Temporal variations and trends of CFC11 and CFC12 surface-water saturations in Antarctic marginal seas: Results of a regional ocean circulation model

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1. Introduction

Ocean tracer observations are a powerful tool to understand the formation and spreading of water masses. Sampling for the chlorofluorocarbons CFC11 and CFC12 has become a routine on many physical oceanography cruises, resulting in a large number of observations, in particular since the WOCE period (Orsi et al., 1999, Orsi et al. (1999), Orsi et al. (1999), Meredith et al. (2001), Smethie Huhn et al. (2008b), Hall et al. (2002), Waugh et al. (2002, 2003), Huhn et al. (2008b)), Rhein et al. (2002), Kieke et al. (2006), Roether (1996), Huhn et al. (2008b), Hall et al. (2002), Waugh et al. (2002, 2003), Huhn et al. (2008b)).

Compared to the “classical” tracers, like oxygen and nutrients, anthropogenic CFC11 and CFC12 have the advantage to be chemically inert. CFCs enter the ocean by gas exchange across the ocean–atmosphere interface. Since their first appearance in the 1930s and up to around the turn of the millennium (Walker et al., 2000), the atmospheric concentrations increased (Fig. 13a), which is reflected in the temporal evolution of their concentrations in the ocean. This transient signal allows one to derive for tracer-carrying water masses:

- tracer ages, for example, Weiss et al. (1985), Thiele and Sarmiento (1990), Doney et al. (1997),
- age/transit time distributions (TTD), for example, Beining and Roether (1996), Hall et al. (2002), Waugh et al. (2002, 2003), Huhn et al. (2008b),
- formation and subduction rates, for example, Broecker et al. (1999), Orsi et al. (1999), Meredith et al. (2001), Smethie and Fine (2001), Rhein et al. (2002), Kieke et al. (2006).

Table 1 lists observed mixed layer saturations in high latitudes, where the CFC saturation is defined as the ratio of the actual concentration to the concentration in equilibrium with the
atmospheric CFC partial pressure. For deeper waters, similarly, one uses the term “apparent saturation”, the reference concentration being the concurrent equilibrium concentration at the ocean surface at the observed temperature and salinity. This saturation is termed apparent, since it ignores the fact that, when the waters actually descended from the mixed layer, the equilibrium concentration was lower than the concurrent one. Consequently, the apparent saturation is lower than the actual.

On the microscopic scale, CFC uptake occurs by diffusion through the oceanic skin layer on top of the mixed layer. The process is rather slow (equilibration time scale for a 100-m deep mixed layer is on the order of one month) so that the actual CFC uptake is controlled by mixed layer processes, essentially the exchange between the mixed layer and deeper layers (mixed layer entrainment/detrainment). The resulting undersaturation (Table 1) defines the air–water CFC gradient, to which the CFC uptake is proportional. Consequently, the apparent saturation is lower than the actual.

In the Southern Ocean, the interaction with sea ice, the ice shelves, and the atmosphere transforms local water masses into deep and bottom waters. On broad continental shelves, the accumulation of High Salinity Shelf Water (HSSW), due to brine release by sea ice formation, initiates two known mixing processes, namely:

- The Foldvik- or ISW-process (Foldvik et al., 1985): HSSW flows into ice shelf caverns where it is modified to Ice Shelf Water (ISW) due to the interaction with the ice shelf base.
- The Foster and Carmack (1976) process: Locally formed HSSW mixes with pycnocline waters penetrating onto the continental shelf.

Both mixing products descend along the continental slope under entrainment of ambient water masses to form deep or bottom water, depending on the entrainment rate.

During the transition from winter to summer, melting sea ice forms a seasonal halocline at 20–50 m depth (Carmack, 1974). The Antarctic Surface Water (ASW) above has temperatures and salinities ranging from −1.8 to 2.0 °C and from 33.0 to 34.3, respectively. The deeper layer, called Winter Water (WW) (Carmack, 1974), maintains the characteristics of the Winter Mixed Layer (WML) with temperatures near the surface freezing point.

Since the beginning of CFC observations in the Southern Ocean marginal seas in 1985 (Mensch et al., 1996), observations, which have primarily been collected during the austral summer, remain sparse in space and time. Therefore, it has been common to assume a time-invariant saturation on the basis of the available data (Table 1).

Existing CFC observations in surface waters are far from resolving the seasonal to interannual variability (Section 3). Thus,

Table 1
Observed CFC saturations in the ocean mixed layer.

<table>
<thead>
<tr>
<th>Region year</th>
<th>Saturation (%)</th>
<th>Source</th>
<th>Abbr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shelf water mass at Antarctic’s Periphery</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unspecified</td>
<td>40–60</td>
<td>Orsi et al. (2001)</td>
<td></td>
</tr>
<tr>
<td>Ross Sea</td>
<td>1984 CFC11: 64</td>
<td>Trumbore et al. (1991) and Smethie and Jacobs (2005)</td>
<td>R:1</td>
</tr>
<tr>
<td></td>
<td>1994 60–70/90</td>
<td>Orsi et al. (2002)</td>
<td>R:3</td>
</tr>
<tr>
<td></td>
<td>2000 CFC11: 84</td>
<td>Smethie and Jacobs (2005)</td>
<td>R:4</td>
</tr>
<tr>
<td>Wilkes Land</td>
<td>1994 70</td>
<td>Orsi et al. (2002)</td>
<td>R:1</td>
</tr>
<tr>
<td>Amery Ice Shelf, Prydz Bay</td>
<td>1994 70</td>
<td>Orsi et al. (2002) and Haine et al. (1998)</td>
<td>A:1</td>
</tr>
<tr>
<td>Central Weddell Sea</td>
<td>1987 90</td>
<td>Mensch et al. (1996)</td>
<td>W:2</td>
</tr>
<tr>
<td>Western Weddell Sea</td>
<td>1992 55–85</td>
<td>Mensch et al. (2000)</td>
<td>W:1</td>
</tr>
<tr>
<td></td>
<td>2004 68–70</td>
<td>Huhn et al. (2008a)</td>
<td>W:5</td>
</tr>
<tr>
<td>Southern Weddell Sea, in front of the Filchner Ice Shelf</td>
<td>1985 85</td>
<td>Mensch et al. (1996)</td>
<td>F:1</td>
</tr>
<tr>
<td></td>
<td>1987 65</td>
<td>Mensch et al. (1996)</td>
<td>F:2</td>
</tr>
<tr>
<td></td>
<td>1987 70–75</td>
<td>Schlosser et al. (1991)</td>
<td>F:3</td>
</tr>
<tr>
<td></td>
<td>1993 85–90</td>
<td>Gammelsrød et al. (1994)</td>
<td>F:4</td>
</tr>
<tr>
<td>Labrador Sea (Northern hemisphere)</td>
<td>1986 60</td>
<td>Wallace and Lazier (1988)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1997 CFC11: 90 ± 8</td>
<td>Azetsu-Scott et al. (2005)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1997 CFC12: 95 ± 9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The abbreviations of the last column are for reference further below. Separately reported values for CFC11 and CFC12 are indicated.
we have to use a regional ocean circulation model (Section 2) to obtain more detailed information concerning the oceanic CFC saturation. The CFC input function can be expressed as a product of the unknown surface saturation together with the well-known atmospheric concentration history (Walker et al., 2000) and solubility (Warner and Weiss, 1985). The model validation follows in Section 4, which includes a detailed description of the available observed surface-water CFC saturations (Section 4.2) and the simulated CFC surface saturation distribution (Section 4.3). The strength of seasonal saturation cycles and long-term trends in the presence of sea ice are addressed in Section 5. We analyze the processes that control the CFC surface saturations and present correlations and multi-linear regression analysis between a variety of parameters and the CFC surface saturations to confirm our findings and to show the prediction capability of the CFC surface saturation cycle (Section 6.1). The discussion includes the effects of a time-dependent versus an invariant saturation on bottom/deep water formation rates based on CFC inventories (Section 6.2), and the paper ends with concluding remarks (Section 7).

2. The model

Our model is the regional ocean circulation model BRIOS-1.0, a version of the z-coordinate primitive equation model SPEM (Haidvogel et al., 1991), adapted to the Southern Ocean by adding the major ice shelf caves and their interaction with the ocean (Beckmann et al., 1999). The domain comprises the circumpolar ocean between 50°S and 82°S, has a resolution of 1.5° × 1.5 cosφ in the Atlantic Sector, which increases gradually to 6.75° × 1.5 cosφ outside the Atlantic, and has 24 terrain-following vertical coordinates to better represent both mixed layer and wind-induced, near-surface mixing.

The parameterization of vertical mixing in the Southern Ocean is critical for a realistic representation of the observed hydrographic structure (Timmermann and Losch, 2005; Timmermann and Beckmann, 2004; Beckmann et al., 1999) and certainly influences the uptake of tracers, as shown by Doney and Jenkins (1988) and Haine and Richards (1995). The vertical viscosity and diffusivity are computed as Richardson-number-dependent functions according to Pacanowski and Philander (1981). An explicit scheme was employed for vertical diffusivity, which is the most critical value as sensitivity studies of initial parameters revealed. The weak stratification in the salinity-dominated regime reacts very sensitively to large vertical diffusivities, which unrealistically homogenize rapidly the Weddell Sea down to 2000 m depth. Therefore, the maximum diffusivity is κ = 0.01 m² s⁻¹ in case of small or negative Richardson numbers. Under the assumption of a continuous forcing, this maximum vertical diffusivity is analogous to convective processes, which homogenize within a day a water column of 30 m thickness. This is a reasonable assumption for a grid size of hundreds to thousands kilometers.

The used sea ice concentration climatology (A) agrees on the large scale reasonably well with satellite and ULS data (Timmermann, 2000); details of the coupled sea ice-ocean model version are described by Timmermann et al. (2002).

The tracer input is implemented as a flux boundary condition according to Asher and Wanninkhof (1998). It is controlled by the concentration gradient across the air–sea interface, with the wind velocity modulating the flux rate (Wanninkhof, 1992). Since sea ice prevents gas exchange, the flux is reduced by the grid box fraction covered with ice (A) according to England et al. (1994). The gas exchange is obtained as

$$F_C = \frac{S_{\text{eq}} - S}{A} (1 - A) \frac{u^2}{Sc},$$

where $k_0$ is the piston velocity—derived from bomb-produced radiocarbon invasion rates into the ocean and, hence, includes implicitly the Schmidt number for $^{14}$C according to England et al. (1994), $p_{\text{atm}}$ the temporal evolution of the atmospheric concentration (Walker et al., 2000), $s_r$ the solubility (Warner and Weiss, 1985), $c_{\text{eq}}$ the equilibrium concentration, $S$ the surface concentration, and Sc the Schmidt number (Zheng et al., 1998). The wind influence is considered by using a computed spatial seasonal cycle of squared winds ($u_{10}^2$), which represents a climatological mean state. In the northern relaxation zone, the subsurface CFC concentrations are nudged towards zero, considering that the water masses that flow towards the deep and bottom water formation sites have negligible CFC concentrations (Roether et al., 1993). Further details about chlorofluorocarbon boundary conditions and CFC simulation results are found in Rodehacke et al. (2007).

The saturation in each grid box is obtained as the ratio of the modeled concentration driven by the flux boundary condition (Eq. (1)) and the model result in which the ocean surface concentration is held at a solubility equilibrium, i.e.,

$$c(t) = \frac{c_0}{\text{atm}} = \frac{s_r}{\text{atm}} = \frac{100}{\text{atm}} (\text{solubility}) + \frac{100}{\text{atm}} (\text{atm saturated}).$$

This boundary condition implies a nearly infinite gas flux when a surface grid box is under- or oversaturated. To ensure identical conditions for all tracers regardless of their boundary condition, we performed all tracer simulations simultaneously.

3. Observed temporal evolution of CFC11 saturations

Before we validate the model simulations against observations, we inspect two regions, where several cruises measured CFCs. One is located around the South Orkney Island northeast of the tip of the Antarctic Peninsula and the other along the Greenwich Meridian near Maud Rise (Fig. 1).

Five cruises (ANT X/4, ANT XIII/4, ANT XV/4, DOVETAII, and M11/5) operated around the South Orkney Islands between 1990 and 1998 in different months (see Table 2 for further details about the cruises). Under the assumption that a long-term trend does not exist in the data set, the monthly dependence would illustrate the seasonal cycle of the saturation in this region. At the beginning of fall (March, M11/5) the saturations are highest because no sea ice has hampered the gas exchange and a reduced saturation concentration during the warm summer allows to reach the equilibrium concentration. With the beginning of winter the decreasing temperature shifts the equilibrium to higher concentrations which causes an undersaturation (May, ANT XV/4). The northward progression of the sea ice edge reduces the gas exchange and maintains decreasing saturations during winter (June, ANT XIII/4 — August, ANT X/4). The spring melting of sea ice fosters a higher gas flux which reduces the undersaturation (September, DOVETAII). However, we neglected this fact that the sea ice edge and concentration both undergo quasi-cyclic changes known as the
Southern Annular Mode (Lefebvre and Goose, 2005; Hall and Visbeck, 2002; Yuan, 2001). For example, during DOVETAIL the sea ice extent was higher than ours the average state representing sea ice concentrations. In addition, the spatial distribution of the observations is different for each cruise with M11/5 not representing values south of the South Scotia Confluence. If we would neglect M11/5, a linear trend of +1.5%/year (all −0.99%/year) in the saturations would be detected.

Fig. 1. Observed CFC11 saturations in the upper 55 m of the water column around the South Orkney Islands (upper row) and along the Greenwich Meridian above Maud Rise (lower row). The first column shows the saturations against month, the second against time/year, and the last depicts the spatial distribution on a longitude/latitude plot. The large circle represents the mean of each cruise, which are connected by an dashed line. Note the different saturation scale for both locations. In the lower row (not shown for clarity in the upper row), also the corresponding simulated saturations are presented as gray shaded symbols and the corresponding means are connected by a dotted line. (For cruise details see Table 2.)
At the Greenwich Meridian section, near Maud Rise, three cruises between 1992 and 1998 (ANT X/4, ANT XII/3, ANT XIV/4) indicate a slight long-term trend (0.6%/year), but as seen for the region around the South Orkney Islands, the length of the period might be probably too short. The presentation of saturations vs. months shows a clear decreasing trend during winter between May and July, however, the sea ice concentration in the region was exceptionally high in 1992 (ANT X/4), which might have caused an unusual strong undersaturation. Hence, the strong seasonal signal as well as the long-term trend might be exaggerated.

The temporal and spatial coverage of the data is sparse and the definition of regional boundaries, which include even different oceanic regimes as in the case of the South Orkney Islands, certainly affects the temporal signature. If we demand comparable conditions between the cruises, like similar sea ice concentrations, the data base shrinks substantially. Currently, observations of CFC surface concentrations in the (Atlantic sector of the) Southern Ocean are far from resolving, in particular long-term, temporal trends. Therefore only numerical simulations in concert with a relentlessly comparison between observations and simulations yield information about the temporal evolution of saturations in the marginal seas around Antarctica. Since saturation trends and seasonal cycles cannot be validated sufficiently, the model/observation comparison has to rely on the existing data and will be described after the validation of the dynamical model.

4. Model validation

The validation of the dynamical model setup is described by Beckmann et al. (1999) and is partly recapitulated here. The flow field reproduces the known circulation features: the eastward flowing Antarctic Circumpolar Current (ACC), the cyclonic Weddell, Ross and Kerguelen Gyres as well as the Antarctic Coastal Current, where observed rates agree with the simulated transports of both Weddell Gyre cells. Simulated annual mean fields of temperature and salinity (Beckmann et al., 1999, Fig. 9a and b) along the Joinville Island–Cap Norvegia section reproduce well the observed doming of the isolines (Fahrbach et al., 1994, Fig. 7a and b).

A unique feature of this model is the integration of major ice shelf cavities including the ocean–shelf ice interaction. Each cavern has its own signature in the Θ–S space (Rodehacke et al., 2007, Fig. 4). Furthermore, the caverns are a source of relatively cold and fresh water masses, which change, in particular, the properties of the near-surface layers. These are distinctly fresher (up to ~0.22) and cooler (up to ~1.5 °C) (Beckmann et al., 1999, Fig. 13 a and b). Since the water column of the western Weddell Sea is stabilized by these lighter water masses, convection is reduced, which conserves the temperature and salinity of deep water masses.

As the Θ–S diagram shows, the model reproduces the linear mixing between ISW and Weddell Deep Water (WSDW). On the continental shelf in front of Filchner–Ronne Ice Shelf (FRIS) observed and simulated hydrographic properties and helium/lethal neon saturations, which are strongly determined by the addition of basal melt due to ocean–ice shelf interaction, indicate that the model reproduces the general hydrographic structure and the ISW outflow. Furthermore, the analysis highlights the importance of the ocean–ice shelf interaction but also suggests that model resolution might be too coarse to prevent warm and salty water masses from penetrating onto the continental shelf (Rodehacke et al., 2006). Nevertheless, a comprehensive treatment of the sub-ice shelf environment and the related freshwater fluxes seems to be important for an adequate representation of observed local and large-scale hydrographic conditions (Hellmer, 2004).

For the model setup used here, the spread of CFC-carrying water masses indicates the paths of newly formed deep and bottom water (Rodehacke et al., 2007). In agreement with observations (e.g. Baines and Condie, 1998), the model reproduces the main deep and bottom water formation sites in, e.g., the Ross Sea and the southwestern Weddell Sea (Rodehacke et al., 2007, Fig. 8). These areas are located on the continental shelves with depths commonly shallower than 500 m. The upper 100 m of the water column are therefore represented by nine (seven) layers for a depth of 500 m (1000 m).

Along two sections following the Greenwich Meridian (Rodehacke et al., 2007, Fig. 10) and the WOCE S4R from Joinville Island to Cap Norvegia (Rodehacke et al., 2007, Fig. 9), vertical simulated CFC distributions show a well ventilated upper mixed layer, which is separated from lower water masses by a sharp concentration gradient. The simulated gradient seems to be stronger than the CFC observations suggest. Along the coast, wind induced downward Ekman pumping deepens the mixed layer, which is in accordance with observations. In addition, CFC-inventories along the
Greenwich Meridian (Rodehacke et al., 2007, Section 6.1), which are dominated by mixed layer concentrations, agree reasonably well with observations from the years 1992, 1996, and 1998 (Rodehacke et al., 2007, Section 6.1). However, the ventilation of water masses below $\approx 1580$ m is underestimated, the model does not reproduce subsurface cores clearly separated from the surface mixed layer, and the cores are, in general, too wide probably caused by an insufficient horizontal resolution (Rodehacke et al., 2007). The latter agrees with the results from models of similar resolution (e.g. Fichefet and Goosse, 1999; Doney and Hecht, 2001; Dutay et al., 2002).

Profiles of CFC concentrations at several locations north of the Weddell Gyre (Rodehacke et al., 2007, Fig. 13) show that the vertical structure agrees reasonable well with observations. However, the observed CFC concentration at profile #7 in the center of Drake Passage penetrates unusually deep $\approx 750$ m, which seems to be associated with the Polar Front (Roether et al., 1993). The model does not resolve the frontal system and therefore cannot reproduce this feature (Rodehacke et al., 2007).

4.1. Mixed layer depth along the Greenwich Meridian

Since the temporal evolution of the mixed layer depth (MLD) influences the CFC uptake and saturation (Table 7), we validate simulated MLDs against observed ones. The comparison is restricted to the repeatedly sampled Greenwich Meridian, which allows us to infer the deduced MLD uncertainty. Beginning at the surface, a density increase by 1% defines the pycnocline, which is the base of the mixed layer.

The observed MLD (Fig. 2) generally amounts to 50–200 m and reaches the sea floor south of Maud Rise (65 S). A MLD equal to the bottom depth does not necessarily imply a homogenized water column. Since both cruises, ANT XIII/3 and ANT XV/4, occupied the Greenwich Meridian in May/June, their differences might be related to natural variability. In addition, neighboring observations also show distinct depth variability, like during ANT XIII/3, in the range of 75–140 m at 59 S or during ANT XV/4 ranging from 600 to 4800 m at 67 S. The latter might be attributed to the local conditions above Maud Rise, where the interaction between the complex flow regime and topography lifts water masses to the surface as simulations (Beckmann et al., 2001) and the observed upwelling of subsurface water masses (Muench et al., 2001) reveal.

In the north the simulated MLD (Fig. 2) ranges from 45 to 180 m, which is beneath the upper two model layers of enhanced background diffusivity ($\chi_{\text{back}}^2$, Section 2). The sequence of the MLD against latitude from February to August reveals that the depths are nearly temporally invariant from February to April when sea ice is absent or melting. With the beginning of winter sea ice formation releases salt into the surface layer, which decreases the density gradient between surface and deeper layers and thus increases the MLD. Since the stratification is weak, the mixed layer can reach the bottom at the southern edge of the section.

The simulation agrees with the observed mixed layer depths north of 54 S and south of 60 S. Although in the south the model tends to underestimate the MLD, the natural variability along the complete section is larger than the mismatch. The simulated MLD local minimum around 55 S, while the observed MLDs increase towards north, is only manifest in the logarithmic depiction. The observed (ANT X/4, ANT XIII/3, and ANT XV/4) and simulated surface temperatures and surface salinities coincide along the Greenwich Meridian, except for salinity between 54 S and 60 S. Here, the simulated surface salinities decrease smoothly towards north while the observed salinities stay nearly constant up to 56 S where they decrease abruptly by 0.1–0.15 (ANT XIII/3, ANT XV/4). This is probably related to the front which separates the so-called “cold regime” and “warm regime” (Gordon and Huber, 1984; Schröder and Fahrbach, 1999).

The difference between observed and simulated surface salinity is strongly related to the coarse model resolution, which does not resolve the frontal systems. If we would replace the simulated

![Fig. 2](image-url) Observed and simulated mixed layer depth along the Greenwich Meridian (logarithmic ordinate). Symbols represent deduced values from observed bottle data for the listed cruises (see also Table 2), while simulated values for different months are represented by lines for a sequence of several years. The latter causes for example slightly different depths in July around 66.5 S. If the observed mixed layer depth equals the depth of the deepest observation, its symbol is combined with a gray star. For clarity, observations are grouped in bands of 1. The model topography is added as gray thick line and the model layers south of 71 S are located underneath the Ekström Ice Shelf. The seamount Maud Rise is marked.
surface salinities with observations, the MLD difference between 54 S and 60 S would vanish completely, indicating an acceptable representation of the subsurface density stratification in our model. The impact of the mixed layer difference on the CFC saturation along the Greenwich Meridian is discussed below (cf. Fig. 7).

4.2. Comparison of modeled and observed surface-layer saturations

Validating the modeled CFC surface-water saturations against observations is a crucial step in our analysis. One has to consider that the model is driven by a recurring annual cycle, so that the forcing does not include the observed extremes of, for example, sea ice concentration or wind speed. Furthermore, since we also compare observations at a single point with simulated, averaged values of a model grid box, we cannot expect to obtain a perfect match. In fact, the modeled CFC11 saturations (Fig. 3) appear systematically high for the observed lower saturations and fall short of the supersaturations the model grid box, we cannot expect to obtain a perfect match. Furthermore, since we also compare observations at a single point with simulated, averaged values of a model grid box, we cannot expect to obtain a perfect match. In fact, the modeled CFC11 saturations (Fig. 3) appear systematically high for the observed lower saturations and fall short of the supersaturations of up to 110% (cruise M11/5). To assess this situation, we address the distribution of the model-data discrepancies in the model’s Weddell Sea sector. We deduce an objective criterion for the inherent or natural CFC saturation spread in the upper surface layer, based on the maximum differences among the observed CFC11 saturations at each profile down to 55 m (Fig. 4). We also check the differences in sea ice concentration between observations and simulation. The comparison is summarized in Section 4.4.

Under the most valid assumption that the upper 55 m of the water column are well mixed, the CFC variability of observed CFC saturations in the upper 55 m represents the natural spread of saturations. We interpret this quantity as natural uncertainty and call it “spread”, which represents the “error bar” of the observed saturation within a homogenized water column during a cast. This variability or spread is much larger than the accuracy of measurement and represents the allowed/acceptable mismatch between single observation and simulation.

4.2.1. CFC11 saturation spread ranges and model-data biases

For the model’s Weddell Sea sector, the spatial distribution of CFC11 saturation differences between observations and simulation are shown in Fig. 4. If more than one observation exists at any position, all differences between these observations and the simulated values were considered. In general, we take for each single observation the spatially nearest simulated value of the same period.

Along the Greenwich Meridian, the simulated CFC11 saturations deviate by up to +20% absolute (observed saturation minus simulated saturation \( S_{\text{obs}} - S_{\text{sim}} \)); Figs. 4 and 7) from the corresponding observed values for all cruises (ANT X/4, ANT XIII/4, ANT XV/4, and M11/5, Table 2) which took place between February and June. The extreme mismatches between −48% and +16% absolute (observation minus simulation) are predominantly located at the dynamically active edge of the Weddell Gyre (coastal current, polar front, and sea ice edge). The maximum CFC11 spread along the meridian is less than 5% absolute and reaches 18% absolute only within the coastal current. East of the Greenwich Meridian (ANT XIII/4, M11/5, and SO4i), the differences are mostly lower than +10% absolute and do not exceed +20% absolute, while the spread reaches values of up to 6% absolute. In the sea-ice-free Drake Passage (M11/5) the saturation differences are between −22% and +16% absolute with a spread below 12% absolute, whereby large differences and high spread do not always coincide. In the southern Weddell Sea (ANT XII/3), the spread is below 16% while the differences are between −23% and +37% absolute. Here, shallower observations tend to show a better agreement with the simulation. A vast region of large discrepancies and high spreads is clustered east of the tip of the Antarctic Peninsula (Fig. 4, 57 S to 66 S, 32 W to 60 W). The saturation differences range from −48% to +16% absolute whereas the spread reaches values of up to 30% absolute. Evidently, the model-data differences consistently exceed the data spreads according to our criterion.

In general, the CFC saturation spread in the upper 55 m is 10%–20% absolute (Table 2). A higher spread often occurs in profiles for which the observed temperature and salinity spread is also high. This indicates that the assumption of a homogeneous CFC concentration in the upper 55 m might be invalid at some locations because of distinct vertical temperature and salinity gradients. The gradients might be caused by melting sea ice,
which freshens the upper water column and splits the Winter Mixed Layer (WML) into Antarctic Surface Water (ASW) and WW (Carmack, 1974). Since WW has no contact with the atmosphere, a distinct CFC undersaturation, which has developed during the preceding winter, is preserved. In contrast, disequilibrium within the ASW is reduced by gas exchange across the ocean–atmosphere interface and by solar heating, which reduces the equilibrium concentration. Therefore, shallower samples have a higher saturation than the deeper ones. However, not all profiles with a high CFC saturation spread are related to an enhanced spread in temperature and/or salinity nor does a high temperature and/or salinity spread cause an increased saturation spread. Thus, a clear relationship between CFC saturation and temperature or salinity spread does not exist.

In the simulations, the maximum spread of the CFC concentrations, computed for the period of observations, is only 2.5%, and the corresponding temperature and salinity spreads are 0.24 and 0.047, respectively (Table 2). Furthermore, the observed strong stratification is not reproduced, in particular in the deep basins. This might be caused by the vertical extension of the two uppermost model layers, set to 0.46% and 0.59% of the entire water column. Hence, for a depth of 5500 m in the central basins the two uppermost layers are 25 and 32 m thick. This coarse vertical resolution together with elevated mixing in shallow layers, due to the representation of wind-induced turbulence, causes smaller spreads compared to the observations.

The discrepancy between observation and simulation is generally higher for deeper samples, which are potentially located in the lower-saturated WW. Furthermore, if the upper ocean is highly stratified and if observations are only available at the standard depth of 50 m below the ASW, these observations may insufficiently represent the saturation at the ocean surface. Therefore, our comparison between simulation and observations, which for some cruises predominantly consisted of deeper observations, might be biased, which might partly explain the deviation between observation and simulation.

4.2.2. Bias in sea ice concentrations

To address the effects of sea ice concentration further, Fig. 5 shows model-data comparisons like in Fig. 3, but subdivided according to model-observation differences in sea ice concentration.

We use sea ice concentration differences one month prior to the observations to consider that the air–sea equilibration takes several weeks and the maximum simulated saturation occurs two months after the sea ice concentration minimum (Section 5.1). The grid size of the observed sea ice concentration data is 25 × 25 km. The accuracy of total sea ice concentration (\(\delta A\)) is approximately 5% (Cavalieri et al., 1996, updated 2005, update 2005), but might be lower when melt ponds exist, in view of approximately 15% accuracy in the Arctic during summer (Cavalieri et al., 1996, updated 2005, updated 2005).

The neglect of sea ice drift should introduce small errors. Strong sea ice concentration gradients are unlikely within large-scale sea ice fields, as sea ice and the upper surface waters flow nearly parallel (Kottmeier and Sellmann, 1996), and the rate of displacement is small. The observed mean sea ice drift velocity amounts to 0.2 cm/s = 5.2 km/month (Kottmeier and Sellmann, 1996), except within the coastal current where the velocity reaches 6 cm/s = 155 km/month, corresponding to a displacement of six grid cells in the sea ice concentration data set.

Selecting only data with sea ice discrepancies <15% (Fig. 5, upper left), the CFC saturation discrepancies range from +10% to −20%, with an average near −10%. A similar result is obtained for even more negative values of the sea ice discrepancy (Fig. 5, upper right). For more positive sea ice discrepancies (Fig. 5, lower right), however, the saturation discrepancies show a large scatter and average appreciable lower (approximately −20%). During the DOVETAIL cruise (1997, months 8–9) the observed sea ice concentration one month prior to sampling was up to 76% higher than in the simulation. Upstream, at the tip of the Antarctic Peninsula, the simulated sea ice cover vanishes earlier than observed, because the model air-temperatures are too high, amplifying sea ice melting and enabling an enhanced CFC uptake of the northward flowing water masses. This causes the simulated CFC saturations to be higher than
observed. On the other hand, if the observed sea ice concentration is lower, the corresponding observed saturations are sometimes distinctly higher than the simulated ones, for example in front of Filchner–Ronne Ice Shelf (FRIS) (ANT XII/3).

A higher simulated saturation for locations of higher sea ice concentrations seems to contradict our expectations (Fig. 5, upper right). This occurs predominate ly along the Greenwich Meridian south of the ACC (Fig. 6). One month prior to and at the time of the CFC observations the sea ice concentration is higher than observed (Fig. 7). Any sudden local sea ice melting and incipient CFC fluxes therefore can be excluded to account for the difference.

East of the Greenwich Meridian sea ice retreats early and completely during the summer. The region is characterized by the inflow of CFC enriched surface water masses from the year-round ice-free ACC. Since the model does not resolve the frontal system which clearly separates the surface layers of the Weddell Gyre from the ACC, higher-saturated surface water masses can penetrate into the gyre at its northern edge. In addition, a tongue of elevated CFC saturated surface waters extends toward the Greenwich Meridian along the Antarctic coast, as it is even seen in a mean field (Fig. 9). In the coastal current the saturation difference increases by some 20% and changes sign under still high sea ice concentration differences (Fig. 7). Therefore, in the model the inflow of higher-saturated surface waters compensates for the expected lower CFC saturation under a stronger than observed sea ice cover. This clearly shows the influence of local differences in the CFC-uptake controlling parameter on the difference between observed and simulated saturation and highlights the need to capture adequately the contribution of tracers remotely exchanged between atmosphere and ocean.

A final item are the model/data CFC saturation differences as a function of season (Fig. 8). Beyond appreciable scatter, one finds a trend of lowest discrepancies in austral summer (February) and generally higher ones at the end of winter (August/September), differing by close to 25%. All large differences are related to cruises operating in the northwestern Weddell Sea near the sea ice edge (ANT X/4 end of July, ANT XIII/4 end of May, ANT XV/4 begin of April, DOVETAIL) where the modeled sea ice concentration is too low because sea ice melts too early (Timmermann et al., 2002).

4.3. Simulated spatial distribution of the CFC surface saturation

The simulated mean saturations of the surface layer (Fig. 9) are calculated for the period covered by all measurements in Table 2 and represent predominantly summer conditions. A comparison
with the observed distribution is given by Rodehacke et al. (2007, Fig. 5).

In parts of the Antarctic Circumpolar Current, the mixed layer is saturated by up to 103% (Fig. 9), caused by temperature-related processes (Section 6.1), while in a small band around Antarctica the saturation drops below 95%, emphasizing the retreat of the winter sea ice. Starting at the Greenwich Meridian, a tongue of higher-saturated waters spreads westwards to the southern Weddell Sea. However, low saturations exist from the Filchner–Ronne Ice Shelf to the Larsen Ice Shelf (60%), extending into the central Weddell Sea, in front of the Ross Ice Shelf (70–80%), and in the ice shelf caverns (< 55%) (Section 5.3). In general, the saturation decreases towards Antarctica, and regions covered with perennial sea ice are characterized by lower saturations.

4.4. Summary of the comparison between observed and simulated CFC saturations

The comparison reveals certain biases between observed and simulated saturations, superimposed on an appreciable scatter.
There appears to be a general bias of simulated saturations being too high by about 10% (Fig. 5, upper left and right; Fig. 4), with the exception of regions with low simulated sea ice concentration compared to the observations (Fig. 5, lower right). These regions appear to be particularly problematic. A seasonal trend also exists (Fig. 8), however, the related observations occurred at the northern tip of the Antarctic Peninsula known to have too high simulated saturations (Fig. 4). The orange spot northeast of the Antarctic Peninsula is strongly determined by the high density DOVETAIL observations (65 observations at this location, Table 2, compare Fig. 5, lower left). Sea ice appears to act as a principal control, modulating the ocean’s uptake of gases by suppressing the gas fluxes. Therefore, much of the biases and the scatter appear to be related to the sea-ice simulations. Since the model is forced with a recurring seasonal climatological cycle, differences between the actual and climatological sea ice concentration have to be expected.

The model uses as vertical coordinate the terrain-following s-coordinate. Therefore, layer thicknesses depend on water depth, resulting in a top-layer thickness of up to 25 m in the deep basins. The presence of enhanced wind-induced turbulence homogenizes the concentrations within the two upper-most model layers. This and the inadequate vertical resolution in the deep basins cause an insufficient representation of the separation of the WML into ASW and WW during summer. However, the slightly underestimated mixed layer depth along the Greenwich Meridian (Latitude range 54°S and 60°S, Fig. 2) does not cause the differences between the
observed and simulated surface saturation. Furthermore, the upper 100 m are resolved by nine layers in the deep/bottom water formation sites on the continental shelves (depth ≈ 500 m) with a top layer thickness of 0.46 m.

Since for some cruises only observations in the WW layer are available, which are generally lower in saturation than for the top ASW layer, our comparison might be biased by too low reference values. If we (a) restrict the comparison to the upper 20 m, (b) consider differences in sea ice concentration before and at the time of the measurements, and (c) apply an uncertainty of 10–20%, derived from the CFC saturation spread in the upper 55 m (Fig. 4), we obtain a better match between observation and simulation and a reduced range of differences. However, the observed saturations (upper 55 m) at section cross-overs show typical differences of 5–10% absolute in open-ocean regions and 10–20% absolute in regions covered with perennial sea ice. This strong variability appears to be controlled by the actual environmental conditions before and during the field measurements.

The observed state might be better represented with a higher vertical and horizontal resolution, a more sophisticated scheme for the mixed layer, and the use of the sea ice extent based on satellite observations. Further sources for errors are the neglect of extremes in the forcing fields and the comparison of "noisy" point measurements with spatially averaged simulated values. When interpreting the simulations, addressed in the following, one has to keep in mind the limitations and uncertainties of the observations and the model as the model/data comparison revealed. However, the comparison showed that the simulations agree with reality to an acceptable degree.

5. Seasonal and long-term evolution of the simulated CFC surface saturation

We evaluate the seasonal and long-term temporal evolution of the simulated saturations in the vicinity of the main deep and bottom water formation sites of the Southern Ocean, located in the Ross Sea, Prydz Bay in front of the Amery Ice Shelf (AIS), and southwestern Weddell Sea (Baines and Condie, 1998; Rodehacke et al., 2006, 2007).

5.1. Seasonal cycle of the CFC saturations

For the all-season ice-free areas, the simulated surface saturation shows a distinct seasonal cycle with values between 87% and 105%. Triggered by sea ice formation, the continental shelf in front of FRIS (hereafter called FRIS Shelf; areas are defined in Fig. 10) is homogenized by winter convection, primarily in June and July. This process transports surface waters to greater depth and mixes them with ambient water masses of lower concentration and saturation. On the broad continental shelves deep convection initializes the formation of HSSW, which contributes to the formation of deep and bottom water and causes reduced sub-surface saturations compared to surface values.

Highest amplitudes of the seasonal saturation cycle exist in front of FRIS and RIS (Table 3, Fig. 11a, d). For the FRIS Shelf, the CFC11 saturation varies at the surface and in the whole water represents by 28% and 2% (Table 3), respectively (simulated surface values are those of the top layer, while whole water column represents a grid box volume-weighted top-to-bottom average). In the Ross Sea, the corresponding values amount to 66% and 2%, respectively. The high surface value is due to the strong seasonal cycle of sea ice concentration combined with convection, which entrains low-saturated water masses into the surface layer. The maximum saturation overlaps in time with an increasing sea ice concentration that stops a further relaxation of the concentration disequilibrium (Fig. 11a–d). In general, the saturation reaches its maximum two month after the sea ice concentration minimum (Fig. 11a–d).

From September to November the surface layer and water column saturations in front of FRIS are virtually equal, because during winter water mass transformation homogenizes the water column (Fig. 11a). In front of RIS the surface layer values fall even below the water column mean (Fig. 11d), because low-saturated water masses, which flow out of the RIS cavern, are mixed into the surface layer. As will be discussed for the FRIS cavern below (Section 5.3), the saturation of water masses decreases while passing through the cavern with inflow at the bottom and outflow in the upper layers (Fig. 14). Since a high sea ice concentration in the southern Ross Sea during winter inhibits CFC uptake from the atmosphere, the flow of water masses from the RIS cavern into the surface layer outside reduces its saturation below the corresponding water column mean.
The seasonal evolution is different for the areas Weddell Sea I/II and Prydz Bay. A large fraction of the water column of Weddell Sea I/II is not directly ventilated and remains mostly stratified during the year. Here, a significant fraction of the water column is characterized by old and, hence, less saturated water masses. These are ventilated by slow vertical mixing either from regions of deep convection, like the FRIS Shelf, or from the Antarctic Coastal Current as described for the Weddell Gyre by Hoppema et al. (2001).

In the model, the Prydz Bay area is continuously flushed by the coastal current, which carries freshly ventilated waters from sources like the Ross Sea, Wilkes Land, and Adélie Coast (Rodehacke et al., 2006, 2007). Since sea ice retreats relatively early upstream of Prydz Bay, the surface layer comes relatively close to equilibrium during summer (Figs. 9 and 11c). Enhanced coastal Ekman pumping in the Indian Ocean, driven by katabatic winds, and winter convection triggered by sea ice formation both ventilate also deeper levels of the coastal current. However, the missing seasonal cycle in the deep water column and a negligible long-term trend (Section 5.2) indicate that a constant supply of older water masses overwhelms the surface influence and reduces the seasonal-cycle amplitude at depth.

The “total surface” saturation in Tables 3 and 4 (lower row) are the grid box volume weighted mean of either all ocean surface grid boxes (table column: surface) or all grid boxes from the surface to the bottom (table column: water column). In summer the high saturation of the total surface has three causes. (a) Since the sea ice retreats considerably during summer around Antarctica (e.g. Gloersen et al.,

Fig. 11. Seasonal cycle of the simulated CFC11 (magenta) and CFC12 (green) saturations for the surface (top model layer) and water column (a) in front of FRIS, (b) the Weddell Sea II, (c) Prydz Bay, and (d) the Ross Sea. For each region the upper panel shows the temporal evolution of the sea ice concentration. Note the different scales for sea ice concentration and saturation. Observations are depicted by vertical bars (range of values), where Ant XII/3 is in front of FRIS, representing its mean value and standard deviation (Table 2). The abbreviations for the other cruises are listed in Table 1. If values are outside of the time axis, they were adjusted by applying the simulated linear annual mean saturation increase (Table 4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
1992), the mean summer sea ice concentration is low. This permits an enhanced CFC uptake, in particular, in the transition zone between the year-long ice-free ACC and Antarctica’s margin. (b) For northern grid boxes the mixed layer reaches an equilibrium concentration in summer (Fig. 9), because stable summer stratification suppresses water mass exchange with lower-saturated deeper layers. (c) Since the volume ratio of the grid boxes at latitudes 50°S : 65°S : 70°S is 1.88 : 1.2 : 1, the northern higher-saturated boxes dominate the volume weighted mean.

Along the path of freshly ventilated water masses from the Filchner Trough to the South Sandwich Islands, the seasonal cycle is only pronounced near the deep and bottom water formation sites (Fig. 12), where also the saturation is highest. A detailed description of the spreading of CFC-containing, freshly ventilated

| Table 4 |
| Simulated mean CFC saturations $s_{CFC}$ at the surface for selected areas in January (summer) of the years 1990 and 1998. |

<table>
<thead>
<tr>
<th>Year</th>
<th>Area</th>
<th>$s_{CFC11}$ (%)</th>
<th>$\Delta s_{CFC11}$ (%/year)</th>
<th>$s_{CFC12}$ (%)</th>
<th>$\Delta s_{CFC12}$ (%/year)</th>
<th>$\Delta s_{CFC11}$ %</th>
<th>$\Delta s_{CFC12}$ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>FRIS cavern</td>
<td>23.7</td>
<td>1.4</td>
<td>23.7</td>
<td>1.2</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>FRIS shelf</td>
<td>50.2</td>
<td>0.9</td>
<td>49.3</td>
<td>0.7</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Weddell Sea I</td>
<td>66.0</td>
<td>0.5</td>
<td>65.2</td>
<td>0.4</td>
<td>5.4</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>Weddell Sea II</td>
<td>68.6</td>
<td>0.5</td>
<td>67.9</td>
<td>0.4</td>
<td>4.2</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>RIS cavern</td>
<td>22.2</td>
<td>0.6</td>
<td>22.1</td>
<td>0.6</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Ross Sea</td>
<td>63.6</td>
<td>0.1</td>
<td>62.6</td>
<td>0.1</td>
<td>–10.3</td>
<td>–9.9</td>
</tr>
<tr>
<td></td>
<td>Prydz Bay</td>
<td>79.0</td>
<td>0.1</td>
<td>78.2</td>
<td>0.1</td>
<td>–6.3</td>
<td>–5.9</td>
</tr>
<tr>
<td></td>
<td>Total surface</td>
<td>88.8</td>
<td>0.1</td>
<td>88.5</td>
<td>0.1</td>
<td>1.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

$\Delta s_{CFC}$ is the mean rate of change per year. The yearly mean saturation can be obtained by adding $s_{offset}$ $s_{CFC11}$ or $s_{offset}$ $s_{CFC12}$, respectively, to the January-1-saturations $s_{CFC}$. The offset is based on the year 1998; the temporal evolution of the offset is negligible for the period 1990–1998 (Fig. 11).

Fig. 12. Simulated path of freshly ventilated water masses and the seasonal saturation cycle in the Weddell Sea bottom layer in 1998. The upper panel shows the CFC11 saturation for each month in the model’s bottom layer (solid lines) and the corresponding depth according to the model topography (crosses connected by a dotted line; compare to lower right panel). The lower left panel depicts the seasonal amplitude (maximum–minimum) of the saturation along the path (original and smoothed with a 15-points moving average) and the standard deviations (see embedded legend). The lower right panel shows the distribution of CFC11 concentration in the bottom layer of the south/western Weddell Sea with depth contours 500, 1000, 2000, 3000, and 4000 m. In all panels numbers in gray squares represent positions along the path. LIS, Larsen Ice Shelf; So O, South Orkney Island; So S, South Sandwich Islands. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
waters is given by Rodehacke et al. (2007). Further downstream and down the continental slope (beyond position 10 in Fig. 12) the saturation drops. The enhanced seasonal cycle and the slightly elevated seasonal mean saturation between position 20 and 28 are related to the formation of water masses in front of LIS, which is confirmed by independent observations (Huhn et al., 2008a; Fahrbach et al., 1995; Weppernig et al., 1996). The seasonal cycle vanishes and the saturation settles to a constant value of about 35% as the flow reaches the northern tip of the peninsula and advances to the South Sandwich Islands.

5.2. Long-term evolution of the CFC saturation

The simulated saturations are rising steadily, apart from somewhat variable values prior to 1950 (Fig. 13). The near-exponential growth of the atmospheric concentrations after 1960 coincides with a reduced increase of the surface saturations, which grew again around 1978 when the atmospheric rate of increase became nearly linear. After 1990 (1995) the atmospheric CFC11 (CFC12) concentrations approached a constant level which induced even slightly higher saturation growth rates in the surface layer.

Early on, the CFC12 saturation exceeded that of CFC11 because CFC11 was released to the atmosphere several years later (1937 vs. 1946) (Walker et al., 2000) so that its relative growth rate was larger, but during the 1970s the differences vanished.

Saturation growth rates (Table 4) are high where surface concentrations are low, often related to a compact ice cover (FRIS and RIS caverns) or to high, year-round sea ice concentrations (FRIS Shelf; Fig. 11, Table 3) that impede air–sea exchange. Another factor might be the mixed layer entrainment that brings tracer-poor water to the surface. The latter reduces the concentration and saturation at the surface, both controlled by growing atmospheric tracer concentrations.

The comparison of the simulated surface saturations with observed ones (Table 1) reveals that in front of FRIS the latter are

![Figure 13](image-url)
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(slightly) higher than simulated. However, in 1985 the observed
sea ice concentration (Gloersen et al., 1992) was partly less than
the average sea ice concentration that drives our model, which
allowed exceptional high saturations of 85% (Mensch et al.,
1996) compared to simulated of approximately 50%. The observed
saturation in the central Weddell Sea is captured by the model
for both Weddell Sea I/II, although we compare point measure-
ments, which range from 65% to 90%, with simulated areal
means. The observed saturation of 35% in the Filchner Trough
(Schlosser et al., 1991) and the late summer surface CFC11
saturations in the Ross Sea of 72–95% in 2000/2001 (Rivaro et al.,
2004) also agree with our simulated values of 68–91% for the
period February-1999 to May-1999 (Table 4) even if we add the
deduced trend (Fig. 11d) of 0.1%/year. Additional summer saturations
(Table 1, Smethie and Jacobs, 2005) observed in the Ross Sea
range from 64% (CFC11) to 79% (CFC12) in January/February-1984
(February-1994: 74–79% and February/March-2000: 84–90%).
These values are reproduced by our simulated CFC11 and CFC12
saturations of 61–79% in January/February 1984, 78–80% in
February 1994, and (extrapolated from January 2000) 82–92% in
February/March 2000.

5.3. Saturation beneath the Filchner–Ronne Ice Shelf

Weddell Sea shelf water masses carry the CFC signal into the
FRIS cavern driven by the so-called “ice pump” (Lewis and Perkin,
1985). The CFC saturation and its seasonal cycle are largest near
the bottom indicating that the model inflow occurs mainly at
depth (Fig. 14b), which is in agreement with hydrographic
observations of Nicholls (1997a), Nicholls et al. (2001), and
Nicholls and Makinson (1998). The inflow mixes with water
masses of lower CFC concentration/saturation. At shallower depth
the reduced amplitude of the seasonal cycle’ and the lower
saturation both characterize an outflow which is a mixture of
different water masses formed at previous times with lower
saturations. The FRIS cavern shows the highest mean saturation
growth rate of 1.4%/year (Table 4), which even exceeds the
 corresponding seasonal cycle of 1% (min–max) absolute (Table 3).

6. Discussion

To understand the processes governing the simulated satura-
tions we investigate processes that can potentially influence the

Fig. 14. Temporal evolution of mean CFC11/12 saturation within FRIS; (a) long-term evolution (after 1980 the seasonal cycle is added), (b) higher resolved temporal
evolution CFC11 of surface, water column, and bottom layer saturations.
surface saturations. The analysis is completed by presenting correlations between 14 parameters and surface saturations as well as a multi-linear regression analysis for subsets of parameters. The capability to predict the surface saturation cycle is illustrated by utilizing SST, SSS, and sea ice concentration together with weights obtained from the multi-linear regression analysis. Ultimately, we show how a constant saturation instead of its temporal evolution can lead to incorrect results. We inspect exemplarily deep/bottom water formation rates from CFC inventories in the ventilated abyssal ocean.

6.1. CFC-saturation and its dependence on physical parameters

Wherever dense surface water masses sink and are replaced by low-concentrated and low-saturated sub-surface water masses, a surface saturation below the equilibrium is produced. Therefore, a low-saturated surface marks areas where deep and bottom water might be formed or intermediate water might be subducted.

Sea ice formation triggers convection and thus downward tracer transport along Antarctica’s periphery, causing the distinct mixed layer’s seasonal cycle of the saturation (e.g., Fig. 11). This might be amplified by a year-round Ekman transport in some coastal areas. The CFC’s solubility (Warner and Weiss, 1985) shows for low temperatures a strong temperature dependence, which shifts the equilibrium concentration and is believed to control the surface saturation in the temperate ocean.

6.1.1. Correlation between CFC surface saturations and environmental parameters

The CFC surface saturation is controlled by a complex interplay of several processes. Table 7 lists correlations between potentially relevant parameters and the simulated CFC surface saturation in the model. The parameter values that enter the analysis are based on calendar monthly means averaged over the 1998–2000 period (Table 5).

For a subset of the parameters, which are assumed to be linearly independent, a multi-linear regression analysis (von Storch and Zwiers, 2003) was performed to determine the order of the multiple parameters and the extent to which they can predict the simulated variability (Table 6). The single parameter of highest regression is first determined and then we add consecutively the parameter which causes the next strongest increase in regression (Fig. 15). Since we consider the combined effect of the most important parameters and a constant element, the order should be different to the one of decreasing correlations, because the latter describes the strength of the linear relation between the CFC saturation and a single parameter.

The correlations and regressions for the parameters, obtained for the areas illustrated in Fig. 10, are listed in Tables 6 and 7, respectively. For most regions SST, SSS, and mixed layer depth show highest regression coefficients (Table 7), and together with sea ice concentration they dominate the predictability of the seasonal cycle of surface saturation (Table 6). However, the same basin might comprise regional differences like it is the case for in the Weddell Sea I and Weddell Sea II.

Weddell Sea I has a hight correlation with SST, while in contrast, Weddell Sea II shows a negligible SST correlation but a strong one with vertical advective transport through the 100 m level. The main difference between Weddell Sea I and Weddell Sea II is that the former covers the area in front of the Riser-Larsen Ice Shelf. At the beginning of spring a tongue of higher-saturated surface water advances there toward FRIS (Fig. 9). Therefore, Weddell Sea I undergoes a higher variability in the sea ice concentration (area averaged difference between maximum and minimum sea ice concentration) of \( \overline{\Delta A} = 50.3\% \), which causes a higher seasonal variability in its saturation \( \Delta S_{\text{CFC11}} = 22\% \) (Weddell Sea II: \( \overline{\Delta A} = 45.4\% \), \( \Delta S_{\text{CFC11}} = 16\% \)).

Salinity as such has a minor effect on the CFC equilibrium concentration. Its main effect is to induce density changes which trigger convection that entrains lower-saturated waters into the mixed layer and thus causes salinity to be highly correlated with the CFC saturation. If we would restrict the multi-parameter regression analysis to parameters detectable by satellite—magnitude and temporal evolution of SST (Barron and Kara, 2006), SSS (Michel et al., 2005; Maes and Behringer, 2000), A (sea ice concentration, Spreen et al., 2008; Comiso et al., 1997) as well as \( u_\text{wind} \) (wind velocity, Bentamy et al., 2003)—and if their precisions would be high enough, we could infer 88–99% of the simulated CFC11 saturation variability (\( R^2 \geq 0.79 \), Table 6).

6.1.2. Prediction of the seasonal surface saturation cycle

By increasing the number of added parameters in the multi-linear regression list, the weights of already integrated ones change. Some of them become eventually negligible. For example, based on parameters detectable by satellite, the relative weight of the SST’s temporal evolution (\( \partial S / \partial t \)) decreases continually from 21 and vanish to insignificant values at the end on the FRIS Shelf (lower Table 6). Therefore, some already added parameters can be safely removed from the list of important parameters without significantly reducing the prediction capability. The number of parameters in Table 6 might be different if we would remove parameters with extremely low weights. In addition, a “pool position” in the multi-linear regression list does not necessarily identify parameters of highest relevance but of high prediction capability. For example, the vertical mixing coefficient \( \nu_{\text{mix}} \) leads in Weddell Sea I and Weddell Sea II the upper Table 6 but has a far lesser correlation (Table 7) of 60–75% than SSS (90%).

Hence, we recommend for real data applications to use correlations and multi-linear regression analysis in concert to identify driving parameters. However, since mostly SSS, SST, and sea ice concentrations (A) only are available, the regression analysis might be sufficient to predict the saturation’s seasonal cycle.

Based only on observed bottle data of CFC11 saturation, temperature, and salinity together with the above discussed satellite derived sea ice concentration during and one month before the time of observation, the multi-parameter regressions explain 77% of the saturation variability around the South Orkney Island (Fig. 1, upper row) and 82% along the Greenwich Meridian near Maud Rise (Fig. 1, lower row). Temperature and salinity together explain 73% of the observed CFC11 saturation variability around the South Orkney Islands (80%, \( R^2 = 0.64 \) near Maud Rise). The surface salinity alone predicts the saturation variability to 70% (78% near Maud Rise), while the predictability drops to 47% (57% near Maud Rise) if we use temperature only. This emphasizes again the above-mentioned importance of SSS, though indirect, for the CFC surface saturation cycle.

<table>
<thead>
<tr>
<th>Area</th>
<th>( r^2 )</th>
<th>Var. (%)</th>
<th>( \hat{\beta}_0 )</th>
<th>( \hat{\beta}_1 )</th>
<th>( \hat{\beta}_2 )</th>
<th>( \hat{\beta}_3 )</th>
<th>( \hat{\beta}_4 )</th>
<th>( \hat{\beta}_5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>North 0.62 79</td>
<td>50.09</td>
<td>6.789</td>
<td>-1.333</td>
<td>-1.840</td>
<td>( &lt; 10^{-6} )</td>
<td>( &lt; 10^{-6} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>South 0.67 82</td>
<td>1024</td>
<td>1.363</td>
<td>-29.95</td>
<td>0.8077</td>
<td>0.01035</td>
<td>0.01162</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Weights are truncated to four significant digits. The explained variability is shown in column “var.”.
For both regions we use the weights related to the lower Table 6, together with model fields (SST, SSS, sea ice concentrations, and their derivations), to compute the surface saturation (Fig. 16). The equation to calculate the saturation is 

\[ s(t) = \hat{\beta}_0 \mathbf{+} \sum_{i=1}^{5} \hat{\beta}_i \hat{p}_i(t), \]

where \( \hat{\beta}_0 \) is the constant element and \( \hat{\beta}_i, i \geq 1 \) are the weights of the following input fields \( \hat{p}_i \) like SST, SSS, and sea ice concentration according to Table 6.

The first parameter beside the constant element, already mimics reasonably the simulated reference cycle, which is the directly simulated saturation. Two to three parameters imitate

![Fig. 15. R–square of multi-linear parameter analysis versus number of considered parameters (\( \Theta, S, \frac{\partial S}{\partial t}, \frac{\partial \Theta}{\partial t}, D_d, A, \frac{\partial A}{\partial t}, \frac{\partial D_d}{\partial t}, u_{100}, u_{10m}, \nu_{\Theta, S} \)) which account for the CFC11 flux variability. The horizontal dashed line marks the 96% level. For each curve is the order of the considered parameters given in Table 6. The description of the parameter occurs in Table 7. See text for further details.](image)
Table 7

<table>
<thead>
<tr>
<th>Area</th>
<th>$\Theta$</th>
<th>$S$</th>
<th>$\rho$</th>
<th>$\Theta/dt$</th>
<th>$S/dt$</th>
<th>$\rho/dt$</th>
<th>$D_d$</th>
<th>$A$</th>
<th>$\partial D_d/dt$</th>
<th>$\partial A/dt$</th>
<th>$\psi_{100 \text{m}}$</th>
<th>$u_{10}$</th>
<th>$S^{\text{flux}}$</th>
<th>$\nu_{\Theta,S}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRIS Shelf</td>
<td>45 ± 16</td>
<td>-88 ± 7</td>
<td>-88 ± 7</td>
<td>-88 ± 7</td>
<td>30 ± 22</td>
<td>37 ± 20</td>
<td>37 ± 20</td>
<td>-81 ± 12</td>
<td>-43 ± 23</td>
<td>-8 ± 26</td>
<td>81 ± 11</td>
<td>-91 ± 6</td>
<td>32 ± 21</td>
<td>-36 ± 24</td>
</tr>
<tr>
<td>Weddell Sea I</td>
<td>88 ± 5</td>
<td>-90 ± 4</td>
<td>-90 ± 4</td>
<td>-90 ± 4</td>
<td>21 ± 26</td>
<td>40 ± 19</td>
<td>40 ± 19</td>
<td>-80 ± 11</td>
<td>-15 ± 26</td>
<td>22 ± 26</td>
<td>89 ± 14</td>
<td>-58 ± 20</td>
<td>11 ± 24</td>
<td>-66 ± 17</td>
</tr>
<tr>
<td>Weddell Sea II</td>
<td>17 ± 24</td>
<td>-90 ± 4</td>
<td>-90 ± 4</td>
<td>-90 ± 4</td>
<td>7 ± 26</td>
<td>40 ± 19</td>
<td>40 ± 19</td>
<td>-82 ± 10</td>
<td>-16 ± 26</td>
<td>15 ± 26</td>
<td>85 ± 9</td>
<td>-81 ± 7</td>
<td>16 ± 24</td>
<td>-65 ± 18</td>
</tr>
<tr>
<td>Prydz Bay</td>
<td>-14 ± 24</td>
<td>-94 ± 3</td>
<td>-94 ± 3</td>
<td>-94 ± 3</td>
<td>5 ± 26</td>
<td>2 ± 25</td>
<td>2 ± 25</td>
<td>85 ± 9</td>
<td>-56 ± 20</td>
<td>-33 ± 21</td>
<td>67 ± 12</td>
<td>94 ± 10</td>
<td>42 ± 18</td>
<td>-29 ± 25</td>
</tr>
</tbody>
</table>

$\Theta$, sea surface temperature (SST); $S$, sea surface salinity (SSS); $\rho$, sea surface density; $D_d$, mixed layer depth; $A$, sea ice concentration; $\psi_{100 \text{m}}$, advective transport across the 100–m depth level; and $u_{10}$, 10-m wind speed. $S^{\text{flux}}$ is the salinity flux across the ocean surface (in ice free areas it is salinity times evaporation minus precipitation, $S(E - P)$; in partly ice covered areas the salt input by growing/melting sea ice is included). The vertical mixing coefficient is $\nu_{\Theta,S}$ (Pacanowski and Philander, 1981). Partial fractions are related to $\partial/dt = 1$ month. The maximum correlation is indicated by a gray box for each area, while correlations higher/lower than 80% = $\nu_{\Theta,S}$ are shown in bold. The 95% uncertainty range of the correlations are presented. The correlations between CFC11 and CFC12 fluxes are between 98.6% (Maud Rise) and 99.99% (Pacific Sector). Areas are defined in Fig. 10.
the cycles quite well, while more than three parameters improve the reproduction further to a limited degree only. This is in agreement with Fig. 15. However, even with five parameters the prediction does not perfectly match the lower part of the reference curve’s declining branch in front of FRIS (Fig. 16).

To further investigate the potential of the method, we determine the seasonal cycle of the CFC11 surface saturation exemplarily for two segments along the Greenwich Meridian based on data. The northern section, labeled “North”, covers the latitude range 53–59 S near the northern edge of the Weddell Gyre, while the southern section near Maud Rise, labeled “South”, extends from 62 S to 70 S. The latter has been discussed in Section 3 (Fig. 1).

Based on the observed temperature, salinity, and CFC bottle data taken during the cruises ANT X/4, ANT XIII/4, ANT XV/4, and M11/5 (Table 2) together with satellite derived sea ice concentrations during the observations as well as one and two month before (Cavalieri et al., 1996, updated 2005) we calculated for each segment the weights (\(\hat{\theta}\)) together with the input fields of SST (\(\hat{\theta}_{\text{SST}}(t)\)), SSS (\(\hat{\theta}_{\text{SSS}}(t)\)), and sea ice concentrations (A) were used to predict the saturation cycle (Fig. 17):

\[
p_{\text{CFC11}}^{\text{Pred}}(t) = \hat{\theta}_0 + \hat{\theta}_1 \theta_{\text{SST}}(t) + \hat{\theta}_2 \theta_{\text{SSS}}(t) + \hat{\theta}_3 A(t)
+ \hat{\theta}_4 A(t - \Delta t) + \hat{\theta}_5 A(t - 2.4t),
\]

(3)

where \(\Delta t\) represents the temporal shift of one month.
As input fields we averaged climatological monthly mean SST and SSS data of the World Ocean Atlas 2005 (1 × 1 - version; http://iridl.ldeo.columbia.edu/SOURCES/.NOAA/.NODC/.WOA05/. Grid-1x1/.Monthly/.an, Locarnini et al., 2006; Antonov et al., 2006) between 5 W and 5 E and the corresponding latitude range to obtain monthly means for each area. As sea ice data we utilized NASA’s ISLSCP GDSLAM sea ice concentrations of the years 1987–1988 (A. Nomura and R. Grumbine, personal communication, 1995 http://iridl.ldeo.columbia.edu/SOURCES/.NASA/.ISLSCP/.GDSLAM/.Snow-Ice-Oceans/.sea/.sea_ice/.seaice) to determine the monthly means. These sea ice concentrations are not necessarily completely consistent with the climatological hydrographic fields, which were obtained by objective interpolation of available observations. This might introduce errors, but we want to demonstrate primarily the potential of the concept.

The predicted seasonal cycles are reasonable and run parallel to the observed connected means (Fig. 17). The use of the actual sea ice concentration is sufficient for “North” while for “South” the weights of the two previous months are also important (Table 5). The latter coincides with our deduced time lag of 2 month between sea ice concentration minimum and surface saturation maximum. Salinity (temperature) controls the saturation prediction stronger in the South (North), reflecting the smaller temperature amplitude during the year in the South. In the North, the regression based saturation cycle (prediction) represents the observed period better than the simulation, which is characterized by a reduced seasonal amplitude probably due to the overestimated inflow of surface water masses form the ACC (Section 4.2.2). Even the high saturation in February of 107% might be realistic as comparably high values in Drake Passage (M 11/5) reveal (Fig. 3). Further studies, however, have to be performed to verify the potential of satellite-based saturation estimates, which is beyond the scope of this paper.

With the developed prediction capability of the seasonal surface saturation cycle, we might be able to deduce long-term trends in the future. For each area and cruise averages of SST, SSS, sea ice concentrations, and CFC saturations have to be computed. These averages enter the multi-linear parameter analysis to construct a seasonal cycle. After projecting the observed mean CFC saturation on one common month, we might we able to validate the yearly trends presented in Table 4. The accordingly computed trend amounts +0.5%/year for the strongly by sea-ice-influenced section “South” which agrees well with rates obtained for regions of distinct sea ice concentration like Weddell Sea I/III (Table 4). These long-term trends are a fundamental property as shown in the next section about the temporal evolution of deduced deep/bottom water formation rates, which is not compellingly identical with the actual rate.

6.2. CFC inventory-based deep/bottom water formation rate estimates and their dependence on the temporal evolution of CFC saturations

It is quite common to assume tracer surface saturations to be time-invariant because of the lack of observation-deduced saturation histories. Since these histories are fundamental for obtaining tracer-based quantities, we address the effect of a neglected temporal evolution by analyzing exemplarily the formation rate of deep and bottom waters based on tracer inventories, i.e., \( \int c(t) dV \). In view of mass conservation, one assumes that the inventory in the abyssal ocean is proportional to the mean formation rate (P) ventilating the tracer-carrying volume as well as the integrated history of the tracer input (\( \int \mathcal{S}(t) \cdot p_{\text{atm}}(t) dt \)):

\[
P(t_{\text{ref}}) = \frac{\int c(t_{\text{ref}}) dV}{\int_{t_{\text{ref}}}^{t_{\text{ref}}} \mathcal{S}(t) \cdot p_{\text{atm}}(t) dt}.
\]

where \( \mathcal{S} \) is the solubility function, \( p_{\text{atm}} \) the atmospheric CFC history, and \( \mathcal{S}(t) \) the spatial mean saturation at the formation site for time \( t \) (e.g., equation in Orsi et al., 1999, p. 94). The ocean is assumed to be in steady-state and, therefore, temperature, salinity, and ultimately the solubility in the formed water masses do not change and are considered to be time-invariant. Since water masses in the Antarctic marginal seas are primarily formed...
where values above (below) 100% represent an over-estimate (under-estimate) of the formation rate.

Assuming (a) a given tracer inventory in the abyssal ocean and (b) two different tracer input histories during the formation of the water masses that ventilate the same abyssal ocean tracer inventory, we would obtain two different formation rates according to Eq. (4). In Eq. (5) we assume implicitly a given tracer inventory and explicitly two different tracer input histories, which differ only in the temporal evolution of the saturation during water mass formation. The temporal evolving saturation represents the true reference state, though a temporal invariant saturation, based on available summer values, is the common case in the literature.

To estimate the systematic error of this approach, we examine CFC11 in front of FRIS. This area is believed to be the dominant formation site in the Atlantic sector, in which 60% of the Southern Ocean’s deep and bottom waters are supposed to be formed (Orsi et al., 1999). The error can be expressed as the ratio of the formation rates, considering a constant saturation \( \left( P(t_{ref}, <S(t_{ref})> = \text{const}) \right) \) and the temporal evolving saturation \( \left( P(t_{ref}, <S(t)> \right):\)

\[
P(t_{ref}, <S(t)> = \frac{\int_{t_{0}}^{t_{ref}} S(t) p_{atm}(t)dt}{\int_{t_{0}}^{t_{ref}} p_{atm}(t)dt} = \text{const.}
\]

where values above (below) 100% represent an over-estimate (under-estimate) of the formation rate.

In the case of a constant saturation we use the simulated value at the time to which the inventory refers \( t_{ref} \) instead of the entire saturation history up to \( t_{ref} \) (Fig. 13a). For example, if the reference time is 1998, the atmospheric CFC11 history covers the entire period up to that year, while the constant saturation \( <S(t_{ref} = 1998)> \) is 57% (Table 4). This is a fairly generic case.

We find that ignoring the temporal evolution induces a systematic error of up to 10% for the year 2000. The inventories are always underestimated, but the deviation is smaller at earlier times because of the nearly exponential atmospheric tracer history. Therefore, the tracer was mostly concentrated along the spreading path close to the formation site, i.e., the inventory was very young. The non-linear evolution in Fig. 18 reflects the addition of remotely ventilated waters in the model.

Fig. 18 also includes results for the constant saturation referring to a time 5 and 10 years prior to the inventory reference time. These are cases where the saturation in front of FRIS was observed, e.g. in 1995 (ANT XII/3), while the CFC data representing the inventory reflect the condition of year 2000 for a 5-year shift. Accordingly, the 10-year shift uses the same observed surface saturation (1995), while the concentration in the ventilated inventory reflects the condition of year 2005. Formally, the deviations become lower because the actual saturations increase in time, but the differences between the curves are quite non-linear. If we would keep instead the tracer inventory fixed to the year 2000, the saturations are observed 5 (10) years earlier, in 1995 (1990) with \( <S(t_{obs} = 1995)> = 55% \) \( <S(t_{obs} = 1990)> = 51% \). It is not an option to correct the missing long-term saturation trend by introducing a time shift, because the selection of a time shift is a rather arbitrary matter.

Other fundamental objections have been raised (Hall et al., 2007) concerning the estimation of formation rates via (5), because it neglects the important role of horizontal mixing. Here, we illustrate the effect of evolving surface saturation on commonly made formation rate estimates. Such evolution would also affect the estimates of the more general ‘ventilation-rate distribution’ from tracers, as discussed in Hall et al. (2007).

7. Conclusions

Using a regional OGCM, we conducted for the first time a detailed study of the CFC (surface) saturations and its dependence on various parameters for different regions, including the major deep and bottom water formation sites in the Southern Ocean, which are important contributors to the ventilation of the global abyss. We found that the simulated saturations of the surface layer are subject to a pronounced seasonal cycle, and that the time lag between the sea ice concentration minimum and the saturation maximum amounts to two months.

Due to water mass formation by deep convection on continental shelves, the seasonal saturation signal penetrates to great depths. Along the spreading path of the freshly ventilated water masses, the seasonal cycle becomes eroded by mixing and the entrainment of ambient, CFC-poor waters. In addition to the seasonal cycle, all analyzed areas exhibit a significant long-term increase of the surface saturations, 0.1–0.3%/year (in the 1990s). Near deep and bottom water formation sites, saturation increases in the whole water column including the bottom layer and also further away as the newly formed waters spread out. The long-term increase of the CFC saturation is strongest within the FRIS cavern (1.4%/year). The increasing atmospheric CFC mixing ratios, suppression of gas exchange by the ice cover, and mixture of freshly ventilated but still undersaturated waters combined with a multi-year composition of very low saturations, cause this strong temporal increase.

In ice-free regions the equilibrium concentration/saturation and hence the flux depends strongly on the SST. When surface water looses buoyancy sufficiently, low-saturation waters are entrained into the mixed layer, triggering a flux from the atmosphere to the ocean and causing elevated seasonal saturation cycles. However, areas characterized by high amplitudes of the seasonal saturation cycle are not necessarily deep and bottom water formation sites, such as the Pacific Sector and Maud Rise.
In ice-covered areas low-mixed layer saturations arise from entrainment of low-concentration deep waters while the ice cover suppresses gas exchange. This leads to a strong tracer flux into the ocean and raising saturation levels when the sea ice retreats. The Maud Rise area demonstrates that high CFC saturation amplitudes developed during the year (Fig. 16) are not necessarily confined to deep and bottom water formation sites, since here the interaction of the flow with topography lifts deeper water masses to be entrained into the mixed layer (Muench et al., 2001).

The correlation analysis in concert with the multi-linear regression analysis identifies SST, SSS, salt flux, and mixed layer depth as important factors controlling the seasonal cycle of the CFC surface saturation in sea ice controlled areas. High amplitudes of the surface saturation seem to be a necessary but not sufficient condition to identify deep and bottom water formation sites. Based only on SST, SSS, and sea ice concentration we presented the capability to reproduce the seasonal CFC surface saturation cycle by utilizing the weights obtain from the multi-linear regression analysis. The two most important input parameters already reproduce to a high degree the simulated saturation (Fig. 16), demonstrating the high potential of the method.

For two different sections along the Greenwich Meridian only observed CFC11 saturations (bottle data), temperature, and salinity together with satellite derived sea ice concentrations were considered to determine weights. These weights, climatological SST, SSS fields (WOA05), and sea ice concentration of the years 1987–1988 were used to determine the full seasonal saturation cycle. The predicted surface saturation cycles seem to be realistic and agree reasonably well with the few existing observations. Therefore, this method should work similarly for other gaseous tracers. Whether biologically active gases, like oxygen, also can be predicted has to be shown in future studies.

Assuming the area in front of FRIS to be representative for the formation of deep and bottom waters (e.g., Weddell Sea Bottom Water) in the Southern Ocean, the formation rates based on tracer inventories are underestimated by up to 10%, if time-invariant instead of realistic (i.e., temporally increasing) saturations are used (Fig. 18). Since the discrepancy increases in (calendar) time, the method using constant surface saturation suggests an erroneous decline of the formation rate with time. Therefore, any noted reduction of water mass ventilation based on tracer inventories should be critically questioned and confirmed by other tracer-independent means.

Further model studies with an improved representation of the mixed layer should be performed to confirm our results. In addition, a comparison between model runs conducted with climatological and daily forcing should be performed to deduce the influence of varying environmental conditions on the results presented here. Since a realistic tracer input is essential for other deduced properties like transient time distributions (Beining and Roether, 1996; Hall et al., 2002; Huhn et al., 2008b), further tracer simulations for all deep and bottom water formation as well as subduction sites should be performed to provide a complete set of CFC surface saturation histories.

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