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Fluxes of dissolved aluminum and manganese to the Weddell Sea and indications for manganese co-limitation

Rob Middag, a,b,1,* Hein J. W. de Baar, a,c Maarten B. Klunder, a and Patrick Laan a

a Royal Netherlands Institute for Sea Research (Royal NIOZ), Den Burg, Texel, The Netherlands
b Department of Ocean Sciences & Institute of Marine Sciences, University of California at Santa Cruz, Santa Cruz, California
c Department of Ocean Ecosystems, University of Groningen, Groningen, The Netherlands

Abstract
The trace metals aluminum (Al) and manganese (Mn) were studied in the Weddell Sea in March 2008. Concentrations of dissolved Al ([Al]) were slightly elevated (0.23–0.35 nmol L⁻¹) in the surface layer compared to the subsurface minimum (0.07–0.21 nmol L⁻¹) observed in the winter water. Atmospheric deposition is the main source of Al to the central Weddell Sea (22 μmol m⁻² yr⁻¹), and the residence time of dissolved Al in the upper mixed layer is ~ 0.8 yr. The flux from the shelf and slope regions equals about 50% of the atmospheric input of Al to the western Weddell Sea. The highest [Al] in the Weddell Sea bottom water (WSBW) is related to the formation of deep water, and the associated downward flux is in the range of 3–10 μmol Al m⁻² yr⁻¹. The concentrations of dissolved Mn ([Mn]) were depleted in the surface layer, likely as a result of biological uptake, as indicated by the correlation among Mn, major nutrients, and fluorescence. The significant negative relation between the ΔMn:AP ratio and the ambient concentration of dissolved iron indicates iron-Mn co-limitation. The flux of Mn from the continental margin is about 2.2 times greater than atmospheric input (1.1 μmol m⁻² yr⁻¹). The flux of both Al and Mn from the continental margin indicates melting of continental ice (icebergs) or direct continental runoff. The slightly elevated [Mn] in the WSBW is due to a relatively small flux of 1 μmol Mn m⁻² yr⁻¹ associated with WSBW formation.

The oceanic distribution of dissolved trace metals is determined by the sources, sinks, and internal cycling of these elements. Dissolved aluminum (Al) occurs in a wide concentration range (< 0.1–174 nmol L⁻¹) in the world oceans (Orians and Bruland 1986; Hydes et al. 1988; Measures et al. 2005), with much higher concentrations in the Atlantic Ocean compared to the Pacific Ocean. This offset between ocean basins is caused by the relatively short deep ocean residence time of 50–200 yr (Orians and Bruland 1986), compared to the 1000 yr timescale of deep ocean circulation. In surface waters, Al has an even shorter residence time, on the order of 4 weeks to 4 yr (Orians and Bruland 1986), as a result of removal of the particle-reactive Al from the water column (Hydes 1979; Gehlen et al. 2002). The main source of Al to the surface of the open ocean is atmospheric deposition, and the concentration of dissolved Al ([Al]) in the surface layer can be related to the atmospheric input (Measures et al. 2005; Han et al. 2008). The sediments of the continental margins act as a sink of Al when undisturbed, but sediments can also be an Al source when the sediments are resuspended (Mackin and Aller 1984; Moran and Moore 1991). Additional Al input into the deep ocean has been suggested to occur via diffusion from the sediments (Hydes 1977), pressure-dependent solubility of Al-containing particles (Moore and Millward 1984), and shelf water input via deep slope convection (Measures and Edmond 1992; Middag et al. 2009, 2011b). This deep slope convection source combined with atmospheric input, melting of continental ice with entrained particles, and input from sediments of the continental margins are the most likely sources of Al in the Weddell Sea.

Dissolved manganese (Mn) occurs in a much smaller concentration range in the open ocean, with surface concentrations ranging between 0.1 and 25 nmol L⁻¹, and there are generally low and quite uniform concentrations in the deep ocean (Landing and Bruland 1980; Statham et al. 1998). The typically elevated concentrations of dissolved Mn ([Mn]) in the surface layer in most ocean regions are mainly the result of photoreduction of Mn oxides (Sunda et al. 1983), but they can also be due to atmospheric input (Landing and Bruland 1980; Baker et al. 2006). In addition to atmospheric input, other potential input sources of Mn to the Weddell Sea are reductive dissolution from sediments (anoxic or suboxic) (Pakhomova et al. 2007) or melting of continental ice with entrained particles. However, in the Southern Ocean the surface [Mn] is known to be very low (Martin et al. 1990; Westerlund and Öhman 1991), most likely as a result of very limited input in combination with active removal by the Antarctic algal community (Sedwick et al. 1997; Middag et al. 2011a).

Several iron (Fe) fertilization experiments in bottles (De Baar and Boyd 2000) and in situ (De Baar et al. 2005) have shown that Fe and light are key limiting factors for phytoplankton growth in the Southern Ocean. Dissolved Mn has also been suggested (Martin et al. 1990) to be potentially (co-)limiting. This has been shown in laboratory experiments (Peers and Price 2004) and to some extent in bottle incubations in the field (Buma et al. 1991; Coale 1991). However, the latter shipboard bottle incubations in the Southern Ocean are ambiguous since a positive

* Corresponding author: rmiddag@chemistry.otago.ac.nz
1 Present address: University of Otago, Dunedin, New Zealand
response to Mn addition is not always observed (Buma et al. 1991; Scharek et al. 1997; Sedwick et al. 2000), which indicates that in some parts of the Southern Ocean the ambient [Mn] is in adequate supply (i.e., not limiting). Mn is needed for various biological processes in cells, most notably in the Photosystem II (PS II) for the splitting of water by photoautotrophs to supply electrons to the reaction center of PS II (Sunda et al. 1983; Raven 1990). It has been shown that Mn is also essential in the superoxide dismutase (SOD) enzymes of marine diatoms (Peers and Price 2004; Wolfe-Simon et al. 2006), especially under Fe-deficient circumstances. Under Fe-deficient conditions, the efficiency of PS II decreases (Greene et al. 1992; McKay et al. 1997) and in addition, more reactive oxygen species (ROS) are formed, such as superoxide and hydroxyl radicals. The ROS indeed are highly reactive and therefore destructive for the cell, especially because the ROS cannot diffuse across cell membranes and must be destroyed by SOD at the site of production. The depletion of Mn in constant proportion to the depletion of phosphate, which has been observed in the surface waters of the Southern Ocean (Middag et al. 2011a), confirms that Mn is indeed an essential element. In combination with the effects of Fe and light limitation, Mn might have the potential to control production in the high-nutrient, low-chlorophyll regions of the Southern Ocean (Middag et al. 2011a). To trace biological Mn uptake and subsequent export, a traditional tracer of particle export, such as the disequilibrium between thorium-234 and uranium-238 ($^{234}$Th:$^{238}$U), can be used (Middag et al. 2011a).

The Weddell Sea is one of the most remote and inaccessible ocean regions in the world because of its ice cover and harsh climate. Therefore, the distribution of dissolved trace metals like Al and Mn in the Weddell Sea has thus far not been extensively studied. Here data from 11 stations are reported with high vertical resolution along a transect in the Weddell Sea in late austral summer that permits a more detailed assessment of the distributions of Al and Mn. This study aims to provide a comprehensive overview of the distribution as well as the cycling of Al and Mn in the Weddell Sea.

Methods

Samples were taken aboard R/V Polarstern during expedition ANT XXIV/3 (10 February 2008–16 April 2008) from Cape Town, South Africa, to Punta Arenas, Chile. Along a transect crossing the Weddell Sea from the main Antarctic continent toward the Antarctic Peninsula, eight full-depth and three upper–water column trace metal (TM) stations were sampled in March 2008 for trace metals and nutrients (Fig. 1). At the TM stations, seawater was collected using 24 internally Teflon-coated, 12 liter Go-Flo samplers (General Oceanics) mounted on an all-titanium frame (Titan) connected to a Kevlar wire and controlled from onboard. The 11 deployments of the Titan all-titanium conductivity–temperature–depth (CTD) sampling system resulted in a total of 188 samples that were analyzed for both Al and Mn. The complete relational database is presently available from corresponding author; it includes specific flags for suspect and rejected outlier values (for definition, see Middag et al. [2011a,b]) and will eventually be available at the international Geotraces datacenter (http://www.bodc.ac.uk/geotraces/). Regular CTD rosette hydrocasts were done in addition to the special trace metal hydrocasts. These regular hydrocasts were done at separate stations and as additional hydrocasts at most TM stations, as not all samples needed for other analysis could be taken from the all-titanium trace metal sampling system. The salinity (conductivity), temperature, and depth (pressure) were measured with two different CTDs of same type (Seabird SBE 911+): one from the Netherlands Institute for Sea Research (NIOZ), mounted on the all-titanium trace metal sampling system for TM hydrocasts, and one from the Alfred Wegener Institute (AWI) on the regular CTD rosette used for regular hydrocasts. Both had been calibrated before
Dissolved Al and Mn in the Weddell Sea

and after the expedition by the company (Seabird). Moreover, the conductivity sensors were calibrated during the cruise against salinity samples measured onboard.

Samples for Al and Mn analysis were collected from the Go-Flo bottles in a class 100 clean room environment. The water was filtered directly from the Go-Flo sampler through a 0.2 µm filter capsule (Sartocon-300, Sartorius) under nitrogen pressure (0.15 MPa). Therefore, all trace metal data reported in this article are categorized as “dissolved.” The low-density polyethylene bottles (LDPE, Nalgene) used for the storage of reagents and samples were cleaned according to an intensive three step cleaning procedure, as described in Middag et al. (2009). Filtered seawater samples were taken in cleaned LDPE sample bottles (125 mL) from each Go-Flo sampler. All sample bottles were rinsed five times with the sample seawater prior to being filled. Samples for Mn were acidified with 12 mol L\(^{-1}\) ultraclean HCl (Baseline \(^{\text{®}}\) Hydrochloric Acid, Seastar Chemicals) to 0.024 mol L\(^{-1}\) HCl solution. Samples of the SAFe intercalibration program were analyzed. The resulting [Mn] for both S (0.73 nmol L\(^{-1}\); \(n = 1\)) and D2 from 1000 m (0.32 ± 0.01 nmol L\(^{-1}\); \(n = 37\)) agree with the majority of the labs contributing to the consensus value (Middag et al. 2011a).

The samples for inorganic major nutrients nitrate (NO\(_3\)), nitrite (NO\(_2\)), phosphate (PO\(_4\)), and silicate (Si(OH)\(_4\)), herein to be referred to as Si, were stored in a refrigerator and analyzed usually within 10 h and always within 16 h on a Technicon TrAAcs 800 autoanalyzer. The reproducibility of an internal laboratory standard mixture of Si, PO\(_4\), and NO\(_3\) was measured daily and typically within 0.7% of its average value (Middag et al. 2011a).

Hydrography

The Weddell Sea is an important region for the formation of dense Antarctic bottom water (Fahrbach et al. 2004) and therefore plays a vital role in the global thermohaline circulation. There is the subpolar, cyclonic, Weddell Gyre that circulates in the Weddell Sea basin (Fig. 1). The water in the Weddell Sea can be classified in four main water masses based on their potential temperature (\(\theta\)) and salinity, as described by, among others, Fahrbach et al. (2004) and Klatt et al. (2005) and as briefly summarized here (Fig. 2). The relatively fresh (salinity < 34.6) Antarctic surface water (AASW) constitutes the upper water layer. The winter water (WW) is the even colder water layer that creates a temperature minimum around ~ 100 m depth. The WW is a remnant of the surface water during the past winter that kept its low temperature while the overlying water was warmed throughout the summer. Water in the Weddell Sea is largely replenished by the Antarctic circumpolar current, mainly by lower circumpolar deep water. This lower circumpolar deep water is referred to as warm deep water (WDW; \(\theta > 0.0 \, ^\circ\text{C}, \text{salinity} > 34.6; \sim 200–1500 \text{ m depth}\) after it separates from the Antarctic circumpolar current and enters the Weddell Gyre at intermediate depths. Underlying the WDW is the Weddell Sea deep water (WSDW), which is more saline and has a lower potential temperature (\(-0.7 \, ^\circ\text{C} < \theta < 0.0 \, ^\circ\text{C}; \sim 1500–4000 \text{ m depth}\)). The WSDW is believed to be formed by mixing between WDW and the underlying Weddell Sea Bottom Water (WSBW), but there is also evidence that WSDW is formed directly from surface waters and modified WDW (Klatt et al. 2005). Over the shelves, close to the Antarctic continent, the AASW gains density during sea ice formation by cooling and brine rejection and sinks along the continental slope to form the coldest (\(\theta < -0.7 \, ^\circ\text{C}\)) WSBW lying at the bottom. The WSBW and WSDW are a source of Antarctic bottom water that is observed in the deep Atlantic Ocean.
Results

**Dissolved aluminum**—In AASW, [Al] was generally low (< 0.5 nmol L⁻¹) (Fig. 3), and with increasing depth [Al] decreased to a subsurface minimum around the temperature minimum of the WW (Fig. 4). Deeper than this subsurface minimum, [Al] increased into the WDW and remained relatively constant in the upper parts of the WSDW (0.35–0.45 nmol L⁻¹). From about 2500–3000 m downwards [Al] started to increase to the highest values of up to 1.5 nmol L⁻¹ in the WSBW (Figs. 3, 4). The lowest [Al] was observed in the AASW at the five stations in the central Weddell Sea, with an average of 0.29 nmol L⁻¹ and 0.13 nmol L⁻¹ in the upper 25 m and at the subsurface minimum, respectively (Table 1). Over the continental slope of the Antarctic Peninsula, higher [Al] was observed in the upper 25 m and at the subsurface minimum, with an average [Al] of 0.36 nmol L⁻¹ and 0.19 nmol L⁻¹, respectively (Table 1). Higher concentrations in the upper 25 m throughout the Weddell Sea, compared to the subsurface minimum, indicate a surface source. Moreover, [Al] was negatively correlated with salinity in the upper 25 m (Fig. 5), indicating that [Al] is related to freshwater input, which most likely comprises melting sea ice that accumulated atmospheric dust. The highest [Al] was observed in WSBW (1.1–1.6 nmol L⁻¹), but concentrations were also elevated near the sediments over the continental shelf and continental slope (Fig. 3). Near the sediments of the shallow shelf sea (∼ 400 m), [Al] was close to 0.5 nmol L⁻¹, and near bottom concentrations increased downward along the slope from 0.81 nmol L⁻¹ at 2450 m depth to 0.94 nmol L⁻¹ at a depth of 4000 m. Only in the deep basin was the highest [Al] observed in the WSBW (above 1 nmol L⁻¹). The low [Al] in AASW, which is the initial source of WSBW, as well as increasing [Al] with increasing depth over the slope show that [Al] increases during the descent of waters originating on the shelf as they become WSBW.

**Dissolved manganese**—In AASW of the central Weddell Sea, [Mn] was low (< 0.2 nmol L⁻¹), but [Mn] was strongly elevated over the continental shelf and slope (Fig. 6). In the central Weddell Sea, [Mn] in surface waters was depleted below 0.2 nmol L⁻¹, followed by a subsurface maximum around 100 m depth (Fig. 4). This is similar to observations along the zero meridian (Middag et al. 2011a), where depleted surface concentrations and a subsurface maximum were also observed. Deeper than the subsurface maximum, [Mn] decreased to a mid-depth minimum of 0.09 nmol L⁻¹ (SD = 0.01 nmol L⁻¹; n = 7) at 1750–2000 m depth in the upper parts of the WSDW. Below this mid-depth minimum, concentrations increased slightly with increasing depth to concentrations in the range of 0.12–0.19 nmol L⁻¹ in the WSBW (Fig. 6). Over the continental slope, surface [Mn] was higher (around 0.25 nmol L⁻¹) than in the central Weddell Sea, but it still showed relative surface depletions compared to the subsurface maximum. When plotting [Mn] shallower than the subsurface maximum vs. the macronutrients, clear positive correlations are observed with PO₄
and NO₃, a moderate positive correlation with Si, and a negative correlation with fluorescence (Fig. 7). All of these correlations indicate biological uptake.

High [Mn] was observed in the shallow shelf sea (Sta. 222) near the Antarctic Peninsula (Fig. 6), with concentrations in the range of 1.3–1.5 nmol L⁻¹ between 100 and 150 m depth, just below the pycnocline. Close to the sediments (≈ 450 m depth), [Mn] was approximately 0.65 nmol L⁻¹. These concentrations are elevated with respect to similar depths in the central basin, but the highest concentrations appear to be unrelated to the local sediments, since no steep increase toward the sediments was observed. From the shelf into the deep basin (over the continental slope), [Mn] near the sediments decreased to 0.37 nmol L⁻¹ at 2450 m and 0.17 nmol L⁻¹ at 4000 m and ranged between 0.12 and 0.19 nmol L⁻¹ in the deep WSBW. Like [Al], WSBW [Mn] is relatively elevated compared to the concentrations in the overlying WSDW. However, contrary to the distribution of Al (see Results: Dissolved aluminum), [Mn] decreased seaward along the continental slope as the depth increased.

Discussion

Previously reported Al in the Weddell Sea—Observed [Al] in AASW is lower than the surface concentrations previously reported by Sañudo-Wilhelmy et al. (2002) over the continental slope in the western Weddell Sea. They report an average [Al] of 3.17 (SD = 1.33 nmol L⁻¹; n = 14) for surface waters of the Weddell Sea, with a lowest observed concentration of 1.21 nmol L⁻¹. These concentrations are an order of magnitude greater than the current concentrations reported here of 0.36 nmol L⁻¹ (see Results: Dissolved aluminum) in the same region (over the slope), with a maximum observed concentration of 0.56 nmol L⁻¹. This discrepancy may indicate large temporal variability in surface [Al], but an overestimation of the actual concentrations of Al in the Weddell Sea by Sañudo-Wilhelmy et al. (2002) cannot be excluded either. This stresses the importance of the use of standard reference water, such as the Geotraces or SAFe reference samples (www.geotraces.org/science/intercalibration), for the sake of later comparisons. The use of reference samples would not reveal any problems in sampling, but it does validate the analyses performed.

Observed [Al] in the central Weddell Sea also appears lower than the range of 1–5 nmol L⁻¹ over the entire water column reported by Moran et al. (1992). The discrepancy with the present data is most likely related to the method used by Moran et al. (1992), which is a predecessor of the method currently used and has a reported precision of ± 0.5 nmol L⁻¹ and a detection limit of 1–1.5 nmol L⁻¹.

Fig. 3. Concentrations of dissolved Al (nmol L⁻¹) over the entire water column at all 11 stations across the Weddell Sea. (A) The upper 1000 m of the water column; (B) the deeper 1000–5000 m part of the water column. Of the 188 samples analyzed for Al, 21 samples (11.2%) were suspected outliers and therefore were not further used in the figures. Abbreviations: AASW, Antarctic surface water; WDW, warm deep water; WSDW, Weddell Sea deep water; WSBW, Weddell Sea bottom water. Station numbers are indicated on the figure.
These precision and detection limit values are in the same range of the [Al] reported here (0.1–1.5 nmol L$^{-1}$), indicating that (in retro-perspective) the previous method is not as suitable for determining [Al] at the low concentrations that exist in the Weddell Sea.

Previously reported Mn in the Weddell Sea—Westerlund and Öhman (1991) have reported an extensive data set for dissolved Mn in the Weddell Sea. The shape of the vertical profiles reported was similar to the observations presented here, although the subsurface maximum and mid-depth minimum are not always obvious in the profiles of Westerlund and Öhman (1991), most likely as a result of the lower sampling resolution with depth. Their reported [Mn] for 50 m (their shallowest sampling depth) in the central Weddell Sea was approximately 0.3 nmol L$^{-1}$. This concentration is higher than the current average concentration reported here at 50 m depth: 0.2 nmol L$^{-1}$ (SD = 0.04 nmol L$^{-1}$; $n = 8$). Similarly, [Mn] at the mid-depth minimum around 2000 m depth was $\sim$ 0.2 nmol L$^{-1}$ higher than the present concentration of 0.09 nmol L$^{-1}$ (see Results: Dissolved manganese). The offset of $\sim$ 0.1 nmol L$^{-1}$ between the past data of Westerlund and Öhman (1991) and the data set presented here again stresses the importance of the use of clean sampling techniques and standard reference water, such as the Geotraces or SAFe reference samples. Nevertheless, despite the small offset between the actual concentrations, there is relatively good agreement on the distribution of [Mn].

Surface ocean fluxes of Al—Atmospheric input of Al into the Weddell Sea is affected by the accumulation of dust by sea ice (and thus Al), which is released upon melting of the sea ice. Indeed, [Al] in the upper mixed layer correlated negatively with salinity, indicating melting ice is a source of

### Table 1. Concentrations of Al and Mn in the surface waters and WSBW.

<table>
<thead>
<tr>
<th></th>
<th>[Al] (nmol L$^{-1}$)</th>
<th>SD</th>
<th>[Mn] (nmol L$^{-1}$)</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AASW Central Weddell Sea (five stations)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper 25 m</td>
<td>0.29</td>
<td>0.04</td>
<td>0.14</td>
<td>0.04</td>
</tr>
<tr>
<td>Subsurface minimum or maximum (~100 m)</td>
<td>0.13</td>
<td>0.04</td>
<td>0.23</td>
<td>0.03</td>
</tr>
<tr>
<td>Upper mixed layer (~50 m)</td>
<td>0.25</td>
<td>0.07</td>
<td>0.16</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>AASW over the continental slope and shelf (six stations)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper 25 m</td>
<td>0.36</td>
<td>0.13</td>
<td>0.61</td>
<td>0.50</td>
</tr>
<tr>
<td>Subsurface minimum or maximum (~100 m)*</td>
<td>0.19</td>
<td>0.03</td>
<td>0.25</td>
<td>0.03</td>
</tr>
<tr>
<td>Upper mixed layer (~50 m)</td>
<td>0.30</td>
<td>0.13</td>
<td>0.53</td>
<td>0.42</td>
</tr>
<tr>
<td>WSBW</td>
<td>1.37</td>
<td>0.18</td>
<td>0.19</td>
<td>0.11</td>
</tr>
</tbody>
</table>

* Only at the three full-depth stations over the continental slope could an Al minimum be determined (not enough vertical resolution on the upper water column stations). Similarly, a Mn maximum was only determined at the full-depth stations, not at the shelf station, as a result of Peninsula influence.
Al (Fig. 5). Melting icebergs derived from the continents are potentially a source of Al as well, although at the time of sampling the transect was mainly covered with sea ice, except near the Antarctic Peninsula. Unfortunately, there are, to the best of our knowledge, no direct measurements of dust deposition to the Weddell Sea. There are estimates that give a considerable range for estimated atmospheric dust deposition, ranging from < 0.01 g dust m$^{-2}$ yr$^{-1}$ (Duce et al. 1991) to 0.29 g dust m$^{-2}$ yr$^{-1}$ (Han et al. 2008). Using a different model and actual measurements in the Southern and Pacific Oceans, Wagener et al. (2008) estimated a dust deposition to the Weddell Sea of approximately 0.01 g dust m$^{-2}$ yr$^{-1}$ (taken from their fig. 6). Assuming that continental dust consists of 7.96% Al and that 5% of this Al dissolves (Han et al. 2008), the flux of Al to the Southern Ocean is between 1 and 43 μmol Al m$^{-2}$ yr$^{-1}$. Moran et al. (1992) calculated a flux of Al from continental ice (icebergs) to the surface waters of the Southern Ocean of 0.6 μmol Al m$^{-2}$ yr$^{-1}$. Substituting calculations for Fe by Shaw et al. (2011) with abundance and solubility of Al, an input of 700 μmol Al m$^{-2}$ yr$^{-1}$, via icebergs, to the Southern Ocean can be calculated. Thus, relative to Southern Ocean atmospheric input, there is a wide range of estimates for the input of Al by icebergs, from almost negligible to roughly 3 orders of magnitude greater. However, the influence of melting continental ice is most likely only of local significance. This is supported by the observations of Lin et al. (2011), who concluded that for Fe, release of icebergs is episodic and produces a spatially heterogeneous environment. The relatively low and uniform concentrations (averaged [Al] is 0.25 nmol L$^{-1}$;
Table 1) in the upper mixed layer (~ 50 m) in the central Weddell Sea indicate that icebergs are not of significant influence to the AASW in the central Weddell Sea. As for Fe, iceberg melt would give rise to locally elevated [Al], given the much higher reported Al content of glacial ice (0.09 nmol Al g ice⁻¹; Moran et al. 1992) vs. sea ice (up to ~ 0.007 nmol Al g ice⁻¹; Lannuzel et al. 2011). Moreover, extrapolation to near zero salinity of the observed relationship between salinity and [Al] (Fig. 4) results in values of ~ 10 nmol L⁻¹, which are comparable with the observations for sea ice (Lannuzel et al. 2011). Therefore, continental ice melt is most likely insignificant in this large area of the Weddell Sea, where virtually no icebergs were observed, and [Al] can be assumed to be the result of limited atmospheric input to the region.

When assuming that the surface layer is in steady state and that atmospheric input (either direct or indirect through melting sea ice) is the only relevant input source of Al to the surface layer, the residence time of Al can be calculated (De Baar and De Jong 2001). Since the Weddell Sea is completely covered by sea ice in winter, winter overturning via storms (as is present elsewhere in the world’s oceans) is not a significant factor for the central Weddell Sea. All dust deposition will enter the water column only in the spring/summer, when the ice is melting or has disappeared. Thus, the summer mixed layer is representative of the water column at the time of Al input. However, in winter, WW is the uppermost water layer and extends deeper than the summer mixed layer (see Hydrography). Since dust input into AASW is mixed with WW annually, it might be more representative to use the upper 100 m (AASW plus WW) of the water column as the surface layer to calculate the residence time. Further uncertainty is introduced by the assumption that the observed [Al] at the time of sampling is representative of annual concentrations. Unfortunately, there are no water column measurements for the central Weddell Sea in winter, as the harsh environmental conditions during the Antarctic winter pose enormous logistical challenges. Nevertheless, WW can be considered a remnant of the surface layer as it existed during winter (Hoppe et al. 2007), after summer dust input and scavenging removal due

Fig. 7. Concentrations of dissolved Mn (nmol L⁻¹) vs. concentrations of PO₄ (µmol L⁻¹), NO₃ (µmol L⁻¹), Si (µmol L⁻¹), and fluorescence above the Mn subsurface maximum in the central Weddell Sea and over the continental slope. Linear regressions are shown in the graphs; for PO₄ (µmol L⁻¹), R² = 0.88; n = 25; and p < 0.001; for NO₃ (µmol L⁻¹), R² = 0.79; n = 25; and p < 0.001; for Si (µmol L⁻¹), R² = 0.30; n = 25; and p = 0.004; and for fluorescence, R² = 0.67; n = 25; and p < 0.001.
to summer primary production have come to equilibrium. Therefore, an alternative approach is to define the (year-round) surface layer as the layer above the WW θ minimum (see Hydrography) and to assume that the [Al] observed in WW is representative for the surface layer in steady state. Since the sampling resolution in the surface ocean included a sample at 100 m (close to the θ minimum) and the next sampling depth was 150 m, well below the θ minimum, the observed [Al] close to 100 m can be used as the representative value.

There are errors associated with the calculation of the residence time as a result of the assumptions that inherently need to be made. The largest source of error is the range of Al input via dust deposition (1–43 μmol Al m⁻² yr⁻¹), due to the wide range of dust deposition input estimates as well as the assumption that 5% of the dust dissolves. For simplicity, we will use the mean of the range of dust deposition (0.15 g dust m⁻² yr⁻¹; 22 μmol Al m⁻² yr⁻¹; Fig. 8), but it should be noted that if the full range were to be used in the calculation, the resulting residence time would also have an order of magnitude range (0.3–15.5 yr; Table 2). When using the mean range for Al deposition via dust, the resulting residence time for the AASW ranges between 0.6 and 1 yr (Table 2). From now on we will assume that the use of the WW approach is most representative for Al, as this resembles the surface layer in steady state and yields an average value (0.8 yr) intermediate between the 50 m and 100 m surface layer approach. Nevertheless, calculated values based on the different scenarios are reported in Table 2. For the western Weddell Sea (over the continental shelf and slope), [Al] in the upper mixed layer of AASW is slightly higher, at 0.30 nmol L⁻¹, than the value in the central basin, 0.25 nmol L⁻¹ (Table 1). This is most likely due to input from the Peninsula, as is also observed in the Drake Passage (Middag et al. 2012). The transport mechanism could be icebergs, as these were numerous in this region near the Peninsula, the start of what is known as iceberg alley (Shaw et al. 2011). Using the same assumptions as described above for the central Weddell Sea (WW approach and mean range of dust deposition) results in a residence time on the order of 1.2 yr (Table 2) for the western Weddell Sea over the continental shelf and slope. The estimated residence times (0.8 and 1.2 yr) are in the

![Conceptual model of the fluxes of Al and Mn to the Weddell Sea and the distributions in the different water masses](image-url)

Fig. 8. Conceptual model of the fluxes of Al and Mn to the Weddell Sea and the distributions in the different water masses. The input and WSBW flux calculations are discussed in the text (see Discussion); the export fluxes from AASW are calculated by closing the budget.
results in an estimated flux of 0.15 g m$^{-2}$ yr$^{-1}$; and the average-dust scenario uses 0.01 g dust m$^{-2}$ yr$^{-1}$. The 50 m surface layer definition uses the average trace metal concentration in the upper 50 m; the 100 m surface layer definition uses the average trace metal concentration in the upper 100 m; and the WW surface layer definition uses the [Al] in the WW as representative for the surface layer with a thickness of 100 m.

Around the depth of the WW there is a Mn maximum (see Results: Dissolved manganese). This maximum is most likely related to remineralization below the surface mixed layer (see Discussion: Biological uptake of manganese), which is a seasonal event related to summer primary production and is not representative of the surface layer in winter steady state.

Since there are no data for [Mn] during wintertime in the Weddell Sea either, there is no reliable estimate of what the concentrations in the surface layer would be during wintertime after summer dust input, biological uptake, and remineralization have come to equilibrium. This leaves the 50 m and 100 m approach to define the surface layer. As a result of the large gradient in [Mn] between the surface mixed layer and the subsurface maximum, these two approaches result in approximately a factor of 2 difference in residence time (Table 2). Additionally, the range of estimated dust deposition has an effect of almost 2 orders of magnitude on the estimated residence time, demonstrating the need for reliable estimates or measurements. Even the shortest estimated residence time in the central Weddell Sea, 3.9 yr, seems relatively long for an element that is being depleted by biological uptake (see below). For example, the residence time for Fe in the surface ocean is estimated to be on the order of 1–5 months (De Baar and De Jong 2001). This indicates that there may be a non-negligible Mn input from continental margins that affects the distribution in AASW of the central Weddell Sea. Alternatively, the depletion of Mn by biological uptake in the summer mixed layer and subsequent export and remineralization in WW, followed by resupply of this remineralized Mn to the overlying water in winter, might represent an effective recycling mechanism.

As is the case for Al, the surface concentrations of Mn in the upper 50 m are higher near the Peninsula (0.53 nmol L$^{-1}$) compared to those of the central Weddell Sea (0.16 nmol L$^{-1}$; Table 1). When assuming that the residence time is the same near the Peninsula as in the central Weddell Sea, as done previously for Al, an estimate for the magnitude of the continental flux can be made. The difference of 0.37 nmol L$^{-1}$ Mn (central basin vs. near the Peninsula) would imply a flux from the Peninsula of ~2.4 μmol Mn m$^{-2}$ yr$^{-1}$ to the mixed layer of AASW over the continental shelf and slope (Fig. 8). This flux is 2.2 times greater than the mean range of Mn input via dust deposition, indicating that the influence of the continent

### Table 2. Residence time estimates in years based on different dust scenarios and surface layer definitions.

<table>
<thead>
<tr>
<th>Surface layer definition</th>
<th>Central basin</th>
<th>Western Weddell Sea (over slope and shelf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 m</td>
<td>100 m</td>
</tr>
<tr>
<td></td>
<td>WW</td>
<td>WW</td>
</tr>
<tr>
<td>Al Mn Al Mn Al Mn Al Mn Al Mn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average dust</td>
<td>0.6 7.5 1.0 17.3</td>
<td>0.8 23.8 1.3 44.3 1.2</td>
</tr>
<tr>
<td>Low dust</td>
<td>0.3 3.9 0.5 8.9</td>
<td>0.4 12.3 0.7 22.9 0.6</td>
</tr>
<tr>
<td>High dust</td>
<td>8.4 112 15.5 259</td>
<td>11.7 358 19.2 664 17.4</td>
</tr>
</tbody>
</table>

The low-dust scenario uses a dust input of 0.01 g dust m$^{-2}$ yr$^{-1}$; the high-dust scenario uses an input of 0.29 g dust m$^{-2}$ yr$^{-1}$; and the average-dust scenario uses 0.15 g dust m$^{-2}$ yr$^{-1}$. The 50 m surface layer definition uses the average trace metal concentration in the upper 50 m; the 100 m surface layer definition uses the average trace metal concentration in the upper 100 m; and the WW surface layer definition uses the [Al] in the WW as representative for the surface layer with a thickness of 100 m.
and its margins is of significant importance for the distribution of Mn, as was also observed in the Drake Passage (Middag et al. 2012). The highest [Mn] at stations over the shelf was observed just below the pycnocline and not near the bottom, indicating that the local sediments are not the main source (see Results: Dissolved manganese). The source of Mn could be a surface source, such as direct land runoff or melting of continental ice, or the result of reducing sediments at similar potential density as the observed Mn maximum, followed by lateral advection over the shelf. Since both Al and Mn were elevated in surface waters over the shelf and slope, at least part of the flux of these metals has to come from melting of continental ice or direct land runoff, since these can be a source for both metals. For Mn, but not for Al, reducing shelf sediments can also be a source, as indicated by lower [Mn] progressing from generally more reducing shelf sediments to less reducing slope sediments (Fig. 6). It seems the effect of the flux from the Peninsula and/or its margins into the AASW of the central Weddell Sea is nullified by biological uptake of Mn (see Discussion: Biological uptake of Mn), leading to the low observed concentrations in the central basin. The residence time reported here, assuming merely atmospheric dust input as the only source of Mn to the AASW of the central Weddell Sea, is therefore likely an overestimation. When taking the influence of the Peninsula and its margins into account as well, the true residence time is likely to be shorter than the estimates in Table 2.

WSBW fluxes of Al and Mn—In WSBW, [Al] was elevated, at an average value of 1.37 nmol L$^{-1}$ (Table 1), compared to the values associated with the upper parts of WSDW (around 2000 m), where [Al] was in the range of 0.35 to 0.45 nmol L$^{-1}$ (see Results: Dissolved aluminum), with an average of 0.40 nmol L$^{-1}$ ($SD = 0.07$ nmol L$^{-1}$; $n = 13$). The elevated [Al] in WSBW is most likely a result of deep-water formation during sea ice formation by cooling and brine rejection and the sinking of the WSBW along the continental slope to the deep Weddell Sea (see Hydrography). In fact, the potential temperature of the surface waters over the continental shelf was approximately $-1.83^\circ C$—very close to the freezing point of seawater (approximately $-1.88^\circ C$ at the observed salinity of 34.1). Elevated [Al] related to deep-water formation has also been observed in the Arctic Ocean (Middag et al. 2009), Greenland and the Norwegian Sea (Measures and Edmond 1992), and in the Weddell basin along the zero meridian (Middag et al. 2011b). Similarly, [Mn] was elevated to an average concentration of 0.19 nmol L$^{-1}$ (Table 1), which, along with the elevated [Al], is most likely due to WSBW formation. Assuming [Al] would have been 0.40 nmol L$^{-1}$ (WSDW concentration as well as AASW concentration in the source region) in the deep Weddell Sea, the flux of Al associated with deep-water formation can be estimated. The residence time of Al is on the order of 50–150 yr in the deep Pacific Ocean (Orians and Bruland 1986). Taking this range for the residence time of Al for the deep Weddell Sea and an average thickness of the WSBW layer of 500 m, the flux of Al to the WSBW would be in the range of 3 to 10 $\mu$mol Al m$^{-2}$ yr$^{-1}$ (Fig. 8).

Assuming [Mn] would have remained around 0.09 nmol L$^{-1}$, as observed at the mid-depth minimum in the upper parts of the WSDW, combined with a residence time of 50 yr (Landing and Bruland 1980) results in a flux of Mn to the WSBW of 1 $\mu$mol Mn m$^{-2}$ yr$^{-1}$ (Fig. 8). The deep-ocean [Al] and [Mn] are relatively constant (compared to surface concentrations), and, thus, the error on these flux calculations comes mainly from the assumptions for residence time.

The flux of Al associated with WSBW formation is slightly less per square meter of ocean compared to the flux from the Peninsula to the upper mixed layer of the AASW. However, the deep-water formation flux is affecting an estimated 500 m of vertical water column, whereas the surface flux is only affecting the upper mixed layer (about 50 m). The recent contact with the atmosphere, ice, and continental shelf sediments is a general source of trace metals and trace metal-rich particles to WSBW source water. In combination with scavenging and biological uptake, this leads to the formation of trace metal-rich particles in these surface waters near the Peninsula. During the sinking of the newly forming WSBW along the slope, more particles, as well as sediment pore waters, can get resuspended from the sediments. The particles can partly dissolve as a result of pressure-dependent solubility (Moore and Millward 1984) combined with a decreasing scavenging intensity during deep slope convection into the deep ocean (Middag et al. 2009). The increasing [Al] with increasing depth along the slope sediments most likely represents these processes of additional input in combination with reduced scavenging export.

The flux of Mn to the deep Weddell Sea appears small compared to the surface ocean fluxes, especially considering that the deep-water formation flux originates from the surface ocean near the Peninsula. However, along the continental slope, [Mn] decreased with increasing depth, with the lowest concentrations in the WSBW (Fig. 6). This indicates that, contrary to the flux of Al, the flux of Mn associated with the deep-water formation is attenuated during deep slope convection (Fig. 8). The causes of decreasing [Mn] are most likely microbiobly mediated oxidation and subsequent precipitation and loss from the water column as well as entrainment and mixing of adjacent waters with lower [Mn], such as the WSDW.

Biological uptake of Mn—The distribution and concentrations of Mn in the Weddell Sea are very similar to the observations in the Weddell basin along the zero meridian (Middag et al. 2011a). Along the zero meridian there was also a subsurface maximum, mid-depth minimum, elevated WSBW concentrations, and biological uptake (indicated by the correlation of Mn with nutrients and fluorescence). As observed in the Weddell Gyre along the zero meridian (Middag et al. 2011a), depleted surface [Mn] corresponded with depleted $^{234}$Th : $^{238}$U ratio values in the AASW of the central Weddell Sea (Rutgers van der Loeff et al. 2011, see their fig. 2b). Briefly, the $^{234}$Th : $^{238}$U values of less than 1 are evidence of loss by scavenging and export of particles into deeper layers. It should be noted that $^{234}$Th : $^{238}$U ratios smaller than 1 are attributed to extracellular
adsorption of $^{234}$Th onto settling biogenic particles. Therefore, the similarity between the Mn depletion and the $^{234}$Th/$^{238}$U ratio shows that Mn is depleted in the surface layer by biological removal; however, it does not distinguish between intracellular uptake of Mn and extracellular adsorption of Mn onto settling biogenic particles. The rationale behind using only the Mn data shallower than the subsurface maximum for the correlation (Fig. 7) is extensively described by Middag et al. (2011a). Briefly, at similar depths to the Mn maximum, the $^{234}$Th/$^{238}$U ratio was near or above 1. This indicates either no export or net remineralization at this depth, as also indicated by the local Mn maximum. The Mn and nutrient concentrations at the depth of the Mn maximum were therefore most likely not representative of the biological uptake but rather of remineralization. In contrast, all Mn and nutrient concentrations above the depth of the Mn maximum do indicate biological uptake; hence, these represent the data used for the correlations.

The slope of the Mn–PO$_4$ relation was similar to the one observed in the ACC and Weddell Gyre along the zero meridian (Middag et al. 2011a). The slope of the Mn–PO$_4$ relation equals the dissolved $\Delta$Mn:$\Delta$PO$_4$ due to biological uptake, assuming relatively uniform Mn and PO$_4$ concentrations before biological uptake in summer. This slope can be taken as representative for the Mn:PO$_4$ uptake ratio and thus the cellular Mn:PO$_4$ ratio of the phytoplankton. The assumption of relatively uniform Mn and PO$_4$ concentrations before biological uptake in summer is supported by the observation of the correlations themselves, as a large spread of initial Mn and PO$_4$ concentrations would have obscured the underlying correlation. From here on we will use the $\Delta$Mn:$\Delta$PO$_4$ notation for the value that equals the slope of the observed correlations. The observed $\Delta$Mn:$\Delta$PO$_4$ matches the extended Redfield ratio concept value of $\sim 0.4 \times 10^{-3}$ mol mol$^{-1}$ offered by Bruland et al. (1991), supporting this hypothesis. The observed ratio is slightly lower than the value of $1 \times 10^{-3}$ mol mol$^{-1}$ reported by Kuss and Kremling (1999), indicating there is spread in the ratio between different regions and phytoplankton communities. Consistent with this notion, there appears to be a trend of an increasing $\Delta$Mn:$\Delta$PO$_4$ from north to south, as tentatively suggested by Middag et al. (2011a) based on observations in the ACC and the Weddell Gyre along the zero meridian. The current observations in the Weddell Sea show even lower $\Delta$Mn:$\Delta$PO$_4$, providing additional support for this hypothesis. It was suggested that the $\Delta$Mn:$\Delta$PO$_4$ could be related to the ambient dissolved Fe availability, as the need for Mn by diatoms, the dominant phytoplankton class, increases under decreasing Fe concentrations (Middag et al. 2011a). Moreover, a decrease was previously observed in the cellular Mn:phosphorus (P) ratio for diatoms from $0.42 \times 10^{-3}$ mol mol$^{-1}$ to $0.22 \times 10^{-3}$ mol mol$^{-1}$ after an in situ Fe fertilization experiment in the Pacific sector of the Southern Ocean (Twining et al. 2004). Plotting the $\Delta$Mn:$\Delta$PO$_4$ observed in the Atlantic sector (from Middag et al. [2011a] and the current observations) and the Mn:P ratio for diatoms observed in the Pacific sector of the Southern Ocean vs. the Fe concentrations (see Fig. 9) does indeed result in a significant correlation ($p = 0.001$; Fig. 9). This increase of the Mn:PO$_4$ ratio with decreasing Fe concentrations is consistent with the hypothesis of elevated Mn requirement of the diatom-dominated phytoplankton community under low-Fe conditions (Middag et al. 2011a). The extremely low surface [Mn] in the surface layer reported here for the Weddell Sea and for the Atlantic section of the Southern Ocean (Middag et al. 2011a), in combination with the low concentrations of Fe, would potentially be limiting to the diatom community. Supplying diatoms with only additional Fe would alleviate only part of this co-limitation, as Mn is still needed for photosynthesis and SOD, even if there is ample Fe. This would imply that the high-nutrient, low-chlorophyll conditions in parts of the Southern Ocean are not only due to Fe and light limitation but may also result from Mn depletion. One
realizes that natural Fe fertilization through atmospheric dust input coincides with Mn input, as Mn is another major crustal component of atmospheric dust. The Fe hypothesis, whereby increased dust input during the Last Glacial Maximum (Martin 1990; De Baar et al. 2005) was responsible for the lower CO₂ concentrations during glacial maxima, could potentially be a combined Fe and Mn fertilization. The surface depletion of Mn in the remote Southern Ocean is discernible because of a lack of external Mn sources to these surface waters. This is in contrast with the surface waters of other oceans, in which plankton uptake is more than compensated by ample Mn supply from dissolution of dust, from rivers, and from anoxic margin sediments (Landing and Bruland 1980; Sunda et al. 1983; Pahomova et al. 2007).

The results presented here have illustrated the need for reliable dust input estimates to remote ocean regions like the Weddell Sea to properly constrain trace metal budgets. Additionally, the influence of icebergs on the overall metal distributions and concentrations warrants further research. The surface Weddell Sea [Al] presented here is lower than that currently used in Al-based dust deposition models and would influence these model results. The use of reference samples is critical to be able to distinguish between variability in analyses performed vs. temporal or spatial variability in the metal distributions. The potential role of Mn as a (co-)limiting nutrient element in the Southern Ocean needs to be further investigated. To do so, in controlled experiments, not only does the dissolved Fe concentration need to be monitored but the dissolved Mn concentration must be monitored as well.

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