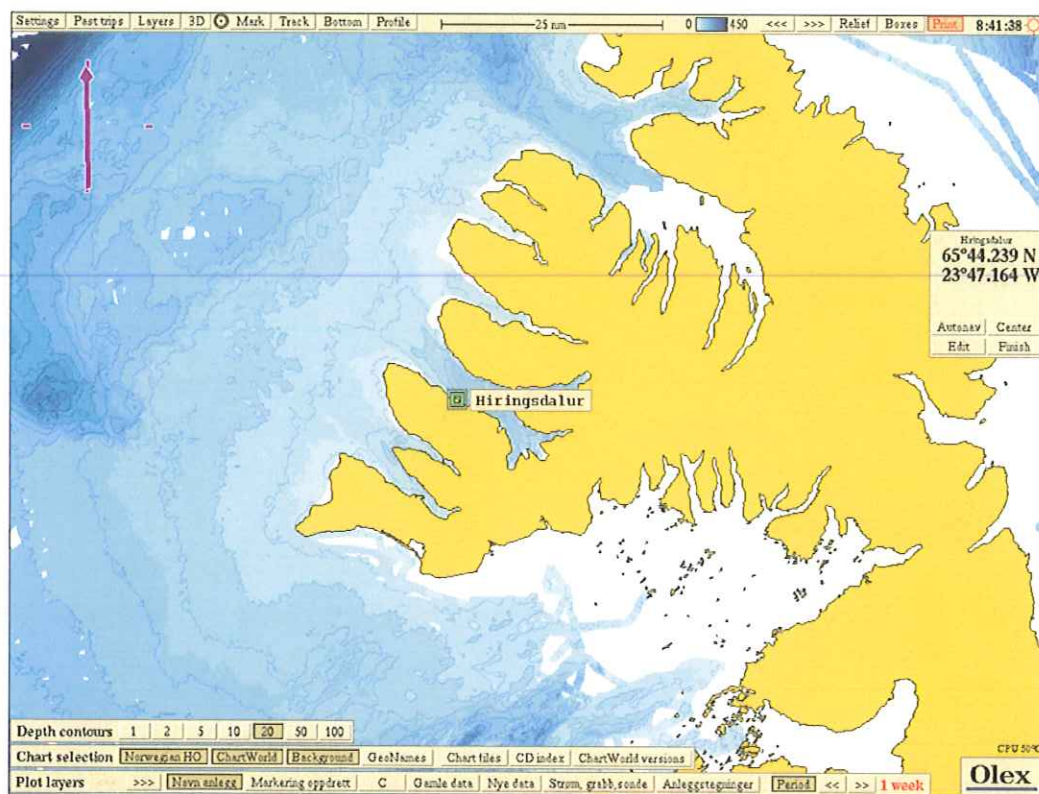


Environmental monitoring (MOM B) of marine  
finfish farms

**Hringsdalur**  
in

Vestur-Barðastrandarsýsla County

October 2013



Title

Environmental monitoring (MOM B) at finfish farm site  
Hringsdalur  
October 2013

**Summary:**

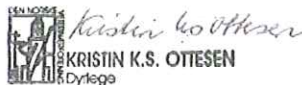
The site is in October 2013 classified by NS 9410 to the site condition 1 (Best score). Considerations on fauna, visual and sensory parameters show no signs of organic load under the planned site. The fauna is rich and consists of a variety of species.

Date 25/11-13

For  
Helgeland Havbruksstasjon AS

*Are A. Moe*

For  
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**Environ monitoring site Hringsdalur**

**Information of client :**

Report title:	Hringsdalur MOM B 22.10.13		
Report-number:	AR131125A	Farming site name:	Hringsdalur
Site number:		Map coordinates:	65° 44.239' N 23° 47.164' W
Region	Vestfirðir	County:	Vestur- Barðastrandarsýsla
Production license:	3400 ton	Site manager:	Víkingur Gunnarsson
Assigner:	Arnarlax AS, Kristian B. Matthiasson		

**Biomass / production status of the date of the investigation :**

Fish group:	No fish at site	Biomass at site:	0 ton
Amount feed out:	0 ton	Quantity produced:	0 ton
<b>Type/ time for investigation</b>			
Max biomass:		Follow-up investigation:	
Fallowed:		New site / expansion:	x

**Results from B investigation / NS-9410- investigation (main results) :**

Parameter group and index		Parameter group and condition	
Gr. I Animals:	0,0	Gr I Fauna:	A
Gr. II pH/Eh:	0,0	Gr II pH/Eh:	1
Gr. III Sensory:	0,59	Gr III Sensory:	1
Gr II+III:	0,30	Gr. II + III:	1
Date fieldwork:	22/10-13	Date report:	25/11-13
Average site condition, according NS 9410:		1	
Responsible fieldwork:	Are A. Moe	Signature:	Are A. Moe



## **Contents**

Overview of tables .....	5
Overview of pictures .....	5
1. Introduction .....	6
2. Material and methods .....	8
2.1. Equipment .....	8
2.2. Preparation of equipment .....	8
2.3. Sampling .....	8
2.4. Inspection of samples .....	9
2.5. Evaluation of results .....	10
3. Site Hringsdalur .....	12
3.1. Objective of the survey .....	13
3.2. Production history .....	13
3.3. Position of sampling stations .....	13
3.4. Bottom topography of the site Hringsdalur .....	15
4. Results .....	17
4.1. Field investigation of the bottom sediments .....	17
4.1.1. Chemical and sensory sediments parameters .....	17
4.1.2. Faunal investigation .....	17
4.2. B-investigation, forms and tables .....	18
5. Summary of environmental condition at site Hringsdalur .....	21
5.1. MOM B investigation .....	21
6. Literature .....	22
7. Appendix .....	23
7.1. pH and Redox potential .....	23
7.1.1. Utility .....	23
7.1.2. Principle .....	23
7.1.3. Choice of measuring equipment .....	24
7.1.4. Temperature control .....	25
7.1.5. Calibration of pH .....	25
7.1.6. Control of Redox potential .....	26
7.1.7. Deflection /response time .....	27

## Overview of tables

Table 1. Description of stations with depth and GPS position, Hringsdalur 22/10-13 ....	14
Table 2. Form for sampling locations, Hringsdalur 22/10-13. *Estimates of individuals in group.....	18
Tabell 3. Form for samples, Hringsdalur 29/1-13. ....	19
Table 4: Information from B investigation (partial results) .....	21
Table 5: Half-cell potentials at different temperatures for two Radiometer reference electrodes .....	24
Table 6: Frequency of B-investigations at the site (local impact zone) in relation to impacts at the site (site condition). Site condition 4 corresponds with unacceptable conditions.....	28

## Overview of pictures

Figure 1. Bathymetric map around the farming site Hringsdalur .....	12
Figure 2. Sampling stations at Hringsdalur 22/10-13, red cross with the station name marks the position for grabbing at the main image.....	13
Figure 3. Depth data in the area of the site, box markings from sonar is marked purple at inset image.....	15
Figure 4. 3D seafloor view under the site Hringsdalur seen from north .....	16
Figur 5. 3D seafloor view under the site Hringsdalur seen from west.....	16
Figure 6. Overview of condition at the different stations. * See table 4 for index-color based on condition.....	20
Figure 7. Schematic illustration of the $E_h$ gradient in marine sediment measured with a platinum electrode before (upper scale) and after (lower scale) contact with hydrogen sulphide .....	27
Figure 8. Point allocation based on redox potential and pH value .....	28

## **1. Introduction**

The aquaculture industry aims to ensure favourable environmental conditions for farmed fish in order to promote optimum fish health and growth. The industry aims to avoid unnecessary environmental impact from fish farms, or that the aquaculture activities harm the surroundings.

Overloading of sites and accumulation of organic material in the form of waste feed pellets and excrement can be a fundamental cause of stress, poor growth and disease, with the associated spread of infectious agents and need for medication. Organic material can therefore be influential for several types of environmental impact, even if the effect is greatest on the bottom under the cages.

Fish farm effluent consists of large particles (waste feed pellets and intact faecal pellets), smaller suspended particles (feed dust and broken faecal pellets) and dissolved material (nutrients, organic compounds etc.). These types of effluents have different potential dispersal kinetics, and affect the water column and sea floor at varying distances from the fish farm. A greater impact is accepted under a fish farm than further out into the recipient. Around a fish farm, various zones are formed, which are affected to different degrees, and where different environmental standards are used. An environmental monitoring called B-investigation (MOM B in NS 9410) is primarily used under and near a fish farm where most of the larger particles are deposited. This does not normally extend beyond 15 m from the fish farm.

The B investigation comprises a simple trend monitoring of the bottom conditions under a fish farm. Because the survey is repeated regularly, at intervals determined by the extent of the environmental impact, the development of the environmental impact can be followed successively. Both the average condition at the site and the conditions under different parts of the fish farm are revealed. The B-investigation comprises many different parameters and is therefore less sensitive to anomalies in individual parameters.

The division between acceptable and unacceptable sedimentary conditions is set as the highest level of accumulation within which burrowing bottom fauna can survive in the sediment.

Sampling is carried out using a hand-held grab deployed from the cage or boat. A minimum of 10 grab-samples is taken from the area under and near the fish farm. Sampling is carried out according to ISO 12878, NS9410, NS-EN ISO 5667 and NS-EN ISO 16665. The survey is carried out by personnel with the necessary training and competence.



The B-investigation encompasses three groups of sediment parameters (see Table 3). All parameters are assigned points, according to the extent to which the sediment is affected by organic material. The higher the points, the more affected the sediment:

- Faunal investigation (Group I): Investigation where the presence or absence of animals larger than 1 mm in the sediment is recorded. Presence of animals gives 0 points: no animals or presence of *Malacoceros fuliginosa* gives 1 point.
- Chemical investigation (Group II): Quantitative survey where the pH and redox potential ( $E_h$ ) is measured in the sediment. The recorded pair of measurements for pH/ $E_h$  is awarded points according to figure 8 in the appendix.
- Sensory investigation (Group III): Qualitative investigation where sediment outgassing, smell, consistency, colour, grab volume and thickness of the layer of deposits is recorded. Presence of gas bubbles gives 4 points, absence of gas bubbles gives 0 points; pale/grey sediment gives 0 points, brown/black sediment gives 2 points; absence of smell gives 0 points, some smell 2 points and strong smell 4 points; firm consistency gives 0 points, soft consistency 2 points and loose consistency 4 points; a grab volume less than  $\frac{1}{4}$  gives 0 points, a volume between  $\frac{1}{4}$  and  $\frac{3}{4}$  gives 1 point and a volume over  $\frac{3}{4}$  gives 2 points; an accumulation of organic material on the sediment of less than 2 cm gives 0 points, between 2 and 8 cm gives 1 points and over 8 cm gives 2 points.

The repetition frequency of the B-investigation at the site is as shown in Table 6 in the Appendix. The time of survey is determined by the production cycle at the site. Sampling is primarily carried out during periods of intensive production.

Should the conditions under the fish farm be unacceptable (Condition 4), an extended B-investigation may be carried out to ensure a correct evaluation of the site. This primarily encompasses a larger number of samples, but may also be extended to include additional parameters such as total organic carbon (TOC), medication (anti-parasitic and antibiotic compounds), total nitrogen, phosphor, zinc and copper.

The monitoring programme is assessed regularly and adjusted as necessary according to the results obtained.

## **2. Material and methods**

The B investigation was performed the 22. October 2013. Fieldwork and reporting is done by Are Andreassen Moe at Helgeland Havbruksstasjon AS. The investigation is carried out after ISO 12878, NS-EN ISO 16665, NS9410 and NS-EN ISO 5667.

### **2.1.Equipment**

The following equipment was used:

- Winch: A fixed boat winch was used to retrieve grab samples.
- Grab: A grab with a sampling area of at least 200 cm<sup>2</sup> is used. The grab close fully such that water and sediment does not leak out during hauling to the surface, and it is equipped with hinged flaps on the top, to allow inspection of Group II and Group III parameters.
- pH measurement equipment: A field pH meter was used (HQ40d from Hatch Lange), together with buffer at pH 4.0 and 7.0 and distilled water.
- Redox measurement equipment: A field redox meter (Radiometer) with redox electrode, reference electrode and redox buffer. A platinum (Pt) redox electrode is used, and an Ag | AgCl electrode filled with KCl solution was the reference electrode.
- Miscellaneous: Sieve with round mesh holes of 1 mm diameter, white plastic bath of dimensions appropriate to an open grab, volume measure for grab contents, plexi-glass cylinder for sub-sampling, magnifying glass (5x enlargement), electrode holder, disinfectant solution.

### **2.2.Preparation of equipment**

Upon arrival at the site, the pH and redox electrodes was assembled and calibrated according to the manufacturer's instructions:

- pH, redox and reference electrodes are fastened to a holder such that the sensors are at precisely the same height (avoid direct sunlight). The pH electrode is calibrated in a buffer solution of pH 4.0 and 7.0. The buffer temperature was equivalent to that of the sea water.
- The electrodes are immersed into a beaker containing sea water or sea water buffer and stirred occasionally. The electrodes are ready for use after 30 min.

### **2.3.Sampling**

The text in this section relates to completion of Table 3. The samples are taken in such a way as to be as representative as possible of the bottom conditions at the fish farm.

Sampling is carried out in accordance with the following guidelines: A minimum of 10 samples are taken, evenly spread across the sampling area. If the fish farm consists of dispersed cages, at least one sample is taken at each cage, independent of the number of cages. The sampling positions are marked on the fish farm cage map, and are revisited during future sampling. During sampling, if the grab is empty on retrieval, another



attempt is made. If the second attempt is also unsuccessful, the bottom is likely to be rocky, without accumulation of organic material. This is noted in Table 2.

#### **Compact cage group**

The sampling area comprises the entire area under the cage group to its outer edges. If samples taken at the outer edges are strongly affected (condition 2 or 3), further samples are taken out into the transitional zone.

#### **Dispersed cages**

The samples are primarily taken beside the cages, particularly downstream of the prevailing current and towards the deepest area. Should there be many cages in an area, samples are also taken between the cages.

### **2.4. Inspection of samples**

The sample is inspected and the results noted in table 2. Form for sampling locations. Further details on pH and redox measurements are given in 8.1 in the Appendix.

The following procedure is applied:

- The closed grab is placed in the plastic basin and the top flaps are opened. pH, redox and reference electrodes are pushed 1 cm into the sediment. If necessary, the overlying water may first be drained off. The electrodes are held as steady as possible; the pH value is read when the given value is stable and the Eh value is read when the drift is less than 0.2 mV/s. Should stable values not be obtained within five minutes, the drift is marked by arrows. The values obtained are noted in table 3. For redox measurements, Eh is calculated by adding the half-cell potential of the reference electrode (at the relevant temperature) to the measured value (see 8.1 in the Appendix).
- The electrodes are rinsed in sea water and any water droplets are removed with absorbent paper. During extended pauses, the electrodes are put into sea water of the same temperature as the samples. The electrodes are controlled in freshly collected sea water or sea water buffer at ½ hour intervals (see 8.1 in the Appendix).
- A core sample is taken via the flaps on the upper side of the grab before the sediment is emptied into the basin, to be used for assessment of some of the Group III-parameters. Alternatively, the grab may be opened such that the sediment gently slides into the basin. The sediment is now assessed in terms of the Group III parameters, and the assigned points are noted in Table 3.
- The sediment in the basin is sieved through a mesh screen of 1 mm pore size. The material remaining on the mesh screen is transferred to a white tray and is surveyed under a hand-held magnifying glass (5x enlargement). Presence of animals in the sample is noted as 0 and absence is recorded as 1 in Table 3. Exception: A sample containing only the bristleworm *Malacoceros fuliginosa* is still assigned a point of 1. This species is capable of living on the surface of heavily affected sediments and is therefore not considered as infauna (animals living within the sediment).

## **2.5.Evaluation of results**

Table 3 is further used both to determine the sediment condition with respect to each parameter group as well as to determine the average condition for the site.

The following are determined for each parameter group:

1. "Condition (sample)" (sediment condition for each individual sample)
2. "Index" (average value of all samples)
3. "Condition (Group)" (average condition for each parameter group).

Finally, the "average site condition" is determined based on the results from all three parameter groups.

Group I parameters (animals): This group distinguishes only between acceptable and unacceptable conditions at the site. The average value of the points for all samples is calculated and noted under "index".

If more than half of all the samples contain animals (Index < 0.5), "Condition (Group I)" is deemed acceptable (A) (corresponds with conditions 1, 2 or 3). If less than half of the samples contain animals, (Index  $\geq$  0,5), "Condition (Group I)" is set to 4 (unacceptable).

In certain circumstances, if the bottom is hard and the retrieved grab contains a low volume of material (less than  $\frac{1}{4}$  full), the amount of material may be too small for animals to be sampled. For this reason, it is only required that at least half the samples shall contain animals.

Exception: Samples taken on rocky bottoms where organic material is scooped up, but which do not contain primary sediment (and therefore no infauna), cannot be expected to contain animals and Group 1 parameters are excluded. As a result, these samples are not included in calculation of the average value for Group I parameters.

Group II parameters (pH/E<sub>h</sub>): The pair of figures for measured pH and corrected E<sub>h</sub> for each sample is plotted onto the figure in Appendix D. The figure distinguishes five intervals, to which each is allotted points. The recorded points are noted under "pH/E<sub>h</sub>".

"Condition (sample)" is read from Table 3 by using the points allotted for "pH/E<sub>h</sub>" for each individual sample.

The average value of the points for all samples is calculated and noted under "Index".

"Index" is entered in Table 3 and "Condition (Group II)" is read and recorded.

Group III parameters (sensory): The sum of points is calculated for each sample.

In order to compare directly points for Group III with points for Group II parameters, a "corrected sum" is calculated for each sample by multiplying the sum with 0.22.

"Condition (sample)" is read from Table 3 by using the value for "corrected sum" for each individual sample.

The average value of all corrected sums is calculated and recorded under "index".

## Environmental monitoring (MOM B) Hringsdalur October 2013

"Index" is entered into Table 3 and "condition (Group III)" is obtained and recorded.

Group II & III parameters: For each individual sample, the average value of "pH/E<sub>h</sub>" and "corrected sum" is calculated and entered under "average value (Groups II & III)".

"Condition (sample)" is read from Table 3 by using the "average value (Groups II & III)" for each individual sample.

Thereafter, the "index" is calculated by taking the average value of all samples.

"Index" is entered into Table 3 and "condition (Group II & III)" is obtained and noted.

Average site condition: Using "condition (group I)" and "condition (groups II & III)" the "average site condition" is given in Table 3.



### 3. Site Hringsdalur

The fish farm site Hringsdalur is placed in Vestur-Barðastrandarsýsla county, Vestfirðir region. The site is placed north of Hólstrangar and Hvilftarsker, south in Arnarfjörður.

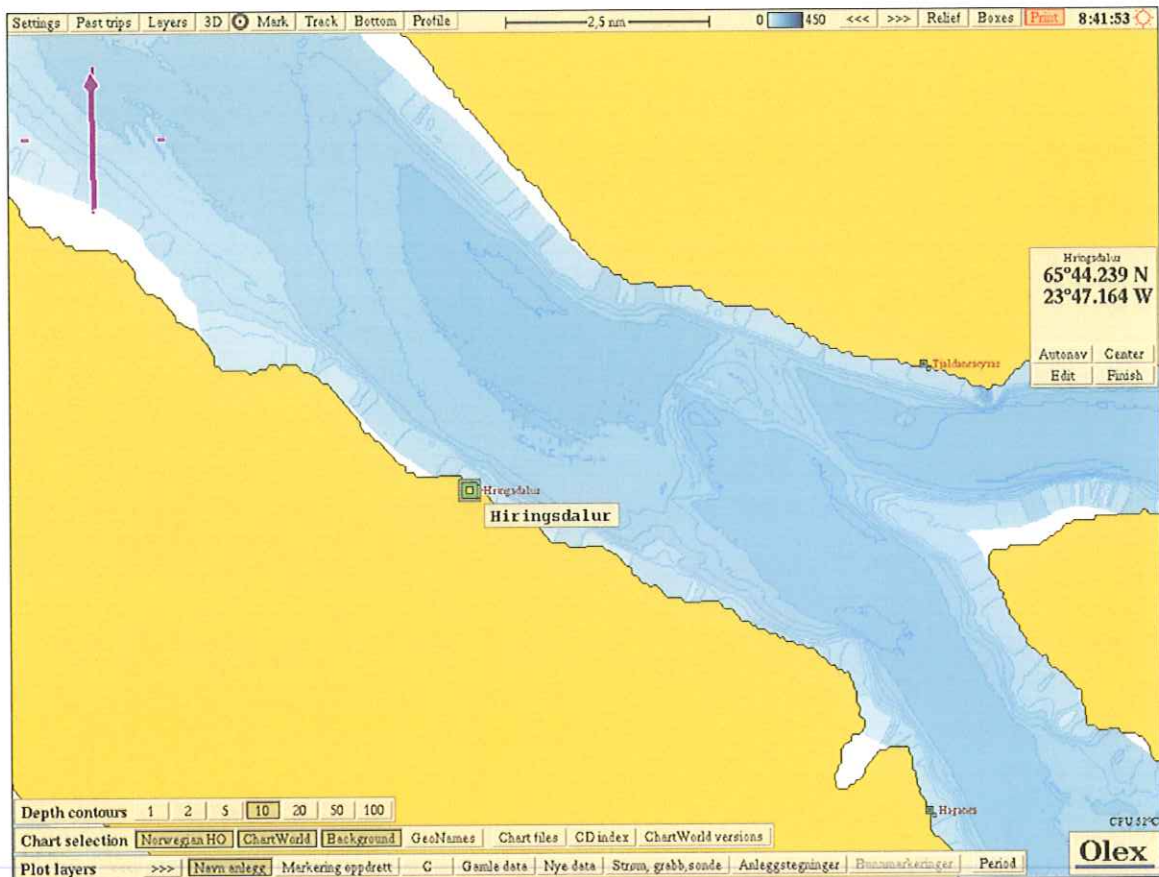


Figure 1. Bathymetric map around the farming site Hringsdalur

### 3.1. Objective of the survey

The main reason for this environmental assessment is that Arnarlax is planning to start fish farming at the area of the investigation. It was therefore done a baseline survey in the area of the planned site.

### 3.2. Production history

It has never been produced fish at the site/area of the investigation.

### 3.3. Position of sampling stations

Position of the sampling stations is based on the guidelines of ISO 12878 and NS 9410. Sampling stations covered the site and the area around. At the time of the monitoring there were no cages at the site. It is planned that the plant will consist of six polar circle cages.

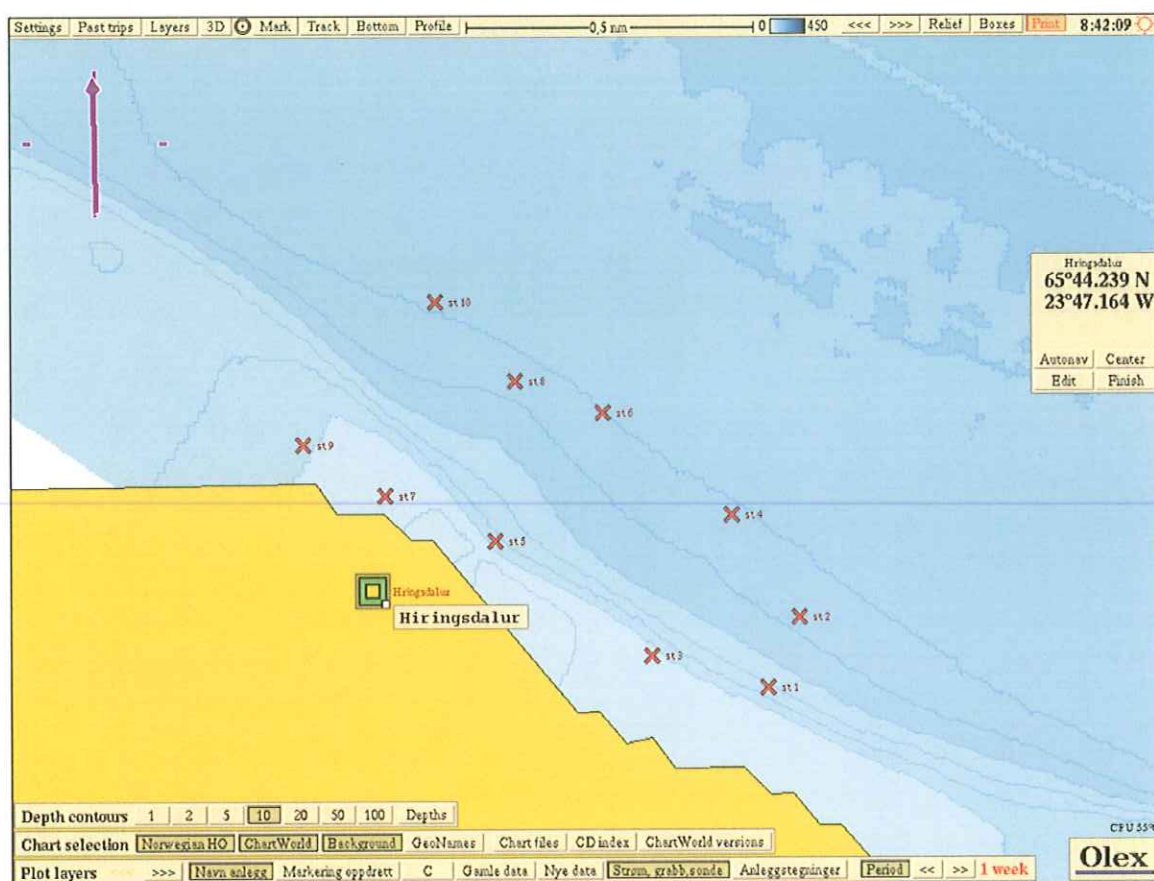


Figure 2. Sampling stations at Hringsdalur 22/10-13, red cross with the station name marks the position for grabbing at the main image.

It was taken 15 grab samples which 10 samples had content that was suitable for pH/ E<sub>h</sub>- measurements. Invalid samples were due to rock /gravel in the grab opening so that the contents spilled out.

## *Environmental monitoring (MOM B) Hringsdalur October 2013*

*Table 1. Description of stations with depth and GPS position, Hringsdalur 22/10-13*

St	Description	Depth	North		Min	Sec	Vest		Min	Sec
1	Mud with elements of silt. >2 Crustaceans, >1 Molluscs and >5 Bristleworms.	47	65	0	44	060	23	0	45	501
2	Silt with elements of sand and mud. >3 Molluscs and >40 Bristleworms.	72	65	0	44	179	23	0	45	364
3	Sand on rocky bottom. 1 Echinoderm and 1 Crustacean.	26	65	0	44	116	23	0	45	989
4	Silt with elements of sand and clay. >50 Bristleworms.	80	65	0	44	357	23	0	45	640
5	Sand with elements of silt. >3 Molluscs and >50 Bristleworms.	40	65	0	44	320	23	0	46	643
6	Silt with elements of sand. >5 Molluscs and >60 Bristleworms.	81	65	0	44	537	23	0	46	178
7	Shell-sand. 2 Crustaceans, 1 Mollusc and 3 Bristleworms.	24	65	0	44	403	23	0	47	106
8	Silt with elements of sand. >80 Bristleworms.	77	65	0	44	596	23	0	46	545
9	Shell-Sand with elements of sand on rocky bottom. 1 Crustacean.	30	65	0	44	493	23	0	47	450
10	Silt with elements of sand. >70 Bristleworms.	82	65	0	44	735	23	0	46	876



### 3.4. Bottom topography of the site Hringsdalur

The site Hringsdalur is situated on the southern side of Arnarfjörður. It is approx. 40-90 meters deep under the site and a moderate degree of sloping bottom to the northeast.

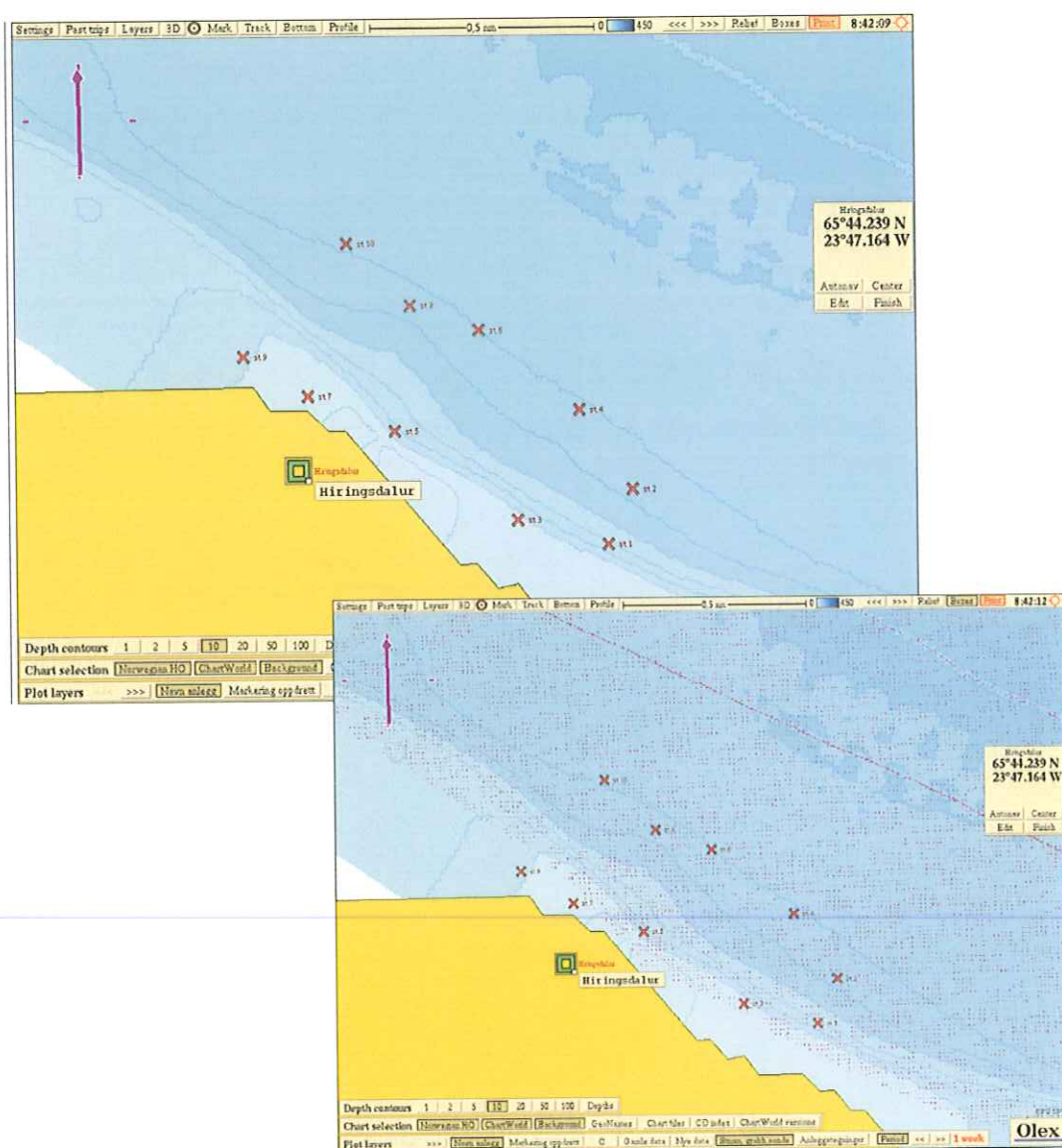


Figure 3. Depth data in the area of the site, box markings from sonar is marked purple at inset image.

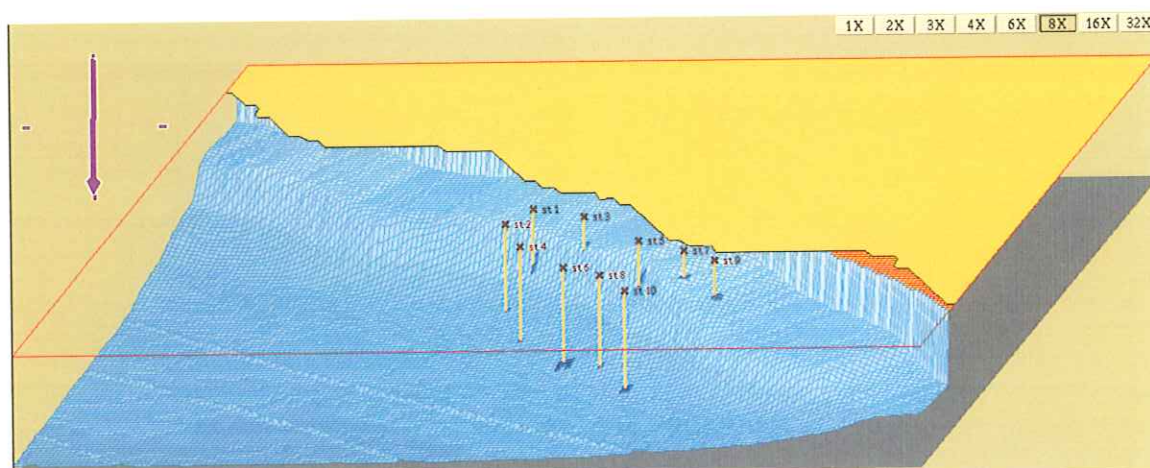
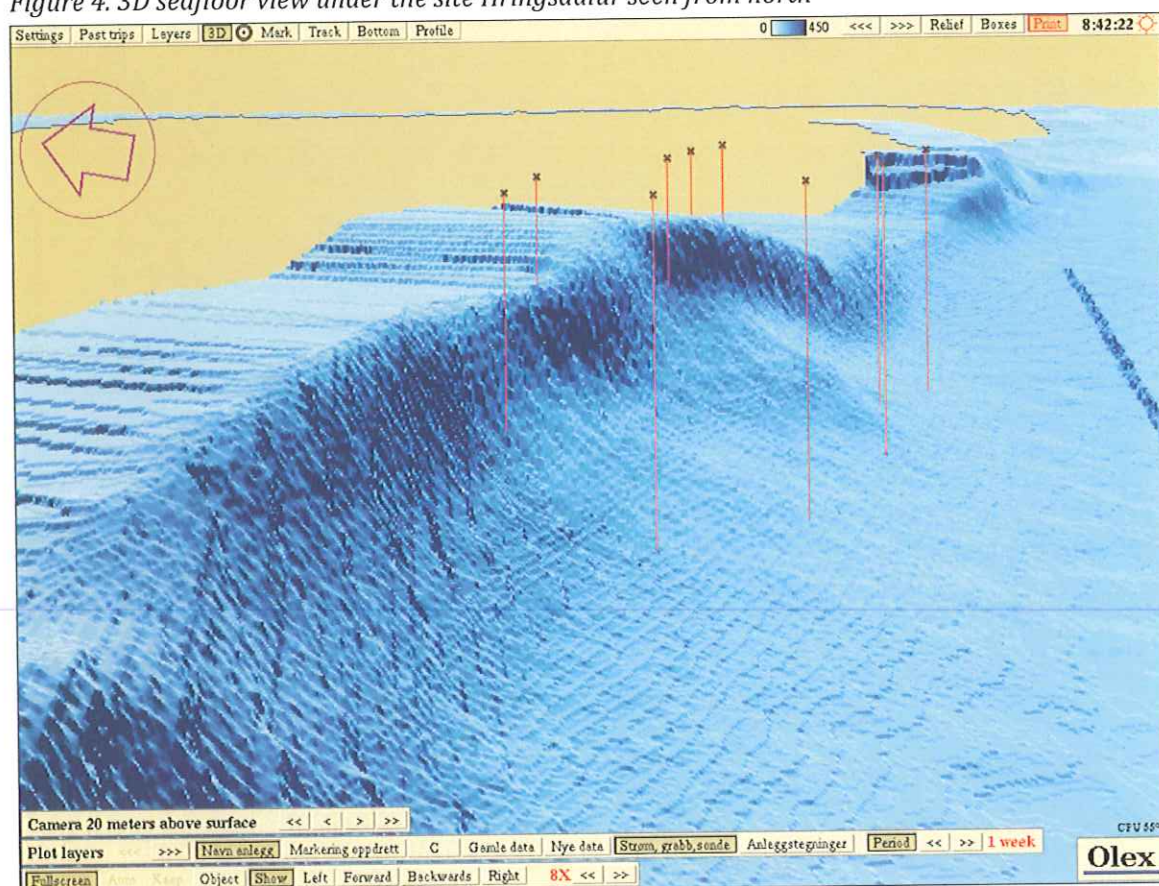


Figure 4. 3D seafloor view under the site Hringsdalur seen from north



Figur 5. 3D seafloor view under the site Hringsdalur seen from west



## **4. Results**

### **4.1. Field investigation of the bottom sediments**

#### **4.1.1. Chemical and sensory sediments parameters**

Sampling points in and around the plant consisted mainly of sand mixed with shell-sand and/or gravel.

The sediments had some signs of organic load relative to NS9410. At station 1 and 2 the sediment had a brown/black color, the rest of the stations had an pale/grey color. The consistency was firm at 6/10 stations and soft at 4/10 stations. According to NS9410 brown/black sediments and soft sediments gives 2 extra points. The points have also been given in this case, even though the color is probably natural for the environment at the station and not a sign of organic load. There were no smell of H<sub>2</sub>S or outgassing at the stations and the samples smelled of fresh sea.

Field measurements of pH and E<sub>h</sub> got points score 1 (best score) based on figure 7 in the appendix and NS9410.

#### **4.1.2. Faunal investigation**

I NS9410 is the division between acceptable and unacceptable sedimentary conditions set at the highest level of accumulation within which burrowing bottom fauna can survive in the sediment.

There was borrowing bottom fauna in 10/10 stations under the planned site. The fauna was diverse, and it consisted of different species crustaceans, molluscs and bristleworms, some of the species found are considered sensitive of organic load.



## 4.2.MOM B, forms and tables

Table 2. Form for sampling locations, Hringsdalur 22/10-13. \*Estimates of individuals in group.

\*\* Number of individuals are noted.

Sampling location (nr)	1	2	3	4	5	6	7	8	9	10
Depth (m)	0	0	0	0	0	0	0	0	0	0
Number of sampling attempts	1	1	3	1	2	1	1	1	3	1
Out gassing (in sample)										
Bottom type	Gravel									
	Shell-sand									
		(x)	(x)	(x)	x	(x)		(x)	(x)	(x)
	x	(x)								
	(x)	x		x	(x)	x		x		x
				(x)						
Rocky bottom			(x)						(x)	
Stony bottom										
*Echinoderms			1							
*Crustaceans	>2		1				2		1	
*Molluscs	>1	>3			>3	>5	1			
*Bristleworms	>5	>40		>50	>50	>60	>3	>80		>70
Other animals										
** <i>Malacoceros fuliginosa</i>										
Beggiatoa										
Feed pellets										
Excrement										
Comments	Mud with elements of silt. >2 Crustaceans, >1 Molluscs and >5 Bristleworms.	Silt with elements of sand and mud. >3 Molluscs and >40 Bristleworms.	Sand on rocky bottom. 1 Echinoderm and 1 Crustacean.	Silt with elements of sand and clay. >50 Bristleworms.	Sand with elements of silt. >3 Molluscs and >50 Bristleworms.	Silt with elements of sand. >5 Molluscs and >60 Bristleworms.	Shell-sand. 2 Crustaceans, 1 Mollusc and 3 Bristleworms.	Silt with elements of sand. >80 Bristleworms.	Shell-Sand with elements of sand on rocky bottom. 1 Crustacean.	Silt with elements of sand. >70 Bristleworms.

# Environmental monitoring (MOM B) Hringsdalur October 2013

Tabell 3. Form for samples, Hringsdalur 29/1-13.

Gr		1	2	3	4	5	6	7	8	9	10	Ind	
I	Parameter												
	Points												
Animals > 1mm	Yes (0) No (1)	0	0	0	0	0	0	0	0	0	0	0	
	Condition gr. I	A											
II	pH	Measured Value	7,8	7,6	7,7	7,7	7,8	7,8	7,7	7,8	7,8	7,8	
	Eh (mV)	Measured Value	-68	-61	-48	-59	-38	-43	-50	-48	-39	-69	
		ref.pot	234	234	234	234	234	234	234	234	234	234	
	pH/Eh	Points, Appendix, figure 8	0	0	0	0	0	0	0	0	0	0	0,00
		Condition (Sample)	1	1	1	1	1	1	1	1	1	1	
	Condition gr. II	1	1	1	1	1	1	1	1	1	1	1	
		Buffer temp	5	seawater temp.	6,9	sediment temp.	4,8						
	Ph seawater:	8,0	Eh seawater:	67	Ref. elekt. pot. (mv)								
	III	Outgassing	Yes (4) No (0)	0	0	0	0	0	0	0	0	0	0
Colour		Pale/grey (0)			0	0	0	0	0	0	0	0	
		Brown/black (2)	2	2									
Smell		None (0)	0	0	0	0	0	0	0	0	0	0	
		Medium (2)											
		Strong (4)											
Consistency		Firm (0)	0		0		0	0	0		0		
		Soft (2)		2		2				2		2	
		Loose (4)											
Grab-volume (v)		v < 1/4 (0)			0						0		
		1/4 < v < 3/4 (1)							1				
		v > 3/4 (2)	2	2		2	2	2		2		2	
Thickness of deposits (t)		t < 2 cm (0)	0	0	0	0	0	0	0	0	0	0	
		2 < t < 8 cm (1)											
		t > 8 cm (2)											
Sum			4	6	0	4	2	2	1	4	0	4	
Corr. Sum (0,22)			0,88	1,32	0	0,88	0,44	0,44	0,22	0,88	0	0,88	0,59
Condition (sample)			1	2	1	1	1	1	1	1	1	1	
Condition gr. III			1										
Average value group II og III		0,44	0,66	0	0,44	0,22	0,22	0,11	0,44	0	0,44	0,30	
Condition gr. II og III		1											
pH/Eh Corr.sum Average value	Condition (gr. II & III)												
	< 1,1	1											
	1,1 -< 2,1	2											
	2,1 -< 3,1	3											
	-> 3,1	4											
Condition													
Group I		A											
Group II and III		1,2,3,4											
Average value for site		1,2,3,4											
4		1,2,3											
4		4											
AVERAGE SITE CONDITION												1	

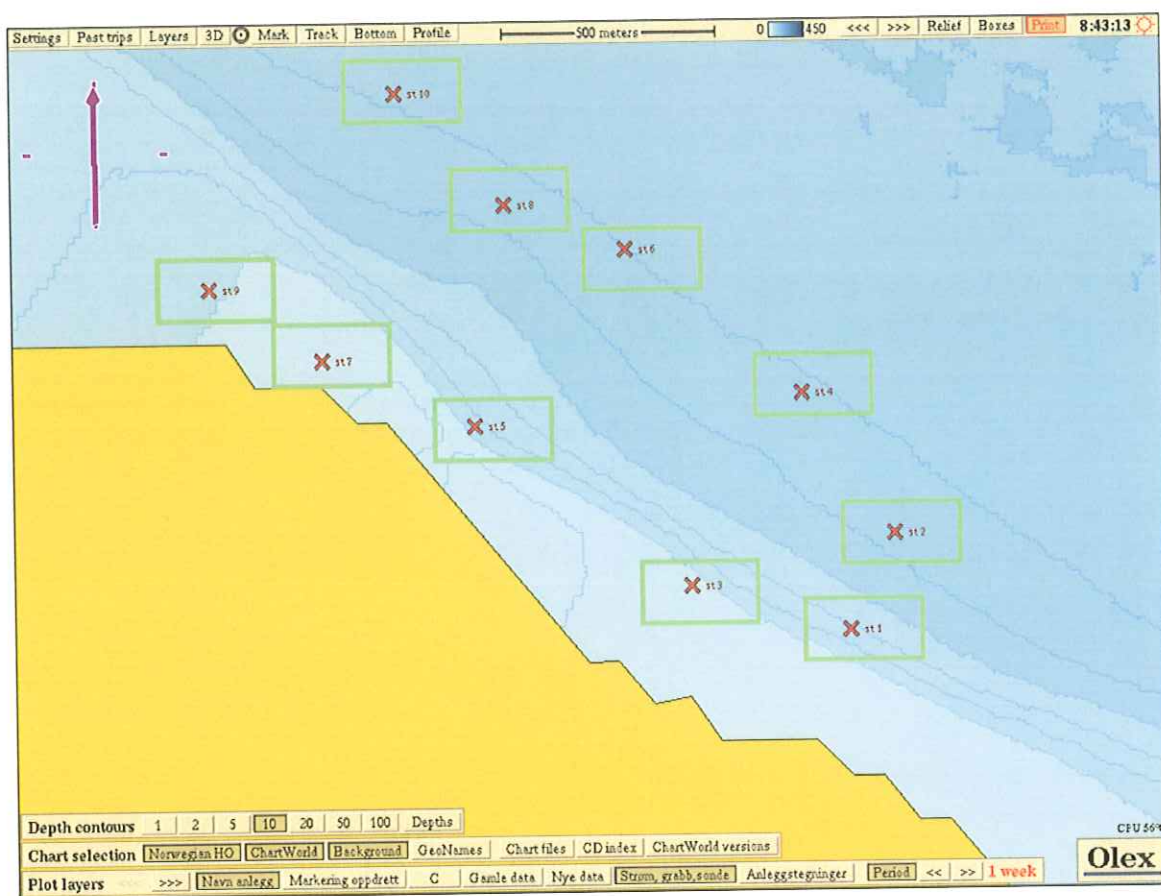


Figure 6. Overview of condition at the different stations. \* See table 4 for index-color based on condition.



## 5. Summary of environmental condition at site Hringsdalur

### 5.1.MOM B investigation

Summary of results are given in table 4.

The site is in October 2013 classified by NS 9410 to the site condition 1 (Best score). Considerations on fauna, visual and sensory parameters show no signs of organic load under the planned site. The fauna is rich and consists of a variety of species.

*Table 4: Information from B investigation (partial results)*

Results from B investigation/NS-9410-Investigation (partial results):				
No. Sampling locations:	10	No. Of sampling attempts	15	
Bottom type: (table 2)	Dominating:	Less dominating:	Least dominating:	
	Sand and Silt	Shell-sand and mud	Clay	
No. Sampling locations (group II and III) with following condition (information from table 3) :				
Condition 1	10	Condition 3	0	
Condition 2	0	Condition 4	0	
Index and B investigation condition (1-4)				
Index-number illustrated	1	2	3	4
	↑			

## **6. Literature**

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## 7. Appendix

### 7.1. pH and Redox potential

#### 7.1.1. Utility

The B-investigation is suited to field work, and the given procedure can be applied for determination of pH and redox potential in sea water and marine sediments. In principle, the procedure may be used for samples collected with a water sampling device, a cylindrical core sampler, box core sampler or a grab.

NOTE The procedure does not aim to operate at a precision level equivalent to that achieved under ideal laboratory conditions. The aim is that different operators with individually selected equipment shall achieve results repeatable to within  $\pm 0.1$  pH units and  $\pm 25$  mV  $E_h$ .

Thermodynamic assessment of  $E_h$  measured using platinum electrodes is not recommended. The parameter is used only as an empirical environmental parameter associated with a contamination gradient.

#### 7.1.2. Principle

pH and  $E_h$  are general chemical parameters controlled by acid-base and the reduction-oxidation equilibrium in the sample. The parameters can be determined non-destructively using electrodes inserted directly into the sample without the addition of chemicals. In the marine environment, the  $E_h$  value varies from +400 mV in surface water at atmospheric equilibrium to -200 mV in anoxic sediments or bottom water in fjords and basins with poor water exchange. The pH value normally varies between 8.0 and 8.1 in surface water down to 7.0 in naturally anoxic water masses and sediments.

In principle, pH ( $= -\log\{H^+\}$ ) and pE ( $= -\log\{e^-\}$ ) are analogue expressions for the negative logarithm of proton and electron activity. The relationship between pE activity and the  $E_h$  potential is obtained by the Nernst equation:

$$E_h = (RT/nF)\ln\{e^-\} = 0,056 \text{ pE} \quad \text{at } 10^\circ\text{C},$$

where:

R is the molar gas constant;

T is the absolute temperature;

n is the number of particles and

F is Faradays constant.

It is important to note that the observed resting potential in the sample ( $E_{obs}$ ) is equivalent to the difference between half-cell potential of the redox electrode ( $E_h$ ) and the reference electrode ( $E_{ref}$ ):

$$E_{obs} = E_h - E_{ref}$$



To determine the redox potential, the half-cell potential of the reference electrode must be known and added to the observed potential:

$$E_h = E_{obs} + E_{ref}$$

*Table 5: Half-cell potentials at different temperatures for two Radiometer reference electrodes*

t (°C)	Ag AgCl E <sub>ref</sub> (mV)	Calomel E <sub>ref</sub> (mV)
0	236.55	-
5	234.13	272.83
10	231.42	271.87

For further information check out the supplier of the reference electrode. They should be able to supply the precise E<sub>ref</sub> at the relevant measuring temperatures. Table A.1 shows the half-cell potentials for two commercially available electrodes.

### 7.1.3. Choice of measuring equipment

The two alternatives given in Table 5 are examples of equipment tested in the field, but should not be considered as binding. The requirements for accuracy are such that most general field instruments and electrodes are suitable.

A platinum (Pt) redox electrode is used, and an Ag | AgCl electrode filled with KCl solution is suitable as a reference electrode.

The reference electrode must not contain metal ions that can lead to clogging of the salt-bridge when used in sulphidic samples. Calomel electrodes contain mercury and, if possible, should be avoided in field surveys.

ISFET technology (Ion Specific Field Effect Transistor) for measurement of pH is newer and less well-tried than traditional glass electrodes. An important advantage with ISFET sensors is that they are very robust compared with glass electrodes and tolerate drying during transport and storage (they require storage in air). One disadvantage with the first models that appeared on the market was that the shape of the electrode tips was unsatisfactory for penetration into the sediment sample. The measuring accuracy is sufficient for the present purposes. The response time and stability over time appears to be at least as good as, and possibly better than, glass electrodes.

#### 7.1.4. Temperature control

All electrode potentials are temperature dependent. Temperature control is particularly important for pH measurements. Low temperature sensitivity is an important criterion for the choice of buffer solution and reference electrode.

Ideally during pH measurement, the sample and the buffer should be at the same temperatures. To achieve the above-mentioned replicability, it is sufficient that the samples are measured at a temperature that deviates less than 5 °C from the *in-situ* temperature, i.e. the temperature of the sample before it was removed from the sea floor. The temperature in the bottom water and sediments at Norwegian fish farms is often between 5 °C and 10 °C. Over large parts of the year, the air temperature will be approximately similar, or lower. The recommended working temperature for calibration and measuring is therefore between 5 °C and 10 °C. A refrigerator, ice or buckets of sea water are simple, readily available means of maintaining the recommended working temperature.

If the pH meter is equipped with temperature compensation, variations between samples and between sample and buffer are compensated for, but changes in pH as a result of temperature changes during storage are not.

No particular attention is paid to temperature during measurement of the redox potential, but during conversion from cell potential to  $E_h$ , the half-cell potential of the reference electrode is used at the appropriate working temperature (Table C.1).

#### 7.1.5. Calibration of pH.

Two-point calibration of pH is carried out at the site before the start of the measurements. The instrument user manual must be followed. Two buffers are used, with pH values of 7.0 and 4.0, respectively. The pH- $E_h$  diagram (Appendix D) is based on calibration in low ionic strength buffers (regular NBS or IUPAC buffers).

After calibration, the electrodes are placed in sea-water. Sea water has a higher salinity than the buffer solutions. This affects the diffusion conditions of the electrodes and causes some problems, such that it may take some time before the electrode gives a stable pH reading. The work should therefore be organised such that the electrodes are allowed to stand in sea water for approximately ½ hour before the measurements are started, preferably with occasional stirring. A somewhat longer response time may be expected during the first measurements after a calibration. During measurements, the electrodes are rinsed in sea water only. Alternatively, fresh water may be used with an additive of 30 -35 g salt (NaCl) per litre, but this cannot be used as a pH-buffer in the same way as sea water.



The pH of sea water is approximately 8.0 - 8.1 with only slight variation. In deep water, the pH can be somewhat lower, but seldom less than 7.6. Sea water is well buffered and freshly collected sea water may therefore be used as a working buffer to control the electrode during measurements, but care should be taken to avoid local conditions that may affect the pH, such as industrial effluent, algal blooms and brackish water layers.

It should not be necessary to re-calibrate a good pH electrode between measurements, but it should be controlled regularly in the working buffer, for example at ½ hour intervals. Should this reveal systematic deviation, the results may be corrected after the measurements are completed. Should there be a persistent deviation of more than 0.2 pH units from the value first measured, the operator should consider recalibrating the electrode and, if possible, repeating measurements.

#### **7.1.6. Control of Redox potential**

It is not necessary to calibrate platinum electrodes. However, the entire redox cycle should be controlled in a solution with a known redox potential, such as a redox buffer solution. Such a solution can be made by dissolving 1.0974 g  $\text{K}_3\text{Fe}(\text{CN})_6$ , 1.2278 g  $\text{K}_4\text{Fe}(\text{CN})_6$  and 7.4551 g KCl in 1000 ml distilled water. This solution has a stable  $E_h$  of 430 mV at 25 °C, decreasing at lower temperatures. Between temperatures of 5 °C – 10 °C, the sum of the measured cell potential ( $E_{\text{obs}}$ ) and the specified half-cell potential ( $E_{\text{ref}}$ ) should be between 400 mV and 430 mV.

An unstable pH/mV signal during measurement may be due to clogging of the salt-bridge or the salt-bridge not being covered by the sample. If the salt-bridge is clogged by sediment particles or precipitation, the electrode is damaged and must be replaced (refers to glass pH electrodes and reference electrodes, not ISFET or platinum electrodes).

Other causes of technical problems may be a weak battery, dampness or corrosion in the electrical contacts, static electricity or electrical noise from nearby electrical installations.



#### 7.1.7. Deflection /response time

The response time, i.e. the time taken before the instrument shows a stable value, is dependent on the composition of the sample and can be lengthy for  $E_h$  measurement. Assuming that a maximum of 4 to 5 minutes is available for each sample, it is important to establish routines that give as repeatable as possible results within this time-frame.

After the electrodes are inserted into the sample, there is an exponential decrease in deflection. A deflection of less than  $\pm 25$  mV from the stable value is usually achieved within 1 to 2 minutes. A deflection of up to 0.2 mV per second at the moment of measurement is considered acceptable.

In certain circumstances, it may not be possible to fulfil even such relatively “mild” requirements as to deflection within a realistic time-frame. This is particularly the case in the transition from reduced to sulphide-free sediment samples. Sulphide is adsorbed to platinum electrodes and can affect measurements in weakly-buffered samples several hours after contact. As illustrated in Figure 7, this can result in poor replicability in samples with high  $E_h$  values recorded within the maximum acceptable waiting time (5 min.). Sulphide absorption does not affect the readings in the redox buffer or sediment samples with a redox potential lower than approximately 100 mV. The B investigation is not affected either, because the assessments of condition (See introduction) do not differentiate values  $E_h > 100$  mV.

If the measurements are always carried out first on a sulphidic sample, or even sea-water to which a small crystal of sodium sulphide ( $\text{Na}_2\text{S}$ ) has been added, the measuring area is reduced at the upper end of the gradient, but the replicability is improved over the entire measuring area as a whole.

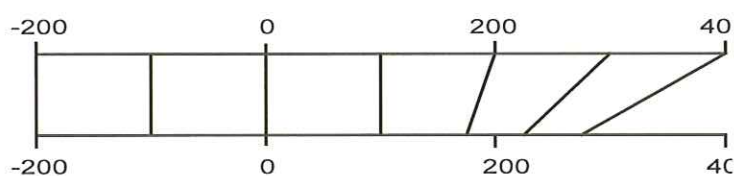


Figure 7. Schematic illustration of the  $E_h$  gradient in marine sediment measured with a platinum electrode before (upper scale) and after (lower scale) contact with hydrogen sulphide

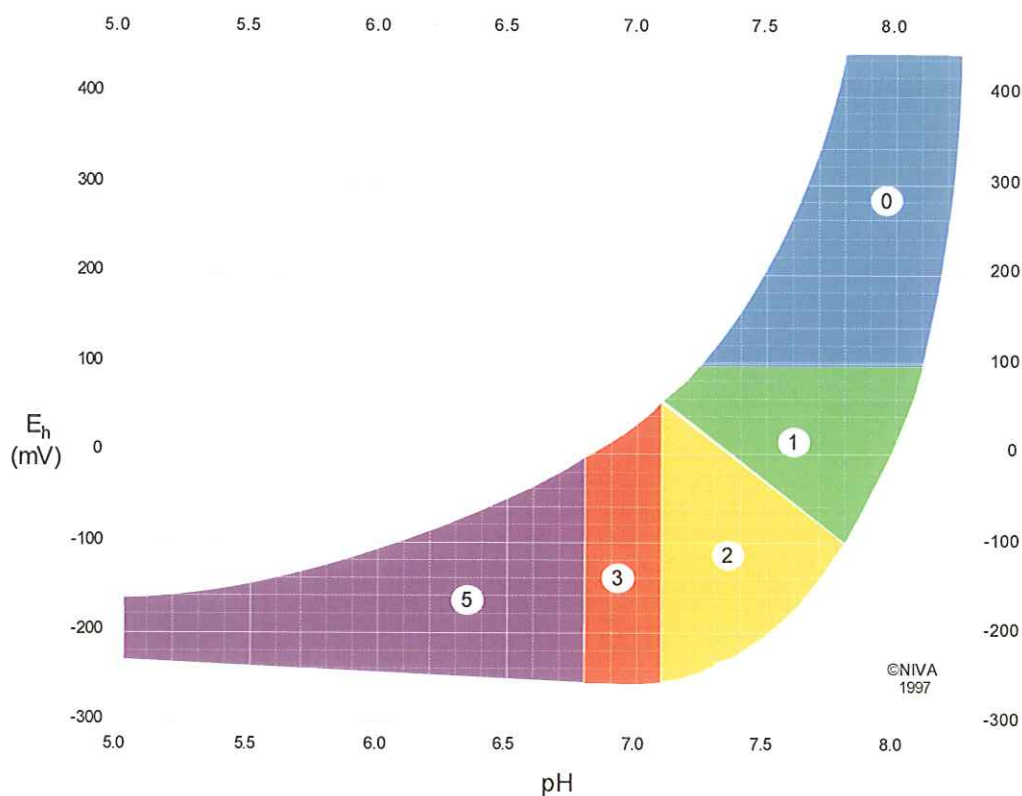


Figure 8. Point allocation based on redox potential and pH value

Table 6: Frequency of MOM B investigations at the site (local impact zone) in relation to impacts at the site (site condition). Site condition 4 corresponds with unacceptable conditions

Site condition	Monitoring level
	B-investigation
1	every 2 years
2	annually
3	every 6 months
4	eventual extended B-investigation