

**Dissolved inorganic carbon
and organic carbon in mires
in the Forsmark area**

A pilot study

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December 2011

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Abstract

Dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) are the large dissolved carbon pools in mires. They are both related to a number of factors such as groundwater flow, minerogenic influence and peat properties, which all are more or less related to peatland development stage. In a scenario of a release of radionuclides from an underground repository containing radioactive material, behaviour of these pools during the mire ontogeny will be of importance for the understanding of how C-14 will constitute a potential risk to humans and non-human biota.

In this pilot study, DIC and DOC concentrations were investigated for three mires representing a potential sequence of peatland development in a coastal area at Forsmark in central Sweden characterized by land upheaval, a flat topography and calcareous content in the soil. The mires were chosen based on difference in height above the sea level, covering approximate 1000 years, and characteristics based on their vegetation. Water samples were collected during August from all three mires at two different depths in the anoxic layer of the mires, by extracting water from peat obtained with a peat corer.

DIC concentrations were related to the age of the mires, with the lowest concentrations in the highest located mire. There was a positive correlation between pH and DIC, where the higher DIC concentrations were found in the “richer” fens. DIC concentrations were also positively related to the conductivity within and between the mires, where conductivity would be a proxy for the dominating cation Ca^{+2} associated to the calcareous-influenced groundwater. DOC concentrations were highest in the oldest mire, but were similar in the younger mires. No patterns were found between DIC and DOC, and the peat bulk density. The report ends with suggestions on how a continued study could be improved.

Sammanfattning

Löst oorganiskt kol (DIC) och löst organiskt kol (DOC) är de stora lösta kolpoolerna i myrar. De är båda relaterade till ett antal faktorer som grundvattenflöde, minerogent inflytande och torvegenskaper, som alla i sin tur är mer eller mindre relaterade till torvmarkens utveckling. I ett scenario med ett utsläpp av radioaktiva ämnen från en underjordisk anläggning kommer dessa pooler vara av betydelse för förståelsen av hur C-14 kommer att utgöra en potentiell risk för människor och icke-mänsklig biota.

I denna pilotstudie undersöktes DIC- och DOC-koncentrationer i myrar som representerar en potentiell sekvens i successionen i ett kustområde vid Forsmark i mellersta Sverige. Området präglas av landhöjningen, en platt topografi och kalkhaltig jord. Myrarna valdes utifrån skillnaden i höjd över havet, som sträcker sig över ca 1000 år, och egenskaper baserat på deras vegetation. Vattenprover samlades in under augusti från alla tre myrarna på två olika djup i det syrefria lagret, genom att extrahera vatten från torv som plockats upp med en torvprofilsprovtagare.

DIC-koncentrationen var relaterad till myrarnas ålder, med de lägsta halterna i den högst belägna myren. Det fanns en positiv korrelation mellan pH och DIC, där de högre DIC-halterna fanns i ”rikare” kärr. DIC-halterna var också positivt relaterade till konduktivitet inom och mellan myrarna, där konduktiviteten kan antas vara en proxy för den dominerande katjonen Ca^{+2} som är associerad till det kalkpåverkade grundvattnet. DOC-halterna var högst i den äldsta myren, men var lägre i de yngre myrarna. Inga samband hittades mellan DIC och DOC, och torvens torrdensitet. Rapporten avslutas med förslag på hur en fortsatt studie skulle kunna förbättras.

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1 Introduction

In the safety assessment SR-Site, the potential exposure of radionuclides to humans and non-human biota was estimated using a model that is dependent on a large number of parameters (SKB 2010, Avila et al. 2010). For parameters describing pools and fluxes of dissolved carbon in mires, data were few or non-existing, both from the site and in literature (Löfgren 2010). In the forthcoming safety assessment for a repository containing waste of low or middle activity, the radionuclide C-14 will become important in terms of exposure in the case of a potential release of radionuclides from the repository. It is therefore adequate to further increase the knowledge of the parameter estimates used to describe the pools of dissolved inorganic carbon (DIC) in the Forsmark region. At the same time, estimates of concentrations of dissolved organic carbon (DOC) in mires were included in the sampling campaign, because of few estimates from mires in this region.

This document reports the results from this first attempt to increase the knowledge of dissolved carbon pools in mires of Forsmark. This activity was performed during supplemental site investigations for the SR-PSU safety assessment. The work was carried out in accordance with activity plan AP SFR-10-003, which is SKB's internal controlling document.

In the sampling campaign, data were collected from three mires in August 2010 and from one mire in late October 2010 (Table 3-2). The results are stored in the primary database (SICADA) and are traceable by the activity plan number.

2 Objective and scope

The calcareous content of the Quaternary deposits around Forsmark is typical for the north-eastern part of Uppland. The deposits originate from the latest glacial period and is more evident closer to the coast of the Baltic, where the more recently uplifted areas have been less exposed to weathering (Hedenström and Sohlenius 2008). The lime content in the regolith is manifested as a high pH in lakes and mire, where lakes are classified as oligotrophic hard water lakes (Andersson 2010) and mires are dominated by rich or extreme rich fens (Göthberg and Wahlman 2006). This has implications for the components of the carbonate system; dissolved CO_2 , HCO_3^- and CO_3^{2-} , which together constitute the potential pool of dissolved inorganic carbon in the water. For mires with pH less than 6, H_2CO_3 is the dominating component, and when pH is between 6.5 and 10, HCO_3^- is the dominating component.

The concentrations of DIC in mires has earlier been investigated by (Nilsson and Bohlin 1993) in the northern part of Sweden representing mires having a pH less than 6. Continuous monitoring of DIC and DOC concentration has been performed in lakes in the area, but there is today no data describing DIC or DOC from mires in the Forsmark region. This document describes the first attempt to estimate concentrations of DIC and DOC from three representative mires around Forsmark and, if possible, to relate these concentrations to different factors such as vegetation, peat density, margins within the mire, depth, and to age of the mires. The three mires represent a potential peatland development gradient, where the first mire surrounds a small lake water surface, the second lacks a lake water surface and the third has vegetation elements indicating a later stage (see 3.1.3). This order of development is also supported by their location in relation to the current sea level (Table 3-1).

3 Methods

Three mires were investigated during the vegetation period 2010 (Figure 3-1). The main sampling effort was made during 26th to 27th of August and one additional sampling was made 22th of October at Stenrössmossen. The sampling of DOC, DIC, additional chemical parameters and bulk density samples were made by Micke Borgiel (Sveriges Vattenkologer AB) and Anders Löfgren (EcoAnalytica).

3.1 The investigated mires

3.1.1 Labboträsk I

The youngest of the three investigated mires is the mire surrounding the small Lake Labboträsk, located in the northern part of the mire area (Figure 3-1, 3-2). This lake is included in a long-term surface monitoring programme for chemical sampling and has also been described with a carbon budget (Andersson 2010). It is therefore possible to relate measurements in the mire to long-term

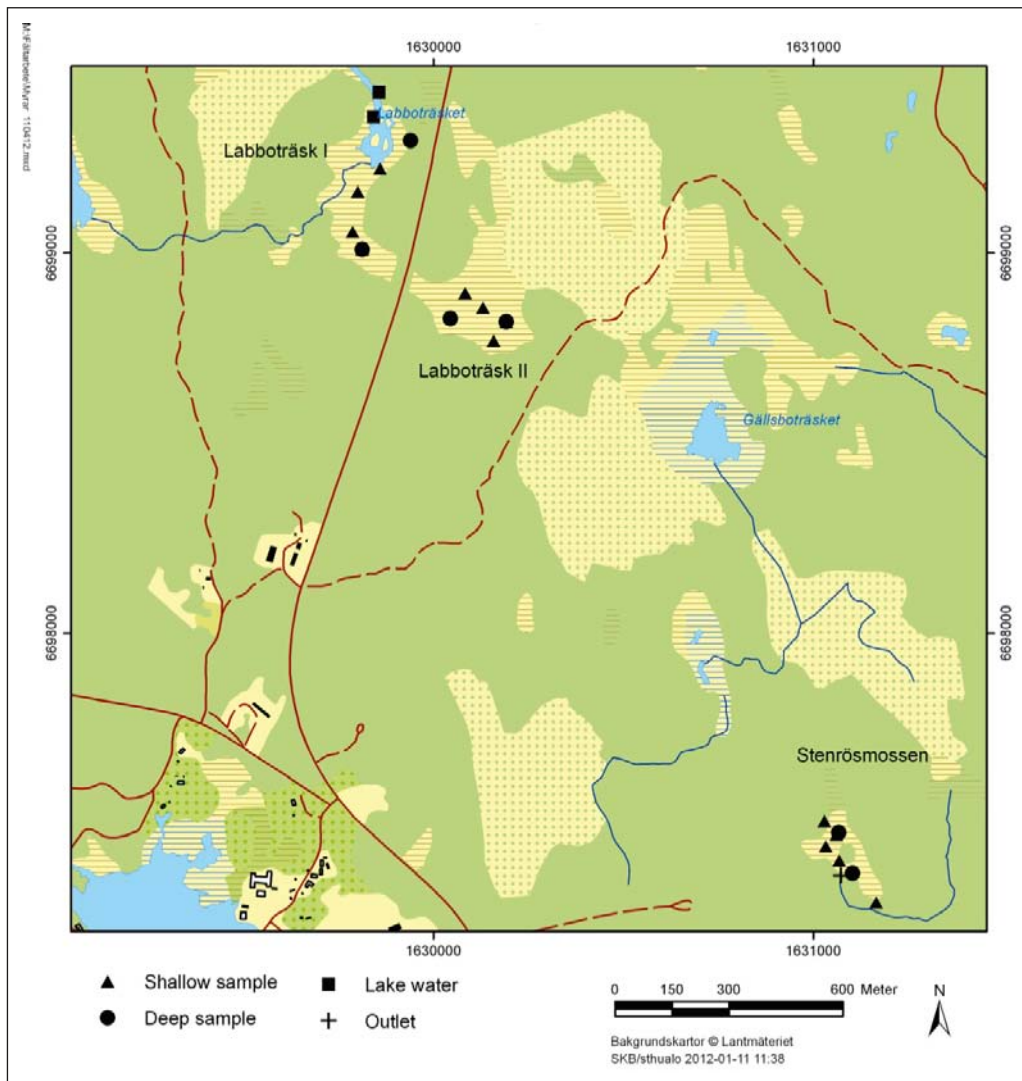


Figure 3-1. The location of the investigated mires and the location of individual samples within the mires in the Forsmark regional investigation area. Symbols show if surface water or peat cores have been sampled. At some of the shallow sample localities also an additional deeper sample was made below the shallow sample.

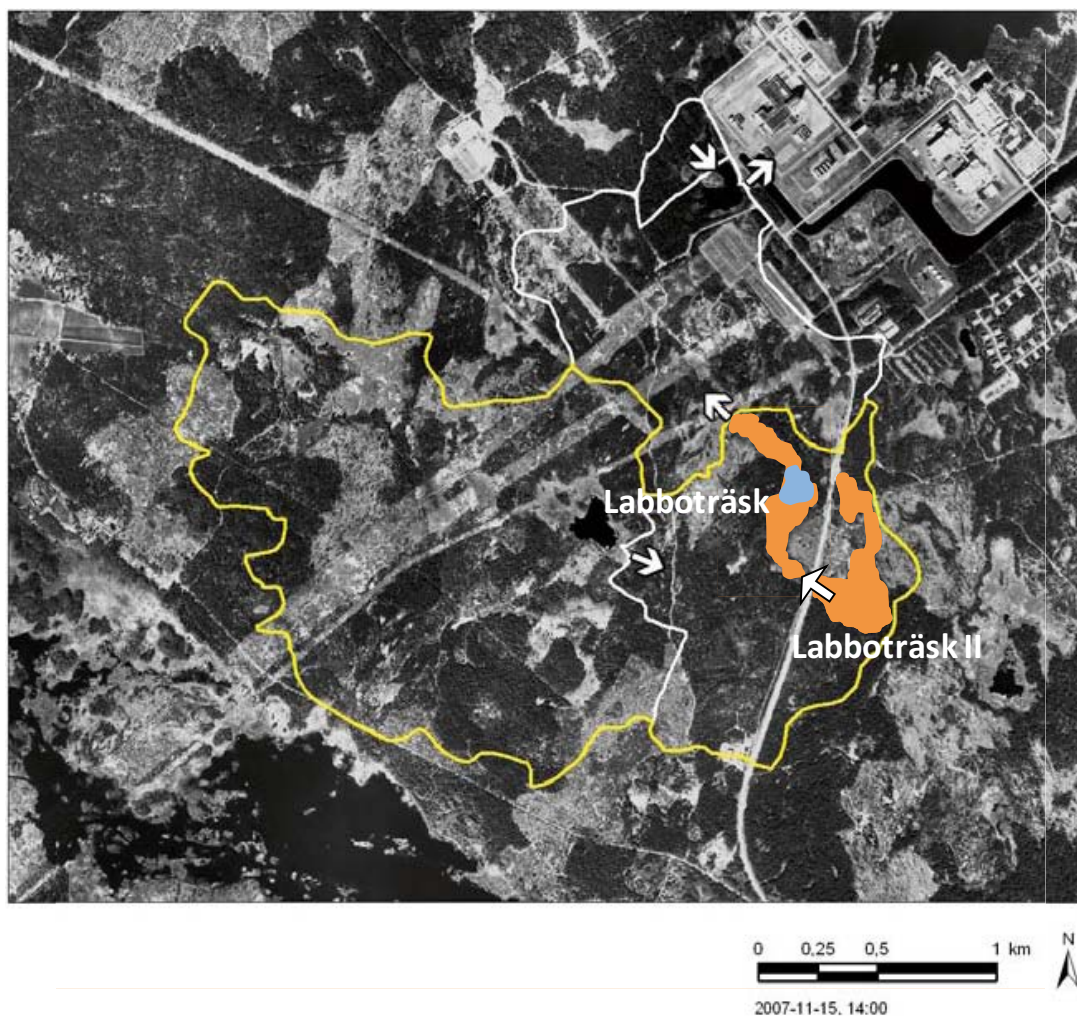


Figure 3-2. Lake Labboträsk and its catchment marked with yellow boundaries from (Brunberg et al. 2004). Orange shows the extent of the mire and blue is the lake. Arrows indicate stream flow directions. Labboträsk II is the upstream mire, situated east of the road and Labboträsk I is situated west of the road.

measurements in the lake. The mire has an approximately 2 m deep layer of peat and clay gyttja above a sand layer, postglacial clay and finally till in the bottom (Sohlenius and Hedenström 2009). The vegetation is mainly dominated by *Phragmites australis*, but becomes less dense in the southern part of the lake. Measurements of DIC in lake water suggest an annual median value of 29 mg L^{-1} , a max value of 56 mg L^{-1} and a large variation during the year (Figure 3-3). The median value for the lakes in Forsmark has been estimated to 21 mg L^{-1} (Tröjbom and Söderbäck 2006). The highest DIC concentrations are found during the early winter, and low concentrations are found during late summer and autumn (Figure 3-3).

3.1.2 Labboträsk II

The second mire is located upstream from the mire surrounding Lake Labboträsk and is referred to as Labboträsk II. Due to the higher location above the sea level (Table 3-1), it is older than Labboträsk. This difference in age is also seen in the overall vegetation pattern, where *P. australis* is much less dominating in Labboträsk II resulting in more diverse and dominant field (herbs and sedges) and bottom (bryophytes) layers. Furthermore, the bryophyte species are restricted to “brown mosses” in Labboträsk I, whereas also some *Sphagnum* species are present in Labboträsk II, suggesting a lower pH in Labboträsk II (e.g. Table 3-1). There is also no open water present in Labboträsk II, but the mire is connected to Labboträsk I through a pipe under the road (Figure 3-1).

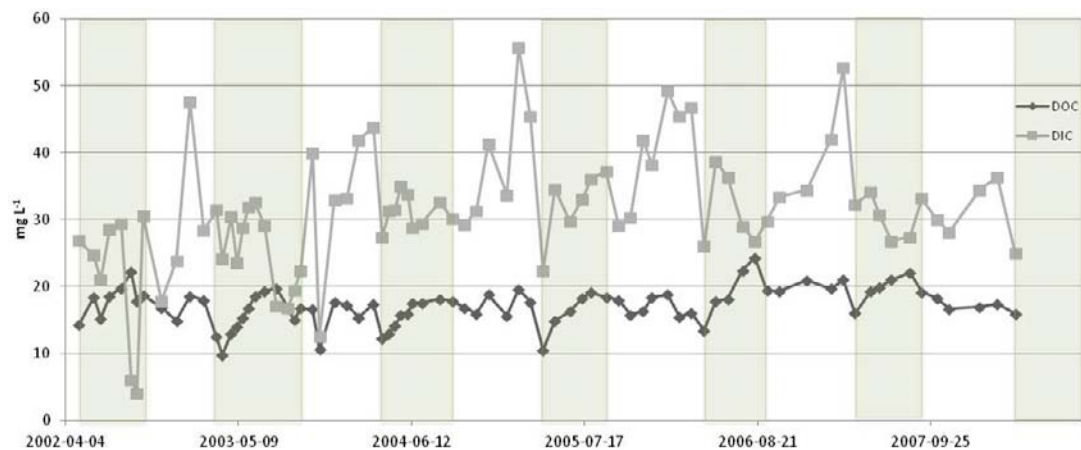


Figure 3-3. Measurements of dissolved inorganic carbon and dissolved organic carbon (mg L^{-1}) during 6 years in water from Lake Labboträsk show a large seasonal variation. Shaded areas indicate the vegetation period April to September. The variation in DOC concentration is small in comparison to that of DIC. Generally, DIC and DOC seem to fluctuate synchronously except in the later part of the vegetation period, where they may go in opposite directions (Data from SICADA).

3.1.3 Stenrössmossen

The oldest mire among the three is Stenrössmossen, which have characteristics of both a fen and of more bog-like environments (Göthberg and Wahlman 2006). The fen-like central parts are dominated by brown mosses and/or grasses/sedges. Parts of the mire is dominated by *Sphagnum* with less sedges and in some adjacent areas there is *Pinus sylvestris* forest on deep *Sphagnum* peat. These parts have been affected by earlier draining activities, seen as a high degree of humification in the top layer, the dominance of *Hylocomium splendens* in the bottom layer and the presence of large *Pinus sylvestris*. Peat stratigraphy and pH (Table 3-1) has been investigated in this mire by Fredriksson (2004) and the sampling for this study was made at the same locations as in Fredriksson (2004).

3.2 Water sampling and analysis

On each mire, sampling points were located with the aim of including different vegetation types and locations in relation to the outlet (see Figure 3-1, Table 3-2). In Stenrössmossen locations were chosen in accordance with the earlier investigation by Fredriksson (2004).

Each sampling point was located or, if not previously investigated, given coordinates using a GPS (Figure 3-1). All sampling points were located in a hollow. This means that all points were regarded to be wet in comparison to a drier hummock. Generally, none of the mires had any pronounced hollow-hummocky pattern, mainly due to their low age. Some parts of the oldest mire, Stenrössmossen, showed a slight hollow-hummocky pattern. At each sampling point the vegetation was described and the depth to water table was estimated using a PVC-pipe ($\text{Ø}=0.015$ m) and a laser plumb. At most sample points the water table was close to or just below the vegetation surface at the sample occasions.

Table 3-1. Information describing the mires that were sampled in the investigation. Time since isolation assumes a shoreline regression of 6 mm per year.

Mire	m.a.s.l. (m)	Time since isolation (year)	pH	Peath depth (m)	Reference
Labboträsk I	2.7	450	6.7–8.4 (lake water) (1)	1–2 ⁽²⁾	1) SICADA 2002–2008 2) Sohlenius and Hedenström 2009.
Labboträsk II	3–5	500–800	–	–	
Stenrössmossen	8.2–9.1	1,400–1,500	5–8	1–1.2	Fredriksson 2004

A peat corer with the diameter of 0.1 m was used to collect a peat profile approximately down to 0.7 m. The samples were taken below the oxic zone and the depth 0.35 m was identified to be located in the anoxic zone in all mires. Immediately after the peat profile was brought to the surface, water was pressed from a ten cm peat sample (0.35 m to 0.45 m divided into two vertical slices). Each slice was squeezed and the water was collected in bottles. This method has given reliable estimates in other studies e.g. Nilsson and Bohlin (1993).

The water from each peat sample was collected in the order; DIC, DOC (if sampled) and a sample for determination of alkalinity and pH in the lab. Water for the DIC and DOC analyses was put in 10 mL bottles, leaving a head space of approximately 2 mL. A third bottle was filled with the water left for additional water analysis, such as alkalinity, pH and conductivity (Table 3-3). The samples were stored cold during transport and the DIC and DOC samples were put in a freezer until they were analysed.

When the peat corer was removed with the peat profile a multi parameter sonde was immediately pressed down in the hole to the approximate depth of 0.3 m. The multi parameter sonde (YSI 600 QS) with a connected terminal (YSI 650 MDS) for logging data measured pH, water temperature, oxygen, redox potential as well as electrical conductivity (see Appendix 2). Calibration of the sonde was conducted according to the measurement system description SKB MD 910.003 before the measurements. At some sampling points, an additional deeper core was removed in close vicinity to the first shallow core (Figure 3-1). The same procedure was used for taking the deeper water sample as for the shallow water sample, but the sonde could not be used in the deep hole.

At Lake Labboträsk, two samples were also taken from the lake water surface (0.5 m depth) following the methodology of the surface water monitoring program (Qvarfordt et al. 2008).

Early tests using a syringe and a filter with a 4 µm pore size to remove particulate matter turned out to be difficult due to the large amount of particulate matter in the water from Stenrössmossen. Therefore, the analysis of DIC and DOC was preceded by centrifugation (4,000 rpm) to remove particulate matter. This procedure would be comparable with a pre-filtering procedure using filters. DIC samples were introduced into an inorganic carbon (IC) reactor vessel (filled with 25% H₃PO₄) to convert all IC to CO₂. DOC samples were treated with acid and bubbled with CO₂ gas to remove IC before analysis. The analyses were performed by “high temperature (680°C) catalytic combustion” on a Shimadzu TOC-5000. Measurement uncertainty for DOC estimates is described by using the 95% confidence interval of a separate test, which is 8% of the expected values. The measurement uncertainty is expected to be similar for DIC, but has not been tested separately.

3.3 Estimating the bulk density

The dry bulk density of the peat containing the sampled water was estimated for 16 of the 32 water samples. Peat from where the water was collected was taken from a known volume (83.1 cm³) and dried in 105°C for 24 hours to estimate the dry bulk density. This was done from most of the sampling localities during the field campaign in August (see data in Appendix 2).

Table 3-2. Number of water samples distributed among mires, depth, season and additional samples. All samples were collected during late August except for those marked with *, which were collected in late October.

Mire	Shallow sample	Deep sample	Additional samples
Labboträsk I	5	2	2 (lake water)
Labboträsk II	5	2	–
Stenrössmossen	6+6*	2+2*	1* (Outlet)
Summa	24	8	3

Table 3-3. Properties that were estimated for each sampled locality. DOC and peat bulk density were estimated for a subset of samples.

Measured properties	Analysed with	Analysed by
Dissolved CO ₂ (DIC)	Infrared gas analyser	Dept of Systems Ecology, Stockholm University
Dissolved organic carbon (DOC)	Infrared gas analyser	Dept of Systems Ecology, Stockholm University
pH (field)	Sonde	Field crew
Temperature (field)	Sonde	Field crew
Oxygen(field)	Sonde	Field crew
Conductivity (field)	Sonde	Field crew
pH (lab)	Titration	SKB-lab Forsmark
Alkalinity (lab)	Titration	SKB-lab Forsmark
Conductivity (lab)		SKB-lab Forsmark
Peat bulk density		SGU, Uppsala
Water table depth	Pipe and laser plumb	Field crew
Vegetation		Field crew

3.4 Analyses and interpretations

3.4.1 Field and lab estimated pH

pH was not possible to estimate in the field in the deeper holes, but was estimated from water samples in the lab. pH is partly dependent on the temperature and the pattern in Figure 3-4 shows the systematic difference between the field estimated pH and estimates made in the lab at +25°C for the shallow samples. Comparing the intercepts of a linear plot between pH in the field and in the lab, and the 1:1 line suggests that lab pH was approximately 0.4 units higher compared to the field estimates. This deviance is mainly due to the temperature dependency of pH (Wetzel 2001). The lab pH was used in the comparisons below if otherwise not stated.

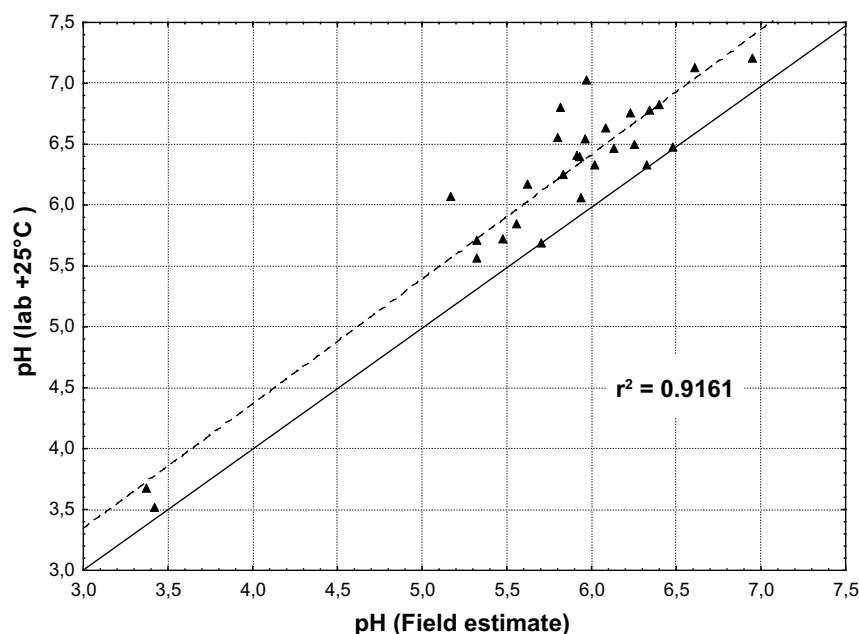


Figure 3-4. Illustration of the deviance between field estimated and lab estimated pH of the mire water.

3.4.2 Precipitation before the sampling campaign

Precipitation events may to some extent affect the sampling results and thereby affect the representativeness of the estimates. 2010 was a rainy year and this was also seen during the two periods before the sampling in August (Table 3-4). This suggests that the mires during 2010 were wetter than during a more normal year, at least compared with the last 8 years. Moreover, the rainfall during the last 10 days before the sampling suggests a flush of surface water from the catchment areas surrounding the mires. Relatively, this flush was probably larger for Labboträsk I than for the two other mires, due to its larger catchment area in relation to the mire/lake area. Labboträsk I is also the only mire with both a distinct inlet and outlet indicating a higher water turnover (Figure 3-1).

3.5 Comparison of samples from lake water with samples from the ongoing surface water monitoring program

A comparison of sampled lake water from Lake Labboträsk with long-term monitoring estimates of DIC and DOC from the same lake could indicate discrepancies due to a somewhat different pretreatment of the samples (centrifugation instead of filtering, see 3.2). Samples taken two weeks earlier and estimates from earlier years compared to the two samples taken in the lake during the summer campaign show that the DIC estimate during this field campaign was much higher (Table 3-5). The alkalinity was also much higher, giving the high DIC estimate confidence. Moreover, the low pH at the sampling occasion is in accordance with the high DIC value (a negative correlation). The high DIC estimate from this study is similar to the high late winter values found in the lake during February and Mars (see Figure 3-3). The DOC estimates were close in agreement. In conclusion, this comparison does not suggest any large discrepancies due to the pretreatment. However, the large difference in the DIC estimates is difficult to explain, but is supported by correlated parameters such as alkalinity and pH. A possible explanation could be related to the precipitation events just prior to the sampling occasion suggesting a large flush of carbonate-enriched surface water (see 3.4.2).

Table 3-4. Precipitation between 2003 and 2010 partitioned into amounts falling during 10 and 20 days before the sampling date of the 26th of August and the total yearly precipitation. Data is from the meteorological station Högmasten situated approximately 2 km NE of Lake Labboträsk (from SICADA).

Year	10 days before (mm)	20 days before (mm)	Total (mm)
2003	25	43	–
2004	22	26	488
2005	4	62	565
2006	11	49	537
2007	11	25	440
2008	39	124	812
2009	35	41	591
2010	64	94	701

Table 3-5. Comparison of measurements on surface water from Lake Labboträsk (26 of August 2010) with data from the surface monitoring programme in Forsmark (mid August to early Sept). Values within brackets denote the range during 2002–2008.

Lake Labboträsk	DIC (mg L ⁻¹)	DOC (mg L ⁻¹)	Alkalinity (HCO ₃ , mg L ⁻¹)	pH (at 25°C)	Temp. (°C)
2003–2009 (Aug–Sept., N=7))	33 (4–56)	20 (10–24)	196 (129–391)	7.7 (6.9–8.3)	15.4
2010 (10 th Aug., N=1)	24	19	160	7.7	18.7
2010 (26 th Aug., N=2)	51	20	239	7.0	14.9

4 Results and discussion

4.1 DIC and DOC concentrations

The estimated DIC concentrations in the samples from the three mires ranged between 2 and 75 mg L⁻¹. A similar range was found by Nilsson and Bohlin (1993) who measured DIC in 12 mires in northern Sweden (between 12 and 78 mg L⁻¹ of individual samples) during August and September. That study was considered to represent a large range of origins, water regimes, depths and nutrient status to be found in the anaerobic zone of mire ecosystems in the northern boreal zone. These mires did, however, only represent mires with relatively low pH where all inorganic carbon occurs as CO₂, which is not the case for the mires in the Forsmark region, where approximately 20 to 50% of the inorganic carbon occurs as HCO₃⁻ in the interval between pH 5.7 and 6.4 (Wetzel 2001). The mean DIC concentration for nine of the mires where shallow samples (between 0.3 and 1.2 m) were taken by Nilsson and Bohlin (1993), was 33 mg L⁻¹. This is comparable to the concentrations found in Labboträsk II (Table 4-1).

The measurements of DOC in the three mires ranged between 25 and 84 mg L⁻¹ (and one extreme sample with 161 mg L⁻¹ representing a drained part of the Stenrösmossen with *Sphagnum* peat). Tahvanainen (2004) investigated the water-saturated oxic layer of 36 mires in Finland, classified according to a poor – rich gradient and found a range in DOC concentrations between 5 and 85 mg L⁻¹.

4.1.1 Variation among the Forsmark mires

The distribution of DIC estimates among the mires is shown in Figure 4-1, where also the two samples from the lake water surface are indicated. DIC concentrations increase from the oldest mire to the youngest (using summer measurements, Friedman ANOVA, N=7, df=2, $\chi^2=12.3$, p=0.002). The pH of fens in the Forsmark region is largely dependent on the inflow of groundwater enriched with carbonates originating from the till (Hedenström and Sohlenius 2008). A low inflow or more stagnant conditions suggest that pH is more dependent on local processes such as respiration (produces CO₂) or acidifying processes by vegetation (i.e. *Sphagnum*). Consequently, pH in the mire could therefore be correlated to the peatland developmental stage, where higher DIC concentrations would indicate a higher inflow of carbonate-enriched groundwater into the mire. Such patterns has also been correlated to concentrations of major cations associated to groundwater, i.e. Ca⁺² and Mg⁺² (Sjörs and Gunnarson 2002, Tahvanainen et al. 2003). A relevant proxy for these cations is the conductivity (i.e. Sjörs and Gunnarsson 2002), and the values in Table 4-1 support the hypothesis of a partly groundwater-induced pattern. One confounding variable of this aspect is that Labboträsk I has the largest catchment area and thereby has a larger inflow of shallow groundwater apart from being the youngest mire, whereas Labboträsk II and Stenrösmossen are of similar size in regard to the relation between size and catchment area. Consequently, age would be a main contributor to differences between at least these two mires. Another interpretation of patterns in DIC and conductivity among samples could be that the inflowing groundwater is heavily depleted in DIC and Ca⁺² in higher locations due to long-term leaching. Webster and McLaughlin (2010) also investigated a rich (pH= 5.7), an intermediate (pH=5.5) and a poor fen (pH=4.4) representing a successional gradient in Canada. They found similar patterns for Ca⁺², conductivity, DIC and DOC concentrations, and their sequence represented fens with a lower pH (Table 4.1). They concluded that DIC dynamics were strongly controlled by contribution from carbonate minerals.

Table 4-1. Mean values for some parameters distributed among the Forsmark mires and seasons. Deep samples were excluded and also the estimates from the sampling point on Stenrösmossen characterised by an extremely high DOC, low DIC and pH, which is regarded typical for a bog-like environment e.g. Tahvanainen (2004) (see also Figure 4-1).

Mire	Season	Temp (° C)	pH (Field)	DIC (mg L ⁻¹)	DOC (mg L ⁻¹)	EC (mS m ⁻¹)	N
Labboträsk I	Summer	14	6.4	46	43	69	5
Labboträsk II	Summer	13	6.0	32	38	40	5
Stenrösmossen	Summer	13	5.7	14	61	15	5
	Autumn	4	5.7	15	54	17	5

The DOC concentration was higher in the older fen Stenrössmossen than in the two other fens (Table 4-1). Tahvanainen (2004) found a pattern in DOC concentration connected to the poor – rich fen categorization (pH) when mires with similar geochemical settings (granitoid bedrock/metabasite) were compared. High DOC values were connected to low pH values. This pattern suggests that the DOC concentration could be related to the peat development stage of the mire, where older mires have more stagnant hydrological conditions and are more affected by autochthonous processes, such as heterotrophic respiration. This is also indicated in Figure 3-3, where the lowest DOC concentrations are found at high water turnover during spring in Lake Labboträsk. Furthermore, Chanton et al. (2008) suggested that this pattern could partly be an effect of a mixed redox zone in fens, where vascular plants produced more reactive DOC in the rhizosphere, in combination with oxygen transport into the rhizosphere, resulting in a more rapid mineralisation. In a *Sphagnum*-dominated environment with less oxygen, more refractory DOC would be produced and accumulated over time.

4.1.2 Variation within mires

Location within the mire and vegetation

In Stenrössmossen there is an increasing trend in the DIC concentration as a function of the distance to the outlet from the mire (Figure 4-2). DOC showed the opposite trend. This pattern could suggest an effect of increasing water movement, but the distance is confounded with differences in the vegetation. The samples with the lowest DIC concentrations and the highest DOC concentrations were from the oldest part of Stenrössmossen dominated by late successional species, such as *Pinus sylvestris*, deep *Sphagnum* peat and hydrologically more stagnant conditions. The opposing trends may suggest that a large part of DIC and DOC have different origin, where DIC mainly is transported with the water entering the mire, whereas DOC is produced locally within the wetland. Nilsson and Bohlin (1993) found that DIC concentration was positively correlated to *Sphagnum* peat and negatively correlated to *Carex* peat. This pattern could not be seen in this investigation, mainly due to the fact that *Sphagnum* peat is rare in this young area where rich fens dominate. The few sampled locations with *Sphagnum* peat rather showed the opposite pattern and do probably represent more stagnant hydrological conditions (in the very left of Figure 4-2).

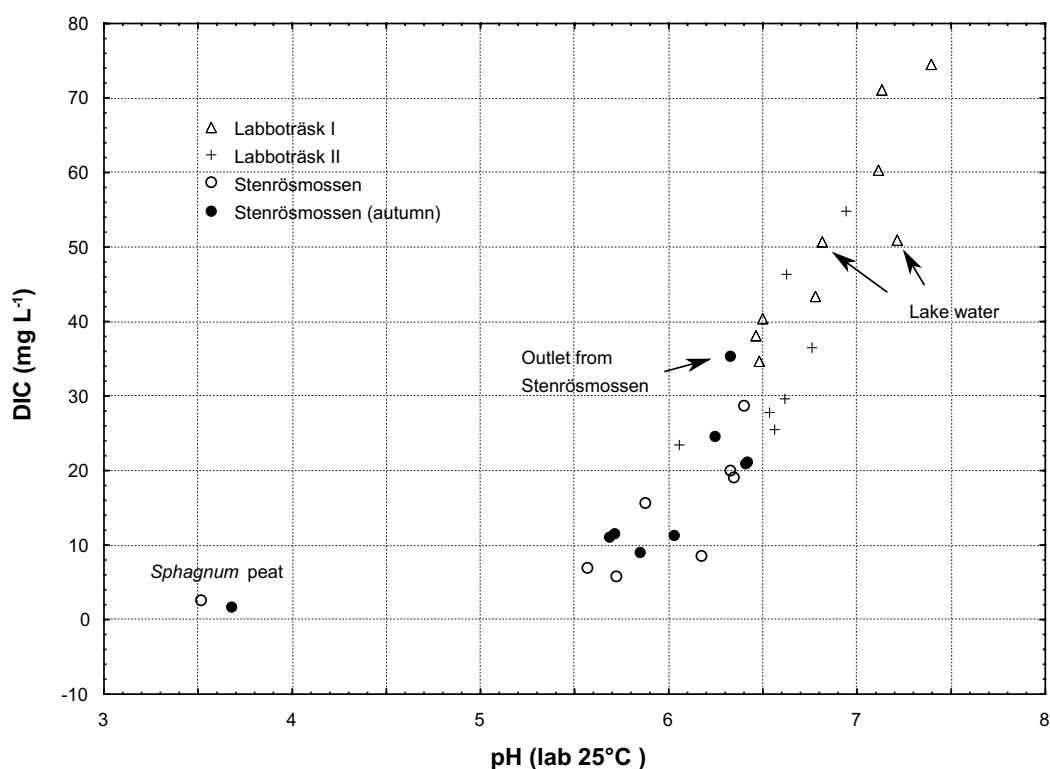


Figure 4-1. The relationship between pH and DIC in the developmental gradient from the oldest mire on the left to the youngest on the right including both shallow and deep estimates.

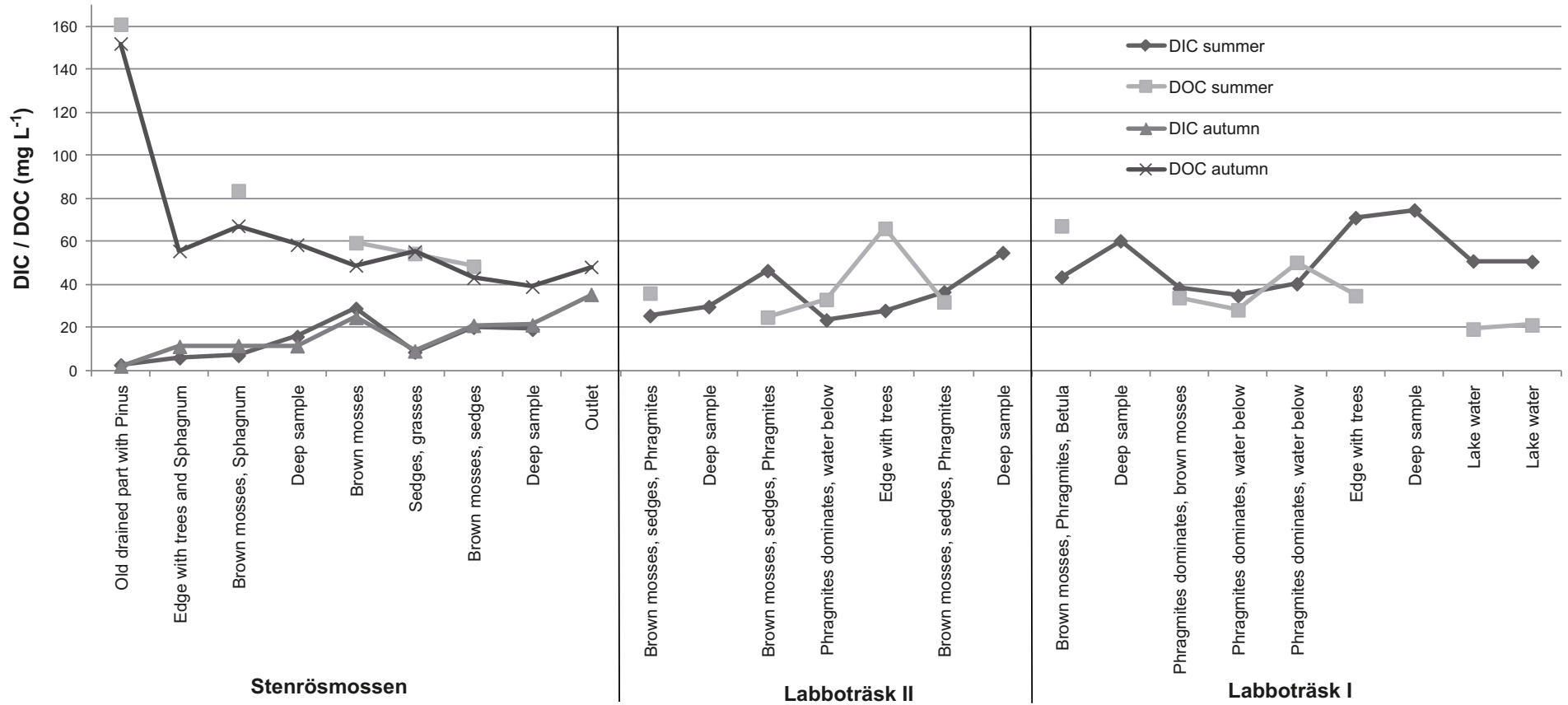


Figure 4-2. Pattern of DIC and DOC concentrations among vegetation types, deep and shallow cores, and location within the mire, where samples have been arranged according to their distance to the outlet from the mire. Stenrösmossen is the oldest highest located fen and is not connected to the other two fens. Labboträsk I and II are connected through a pipe under a road. The text “water below” on the horizontal axis indicates that there is a free water volume beneath the Phragmites root mat.

Waddington and Roulet (1997) found the highest DIC values in the margins of the peatland (compared to the bog plateau) in a peatland in northern Sweden measured regularly during two consecutive years. In the present study the highest DIC values (shallow and deep) were recorded at a forested margin of the fen in Labboträsk I (Figure 4-2).

Depth

In total, six deeper cores from the summer campaign were analysed. The overall pattern was that DIC concentrations were higher in the deeper section (Wilcoxon matched pair test, $Z=1.99$, $p<0.05$). This pattern was also found by Nilsson and Bohlin (1993) and was in that case suggested to be an indication of incoming groundwater.

Seasonal variation

A comparison between sampling occasions in the anoxic layer in Stenrössmossen suggests small differences in DIC and DOC concentrations during the year (Table 4-1, Figure 4-1 and 4-2). It should however be noted that sample sizes are small and there are only two sampling occasions. The first occasion would represent stagnant hydrological conditions during a period with high photosynthesis and decomposition, in comparison with the occasion with higher hydrological flows, lower photosynthesis and decomposition (but see 3.4.2).

In lakes, the seasonal variation in DIC concentration is regarded to mainly be a function of biotic processes during the vegetation period, where DIC is consumed by autotrophic organisms (Wetzel 2001). Low DIC concentrations are therefore found during periods of high photosynthetic activity (Figure 3-3) (also a diurnal pattern). This metabolic consumption of DIC may also cause precipitation of calcite (CaCO_3), which has been observed in the sediments of Lake Labboträsk (Sohlenius and Hedenström 2009). Moreover, there are physical constraints to the solubility of CO_2 in water determined by temperature, where a decrease in temperature from $+20^\circ\text{C}$ to $+4^\circ\text{C}$ increases the solubility by 75%.

In a mire, all photosynthetic activity is found in the field and bottom layers (mainly bryophytes in Stenrössmossen). Bryophytes primarily take up their carbon from the atmosphere, but hollow species are likely to take up dissolved inorganic carbon forms (DIC) from the surrounding water (e.g. Price et al. 1997). Generally, the peak of the vegetation period also implies lower water tables and therefore an additional limit to the potential uptake of DIC from the mire surface water. DIC in water is partially formed during heterotrophic respiration (both aerobic and anaerobic) and would continuously be added during the vegetation period. However, approximately 60 to 90% of the respiration is occurring in the oxic upper layer (Malmer and Wallén 2004), which suggests that most of the CO_2 is entering the atmosphere without being dissolved in the water or transported down into the anoxic layer. Correspondingly, Tahvanainen and Tuomaala (2003) found evidence for diurnal variation reflecting acidifying effects of CO_2 in the upper water-saturated oxic layer. Furthermore, DIC accumulation in the anoxic layer would be obscured by groundwater flows (and degassing from the mire surface) (Siegel and Glaser 1987). Also Waddington and Roulet (1997) found relatively small differences in DIC concentration between dry and wet seasons in the margin of a larger peatland. The largest differences were found in the ombrotrophic part of the wetland.

The pattern seen in Figure 4-2 suggests a somewhat higher concentration of DOC in 4 of 5 localities within Stenrössmossen during the summer. A similar pattern was found by Tahvanainen et al. (2003) in a boreal, moderately rich fen. This could be attributed to high photosynthesis and decomposition with more stagnant hydrological conditions.

Measurements in Lake Labboträsk from the ongoing surface monitoring program show that DOC is less prone than DIC to seasonal variation (Figure 3-3). Interestingly, DIC and DOC concentrations covary during the winter season, but goes in different directions during late summer. This is consistent with a pattern in DIC and DOC concentrations that is groundwater driven outside the vegetation season and partly driven by assimilation and decomposition during the late summer. Briefly, this could suggest that mires that are more affected by groundwater flow, e.g. Labboträsk I and II, would be expected to show a larger seasonal variation in DIC concentrations than Stenrössmossen, where a low inflow of DIC during spring and autumn is replaced by the input of DIC from decomposition during summer.

4.2 Dry bulk density of peat

The results suggest no large differences in dry bulk density of peat between mires, but the dry bulk density tended to be lower in the deeper samples compared with samples from 0.35 m (Figure 4-3). For Labboträsk I and II this was evident due to the shallow dense root mat that could be found floating on the water or less dense material. Interestingly, this pattern seems to be present also in Stenrösmossen. A pattern with a higher peat bulk density closer to the surface could be a consequence of a higher degree of humification (indicating oxidized conditions), but this was only found in one coring location below 0.35 m in Stenrösmossen (Fredriksson 2004). Therefore, a decreasing peat bulk density with depth suggests that the continuous peat compactation is still progressing in Stenrösmossen. Differences in bulk density would suggest overall differences in water permeability for the three fens, but the bulk density samples did not reflect such a pattern (Figure 4-3). Instead, differences in potential water mobility between mires are inferred from the presence of areas where deep peat samples were impossible to sample, due to loose material (see Figure 4-2) or absence of material and the presence of quag mires (Sw. gungflyn) in the both younger fens. Consequently, the potential water mobility is higher in the two younger fens compared with Stenrösmossen.

DIC concentration was not related to the density of the peat (Figure 4-4). Other studies have shown that the degree of decomposition (as von Post index) was correlated to production of CO₂ from decomposition, e.g. Scanlon and Moore (2000). This pattern does, however, depend upon the hydrological condition and e.g. Nilsson and Bohlin (1993) concluded from their study that the strong relation between DIC and depth indicated that hydrological conditions may be more important than the peat type.

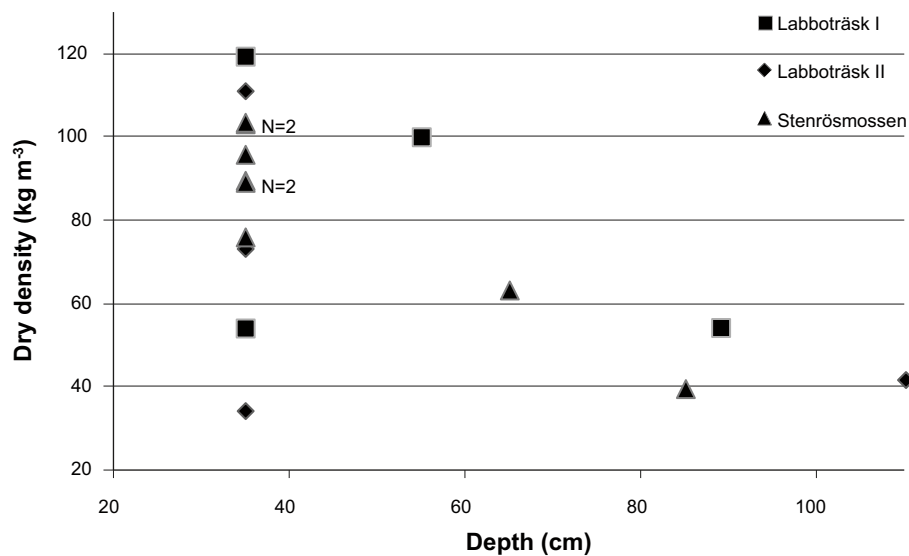


Figure 4-3. Relationship between depth and dry density of the peat for the three mires.

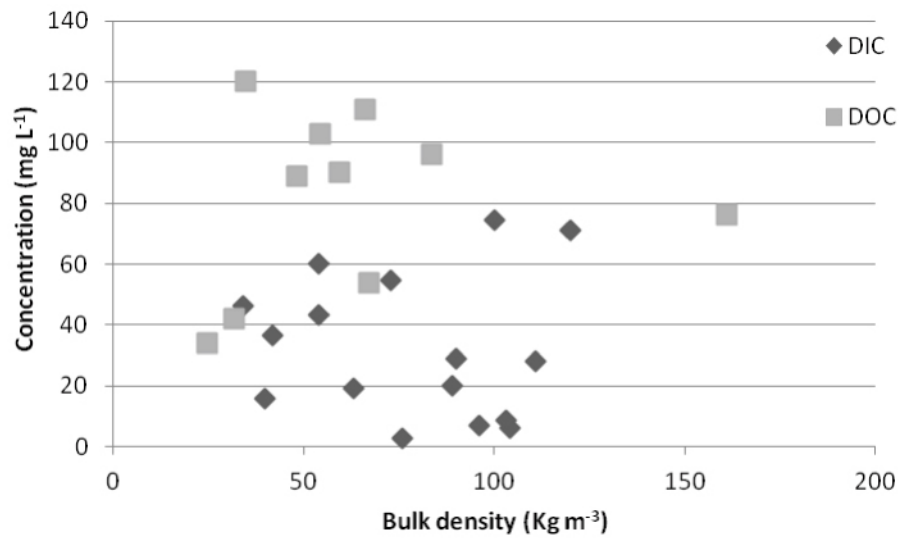


Figure 4-4. DIC and DOC concentrations plotted against the dry weight density of the peat containing the sampled water.

5 Concluding summary

The present study, although based on few replicates, suggests differences in DIC concentrations among mires of different ages in an area like Forsmark, characterized by calcite-rich deposits and high groundwater pH. A small difference also seems valid for DOC concentrations, but seems to be more prevalent in older developmental stages. DIC measured in the anoxic layer is produced during decomposition in the summer, but is also added with increased water influx enriched by the carbonate-rich till in spring and autumn. DOC on the other hand is mainly produced during heterotrophic respiration and by vascular plant roots in the rhizosphere, and concentrations levels off if water influx/turnover increases in the autumn.

Both DIC and DOC seem to be related to pH, however, in opposite ways. pH associated to the poor/rich index of mires also seems to describe the peat development of mires in Forsmark and it would, at least in Forsmark, be possible to use pH as a proxy for mire development. DIC concentrations decreased with mire age, whereas DOC increased. DIC and DOC also seems to be related to the water transport within the wetland and between wetlands, suggesting that a considerable part of DIC either originates from groundwater or is produced during conditions of increased water flow within the mire. No pattern associated to mire edges could be detected, but this may be an effect of a small sample sizes or a failure to locate these edge samples appropriate in time or space.

The small data set from the fen Stenrösmossen suggests that the DIC concentrations in the anoxic layer seem to be quite stable during the autumn compared to the summer. Several factors may contribute to this pattern. The overall low DIC concentration in this mire suggests a relatively small input of carbonate-enriched groundwater.

No correlations were found between DIC and DOC on the one hand, and bulk peat density on the other. From the work with peat corings on the three mires it was possible to infer that water mobility was larger within the two younger mires.

In the planning of a future study it would be relevant to consider the following.

- It would be important to establish permanent installations to minimize the impact on the sampling points at each sampling occasion and to minimize the sampling error. Thereby, the collecting unit would only sample the water that is more or less free to move in the peat, instead of squeezing the peat.
- Samples describing depth profiles. Add samples from the oxic zone as well as samples from below the peat, which would add further information on depth-related patterns.
- This study did not include CH₄ that might reach concentrations corresponding to between 5 to 25% of the dissolved inorganic carbon pool (Nilsson and Bohlin 1993) and figures close to 50% has been reported (Waddington and Roulet 1997) from a bog in northern Sweden.
- By including the major cations, Ca²⁺ and Mg²⁺, and also δ¹³C-DIC values in the sampling program, it could be possible to infer influx of groundwater.
- Including other elements associated with different sources, e.g. atmospheric deposition or rain events, or shallow groundwater.
- Including inert elements, e.g. Rb, Zr and Ti, that could be compared with the more reactive elements, such as Ca²⁺ and different carbon species.

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Table describing the localities for water and peat sampling

Locality	Date	IDCODE	X	Y	Vegetation	Peat type	Water table in relation to ground surface (m)
Stenrössmossen	100826	PFM004421	1631030	6697507	Old drained part with large Pinus. Hylocomium schreberi dominates, Vaccinium uliginosum, Ledum palustre	Sphagnum	-0.24
Stenrössmossen	100826	PFM004419	1631174	6697293	Edge with Betula, Alnus, Picea and Pinus. Sphagnum dominates with Myrica gale.	Carex	-0.05
Stenrössmossen	100826	PFM004416	1631068	6697476	Brown mosses, Sphagnum, with Ledum palustre and Andromeda polifolia.	Carex-bryales	0
Stenrössmossen	100826	PFM004416	1631068	6697476	Deep core	Carex-bryales	0
Stenrössmossen	100826	PFM004415	1631034	6697440	Brown mosses with Vaccinium microcarpum and Ledum palustre	Carex-bryales	0
Stenrössmossen	100826	PFM004417	1631068	6697403	Carex, Molinia caerulea and Myrica gale	Carex-bryales	0
Stenrössmossen	100826	PFM004418	1631104	6697369	Brown mosses, Carex and Ledum palustre	Bryales	0
Stenrössmossen	100826	PFM004418	1631104	6697369	Deep core	Bryales	0
Labboträsk II	100827	PFM007699	6698820	1630192	Brown mosses, sedges, Phragmites	Carex-bryales	0
Labboträsk II	100827	PFM007699	6698820	1630192	Deep core	Phragmites	0
Labboträsk II	100827	PFM007698	6698770	1630159	Brown mosses, sedges, Phragmites	Carex-bryales	0
Labboträsk II	100827	PFM007706	6698857	1630131	Phragmites dominates, Betula Myrica gale and Thelypteris palustris with water below	Phragmites	0
Labboträsk II	100827	PFM007705	6698895	1630084	Edge with Betula, Picea and Alnus trees. Phragmites, V. vitis-idaea and Maianthemum bifolium.	Carex-bryales	-0.25
Labboträsk II	100827	AFM001079	6698828	1630045	Brown mosses, sedges, Phragmites	Carex-bryales	0
Labboträsk II	100827	AFM001079	6698828	1630045	Deep core	Phragmites humified	0
Labboträsk I	100827	PFM007700	6699009	1629813	Betula, Phragmites and Myrica gale. Vaccinium microcarpum and Filipendula ulmaria. Brown mosses dominates. "Gungfly"	Phragmites	0
Labboträsk I	100827	PFM007700	6699009	1629813	Deep core	Phragmites	0
Labboträsk I	100827	PFM007701	6699056	1629788	Phragmites dominates with Carex diandra, Parnassia palustris and brown mosses. "Gungfly"	Phragmites	0
Labboträsk I	100827	PFM007702	6699161	1629801	Phragmites dominates and Myrica gale, water below	None	0
Labboträsk I	100827	PFM007703	6699223	1629860	Phragmites dominates and Myrica gale, water below	None	0
Labboträsk I	100827	PFM007704	6699296	1629940	Edge with Betula, Alnus and Pinus trees.	Woody	0
Labboträsk I	100827	PFM007704	6699296	1629940	Deep core	Woody	0

Locality	Date	IDCODE	X	Y	Vegetation	Peat type	Water table in relation to ground surface (m)
Labboträsk I	100827	PFM1000074	6699422	1629857	Lake	None	0
Labboträsk I	100827	PFM1000074	6699358	1629843	Lake, close to Phragmites border with Utricularia, Potamogeton and Chara species.	None	0
Stenrösmossen	101022	PFM004421	1631030	6697507	Old drained part with large Pinus. Hylocomium schreberi dominates, Vaccinium uliginosum, Ledum palustre	Sphagnum	-0.30
Stenrösmossen	101022	PFM004419	1631166	6697210	Edge with Betula, Alnus, Picea and Pinus. Sphagnum dominates with Myrica gale.	Woody/Carex	0
Stenrösmossen	101022	PFM004416	1631068	6697476	Brown mosses, Sphagnum, with Ledum palustre and Andromeda polifolia.	Carex-bryales	0
Stenrösmossen	101022	PFM004416	1631068	6697476	Deep core	Carex-bryales	0
Stenrösmossen	101022	PFM004415	1631034	6697440	Brown mosses with Vaccinium microcarpum and Ledum palustre	Bryales	0
Stenrösmossen	101022	PFM004417	1631068	6697403	Sedges, grasses and Myrica gale	Bryales	0
Stenrösmossen	101022	PFM004418	1631104	6697369	Brown mosses, Carex and Ledum palustre	Bryales	-0.10
Stenrösmossen	101022	PFM004418	1631104	6697369	Deep core	Bryales	-0.10
Stenrösmossen	101022	PFM007707	1631073	6697362	Outlet, surface water	None	0

Appendix 2

Table describing bulk peat density and chemistry data

IDCODE	Sample depth (m)	Dry density (Kg/m ³)	Temp °C	Cond. (field) (mS/cm)	Cond. (lab) (mS/m)	Salinity (ppt)	O ₂ (%)	O ₂ (mg/L)	pH (field)	pH (lab 25°C)	mbar	DIC (mg/L)	DOC (mg/L)	HCO ₃ -alkalinity (mg/L)
PFM004421	0.35–0.45	76	13.3	0.163	15.3	0.08	40.1	4.19	3.42	3.52	1,001	3	161	
PFM004419	0.35–0.45	104	13.9	0.096	7.9	0.04	29.9	3.09	5.48	5.72	1,000	6		*16.1
PFM004416	0.35–0.45	96	13.6	0.111	10.4	0.05	28.3	2.95	5.32	5.57	1,002	7	84	*27.7
PFM004416	0.85–0.95	40			13.4					5.88		16		*52.0
PFM004415	0.35–0.45	90	13.3	0.228	23.9	0.11	32.2	3.37	5.93	6.4	998	29	59	*116
PFM004417	0.35–0.45	103	12.5	0.117	11.9	0.05	28.3	3.02	5.62	6.17	997	8	54	*42.1
PFM004418	0.35–0.45	89	14.0	0.172	18.6	0.08	45.9	4.73	6.02	6.33	998	20	48	*84.8
PFM004418	0.65–0.75	63			18.4					6.35		19		91.4
PFM007699	0.40–0.50		13.7	0.396	48.9	0.19	32.5	3.38	5.8	6.56	999	25	36	101
PFM007699	0.80–0.90				40.4					6.62		30		*168
PFM007698	0.35–0.45	34	13.3	0.516	49	0.25	28.6	2.99	6.08	6.63	999	46	25	248
PFM007706	0.4		12.8	0.241	24.9	0.12	37.6	3.99	5.94	6.06	1,007	23	33	98.1
PFM007705	0.35–0.45	111	12.6	0.24	28.3	0.11	42.1	4.48	5.96	6.54	1,007	28	66	*150.9
AFM001079	0.35–0.45	42	13.9	0.478	49.9	0.23	29.8	3.08	6.23	6.76	1,004	36	32	237.1
AFM001079	1.10–1.20	73			56.6					6.94		55		321
PFM007700	0.35–0.45	54	13.3	0.647	56.7	0.32	39.7	4.14	6.34	6.78	1,003	43	67	209.5
PFM007700	0.89–0.99	54			76.5					7.11		60		374.1
PFM007701	0.35–0.45		14.5	0.573	66.6	0.28	42.2	4.3	6.13	6.46	1,009	38	34	214.6
PFM007702	0.35–0.45		14.0	0.361		0.17	42.9	4.42	6.48		1,007	35	28	
PFM007703	0.35–0.45		13.2	0.49	47.1	0.24	39.9	4.19	6.25	6.5	1,003	40	50	221.6
PFM007704	0.35–0.45	120	12.8	0.981	105.7	0.49	45.2	4.77	6.61	7.13	1,002	71	35	*477.1
PFM007704	0.55–0.65	100			98.6					7.39		75		471.9
PFM1000074	0.4		15.2	0.43	43.7	0.21	92.7	9.29	6.95	7.21	1,011	51	19	236.1
PFM1000074	0.4		14.5	0.499	43	0.24	51.9	5.28	6.4	6.82	1,013	51	21	241.9
PFM004421	0.35–0.45		7.6	0.166	16.3	0.08	48.7	5.82	3.37	3.68	992	2	152	
PFM004419	0.35–0.45		3.5	0.112	8.78	0.05	23.3	3.09	5.7	5.69	986	11	56	
PFM004416	0.35–0.45		3.7	0.1	12.7	0.05	14.3	1.89	5.32	5.71	991	12	67	155.7
PFM004416	0.70–0.80				16.7					6.03		11	58	110.4
PFM004415	0.35–0.45		3.9	0.207	33.9	0.1	15.6	2.05	5.83	6.25	989	25	49	
PFM004417	0.35–0.45		4.6	0.094	10.3	0.04	14.9	1.93	5.56	5.85	988	9	55	
PFM004418	0.35–0.45		4.4	0.189	17.5	0.09	10.6	1.38	5.91	6.41	987	21	43	*167.1
PFM004418	0.65–0.75				17.7					6.42		21	39	
PFM007707	0		3.2	0.367		0.18	27.2	3.63	6.33		992	35	48	

*For most of the lab measured samples a lot of organic material was present during the measurements and small available volumes made some of the alkalinity estimates somewhat uncertain.