Distributions, trends and inter-annual variability of nutrients along a repeat section through the Weddell Sea (1996-2011)

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Abstract

Nutrient data from five repeat sections spanning 1996 to 2011 crossing the Weddell Sea are presented. These measurements have been standardized against the same reference material, yielding an outstanding internal consistency. The generic structure of the Weddell Gyre and its hydrographic features are visible in the nutrient distributions; variability is largest in the Circumpolar Deep Water (CDW) and only minor in other water masses. The distribution of silicate appears to be very powerful for describing water mass processes in the bottom layer. The distribution of nitrite is described in detail for the first time. Opposed to common knowledge, a considerable part of the abyssal Weddell Sea had detectable nitrite concentrations, hinting at biological activity at these depths. Also the bottom water, which definitely exists on a longer-than-seasonal scale, has a nitrite signature, thus challenging the commonly assumed short life-time of nitrite. We infer significant trends of increasing nutrient concentrations in the surface layer, which are attributed mainly to an increasing rate of upwelling of subsurface water over those 15 years. Also in the depth range of the CDW an increasing trend is found, which indicates that the nutrient supply to the gyre may have increased. In the bottom water, silicate exhibits an increasing trend, which is probably caused by a changing composition of the bottom water, i.e. containing more CDW and less surface water.

Keywords: Phosphate, nitrate, silicate, nitrite, Weddell Sea, upwelling

Introduction

In Antarctic waters, the nutrient concentrations in deep water layers are among the highest in the world oceans – only in the northern North Pacific they are higher. Contrary to almost all other surface waters in the world's oceans, the nutrients in the Southern Ocean do not become seasonally depleted and high concentrations are found all year round everywhere south of the Polar Front. The Southern Ocean is by far the largest coherent High Nutrient Low Chlorophyll (HNLC) region of the world. The growth of the phytoplankton community in the Southern Ocean is not limited by the macronutrients phosphate or nitrate, unlike most other oceans, but rather by the availability of the dissolved micronutrient iron (De Baar et al., 1990; Martin et al., 1990).

The Weddell Sea forms a large embayment, bordered by the Antarctic continent in the south and the Antarctic Peninsula in the west. It is recognized as a source of deep and bottom waters. These dense waters fill all main ocean basins to the north (Deacon, 1979) and can be traced well into the northern hemisphere. The major circulation feature of the Weddell Sea is a large, elongated cyclone: the Weddell Gyre. Relatively warm and saline Circumpolar Deep Water (CDW) from the north, i.e., the Antarctic Circumpolar Current (ACC), enters the gyre, predominantly in the east (Bagriantsev et al., 1989), and constitutes the main source of other water masses within the Weddell Gyre. At all depths, the gyre transports waters westwards, parallel to the Antarctic coast, and then northeastwards, forced by the Antarctic Peninsula. In a belt along the coast, the water flow is very strong within the Antarctic Coastal Current – this current is circumpolar and thus its waters in the Weddell Gyre originate from the Indian sector of the Southern Ocean. Beyond the Antarctic Peninsula, most of the water continues its flow to the east upon meeting the North Weddell Ridge, which forms the physical northern boundary of the Weddell basin and the adjacent Enderby basin to the east. Water mass formation in the south, southwest and west of the Weddell Sea involves the CDW (locally called Warm Deep Water; WDW), and dense surface waters on the continental shelf (Foster and Carmack, 1976; Foldvik et al., 1985). Weddell Sea Bottom Water (WSBW) with potential temperatures < -0.7°C is produced and occupies the sea floor of the Weddell and Enderby basins. Since WSBW is too dense to leave the Weddell basin, it is being mixed as it is lifted up in the water column, transforming into Weddell Sea Deep Water (WSDW) with potential temperatures between -0.7°C and 0°C. Additionally, some WSDW is formed directly, i.e., without going through the WSBW route (Orsi et al., 1993; Weppernig et al., 1996) and some WSDW is imported from the east (Meredith et al, 2000; Hoppema et al., 2001).

With the cold waters originating from the Weddell Sea, dissolved chemical substances (including nutrients and gases) picked up in the region are transferred into all oceans to the north. The conditions in the Weddell Sea thus have implications for the concentrations of nutrients elsewhere. Consumption of nutrients in the high-latitude Southern Ocean eventually has impact on the nutrient availability at lower latitudes (Marinov et al., 2006).

While Pollard et al. (2006) report that the subsurface nutrient concentrations in the Southern Ocean are remarkably constant, long-term increasing concentrations of nitrate and phosphate (but not silicate) were found in the Antarctic Zone of the Indian sector of the Southern Ocean, indicating that changes are occurring indeed (Iida et al., 2013). Here we address the question whether such trends are also occurring in the Weddell Sea. As part of this, we investigate the distribution and variability of the concentrations of the macronutrients nitrate, phosphate, silicate (or silicic acid; hereafter we use the term silicate) and nitrite. Data originate from a section that closes the Weddell Sea from Kapp Norvegia to Joinville Island at the tip of the Antarctic Peninsula (Fig. 1). The section has been occupied on a regular basis since the late 1980s by the Alfred Wegener Institute (e.g., Fahrbach et al., 2011) for hydrographic measurements and other variables such as oxygen, TCO_2 and CFCs (e.g., Huhn et al., 2013). At many of the occupations, nutrients were analyzed.

Data and methods

We present data from FS Polarstern cruises ANT-XIII/4 (1996), ANT-XV/4 (1998), ANT-XXII/3 (2005), ANT-XXIV/3 (2008) and ANT-XXVII/2 (2010/2011). On all these cruises, nutrient analyses were performed by the Royal Netherlands Institute for Sea Research (NIOZ, Texel) on a section between Kapp Norvegia and the tip of the Antarctic Peninsula (Fig. 1). Although there are a few more repeat sections with nutrient data, we have chosen the above occupations because these data were all standardized by the same in-house reference material and thus have been made fully consistent. This procedure is very important to assure data of the highest quality since internationally recognized (but not certified yet) reference material has been available only recently. The CARINA data synthesis project (Key et al., 2010) has shown that the biases between cruises, and between different nutrient laboratories, can be considerable. Biases (inferred from cross-over analysis of deep ocean data) of up to 15% are commonly encountered (Tanhua et al., 2009; Hoppema et al., 2009; Lo Monaco et al, 2010). With the extremely small nutrient gradients in the deep Weddell Sea, such offsets would preclude any possible conclusion on changes or variations.

Nutrient analysis methods

Concentrations of silicate, phosphate, nitrate and nitrite were determined by colorimetric methods after Grasshoff et al. (1983) using the gas segmented continuous flow auto-analyzer TRAACS 800 (Technicon) at all cruises. Briefly, silicate in the water samples reacts with ammonium molybdate forming a yellow complex. After reduction with ascorbic acid, the blue silica-molybdenum complex is measured at 800 nm. To prevent the formation of the blue phosphate molybdenum, oxalic acid is added. In a second channel of the autoanalyzer, phosphate reacts with ammonium molybdate at pH 0.9, while potassium antimonyltartrate is used there as inhibitor. The resulting yellow phosphate-molybdenum complex is reduced by

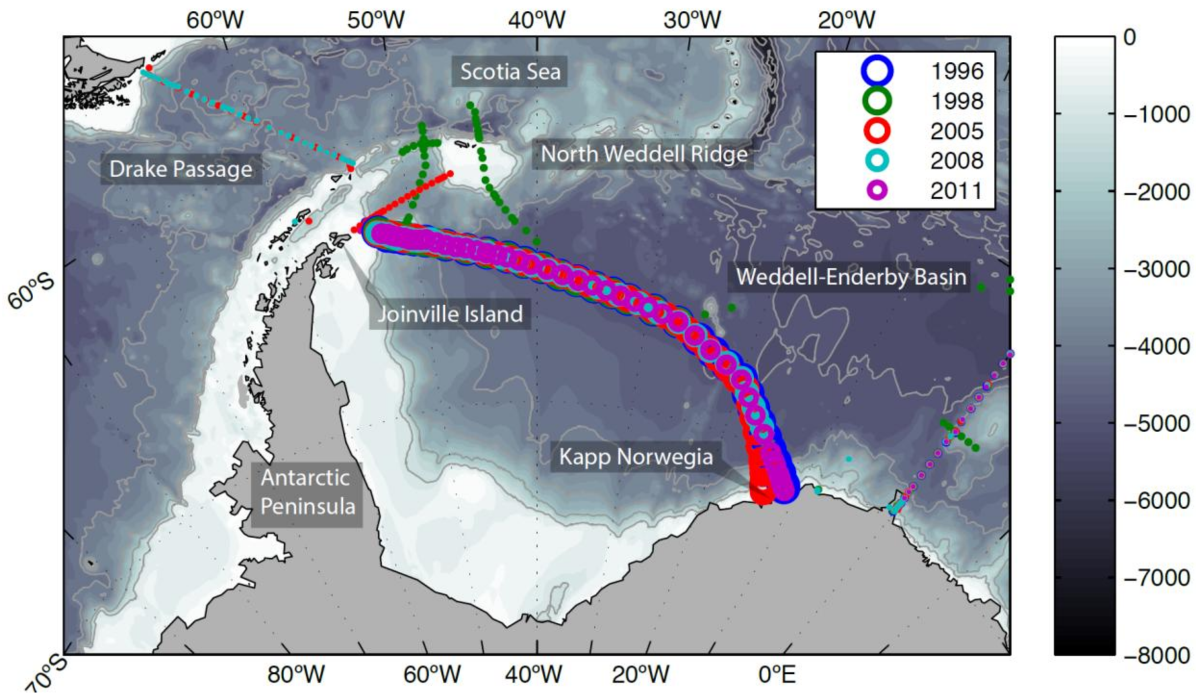

Figure 1

Map of the Weddell Sea, showing overlaid station locations for the five cruises. Samples for nutrient measurements were collected on all stations. Large circles indicate stations used in this study.

ascorbic acid and measured at 880 nm. For the analysis of combined nitrate+nitrite, the water sample is mixed with the buffer imidazole at pH 7.5 and all nitrate in the sample is reduced to nitrite by a copperized cadmium column. To this nitrite, sulfanylamide is added and the resulting diazo compound reacts with naphtylethylenediamine to a pink colored azo complex, which is measured at 550 nm. After subtracting the original nitrite value (as present in the water sample) obtained in the fourth channel, the nitrate value is obtained by difference from the nitrate+nitrite determination.

Standardization

For each nutrient, individual standard samples were prepared every day from stock solutions by diluting with low-nutrient seawater (LNSW). The latter was also used as baseline water. Prepared solutions covered the full range of Southern Ocean nutrient values. Additionally, during every run a single mixed standard containing all nutrients (at the high end of the natural range) was prepared and measured in triplicate for checking the long-term performance of the system and for statistical purposes. The stock solution for this standard water dates from 1998 and contains nitrate, phosphate and silicate in high concentrations, with addition of 20 mg per liter mercuric (II) chloride ($HgCl_2$). It was initially prepared in 1998 and has been used on all subsequent cruises. It is referred to as the Antarctic nutrient cocktail

1998 or ANTCOCK98. It is assumed to be stable over time due to poisoning and storage in a moisture cabinet at 100% humidity, which prevents evaporation. Moreover, it has been shown to be stable in several intercomparison exercises (ICES, Quasimeme) since its production in 1998. In 1996, the first cruise of our data set, a different standard was used for checking the system performance. This 1996 standard was also measured during the next cruise in 1998, thus allowing consistency with the 1998 cocktail to be maintained. All data for the 5 cruises between 1996 and 2011 were normalized to the known value of the Antarctic nutrient cocktail 1998 thus guaranteeing optimum consistency of all nutrient data throughout the years. For each cruise the 'long-term' precision is calculated as the root mean square of the differences of duplicates of the deepest samples of each station, measured in separate runs. We express these standard deviations as the percentage of the mean (deep water) measurement value, i.e., as a coefficient of variation (CV). Precision statistics are presented in Table 1. For all cruises, the CV is generally better than 0.6% for phosphate, silicate and nitrate+nitrite except for 2005 where, due to temperature control problems, the precision for phosphate and silicate is only 1.2%. In 2008, the CV of nitrate+nitrite data was 1%. Data from 2011 are of particularly high quality. The 'short-term' precision is even better: back-to-back analyses of 24 samples (all from different Niskin bottles, but from the same depth) have a CV as low as 0.2% for all nutrients.

Table 1

Overall precision expressed as coefficient of variation (CV; in %), being the relative standard deviation of all duplicates from the bottom water samples analyzed and reanalyzed in the next run

year	PO_4	Si	NO_3+NO_2
1996	0.71	0.76	0.58
1998	0.51	0.64	0.60
2005	1.09	1.28	0.57
2008	0.51	0.48	0.95
2011	0.27	0.29	0.30

In summary, processing resulted in an internally consistent data set with overall precision better than 0.01 μM for PO_4, 0.3 μM for Si, 0.11 μM for NO_3 and 0.01 μM for NO_2. Note that this precision for nitrite is only valid for the 2011 data – data quality of the other years is considered insufficient to warrant further processing, and these pre-2011 nitrite data are not further considered here. Since nitrite concentrations in the deep ocean get very low (see below), we also provide the limit of detection (as 3 times the standard deviation of measurements of 10 samples of LNSW) of 0.0025 μM. Calibration was done with 5 standards spaced equally between 0.01 and 0.51 μM. In the deep ocean, the standard deviation of 24 samples from the same depth for nitrite is 0.0008 μM. Semi-daily measurements of low-nitrite standard showed no trend and very small noise (0.028 ± 0.005, n=23). Together, this strongly suggests that any difference in nitrite concentrations seen in the deep Weddell Sea is real.

Table 2

Statistics on the accuracy of the presented datasets. All our five cruises were brought to the same analytical scale by standardization against NIOZ ANTCOCK98. The most recent two cruises (2008 and 2011) allow for comparison of that scale to the internationally recognized nutrient scale defined by the KANSO-supplied Reference Material for Nutrients in Seawater. Two sets of reference values for the RMNS are given and compared to measurements of the RMNS performed during the 2008 and 2011 cruises

	Kanso RMNS batch AZ				deviation of cruise data of 2011 against		
	KANSO[a]	IC2006[b]	cruise data				
	Nominal value	consensus mean value	2008	2011	KANSO	IC2006	2008
NO_3	41.87	42.4	42.68	42.63	+1.8%	+0.5%	-0.1%
PO_4	3.01	3.03	3.018	3.026	+0.5%	-0.1%	+0.3%
Si	136.3	135.36	135.6	135.2	-0.8%	-0.1%	-0.3%

[a] Nominal RMNS values obtained from *http://kanso.co.jp/eng/pdf/identification_az.pdf*

[b] See Aoyama et al. (2008)

In 2008 and 2011 the then newly available Reference Material for Nutrients in Seawater (RMNS, batch AZ from KANSO; *www.kanso.co.jp/eng/production/*) was also measured to allow traceability of our data to the international nutrient scale. The data presented here have not been adjusted to be on this scale, but rather are found to differ slightly from it (see Table 2). Notably, our results for RMNS batch AZ are in very close agreement with the consensus mean values as determined by the 2006 Intercomparison Exercise for Reference Material for Nutrients in Seawater (Aoyama et al., 2008). Irrespective of the reference values taken as ‘ground truth’, the data presented here are considered ‘accurate’ for use in various backcalculation techniques. The reprocessed data presented here have been submitted for inclusion in the GLODAPv2 data product (Key et al., in preparation) and are available for download at CDIAC:

doi: 10.3334/CDIAC/OTG.CLIVAR_A12_ANT_XXVII_2

doi: 10.3334/CDIAC/OTG.CLIVAR_A12_ANTXXIV_3

doi: 10.3334/CDIAC/OTG.CLIVAR_A12_ANT_XXII_3

doi: 10.3334/CDIAC/OTG.CARINA_06AQ19980328

doi: 10.3334/CDIAC/OTG.WOCE_S04A_ANTXIII_4

Results and discussion

Nutrient sections

Sections across the Weddell Sea showing contoured data of all four nutrients, salinity and potential temperature in 2011 are shown in Fig. 2. All nutrients are relatively low in the surface layer due to net consumption by algae. However, compared to nutrient concentrations elsewhere in the world's oceans, these values are very high – note that the cruises were all in summer and early autumn when the annual minimum nutrient concentrations are expected. Nutrient maxima are found in the Warm Deep Water (WDW) – the subsurface water mass defined by > 0°C, with a lower boundary at about 1200-1700 m (roughly west to east). The depth of the nutrient maximum is variable among nutrients and varies with the location along the section. Clearly, the silicate maximum occurs significantly deeper (i.e., near the lower boundary of the WDW) than that of nitrate and phosphate (which both peak around 400 m). This is caused by the slower rate of dissolution of opal, sinking out of the surface layer, compared to the remineralization of sinking organic matter (Brown et al., 2006) releasing nitrate and phosphate. The value of the nutrient maximum is not constant along the section: the highest maxima generally occur in the western half of the section, although in 1998 and 2008 a reversed situation was observed for nitrate (sections shown in the Supplementary Material). Below the WDW, the nitrate and phosphate concentrations generally decrease to the bottom. The concentration gradients between 1000 m and the bottom at about 5000 m are extremely small; especially for phosphate with only about 0.1 µmol kg^{-1} per 4 km. The fact that such minor gradients are observable at each cruise (only 2011 data shown here; data from

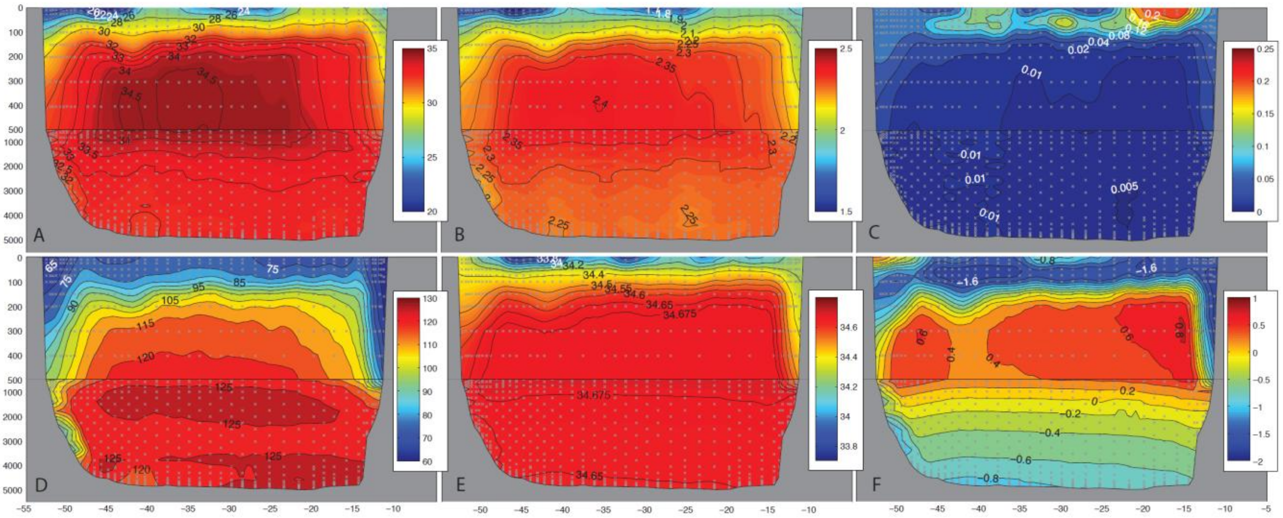

Figure 2

Section plots for the 2011 cruise, showing a) nitrate, b) phosphate, c) nitrite, d) silicate, e) salinity and f) potential temperature (°C). All nutrient concentrations are in µmol kg^{-1}. Note the change of vertical scale at 500 m depth.

other years in the Supplementay Material) is made possible by the high precision of the measurements. For silicate, different layers with local maxima and minima are discerned below the WDW. In the eastern part of the section, a silicate maximum at the bottom is observed that features the highest silicate concentrations of the entire section, with some samples slightly above 130 μmol kg^{-1}. Nitrate and phosphate feature a minimum in the bottom water at the sea floor due to the low-nutrient surface water ingredient of WSBW, but in some near-bottom samples a weak local maximum is observed coinciding with the bottom silicate maximum in the east.

Apparently, the water mass structure of the bottom layer across the section is relatively stable through the years, as deduced from the silicate distribution (Figs. 2d and S6-S10 in Suppl. Mat.). Silicate proves a powerful tracer for processes taking place in the bottom layer because of the large range of silicate concentrations in this layer. Roughly, all repeats show an absolute silicate maximum in the east (15-20°W) and a lateral minimum in the west (45-40°W). Abutting this minimum to the west, at the base of the continental rise (45-48°W), another lateral silicate maximum is situated. Its permanent location, which is hardly variable, suggests that this dense bottom water is rigorously steered by the topography, namely by the base of the continental rise. It must thus be the downstream occurrence of the high-silicate bottom water off Kapp Norvegia being transported as part of the main gyre flow. At a depth of about 4000 m, a silicate maximum spreads all across the basin, whereas right below that, a silicate minimum spreads from the west far into the eastern part of the section. For all occupations, the structure of the bottom layer appears robust, i.e., the layer and its maxima and minima are always present. However, there is some variability in the extent and intensity of the single features in the bottom layer. The silicate-enriched bottom water off Kapp Norvegia spreads across the Weddell basin and is detected approximately up to the middle of the section: From east to west the concentration of silicate decreases. The silicate maximum near the eastern end originates from silicate exchange with the local sediments combined with a bottom water recirculation feature that prolongs the residence time of the bottom water in the region (Hoppema et al., 1998). Also some nitrate and phosphate have been suggested to originate from the sediments (Rutgers van Loeff and Van Bennekom, 1989) which increases their concentrations near the sea floor slightly. Changes in circulation might thus invoke pronounced changes in near-bottom silicate concentrations. In 2005 and 2008 the silicate maximum is the highest with >130 μmol kg^{-1} and also its extension seems to reach further west than in the other years.

At the base of the continental slope (45-48°W) the silicate maximum has a variable magnitude, reflecting its origin upstream off Kapp Norvegia. In 1996 its concentration was the lowest, while in other years it is 120-125 μmol kg^{-1}(Figs. S6-S10 in Suppl. Mat.). Newly formed, denser WSBW with a low-silicate signature, formed in the south and west on the shelves of the Weddell Sea (and in Fig. 2d coming from the east), underrides this silicate-rich water and mixes with it; a silicate maximum is thus induced. On the continental slope the denser WSBW is found (48-50°W) with concentrations below 100 μmol kg^{-1}; in the western part (35-45°W) on the sea floor this dense WSBW is present as water with <120 μmol kg^{-1} or <115 μmol kg^{-1}. Moving into the gyre interior, the low-silicate WSBW forms a silicate minimum where the minimum is continually eroded by mixing with higher-silicate water above and below (the latter water coming from the east).

In the CDW layer, the highest nutrient maximum is strongly associated with the hydrographic structure of the Weddell Gyre. In 1996 the nitrate maximum of >35 μmol kg^{-1} is found between 40-45°W (Fig. S25 in Suppl. Mat.), which corresponds exactly to the location of the axis of the gyre. The latter is recognizable in the temperature distribution (Fig. S5 in Suppl. Mat.); it is the saddle location between the two main cores of gyre flow (with lateral temperature maxima) where the temperature maximum reaches its lowest value of 0.3-0.4°C. In the axis area, the residence time of the water is the longest. Hence, its temperature maximum has been attenuated to the largest extent by mixing with surrounding waters of lower temperatures. Translated to the nutrient distributions, in the axis area a relatively small nutrient maximum would be expected, because mixing with surrounding waters would also tend to reduce the nutrient concentration in the nutrient maximum. However, this is not the case, and instead the axis area features a nutrient maximum (Fig. 2a,b). This is explained by modification of the nutrient distribution by biologically-mediated processes: organic matter produced in the surface layer sinks to greater depths and is degraded there; the main remineralization seems to occur between 300 and 500 m. Because of the longer residence time of the waters in the axis area, nutrients attain higher concentrations there than in surrounding waters. This mechanism was described for the central Weddell Gyre by Whitworth and Nowlin (1987), who differentiated the CDW of the axis area as Central Intermediate Water.

The data from 1996 represent a unique (“classical”) case of nutrient distributions that are influenced by circulation and biological activity. Since we know the location of the inflow of CDW into the Weddell Sea – represented by the highest temperature maximum at 15-20°W (Fig. 2f), we can estimate the enrichment of nutrients that has occurred in the Weddell Sea by simply calculating the difference between the concentrations in the inflow and in the axis area. Consequently, up to about 1.5 μmol kg^{-1} of nitrate and 0.15 μmol kg^{-1} of phosphate were accumulated in the central gyre; this is a lower boundary because the nutrient concentration was at the same time attenuated by mixing (see above). Note that the nutrient concentrations in the inflow and in the outflow (45-50°W) are quite similar, which suggests that during the residence of the water in the main gyre flow the nutrient accumulation is negligible. The nutrient enrichment patch, especially that of nitrate (Fig. 2a), provides a revealing view of the spreading of the waters in the central gyre. Although some local enrichment contributes as well, the waters from the gyre axis appear to spread to the east and eventually subside under the inflow core. These observations show that nutrients serve as powerful tracers for the circulation of the central Weddell Gyre.

In 1998 and 2011 the nitrate maximum occurs at approximately the same position as in 1996 (Figs. S24, S21 and S25 in Suppl. Mat., respectively); however, in 1998 comparably high nitrate concentrations occur further east at 33-27°W. In 2005 (Fig. S23) the nitrate maximum has a similar structure as in 1996, however the core lies somewhat further east at 43-38°W. In

2008 (Fig. S22) the situation is different, with the lateral nitrate maximum clearly at 33°W (and a secondary, lower nitrate maximum at the usual location (40-45°W). This variability is likely the consequence of variations in the circulation of the gyre. The lateral nutrient maximum more to the centre of the gyre seems to point to a temporal slowing down of the gyre transport in the southern and intensification in the northern limb of the gyre. Such flow variations, which occur independently in both limbs of the Weddell Gyre, were previously suggested by Fahrbach et al. (2011). Both the surface layer and the CDW layer are particularly sensitive to such variations.

Nitrite distribution

At all cruises nitrite was measured with the main purpose of separating nitrate from the measured nitrate+nitrite. However, nitrite also has inherent relevance within the nitrogen cycle of the Weddell Sea but only very few publications treat this subject. Only few nitrite data for the Weddell region have been previously published (Nöthig et al., 1991; Cota et al., 1992 and Hoppema et al., 2002a). Nitrite is a dynamic, short-lived intermediate product of nitrification (nitrate formation from ammonium) and is excreted by phytoplankton (Lomas and Lipschultz, 2006); it is generally found in significantly non-zero concentrations only in the oceanic surface layer where often a primary nitrite maximum is found at the base of the euphotic zone (Lomas and Lipschultz, 2006). Interestingly, non-zero concentrations have been observed in the Weddell region in austral winter (Nöthig et al., 1991; Cota et al., 1992). The nitrite distribution in the Weddell Sea is anomalous because of specific circulation features related to deep water production, which we explain in the following. Fig. 2c shows the nitrite distribution during the 2011 cruise, which took place in the austral summer. Active biological production occurred in the surface layer, as suggested by the high nitrite concentrations of up to 0.28 µmol kg^{-1}. At the western and eastern margins, the surface layer is a few hundred meters deeper than in the interior and the nitrite = 0.02 µmol kg^{-1} horizon also descends from 200 to 500 m. The nitrate and phosphate maxima in the Weddell Sea are partly advected from the ACC, and magnified through degradation of organic matter in the gyre interior (Whitworth and Nowlin, 1987; Hoppema et al., 2002b). The source of this water being the deep ACC and abyssal oceans to the north, negligible nitrite concentrations are thus expected and, indeed, observed to be only 0.01 µmol kg-1. We conclude that the decomposition of organic matter at depth of the WDW does not produce a significant amount of nitrite on the time scale of the enrichment of nutrients in the WDW, which is about 3 years (Hoppema et al., 2002b).

Below the upper 200 m, the concentrations in the Weddell Sea are lowest, at around 0.01 µmol kg, with the western part of the section (36-47°W) having slightly higher concentrations (0.01-0.02 µmol kg-1) than the eastern half (0.0075-0.001 µmol kg-1). The nitrite concentrations at or above 0.01 µmol kg^{-1} throughout the water column west of about 36ºW hint at recent nitrite production. Non-zero nitrite concentrations at depths up to 5 km are exceptional in the oceans. We hypothesize that nitrite in this region was produced at all depths by decaying phytoplankton which in a massive event had sunk out of the surface layer. This particular region of the Weddell Sea is known for phytoplankton blooms consisting of *Phaeocystis* species and diatoms (e.g., Schoemann et al., 2005; Bertolin and Schloss, 2009). The massive sinking of blooms in this area was confirmed by observations of conspicuous maxima of Total Organic Carbon in the deep sea (Wedborg et al., 1998). Physical processes are unlikely to cause these enhanced concentrations, as the newly formed bottom water only occupies a thin bottom layer (see below). It is worthwhile noting that the nitrite concentration in the west is clearly larger than in the east (Fig. 2c) and there is no known process for causing stronger vertical mixing in the west.

On the continental slope of the Antarctic Peninsula (the western boundary of the section), a thin layer of nascent Weddell Sea Bottom Water is present (e.g., Fahrbach et al., 1995; Gordon et al., 2001). Coinciding with it there is a layer of enhanced nitrite concentrations: the 0.02 umol kg^{-1} isoline is found as deep as 800 m and higher than usual deep values can be seen to extend down to ~1500m (Fig 2c). At greater depth, 2000 to 4000 m, nitrite is still between 0.005 and 0.01 μmol kg^{-1}. Also the WSBW at the bottom of the Weddell basin has non-zero nitrite concentrations, which often occur as a local maximum. As WSBW is generated from a modified form of WDW and a surface water ingredient (Mosby, 1934; Gordon et al., 2001; Huhn et al., 2008), the enhanced nitrite in the WSBW must originate from the high-nitrite surface water on the shelves where the WSBW is produced. The residence time of the WSBW at the bottom of the central basin is in the order of decades (Huhn et al., 2013) and thus the presence of nitrite, being known to be short-lived with turnover times estimated to be 33-178 days (Buchwald and Casciotti, 2013), is surprising.

Nutrient Trends

To enable calculation of temporal trends, first all data were subsampled onto a common grid (gridpoints were located every 0.5 degrees of longitude and on 27 depth levels, spaced every 20 m near the surface but with progressively larger intervals deeper in the water column; grid point values are influenced by data within approximately one bin length in every direction). The bathymetry was assumed identical for all cruises – this almost conforms to reality as cruise tracks are almost exactly coincident (Fig. 1). At all grid points ordinary least squares linear regressions of the gridded nutrient concentrations against time were performed. At each grid point, the regression is thus performed with 5 data points from 5 different years; note that the 1998 cruise has only data between the Peninsula and 27°W and thus for the region east of 27°W trends were calculated from only 4 cruises. Contour plots with rates of change of phosphate, nitrate and silicate are shown in Fig. 3. For all variables there are both regions with increases and regions with decreases. Particularly in the deeper Weddell Gyre most of the increases and decreases appear to be insignificant (at the 0.05 level). These insignificant trends are likely statistical artifacts of the usual variability in the Weddell Sea due to variations in circulation and/or export plus remineralization of organic matter. Conversely, in the surface layer (the upper 100 m) all variables show significant increases along part of the transect (nitrate, phosphate) or nearly the entire transect (silicate). The increase of nitrate during the 15 years period is typically about 1.5 μmol kg^{-1}, for phosphate this is 0.05 μmol kg^{-}

[1] and for silicate a rather astounding 20 µmol kg^{-1}. For silicate, a regression through measured values (as opposed to grid points) gives quite similar results (Fig. 4), yielding a rate of silicate increase of 1.5 ± 0.0 µmol kg^{-1} yr^{-1}. Also in the depth range 300-500 m, i.e. in the upper WDW layer, some statistically significant upward trends are found (Fig. 3).

The most conspicuous feature in the nutrient trends along the Weddell section is certainly the concurrent increases of all nutrients in the surface layer. Enhanced nutrient concentrations in the surface layer have two possible explanations. First, since nutrients are consumed by phytoplankton and cyanobacteria in the euphotic zone, higher nutrient concentations after 15 years would imply reduced photosynthesis during that time period. Second, as the surface layer in the Weddell Sea is eventually formed through upwelling and entrainment of subsurface water, the increased nutrient concentrations might have been caused by an enhanced rate of upwelling of nutrient-charged deep water.

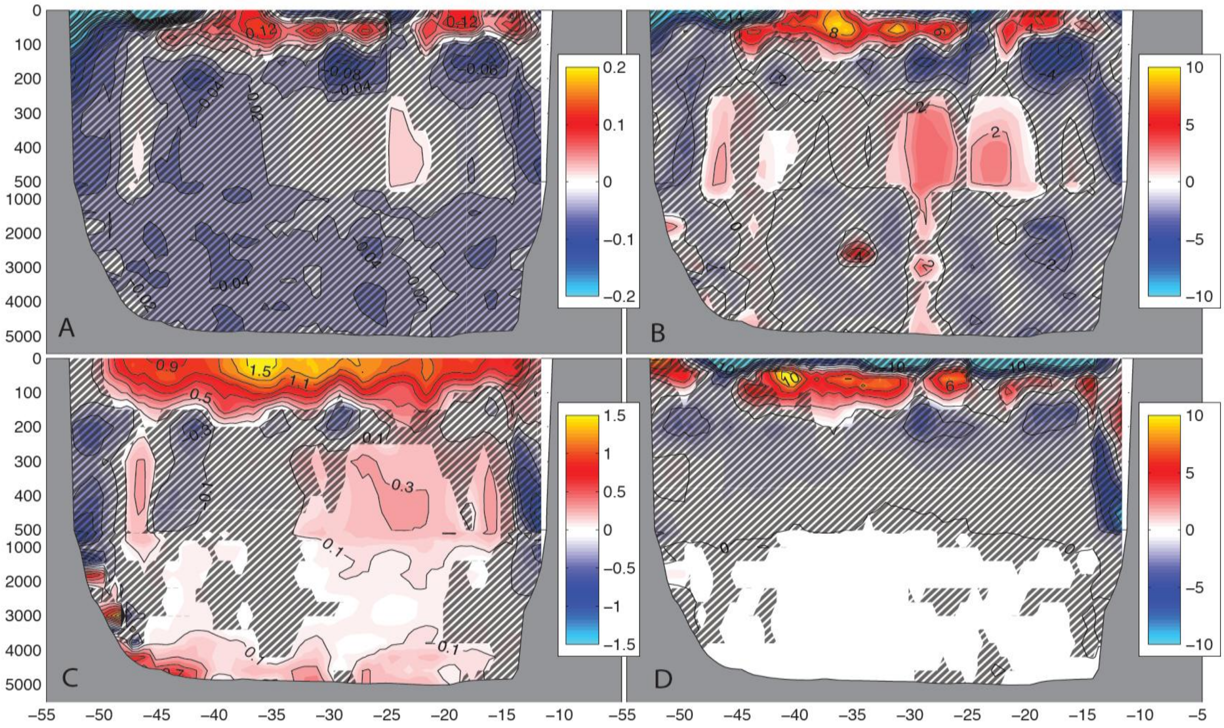

Figure 3

Inferred time rates of changes for a) nitrate (in µmol kg^{-1} year^{-1}), b) phosphate (in nmol kg^{-1} year^{-1}), c) silicate (in µmol kg^{-1} year^{-1}) and d) salinity (in ppm year^{-1}) along the Weddell Sea section. Trends in hatched parts of the section are not statistically significant at the 0.05 level.

Phytoplankton blooms are frequent in the Weddell Sea (e.g., Lancelot et al., 1993; Krell et al., 2005), but trends in biological activity have to our knowledge as yet not been reported. Trends in the wider Southern Ocean, on the other hand, have been observed (e.g., Atkinson et al., 2004) and several studies suggest that the recent positive trend in the Southern Annular Mode (SAM) must be followed by changes in physical forcing and subsequent changes in the biological systems (e.g., Arrigo et al., 2008; Wang and Moore, 2012; Hauck et al., 2013). Hence, although changes in biological activity are likely, there is presently no evidence for it in the Weddell Sea.

To investigate the role of upwelling, we additionally calculated the rate of change along the salinity section, a parameter that is not biologically-mediated. Fig. 3d shows that in the central part of the gyre, significant increases in salinity over 15 years are observed in the surface layer below about 50 m. That no significant changes in salinity are observed in the upper 50 m is due to seasonal sea-ice formation and melting, which result in strong variations in salinity. The observed trend occurs in the Winter Water (the temperature-minimum layer), which is separated from the upper surface layer by the seasonal pycnocline. An increase in surface layer salinity in the eastern Weddell Gyre between the 1990s and the mid-2000s was previously observed by Behrendt et al. (2011). Although processes in the western and eastern Weddell Gyre are not necessarily congruent, this is a strong indication of gyre-wide salinity elevation.

The explanation of an increase in salinity as observed in Fig. 3d could also be an increase of sea-ice formation during this period: more sea ice produced would release more brine into the surface layer, especially in winter, and thus increase the salinity of the Winter Water. The sea-ice extent of the Southern Ocean has been found to increase during the period of our investigation (e.g., Parkinson and Cavalieri, 2012). However, for the wider Weddell region these trends have been quite low and along our Weddell Sea section the trends have been insignificant or even negative (Holland and Kwok, 2012). Moreover, the latter authors showed a decreased northward export of sea ice from the Weddell region. Concluding, the most plausible explanation for the inferred positive nutrient trends in surface waters is definitely enhanced upwelling of high-salinity, high-nutrient subsurface water.

For phosphate and silicate (and to minor extent also nitrate), significant trends are also observed in the depth range 300-500 m for appreciable parts of the section (Fig. 3b,c). This depth range represents the core flow of the WDW, i.e., the temperature maximum. The core of the WDW inflow and outflow is quite variable in intensity (and location), caused by both variable water transport of the gyre, (re-)circulations and mixing processes in and around the WDW core. It is surprising, though, that the nutrient concentrations in the WDW core are not just varying, but have rather increased significantly in the 1996 to 2011 period. Nutrient concentrations in the WDW core are not appreciably modified through degradation of organic matter, unlike in the central part of the gyre (see above). It must then be the lateral supply of phosphate and silicate to the Weddell Sea (from the ACC to the north) that has changed in these 15 years. This idea is furthermore supported by the observation that only nutrient increases appear to be significant (Fig. 3a,b,c) and not nutrient decreases, indicating that over these 15 years the Weddell basin has accumulated nutrients, rather than redistributed nutrients. The ultimate cause must be a change in circulation.

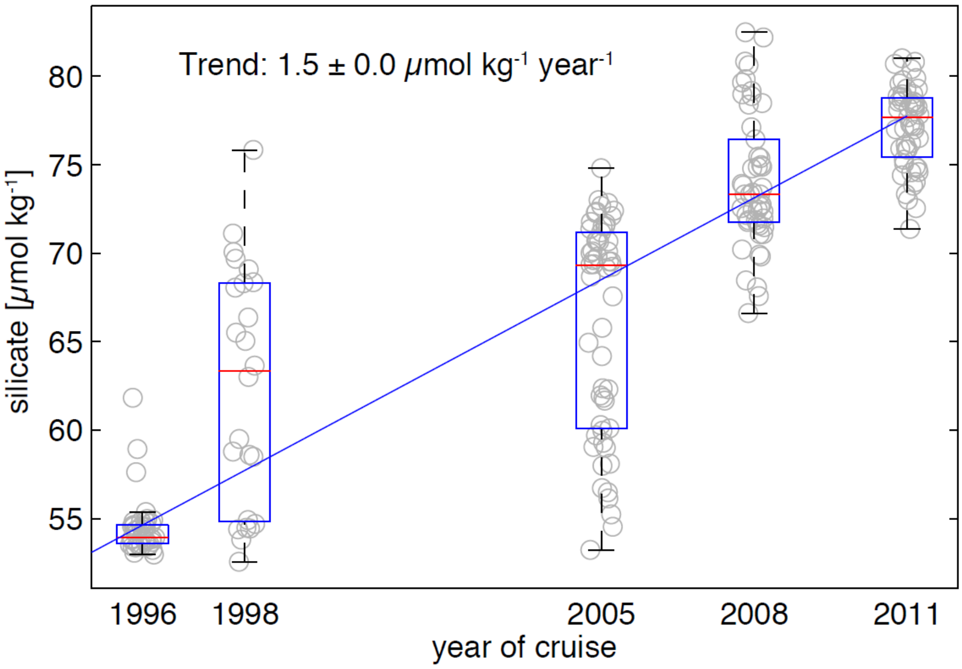

Figure 4

Time trend of silicate in Weddell Sea surface water (40ºW−20ºW; 0−80 m) represented by a box-and-whisker plot. The whiskers show the minimum and maximum of all data. In the 1996 data there are some high outliers.

Contrary to the other nutrients, a significant increase of silicate has occurred in the layer at and near the bottom (Fig. 3c). This tallies with observations on the Prime Meridian to the east, where a notable increase in silicate in the Weddell Sea Bottom Water was found (Van Heuven et al., 2014). It should be mentioned that in the WSBW on the Prime Meridian also a slight but significant increase of nitrate was detected over 35 years of observations (Van Heuven et al., 2014), contrary to the present study, which does not find a nitrate increase in the bottom water of the central Weddell Sea. It should be noted, though, that the nitrate increase at the Prime Meridian covers a much longer time span; only accounting for the time period 1996-2011 (like in the present study) on the Prime Meridian, no significant nitrate increase can be detected (see Van Heuven et al., 2014). The trend of increasing silicate concentrations on the Prime Meridian was accompanied by a trend of decreasing dissolved oxygen concentrations and increasing TCO_2 concentrations. Van Heuven et al. (2014) argued that all those trends can be explained by a modified mixing process generating WSBW. The mixing recipe of the main components, WDW and surface shelf water, is likely to have changed towards a greater proportion of the former. It seems that the elevated silicate concentrations in the Weddell Gyre interior align with this. Fig. 5 shows the subsurface nutrient concentrations over the western continental slope as a function of their potential temperature. The part of the plot where the concentration are the lowest characterize the nascent WSBW. It is manifest that the nutrient properties of the WSBW have not changed during these 15 years. This is further evidence for our statement that observed changes in the WSBW result from changing contributions of source water types to the formed WSBW (i.e., changes along the mixing line).

With regard to silicate, it should be realized that major fluxes from the sediments exist, which increase the concentration in the near-bottom layers; up to 50 µmol kg^{-1} of enrichment is possible in the Weddell-Enderby basin (Edmond et al., 1979). Due to changes in circulation in the bottom portions of the gyre, the residence time of bottom water parcels may increase, thus prolonging the contact times of those water parcels with the sediment and subsequently increasing concentrations of dissolved silicate. This process may play an additional role in the accumulation of silicate in the deep Weddell Gyre. This holds much less for nitrate and phosphate, which do indeed not exhibit rates of increase in the bottom layer; the concentrations of those nutrients are only slightly influenced by exchanges with the seafloor (Rutgers van der Loeff and Van Bennekom, 1989; Hoppema et al., 1998).

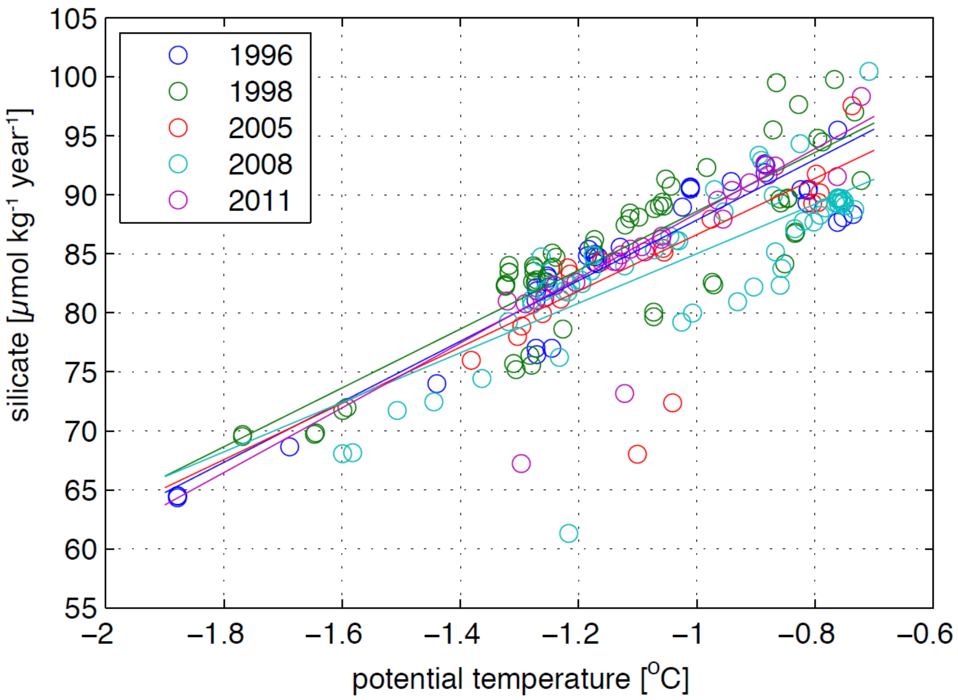

Figure 5

Regressions of silicate against potential temperature for all near-bottom, on-slope WSBW samples [>50 m deep, <500 m from bottom, potential temperature<−0.7ºC, 55ºW-50ºW] indicates that the source water type has maintained a silicate = ~65 µmol kg^{-1} characteristic over the 15 years of this study.

It is also revealing to inspect the locations where no significant silicate trends were observed. This aims especially at the silicate minimum centered at 3500 m and extending from its core hugging the eastern continental slope (clearly observable in section of 2005, see Fig. S8 in Suppl. Mat.). This silicate minimum corresponds to a CFC maximum observed by Hoppema et al. (2001), which finds its origin in the Indian sector of the Southern Ocean (Mantisi et al., 1991). The CFC maximum proves that it is Weddell Sea Deep Water with a surface water ingredient, likely from Prydz Bay or nearby Cape Darnley (Yabuki et al., 2006; Ohshima et al., 2013); this surface water component also causes the minimum in silicate in the deep Weddell Sea. The fact that no silicate trend is detected in this ventilated water mass (Fig. 3c; at 3500m, 15ºW) suggests that the processes determining the silicate concentration in Prydz Bay and surroundings have not significantly changed, i.e., apparently no enhanced upwelling in the gyre circulation of Prydz Bay (Smith et al., 1984) like in the Weddell Gyre. Couldrey et al. (2013) did find changes (i.e., warming) in this water mass during the time period of our observations, and attributed this to enhanced entrainment of CDW. This would potentially cause changes (likely an increase) in silicate concentration in the core, but apparently these are not sufficiently large (or have been attenuated underway) to be observed in the Weddell Gyre.

General discussion

From the positive nutrient trends in the surface layer, confirmed by a corresponding trend in salinity, we deduce that upwelling of subsurface water in the central Weddell Gyre has increased between the mid-1990s and 2011. Since the upwelling in the gyre interior is eventually caused by the divergent flow of the gyre, we surmise that the gyre transport and flow have concomitantly intensified. An indication of increased gyre flow is indeed found in the geopotential anomaly at the Prime Meridian, which shows, though with large variations, an increase between the mid-1990s and 2005 (Fahrbach et al., 2011). Increased upwelling in the Southern Ocean is the expected consequence of the observed intensification of the westerly winds that project onto the more positive phase of the Southern Annular Mode (Hall and Visbeck, 2002). Waugh et al. (2013) used CFC distributions to show that a modification of water mass ventilation in the Southern Ocean has occurred, where in the southern regions the age of the deep water masses has increased, meaning that it takes more time for those water masses to be ventilated. They further explain that those changes are fully consistent with the elevated and poleward moving westerlies due to the SAM pattern changes which strengthen the Ekman divergence and thus upwelling. Also in the Weddell Sea the ventilation of all water masses has decreased since the 1980s and the ages have increased accordingly (Huhn et al., 2013). In sum, the trends in nutrient data are fully consistent with the larger-scale modifications in wind field and circulation due to gradual phase changes of the SAM, which in turn result from the impact of certain anthropogenic activities on processes of climatic relevance, i.e., the ozone depletion over the Antarctic and the increased greenhouse gases in the atmosphere (Thompson and Solomon, 2002).

Accompanying the nutrients, we can expect that the concentrations of other chemical species, in particular iron, have increased likewise due to elevated upwelling of subsurface waters, since the latter feature high iron concentrations in the Weddell Sea (Klunder et al., 2011). The increased iron availability might enhance primary productivity because iron limits productivity in the Southern Ocean, including the offshore Weddell Sea (De Baar et al., 1990; Martin et al., 1990). Enhanced productivity would tend to draw down CO_2 and nutrients and this would counteract the nutrient increase. A modeling study by Hauck et al. (2013) found strong indications for this mechanism and concluded that enhanced biological activity and export of carbon to depth is a significant factor. Our results reveal that there is a net increase in nutrients, which indicates that upwelling of nutrients into the surface layer must be the dominant process. Any possible enhancement of biological activity (which tends to decrease nutrients) following increased upwelling thus did not compensate for the increase of nutrients by upwelling. Only a slight response of primary productivity was suggested in a modeling study by Lenton et al (2009), because of a higher iron demand of the phytoplankton in iron-replete conditions.

Silicate appears to be a useful indicator for processes occurring in the bottom layer. We found strong indications that the flow of silicate-rich bottom water at the base of the continental rise is continuous between the east and the west end of our section that cuts accross the Weddell basin. The dense water that arrives at the tip of the Peninsula has only some attenuated characteristics as compared to its source. This brings up an issue with bottom water formation at the southern shelves of the Weddell Sea. In this region very dense bottom water is produced, which in its nascent state flows down the continental slope. If the sinking would be finished off the southern shelves, this dense water would meet the silicate-rich bottom water within the gyre flow, the latter of which, however, is somewhat less dense than the newly formed WSBW. In that case, the WSBW from the shelves would be taken up into the main gyre flow. But then it would be unlikely to find on our section the high-silicate water to the west of the new WSBW from the southern shelves. Therefore, we conclude that the newly formed WSBW from the southern shelves keeps hugging the continental slope all its way through to the tip of the Antarctic Peninsula. Only downstream of that, the ventilated, low-silicate bottom water makes its way south into the gyre interior.

Conclusions

Five sections across the Weddell Sea with high-quality nutrient data showed statistically significant increases of all nutrients in the surface layer between 1996 and 2011. Increased rates of upwelling are determined to be the main cause. Within a divergent cyclonic gyre, increased upwelling into the surface layer arises from intensification of the gyre flow. For the latter, in turn, the recent more positive phase of the Southern Annular Mode may be causative. This has brought a recent intensification of the westerly winds and a more southern course. Such conditions could also enhance the flow and transport of the Weddell Gyre, whose northern limb is part of the west wind drift.

We believe that the increase of silicate in the bottom water, as also observed on the Prime Meridian (Van Heuven et al., 2014), indirectly stems from the same changes in the climate system. The composition (i.e. the mixing fractions) of the water masses that produce the

WSBW has changed: The share of WDW has grown at the expense of the surface water component. Interestingly, this has most probably occurred via the properties of the surface water: Since the upwelling of WDW into the surface water has increased, the composition of the surface water has changed due to a higher contribution of upwelled WDW. Finally, this has probably led to a WSBW variant with overall more WDW as compared to pure, ventilated surface water.

We have systematically examined the nitrite distribution in the Weddell Sea. Nitrite is commonly known to be a short-lived species, which means that it generally only occurs in significant amounts in the surface layer. We found significant non-zero nitrite concentrations all through the water column in the western Weddell Sea. Additionally, main hydrographic features like the thin WSBW layer on the western continental slope had their own nitrite signature. And even in the WSBW on the sea floor of the gyre interior, detectable nitrite concentrations were found. This obviously challenges the asserted short life time of nitrite, or what we see here is a characteristic typical to the cold waters of the Weddell Sea.

Acknowledgments

This work was supported through EU project CARBOCHANGE ‘Changes in carbon uptake and emissions by oceans in a changing climate’, which received funding from the European Community’s Seventh Framework Programme under grant agreement no. 264879. We gratefully acknowledge the dedicated support of crew and participants in the collection of the data used in this study, with specific mention of the efforts of Evaline van Weerlee. We dedicate this work to the late Eberhard Fahrbach, who was chief scientist on all cruises reported here.

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Supplementary Material

Contour plots for each of the five cruises, for each of the six discussed parameters nitrate, nitrite (only 2011), phosphate, silicate, salinity and potential temperature.