300	9400	1500
MB 25	692-2	4,6	560	14800	4700	4100
MB 25	692-3	6-7	290	11000	5100	4700
MB 25	692-4	8-9	1260	16900	15000	3700
MB 25	692-5	9-10	610	9600	3000	1600
FB 1-1		4.5	2300	10700	6900	726
FB 1-3		5.7	11000	13700	3000	3108
FB 1-5		6.7	<3400	18400	3500	2683
FB 1-7		7.7	<3700	19200	2800	

Appendix 2

Results from measurements of sulphate reduction rates. Received from Bioforsk by email
02.05.2008

Miljøovervåkning i kulturlag ved kaifronten av Bryggen i Bergen med spesiell fokus på aktivitet av sulfatreduserende mikroorganismer

Bakgrunn

I forbindelse med installering av miljøbrønner i kaifronten av Bryggen i Bergen ble det tatt jordprøver til videre undersøkelser på laboratoriet. I denne forbindelse var det aktuelt å vurdere effekten av sjøvannsinnntrengning på nedbrytningen av kulturlagene. Bakgrunnen for dette er at kulturlagene ikke inneholder oksygen, men under slike forhold kan sulfat brukes av mikroorganismene til å bryte ned organisk materiale. Under forhold hvor det verken finnes oksygen eller sulfat, men bare produseres metan, vil nedbrytning av trevirke kunne ta mer enn tusen år. Nedbrytning er også vanligvis langsommere med sulfat enn med oksygen, men det er ikke kjent i hvilken grad høy sulfatkonsentrasjon vil kunne stimulere nedbrytningen, og det ble derfor foreslått å undersøke dette nærmere. Denne kunnskapen kan sammen med den hydrologiske modelleringen komplettere risikovurderingen av de faktorene som fører til nedbrytning av kulturlagene ved Bryggen i Bergen, samt bidra i vurderingen av effekten av økt saltvannsinnntrengning som er forventet i forbindelse med klimaendringen.

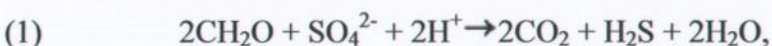
Litt om sulfatreduserende bakterier

Mikrofloraen i marine miljøer som har tilgang på mye organisk materiale, er dominert av heterotrofe mikroorganismer som lever av å bryte ned dette organiske materiale. Tilførselen vil kunne være spesielt stor i forurensede fjorder med sterk algevekst, eller steder med tilførsel av organisk materiale fra utslipp av kloakk eller utslipp fra industri, for eksempel fra treforedling og trevareindustri. Dersom sediment eller kulturlag inneholder oksygen, så vil det aller øverste laget av sedimentene eller jordlagene være dominert av aerobe mikroorganismer. Disse organismene benytter oksygen som oksidasjonsmiddel. I sedimenter vil det aerobe laget bare være noen millimeter eller centimeter dypt, avhengig av tilgangen på organisk materiale, permeabilitet og temperatur. I jord vil mektigheten av laget være avhengig av miljøforholdene. Andre oksidasjonsmidler som vi kan finne i disse øverste lagene, kan være nitrat og treverdige jern (Ronald M. Atlas og Richard Bartha, 1981). Under disse øverste lagene finner vi anaerobe sulfatreduserende bakterier som benytter sulfat som oksidasjonsmiddel.

Sulfatreduserende bakterier er spesielt viktige i sjøvannssedimenter og kulturlag som er påvirket av sjøvannsinnntrengning siden sjøvann inneholder store mengder sulfat - ca. 2,8 gram per liter sjøvann. Til sammenligning inneholder sjøvann som er mettet med luft, bare 8 til 10 mg O₂ per liter. Derfor vil sulfatreduserende bakterier stå for en stor del av mineraliseringen av organisk materiale i marint miljø. Sulfatreduserende bakterier er ansvarlige for opp mot halvparten av den totale mineraliseringen av sedimentert organisk materiale i grunne sedimenter (Kasten, S. og B.B. Jørgensen, 2000), og vi vil anta at det samme gjelder for kulturlag i marint miljø så lenge tilgangen på sulfat og organisk substrat er tilstrekkelig.

Sulfatreduserende bakterier er strengt anaerobe og prosessen vil hemmes, eller stoppe fullstendig opp i nærvær av oksygen eller nitrat. De utgjør en svært heterogen gruppe, både morfologisk og fysiologisk, men har til felles at de kan benytte sulfat i stedet for oksygen som oksidasjonsmiddel og de danner hydrogensulfid (H₂S) i stedet for vann (H₂O) som redusert sluttprodukt.

Sulfatreduserende bakterier lever stort sett på gjæringsproduktene fra anaerob gjæring som for eksempel hydrogen (H₂), maursyre, eddiksyre, propionat, melkesyre, høyere rette og forgrenede fettsyrer, enkle alkoholer og andre mindre organiske forbindelser, men de kan ikke leve på sukker og aminosyrer, parafiner eller naturlige polymerer (F. Widdel, 1986). Forholdet mellom forbruket av sulfat ved oksidasjon av organisk materiale kan forenklet beskrives med følgende uttrykk:



Ved å måle hvor fort sulfatreduksjonen foregår, så får vi også et mål på hvor raskt nedbrytningen av det organiske materialet foregår. De mikroorganismene som gjennom hydrolyse og gjæringsprosesser forsyner sulfatreduserende bakterier med gjæringsprodukter, kaller vi i det etterfølgende for primærnedbrytere.

Metodikk

Aktiviteten til sulfatreduserende bakterier kan bestemmes på flere måter, og valg av metode vil være avhengig av problemstilling og hvor høy aktiviteten er forventet å være. I denne sammenheng var det aktuelt å vurdere tre ulike metoder:

1. Hvis man skal få et mål på aktiviteten slik den er i uforstyrrede sedimenter med lite sulfat, vil bruk av radiomerket sulfat være et naturlig valg. Radiomerket sulfat leveres bærerfri slik at den mengden som tilføres blir ubetydelig i forhold til konsentrasjonen i prøven (selv i ferskvann). Inkubasjonstiden vil være kort, fra noen minutter til timer eller noen få dager, og avhengig av bakterienes aktivitet slik at forholdene endres minimalt.
2. Radiomerket sulfat kan også være å foretrekke dersom sulfatkonsentrasjonen er høy og dersom aktiviteten er svært lav, fordi man kan måle akkumulert radiomerket sulfid etter relativt kort tid (timer til dager). Hvis aktiviteten er tilstrekkelig høy eller inkubasjonstiden er lang (dager til uker), kan man også måle nedgangen i radiomerket sulfat.
3. Den enkleste framgangsmåten å måle nedbrytningshastigheten er å måle nedgang i sulfatmengden direkte. Slike målinger kan gjøres med kjemiske metoder eller med ved hjelp av såkalt turbidimeter. Denne metoden forutsetter imidlertid relativ høy nedbrytningsaktivitet. Hvis nedbrytningsaktiviteten er lav, blir nøyaktige målingene meget tidkrevende.

I utgangspunktet var planen å måle aktiviteten i prøver med og uten tilsetning av sulfat, ved hjelp av radioaktivt merket sulfat ($\text{Na}_2^{35}\text{SO}_4$). Siden prøvematerialet inneholder svært mye flis og trebiter så var det ikke nok materiale til å gjennomføre begge deler. Det hadde også vært en fordel å kunne gjennomføre et preliminært forsøk for å få et mål på aktiviteten slik at prøvetakingsintervaller kunne bestemmes. Planene måtte derfor omarbeides noe, slik at vi kunne få mest mulig informasjon ut fra det materialet vi hadde til rådighet.

Det ble da tatt utgangspunkt i analyser av klorid og sulfat som allerede var gjennomført, for å se om disse resultatene kunne gi noe informasjon om aktiviteten i prøvene. Klorid utgjør ca 55 % av saltinnholdet i sjøvann, og selv om saltinnholdet varierer vil forholdet mellom sulfat og klorid være nær konstant ($\text{mg SO}_4/\text{mg Cl} \sim 0,14$). Saliniteten i havet utenfor Bergen er 32 ‰, men vi har antatt at den ligger nærmere 20 ‰ i indre havn.

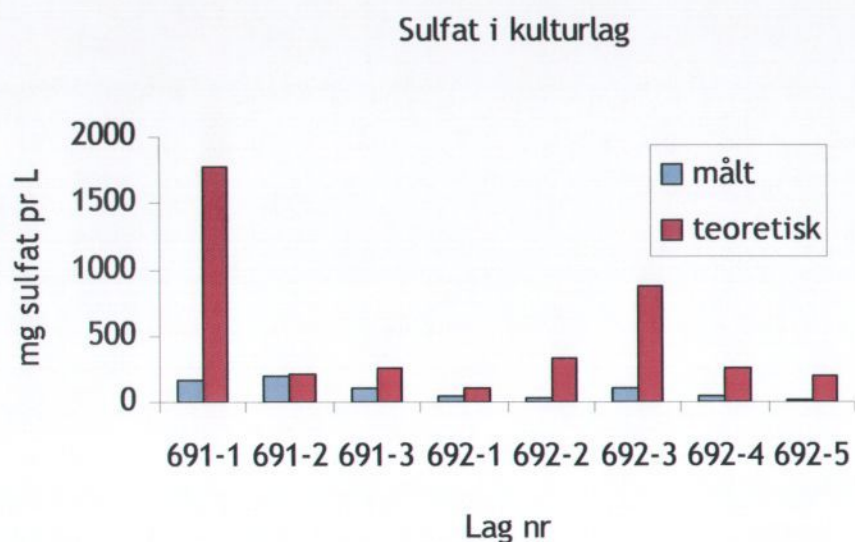
På denne bakgrunn ble det bestemt å gjennomføre ett korttidsforsøk over 24 timer med radiomerket sulfat der det også ble tilsatt fortynnet sjøvann i henhold til kloridkonsentrasjonen i prøvene. Forsøket med radioaktivt merket sulfat ble gjennomført etter metodene som er beskrevet av Westermann & Ahring (1988). Til hver 50 ml serumflaske (Bellco) ble det veid inn 5 g sediment som ble tilsatt 5 ml fortynnet sjøvann. Prøvene ble forhåndsinnkubert i 24 timer før tilsetning av tracer. Hver prøve ble innkubert i 0, 1, 2, 3, 12 og 24 timer etter tilsetning av $10 \text{ KBq } ^{35}\text{S-Na}_2\text{SO}_4$. Aktiviteten bestemmes ved å måle på mengden merket sulfid som er produsert. Til resten av prøvematerialet ble det tilsatt rent sjøvann og disse prøvene ble innkubert i 32 dager før sulfat ble målt. I begge forsøkene ble reaksjonen stoppet ved tilsetning av Zn-acetat. Sulfat ble bestemt etter turbidometrisk metode (Tabatabai, 1974). Deretter ble ca 1 gram av disse prøvene brukt som podemateriale til nye kulturer for å undersøke effekten av å tilsette eddiksyre og cellulose. Eddiksyre kan utnyttes direkte av sulfatreduserende bakterier, mens cellulose må hydrolyseres og fermenteres før videre nedbrytning via sulfatreduksjon. Økt sulfatreduksjon etter tilsetning av eddiksyre vil indikere at aktiviteten til sulfatreduserende bakterier er karbonbegrenset, mens økt aktivitet etter tilsetning av cellulose i tillegg vil indikere noe om forekomst og aktivitet til primærnedbryterne. Alle kulturer ble innkubert ved 10^0 C .

Resultater og diskusjon

Kjemiske analyser av sedimenter

Kloridkonsentrasjonen i prøvene tyder på at sjøvannsinntrengingen er begrenset i de fleste sjikt (fig 1). I prøven 691/1 fra brønn 24 er imidlertid inntrengingen fullstendig hvis vi antar at saliniteten er ca 23 ‰.

Bortsett fra i 691/2, 691/3 og 692/1 var sulfatkonsentrasjonen mye lavere enn en skulle forvente ut fra kloridkonsentrasjonen. I jordlag hvor sulfatkonsentrasjonene er lavere enn forventet kan det ha foregått en betydelig sulfatreduksjon, enten før prøven ble tatt eller underveis før analysene ble gjennomført. Hvis transporten først og fremst er styrt av en konsentrasjonsgradient, vil mest sannsynlig mesteparten av sulfatreduksjonen ha foregått i over- eller foranliggende kulturlag før sulfat har trengt inn til der prøvene er tatt. I havnesedimenter hvor det er rikelig tilgang på organisk materiale, vil sulfatkonsentrasjonen ofte være mindre enn 100 mg L^{-1} allerede 25 cm under sedimentoverflaten, mens saltholdigheten er relativt uforandret på mange meters dyp. I 691/2 var det ingen forskjell på teoretisk og målt sulfatkonsentrasjon. I utgangspunktet vil vi forvente at aktiviteten vil være lav i prøver der forholdet mellom målt og teoretisk sulfat er nær 1.



Figur 1. Teoretisk sulfatkonsentrasjon viser graden av sjøvannsinntrenging. Sulfatkonsentrasjon ved salinitet på 23 ‰ er 1782 mg L^{-1} .

Bortsett fra den ene prøven 691/2 ga ikke disse resultatene noe entydig svar på hvilke sedimenter som var mer eller mindre aktive. Vi valgte derfor å gjennomføre et kortidsforsøk med merket sulfat og et langtidsforsøk med ekstra tilsetning av sulfat på alle sedimentene. Det ble vurdert å spare en av prøvene fra hvert sediment og innkubere denne i en uke eller 14 dager med merket sulfat, men siden vi ikke hadde nok materiale til parallelle prøver ble det bestemt å beholde alle prøvene til korttidsforsøkene slik at vi kunne få et best mulig bilde av reduksjonsforløpet. Det som var igjen i prøveglassene, inklusiv flis, stein og annet rask ble tilsatt 5 ml sjøvann og innkubert i 32 dager.

Korttidsforsøk med $^{35}\text{S-Na}_2\text{SO}_4$

Det kunne ikke påvises radioaktivt merket sulfid i prøvene. Vi kan likevel beregne hvor høy aktiviteten maksimalt kunne ha vært. Bakgrunnsaktiviteten i sulfidfellene var 20 cpm mL^{-1} og vi regner 40 cpm (0,67 Bq) som en nedre grense for å kunne påvise aktivitet i sedimentet. Denne differansen betyr at ca 0,3 % av det som ble tilsatt i prøven er syreflyktig sulfid. Hvis vi videre går ut fra prøven med høyest teoretisk sulfatkonsentrasjon og justerer for 6 % diskriminering av ^{35}S i forhold til ^{32}S og at syreflyktig sulfid utgjør 70 % av totalt produsert sulfid blir maksimal reduksjonsaktivitet $8,1 \text{ mg sulfat L}^{-1} \text{ dag}^{-1}$. Tilsvarende beregninger er gjort for alle prøvene og fremstilt i tabell 1 nedenfor. Alle verdiene ligger innenfor det som ofte måles i organiske sedimenter i marint miljø ($0,2 - 20 \text{ mg sulfat L}^{-1} \text{ dag}^{-1}$). At vi ikke kunne påvise radioaktiv sulfid, skyldes antagelig at aktiviteten var lavere enn dette. Hvis det hadde vært mulig å gjenta forsøket, kunne vi økt følsomheten ved å tilsette mer merket sulfat. I tillegg kunne vi ha økt inkubasjonstiden og redusert volumet av sulfidfellene. Forsøket kunne imidlertid ikke gjentas siden vi hadde for lite materiale (sediment).

Tabell 1. Teoretisk maksimal sulfatreduksjon i kulturlag

Lag nr	mg SO ₄ L ⁻¹ dag ⁻¹
691-1	8,1
691-2	0,9
691-3	1,2
692-1	0,5
692-2	1,5
692-3	4,0
692-4	1,2
692-5	0,9

En annen forklaring kan være at metoden vi har brukt bare ekstraherer syreflyktig sulfid, det vil si fra jernsulfid (FeS) og løst sulfid, men ikke pyritt og elementært svovel. Hvis dannelsen av pyritt og andre ikke syreflyktige svovelforbindelser skjer raskt, vil aktiviteten naturligvis kunne bli undervurdert. Vanligvis er imidlertid den syreflyktige fraksjonen størst og som regel tilstrekkelig til å gi et rimelig estimat på aktiviteten.

Langtidsforsøk

Disse forsøkene ble stoppet med Zn-Acetat etter 32 dager og sentrifugert før supernatanten ble analysert for sulfat. I dette forsøket ble alle prøvene tilsatt samme mengde sulfat, men fordi vanninnholdet i prøvene var noe forskjellig ble utgangskonsentrasjonen tilsvarende forskjellig.

Tabell 2. Sulfatkonsentrasjoner og målt aktivitet i kulturlag

Lag nr	Start sulfat mg L ⁻¹	Slutt sulfat mg L ⁻¹	Aktivitet mg L ⁻¹ dag ⁻¹
691/1	646	242	12,6
691/2	1115	757	11,2
691/3	1237	1596	-11,2
692/1	615	450	5,2
692/2	538	358	5,6
692/3	646	482	5,1
692/4	583	239	10,7
692/5	780	381	12,5

Den høye sluttkonsentrasjonen av sulfat i 691/3 kan skyldes oksidasjon av sulfid siden glasset var sprukket. Bortsett fra 691/3 er aktiviteten som ble funnet i dette forsøket, tilstrekkelig til at radioaktiv sulfid kunne vært påvist etter 24 timer selv om det ligger helt på grensen. En forklaring kan være at det tar mange dager etter tilsetning av sulfat før aktiviteten øker. I et stabilt uforstyrret system er aktiviteten i stor grad bestemt av den romlige fordelingen av de elementer som inngår i prosessen og hvor raskt diffusjonen av de forskjellige elementene foregår. I dette tilfellet er de viktigste elementene sulfat og ulike karbonforbindelsene. Ved å manipulere med prøvene vil diffusjonsbegrensningene opphøre for kortere eller lenger tid. Hvorfor det tar mange dager før aktiviteten øker kan skyldes at det først er primærnedbryernes aktivitet som øker. Det tar antagelig litt tid før karbontilgangen øker så mye at det får betydning for aktiviteten til de sulfatreduserende bakteriene. Dette betyr at det var riktig å la prøvene stå i ro i lang tid etter at de var tatt. Selve prosessen med prøvetakingen og fordelingen av delprøver til de ulike undersøkelsene kan i seg selv ha ført til økt aktivitet i prøvene. At det ikke ble påvist aktivitet i kortidssforsøket kan derfor bety at aktiviteten er betydelig lavere i uforstyrrede kulturlag enn det som ble målt i langtidsforsøket.

Betydningen av primærnedbrytere og karbontilgang ble undersøkt nærmere ved hjelp av kulturene som ble tilsatt eddiksyre og cellulose. Eddiksyre kan brytes ned direkte av sulfatreduserende bakterier, mens cellulose først må hydrolyseres og fermenteres av primærnedbrytere til melkesyre, eddiksyre, etanol med mer. Det var ingen målbar forskjell i sulfatkonsentrasjonene etter 5 uker, men det var likevel mulig å påvise forskjeller siden ingen av kulturene som bare var tilsatt sulfat, luktet hydrogensulfid. Luktterskelen for hydrogensulfid er så lav at den kan merkes allerede når konsentrasjonen er $5 \mu\text{g L}^{-1}$ luft. 6 av kulturene som var tilsatt eddiksyre luktet hydrogensulfid, mens bare en av kulturene som var tilsatt cellulose, luktet sulfid. Dette var kulturen som var podet, med materiale fra sedimentet med størst grad av sjøvannsinntrenging (691/1). Dette sedimentet har tydeligvis fortsatt en stor populasjon av cellulosenedbrytende mikroorganismer. En slik populasjon kan antagelig bare opprettholdes over lang tid under forhold med god tilgang på cellulose. Denne cellulosen må enten komme fra nedbrytning av organisk materiale i sedimentet, eller med regelmessig inntrenging av sjøvann eller overflatevann som inneholder mye organisk materiale. Hvis det har vært mindre gode bevaringsforhold i denne delen av sedimentet, kan det bety at inntrenging av sjøvann er lite gunstig, men det behøver ikke nødvendigvis bare skyldes økt sulfatreduksjon.

Resultatene for de ulike lag i tabell 2 er ikke direkte sammenlignbare siden prøvene ikke inneholdt like mye sediment. I tabell 3 er resultatene omregnet i forhold til mengde tørrstoff i prøven. Videre har vi brukt ligning (1) til å regne ut hvor mye karbon som blir mineralisert via sulfatreduksjon. Som eksempel, har vi også vist hvor mye cellulose dette tilsvarer, samt hvor lang tid det tar å bryte ned 500 gram cellulose under forsøksbetingelsene i vårt laboratorieforsøk.

Tabell 3. Sulfatreduksjon og karbonmineralisering i kulturlag

Lag nr	mg Sulfat kg^{-1} dag $^{-1}$	mg C kg^{-1} dag $^{-1}$	mg Cellulose kg^{-1} dag $^{-1}$	mg Cellulose år $^{-1}$	Antall år før all cellulose er nedbrutt
691/1	9,2	2,3	5,7	2091	239
691/2	13,3	3,3	8,3	3044	164
691/3				0	
692/1	5,6	1,4	3,5	1285	389
692/2	7,7	1,9	4,8	1765	283
692/3	5,3	1,3	3,3	1209	414
692/4	23,5	5,9	14,7	5358	93
692/5	14,3	3,6	9,0	3268	153

Nedbrytningen av ren cellulose kan naturligvis gå mye fortare enn dette også under anaerobe forhold, men aktiviteten må likevel karakteriseres som høy. Hvis vi kunne ha målt på uforstyrrede prøver, ville aktiviteten sannsynligvis vært betydelig lavere. Det hadde ikke vært mye godt bevart treverk igjen i disse prøvene hvis nedbrytningen hadde gått så fort som i dette forsøket. Forsøket med merket sulfat tyder også på at aktiviteten var lavere i utgangspunktet. Dette kan indikere at sulfatinntrenging og kanskje spesielt kombinert med andre mekaniske forstyrrelser, vil kunne ha stor betydning for bevaringsforholdene.

Forøvrig foreligger undersøkelser som kan tyde på, at sulfatreduserende bakterier kan bidra til økt hydrolyse av polysakkarider (se bla.a to referanser nedenfor). De undersøkelsene som er referert, er imidlertid gjennomført med den hensikt å optimalisere avfallsbehandling, og resultatene er ikke uten videre overførbare på vår problemstilling. Dersom dette skal belyses nærmere, må det gjennomføres sammenlignende nedbrytningsforsøk med cellulose under sulfatreduserende og metanogene/sulfatbegrensede forhold. Dette kan antagelig best gjennomføres med ^{14}C -merket cellulose siden konsentrasjonen av mikrobielt tilgjengelig cellulose bør holdes på samme nivå som under naturlige forhold.

Sandeep Pareek, Jun-Ichi Azuma, Yoshihisa Shimizu and Saburo Matsui, 2000. Hydrolysis of newspaper polysaccharides under sulfate reducing and methane producing conditions. *Biodegradation*, 11(4): 229-237

K.J. Whittington-Jones, J.B. Molwantwab and P.D. Roseb, 2006. Enhanced hydrolysis of carbohydrates in primary sludge under biosulfidogenic conditions. *Water Research* 40(8):1577-1582

Appendix 3

Results from water analysis from dipwells at the quay front (Eurofins)

mg/L	MB9	MB12	MB24	MB25	MB26	MB27	FB1, 1.5	FB1, 3.0	FB1, 4.5	FB1, 6.0	FB1, 7.5	FB1, 9.0
Na ⁺	4600	450	4200	150	3100	4800	150	1000	1000	400	280	200
K ⁺	160.0	46.0	170	11	120	190	12	43	48	35	30	26
Ca ⁺⁺	210	350	220	140	130	910	39	340	230	520	230	200
Mg ⁺⁺	580.0	75	530	11	210	220	13	44	38	40	29	26
Mn ⁺⁺	0.16	0.25	0.06	0.57	0.26	0.51	0.3	1.9	1.2	3.0	1.1	1.2
Fe ⁺⁺	7.30	6.00	2.10	21	6	19	6	23	35	95	16	25
NH ₄ ⁺	12.00	110.00	8.80	18	83	240	1	54	74	61	49	30
Cl ⁻	8300	860	8300	310	3900	6400	180	1100	1100	590	410	260
SO ₄ ⁻	1200.0	16.0	1100.0	18.0	270.0	34.0	35.0	27.0	6.3	5.7	4.8	6.5
NO ₃ ⁻	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5
P-tot	3.00	7.20	1.80	9.40	11.00	13.00	3.80	3.80	27.0	13.0	9.8	6.8
HS ⁻	too high	too high	too high	0.15	2.50	21.00	0.00	n.m.	0.20	0.11	0.10	0.05
HCO ₃ ⁻	281	1560	232	340	1140	330	198	89	1070	907	936	895
F ⁻	0.420	0.190	0.43	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
O ₂	0.4	0.5	0.6	0.4	0.4	0.6	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
CH ₄	3	21	3.9	0.09	16	18	6.4		8.9	13	0.44	2.4
Hardness H	163	65.8	152	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
pH	7.2	6.9	7	6.6	6.5	6.7	7.9	7.3	6.9	6.9	7.1	7.4
Conduct. (mS/m)	1670	329	1747	133	863	1460	81	470	340	118	192	147
Total dissolved solids (TDS)	18000	2600	17000	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Colour	Black	Black	Grey w. particles	Grey/brown	Colourless	Brown			Brown	Brown	Brown	
Temperature	8.3	9.8	9.4	12.9	10.7	12.3	15.9	n.m.	14.3	16.4	14.6	16.4
Comments	H ₂ S smell	H ₂ S smell	H ₂ S smell	H ₂ S smell	H ₂ S smell	H ₂ S smell		tube blocked		H ₂ S smell		H ₂ S smell

All results are in mg/L unless otherwise stated. n.m. means "not measured". The oxygen measurements were made in the field, and the levels given here are at the detection limit of the method – i.e. they are due to the instrument and pollution during sampling. All dipwells are considered to be anoxic, based on the results from measurements of reduced species.