Chapter 4

Fluvial and hydrothermal input of Manganese into the Arctic Ocean

Abstract:
A total of 773 samples were analysed for dissolved manganese (Mn) in the Arctic Ocean aboard R.V. Polarstern during expedition ARK XXII/2 from 28 July until 07 October 2007 from Tromsø (Norway) to Bremerhaven. Concentrations of Mn were elevated in the surface layer with concentrations of up to 6 nM over the deep Basins and over 20 nM in the Laptev Sea. The general distribution of Mn through the water column is consistent with previous studies, but the absolute concentrations of the previous studies appear to be slightly higher than currently reported.

The concentrations of Mn were elevated in the surface layer and this can be related to fresh water input. This was visible in the strong negative correlations observed between dissolved Mn and salinity. Using the correlations between Mn and salinity and the correlation between Mn and the quasi conservative trace water mass tracer PO_4^*, shows fluvial and melt water input and that the surface water was of Pacific and Atlantic origin. A large portion of the Mn delivered by the Arctic rivers is removed in the shelf seas and does not pass into the central basins. Most likely a benthic flux is at the origin of the elevated concentrations of Mn near the sediments in the Barents and Kara Seas. These elevated concentrations of Mn apparently affected the deep basins as well, as maxima in the concentrations of Mn were observed that corresponded with lowered transmission over the continental slope.

The concentrations of Mn were extremely low in the deep Makarov Basin (~50 pM) and slightly higher in the Eurasian Basin (~0.1 nM) outside the influence of the hydrothermal activity. A maximum in the concentration of Mn corresponded with anomalies in light transmission, potential temperature and dissolved iron, confirming the hydrothermal origin. The hydrothermal plume was observed throughout the Nansen Basin and over the deep Gakkel Ridge around 2500 m depth and a smaller plume was observed around 3200 m. The concentration of Mn at the Mn maximum around 2500 m depth decreased exponentially according to a first order scavenging model. Calculating the residence time from this first order scavenging model suggested a counter clockwise current that flows along the Gakkel Ridge towards Greenland and Fram Strait and subsequently along the Eurasian continental slope.

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4.1. Introduction

The Arctic Ocean is one of the least studied oceans in the world due its inaccessibility and the hostile weather circumstances. From studies into the physical properties of the Arctic Ocean it has been recognised the Arctic Ocean is a significant source of North Atlantic Deep Water (Rudels et al., 2000) and therefore of interest for the global thermohaline circulation. Much less is known however, about the biogeochemical cycles and trace metal distributions. With the GEOTRACES program within the International Polar Year this is changing due to four expeditions with a GEOTRACES team onboard in the Arctic region. Here is presented a comprehensive distribution of manganese (Mn) as determined on one of these expeditions, ARK XXII/2 aboard R.V. Polarstern in 2007.

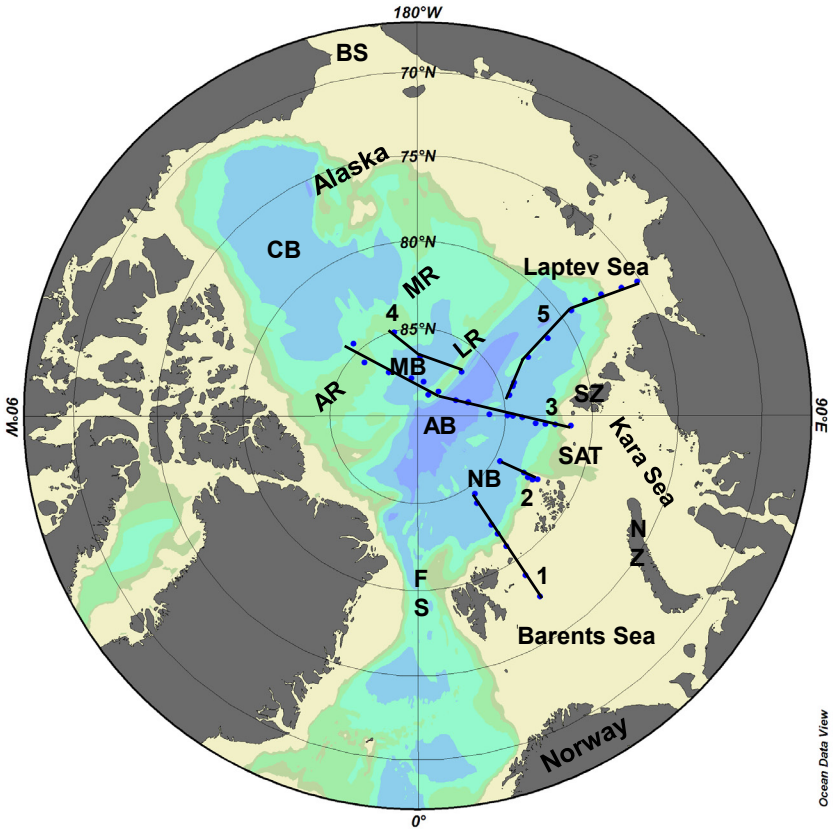

Figure 1 *Stations for trace metal sampling during ARK XXII/2. Transects are indicated by numbered lines as discussed in the same sequence in the text. Transect 1 goes from the Barents Sea into the Nansen Basin. Transect 2 also goes from the continental shelf into the Nansen Basin, just west of the St Anna Trough. Transect 3 goes from the continental shelf, east of the St Anna Trough, into the Nansen and Amundsen Basin, over the Lomonosov Ridge into the Makarov Basin and onto the Alpha Ridge. Transect 4 goes from the Mendeleyev Ridge into the Makarov Basin and extends until just in the Amundsen Basin. Transect 5 follows the deep Gakkel Ridge and extends into the Laptev Sea. AB: Amundsen Basin, AR: Alpha Ridge, BS: Bering Strait, CB: Canada Basin, FS: Fram Strait, GR: Gakkel Ridge, LR: Lomonosov Ridge, MB: Makarov Basin, MR: Mendeleyev Ridge, NB: Nansen Basin, NZ: Novaya Zemlya, SAT: St Anna Trough, SZ: Severnaya Zemlya*

Sources of dissolved Mn to the Arctic Ocean could be its extensive shelf seas, like on the Eurasian side, the Barents Sea, Kara Sea and Laptev Sea. Furthermore the outflows of the Lena, Ob and Yenisey rivers enter the Laptev Sea (Guay and Falkner, 1997). Moreover, hydrothermal activity has been observed over the Gakkel Ridge in the Arctic Ocean (Edmonds et al., 2003). Photo-reduction and atmospheric input on the other hand, might be less significant due to the sea ice cover and the relatively small atmospheric dust flux to this remote ocean. Nevertheless, in the Arctic Ocean the distribution of Mn will most likely be controlled by a combination of all these processes.

4.2 Results

Samples were taken aboard Polarstern during expedition ARK XXII/2 from 28 July until 07 October 2007 from Tromsø (Norway) to Bremerhaven. The Arctic Basin was sampled in five transects where for dissolved Mn 44 trace metal stations (of which 27 deeper than 2000 metres) were sampled with a total of 773 samples. Of the 773 samples analysed for Mn, 11 samples (1.4%) were suspected outliers and therefore not further used in the data analyses and figures here presented. Two transects covered the Makarov basin as well as the Eurasian basin, the latter consisting of the Nansen and Amundsen basins, separated by the deep Gakkel Ridge (Figure 1).

4.2.1. Hydrography

In Figure 1 the transects and stations are plotted. The hydrographical features of the Eurasian and Makarov basins have been described in detail by Anderson et al. (1994) and Rudels et al. (2000) and briefly summarised by Middag et al. (2009) (Chapter 3). Latter summary is presented in this Chapter again for the convenience of the reader.

Atlantic water is flowing into the Eurasian Arctic basins via Fram Strait and the Barents Sea along the continental slope with the counter clockwise boundary current, influencing the surface and intermediate waters. The boundary current is modified by shelf processes and near the continent a branch crosses over the Lomonosov ridge that separates the Eurasian basins from the Makarov basin while another branch flows along this ridge. The branch of the boundary current that crosses the Lomonosov ridge influences the water column of the Makarov basin. The formation of dense water on the shelves and subsequent slope convection influence the deepest parts of the water column in the Eurasian basin.

Pacific water is flowing in through the Bering Strait over the Siberian shelves and mixes with the freshwater input of the Siberian rivers, creating strong stratification in the central Arctic Ocean. The Pacific inflow influences the water column of the Makarov Basin and the influence can extend into the surface layer of the Amundsen Basin. The Surface Mixed Layer (SML) is shallow, typically extending to 25 metres depth in the central Arctic Ocean. Below the SML there is an upper halocline in the Makarov Basin that sometimes extends into the Amundsen Basin. The upper halocline is marked by a nutrient maximum and is of Pacific origin. In the Nansen and Amundsen Basins the lower halocline is more profound, marked by a minimum in nitrate and nitrite. Below the haloclines, the Atlantic Layer Water (ALW) is found, generally extending to about 600 m depth. The warmer and more saline ALW does not cross over the Lomonosov Ridge into the Makarov Basin due to a strong front in temperature and salinity over the Lomonosov Ridge. However, following the boundary current the Atlantic water flows into the Canadian Basin via the shelf edge. Mixing of this ALW with shelf water results in a relatively colder less saline ALW in the Canadian Basin compared to the Eurasian Basin. Below about 800 metres the Makarov Basin becomes warmer and more saline than water at a similar depth in the Eurasian Basin. This difference remains the case throughout the intermediate depth and deep basin waters.

In the deep basins below the ALW several water masses have been distinguished such as the Intermediate Depth Water (IDW) which is a mixture of overlying ALW and underlying Eurasian Basin Deep Water. Finally below the latter Eurasian Basin Deep Water one may find Eurasian Basin Bottom Water.

In the following paragraphs the water masses are briefly described per transect based on the more detailed description in Middag et al. (2009) (Chapter 3).

4.2.2. Transect 1 and 2

Transect 1 (Figure 1) consisted of seven vertical profiles and transect 2 of five profiles. Over the continental shelf (Barents Sea) five profiles were sampled, four profiles were sampled over the continentals slope and three in the deep Nansen Basin. The Barents Sea profiles had a depth of around 200 m and in the Nansen basin the depth increased to over 4000 m.

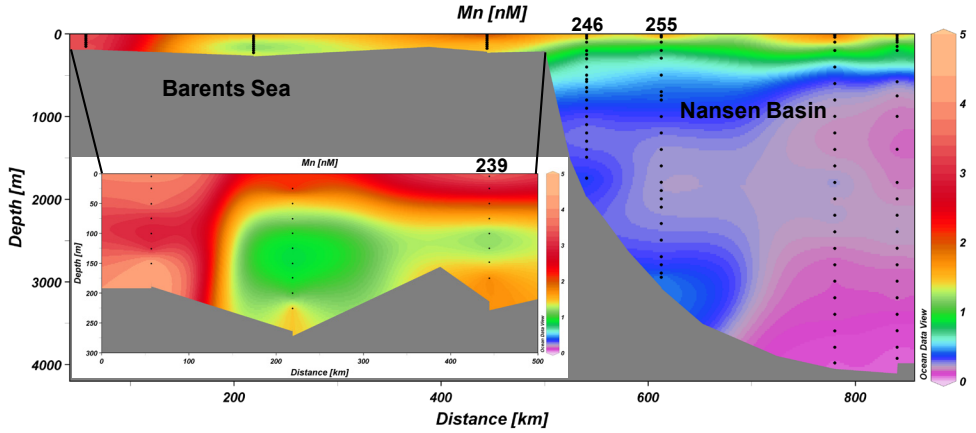

Figure 2a *Concentrations of dissolved Mn (nM) over the entire water column in transect 1. The concentrations of Mn in the Barents Sea are shown in the inset at the bottom left. From this figure three suspected outliers were omitted. Station numbers indicated are used in Figure 3 and 4.*

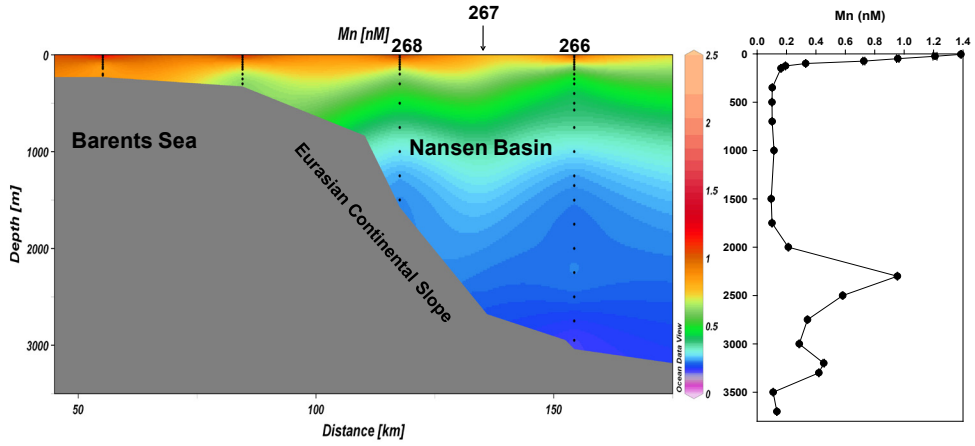

Figure 2b *Concentrations of dissolved Mn (nM) over the entire water column in transect 2. The concentrations of Mn in the deepest part of the Nansen Basin (not shown in colour plot) are shown as a vertical profile versus depth the inset at the bottom left to avoid excessive interpolation. From the colour plot two suspected outliers were omitted. Station numbers indicated are used in Figure 4, station 267 indicates the position of the regular hydrocast.*

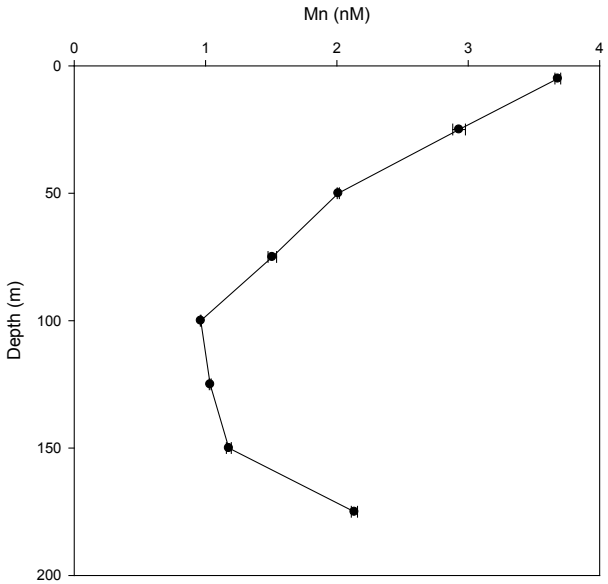

Figure 3 *Dissolved Mn (nM) as a vertical profile versus depth in the Barents Sea (of transect ,1 station 239, see Figure 2a)*

In these transects, as well as in the following transects, several water layers were encountered as described in more detail by Middag et al. (2009) (Chapter 3). In the Barents Sea and in the Nansen basin a relatively cold and fresh surface layer was found, which extended to about 75 m depth. Below this layer an Atlantic influenced warmer and more saline bottom layer existed in the Barents Sea. In the Nansen basin the Atlantic and Intermediate Depth Water (AIDW) generally extended until about 2000 m depth, and comprises the ALW with its characteristic potential temperature maximum and extending to about 600 m depth which is underlain by the Intermediate Depth Water over the 600 to 2000 m depth range. Within the Intermediate Depth Water the potential temperature decreased with increasing depth. Deeper than about 2000 m depth, in the Deep Eurasian Basin Water (DEBW), the potential temperature remained relatively constant while the salinity increased.

The concentrations of dissolved Mn for the entire water column are shown in Figure 2 (a and b). In the Barents Sea the concentrations were highest furthest away from the Nansen basin. Towards the Nansen basin the values decreased both in the surface and bottom layer. In the top of the surface layer concentrations of Mn were up to 4 nM in the Barents Sea and as low as around 2 nM in surface layer of the deep Nansen basin. In the Barents Sea concentrations of Mn decreased sharply in the surface layer to a mid depth minimum, followed by an increase towards the sediment (Figure 3). Over the continental slope into the Nansen basin the concentrations of Mn decreased even more sharply from the maximum concentrations in the uppermost surface layer to around 0.35 nM around 200 meter over the continental slope. However, concentrations of Mn started to increase again just deeper than 400 m to a maximum between 500 and 750 m depth at all slope stations. This maximum was most profound at the stations closest to the continental shelf with a maximum value of over 0.6 nM Mn and coincided with lower light transmission, indicating the higher concentrations of Mn were associated with particles (Figure 4). These particles are most likely derived from the continental shelf. Deeper than this Mn maximum over the continental slope, concentrations of Mn were relatively stable around 0.2 nM before they increased towards the sediments.

In the deep Nansen basin, north of the continental slope (not shown in the colour plot to avoid excessive interpolation), concentrations of Mn decreased to approximately 0.25 nM around 200 m (Figure 2b). Below this depth concentrations of Mn decreased with increasing depth towards concentrations of just above 0.1 nM before a Mn maximum (up to 0.95 nM) was observed around 2300 m depth due to hydrothermal input (see text section 4.3.4). Deeper than this maximum the concentrations of Mn decreased to concentrations as low as 0.1 nM at the deep basin stations. Further down the water column concentrations of Mn increased to a second, less profound maximum around 3300 m (up to 0.45 nM). In the deepest part of the water column the concentrations of Mn decreased to values of approximately 60 pM at the greatest sampled depths (almost 4000 m).

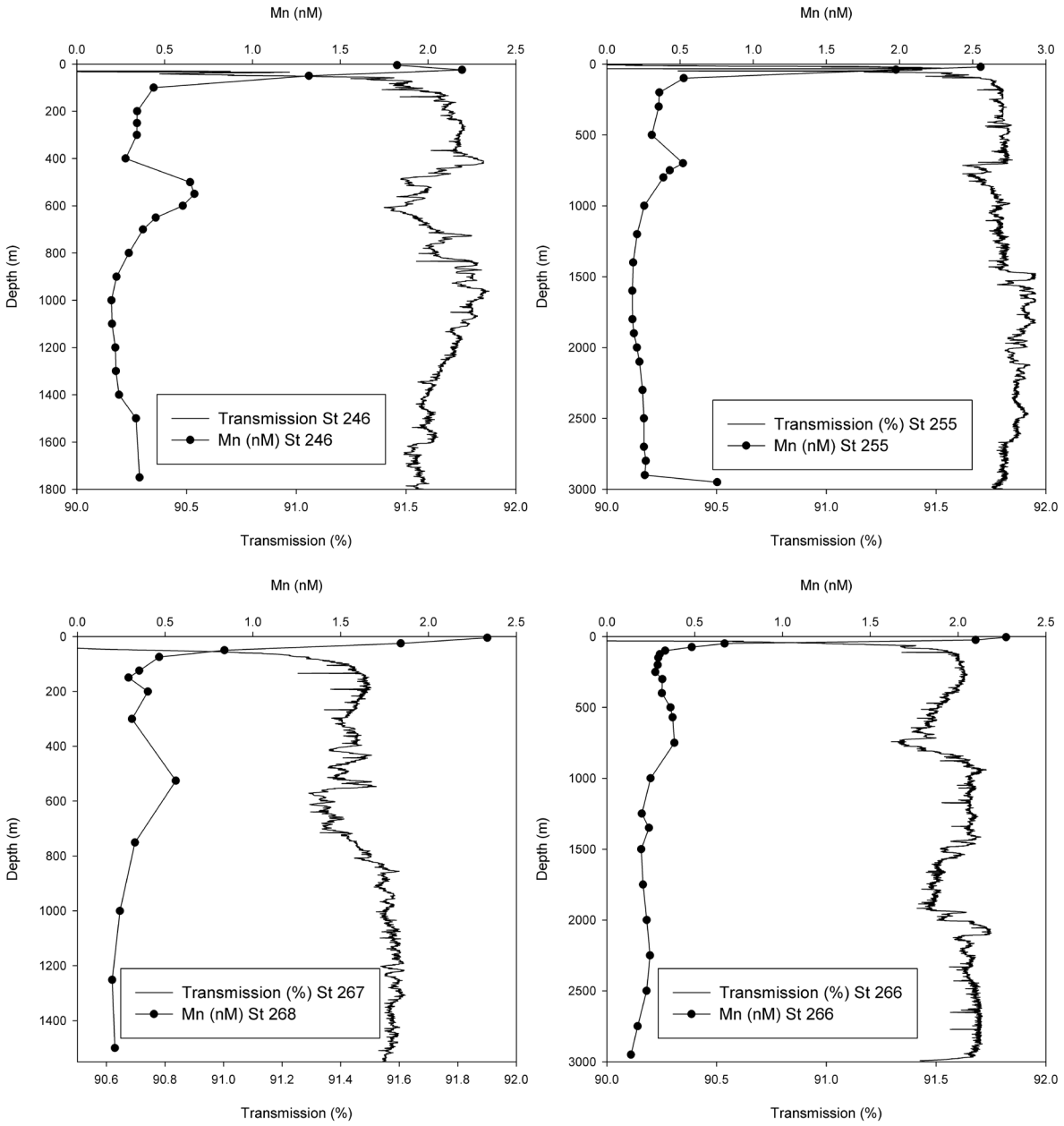

Figure 4 *Dissolved Mn (nM) and transmission (%) as a vertical profile versus depth over the continental slope of transect 1 (upper panels, stations 246 and 255) and 2 (lower panels, stations 267/268 and 266). Left panels show the profiles closest to the shelf, right panels show the profiles closest to the deep Nansen Basin. From the upper and lower left panel (stations 246 and 268) one suspected outlier was omitted. Transmission profile from the lower left panel (transect 2, station 267) is from the regular hydrocast about 9 miles to the north as no concurrent regular hydrocast was done at the trace metal station. Positions of the station numbers are also indicated in Figure 2. Note the different scales between the different panels.*

4.2.3. Transect 3

Transect 3 (Figure 1) is the longest transect with in total 17 stations, crossing the Eurasian and Makarov basin and extending onto the Makarov Ridge (Figure 5). In the Eurasian basin the relatively cold and fresh surface layer extended until about 50 m depth over the shelf and to about 100 m in the Nansen and Amundsen basins. The Atlantic layer underneath the surface layer was relatively warm close to the Eurasian shelf and cools further into the basins away from the shelf (Middag et al., 2009; Chapter 3). In the Makarov basin near the Lomonosov Ridge the surface layer extended to similar depths as in the Eurasian basin, but to about 150 m towards the Alpha Ridge. Furthermore, the surface layer in the Makarov basin was relatively fresh compared to the surface layer in the Eurasian basin due to the Pacific influence in the Makarov surface layer. The Atlantic layer in the Makarov basin was colder compared to the Eurasian basin while the intermediate and deep waters were warmer (see section 4.2.1.).

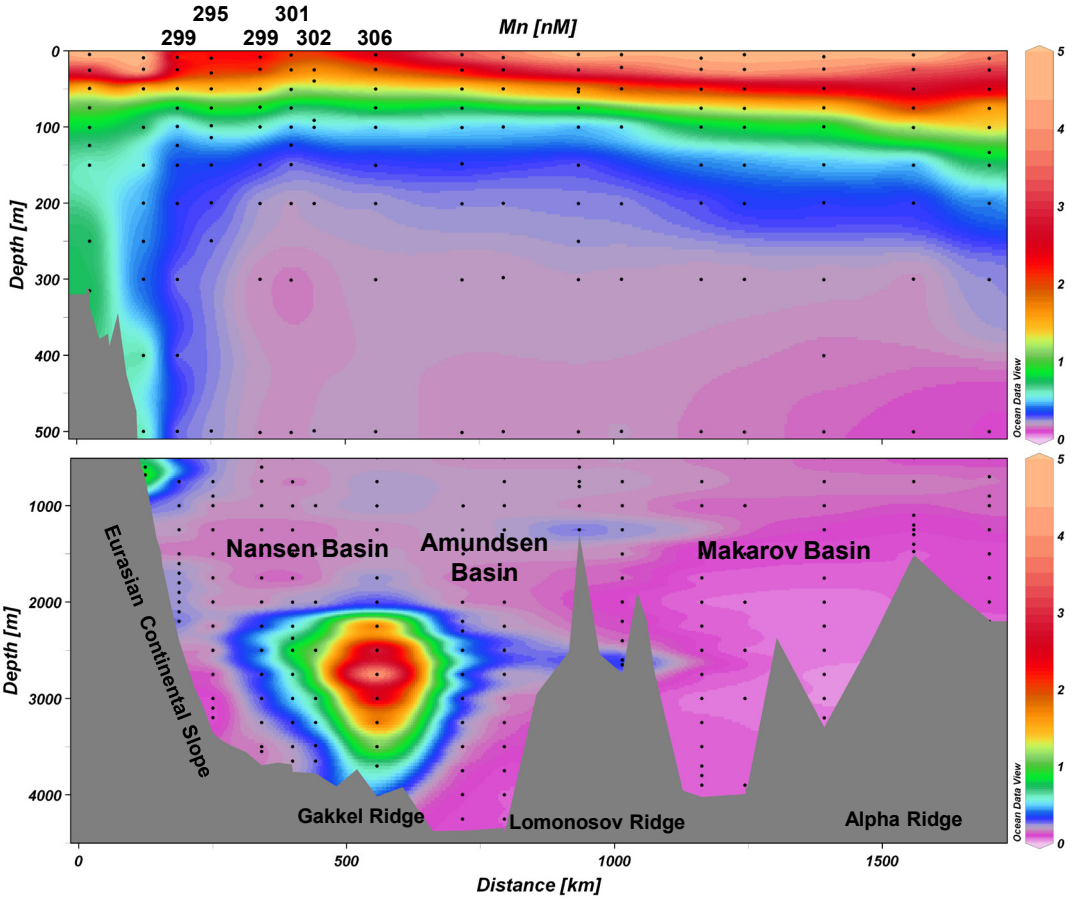

Figure 5 *Concentrations of dissolved Mn (nM) in the upper 500 m of the water column (upper panel) and over the entire water column (lower panel) in transect 3. Two suspected outliers were omitted from this figure. Station numbers indicated are used in Figure 6 and 7.*

The concentrations of Mn in the top of the surface layer were as high as 5 nM around the edge of the continental shelf close to Severnaya Zemlya. Into the Eurasian basin the concentrations of Mn in the top of the surface layer decreased to concentrations of around 2 nM. In the region where the Gakkel Ridge lies in the deep, the surface concentrations started to increase again to higher values. Maximum concentrations of around 5 nM were observed in the top of the surface layer in the middle of the Makarov basin. However, past the middle (geographic) of the Makarov basin,

onto the Alpha Ridge and towards the Canada Basin, the concentrations of Mn started to decrease again to values of around 3.5 nM. The higher concentrations of Mn in the surface layer coincided with lower salinity values indicating a fresh water source for the increased concentrations of Mn (see text section 4.2.6.).

Within the surface layer the concentrations of Mn decreased sharply with depth as seen in the previous transects. Also here, a Mn maximum was observed over the continental slope, located around 1000 m depth at the deeper station halfway the slope. The concentration of Mn at this station was less than 0.2 nM at 500 m depth before increasing to 0.25 nM at 1000 m depth. Unfortunately there was no transmission meter on the trace metal sampling system at the time and a comparison with transmission can only be made when a concurrent regular hydrocast was done which was not the case at this station. However, the Mn maximum coincided with lower transmission, taken from observations at the regular hydrocast about 8 miles to the south (Figure 6), whereas 8 miles further north no transmission minimum was observed anymore. The station over the shallow part of the slope was only 680 m deep and at this station a mid depth minimum of about 0.4 nm at 300 m depth was observed, followed by an increase towards the sediment to a concentration of around 1 nM.

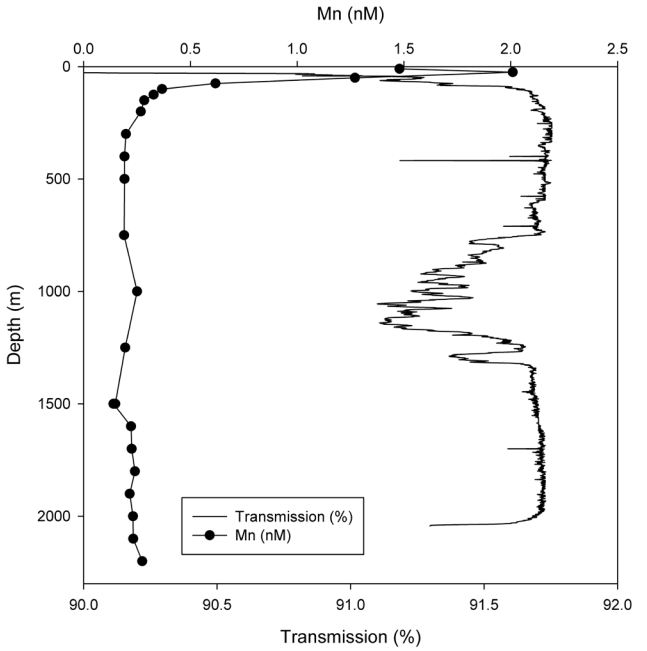

Figure 6 *Dissolved Mn (nM) and transmission (%) as a vertical profile versus depth over the continental slope of transect 3 (station 291, see Figure 5). Transmission profile is from the regular hydrocast about 8 miles to the south as no concurrent regular hydrocast was done at the trace metal station.*

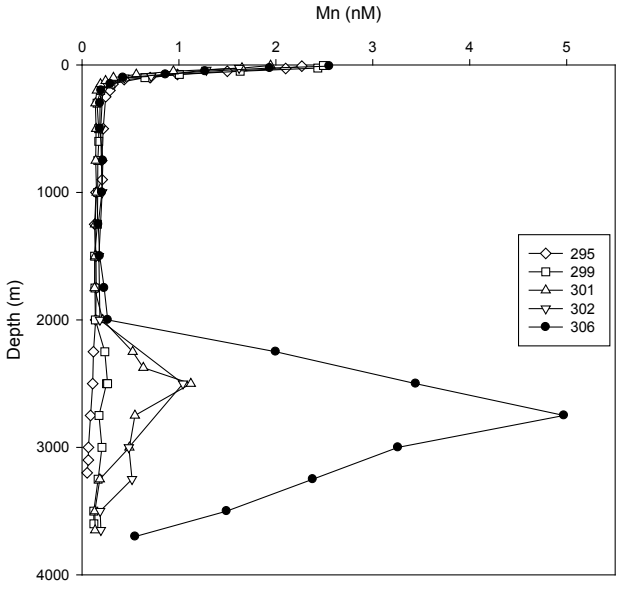

Figure 7 *Dissolved Mn (nM) as a vertical profile versus depth for 5 profiles from south to north in the deep Nansen basin of transect 3. Positions of the station numbers are also indicated in Figure 5.*

In the deep basins the concentrations of Mn below the surface layer decreased to values of around 0.2 nM at 200 m depth while onto the Alpha Ridge concentrations of Mn reached this value around 300 m depth. In the deep basins concentrations of Mn decreased with depth to values below 0.1 nM in the Amundsen basin and to even lower values in the Makarov basin (around 50 pM). Contrary, in the Nansen basin there was a very clear maximum around 2500 m over the entire basin (Figure 7), except for the station at the transition between the continental slope and the deep basin.

At latter station there was a very small maximum somewhat shallower around 2000 m depth. The highest Mn maximum of almost 5 nM was observed at the station over the Gakkel Ridge and the maximum concentrations of Mn around 2500 m depth decreased through the Nansen basin towards the Eurasian continental slope (Figure 7). This decrease of the Mn maximum around 2500 m depth was exponentially with distance from the station over the Gakkel Ridge. This was also the case when plotting the Mn maxima observed in transect 1 and 2 (see text section 4.2.2.) versus distance from the station over the Gakkel Ridge in this transect 3 (Figure 8).

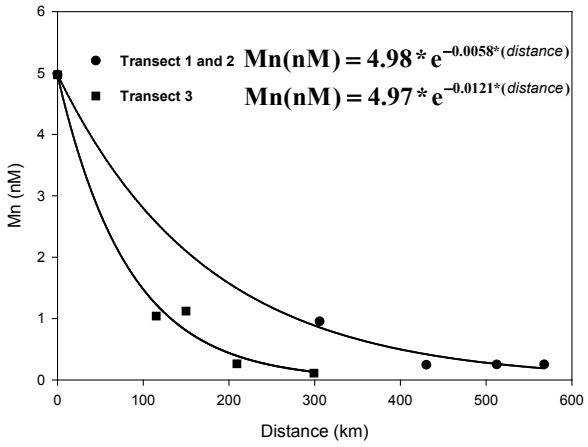

Figure 8 *Concentrations of Mn (nM) at ~2500 m depth (Mn maximum) versus distance (km) from station 306 over the Gakkel Ridge (see Figure 5) for transect 1 and 3 (circles) and transect 3 (squares). Exponential equations are shown in the figure.*

At the station over the Gakkel Ridge also the transmission decreased (Figure 9a) and the potential temperature was elevated (Figure 9b) around 2500 m depth. Moreover, the dissolved Fe concentrations were elevated over the same depth range as Mn (Klunder, in prep).

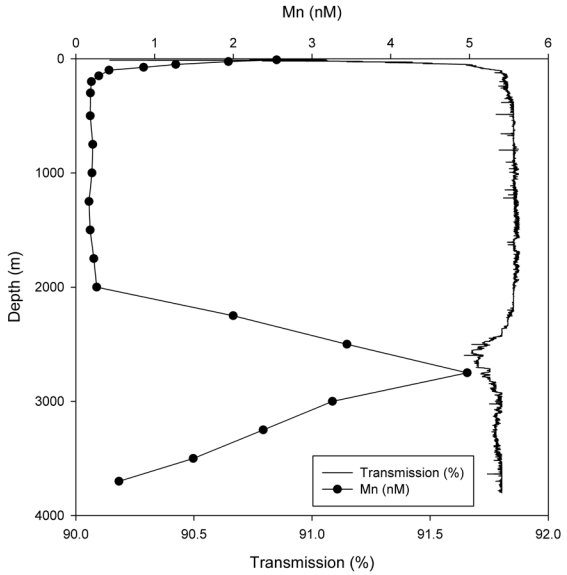

Figure 9a *Dissolved Mn (nM) and transmission (%) as a vertical profile versus depth at the station over the Gakkel Ridge (station 306, see Figure 5).*

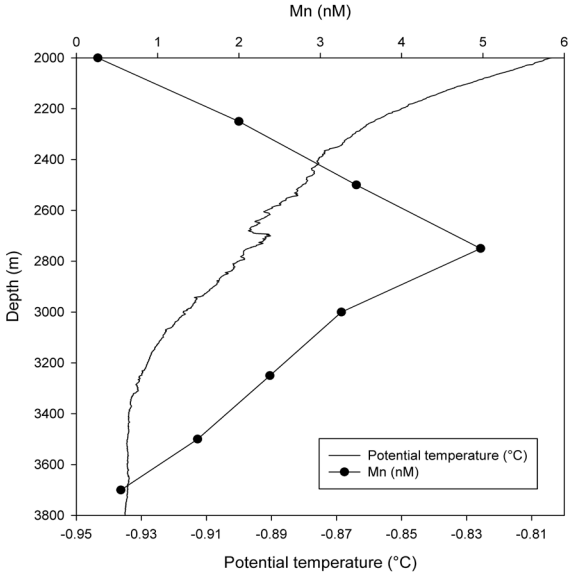

Figure 9b *Dissolved Mn (nM) and potential temperature (°C) as a vertical profile versus depth at the station over the Gakkel Ridge (station 306, see Figure 5).*

4.2.4. Transect 4

The fourth transect consisted of three profiles for Mn. One profile was sampled on the Mendeleev Ridge, one in the Makarov basin and one in the Amundsen basin. The concentration of Mn in the top of the surface layer was with a value of over 5 nM highest in the Makarov basin as was also observed in transect 3 (see text section 4.2.3.) (Figure 10). However, below the surface layer at about 200 m depth the concentration of Mn was near 0.3 nM at all three stations. Deeper than

latter depth the two profiles on the Mendeleev Ridge and in the Makarov basin were very similar and concentrations of Mn were lower than in the Amundsen basin. The concentrations of Mn over the Mendeleev ridge decreased with depth to values below 90 pM, but showed a small increase to just over 0.1 nM at 1950 m depth close to the sediment. In the deeper Makarov basin the concentrations continued to decrease below latter depth to a minimum of about 50 pM at 2750 m. Further down the water column at about 3250 m depth concentrations of Mn increased to values of around 70 pM again and stayed at that level until the greatest sampled depth of 3900 m near the sediment. Below the surface layer in the Amundsen Basin the concentrations of Mn gradually decreased with depth until values of around 0.1 nM at 3000m depth. Below latter depth concentrations of Mn remained around 0.1 nM until an increase to 0.3 nM at the greatest sampled depth of 3850 near the sediments.

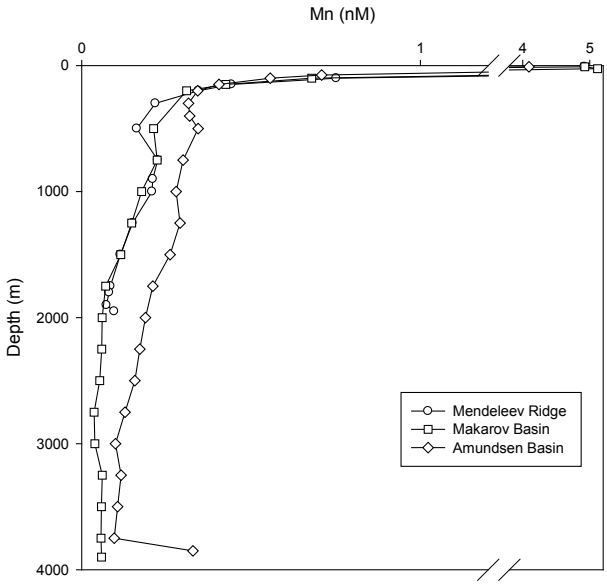

Figure 10 *Dissolved Mn (nM) as a vertical profile versus depth for the three stations of transect 4 over the Mendeleev Ridge (circles), in the Makarov Basin (squares) and in the Amundsen Basin (diamonds).*

4.2.5. Transect 5

The final transect (transect 5, Figure 1) was sampled over the Gakkel onto the continental slope and into the shallow Laptev Sea (Figure 11). The Gakkel ridge that separates the Nansen and Amundsen Basin is quite deep with depths between 4000 and 5200 m. The depth of 5200 m was observed in a deep trench just before the onset of the continental slope. The water masses were very similar to what was observed in the previous transects in the Nansen and Amundsen basins. The cold and relatively fresh surface layer extended to around 100 m in the deep parts of the basin and over the continental slope. The top of the surface layer was the most saline furthest away from the continental shelf and became fresher in the Laptev Sea. In the Laptev Sea the water also became warmer, with the upper parts of this shallow water column (55 – 35 m) being the warmest and least saline (S=29.1). The Atlantic layer was warmest over the continental slope and was colder further away from the slope as was seen in transect 3 (see text section 4.2.3.).

The concentrations of Mn in the top of the surface layer increased from 2 nM furthest away from the shelf to almost 6 nM halfway the continental slope. At the shallowest station over the continental shelf the concentrations decreased to 5 nM before they increased to values over 20 nM (and outside the range of the method used) in the Laptev Sea. The decrease in Mn at the shallowest station over the continental shelf near the edge of the continental shelf corresponded with lower observed values for potential temperature and dissolved Aluminium (Middag et al., 2009; Chapter 3). Within the surface layer over the entire transect the concentrations of Mn decreased steeply with depth as seen in the previous transects. Below the surface layer, the concentrations of Mn were below 0.3 nM at about 200 m depth over the deep Gakkel Ridge and the two deep (deeper than 1500 m) stations over the continental slope. At the two deep stations over the continental slope a Mn maximum of about 0.4 nM was visible around 900 m depth.

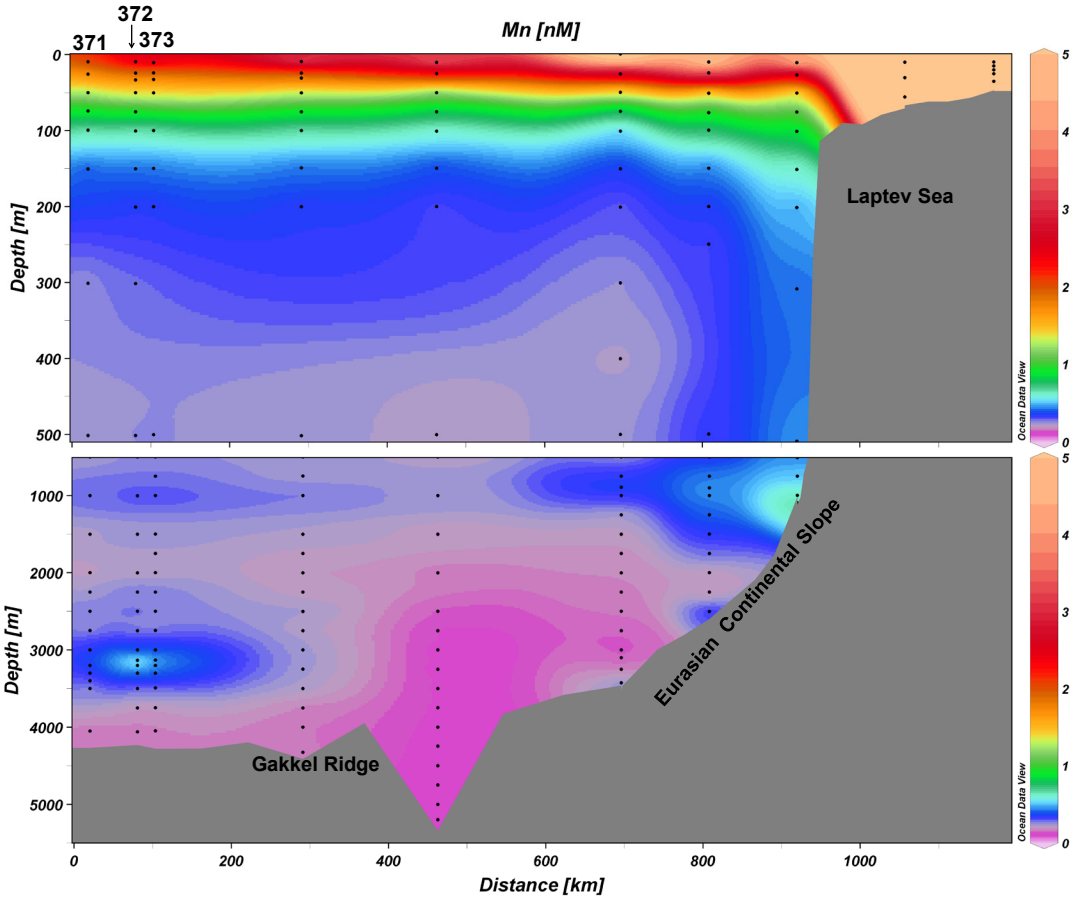

Figure 11 *Concentrations of dissolved Mn (nM) in the upper 500 m of the water column (upper panel) and over the entire water column (lower panel) in transect 5. Concentrations at the shallowest station in the Laptev Sea were out of range of the analytical method. Station numbers indicated are used in Figure 12.*

The Mn maximum at the deepest station coincided with a small transmission minimum as observed over the continental slope in the previous transects. At the other deep slope station halfway the continental slope, however, the Mn maximum did not correspond exactly with the transmission minimum which was observed just below the Mn maximum. Deeper than the Mn maximum the concentrations of Mn decreased to around 0.1 nM again. At the greatest sampled depth close to the sediment, the concentrations of Mn increased to around 0.3 nM and this coincided with a decrease of transmission. At the shallowest station over the continental slope, just before the shelf edge, concentrations of Mn decreased to 0.4 nM at 300 m depth. Below latter depth the concentrations of Mn increased towards the sediment to a value of 0.7 nM at the greatest sampled depth of 1100 m.

Over the deep Gakkel Ridge the three stations furthest away from the continental slope had station numbers 371, 372 and 373 (Figure 11), going into the direction of the slope. At these stations two separate Mn maxima were observed (Figure 12a and 12b) at 2500 m and between 3000 and 3300 m depth, respectively. The middle station of the three (372) had the highest maxima concentrations with values of over 0.3 nM and 1.2 nM at 2500 and 3130 m depth, respectively. Deeper than the observed maxima, the concentrations of Mn at the three stations matched closely as they decreased to values of around 0.15 nM until the greatest sampled depth close to the sediment. The deepest, most profound, Mn maximum coincided with a transmission

minimum (Figure 12a). The transmission minimum was, like the Mn maximum, most profound at the middle station (372). Moreover, the Mn maximum coincided with a potential temperature maximum (Figure 12b) at the middle station (372).

At the station just before the deep trench the Mn maxima around 2500 m and between 3000 and 3300 were still visible in the profile, but they were not very profound. Over the deep trench the Mn maxima were not distinguishable and concentrations were around 0.1 in the deep trench.

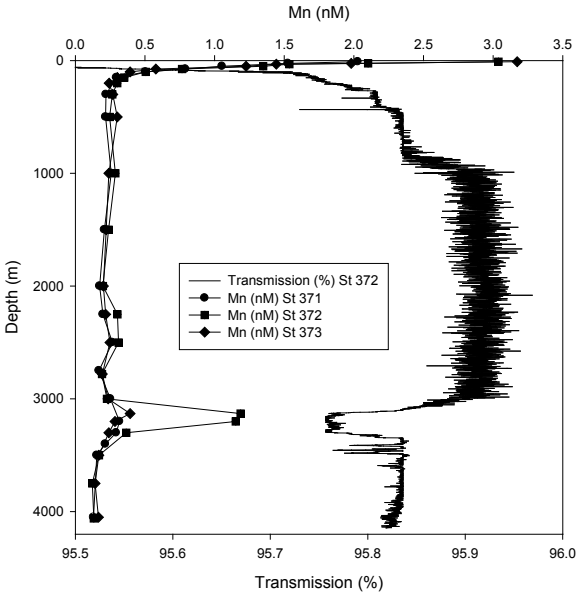

Figure 12a *Dissolved Mn (nM) and transmission (%) as vertical profiles versus depth. Three profiles are shown for Mn over the deep Gakkel Ridge at transect 5 (Figure 11) and one profile for the transmission.*

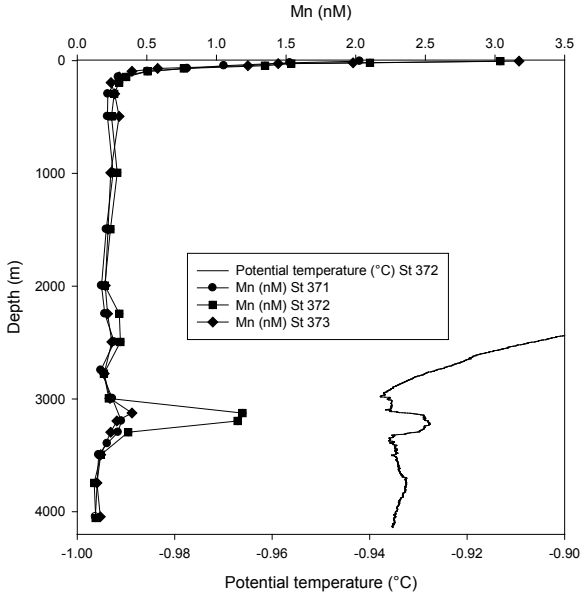

Figure 12b *Dissolved Mn (nM) and potential temperature (°C) as vertical profiles versus depth. Three profiles are shown for Mn over the deep Gakkel Ridge at transect 5 (Figure 11) and one profile for the potential temperature.*

4.2.6. Surface Layer

The highest concentrations of over 5 nM Mn were observed in the top of the surface layer and the concentrations decreased steeply to subnanomolar levels within this surface layer. The relatively cold and fresh surface layer was defined as the upper part of the water column with a potential temperature < 0°C and a salinity < 34.6. Within the surface layer of transect 3, there was quite some variability in the concentrations of Mn observed (see text section 4.2.3.). Within the deep basins of transect 3, the highest surface layer concentrations of Mn were observed in the Makarov basin and the concentrations of Mn decreased onto the Alpha and Lomonosov Ridge. A similar trend was observed for the salinity, which shows in the good negative correlation between Mn and salinity in the surface layer of transect 3 (Figure 13). The high concentrations of Mn correlate with relatively low salinity. This low salinity can be an indication of river input, ice melt or Pacific inflow, which all have relatively low salinity compared to the Atlantic water that flows in via Fram Strait (see text section 4.2.1.). The quasi conservative water mass tracer PO_4^* (Broecker et al., 1985; 1998) that compensates for organic respiration can be used to partly distinguish between the different sources of low salinity water to the surface layer as shown by Ekwurzel et al., (2001). River input and sea ice melt both have a relatively low PO_4^* of ~0.1 and 0.4 $\mu M \cdot kg^{-1}$, respectively, Atlantic water has an intermediate PO_4^* value of ~0.7 $\mu M \cdot kg^{-1}$ and Pacific water has a high PO_4^* -value of ~2.4 $\mu M \cdot kg^{-1}$ (Ekwurzel et al., 2001, their table 1). When plotting Mn versus PO_4^* for the entire surface layer of transect 3, no relation is apparent at first glance.

However, at closer inspection when plotting Mn versus PO_4^* per basin, relations do appear. When plotting only the Eurasian basin of transect 3, a negative correlation appears (Figure 14a). Even though this correlation is quite weak, it is significant ($[PO_4^*][\mu M \cdot kg^{-1}]=-8.4[Mn][nM \cdot kg^{-1}]+5.8$ with $R^2=0.4$ and $P<0.001$). All PO_4^* values are below 0.7 $\mu M \cdot kg^{-1}$, indicating this water is a mixture of Atlantic water and fresh water input from either sea ice or rivers. The negative correlation indicates higher concentrations of Mn are related to this fresh water input.

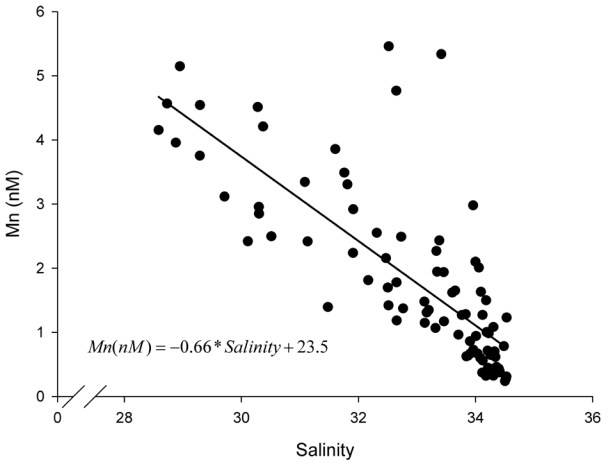

Figure 13 *Dissolved Mn (nM) versus salinity in the surface layer of transect 3. Linear regression is shown in the graph, $R^2=0.62$; n=87 and $P<0.001$.*

For the Makarov basin, however, no general correlation is apparent for the surface layer. Instead, two different correlations appear, both with a negative slope but with different y-axis intercepts (Figure 14b). The correlation with the highest intercept is found in the upper 25 m of the Makarov Basin. Almost all (20 out of 22) PO_4^* values in this correlation are above 0.7 $\mu M \cdot kg^{-1}$. This indicates the water is a mixture of Pacific water and fresh water input from either sea ice or rivers.

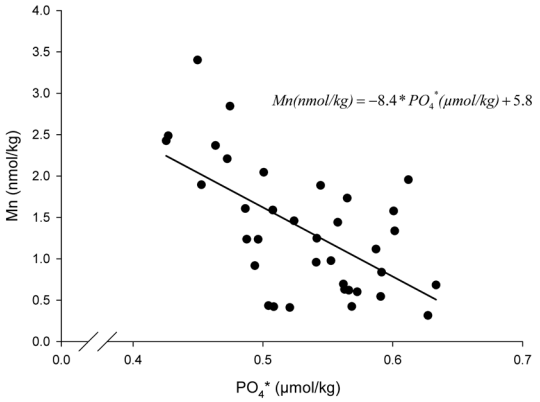

Figure 14a *Dissolved Mn (nmol/kg) versus PO_4^*(µmol/kg) in the surface layer of the Eurasian Basin of transect 3. Linear regression is shown in the graph, $R^2=0.37$; n=36 and $P<0.001$.*

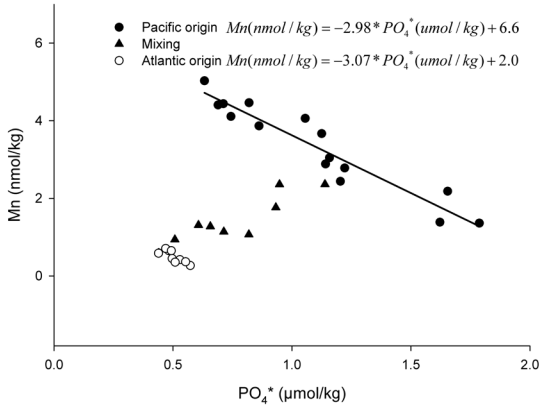

Figure 14b *Dissolved Mn (nmol/kg) versus PO_4^*(µmol/kg) in the surface layer of the Makarov Basin of transect 3. Linear regressions are shown in the graph, Pacific origin $R^2=0.91$; n=15 and $P<0.001$; Atlantic origin $R^2=0.67$; n=9 and $P<0.008$.*

The correlation with the lower intercept (Figure 14b) is found in the deepest part of the surface layer, below about 100 m depth. The highest PO_4^* value in this correlation is 0.57 $\mu M \cdot kg^{-1}$, indicating this water is a mixture of Atlantic water and fresh water input from either sea ice or rivers. The remaining data points in between the two correlations are from depths sampled in between the upper surface layer of Pacific origin and lower surface layer of Atlantic origin. These data points reflect most likely the results of mixing between the water of Atlantic origin with the water of Pacific origin, both affected by fresh water input.

Transect five (see text section 4.2.5.) went from the deep basin into the Laptev Sea. The Lena River drains into the Laptev Sea, delivering fresh water and Mn to the Arctic Ocean. When plotting the dissolved Mn versus salinity in the surface layer, a good correlation appears in the deep basin region when excluding the upper surface (25 m) of the three stations over the continental slope (Figure 15). The concentrations of Mn in the upper surface layer over the slope and in the Laptev Sea are much higher and do not fit the correlation observed over the deep basin.

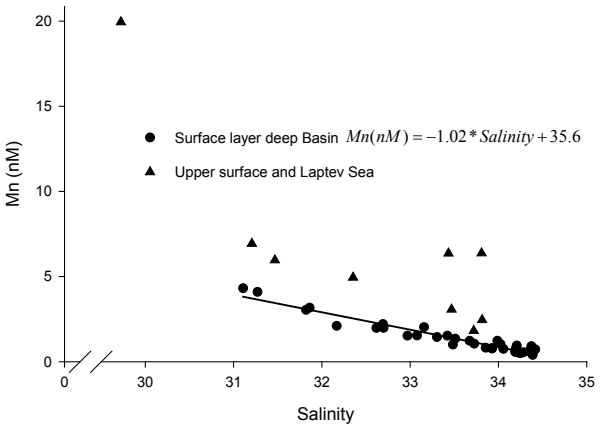

Figure 15 *Dissolved Mn (nM) versus salinity in the surface layer over the deep basin (circles) and the upper surface (25 m) of the three stations over the continental slope (triangles) of transect 5. Linear regression is shown in the graph, R^2=0.94; n=36 and P<0.001.*

4.3 Discussion

4.3.1. Comparison with previously reported Mn in the Arctic Ocean

The here presented transects for dissolved Mn constitute a comprehensive dataset of Mn in the Arctic Ocean. This dataset comprises 773 new values of dissolved Mn over full water column profiles of the deep basins and shelf seas. Previously limited data has been available about the distributions of dissolved Mn in the Arctic Ocean. To the best of our knowledge the only data published on dissolved Mn (0.4 µm filtered in this case) in the central Arctic Ocean is from Yeats (1988). Like the profiles of Mn here reported, the profile reported by Yeats (1988) also shows elevated concentrations of Mn in the surface. This station extended to about 1350 m depth and the lowest concentration of about 0.25 nM was found in the Atlantic Layer. Latter concentration of 0.25 nM in the Atlantic Layer is only slightly higher than the concentrations here reported. The higher concentrations of Mn (around 0.6 nM) in the deeper parts of the water column reported by Yeats (1988) could be the result of the relatively shallow water column depth. The other profile of Mn reported by Yeats (1988) close to Fram Strait was for unfiltered samples and extended to about 2500 m depth. This profile for unfiltered Mn also shows a maximum of Mn at the surface, but the general concentrations are much higher.

Slightly more data on dissolved Mn is available for the Eastern Arctic Ocean near Greenland and the Canadian Archipelago by Campbell and Yeats (1982) and Yeats and Westerlund (1991) (both 0.4 µm filtered). In the Central Baffin Bay near Greenland (Campbell and Yeats, 1982) concentrations of Mn decreased from a surface maximum of about 5.3 nM to 1.6 nM at the greatest sampled depth of 2300 m. This profile shape, a surface maximum and lower concentrations in the deep, is similar to the shape of the vertical profiles of Mn here presented. However, the concentrations of Mn in this enclosed bay appeared to be much higher. The concentrations of Mn in the shelf sea at the edge of the Canada Basin at 81°43.4'N, 93°25.0'W (Yeats and Westerlund, 1991) were considerably lower. A maximum of Mn of 1.58 nM was observed at the shallowest depth of 60 m, followed by a steep decrease to 0.24 nM at 150 m depth and concentrations of 0.51 and 0.26 nM at the greatest sampled depths of 270 and 280 m, respectively. Latter general profile shape and concentrations are comparable to the here reported

data for shallow stations in the shelf seas with the exception of the relatively low concentration of Mn near the sediments in the previous work.

4.3.2. Mn in the Shelf Seas

The here presented concentrations of Mn in the Arctic Ocean were highest in the shelf seas and surface layers of the deep basins. The vertical profiles in the Barents and Kara shelf Seas were characterised by a mid depth minimum and higher concentrations at both the surface and near the sediments (see text sections 4.2.2., and 4.2.3.). The higher concentrations of Mn in the deeper parts of the water column of the Barents and Kara Seas are most likely due to a benthic flux. This benthic flux of Mn by resuspension of the sediment and direct fluxes from the pore water have been described for continental shelves elsewhere (e.g. Heggie et al., 1987; Laës et al., 2007; Slomp et al., 1997; Statham et al., 1998). Moreover, the data here presented shows increasing Mn concentrations below the mid depth minimum in the Barents and Kara Seas, clearly indicating a benthic source. In the Laptev Sea however, high concentrations of Mn were found (see text section 4.2.5.), but no clear increasing trend towards the sediments was observed. These high concentrations of Mn in the Laptev Sea were most likely the result of fluvial input (see text below). The apparent benthic flux of Mn from the sediments was only observed in the Barents and Kara Seas, but its influence also appears to affect the deep basins. At all transects crossing the continental slope, a maximum of Mn was observed that corresponded with lowered transmission (see Figures 4 and 6). This indicates Mn and particles from the shelf seas are transported towards the deep basins. Both the minima of transmission and maxima of Mn fade away with increasing distance from the shelf and are no longer distinguishable as pronounced minima and maxima in the deep basin beyond the continental slope. Even so, the deep concentrations of Mn were higher in the Eurasian Basin compared to the Makarov basin. Whether this is due to the observed hydrothermal input at the Gakkel Ridge (see text section 4.3.4.) or due to input from the shelf seas can not be distinguished based on this data. However, the concentrations of dissolved aluminium and barium were also elevated in the deep Eurasian Basin and it has been argued this was caused by input from the shelf seas via deep slope convection (Middag et al., 2009; Chapter 3). Based on these observations, input from the shelf seas into the deep basins most likely affects the deep distribution of dissolved Mn but this effect can not be further quantified based on the available data presented here.

4.3.3. Mn in the Surface layer

The elevated concentrations of Mn in the surface layer were observed in all transects (see text section 4.2.). The surface layer distribution of transect 3 (see text section 4.2.3.) is most interesting since this transect covers all deep basins and is influenced by both Pacific and Atlantic water and by fluvial input (Ekwurzel et al., 2001). In the surface layer the concentrations of Mn correlated inversely with salinity (Figures 13 and 15) as was also observed by Yeats and Westerlund (1991) and concentrations of Mn correlated with PO_4^* (Figure 14a and 14b). The negative correlation between Mn and salinity indicates a fresh water source for the elevated concentrations of Mn in the surface layer. This fresh water source can be fluvial input, sea ice melt or mixing with relatively fresh Pacific water (Ekwurzel et al., 2001). The concentrations of PO_4^* and the correlations between Mn and PO_4^* combined give insight in the contributions of the different sources (see text section 4.2.6.). The surface layer in the Eurasian basin appears to be mainly Atlantic water with fresh water input from rivers and/or sea ice and the higher concentrations of Mn correspond with the fresh water input (Figure 13 and 14a). In the Makarov Basin two correlations were observed between Mn and PO_4^*, one in the upper surface layer and one in the deepest part of the surface layer, below about 100 m depth (see text section 4.2.6. and

Figure 14b). This shows the upper surface layer of the Makarov basin is mainly Pacific water with river and/or sea ice melt input, whereas the deepest part below 100 m depth is again mainly Atlantic water river and/or sea ice melt input. The surface layer water between the layer of Atlantic origin and the layer of Pacific origin appears to be a mixture of the two layers. No distinction can be made between fresh water input from rivers and from sea ice melt in both the surface layer of the Eurasian and Makarov Basin based on the presented parameters.

The influence of Atlantic, Pacific and fresh water from rivers and sea ice on the surface layer in the Arctic Ocean have already been assessed in previous reports based on conservative tracers (e.g. Anderson et al. 1994; Ekwurzel et al., 2001; Rudels et al., 2000). These assessments give very useful information about the volumes of water from the different sources. However, when considering the importance of these sources for non-conservative constituents like dissolved Mn, the biogeochemical cycling and initial concentrations of Mn should be taken into account. This shows in transect five (see text section 4.2.5. and section 4.2.6.) that extended from the deep basin into the Laptev Sea. When considering the salinities in the upper surface layer and in the Laptev Sea, the concentrations of Mn were higher than would be expected based on the Mn-salinity relation observed in the basin (Figure 15). Therefore, extrapolating the Mn-salinity relations observed in the surface layer of the deep basins to zero salinity (24 and 36 nM Mn) underestimates the Mn delivered to the Arctic Ocean by the Lena River that drains into the Laptev Sea. This is confirmed by Hölemann et al. (2005) who reported concentrations of dissolved Mn between 82 and 1471 nM and concentrations of particulate Mn between 11.6 and 26.4 μmol/g suspended particulate matter. The large range in concentrations of dissolved Mn and fraction Mn in suspended particulate matter is related to variations in the discharge of the river (Hölemann et al., 2005). For the Lena River plume with salinity < 10 in the Laptev Sea in the same time of the year as the data here presented was collected (September), an average concentration of Mn of 111 ± 70 nM has been reported (Hölemann et al., 2005). Latter concentration is also considerably higher than would be expected based on extrapolation of the Mn-salinity relation observed in surface layer of the deep basins. This indicates removal of dissolved Mn in the estuary.

However, besides river discharge also melting of sea ice can be a source of fresh water and elevated concentrations of Mn. There is little data on Mn in (sea) ice in the literature. Townsend and Edwards (1998) found up to 0.55 nM (unfiltered) Mn in Antarctic snow, but these low concentrations are most likely not representative for the Arctic Ocean that is in greater proximity to continental sources. In coastal sea ice in the Ross Sea (Antarctica) concentrations of dissolved Mn between 0.84 and 10.5 nM Mn were observed. Besides dissolved Mn, also particulate Mn was reported with concentrations ranging between 0.13 and 23.2 nM that potentially can dissolve when the sea ice melts (Grotti et al., 2005). Campbell and Yeats (1982) reported trace metal data for Arctic sea ice from the Eastern Arctic Ocean of 17.3 nM dissolved Mn and 26.8 nM particulate Mn. Apparently there can be a wide range of concentrations of Mn in sea ice and the concentrations appear to be higher in the Arctic Ocean. However, the concentrations of Mn in sea ice are much lower than those observed in the Lena River and its discharge and the surface layer concentrations of dissolved Al indicate little input of ice melt (Middag et al; 2009; Chapter 3). Nevertheless, when extrapolating the Mn-salinity relation to zero, the concentrations of Mn of 24 and 36 nM Mn (see text above) are higher than the reported concentrations of Mn in sea ice. The work of Ekwurzel et al. (2001) shows that in the central Eurasian Basin (their Figure 7), the fraction of the surface layer water that constitutes river run off is twice the fraction that constitutes sea ice. This implies that the extrapolation to zero salinity of the Mn-salinity relation observed in surface layer of the deep basins, should render a concentration of Mn of 2/3 the river

Mn concentration and 1/3 sea ice Mn concentration. When taking the lower limit of the Lena River water concentration of Mn of 82 (Hölemann et al., 2005) and the sea ice concentration of Mn of 17.3 (Campbell and Yeats, 1982), the resulting concentration of Mn at zero salinity is about 60 nM. Latter concentration of Mn is about twice the extrapolation values of 24 nM and 36 nM of the Mn-salinity relations observed in the surface layer of the Eurasian basin in transect 3 and 5, respectively. Even when assuming none of the Mn released from melting sea ice would remain in solution in the surface layer, the resulting concentration of 55 nM Mn exceeds the extrapolation concentration of Mn for zero salinity (24 and 36 nM Mn) by almost a factor of 2. This confirms that a considerable fraction of the dissolved Mn delivered towards the Arctic Ocean by river discharge is lost in the estuary and shelf sea. Most likely this is caused by precipitation and scavenging (Salomons and Föstner, 1984; Nolting et al., 1999 and references therein;) Moreover, also for the Mn released by the melting sea ice, precipitation and subsequent loss from the surface layer can not be discounted.

4.3.4. Mn in the deep Deep Basins

The concentrations of Mn in the deep basins are low with concentrations decreasing below 0.1 nM in the Eurasian Basin and even lower to about 50 pM in the Makarov Basin (see text section 4.2.3.). Below the initial steep gradient from relatively high to subnanomolar concentrations in the upper 200 to 300 m the concentrations of Mn are relatively uniform in the remainder of the water column (Figure 10). Concentrations of Mn did tend to decrease slightly with depth from the concentrations observed below the surface layer to the lowest concentrations in the deepest layers. Within the deep basins, usually no increase towards the sediments was observed, indicating no sedimentary flux in the deep basins.

However, this distribution of slightly decreasing concentrations of Mn with depth below the surface layer was not observed near the continental slope due to input of Mn from the shelf seas (see text section 4.3.2.). Moreover, within the deep Eurasian Basin near the Gakkel Ridge elevated concentrations of Mn were observed that coincided with maxima of Fe and potential temperature and a transmission minimum, indicating hydrothermal input (see text sections 4.2.3. and 4.2.5.). Hydrothermal input is a known source of dissolved Mn for the deep ocean (Klinkhammer et al., 1977; Klinkhammer and Bender 1980; Klinkhammer et al., 2001), but there are not many in situ studies on the extent of this hydrothermal influence on the distribution of Mn in the deep ocean.

The Gakkel Ridge is an ultraslow-spreading ridge, but has numerous known sites of hydrothermal activity (Edmonds et al., 2003). Edmonds et al. (2003) located nine primary vent sites along the Gakkel Ridge, of which the most easterly at 85°39’N, 84°50’E was located closest to the observed hydrothermal plume in transects 3 (see text section 4.3.3.). To locate the vent site, Edmonds et al. (2003) used Miniature Autonomous Plume Recorders that recorded temperature and light scattering. The latter is, like the light transmission here reported, indicative of suspended particles. Besides the physical parameters light scattering and temperature anomalies, also some samples were taken for total dissolvable Mn by Edmonds et al. (2003). The depth and the depth range (Between 2000 and 3000 m) at which the plume detected at 85°39’N, 84°50’E based on the light scattering and Mn by Edmonds et al. (2003, their figure 4) was remarkably similar to what was observed for the most profound plume of Mn at 85°55’N, 91°07’E (Figure 9a) presented here. The vertical profiles of total dissolvable Mn had a higher background concentration (~0.1-1 nM) and exceeded 10 nM in the plume compared to the background concentrations and the maximum value of 5 nM dissolved Mn here reported. The higher background concentrations of Mn confirm the remark of Edmonds et al. (2003) that some portion

of the total dissolvable Mn signal could result from leaching of Mn oxide coatings off suspended particles. At the station on top of the Gakkel Ridge with the highest Mn elevation observed in transect 3, also higher concentrations of dissolved Fe and anomalies of potential temperature and transmission were observed (see text section 4.2.3. and Figure 9). This confirms the hydrothermal source of the elevated concentrations of Mn that could be traced throughout the Eurasian basin around the 2500 m depth level.

In transect 5 also maxima of Mn were observed over the deep Gakkel Ridge. The least profound maximum was located around 2500 m and therefore most likely originated from the hydrothermal vent site passed in transect 3 (See text above and text section 4.2.3.). The second, more profound maximum was located between 3000 and 3300 m depth and corresponded with a transmission anomaly, as well as a potential temperature anomaly (see figure 12a and 12b). Unfortunately this particular region was not visited with the Miniature Autonomous Plume Recorders reported by Edmonds et al. (2003). However, the depth range at which the Mn maximum and transmission anomaly here reported were observed, is consist with the depth range for which an additional hydrothermal plume was observed at the closest and several other locations sampled by Edmonds et al. (2003). Furthermore, a maximum of dissolved Mn was observed throughout the Eurasian basin in the 3000-3300 m depth range.

The maxima of Mn of hydrothermal origin that were observed in the entire Eurasian Basin could be related to the enclosed nature of this ocean basin. But at the very least, this shows that the influence of hydrothermal vent activity on the distribution of Mn in the deep Arctic Ocean is more significant than hitherto realised and can indeed extend to distances of over 500 km, as the model of Weiss (1977) predicted. The extend of the hydrothermal effect on the distribution of Mn in other deep ocean basins remains to be studied in more detail but appears to be much greater than expected thus far.

When plotting the maxima of Mn around 2500 m in the Eurasian basin versus the distance from the station in transect 3 on the Gakkel Ridge with the highest concentration of Mn observed (Figure 8), an exponential decrease with distance is observed. When assuming only turbulent mixing is responsible for the dispersion of the Mn plume, i.e. the water mass itself is stagnant, the horizontal plume dispersion from its origin is given by the following equation:

$C_x = C_o * e^{-Ax}$ (Weiss, 1977) (eq. 1)

Where C_x is the concentration of Mn at a distance x, C_o is the concentration of Mn on the Gakkel Ridge with the highest concentration of Mn observed (x=0) and

$A = (\psi / K_H)^{1/2}$

Where ψ is the first order scavenging rate constant and K_H is the horizontal eddy diffusivity which is assumed to be $5*10^6$ cm^2/s (Weiss, 1977).
The residence time τ can be calculated by

$\tau = 1/\psi$

When calculating τ from the exponential relations observed by plotting the maximum of Mn versus the distance gives 2 and 0.4 years for transects 1 and 2 combined and transect 3, respectively. These residence times are much shorter than the 51 years found by Weiss (1977), therefore the assumption that eddy diffusion is the only process of influence for the plume expansion is not correct. This suggests that also deep water circulation has to be taken into account. The shorter residence time derived from transect 3 compared to the one derived from transect 1 and 2 together shows the direction of the deep water circulation is more towards

transect 1 and 2 than along transect 3. However, the short residence time derived from transect 1 and 2 together indicates the circulation pattern is no direct route from the plumes origin towards the Eurasian shelf site of the basin, but actually takes a longer route, leading to the underestimation of the residence time. For transect 3 the actual route must be even longer to lead to the greater underestimation of the residence time. These observations are consistent with a counter clockwise current that flows along the Gakkel Ridge towards Greenland and Fram Strait and subsequently along the Eurasian continental slope as is as suggested by Jones et al. (1995). Besides the deep basin circulation it must also be considered that there are multiple active hydrothermal vent sites (Edmonds et al., 2003). This further complicates the process which can therefore not be described solely by a simple turbulent mixing and scavenging model. However, the observed distribution of Mn around 2500 m at various distances from the Gakkel Ridge in a specific direction can be described with an exponential equation without accounting for currents or multiple sources. This suggests that scavenging removal of Mn plays a major role.

4.4 Conclusions

This comprehensive study of dissolved Mn in the Arctic Ocean shows elevated concentrations in the surface layer with concentrations up to 6 nM. Highest concentrations of Mn were observed in the shelf seas, notably the Laptev Sea with concentrations over 20 nM. In the deep basin the concentrations of Mn decreased steeply from the surface values to very low background concentrations of just below 0.1 nM in the Eurasian Basin and even lower at about 50 pM in the Makarov Basin. The general profile shape is consistent with the three previous studies about dissolved Mn done in the Artic Ocean, although the absolute concentrations of the previous studies appear to be slightly higher.

The elevated concentrations of Mn in the surface layer have a fresh water source and show a negative relation with salinity. Both fluvial input and sea ice melt have to be taken into account as fresh water and Mn source, but fluvial input appears to be the most important in both volume and concentration of Mn. By extrapolating the Mn-salinity relation observed in the surface layer of the deep basin it is confirmed a large portion of the Mn delivered by the Arctic rivers is removed in the shelf seas and does not pass into the central basins.

In the shelf seas a mid depth minimum was observed, indicating a benthic source. From the shelf seas Mn is exported along the continental slope into the deep basin and this process results in higher concentrations of Mn and lower light transmission along the slope. The effect of this Mn input from the slope faded out with distance into the basin and was not observed beyond the continental slope.

In the deep basins the lowest concentrations of Mn were observed. The concentrations of Mn tended to decrease slightly with depth below the initial decrease in the first 200 to 300 m, but were overall quite uniform within the deep basins. The higher concentrations in the Eurasian Basin might be related to the observed input from the shelf seas, but also hydrothermal input plays a role. Distinct hydrothermal activity and Mn input was observed over the deep Gakkel Ridge. The hydrothermal plume of dissolved Mn could be seen in a clear Mn maximum around 2500 m depth throughout the Eurasian Basin and a smaller plume was observed around 3200 m. The Mn concentration at the 2500 m maximum decreased exponentially with distance from the Gakkel Ridge which is consistent with a first order scavenging model (eq.1). However, using the first order scavenging model to calculate the residence time suggests also the deep basin circulation has to be considered to explain the hydrothermal Mn plume dispersion.

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