

Geochemical Data Collection in LOOP4

MapField, 2019-2020

Hyojin Kim, Rasmus Jakobsen, Jens Aamand, Ingelise Møller
& Birgitte Hansen

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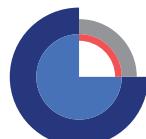
Results from The Innovation Fund Denmark project:
MapField – Field-scale mapping for targeted Nregulation
and management (8855-00025B)

Hyojin Kim, Rasmus Jakobsen, Jens Aamand, Ingelise Møller & Birgitte Hansen

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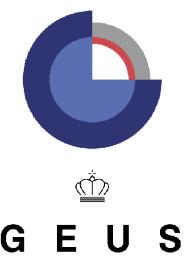
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DE NATIONALE GEOLOGISKE UNDERSØGELSER FOR DANMARK OG GRØNLAND
KLIMA- OG ENERGIMINISTERIET

Data report 2019-2020 MapField

Authors: Hyojin Kim, Rasmus Jakobsen, Jens Aamand, Ingelise Møller & Birgitte Hansen

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1. Introduction

This report summarizes existing data and results of the field campaigns carried out in LOOP4 in 2019 to collect geochemistry data for the MapField project. The geochemistry data includes groundwater chemistry, sediment chemistry, and nitrate reduction rates. We drilled boreholes to collect groundwater and sediment samples. The primary objectives of the geochemistry data collection are to capture transport and evolution of nitrate in the subsurface at the field scale and to quantify the rates of nitrate reduction. This geochemistry data will be input data for an integrated hydro-geochemistry modelling. Here, we describe the methods and results of 2019.

2. Methods

2.1. Field campaign planning

To select the most important drilling sites of the study catchment, preliminary characterization of the subsurface structure and nitrate transport and fate were done using existing data. The existing data encompass 1) tTEM model and geological interpretation of the tTEM model; 2) digital terrain model; 3) water chemistry (pore water, groundwater, and stream water chemistry) focusing on nitrate; 4) groundwater table; and 5) redox zones interpreted from sediment colors.

2.2. Identified hypotheses

Based on this preliminary analysis, hypotheses for the evolution of nitrate in the subsurface were developed, and sampling points for N reduction rates and detailed water chemistry profiling were selected. These hypotheses are related to the optimizerization or the iterative creative processes:

Optimization process:

1. Using 2.5 days for screening the redox conditions and IP (Induced polarization) with the redox-IP-geoprobe is optimal for planning the 3-days drilling campaign for sediment, water and gas sampling

Iterative creative process:

1. There is a significant correlation between redox state and IP at the redox interfaces due to facies change from Fe^{3+} to Fe^{2+} .
2. N reduction in upper clay till is important.
3. N reduction in the unsaturated zone in upper clay till plays a measurable role in the total N reduction.
4. The nitrate leaching and transport through the western sandy geologic windows and along the upper sand layer creates deep redox interfaces important for catchment N transport.
5. In the low-lying Eastern part of the catchment N reduction in the interglacial and meltwater sand plays an important role in N reduction.
6. Exploring different laboratory methods for N reduction rate determination e.g. with and without the use of acetylene.

2.3. Borehole drilling and sample collection

In November 2019, to screen the redox interface of the selected sampling points, a redox probe survey was carried out. Two weeks after the redox probe survey, based on

the screening results, a Geoprobe direct push method was used to collect core samples less than 1 meter from the redox probe points. The drilling was performed by Ejlskov. The core samples were cut and wrapped with aluminum tape in the field for pore-water chemistry (9cm-long), nitrate reduction rates (25cm-long), geochemistry sediment analysis (varying length), and lithological description (varying length). Except the lithology samples, all the core samples were stored in a cooling box in the field.

2.4. Gas sampling well installation

During the drilling campaign, gas sampling wells were installed in selected locations among the geochemistry sampling points. Plastic tubing was cut for a desired length and about 20-30 cm of the bottom end was slotted to allow gas influx. The other end was connected to a two-way valve so that gas sample can be extracted. A 2-inch diameter hole was drilled to a desired depth using Geoprobe and the plastic tubing was inserted. The bottom 30 cm of the hole was filled with sand and the rest was filled with bentonite.

2.5. Water chemistry analysis

In the laboratory, the core samples for the pore water chemistry analysis were centrifuged to extract pore water. The water samples had been stored refrigerated until analysis. The centrifuged water yield varied and analyses were prioritized in the following order at GEUS: 1) Anions by an ion chromatography (IC); 2) ammonium by a Flow Injection Analysis (FIA); 3) Dissolved inorganic and organic carbon by an Infra-red (IR) detection on Shimadzu instrument; 4) Cations and trace elements by an Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS); and 5) Water isotopes by a Cavity Ring Down Spectroscopy (CRDS).

2.6. Sediment chemistry analysis

A number of sediment chemistry parameters were analyzed for at GEUS:

- 1) Sediment Reduction Capacity was determined by oxidation with Ce(IV)
- 2) Fe(III) from less stable Fe-oxides, and Fe(II) compounds soluble at pH 3 were determined by extraction in formic acid at pH 3
- 3) Sediment inorganic and organic carbon as well as total sulfur was analyzed using a LECO furnace.

2.7. Nitrate reduction rate measurements and experiments

Rates of nitrate reduction were measured in the laboratory at GEUS using the acetylene-block method, where the transformation of N₂O to N₂ is blocked by adding acetylene to a closed vial containing sediment, 20 mL of a 1 mmol nitrate solution and a headspace, and following the production of N₂O for up to 2 weeks. The production of N₂O was followed by measuring the concentration in the known headspace of the vial and calculating the concentration in the known water volume.

Many of the incubations from LOOP3 show two phases in the N₂O development. An initial phase, where the development in the N₂O concentrations is very slow, followed by a second phase where the rate in the N₂O development has shifted to a much higher level.

Incubations in other experiments where the porewater was sampled over time strongly indicate that the initial phase where a very slow rate in the N₂O development is seen, is a phase where the last traces of O₂ in the incubation flask are removed. This is supported by the observation that this initial phase is sometimes not seen in incubations where high rates are measured, presumably because in these the traces of oxygen are rapidly removed by a reactive electron donor.

In the cases where there is a second rapid phase and it is adequately well described by a highly linear increase over at least three measuring points this second rapid phase has been used. This implies that many samples have not been included in the calculation of the final rates because the rate determined from only two points has a high probability of being underestimated.

The values are transformed from the rates of development in the N₂O concentration determined pr. gram of incubated sediment into $\mu\text{molN}_2\text{O/l/yr}$ assuming that there are 5.4 kg of sediment pr. liter of groundwater/porewater. In the final calculation this has been multiplied by 2, as each mole of N₂O represents 2 moles of NO₃⁻.

In addition to the rate measurements, experiments to address different aspects of the nitrate reduction and clarify the interpretation of the acetylene block N₂O rate measurements were carried out.

Experiment 1: A 1 mM nitrate solution was added to the nitrate rate incubations, but to clarify whether the rate was dependent on the nitrate concentration we set up 12 sets of 2 incubations with different nitrate concentration (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7,

1.0 (triplicates), 1.5, 2, 3, and 4 mM), using homogenized sediment from 2 core segment. In this experiment there was no acetylene added and the rates were derived from measuring the nitrate concentration in the water over time. To have enough water 300 g of sediment was added to 500 mL bottles and 130 mL of water was added.

Experiment 2: In experiment 2 the N₂/CO₂ atmosphere was changed to a pure He atmosphere and calcite was added as pH buffer instead of CO₂. To see if this affected the measured rates a set of incubations (triplicates), corresponding to the 1 mM nitrate incubations mentioned above, was set up using He as headspace gas and calcite as pH buffer.

To clarify to what extent the rate of nitrate reduction measured by the acetylene block method includes the part of the rate that could be associated with pyrite oxidation rather than oxidation of organic matter Experiments 3 and 4 were set up in parallel. Experiment 3 in large bottles where the concentrations in the water could be followed to derive the rates and Experiment 4 where the acetylene block method was used.

Experiment 3: The experiment was done with clayey sediment from what based on the sediment color was most probably; oxidized, nitrate reducing and reduced sediment. For each type of sediment duplicates with 0, 125 and 250 mg of pyrite pr. 100 g of sediment were set up in 300 ml bottles. The pyrite added came from pyrite crystals that had been crushed and sieved resulting in a powder with a BET surface area of 0.4 m²/g. The headspace was He and 0.5 g of calcite powder pr. 100 g of sediment was added as pH buffer and no acetylene was added. The bottles were sampled for anions, Fe²⁺ and pH, one of the duplicates had an optode sticker mounted inside for measuring oxygen. The headspace gas was sampled and measured for N₂, O₂ and CO₂ by gas chromatography by TCD detection.

Experiment 4: This was parallel to experiment 3, with sediment from 3 apparent redox zones with varying amounts of pyrite, except done in the smaller 120 mL bottles with 100 g of sediment and here acetylene was added as in the normal rate measurements, but here the headspace was He and calcite was used as pH buffer.

2.8. Gas chemistry analysis

Gas samples were collected using plastic syringe. Before sampling, the gas wells were purged to remove the air in the gas well. The gas samples were collected in 3ml (N₂O) and 6ml (CO₂ and O₂) Exetainers®. The samples were duplicated.

The gas samples were analyzed for CO₂ and O₂ using gas chromatography (GC) with a TCD detector, N₂O was measured using a GC using cavity ringdown spectroscopy (CRDS) and N and O isotopes of N₂O also using CRDS.

2.9. Lithology description

Geological descriptions of the sediment samples were carried out at the laboratory at GEUS and are shown in Appendix 1.

2.10. Re-evaluation of redox probe

In February-March 2020, Ejlskov concluded that the redox-probe has been unstable since the summer of 2018 due to a hole in the insulation of the wire connecting the platinum electrode used for measurement of the signal. Ejlskov started troubleshooting the redox-probe and after a few rounds of amendments, the stability of the redox-probe was tested in LOOP2 in April 2020. More test and adjustments were carried out over the summer and autumn resulting in a dual-redox-probe. The final redox-probe measurements were carried out in March 2021 at sample points GeoW-1, GeoW-2, GeoW-3, TL-1, TL-2, IS-1, IS-2, MS-1 and MS-2. At the field campaign in 2021 each sampling point were repeated twice and using the dual probe.

2.11. Water table

Water table measurements were carried out in the field directly in the boreholes left after each redox-probe measurement. At two locations the level of the water table was deeper than the bottom of the borehole. At another location the borehole collapsed immediately after the drill stem was removed and it was not possible to measure the water table. The depth to the top of the collapse in the borehole was measured as it may be an indication of the water table. Water table measurements from the first round of redox probe measurements were used for the well panel plots.

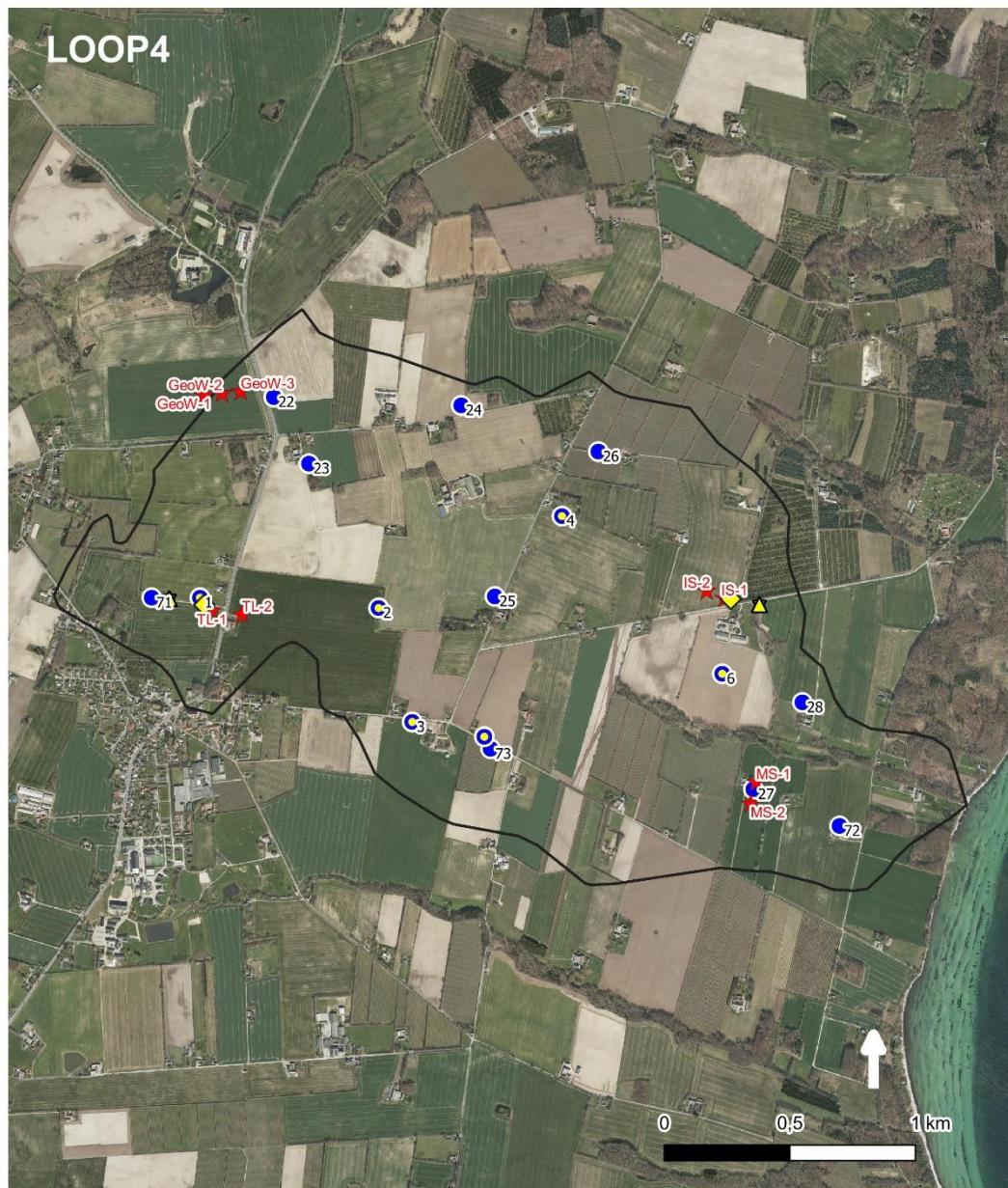
To supplement and validate the information on the water table from field measurement an evaluation of the water table at each sampling point was carried out on existing data reported to the Jupiter database. The Jupiter borehole data including water level and a

terrain grid were read into Geoscene 3D. Profiles crossing existing wells with water table levels and the MapField sampling points were drawn and at each sampling point the water table were interpreted taking the water level in adjacent well as well as the terrain level into account. At sampling points GW-1, IS-1 and IS-2 only interpreted water levels are available.

3. Results

3.1. Existing data

In total, water chemistry and groundwater table observations were available at 20 locations across the catchment (Figure1 and table1). Table 1 summarizes the availability of water chemistry and groundwater level data of LOOP4. Most LOOP monitoring stations have 1-4 filter depths for water sampling. Water chemistry was measured at 40 points and groundwater table is monitored at 21 points. The time-series of nitrate concentrations and groundwater table of each monitoring station are shown in Appendix 2 as an example.



Boreholes

★ MapField investigation boreholes

◆ Gas wells

Existing boreholes

○ LOOP Groundwater + Soil pore water (Station Nr)

● LOOP Groundwater (Station Nr)

▲ other wells

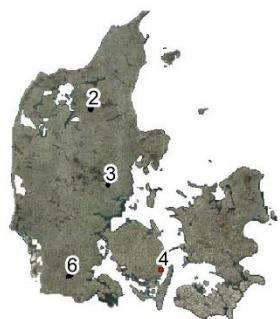


Figure 1. Overview of existing boreholes with geochemistry information, MapField investigation boreholes and gas access wells.

Table 1. List of existing data in LOOP4 (No = number)

LOOP Station Nr	Water chemistry							Groundwater table	
	DGU (X, Y)	Depth (m)	Data period	No of DO samples	No of NO ₃ ⁻ samples	No of Fe(II) samples	No of SO ₄ ²⁻ samples	DGU (X, Y)	Data period (Nr of data)
1	165. 296 (610169, 6110139)	3.0-3.3	1989-1999	0	46	26	17	165. 334 (610172, 6110112)	1990-2017 (1078)
	165. 297 (610169, 6110139)	5.0-5.3	1989-1999	0	62	36	31	165. 394 (610170, 6110139)	2008-2017 (1821)
	165. 299 (610169, 6110139)	3.0-3.3	1989-2017	5	54	35	17		
2	165. 303 (610880, 6110098)	5.0-5.3	1989-2018	17	184	150	44	165. 395 (610881, 6110098)	2009-2017 (436)
	165. 305 (610881, 6110099)	3.0-3.3	1989-2018	14	153	128	31		
	165. 306 (610880, 6110098)	5.0-5.3	1989-2018	18	172	148	40		
3	165. 308 (611014, 6109644)	3.0-3.3	1989-2018	16	165	136	35	165. 336 (611004, 6109654)	1990-2017 (1058)
	165. 309 (611014, 6109644)	5.0-5.3	1989-1994	0	29	21	20	165. 369 (611000, 6109654)	1995-1995 (19)
	165. 311 (611014, 6109644)	3.0-3.3	1989-1995	0	8	1	5		
	165. 312 (611014, 6109644)	5.0-5.3	1989-2018	16	193	155	48		
4	165. 314 (611610, 6110464)	3.0-3.3	1989-1997	0	47	24	24	165. 337 (611587, 6110478)	1990-2017 (1068)
	165. 315 (611610, 6110464)	5.0-5.3	1989-2006	0	82	44	35	165. 396 (611609, 6110464)	2008-2017 (2509)
	165. 317 (611611, 6110464)	3.0-3.3	1989-2017	4	151	119	38		
	165. 318 (611610, 6110464)	5.0-5.3	1989-1997	0	21	7	12		
5	165. 321 (611301, 6109585)	5.0-5.3	1989-2018	11	125	102	33	165. 338 (611307, 6109571)	1990-2017 (853)
	165. 322 (611301, 6109586)	1.2-1.5	1990-1995	0	9	1	1	165. 397 (611302, 6109586)	2008-2017 (1565)
	165. 323 (611301, 6109585)	3.0-3.3	1989-1997	0	33	17	19		
6	165. 326 (612248, 6109836)	3.0-3.3	1992-1995	0	11	4	5		
	165. 327 (612248, 6109836)	5.0-5.3	1989-2018	17	185	150	44		
	165. 328 (612248, 6109836)	1.2-1.5	1990-1995	0	6	0	3		
	165. 329 (612248, 6109836)	3.0-3.3	1989-2017	4	125	101	34		
22	165. 272 (610463, 6110938)	3.0-3.3	1989-1997	0	11	4	6	165. 341 (610449, 6110923)	1901-2003 (62)
	165. 273 (610463, 6110938)	5.0-5.3	1989-1995	0	26	11	16		
23	165. 275 (610603, 6110673)	3.0-3.3	1989-2018	11	90	82	22	165. 342 (610614, 6110609)	1990-2013 (127)
	165. 276 (610603, 6110673)	5.0-5.3	1989-2017	2	77	56	29		
24	165. 278 (611209, 6110905)	3.0-3.3	1989-2001	1	64	48	29	165. 343 (611216, 6110877)	1990-2013 (133)
	165. 279 (611209, 6110905)	5.0-5.5	1989-2018	16	139	124	31	165. 399 (611210, 6110905)	2008-2017 (2594)
25	165. 281 (611343, 6110144)	3.0-3.3	1989-1997	0	34	16	19	165. 344 (611361, 6110154)	1989-1998 (44)
	165. 282 (611343, 6110144)	5.0-5.3	1989-1995	0	30	15	21		
26	165. 283 (611755, 6110721)	1.2-1.5	1989-1993	0	6	1	4	165. 345 (611740, 6110706)	1990-2013 (118)
	165. 284 (611755, 6110721)	3.0-3.3	1989-1997	0	10	5	6		
27	165. 285 (611755, 6110721)	5.0-5.3	1989-2017	5	153	135	36		
	165. 287 (612372, 6109376)	5.0-5.3	1989-1997	0	40	25	25	165. 346 (612366, 6109389)	1990-2013 (135)
28	165. 288 (612372, 6109376)	7.0-7.3	1989-2017	5	143	131	32		
	165. 291 (612567, 6109722)	6.2-6.5	1989-1995	0	32	10	19	165. 347 (612573, 6109713)	1990-2013 (131)
29				0	0	0	0	165. 348 (612759, 6109225)	1989-2005 (25)
71	165. 333 (609977, 6110139)	14.9-15.0	1991-2018	17	509	497	32		

72	165. 159 (612715, 6109230)	18.0-30.0	1991-1997	0	11	10	9		
73	165. 361 (611326, 6109537)	19.0-25.0	1991-1997	0	13	11	11		
Others								165. 34 (609706, 6110247)	1954-2017 (17007)
	165. 35 (612396, 6110112)	16.5-18.5	1956-2003	2	3	8	7	165. 35 (612396, 6110112)	1955-2000 (14)
	165. 167 (610047, 6110136)	32.4-40.4	1979-2018	7	6	11	11	165. 167 (610047, 6110136)	1979-2017 (92)

3.2. Overview of geochemistry sample collection

In November 2019, the redox survey was carried out at nine points and core sampling was carried out at seven points (Figure 1 and Table 2). At GeoWin-1 and GeoWin-2, core samples were not collected because the groundwater table could not be reached. In total 47 core samples for pore water extraction, 34 for the nitrate reduction rate measurements, 43 samples for the sediment geochemistry and 55 samples for the lithology description were collected. In addition, for methodological evaluation of the N reduction rate measurement, 1 and 3 additional cores were collected at till-layer 1 and till-layer 2, respectively. In March 2021, the redox survey was carried out again in all locations. The data obtained in the redox probe survey of 2019 are unstable and should not be used in the interpretations and data analyses.

Table 2. Summary of core samples collected in LOOP4 in the MapField project

Point	DGU (X, Y)	Depth (m)		Nr of samples					Total
		Rx*	Core**	L ¹⁾	S ²⁾	R ³⁾	W ⁴⁾	E ⁵⁾	
GeoWin-1	(610186, 6110944)	7							
GeoWin -2	165. 741 (610257, 6110952)	8	6.05	5	4	4	4		17
GeoWin -3	(610331, 611099)	9							
Till layer-1	165. 742 (610216, 6110085)	11	9.71	8	6	9	9	1	32
Till layer-2	165. 743 (50336, 6110071)	7.5	6.05	8	7	7	7	3	29
IGS-1	165. 744 (612257, 6110135)	5	6.05	6	5		5		16
IGS-2	165. 745 (612186, 6110165)	6	8.29	7	4	4	4		19
MS-1	165. 746 (612383, 6109403)	9	12.14	9	8	6	9		32
MS-2	165. 747 (5125, 6109317)	11	10.93	12	9	4	9		34
Total				55	43	34	47		179

* Redox probe, investigation depths of the second survey; ** Core sampling; ¹⁾ Lithology; ²⁾ Sediment chemistry;
³⁾ N reduction rate; ⁴⁾ Pore water chemistry; and ⁵⁾ N rate experiment

3.3. Overview of gas sample collection

During the Geoprobe campaign, two sets of gas access wells were installed at five depths near IGS-1 and Till layer (TL)-1 points (Figure 1 and Table 3). A set of gas samples was collected a day after the installation. In February of 2020, two set of gas samples were collected again. It is important to note that the exetainers were not purged during these sampling. The exetainers were pre-vacuumed; however, a non-negligible amount of atmospheric air is often found to be remained in the exetainers, resulting in contamination of gas samples. The gas chemistry of the samples collected during 2019 and early 2020 should be carefully interpreted.

Table 3. Summary of gas access wells.

Location	Depth (m)	Nr of sample	Note
IGS	0.5	6	
	1	4	
	2	6	
	3	6	
	4		saturated
TL-1	0.5	2	
	1	-	Saturated
	2	-	Saturated
	3	-	Saturated
	4	2	

3.4. Interpretation of redox zones

The interpreted redox zones are shown in the chemistry tables in Appendix 2 where:

- Redox zone A is the oxic zone
- Redox zone B the anoxic nitrate reducing zone
- Redox zone C is the reduced zone

The evaluation of the redox zones is mainly based on the following indicators:

- The nitrate and sulfate, being redox sensitive water chemical compounds:
 - Stable high nitrate concentrations and low sulfate concentrations indicate oxic conditions
 - Low and/or decreasing nitrate concentrations over depth on agricultural fields indicate nitrate reducing conditions sometimes supported by increasing sulfate concentrations
 - Stable nitrate concentrations below 1-3 mg/l indicate reduced conditions as low concentrations of nitrate could be from ammonium oxidation during sampling

- The sediment content of $\text{Fe}^{2+}/\text{Fe}_{\text{total}}$, where even small amounts of extractable Fe(II) indicate lack of oxygen implying nitrate reducing or reduced conditions
- Color descriptions of the sediment, where reddish, orange, brown colors indicate oxic conditions, and olive, greyish colors indicate nitrate reducing or reduced conditions

The redox probe measurements seem to be able to detect the redox interfaces to some degree.

3.5. Overview of the MapField chemical analyses

The results from the analysis performed in 2019 on pore water and sediment samples are summarized in Appendix 3. Nitrate reduction rate, sediment chemistry and selected water chemistry data are displayed in Appendix 4 together with redox-probe measurement. The background shows the interpreted redox zones.

3.6. Results from extra nitrate reduction rate experiments

To look closer into the nitrate concentration-rate relationship, sediment from LOOP6 and LOOP4 was used for nitrate removal experiments where more initial concentrations were used. The nitrate removal curves for LOOP6 are shown in Figure 2 with the corresponding sulfate measurements.

For most of the bottles there is a very fast initial phase that ends after the first sample. However except for the system without added nitrate (“0 mM”) the nitrate concentration continues to decline at a much lower rate – estimated from the average slope from 236 h and beyond – due to the difference in scale the high concentrations look very flat.

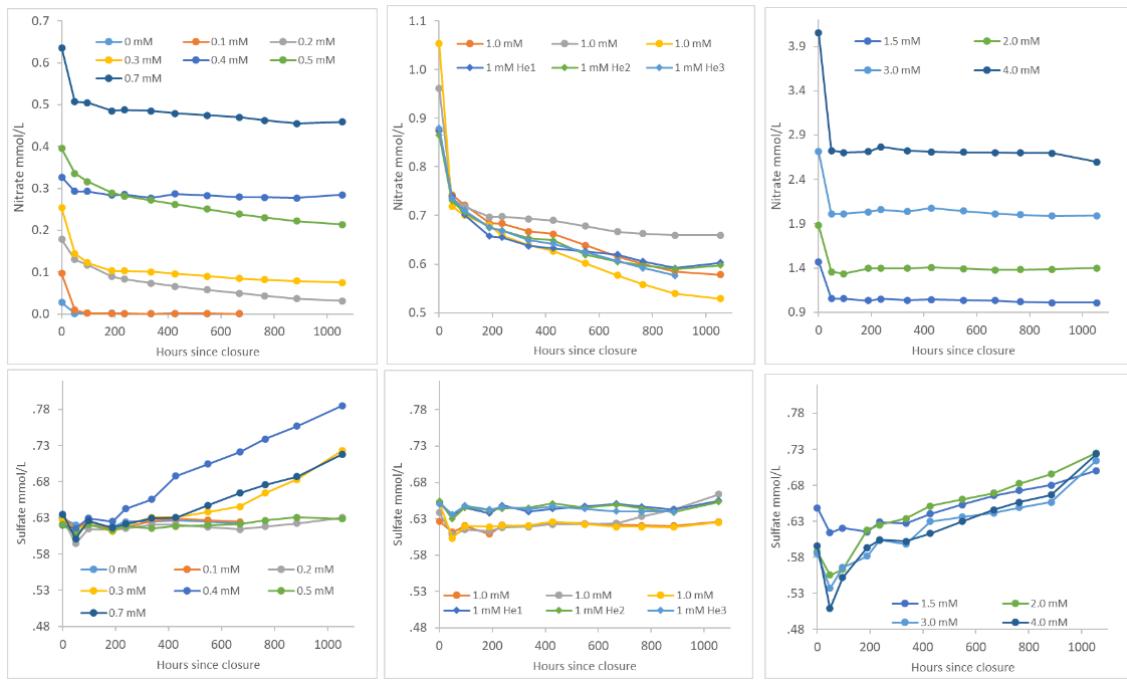


Figure 2: The development of nitrate and sulfate in the nitrate removal rate experiments on homogenized LOOP6 sediment with different initial nitrate concentrations

The middle panel in Figure 3 compares bottles with the normal 7:3 N₂:CO₂ mixture with bottles where the headspace is filled with He and the pH is buffered by the addition of calcite powder. There does not appear to be a systematic difference, the reason for the slightly higher sulfate concentration is not known, but it could perhaps be an impurity in the added calcite.

Two set of rates have been derived. An initial rate ($t(0) \rightarrow t(49h)$) and a later rate taken as the average linear rate from $t(237\text{ h})$ until the last measurement. Both set of rates are plotted as a function of the nitrate concentration in Figure 3, for the entire concentration range and for low concentrations.

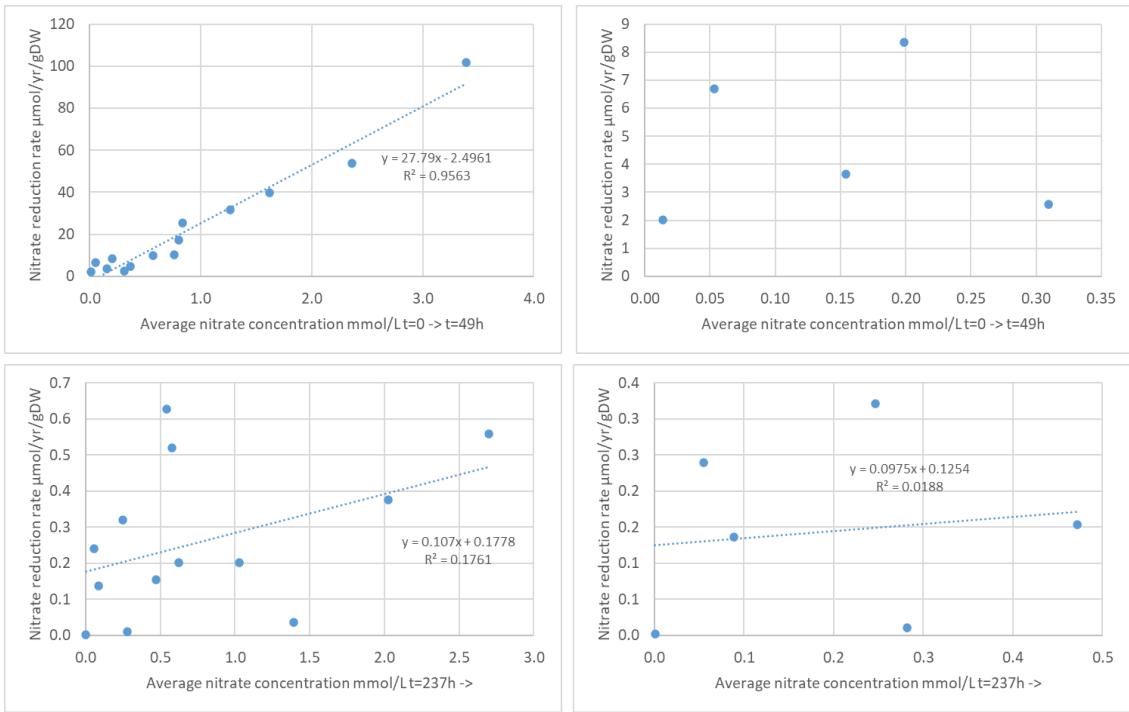


Figure 3: Concentration rate relation for two time intervals for LOOP6 sediments. Right panels are the same as the left panels, except for the range of data which is limited to "low" concentrations in the right panels.

The initial rates appear to be linearly correlated (Figure 3 top left) but the plot to the right focusing on the low concentrations shows that the correlation disappears for low concentrations. For the rates derived for times after 237 h (Figure 3 lower left), there is no significant correlation and for low concentration (lower right) there is no correlation at all. The tendency seen for LOOP3 and LOOP2 sediments, for concentrations below 0.1-0.2 mmol/L, to follow a first order behavior is not apparent in these data. None of the individual nitrate removal curves follow an exponential function. For concentrations above 0.1-0.2 mmol/L LOOP3 and LOOP2 sediments the rates did not show a relation to the concentration.

When the development of nitrate and sulfate seen in figure 2 is compared it differs from bottle to bottle. For 0.3 mM, 0.4 mM, 0.7 mM, 1.5 mM, 2.0 mM, 3.0 mM and 4 mM, there is a clear increase in the sulfate concentration, indicating pyrite oxidation. However, for all the bottles that have clear indications of pyrite oxidation, the ratio between nitrate removal and sulfate production is below the 3:2 ratio you would expect. This indicates that another oxidant than nitrate is oxidizing the pyrite. This could be oxygen, which would indicate leakage, but it is difficult to see how this could lead to rates of sulfate production that are so close from bottle to bottle, though it could be that the limiting factor is the pyrite and the pyrite is evenly distributed. An alternative could

be reduction of Mn-oxides which could be present in some bottles but not others, in spite of the homogenization of the sediment before the experiments were set up. The homogenization could, however, have brought Mn-oxides and pyrit in contact with each other. Mn-oxides could compete with nitrate for both pyrite and organic matter, but again the very similar rates indicate that the rate is controlled by the pyrite reactivity.

For LOOP 4, the observations for nitrate and sulfate are shown in Figure 4. Also, here a test comparing the normal 7:3 N₂:CO₂ mixture with bottles where the headspace is filled with He and the pH is buffered by the addition of calcite powder is shown in the center panels. The results resemble the results for the LOOP6 experiments, though it appears that there is a much higher sulfate concentration in the bottles with He and calcite and here it seems to be released within the first 75-170 hours indicating that the sulfate is associated with the surface of the calcite.

The increase in the nitrate concentration seen for the low concentrations between 192 and 240 hours is due to an addition of extra nitrate as it was observed that the nitrate would otherwise be gone.

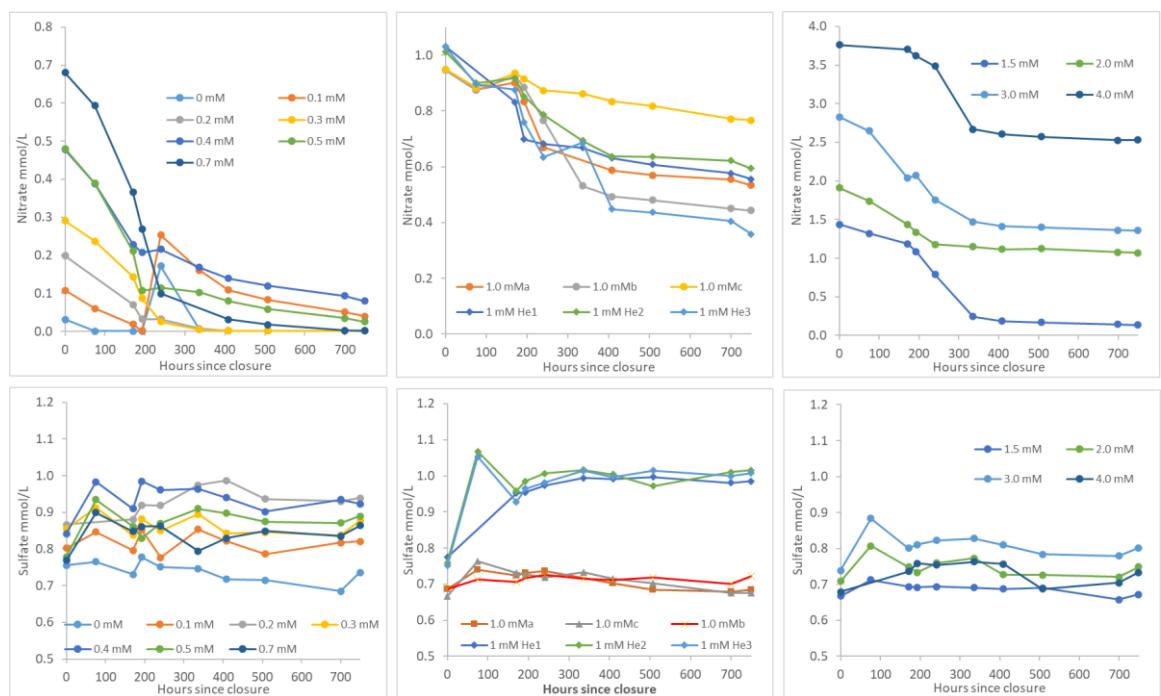


Figure 4: The development of nitrate and sulfate in the nitrate removal rate experiments on homogenized LOOP4 sediment with different initial nitrate concentrations

The curves related to the LOOP4 sediments are not linear, so rates have been calculated for each timestep after 240 hours, discarding the few negative rates that occur due to uncertainty in the analysis. The rates are plotted as a function of the

average nitrate concentration for the corresponding time interval at three different scales in Figure 5. The left panel shows all the rates, where a few outliers of very high rates make it difficult to see if there are any tendencies in the rest of the data, so the center panel is a plot without the outliers indicating a very random distribution. The right most panel shows the data for concentration below 0.1 mmol/L, indicating that, as seen for the experiments using LOOP3 and LOOP2 sediments, at very low concentrations the rate depends on the concentration.

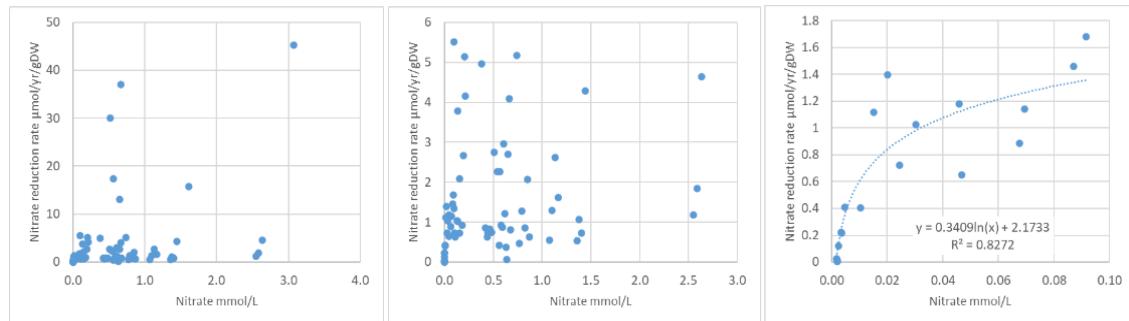


Figure 5: Rates measured by nitrate removal in bottles with LOOP4 sediment. Rates are derived from the slope between sampling points after 240 hours, the concentrations are averages for the interval. Left panel: all rates, Center: High rate outliers removed, Right: rates for concentrations <0.1 mmol/L

The nitrate removal curves for the experiments with initial low concentrations are plotted with an exponential curve fit for times > 240 hours in Figure 6, though the exponential fits have a high R^2 value the coefficients and exponents vary considerable indicating that a simple first order description of the rate is not feasible.

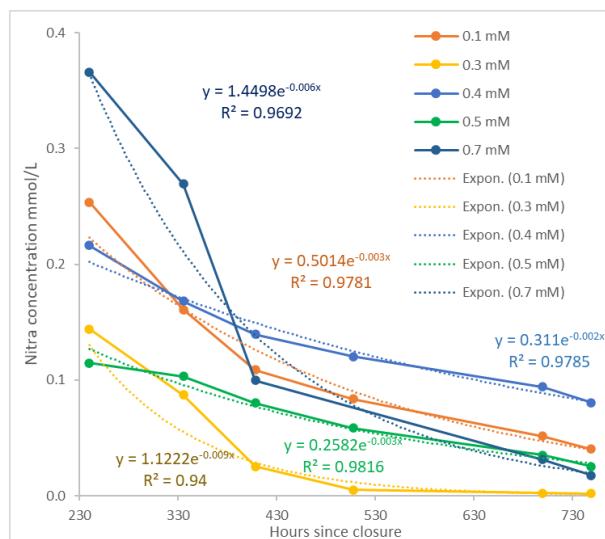


Figure 6: Development in nitrate concentration in LOOP4 sediment bottles with low initial nitrate concentrations and exponential fits.

The last set of experiments performed on LOOP6 and LOOP4 sediments were carried out to see to what extent the effect of pyrite oxidation was the same for rates measured by the acetylene block method and the nitrate removal method. Three types of sediment was used— the types were determined by their color. The sediments were overlying each other at the site. The upper of the sediments called “oxic” was Fe-oxide colored, the intermediate sediment called “nitrate reducing” was olive gray and the sediment called “reduced” was gray. The sediment of each type was homogenized and used for rate measurements by nitrate removal and by the acetylene block method. For each sediment type 2 concentrations of pyrite was added resulting in bottles with 0, 125, and 250 mg pyrite/100 g of sediment. All experiments were done in triplicates giving a total of 27 bottles for both the nitrate removal and the acetylene block measurements. For the experiment using LOOP6 sediment, the bottles were sealed without the headspace being flushed leaving oxygen in the systems as seen from readings of the O₂ optodes placed in 8/9 of the bottles used for each method. The oxygen data are plotted in Figure 20. After 264 hours the bottles were flushed with He removing practically all of the oxygen in the systems.

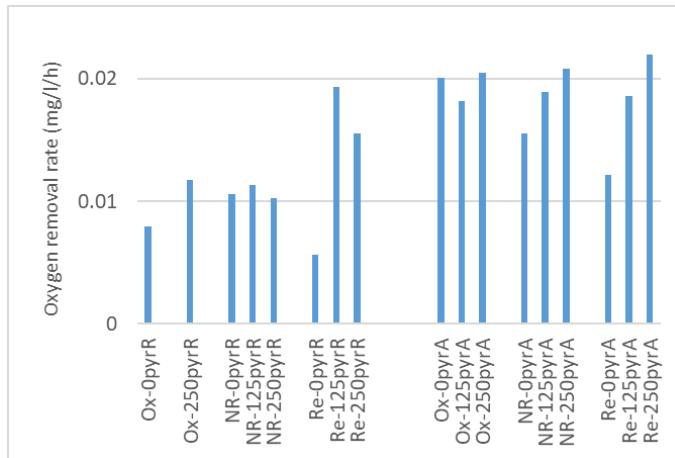


Figure 7: Average rate of oxygen removal during the first 264 hours. All measurements are from the C bottles. The last letter in the name indicates the method R= "nitrate removal", A= "acetylene block". The first letters indicate the sediment Ox= oxic, NR=nitrate reducing, Re=reduced, the number indicates the added concentration of pyrite in mg/100g of sediment

It appears that there is very little difference in the rate of oxygen removal in the bottles, this is however not the case as seen in Figure 7 where the average rate of oxygen removal during the first 264 hours has been plotted. For the nitrate removal experiments the expected higher rate of oxygen removal at higher pyrite concentrations is not clear at all. This is also the case for the oxic sediments for the acetylene method, but for the nitrate reducing and reduced sediments the pattern is the expected with an increment in the rate that is proportional to the added amount of pyrite, though it appears that most of the rate of oxygen removal is not associated with oxidation of the

added pyrite. The oxic sediment was found above the nitrate reducing which was above the reduced, and it appears that in the A bottles there is a clear decrease with depth or the redox state, in the rate of oxygen consumption.

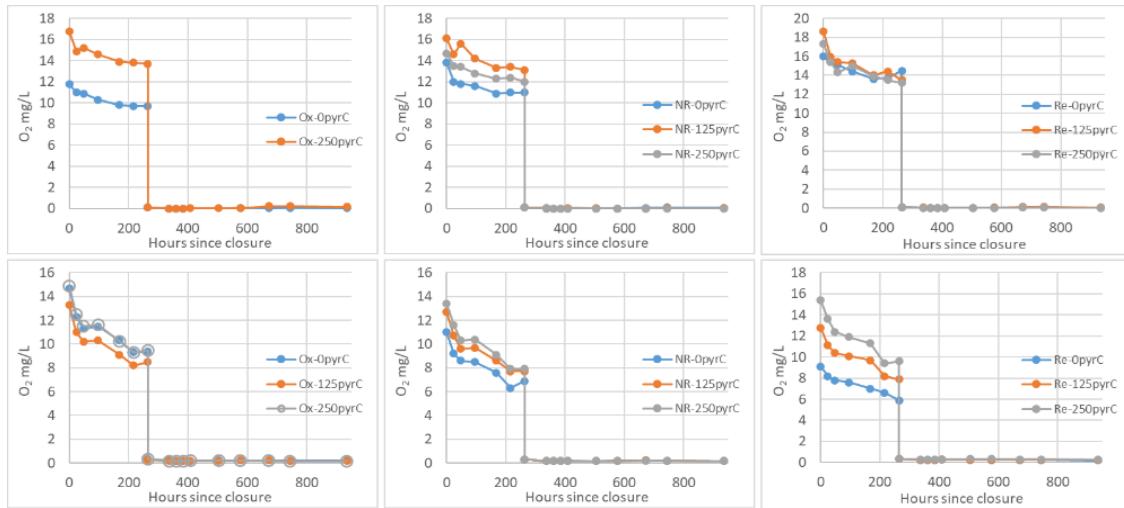


Figure 8: O_2 measurements by optode in the pyrite amended experiment with LOOP6 sediment. The upper half are from the nitrate removal bottles the lower half are from the acetylene block bottles. The first letters indicate the sediment Oxo= oxic, NR=nitrate reducing, Re=reduced, the number indicates the concentration of pyrite in mg/100g of sediment.

The observations for nitrate and sulfate from the nitrate removal experiments are shown in Figure 9 for 950 hours. The vertical line in each plot indicates when oxygen was flushed from the system. It is interesting to note that there is a slow removal of nitrate in the period where there is oxygen in the bottles. This could be due to oxygen free microniches or it could be because nitrate reduction may occur at low rate in the presence of oxygen. There is an acceleration in the rate while oxygen is present, perhaps related to the decrease in oxygen over time, though the decrease is not very large (Figure 9). Bottles with added pyrite have higher rates of nitrate removal both before and after the oxygen has been removed and the rate is in most cases proportional to the pyrite concentration indicating that nitrate is reduced by pyrite both in the presence and absence of oxygen. The rates of nitrate removal are much higher after the removal of oxygen and the rate is proportional to the amount of added pyrite.

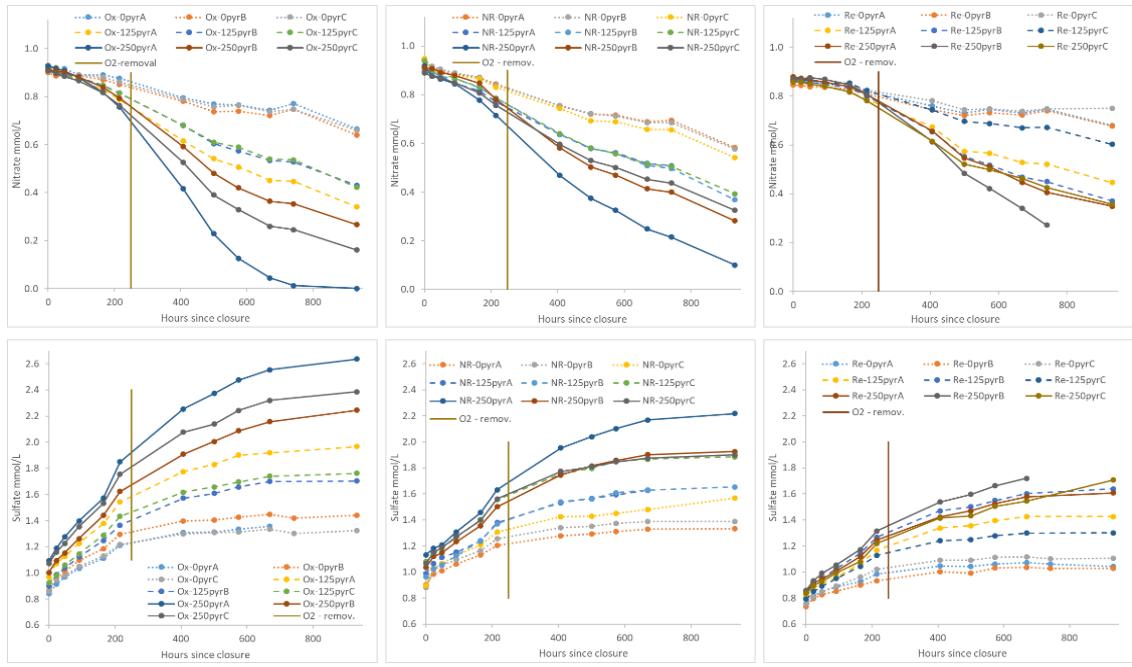


Figure 9: The development in nitrate and sulfate in the nitrate removal rate experiments. The first letters indicate the sediment Ox= oxic, NR=nitrate reducing, Re=reduced, the number indicates the concentration of pyrite in mg/100g of sediment. The last letter indicates the specific bottle of the triplicate. The vertical line indicates when the oxygen was removed.

The sulfate concentration increases rapidly when oxygen is present, indicating that most of the pyrite oxidation occurs with oxygen. The rate is highest in the originally oxic sediment and lowest in the originally reduced sediment. After the oxygen has been removed the sulfate concentration continues to increase, but the rate is lower after the oxygen has been removed. In order to compare the rates of nitrate removal with the rates determined by the acetylene block method, the rate was calculated from the slope in the time interval 407-500 hours to avoid effects of the oxygen.

The development in N_2O from acetylene block rate measurements were somewhat surprising. The data from the “c” bottles (of the a-b-c- triplicates) in which the oxygen was also measured by optodes are shown in in Figure 10. As mentioned in the LOOP2 data report, the N_2O data often show two linear phases, an initial slow phase followed by a longer linear phase which continues until the nitrate runs out. In the parallel nitrate removal and acetylene block experiments described in the LOOP2 data report the rate derived from the 2nd phase showed a better correspondance with the rate determined from nitrate removal over time. It was assumed that the 1st phase represented a period with a small amount of O_2 in the system. The data from these pyrite experiments with presence of oxygen for the first ~250 hours indicate that this is probably not the correct interpretation. The purple vertical line indicates the time for the removal of O_2 from the bottles and it is seen that the 1. phase finishes while there is still O_2 in the system and

in two cases (for the oxic sediment without added pyrite and 250 mg pyrite/100g) the second phase continues linearly across the time at which the oxygen was removed. This is actually rather surprising since the N₂O would also be removed by the He flushing.

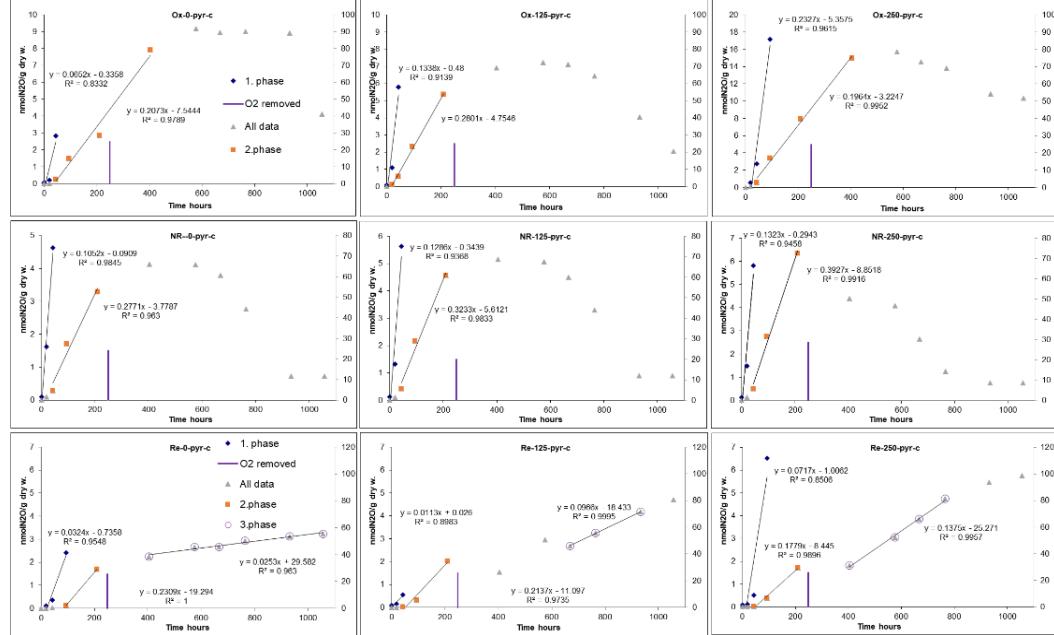


Figure 10: The development in N₂O from the acetylene block experiments. The data are from the same bottles in which the O₂ was measured by optode. As mentioned previously the N₂O data often show two linear phases, an initial slow phase followed by a longer linear phase which continues until the nitrate runs out. In this case there was a third linear phase in the reduced sediment after the oxygen had been removed. The purple vertical line indicates the time for the removal of O₂ from the bottles

For both the oxic and the nitrate reducing sediment the N₂O decreases after around 600 hours in most bottles. This is also surprising because in the nitrate removal bottles there is still nitrate available, it could indicate that the replenishment of the acetylene has not been successful in all bottles. However, in the bottles with reduced sediment there is actually a 3. linearly N₂O increasing phase, here it appears that the more pyrite, the closer the rate is to the 2. phase rate. It is difficult to explain why the replenishment of the acetylene would only be successful in the bottles with reduced sediment. The rates obtained from the three phases are compared with the rates obtained for nitrate reduction and sulfate production (converted to nitrate equivalents) from the nitrate removal experiments in Table 1 and Figure 11.

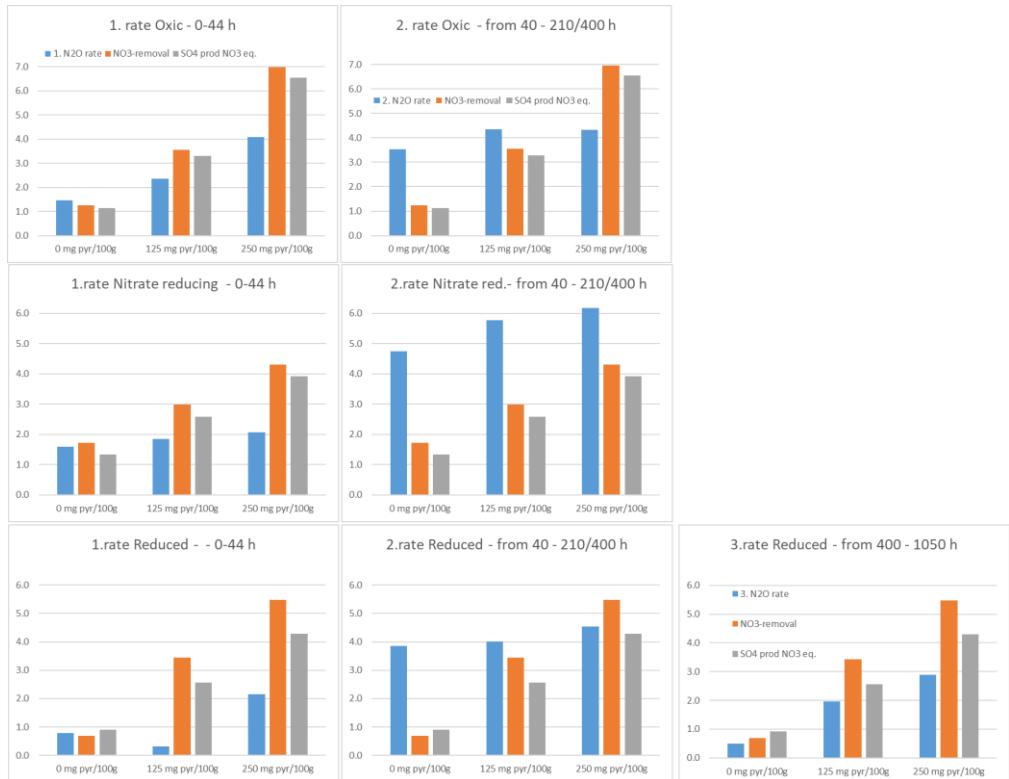


Figure 11: The rate of nitrate reduction (in mmol/kg DryW/yr) from the nitrate removal (407-669 hours) and the acetylene block method and the sulfate production rates from the nitrate removal method (converted to nitrate equivalents). All are the average of triplicates, the nitrate removal and sulfate production data are the same for each row. The period used to derive the rates for the acetylene block method are given in the titles of the panels. Note that it is only for the reduced sediments that acetylene block rates of nitrate reduction after the removal of oxygen are available.

Table 4: Comparison of rates for the pyrite experiments with LOOP6 sediments

Visually est. sediment type	Pyrite mg/100g	1. N ₂ O rate mmol/kg/yr	increase rel. 0 pyr.	2. N ₂ O rate mmol/kg/yr	increase rel. 0 pyr.	3. N ₂ O rate mmol/kg/yr	increase rel. 0 pyr.	NO ₃ -remov. ¹ mmol/kg/yr	increase rel. 0 pyr.	SO ₄ ^{** p.^{1,2}} mmol/kg/yr	increase rel. 0 pyr.
Oxic	0	1.5		3.5				1.2		1.1	
	125	2.4	0.9	4.3	0.8			3.6	2.3	3.3	2.2
	250	4.1	2.6	4.3	0.8			7.0	5.7	6.5	5.4
Nitrate reducing	0	1.6		4.8				1.7		1.3	
	125	1.9	0.3	5.8	1.0			3.0	1.3	2.6	1.2
	250	2.1	0.5	6.2	1.4			4.3	2.6	3.9	2.6
Reduced	0	0.8		3.9		0.5		0.7		0.9	
	125	0.3	-0.5	4.0	0.1	2.0	1.5	3.4	2.7	2.6	1.7
	250	2.2	1.4	4.5	0.7	2.9	2.4	5.5	4.8	4.3	3.4

¹calculated from change between T6 and T9 (407 > 669 hours)

^{**}given in NO₃ equivalents

For the oxic sediment (top row) the increase in the nitrate removal rates and the sulfate production rates are very close when pyrite has been added and the increase appears to be proportional to the amount of pyrite added. Surprisingly there is a small production of sulfate also in the oxic sediment not amended with pyrite. Perhaps some pyrite has become available for oxidation due to the sediment handling and mixing. For the nitrate reducing sediment (center row) there is also a (slightly higher) production of

sulfate in the sediment without added pyrite. The nitrate reduction rate measured by nitrate removal increases linearly with the amount of added pyrite. This is also the case for the sulfate production and the increases appear proportional to the added pyrite. For the reduced sediment (lower row) the rate of sulfate production without added pyrite is lower than seen for the two other sediment types. The increase in the nitrate removal rate after addition of 125 mg/100g of pyrite is rather high but there is a clear increasing trend with the addition of pyrite. The increase in the nitrate removal rate is larger than the increase in the sulfate production rate.

The leftmost column of panels general show that the 1st phase acetylene block rates are about the same as the rates measured by nitrate removal, when no pyrite has been added, but considerably lower when pyrite is added. There is an increase in rates with increasing added pyrite in the oxic and nitrate reducing sediments sediment, but the increase is smaller than the increase seen in the nitrate removal rates and for the reduced sediment the effect is not systematic. In the center panels with the 2. phase acetylene rates, the correlation with the pyrite concentrationis is there but appears to be weaker than the effect on the nitrate removal rates. In most of the experiments (7 of 9) the 2. phase rate is higher than the nitrate removal rate. The average for all nine 2nd phase rates is 4.6 while it is 3.4 mmol/kgDryW/yr for the nitrate removal rates, so given the large variation they are similar. For the reduced sediment there is also a 3rd phase (lower right panel) and it is only for these rates that we are able to compare data where both systems are without oxygen. The 3. phase rate increases systematically with the addition of pyrite, though it increases less than the rate measured by nitrate removal, however, since the absolute N₂O increase rate in the 3. phase is only about 60% of the nitrate removal rate, it can only be seen as an indication that pyrite oxidation is not fully reflected in the rate measured via the acetylene block method.

The pyrite experiments set up with LOOP4 sediments are similar, though here the bottles were made anoxic from the beginning. While the LOOP6 sediments used for the pyrite experiments were sandy, the LOOP4 sediments used for the pyrite experiments were clayey, which may explain the somewhat more complex course of the measurements. The development in the nitrate and sulfate concentrations are shown in Figure 12. Compared to LOOP6, the separation of the curves by the amount of pyrite added is less clear. The oxic sediment (left) shows an initial drop in the nitrate concentration from the initial measured concentration to the next, followed by an increase or stable values until a little past 200 hours. The reason for this is not known, but could perhaps be related to the mixing of the sediment for the setup of the

experiment which might have brought oxidized phases such as Mn-oxides into contact with clay minerals with adsorbed ammonium. The amplitude of the variation in the nitrate concentration during this period seems to be related to the pyrite concentration. The sulfate production on the other hand is low and predictable in terms of being proportional to the amount of added pyrite.

The nitrate reducing sediments (center) show a similar dip in the nitrate concentration, but at a later time and the amplitude is smaller, which perhaps corresponds to the overall smaller removal of nitrate in this group of bottles. The reduced sediments (right) appears to be very reactive and there is a clear response to the addition of pyrite, though not always as expected. The spike in the sulfate concentration a little before 100 hours is not readily explainable. Most of the curves are quite linear from 338-698 hours, therefore, the rate of nitrate removal and sulfate production was calculated from the average slope in this time interval.

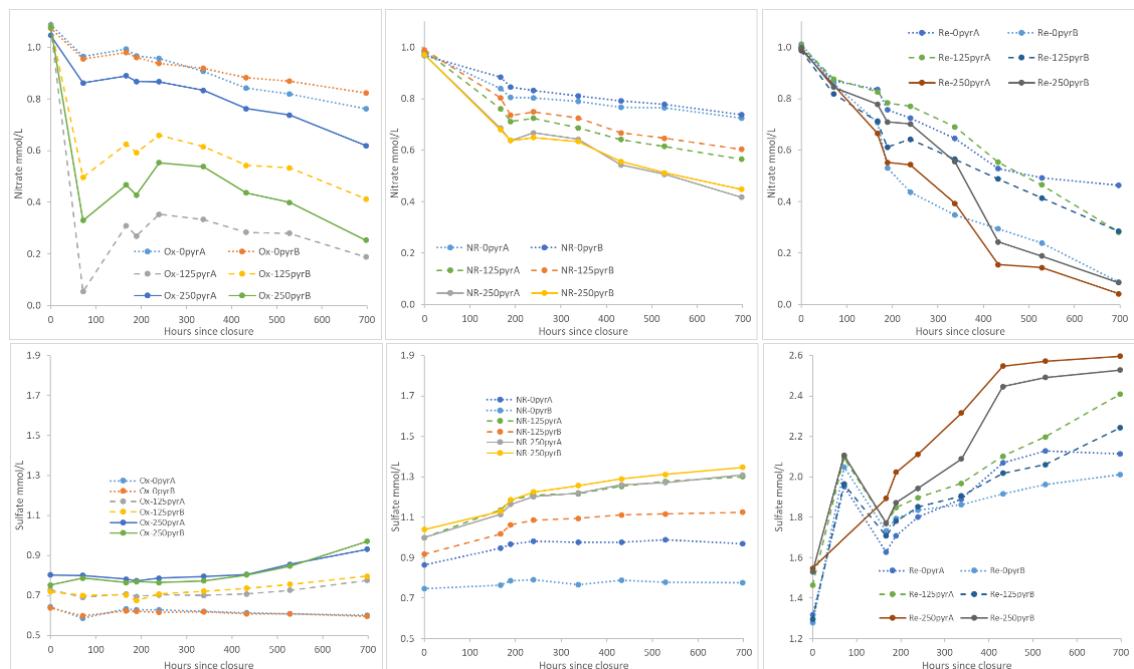


Figure 12: The development in nitrate and sulfate in the pyrite addition experiments carried out with LOOP 4 sediment. The first two letters indicate the redox status of the sediment based on the visual impression. Ox=oxic, NR=nitrate reducing, Re=reduced, the last letter refers to the individual duplicate sample.

The acetylene block data (not shown) contain a 1st and 2nd phase, but the duplicates are sometimes quite different, probably related to the fact that the sediments are more clayey making homogenization difficult. Where LOOP 6 sediments showed a decrease in the N₂O concentration towards the end, the LOOP4 sediments showed a constant N₂O level. This has also been observed when carrying out the normal rate

measurements using the acetylene block method, in both cases this corresponds to the time when the nitrate has been reduced so that the production of N_2O stops. The rate derived from the nitrate removal rate experiments and the acetylene block method are shown and compared in Figure 13 and Table 5.

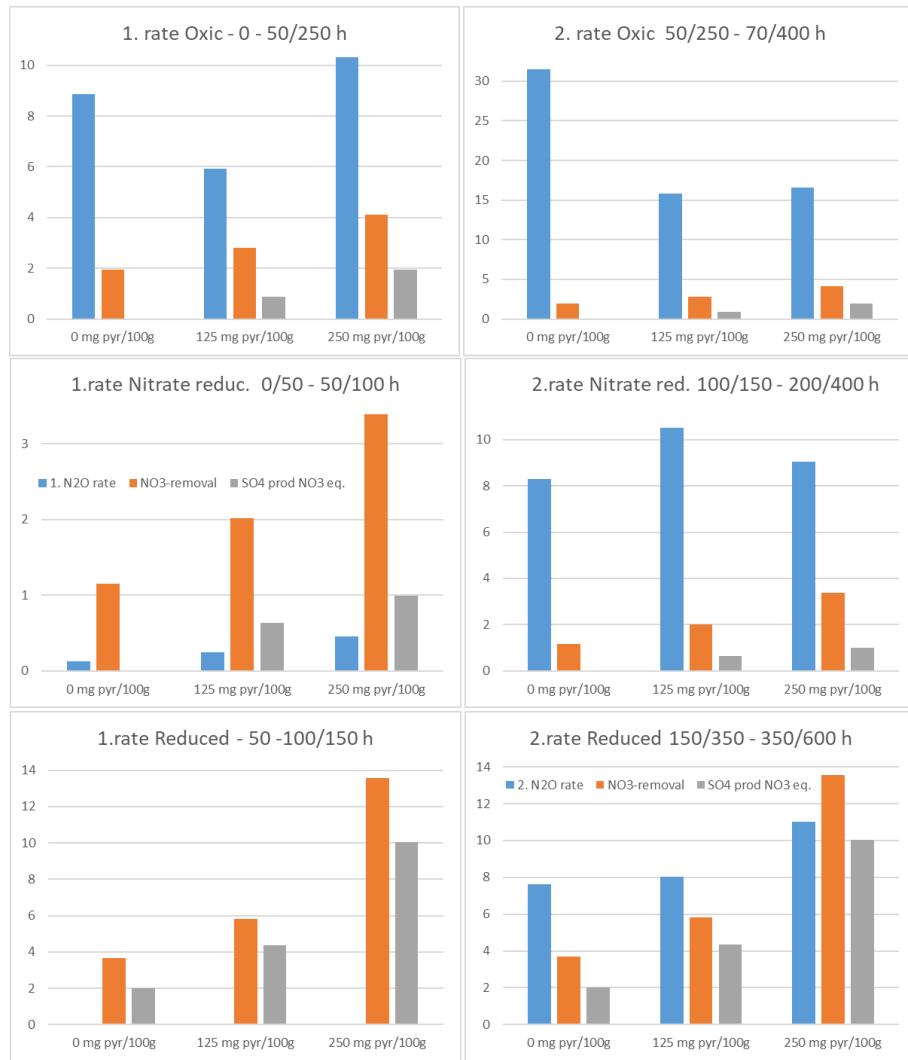


Figure 13: The average rate of nitrate reduction (in mmol/kgDryW/yr) from the nitrate removal (338-698 hours) and the acetylene block method and the sulfate production rates (converted to nitrate equivalents). All are the average of duplicates, the nitrate removal and sulfate production data are the same for each row. The period used to derive the rates for the acetylene block method are given in the titles of the panels. The 1. Rate of the reduced sediments are too small to show in the plot.

Table 5: Comparison of rates for the pyrite experiments with LOOP4 sediments

Visually estim. sediment type	Pyrite mg/100g	1. N ₂ O rate mmol/kg/yr	increase rel. 0 pyr.	2. N ₂ O rate mmol/kg/yr	increase rel. 0 pyr.	NO ₃ -remov. ¹ mmol/kg/yr	increase rel. 0 pyr.	**SO ₄ prod ^{1,2} mmol/kg/yr	increase rel. 0 pyr.
	0	8.9		31.5		2.0		-0.2	
Oxic	125	5.9	-2.9	15.8	-15.7	2.8	0.8	0.9	1.1
	250	10.3	1.4	16.6	-15.0	4.1	2.1	1.9	2.2
	0	0.1		8.3		1.2		0.0	
Nitrate reduc.	125	0.2	0.1	10.5	2.2	2.0	0.9	0.6	0.7
	250	0.5	0.3	9.0	0.7	3.4	2.2	1.0	1.0
	0	0.0		7.6		3.7		2.0	
Reduced	125	0.0	0.0	8.0	0.4	5.8	2.2	4.3	2.3
	250	0.0	0.0	11.0	3.4	13.6	9.9	10.0	8.0
¹ calculated from change between T5 and T8 (338 -> 698 hours)						² given in NO ₃ equivalents			

The 1st phase rates of the oxic sediment are very high, but the 2nd phase rates of the oxic sediment is even higher and both are higher than the nitrate removal rates. None of the acetylen block rates made on the oxic sediment indicate an effect of the added pyrite. The nitrate removal rates and the sulfate production rates show an increase which appears to be very close to the expected, meaning that the increase in rate is approximately twice as high for 250 mg/100 g compared to 125 mg/100 g. The increase in sulfate in nitrate equivalents appears to match the increase in nitrate.

For the nitrate reducing sediment the 1st phase acetylene block rates are much lower than the nitrate removal rates, while the 2nd phase rates are much higher. The 1. phase rates appear to increase proportionally with the added pyrite, but this does not appear to be the case for the 2nd phase rates. The increases in the nitrate removal and sulfate production rates are again proportional to the amount of added pyrite.

For the reduced sediment the 1st phase rate is so low that it doesn't show on the plot, while the 2nd rate is higher than the nitrate removal rate for 0 and 125 mg pyrite /100g and shows an increase with the amount of added pyrite. The increase is, however, smaller than the increase seen in the nitrate removal and pyrite production rates., even though the 2nd phase N₂O rate is generally higher than the nitrate removal rate for 0 and 125 mg pyrite/100g. The increase in the nitrate removal and sulfate production rates from 125 – 250 mg pyrite/100g is much higher than the increase from 0 - 125 mg pyrite/100g. The results indicate that the acetylene block rates only partially measures the rate of pyrite oxidation.

The results also indicate that for clayey sediments like the LOOP4 sediments the rate derived from the 2nd phase in the acetylene block N₂O accumulation is much higher

than the rate determined from the nitrate removal, while for the sandy LOOP6 sediments the rates were similar. It also seems that the difference between the 1st and 2nd phase rates are much higher in the clayey sediments from LOOP4 compared to sandy sediments from LOOP6.

Appendices

Appendix 1: Lithological descriptions of the MapField samples

Appendix 2: Water chemistry of existing data (LOOP, GRUMO and others)

Excel file available

Appendix 3: Water (Appendix3-1 and 3-2), sediment chemistry (Appendix 3-3), denitrification rates (Appendix 3-4) collected in the MapField project

Appendix 4: Well panels illustrating all the collected parameters

Attached separately

The well panels display from left towards right:

Panel 1: Lithology (from Jupiter, Appendix 1)

Panel 2: Sediment color (from Jupiter, Appendix 1)

Panel 3: Redox probe measurement (unstable 2019 data, not to be used in the interpretations, and 2021 data use with caution)

Panel 4: Redox capacity (analysis pending) and N-rate (blue curve)

Panel 5: Sediment chemistry; formic acid extracted Fe(II) and total Fe as well as the Fe(II)/Fe(total).

Panel 6: Water isotopes; δO_{18} and δD .

Panel 7: Concentrations of ammonium.

Panel 8: Concentrations of Cl^- , NO_3^- and SO_4^{2-} and DOC

Panel 9: Concentrations of Ca^{2+} , Mg^{2+} , K^+ and Na^+

Appendix 1: Lithological descriptions of the MapField samples

BORERAPPORT

DGU arkivnr: 165. 741

Borested : Albjergvej 86
5883 Oure

Kommune : Svendborg
Region : Syddanmark

Boringsdato : 7/11 2019**Boringsdybde :** 6,1 meter**Terrænkote :** 47,51 meter o. DNN

Brøndborer : Palle Ejlskov
MOB-nr :
BB-journr :
BB-bornr : LOOP4 - GeoW-2

Prøver

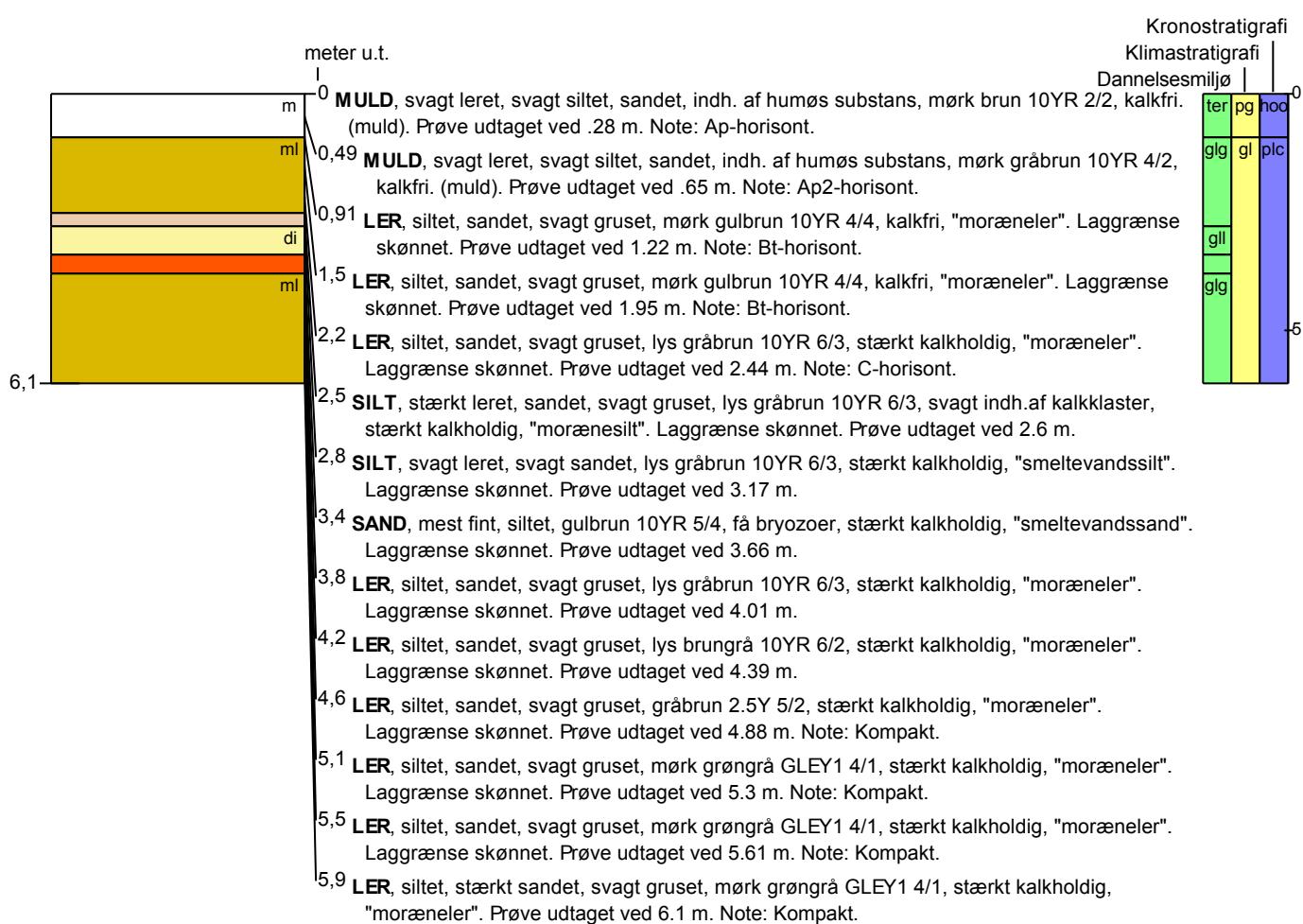
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- antal gemt : 0

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UTM-zone : 32
UTM-koord. : 610257, 6110952

Datum : EUREF89
Koordinatkilde : Brøndborer
Koordinatmetode : Landinspektør

Notater : Boringen består af kernestykker, hvor en del intervaller mangler. Sedimentet er ofte komprimeret eller ekspanderet under prøvetagning. Begge dele giver usikkerhed om prøvedybder.

**Aflejringsmiljø - Alder (klima-, krono-, litho-, biostratigrafi)**

meter u.t.

- 0 - 0,91 terrigen - postglacial - holocæn
- 0,91 - 2,8 glacigen - glacial - pleistocæn
- 2,8 - 3,4 glaciolakustrin - glacial - pleistocæn
- 3,4 - 3,8 glaciofluvial - glacial - pleistocæn
- 3,8 - 6,1 glacigen - glacial - pleistocæn

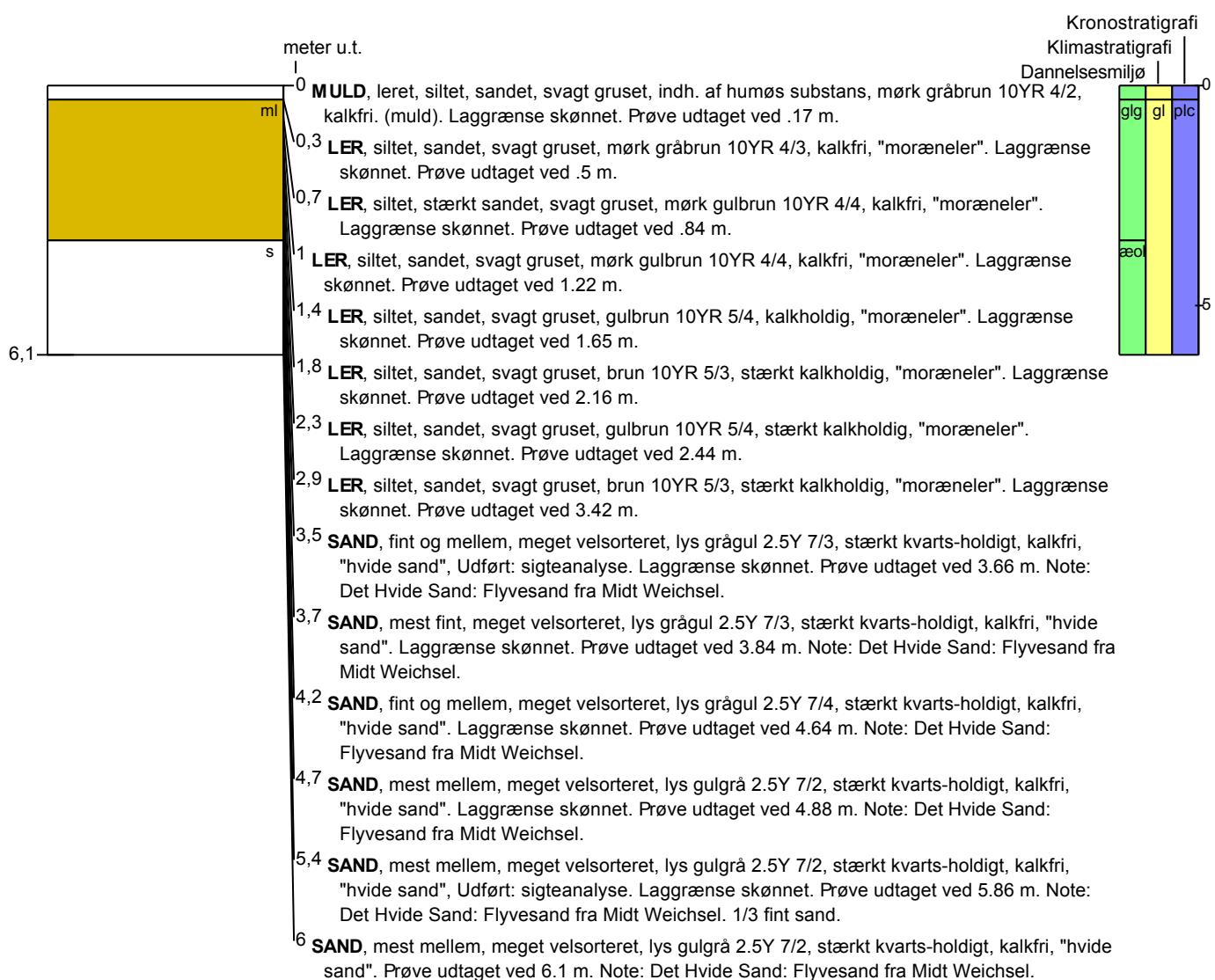
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Borested : Knarreborg Møllevej 13
5883 Oure

Kommune : Svendborg
Region : Syddanmark
Boringsdato : 6/11 2019**Boringsdybde :** 6,1 meter**Terrænkote :** 25,58 meter o. DNN
Brøndborer : Palle Ejlskov
MOB-nr :
BB-journr :
BB-bornr : LOOP4 - IS-1

Prøver
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- beskrevet : 20/5 2020 af : HJG
- antal gemt : 0

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UTM-zone : 32
UTM-koord. : 612257, 6110135

Datum : EUREF89
Koordinatkilde : Brøndborer
Koordinatmetode : Landinspektør

Notater : Boringen består af kernestykker, hvor en del intervaller mangler. Sedimentet er ofte komprimeret eller ekspanderet under prøvetagning. Begge dele giver usikkerhed om prøvedybder.


fortsættes..

BORERAPPORT**DGU arkivnr: 165. 744****Aflejringsmiljø - Alder (klima-, krono-, litho-, biostratigrafi)****meter u.t.**

0 - 0,3 terrigen - postglacial - holocæn
0,3 - 3,5 glacigen - glacial - pleistocæn
3,5 - 6,1 æolisk - glacial - pleistocæn

BORERAPPORT**DGU arkivnr: 165. 745**
Borested : Knarreborg Møllevej 9
 5883 Oure

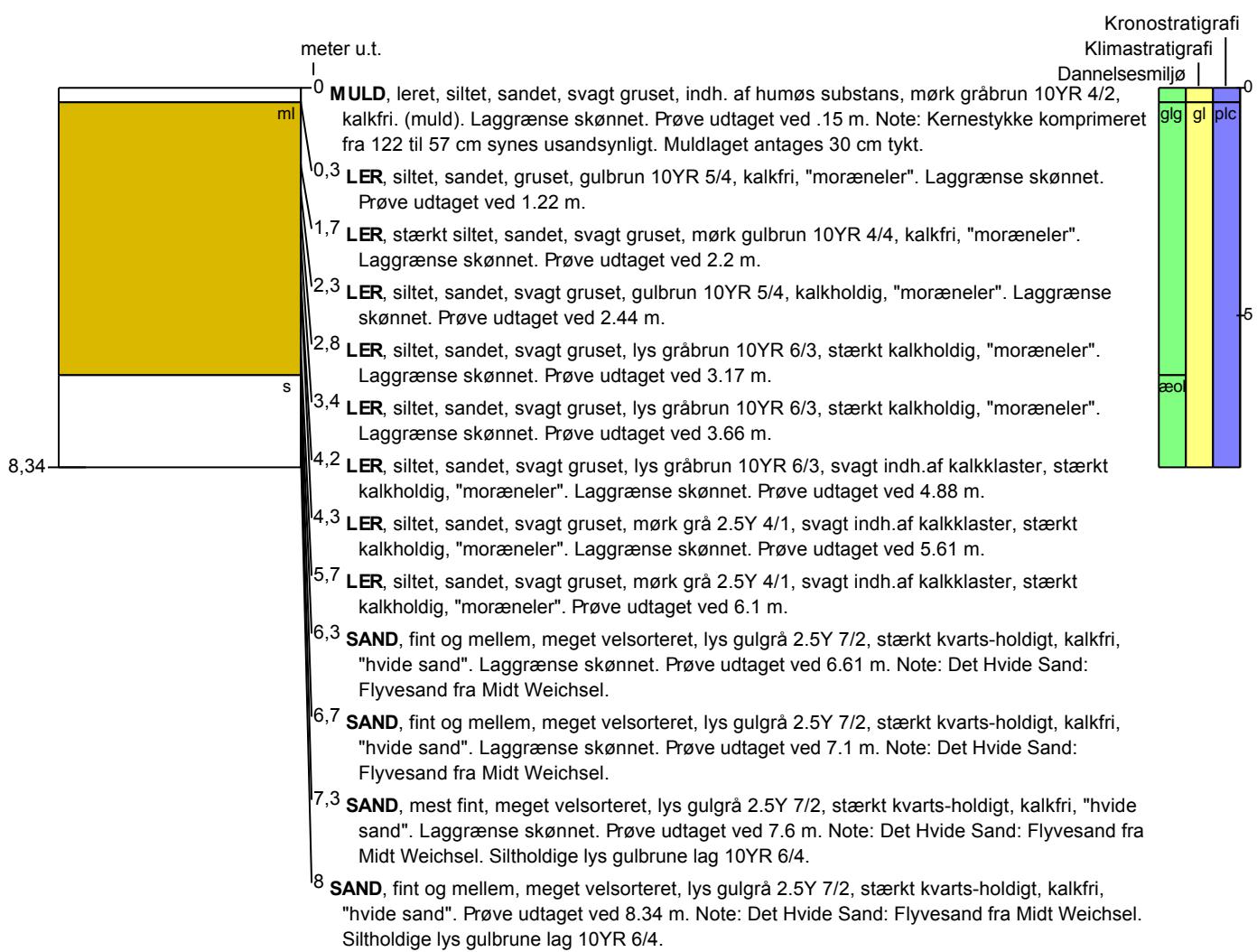
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Region : Syddanmark
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Brøndborer : Palle Ejlskov
MOB-nr :
BB-journr :
BB-bornr : LOOP4 - IS-2

Prøver

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- beskrevet : 20/5 2020 af : HJG
- antal gemt : 0

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UTM-zone : 32
UTM-koord. : 612186, 6110165

Datum : EUREF89
Koordinatkilde : Brøndborer
Koordinatmetode : Landinspektør

Notater : Boringen består af kernestykker, hvor en del intervaller mangler. Sedimentet er ofte komprimeret eller ekspanderet under prøvetagning. Begge dele giver usikkerhed om prøvedybder.
**Aflejringsmiljø - Alder (klima-, krono-, litho-, biostratigrafi)**

meter u.t.

 0 - 0,3 terrigen - postglacial - holocæn
 0,3 - 6,3 glacigen - glacial - pleistocæn
 6,3 - 8,34 æolisk - glacial - pleistocæn

BORERAPPORT**DGU arkivnr: 165. 746**

Borested : Tanghavevej 49
5883 Oure

Kommune : Svendborg
Region : Syddanmark

Boringsdato : 5/11 2019**Boringsdybde :** 12,2 meter**Terrænkote :** 13,76 meter o. DNN

Brøndborer : Palle Ejlskov
MOB-nr :
BB-journr :
BB-bornr : LOOP4 - MS-1

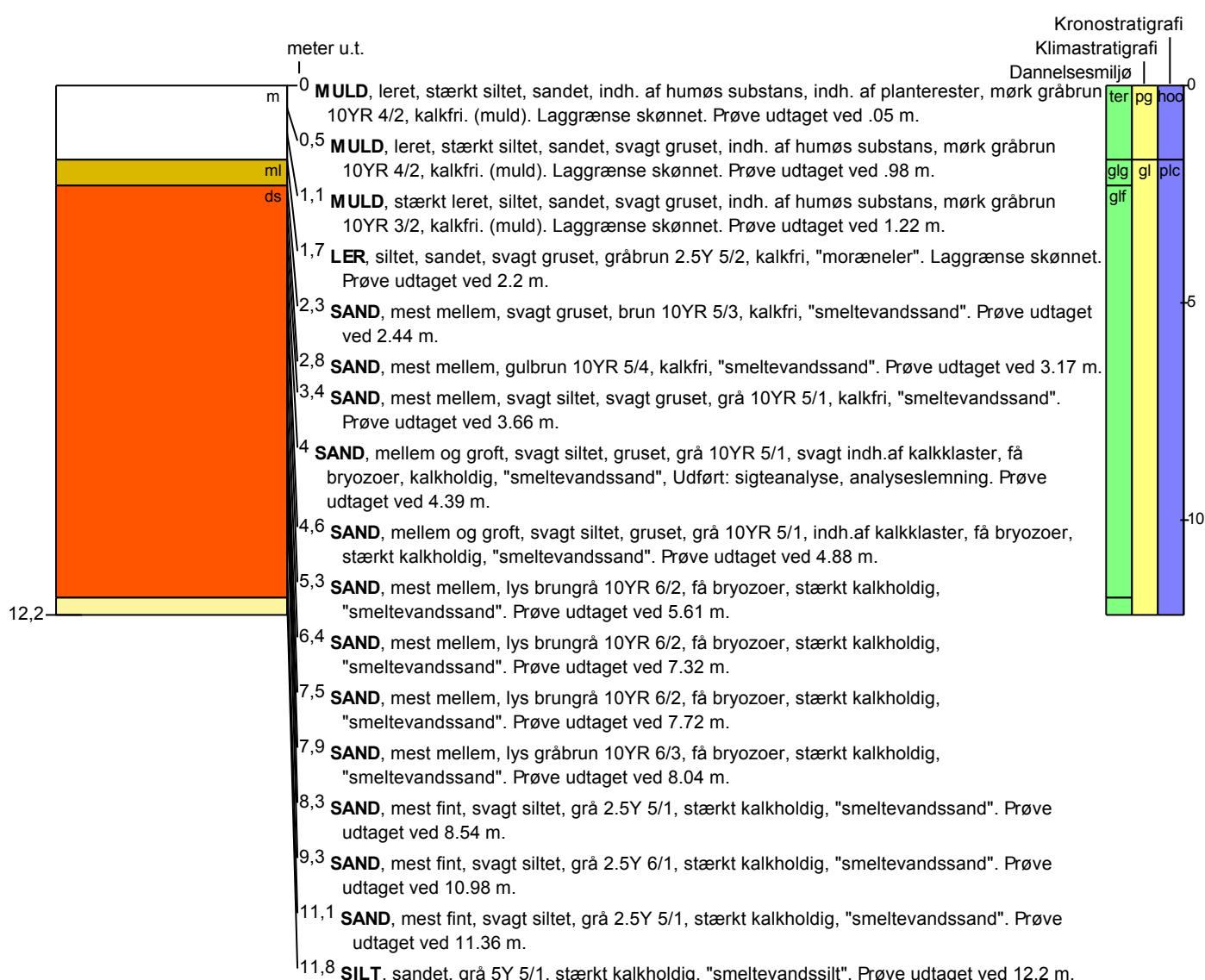
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Boremetode :

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UTM-zone : 32
UTM-koord. : 612383, 6109403

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Koordinatkilde : Brøndborer
Koordinatmetode : Landinspektør

Notater : Boringen består af kernestykker, hvor en del intervaller mangler. Sedimentet er ofte komprimeret eller ekspanderet under prøvetagning. Begge dele giver usikkerhed om prøvedybder.



fortsættes..

BORERAPPORT**DGU arkivnr: 165. 746****Aflejringsmiljø - Alder (klima-, krono-, litho-, biostratigrafi)****meter u.t.**

0	-	1,7	terrigen - postglacial - holocæn
1,7	-	2,3	glacigen - glacial - pleistocæn
2,3	-	11,8	glaciofluvial - glacial - pleistocæn
11,8	-	12,2	glaciolakustrin - glacial - pleistocæn

BORERAPPORT

DGU arkivnr: 165. 747

Borested : Tanghavevej 49
5883 Oure

Kommune : Svendborg
Region : Syddanmark

Boringsdato : 5/11 2019**Boringsdybde :** 10,98 meter**Terrænkote :** 16,72 meter o. DNN

Brøndborer : Palle Ejlskov
MOB-nr :
BB-journr :
BB-bornr : LOOP4 - MS-2

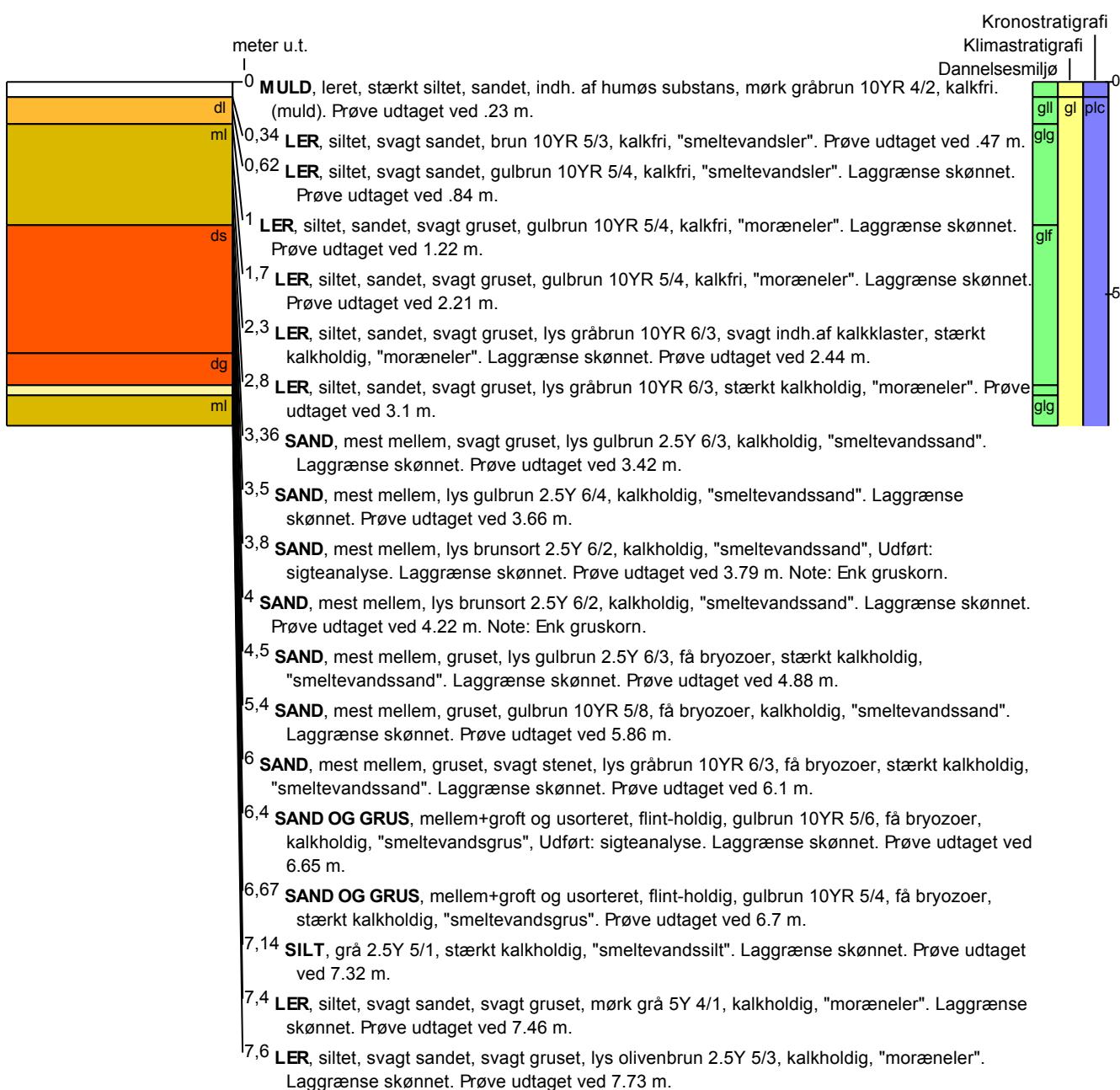
Prøver
 - modtaget : 8/11 2019 antal : 27
 - beskrevet : 26/5 2020 af : HJG
 - antal gemt : 0

Formål : Undersøg./videnskab
Anvendelse :
Boremetode :

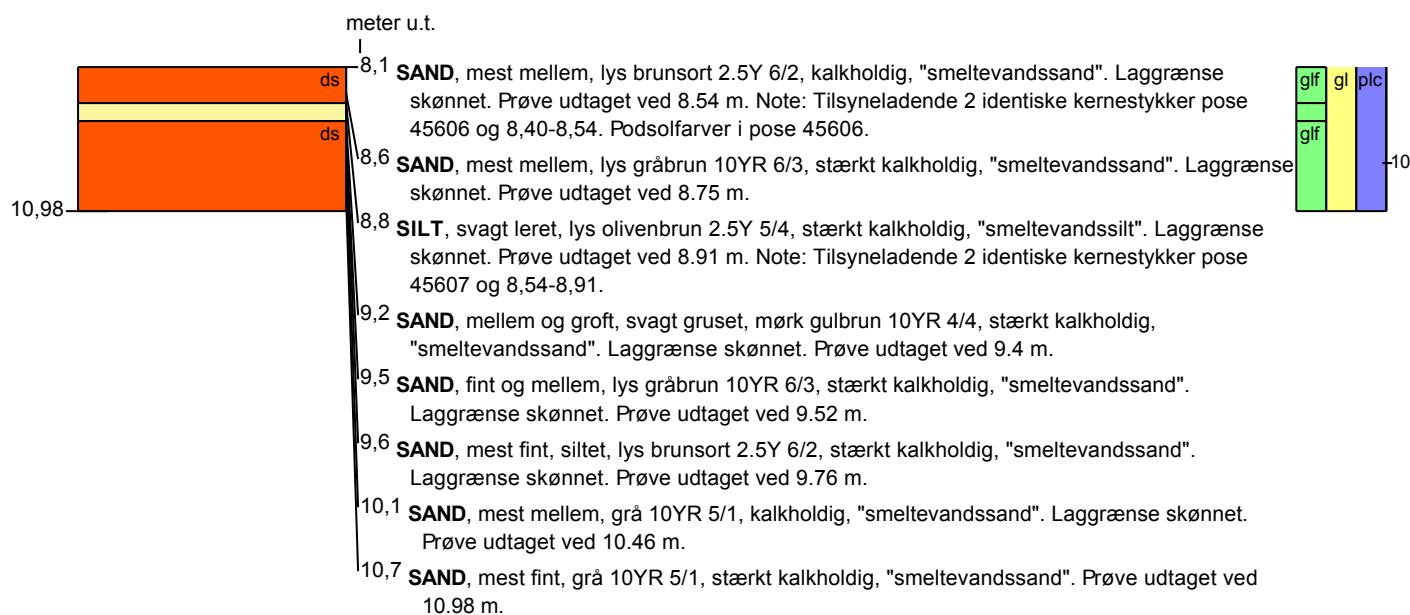
Kortblad : 1312 IINØ
UTM-zone : 32
UTM-koord. : 612361, 6109317

Datum : EUREF89
Koordinatkilde : Brøndborer
Koordinatmetode : Landinspektør

Notater : Boringen består af kernestykker, hvor en del intervaller mangler. Sedimentet er ofte komprimeret eller ekspanderet under prøvetagning. Begge dele giver usikkerhed om prøvedybder.



fortsættes..

BORERAPPORT**DGU arkivnr: 165. 747****Aflejningsmiljø - Alder (klima-, krono-, litho-, biostratigrafi)****meter u.t.**

0	-	0,34	terrigen - postglacial - holocæn
0,34	-	1	glaciolakustrin - glacial - pleistocæn
1	-	3,36	glacigen - glacial - pleistocæn
3,36	-	7,14	glaciofluvial - glacial - pleistocæn
7,14	-	7,4	glaciolakustrin - glacial - pleistocæn
7,4	-	8,1	glacigen - glacial - pleistocæn
8,1	-	8,8	glaciofluvial - glacial - pleistocæn
8,8	-	9,2	glaciolakustrin - glacial - pleistocæn
9,2	-	10,98	glaciofluvial - glacial - pleistocæn

BORERAPPORT

DGU arkivnr: 165. 742

Borested : Landevejen 177
5883 Oure

Kommune : Svendborg
Region : Syddanmark

Boringsdato : 6/11 2019**Boringsdybde :** 9,76 meter**Terrænkote :** 46,43 meter o. DNN

Brøndborer : Palle Ejlskov
MOB-nr :
BB-journr :
BB-bornr : LOOP4 - TL-1

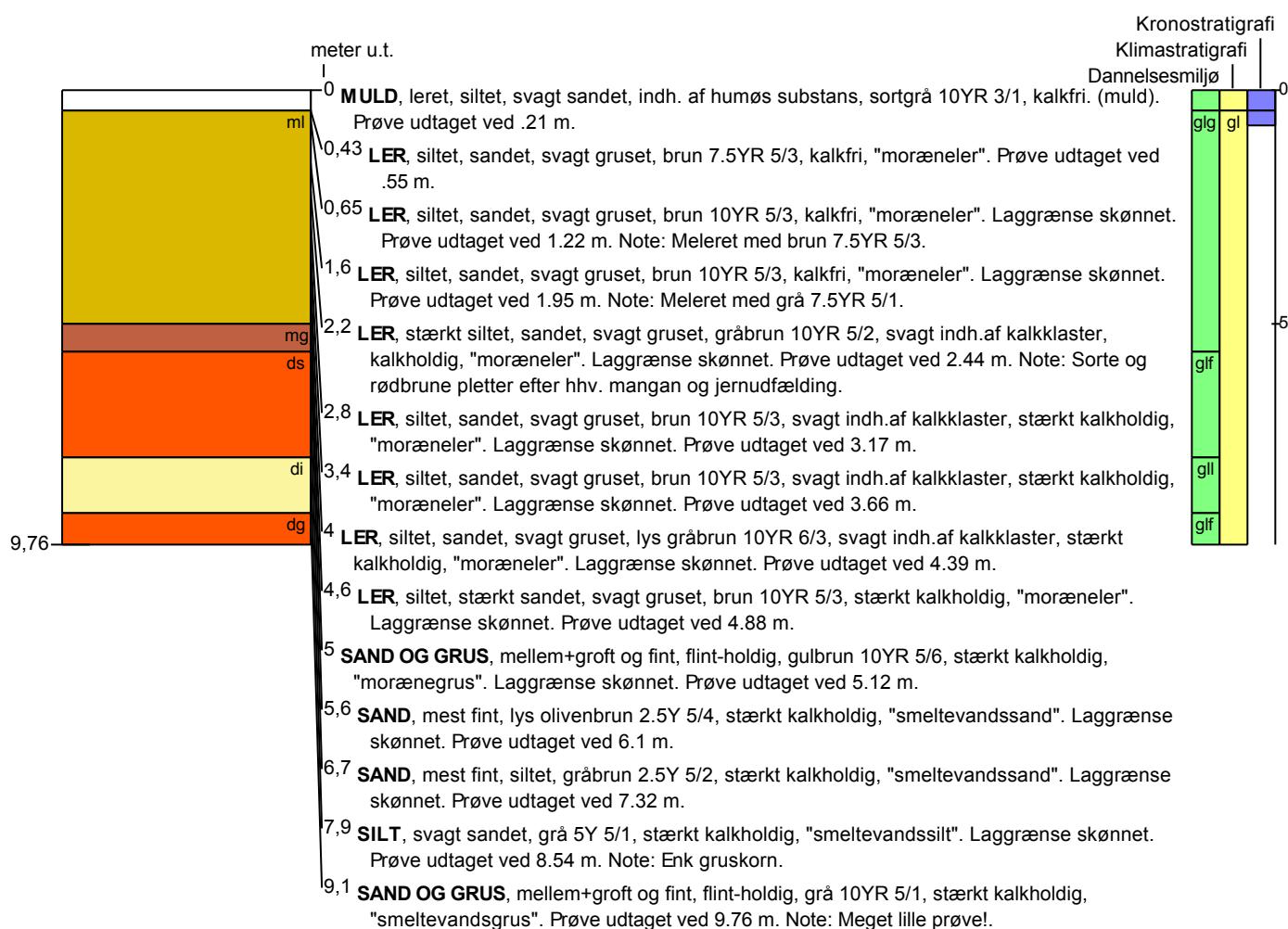
Prøver
 - modtaget : 8/11 2019 antal : 14
 - beskrevet : 19/5 2020 af : HJG
 - antal gemt : 0

Formål : Undersøg./videnskab
Anvendelse :
Boremetode :

Kortblad : 1312 IINØ
UTM-zone : 32
UTM-koord. : 610216, 6110085

Datum : EUREF89
Koordinatkilde : Brøndborer
Koordinatmetode : Landinspektør

Notater : Boringen består af kernestykker, hvor en del intervaller mangler. Sedimentet er ofte komprimeret eller ekspanderet under prøvetagning. Begge dele giver usikkerhed om prøvedybder.



fortsættes..

BORERAPPORT**DGU arkivnr: 165. 742****Aflejringsmiljø - Alder (klima-, krono-, litho-, biostratigrafi)****meter u.t.**

0	-	0,43	terrigen - postglacial - holocæn
0,43	-	0,76	glacigen - glacial - pleistocæn
0,76	-	5,6	glacigen - glacial
5,6	-	7,9	glaciofluvial - glacial
7,9	-	9,1	glaciolakustrin - glacial
9,1	-	9,76	glaciofluvial - glacial

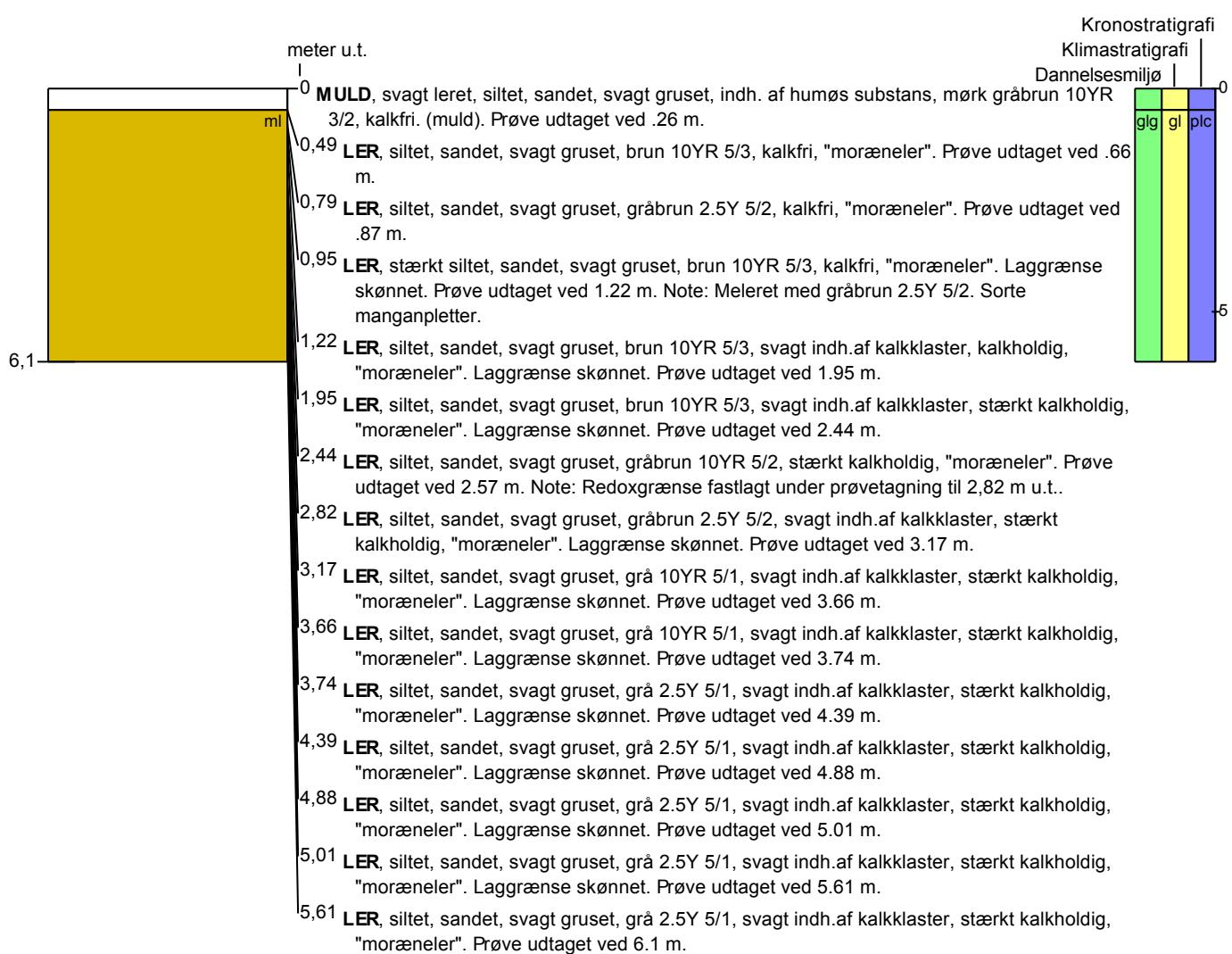
BORERAPPORT**DGU arkivnr: 165. 743**
Borested : Landevejen 176D
5883 Oure

Kommune : Svendborg
Region : Syddanmark
Boringsdato : 7/11 2019**Boringsdybde :** 6,1 meter**Terrænkote :** 44,55 meter o. DNN
Brøndborer : Palle Ejlskov
MOB-nr :
BB-journr :
BB-bornr : LOOP4 - TL-2

Prøver
- modtaget : 8/11 2019 **antal :** 16
- beskrevet : 19/5 2020 **af :** HJG
- antal gemt : 0

Formål : Undersøg./videnskab
Anvendelse :
Boremetode :
Kortblad : 1312 IINØ
UTM-zone : 32
UTM-koord. : 610336, 6110071

Datum : EUREF89
Koordinatkilde : Brøndborer
Koordinatmetode : Landinspektør

Notater : Boringen består af kernestykker, hvor en del intervaller mangler. Sedimentet er ofte komprimeret eller ekspanderet under prøvetagning. Begge dele giver usikkerhed om prøvedybder.
**Aflejringsmiljø - Alder (klima-, krono-, litho-, biostratigrafi)**

meter u.t.

0 - 0,49 terrigen - postglacial - holocæn
0,49 - 6,1 glacigen - glacial - pleistocæn

Appendix 3: Water (Appendix3-1 and 3-2), sediment chemistry (Appendix 3-3), denitrification rates (Appendix 3-4) collected in the MapField project

Appendix3-1. Results of anions, dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), stable isotope of water of LOOP4

LOOPNr	Boreholes	method	DGUnr	Depth (m)	mg/L						$\mu\text{g/L}$	mg/L		%o		
					F ⁻	Cl ⁻	Br	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻		NH ₄ ⁺	DOC	TIC	δO18	δD
LOOP4	GeoW-2	GeoProbe	165. 741	2.25		25.71	0.51	26.15	261.50	39.09	216.47		46.40			
LOOP4	GeoW-2	GeoProbe	165. 741	3.47	0.69	21.32	0.32	8.98	89.82	22.45	70.48	57.85	58.82			
LOOP4	GeoW-2	GeoProbe	165. 741	4.69	3.34	27.30	0.96	29.32	293.20	79.46	157.15					
LOOP4	GeoW-2	GeoProbe	165. 741	5.91	2.24	20.12	0.94	1.56	15.60	431.46	223.48		35.00			
LOOP4	GeoW-2	GeoProbe	165. 741	6.00		34.15	0.54	1.12	11.20	549.61	149.04					
LOOP4	IS-1	GeoProbe	165. 744	2.21	4.03	19.62	0.26	9.03	90.30	73.91	254.36					
LOOP4	IS-1	GeoProbe	165. 744	3.47	1.35	25.10	0.17	24.77	247.70	78.30	176.05					
LOOP4	IS-1	GeoProbe	165. 744	3.89	1.15	13.70	1.28	0.87	8.74	35.23	27.10	139.94	28.66			
LOOP4	IS-1	GeoProbe	165. 744	5.91		50.14	0.54	12.24	122.40	98.48	534.16					
LOOP4	IS-2	GeoProbe	165. 745	3.47	3.78	25.50	0.28	56.62	566.20	91.04	419.37					
LOOP4	IS-2	GeoProbe	165. 745	5.91	4.14	42.94	0.22	3.00	30.00	421.64	377.86					
LOOP4	IS-2	GeoProbe	165. 745	6.91	1.65	29.98	0.27	1.87	18.72	114.14						
LOOP4	IS-2	GeoProbe	165. 745	8.15	4.00	48.26	0.48	3.72	37.20	199.26	84.18		35.37			
LOOP4	MS-1	GeoProbe	165. 746	1.03	1.80	8.94	0.16	2.09	20.90	52.88	139.83		26.93			
LOOP4	MS-1	GeoProbe	165. 746	2.35	0.39	18.90	0.28	41.88	418.77	41.80	57.12	39.43	36.36			
LOOP4	MS-1	GeoProbe	165. 746	3.47	1.70	19.22	0.32	1.50	15.00	48.30						
LOOP4	MS-1	GeoProbe	165. 746	4.69	0.32	21.01	0.36	10.28	102.81	30.09	<6.5ug/l	35.72	74.30			
LOOP4	MS-1	GeoProbe	165. 746	5.91	0.33	24.37	0.52	0.06	0.58	31.33	267.52	48.35	65.24			
LOOP4	MS-1	GeoProbe	165. 746	7.85	0.69	28.94	1.63	0.00	0.00	45.14	32.57	51.09	71.95			
LOOP4	MS-1	GeoProbe	165. 746	8.34	0.48	28.15	2.46	0.00	0.00	47.88	38.16	75.07	64.23			
LOOP4	MS-1	GeoProbe	165. 746	11.66	0.72	32.27	0.28	0.07	0.71	136.17	52.55	65.16	30.23			
LOOP4	MS-1	GeoProbe	165. 746	12.00	0.45	24.96	0.16	0.10	0.97	111.02	50.41	34.93	37.54			
LOOP4	MS-2	GeoProbe	165. 747	2.26	1.57	9.16	0.06	1.32	13.20	83.97	417.93		34.65			
LOOP4	MS-2	GeoProbe	165. 747	5.91	0.18	8.19	0.22	0.10	0.97	24.51	30.18	41.81	64.34			
LOOP4	MS-2	GeoProbe	165. 747	7.00	0.42	11.30	0.39	0.05	0.48	19.94	235.15	64.95	74.23			
LOOP4	MS-2	GeoProbe	165. 747	8.21	0.13	8.91	0.00	0.09	0.89	16.73	98.98	77.94	77.59			
LOOP4	MS-2	GeoProbe	165. 747	9.21	0.39	12.74	0.14	0.12	1.16	21.95	116.48	33.44	54.02			
LOOP4	MS-2	GeoProbe	165. 747	9.57	0.26	14.93	0.11	0.10	1.01	36.20	94.83	48.62	48.03			
LOOP4	MS-2	GeoProbe	165. 747	10.79	0.28	20.61	0.28	0.07	0.67	157.28	506.67	83.67	29.37			
LOOP4	TL-1	GeoProbe	165. 742	2.25	0.38	8.06	0.00	0.00	0.00	14.69	2.00	51.76	53.85			

LOOP4	TL-1	GeoProbe	165. 742	3.47	3.22	18.42	0.12	1.84	18.40	57.10	219.38				
LOOP4	TL-1	GeoProbe	165. 742	4.69	1.24	14.65	0.08	0.94	9.40	32.30	139.22		58.31		
LOOP4	TL-1	GeoProbe	165. 742	6.79	0.22	14.81	0.00	0.00	0.00	35.89	2.00	85.88	67.02		
LOOP4	TL-1	GeoProbe	165. 742	7.13	0.37	14.75	0.00	0.66	6.63	33.46	45.30	59.98	74.36		
LOOP4	TL-1	GeoProbe	165. 742	7.96	0.36	16.93	0.08	0.00	0.00	92.84	14.55	101.09	38.65		
LOOP4	TL-1	GeoProbe	165. 742	8.30	0.62	17.59	0.00	0.00	0.00	209.90	33.16	100.04	49.21		
LOOP4	TL-1	GeoProbe	165. 742	9.23	0.32	22.60	0.24	0.00	0.00	39.68	41.54	92.34	57.37		
LOOP4	TL-1	GeoProbe	165. 742	9.57	0.22	18.56	0.35	0.00	0.00	94.04	84.96	97.99	53.03		
LOOP4	TL-2	GeoProbe	165. 743	2.25	1.02	39.95	0.49	51.16	511.60	60.23	175.35		58.20		
LOOP4	TL-2	GeoProbe	165. 743	2.87		49.70	1.20	2.43	24.32	132.11					
LOOP4	TL-2	GeoProbe	165. 743	3.47	3.22	34.21	0.69	1.07	10.70	230.22	200.02				
LOOP4	TL-2	GeoProbe	165. 743	4.04	1.51	39.27	0.63	1.18	11.80	313.22	153.73				
LOOP4	TL-2	GeoProbe	165. 743	4.69	2.32	36.22	1.10	1.18	11.80	537.40	560.79		22.86		
LOOP4	TL-2	GeoProbe	165. 743	5.31	2.48	51.44	1.00	1.76	17.60	512.66	284.58				
LOOP4	TL-2	GeoProbe	165. 743	5.91	3.12	48.94	0.96	1.50	15.00	225.42	83.67				

Appendix3-2. Results of cations of LOOP4

LOOPNr	Boreholes	method	DGUnr	Depth (m)	mg/L									
					Al	Ba	Ca	Fe	K	Mg	Mn	Na	Ni	Sr
LOOP4	GeoW-2	GeoProbe	165. 741	3.465	0.09	0.27	101.49	0.00	1.29	4.34	0.04	23.11	0.01	0.26
LOOP4	IS-1	GeoProbe	165. 744	3.885	0.08	0.06	64.53		2.07	3.59	0.13	23.31	0.01	0.25
LOOP4	IS-2	GeoProbe	165. 745	6.905	0.10	0.08	65.76		4.63	5.56	0.04	44.73	0.01	0.21
LOOP4	IS-2	GeoProbe	165. 745	8.145	1.39	0.12	68.13	1.57	4.64	6.03	0.08	31.21	0.01	0.16
LOOP4	MS-1	GeoProbe	165. 746	1.025	0.14	0.08	37.16		8.48	4.36	0.04	39.71	0.01	0.26
LOOP4	MS-1	GeoProbe	165. 746	2.345	0.22	0.11	70.75		13.91	5.59	0.03	22.12	0.01	0.26
LOOP4	MS-1	GeoProbe	165. 746	4.685	0.11	0.13	108.80		24.00	7.06	0.15	15.71	0.02	0.23
LOOP4	MS-1	GeoProbe	165. 746	5.905	0.12	0.15	112.96		18.75	7.64	0.25	20.50	0.02	0.29
LOOP4	MS-1	GeoProbe	165. 746	7.845	0.10	0.08	123.69		1.77	6.16	0.14	20.98	0.01	0.28
LOOP4	MS-1	GeoProbe	165. 746	8.34	0.10	0.08	120.43		1.40	6.76	0.18	21.21	0.01	0.26
LOOP4	MS-1	GeoProbe	165. 746	11.655	0.11	0.12	98.83		3.06	3.39	0.11	21.16	0.01	0.27
LOOP4	MS-1	GeoProbe	165. 746	11.995	0.10	0.11	105.42		3.08	3.68	0.18	23.79	0.01	0.29
LOOP4	MS-2	GeoProbe	165. 747	2.255	0.41	0.04	61.96		1.23	11.85	0.08	29.60	0.01	0.29

LOOP4	MS-2	GeoProbe	165. 747	5.905	0.30	0.03	89.12		1.63	7.85	0.09	17.14	0.01	0.25
LOOP4	MS-2	GeoProbe	165. 747	6.995	0.25	0.11	112.07		1.94	4.72	0.09	21.86	0.01	0.27
LOOP4	MS-2	GeoProbe	165. 747	8.205	0.20	0.04	113.83		1.34	4.89	0.28	18.16	0.01	0.26
LOOP4	MS-2	GeoProbe	165. 747	9.205	0.21	0.05	82.43		1.29	4.42	0.26	15.36	0.01	0.20
LOOP4	MS-2	GeoProbe	165. 747	9.565	0.15	0.02	85.79		1.31	4.27	0.10	14.96	0.01	0.21
LOOP4	MS-2	GeoProbe	165. 747	10.785	0.15	0.06	102.45		1.98	5.34	0.18	18.73	0.02	0.27
LOOP4	TL-1	GeoProbe	165. 742	2.245	0.10	0.17	78.65		1.43	4.84	0.02	31.61	0.01	0.33
LOOP4	TL-1	GeoProbe	165. 742	3.465	0.09	0.24	92.33		2.01	3.99	0.03	49.85	0.01	0.25
LOOP4	TL-1	GeoProbe	165. 742	4.685	0.10	0.24	94.69	0.10	1.70	3.92	0.03	31.24	0.01	0.22
LOOP4	TL-1	GeoProbe	165. 742	6.785	0.06	0.15	111.34		1.59	5.02	0.92	14.20	0.01	0.23
LOOP4	TL-1	GeoProbe	165. 742	7.125	0.05	0.09	120.09		1.82	5.35	0.05	17.09	0.01	0.25
LOOP4	TL-1	GeoProbe	165. 742	7.955	0.07	0.07	89.41		2.76	4.47	0.06	15.02	0.02	0.23
LOOP4	TL-1	GeoProbe	165. 742	8.295	0.06	0.11	151.40		3.91	8.17	0.20	21.97	0.07	0.39
LOOP4	TL-1	GeoProbe	165. 742	9.225	0.05	0.09	95.05	0.10	5.48	6.15	0.50	25.50	0.01	0.25
LOOP4	TL-1	GeoProbe	165. 742	9.565	0.07	0.06	118.77	0.00	2.46	6.81	0.09	14.98	0.05	0.25
LOOP4	TL-2	GeoProbe	165. 743	4.685	0.12	0.09	242.17	0.00	5.06	15.25	0.24	45.60	0.03	0.72

Appendix3-3. Formic acid extractable Fe(II), Fe(total), and Fe(II)/Fe(total) of LOOP4

LOOPNr	DGUnr	borehole	Depth (m)	mg/Kg		Fe(II)/Fe(total)
				Fe(II)	Fe(total)	
LOOP4	165. 741	GeoW-2	2.34	-0.1	-3.7	0.02
LOOP4	165. 741	GeoW-2	3.56	11.3	210.4	0.05
LOOP4	165. 741	GeoW-2	4.78	2.1	207.5	0.01
LOOP4	165. 744	IS-1	2.3	5.6	213.4	0.03
LOOP4	165. 744	IS-1	3.56	0.1	22.1	0.00
LOOP4	165. 744	IS-1	3.98	0.1	11.3	0.00
LOOP4	165. 744	IS-1	4.78	0.1	19.4	0.01
LOOP4	165. 744	IS-1	6	0.1	9.6	0.01
LOOP4	165. 745	IS-2	3.56	30.9	214.2	0.14
LOOP4	165. 745	IS-2	6	391.6	457.3	0.86
LOOP4	165. 745	IS-2	7	0.0	12.8	0.00
LOOP4	165. 745	IS-2	8.24	0.2	53.0	0.00
LOOP4	165. 746	MS-1	1.12	5.4	283.3	0.02
LOOP4	165. 746	MS-1	2.225	68.3	182.3	0.37
LOOP4	165. 746	MS-1	2.275	17.4	90.8	0.19
LOOP4	165. 746	MS-1	3.56	49.1	358.3	0.14
LOOP4	165. 746	MS-1	4.78	273.4	594.1	0.46
LOOP4	165. 746	MS-1	6	1.2	218.1	0.01
LOOP4	165. 746	MS-1	8.435	48.3	269.4	0.18
LOOP4	165. 746	MS-1	12.09	645.9	716.5	0.90
LOOP4	165. 747	MS-2	2.345	64.4	332.7	0.19
LOOP4	165. 747	MS-2	3.47	0.6	45.6	0.01
LOOP4	165. 747	MS-2	4.38	3.8	48.7	0.08
LOOP4	165. 747	MS-2	6	227.0	434.7	0.52
LOOP4	165. 747	MS-2	7.09	1.8	205.6	0.01
LOOP4	165. 747	MS-2	8.3	208.4	418.5	0.50
LOOP4	165. 747	MS-2	9.3	312.3	518.6	0.60
LOOP4	165. 747	MS-2	9.66	301.5	620.5	0.49
LOOP4	165. 747	MS-2	10.88	485.7	537.4	0.90
LOOP4	165. 742	TL-1	2.34	1.6	297.8	0.01
LOOP4	165. 742	TL-1	3.56	4.0	173.2	0.02
LOOP4	165. 742	TL-1	4.78	224.2	521.8	0.43
LOOP4	165. 742	TL-1	7.225	75.8	114.3	0.66
LOOP4	165. 742	TL-1	8.415	167.9	205.5	0.82
LOOP4	165. 742	TL-1	9.66	132.8	274.8	0.48
LOOP4	165. 743	TL-2	2.34	140.0	261.7	0.53
LOOP4	165. 743	TL-2	2.96	286.2	312.5	0.92
LOOP4	165. 743	TL-2	3.56	324.7	381.1	0.85
LOOP4	165. 743	TL-2	4.13	390.9	463.1	0.84

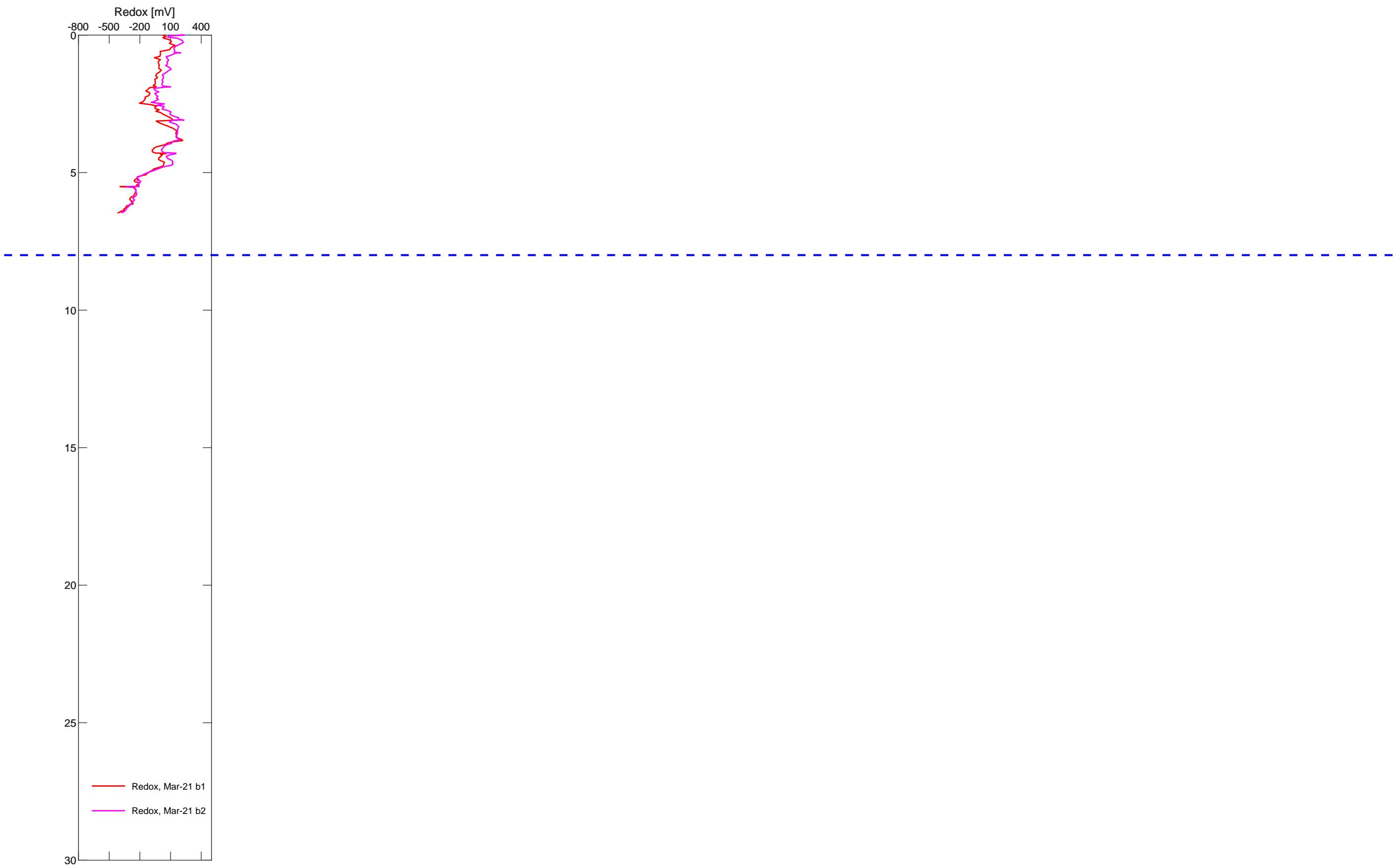
LOOP4	165. 743	TL-2	4.78	473.7	557.8	0.85
LOOP4	165. 743	TL-2	5.4	488.6	562.1	0.87
LOOP4	165. 743	TL-2	6	402.4	468.3	0.86

Appendix3-4. Denitrification rate of LOOP4

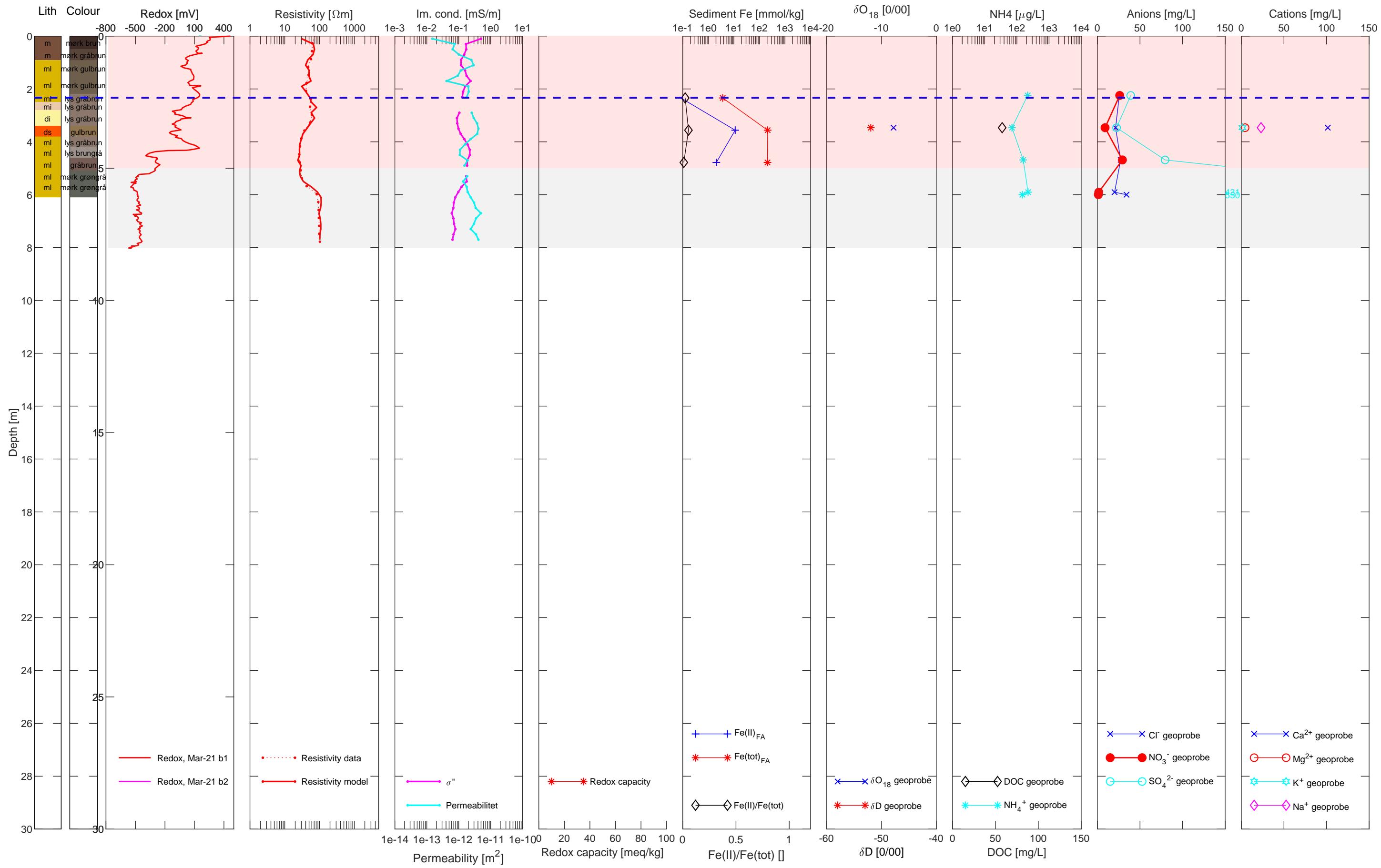
LOOPNr	DGUNr	Borehole	Depth (m)	mg N /yr	
				Repeat1	Repeat2
LOOP4	165. 745	IGS-2	3.3	277.3	131.9
LOOP4	165. 745	IGS-2	5.7	701.3	79.1
LOOP4	165. 745	IGS-2	7.5	38.4	
LOOP4	165. 746	MS-1	11.5	579.7	565.0
LOOP4	165. 746	MS-1	3.3	1735.0	1702.6
LOOP4	165. 746	MS-1	8.2	899.1	610.3
LOOP4	165. 747	MS-2	10.6	436.7	287.2
LOOP4	165. 747	MS-2	8.0	688.6	
LOOP4	165. 747	MS-2	9.0	419.0	397.1
LOOP4	165. 742	TL-1	2.1	358.3	285.5
LOOP4	165. 742	TL-1	3.3	367.3	218.6
LOOP4	165. 742	TL-1	4.5	299.8	249.2
LOOP4	165. 742	TL-1	6.6	585.6	557.6
LOOP4	165. 742	TL-1	7.0	480.8	469.4
LOOP4	165. 742	TL-1	7.8	951.1	854.3
LOOP4	165. 742	TL-1	8.1	1.7	1.3
LOOP4	165. 742	TL-1	9.4	939.1	900.8
LOOP4	165. 743	TL-2	2.1	359.2	264.6
LOOP4	165. 743	TL-2	2.7	456.1	90.0
LOOP4	165. 743	TL-2	3.3	235.1	207.3
LOOP4	165. 743	TL-2	3.9	0.2	0.2
LOOP4	165. 743	TL-2	4.5	358.6	332.5
LOOP4	165. 743	TL-2	5.1	394.2	190.8
LOOP4		TL-2	5.7	340.6	123.2

Appendix 4: Well panels illustrating all the collected parameters

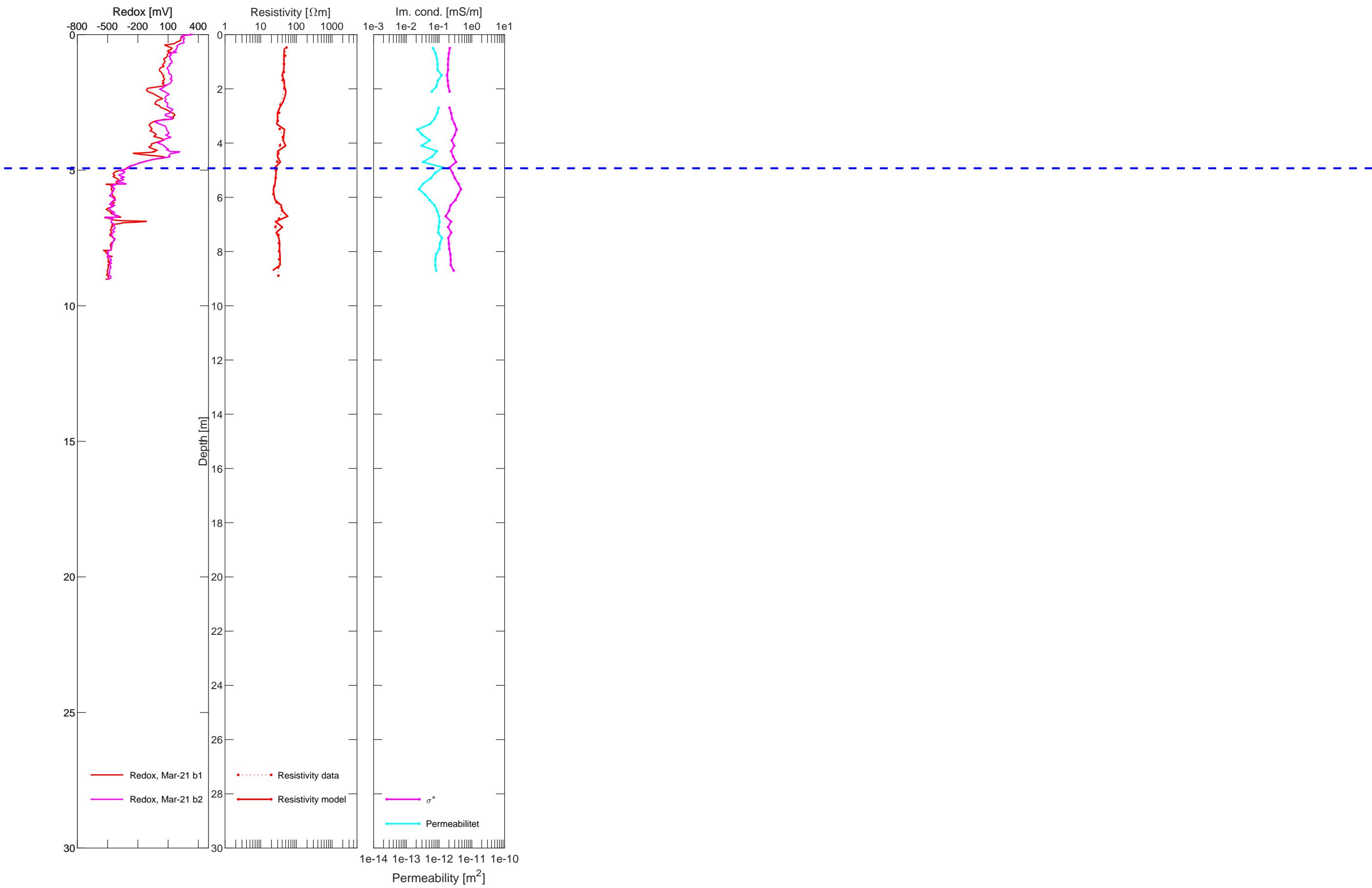
LOOP4 Borehole GW1 , DGUno Geological Window-1,



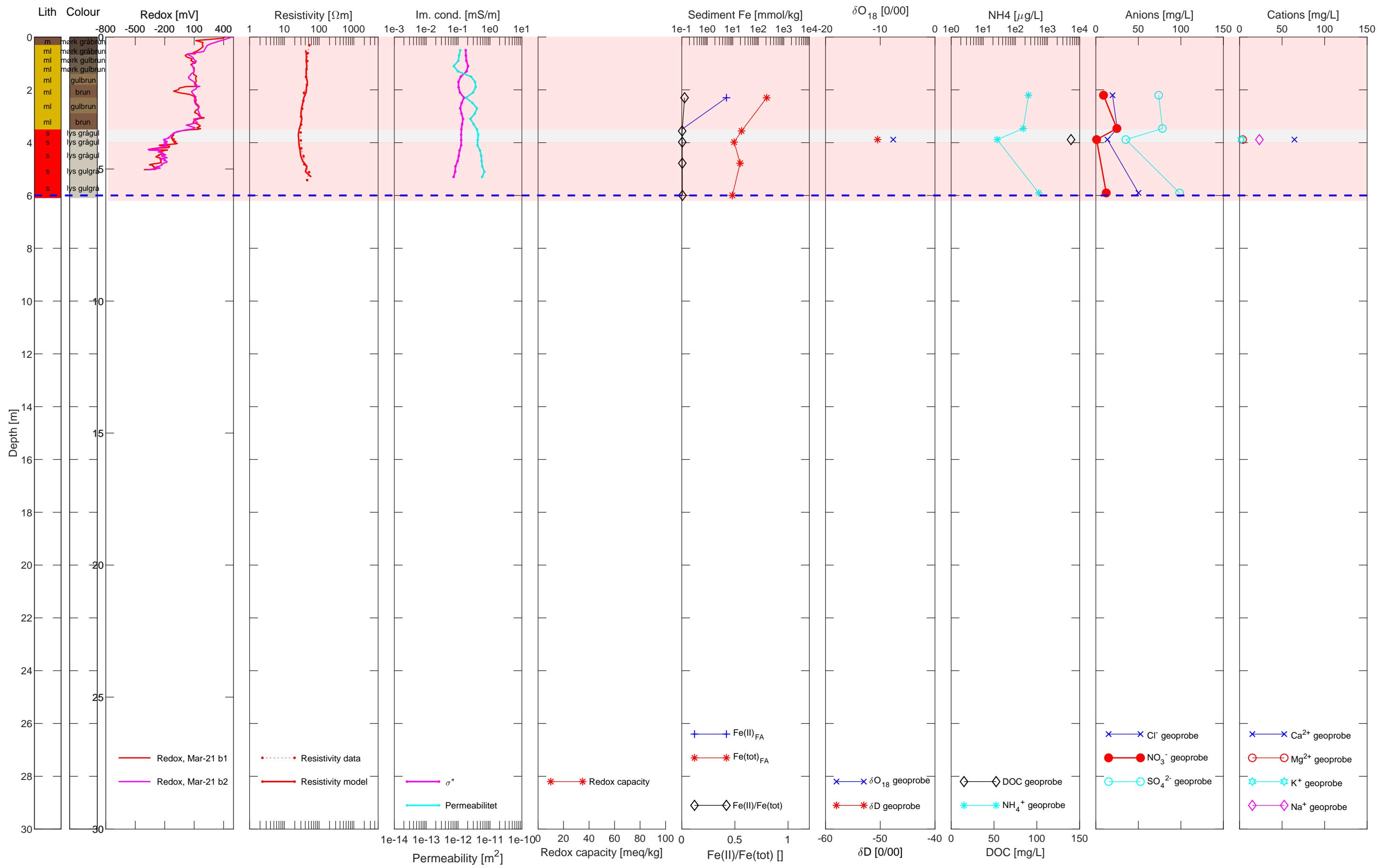
LOOP4 Borehole GW2 , DGUno 165. 741,



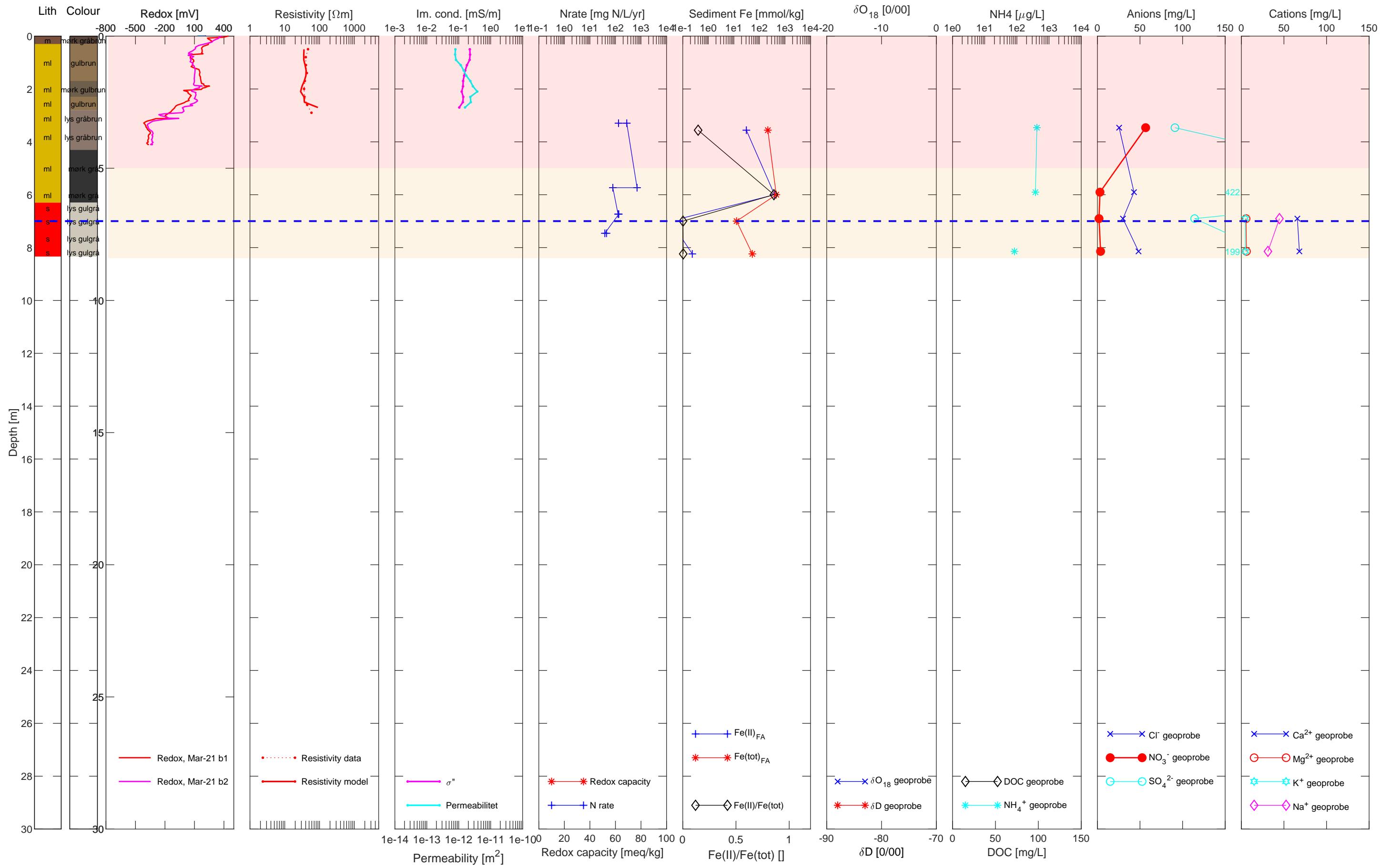
LOOP4 Borehole GW3 , DGUno Geological Window-3,



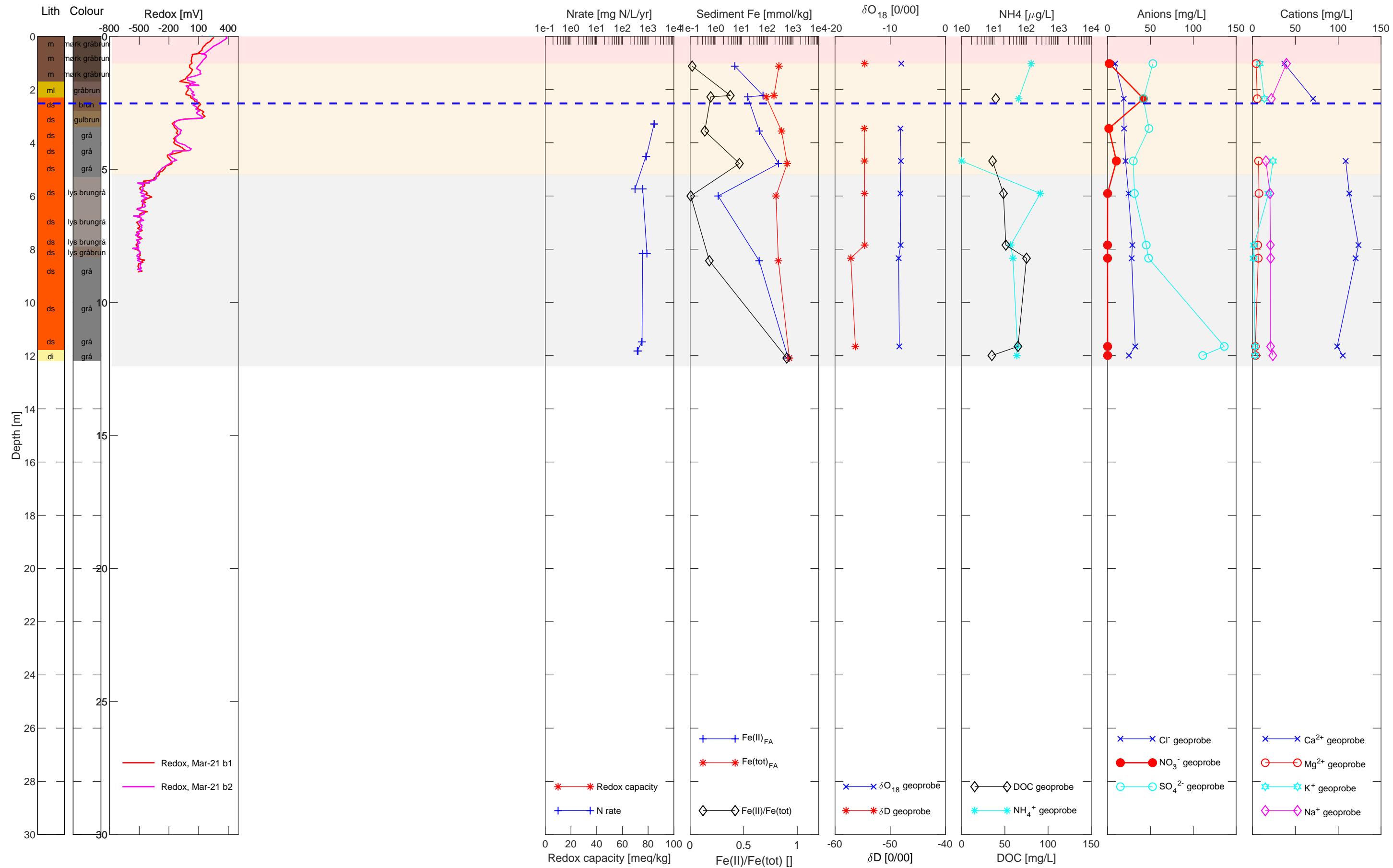
LOOP4 Borehole IGS1 , DGUno 165. 744,



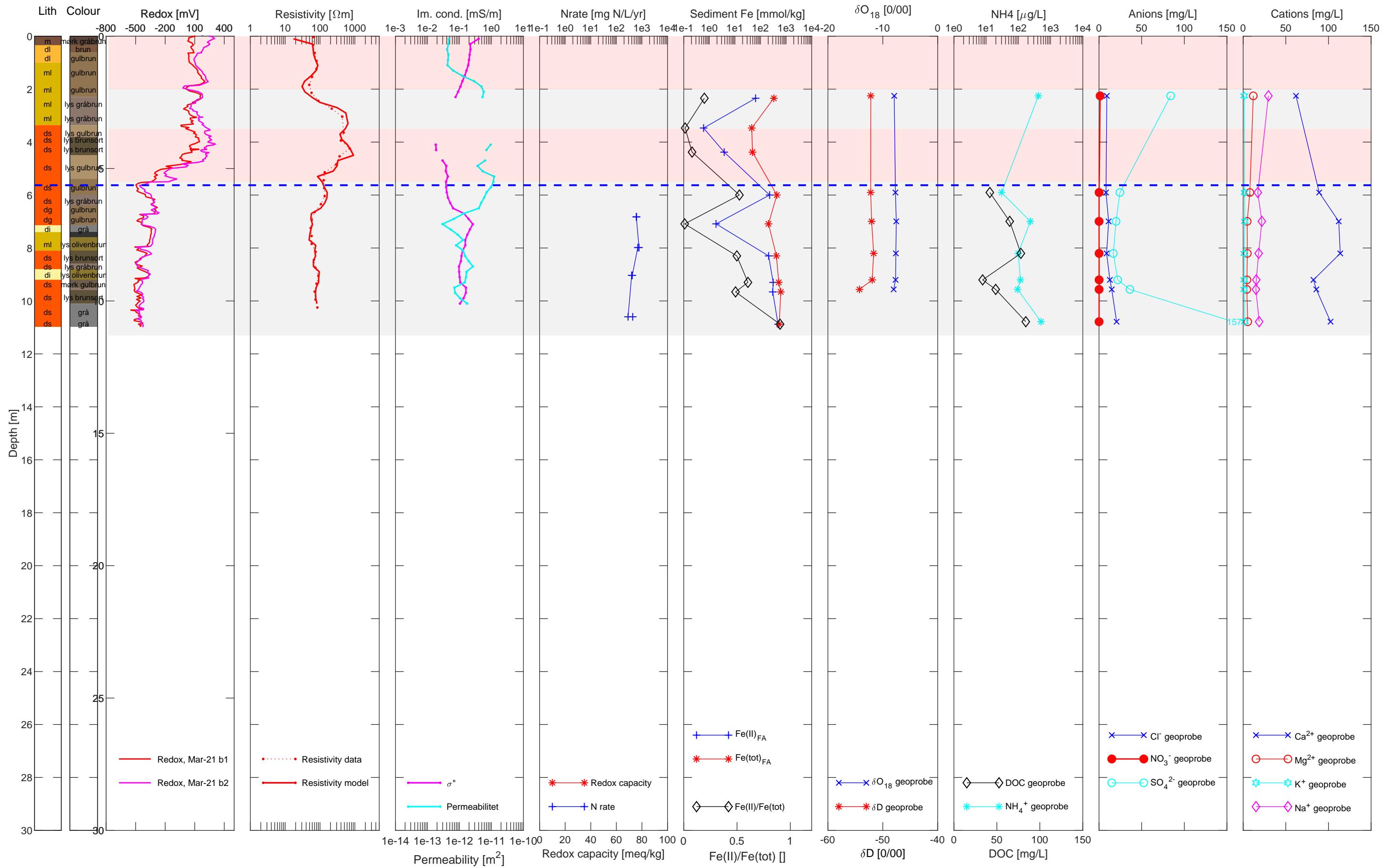
LOOP4 Borehole IGS2 , DGUno 165. 745,



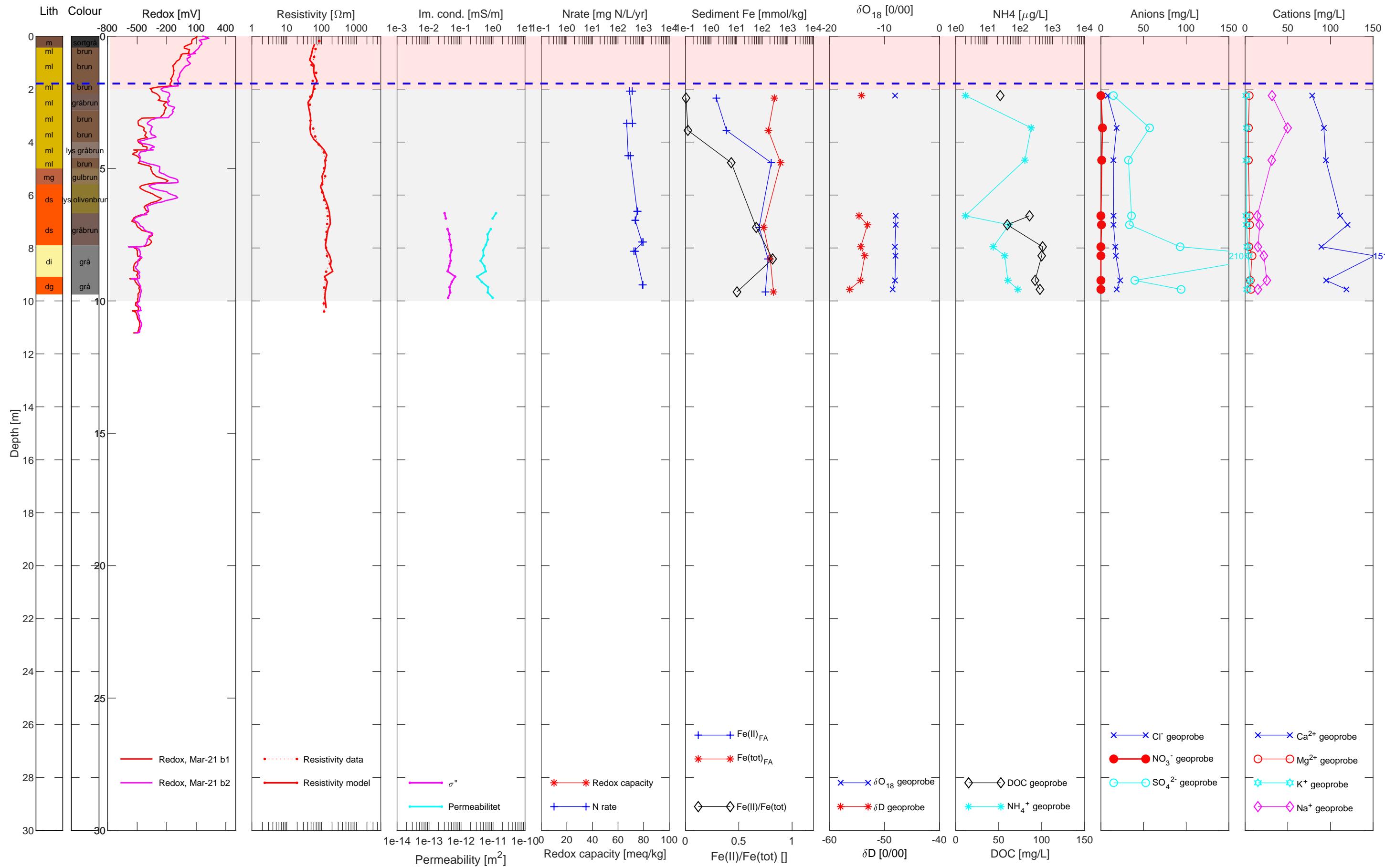
LOOP4 Borehole MWS1 , DGUno 165. 746,



LOOP4 Borehole MWS2 , DGUno 165. 747,



LOOP4 Borehole TIL1 , DGUno 165. 742,



LOOP4 Borehole TIL2 , DGUno 165. 743,

