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Using dissolved oxygen concentrations to determine mixed layer depths in the Bellingshausen Sea

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Abstract

Concentrations of oxygen (O_2) and other dissolved gases in the oceanic mixed layer are often used to calculate air-sea gas exchange fluxes; for example, in the context of net and gross biological production estimates. The mixed layer depth (z_{mix}) may be defined using criteria based on temperature or density differences to a reference depth near the ocean surface. However, temperature criteria fail in regions with strong haloclines such as the Southern Ocean where heat, freshwater and momentum fluxes interact to establish mixed layers. Moreover, the time scales of air-sea exchange differ for gases and heat, so that z_{mix} defined using O_2 may be different to z_{mix} defined using temperature or density. Here, we propose to define an O_2-based mixed layer depth, $z_{\mathrm{mix}}(O_2)$, as the depth where the relative difference between the O_2 concentration and a reference value at a depth equivalent to 10 dbar equals 0.5 %. This definition was established by numerical analysis of O_2 profiles in coastal areas of the Southern Ocean and corroborated by visual inspection. Comparisons of $z_{\mathrm{mix}}(O_2)$ with z_{mix} based on potential temperature differences, i.e. $z_{\mathrm{mix}}(\Delta\theta = 0.2\,^{\circ}\mathrm{C})$ and $z_{\mathrm{mix}}(\Delta\theta = 0.5\,^{\circ}\mathrm{C})$, and potential density differences, i.e. $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}})$ and $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.125\,\mathrm{kg\,m^{-3}})$, showed that $z_{\mathrm{mix}}(O_2)$ closely follows $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}})$. Further comparisons with published z_{mix} climatologies and z_{mix} derived from World Ocean Atlas 2005 data were also performed. To establish z_{mix} for use with biological production estimates in the absence of O_2 profiles, we suggest using $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}})$, which is also the basis for the climatology by de Boyer Montégut et al. (2004).

1 Introduction

The oceanic mixed layer is the top part of the water column where temperature and solute concentrations are vertically homogeneous due to wind-driven turbulent mixing (Lukas and Lindstrom, 1991; Brainerd and Gregg, 1995). This is an important region that directly interacts with the atmosphere through exchange of momentum, heat, moisture, gases and aerosols (Dong et al., 2008). The mixed layer depth (z_{mix}) defines the bottom boundary of the mixed layer and separates it from the pycnocline. Mixing between mixed layer and waters below determines the ventilation of the ocean interior and influences the large-scale circulation (Cisewski et al., 2008; Le Quéré et al., 2003).

The biological response to physical forcing is not always immediate. Likewise, changes in light or micronutrient levels may stimulate rapid biological changes, but are not necessarily reflected in changes of physical properties of the surface ocean. Therefore, physical and biogeochemical tracers cannot be expected a priori to show the same scales of variability. For example, heat exchange is generally faster than gas exchange (Fairall et al., 2000). Mixed layer depths could also be different, depending on whether they refer to temperature or to gases. Moreover, different gases respond at different rates to wind forcing, depending on their solubility, with less soluble gases (e.g. N_2, Ar or O_2) responding more quickly. Therefore, for air-sea gas exchange studies and related topics such as biological production estimates from O_2/Ar ratios ratio and oxygen triple isotopes (Reuer et al., 2007; Kaiser et al., 2005), it is important to have a proper representation of z_{mix} in terms of gas fluxes.

In the Southern Ocean, a strong coupling exists between atmosphere and surface waters due to the lack of physical barriers for the eastward flowing Antarctic Circumpolar Current, leading to pronounced meridional gradients and defined frontal regions. In this marine ecosystem, physical processes are an important driver for biogeochemical processes, such as biological production in the surface ocean .(Rintoul and Trull, 2001; Smith et al., 2008). The Southern Ocean accounts for a significant fraction of oceanic CO_2 uptake (Sarmiento et al., 1998; Sarmiento and Le Quéré, 1996). In particular, Antarctic shelf waters act as a strong sink of atmospheric CO_2 due to high biological productivity, intense winds and high deep-water ventilation rates (Arrigo et al., 2008).

Previous definitions of z_{mix} in the Southern Ocean have used criteria based on physical properties of the water column, such as potential temperature or density (Cisewski et al., 2008; Dong et al., 2008; Gordon and Huber, 1990; Rintoul and Trull, 2001; Verdy et al., 2007). However, temperature and salinity do not always show the same stratification, leading to water column structures such as temperature inversions (i.e. abrupt changes in the temperature profile due to intrusions of water masses), barrier layers (as a result of temperature inversions and at locations where the halocline is shallower than the thermocline) and density-compensated profiles (de Boyer Montégut et al., 2004; Rintoul and Trull, 2001). These structures can develop frequently in high latitude coastal areas, such as the western Antarctic Peninsula (WAP), due to the combined effect of shelf bathymetry and sea-ice dynamics (Ducklow et al., 2006; Williams et al., 2008). In the WAP region, little temperature stratification occurs and the density distribution is dominated by the influence of ice melt on salinity (de Boyer Montégut et al., 2004; Dong et al., 2008).

Most definitions of z_{mix} can be classified into two groups: (a) gradient-based criteria, where z_{mix} is the depth where the vertical gradient of an oceanic property reaches a threshold value (Lukas and Lindstrom, 1991) and (b) difference-based criteria, where z_{mix} is the depth where an oceanic property has changed by a certain amount from a reference value (Levitus, 1992).

Previous comparisons suggested that in order to use gradient-based criteria successfully, well-resolved vertical profiles are needed (Brainerd and Gregg, 1995; Cisewski et al., 2008). For example, Dong et al. (2008) concluded that the presence of anomalous spikes and perturbations in profiles from ARGO floats could lead to erroneously low z_{mix}. The authors found that gradient-based z_{mix} deviates as much as 100 m from difference-based z_{mix}. This was mainly due to limited resolution and noise of the temperature and conductivity float's sensors. Difference-based criteria perform better in such circumstances as well as in regions with temperature inversions or weak upper water column stratification. However, simulations using an ocean general circulation model have shown that a latitude-dependent difference criterion may actually give the best results (Noh and Lee, 2008).

Other z_{mix} definitions include curvature of temperature or density profiles (Lorbacher et al., 2006), combinations of physical criteria (Holte and Talley, 2009), optical measurements (Zawada et al., 2005) and split and merge methods (Thomson and Fine, 2003). These criteria require more complex numerical methods or additional measurements to determine z_{mix}.

O_2 is used as a tracer for water masses, biological activity and air-sea exchange (Jenkins and Jacobs, 2008; Reuer et al., 2007; Körtzinger et al., 2008). Dissolved O_2 responds to the same physical processes (e.g. vertical mixing, horizontal advection, air-sea exchange) as heat. However, since the response of O_2 solubility to changes in temperature and salinity is not linear and immediate, z_{mix} defined solely by differences in potential density does not fully describe the properties of the water column in terms of dissolved O_2 and temperature-associated solubility changes. O_2 also depends on biology and therefore gives a more complete picture of all relevant processes.

It makes sense to define z_{mix} using O_2 concentrations in the context of net and gross biological production estimates, where z_{mix} is used to calculated weighted-average gas exchange coefficients (Reuer et al., 2007). In the Bellingshausen Sea, the main factors controlling the initiation and maintenance of the high algal biomass are physical dynamics, iron and light availability, which are driven by the mixed layer depth variability. According to Boyd et al. (1995), high chlorophyll concentrations in the upper water column of the Bellingshausen Sea remained unchanged for about 25 days during austral summer.

Holte and Talley (2009) compared winter mixed layer depth defined by the 95 % O_2 saturation horizon (Talley, 1999) with results from a recently published z_{mix} algorithm based on combinations of physical criteria. The authors found good agreement between both definitions in data from the World Ocean Atlas 2005 and Argo profiles. In the Southern Ocean, a region with consistent deep mixed layers was identified north of the Subantarctic Front by both methods. However, the 95 % O_2 saturation criterion is not suitable for the detection of shallow mixed layers, particularly in the coastal Southern Ocean where surface cold waters are normally in equilibrium or slightly undersaturated in O_2 for most of the year (Garcia and Keeling, 2001).

Here, we propose to define z_{mix} using a difference criterion based on the relative difference between O_2 concentrations and a reference value at a depth equivalent to

10 dbar. O_2 is commonly measured during hydrocasts and modern electrochemical or optical O_2 sensors give sufficiently stable results for establishing z_{mix}. The corresponding $z_{\text{mix}}(O_2)$ was first obtained through visual inspection of vertical O_2profiles in the Bellingshausen Sea. We summarise the different criteria used to define z_{mix} in global climatologies and in climatologies specific to the Southern Ocean (Table 1) and compare them with $z_{\text{mix}}(O_2)$. Climatologies may be useful where no CTD O_2 data are available to determine $z_{\text{mix}}(O_2)$ for the calculation of wind-speed weighted gas exchange coefficients.

2 Methods

2.1 CTD data acquisition

Vertical profiles of temperature (θ), salinity (S) and dissolved O_2 concentration ($c(O_2)$) were obtained at 253 hydrographic stations in the Bellingshausen Sea (RRS *James Clark Ross* cruise JR165). The cruise took part within the framework of the ACES-FOCAS project (Antarctic Climate and the Earth System-Forcing from the Oceans, Clouds, Atmosphere and Sea-ice) of the British Antarctic Survey.

The Bellingshausen Sea is situated to the west of the Antarctic Peninsula between 75° W and 90° W and is a transition region between continental shelf, shelf breaks and the open ocean. The sampling period consisted of 38 days between 3 March and 9 April 2007, which represent the seasonal shift from late summer to early autumn (Fig. 1). The hydrographic profiles were taken with a *Sea-Bird* 911+ CTD package mounted on a rosette with 12 ten-litre Niskin bottles for the collection of water samples.

The CTD conductivity sensor was calibrated on board against discrete samples analysed with a *Guildline Autosal* 8400B. A constant offset of $+0.034 \pm 0.040$ was found and corrected for. A high-precision reversing thermometer sensor (*Sea-Bird* SBE35) and an O_2 sensor (CTD-O_2; *Sea-Bird* SBE43) were also mounted on the rosette. The CTD data were binned into 2 dbar-depth intervals starting from 1 dbar ($=10^4$ Pa, or about 1 m) to the maximum depth for each station. The CTD-O_2 data were calibrated against discrete samples analysed on board using whole-bottle Winkler titration (Dickson, 1996) with photometric end-point detection. A total of 276 titrations were performed with a repeatability of 0.29 µmol kg^{-1} (0.1 %) based on 76 duplicate samples. The average difference between the non-calibrated CTD-O_2 and Winkler data was (3.9 ± 3.1) µmol kg^{-1}.

For determining z_{mix} using difference criteria, the sensor precision is more important than the absolute accuracy. The sensor precision was estimated from the relative standard deviation of the CTD-O_2 readings within 2 dbar-bins in the mixed layer, which was found to be (0.4 ± 0.3) %, on average.

2.2 Definition of the $z_{\text{mix}}(O_2)$ criterion

To define a z_{mix} criterion based on O_2, all 253 CTD profiles were initially inspected visually. Two profiles could not be used due to sensor problems. Some examples of typical profiles encountered during the survey are depicted in Fig. 2. Subjective, visually determined z_{mix} was then compared to objective, numerically determined z_{mix} to identify a suitable O_2 criterion for z_{mix}. We propose to define $z_{\text{mix}}(O_2)$ as the depth at which $c(O_2)$ has changed by 0.5 % with respect to a reference value at 10 dbar. Brainerd and Gregg (1995) suggested 10 dbar as reference depth to avoid sensor noise in the surface water due to the effect of ship motion. Sensor noise affected our measurements only in the top 5 dbar of most CTD stations. Using this reference depth means that the minimum z_{mix} is 10 dbar. The reference depth of 10 dbar was also chosen for consistency with other studies and to allow comparing our results to climatological data that use the same reference depth.

2.3 Comparison with density- and temperature-based z_{mix} and climatologies

Comparisons between $z_{\text{mix}}(O_2)$ and z_{mix} based on temperature and potential density differences were performed. To compare with z_{mix} data from climatologies, difference criteria used in selected three-widely used climatologies were chosen. A further comparison was made between of $z_{\mathrm{mix}}(\mathrm{O_2})$ and the actual z_{mix} values from the climatologies, interpolated according to location and time of year (Table 1).

Climatologies represent binned and averaged monthly fields. The z_{mix} climatologies by Monterey and Levitus (1997), Kara et al. (2003) and de Boyer Montégut et al. (2004) (referred to as ML97, K03 and BM04 hereinafter and respectively) are widely used in oceanographic studies. The corresponding data were obtained from http://www.esrl.noaa.gov/psd/data/gridded/data.nodc.woa94.html, http://www7320.nrlssc.navy.mil/nmld/nmld.html and http://www.locean-ipsl.upmc.fr/~cdblod/mld.html. ML97 and K03 are based on data from the World Ocean Atlas 1994 (WOA94). BM04 is based on individual CTD profiles obtained from the World Ocean Circulation Experiment (WOCE) and the National Oceanographic Center (NODC) and the latest update includes profiles from Argo floats. The BM04 climatology is obtained by an ordinary kriging of the data distributed in 2^o boxes, with a prediction limited to 1000 km radius. No value is assigned if there are less than 5 data points in a grid box. BM04 includes profiles from mechanical bathythermograph (MBT), expendable bathythermograph (XBT), CTD hydrocasts and profiling floats, providing a range of vertical resolutions from 2.3 m (CTD) to 19.5 m (XBT). The ML97 and K03 climatologies consider a smaller radius of influence (771 km). However, interpolation of data and smoothing were performed within that radius leading to larger uncertainties in the data.

Based on ML97 and BM04, the following criteria were chosen to define z_{mix} based on potential temperature (θ) and potential density (σ_θ) differences: $\Delta\theta = 0.2\,^\circ\mathrm{C}$ and $\Delta\sigma_\theta = 0.125\,\mathrm{kg\,m^{-3}}$ with respect to the surface value; $\Delta\theta = 0.5\,^\circ\mathrm{C}$ and $\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}}$ with respect to the 10 dbar value. These criteria were applied to the same 251 CTD profiles used to determine $z_{\mathrm{mix}}(\mathrm{O_2})$. In addition, $z_{\mathrm{mix}}(\mathrm{O_2})$ was compared with the curvature-based z_{mix} algorithm of Lorbacher et al. (2006) as well as z_{mix} based on the 95 % $\mathrm{O_2}$ saturation criterion (Talley, 1999).

The z_{mix} values from ML97, K03 and BM04 were also directly compared with $z_{\mathrm{mix}}(\mathrm{O_2})$ after linear interpolation to the same month, latitude and longitude. Since these climatologies suffer from poor data coverage in the Southern Ocean, particularly south of 30° S in the Antarctic coastal zone, we planned to use a dedicated Southern Ocean z_{mix} climatology based on σ_θ differences derived from Argo float profiles used for comparison (Dong et al., 2008). However, it turned out that this climatology did not contain any data in the region of study and could therefore not be used.

To further test the $z_{\text{mix}}(O_2)$ criterion, we applied the $\Delta\sigma_\theta = 0.03\,\text{kg}\,\text{m}^{-3}$ criterion to density profiles calculated from 1° by 1°-temperature and salinity climatology in World Ocean Atlas 2005 (WOA05; http://www.nodc.noaa.gov/OC5/WOA05/woa05data.html; (Antonov et al., 2006; Locarnini et al., 2006). Then, the $z_{\text{mix}}(O_2)$ criterion was applied to the O_2 data in WOA05 (Garcia et al., 2006). WOA05 uses the same standard depths and interpolation method for temperature, salinity and oxygen. The O_2 data only comprise results obtained by Winkler titration.

3 Results

3.1 Comparison between $z_{\text{mix}}(O_2)$ from subjective and objective analysis

$z_{\text{mix}}(O_2)$ obtained by subjective visual inspection and by using objective numerical analysis agreed to within 1 dbar for 235 out of 251 stations. For the remaining 16 stations, the objective $z_{\text{mix}}(O_2)$ value was on average (1 ± 5) dbar shallower than its subjective counterpart (Fig. 3). This small discrepancy was caused by the presence of low oxygenated subsurface waters (i.e. Winter Water) that created a weak upper oxycline. The visual inspection disregarded this top oxycline and $z_{\text{mix}}(O_2)$ was defined according to the deeper and more pronounced seasonal oxycline. In the following, the subjective result is used for $z_{\text{mix}}(O_2)$.

The $z_{\text{mix}}(O_2)$ criterion appears to better reflect the O_2 distribution in the mixed layer, compared to the $z_{\text{mix}}(\Delta\sigma_\theta = 0.03\,\text{kg}\,\text{m}^{-3})$ criterion. This is illustrated by six typical profiles (Fig. 2). Vertical profiles for stations 25, 76, 89, 188, 199 and 250, show $z_{\text{mix}}(\Delta\sigma_\theta = 0.03\,\text{kg}\,\text{m}^{-3})$ lying in the oxycline region, deeper than $z_{\text{mix}}(O_2)$. As a consequence, the O_2 concentration is lower at $z_{mix}(\Delta\sigma_\theta = 0.03\,kg\,m^{-3})$ than at $z_{mix}(O_2)$. This difference can lead to an underestimation of the average mixed layer O_2 concentration.

3.2 Comparison between $z_{mix}(O_2)$ and z_{mix} based on θ and σ_θ differences

No significant correlation was observed between $z_{mix}(O_2)$ and z_{mix} based on $\Delta\theta = 0.5\,^\circ C$ (with respect to the surface value) or based on $\Delta\theta = 0.2\,^\circ C$ (with respect to the 10 dbar value). The corresponding correlation coefficients were $r^2 = 0.001$ and 0.111, respectively. $z_{mix}(\Delta\theta = 0.5\,^\circ C)$ was on average (58 ± 51) dbar deeper than $z_{mix}(O_2)$, while $z_{mix}(\Delta\theta = 0.2\,^\circ C)$ was (26±34) dbar deeper. These observations confirm the overestimation of z_{mix} based on temperature in the Southern Ocean providing the importance of using density to define z_{mix} in this area (Figs. 4 and 5a).

Comparison between $z_{mix}(O_2)$ and z_{mix} based on $\Delta\sigma_\theta = 0.125\,kg\,m^{-3}$ with respect to the surface value, $\Delta\sigma_\theta = 0.03\,kg\,m^{-3}$ and $\Delta\sigma_\theta$ due to a temperature change of $0.8\,^\circ C$, $\Delta\sigma_\theta(0.8\,^\circ C) = \sigma_\theta\ (\theta + 0.8\,^\circ C) - \sigma_\theta\ (\theta)$, both with respect to the 10 dbar value, showed a better agreement than for the solely θ–based criteria. The corresponding correlation coefficients were $r^2 = 0.711$, 0.813 and 0.016, respectively. $z_{mix}(\Delta\sigma_\theta = 0.125\,kg\,m^{-3})$ was on average (14 ± 13) dbar deeper than$z_{mix}(O_2)$, while $z_{mix}(\Delta\sigma_\theta = 0.03\,kg\,m^{-3})$ was (3 ± 7) dbar deeper and $z_{mix}(\Delta\sigma_\theta(0.8\,^\circ C))$ was (94 ± 60) dbar deeper (Figs. 4 and 5b). We also confirmed the results obtained based on the $\Delta\sigma_\theta$ criteria visually. Objective and subjective results agreed to within (2 ± 6) dbar for all criteria.

Lorbacher et al. (2006) have defined z_{mix} based on the first extreme curvature in the temperature or potential density profile. Compared to difference criteria, this approach has the advantage of being independent of the actual value of the variable in question. The same is true for $z_{mix}(O_2)$, which uses a relative difference of 0.5 %, independent of the O_2 concentration. The mixed layer depth based on temperature curvature, $z_{mix}(\theta'')$, gave (12 ± 30) dbar deeper values than $z_{mix}(O_2)$; z_{mix} based on density curvature, $z_{mix}(\sigma''_\theta)$, gave (8 ± 14) dbar deeper values (Fig. 4).

Talley (1999) used the 95 % O_2-saturation horizon to identify winter mixed layer depth. We tested this criterion to identify summer/autumn mixed layer depth during our cruise. Away from the shore (stations 90 to 163 and 197 to 253), the 95 % saturation criterion does not give meaningful results because of the presence O_2-undersaturated waters near the surface. Closer to ice shelves (stations 1 to 90 and 166 to 198), biological production is able to overcome this O_2 deficit. The surface O_2 saturation was (100 ± 4) % and $z_{\mathrm{mix}}(95\,\%\ O_2)$ was on average (12 ± 24) dbar deeper than $z_{\mathrm{mix}}(O_2)$ (Fig. 6).

3.3 Comparison of z_{mix} with climatologies

For the following comparisons, the z_{mix} data are presented in meters (rather than dbar) to keep consistent with the climatologies. Comparison between z_{mix} from the selected criteria with the z_{mix} obtained from the same criteria according to the corresponding climatology was done. This means that the $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.125\,\mathrm{kg\,m^{-3}})$, $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}})$ and $z_{\mathrm{mix}}(\Delta\sigma_\theta(0.8\,^\circ\mathrm{C}))$ derived from our profiles was compared with the corresponding values extracted from the ML97, BM04 and K03 climatologies, respectively, for the same month and location were done. Due to the limited spatial coverage of the climatologies in the Southern Ocean, not all profiles had a corresponding climatological z_{mix} value (170 profiles for ML97, 208 profiles for BM04 and 179 profiles for K03 all out of 251). Therefore, the comparisons below were done for the common minimum number of profiles found in the climatologies.

The ML97 and K03 climatologies have a coarse vertical resolution (0, 10, 20, 30, 50, 75, 100, 125, 150, 200, 250, 300, 400, 500, 600, 700, 800, 900, 1000 m), which puts limits on the comparison to in situ z_{mix} data based on profiles with 2 dbar resolution. For some CTD stations, climatological z_{mix} was overestimated by up to 500 m with respect to $z_{\mathrm{mix}}(O_2)$. These values were disregarded for the comparison between climatological z_{mix} and $z_{\mathrm{mix}}(O_2)$. In case of BM04, the vertical resolution varies according to the source of data: PFL data have a vertical resolution of 8.2 m, CTD data 2.3 m, XBT data 19.5 m and UBT data 9.4 m.

Comparisons with z_{mix} from ML97 and B04 showed a good agreement, with $r^2 = 0.628$ for ML97 and $r^2 = 0.604$ for BM04 (data not shown). The ML97 climatology gave (11.9 ± 11.6) m shallower z_{mix} than the in situ data; the BM04 climatology gave (0.7 ± 13.5) m shallower z_{mix}. However, $z_{\mathrm{mix}}(\Delta\sigma_\theta(0.8\,^\circ\mathrm{C}))$ showed poor agreement with the corresponding data from K03 ($r^2 = 0.002$), with z_{mix} based on CTD profiles being (94.4 ± 64.1) m deeper.

We then compared $z_{\mathrm{mix}}(\mathrm{O_2})$ with the density-based z_{mix} in the BM04, ML97 and K03 climatologies. To ensure comparable results, we only used the profiles where data from all climatologies were available, so that the total number of profiles compared was 160 (Table 2). $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}})$ from BM04 showed a positive correlation with $z_{\mathrm{mix}}(\mathrm{O_2})$ ($r^2 = 0.542$) and was on average (6 ± 11) m deeper than $z_{\mathrm{mix}}(\mathrm{O_2})$. $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.125\,\mathrm{kg\,m^{-3}})$ from ML97 also showed a positive correlation with $z_{\mathrm{mix}}(\mathrm{O_2})$ ($r^2 = 0.542$), and was on average (1 ± 11) m shallower than $z_{\mathrm{mix}}(\mathrm{O_2})$. No correlation was found between z_{mix} from K03 and $z_{\mathrm{mix}}(\mathrm{O_2})$, with $z_{\mathrm{mix}}(\mathrm{O_2})$ on average (15 ± 14) m deeper (Table 2).

Our observations show that $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}})$ is most similar to $z_{\mathrm{mix}}(\mathrm{O_2})$. The BM04 climatology showed the best coverage in the Southern Ocean, and has the advantage of having a higher vertical resolution than to the other climatologies.

3.4 $z_{\mathrm{mix}}(\mathrm{O_2})$ compared with z_{mix} based on WOA05 density and oxygen profiles

The criterion z_{mix} ($\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}}$) was applied to density profiles taken from objectively analysed fields of temperature and salinity data from WOA05. We then compared the results obtained from these observations to the z_{mix} using the same density criterion and the oxygen criterion both in our CTD profiles. For the WOA05 profiles we could only find matching data for 120 out of 251 CTD profiles, due to the limited spatial coverage of WOA05. A poor correlation was found for both comparisons ($r^2 = 0.048$ and 0.043, respectively), with $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}})$ based on CTD data being (17 ± 17) m deeper than based on WOA05. These differences are likely due to the scarce WOA05 data in the Southern Ocean and their limited vertical resolution (10 m) (Table 2).

To test the $z_{mix}(O_2)$ criterion with other O_2 profiles, we used historical O_2 profiles from WOA05 located at the same geographical location than our CTD stations. Our results show a positive correlation ($r^2 = 0.412$) between z_{mix}(CTD-O_2) and z_{mix}(WOA05-O_2). On average, z_{mix}(WOA05-O_2) was (8 ± 12) dbar shallower than z_{mix}(CTD-O_2).

4 Discussion

Defining z_{mix} based on potential temperature can lead to deeper values than $z_{mix}(O_2)$, which is defined based on the vertical O_2 distribution. The $\Delta\theta = 0.5\,^\circ\mathrm{C}$ and $\Delta\theta = 0.2\,^\circ\mathrm{C}$ criteria lead to z_{mix} located within the oxycline. These criteria tend to underestimate the average mixed layer O_2 concentration. Potential density-based z_{mix} values are in better agreement with $z_{mix}(O_2)$, particularly for the $\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}}$ criterion.

To explain the discrepancy between temperature and density-based z_{mix}, we checked for the presence of barrier layers and temperature inversions in the area of study. Barrier layers are thought to be formed by melting sea ice, although the mechanisms for the formation and destruction of barrier layers in the Southern Ocean are not well understood (de Boyer Montégut et al., 2007). Our results showed that barrier layers were present in 43 % of the CTD profiles. The barrier layer thickness ranged from 2 to 93 m. Barrier layers were also encountered below the seasonal mixed layer, but do not influence $z_{mix}(O_2)$. The seasonal variability of the barrier layers, influenced mainly by the water column stratification, is expected to correspond to that of $z_{mix}(O_2)$. The deepening of z_{mix} during autumn and winter will lead to low-O_2 waters entering the ML from the barrier layer below and subsequent destruction of the barrier layer.

Comparison between in situ $z_{mix}(O_2)$ with z_{mix} climatologies showed a good agreement for the ML97 and BM04 climatologies. BM04 has several advantages over ML97 and K03: (1) It includes Argo data up to 2008, giving better data coverage, especially in high latitudes (ML97 and K03 covered 71 % and 68 % of the occupied stations respectively, while BM04 83 %), (2) BM04 uses non-interpolated, non-averaged profiles, which avoids the creation of artificially smooth profiles as in ML97 and K03; (3) ML97 and K03 have limited vertical resolution and use discrete intervals; (4) non-averaged profiles allow identification of upper water structures such as barrier layers and temperature inversions; (5) a difference-criterion based on temperature or density with a wide threshold (such as in ML97 and K03), can lead to an overestimation of z_{mix}. De Boyer Montégut et al. (2004) reasoned that a wider threshold might be better for averaged-profiles with a coarser and smoother resolution.

Both the ML97 and K03 temperature criteria have been applied for areas where sharp temperature stratification in the upper water column is present (i.e. tropical and sub-tropical oceanic areas). The larger temperature difference of the K03 criterion produces z_{mix} values higher than those of ML97.

Argo float data such as used in the latest update of the BM04 climatology provide new insights for seasonal z_{mix} investigations in a region where the lack of data during austral winter from direct observations collected on board research ships is considerable. Argo floats with O_2 sensors have been launched since 2007, a few of them in the Southern Ocean. However, these floats are only located in deep waters and the coarse vertical resolution that the Argo profiles provide ($\approx$10.5 m) are important limitations for detection of shallow summer z_{mix} in the coastal region of the Southern Ocean. Due to this, the climatology by Dong et al. (2008) is limited to 30° S to 65° S excluding the location of the Bellingshausen Sea (i.e. 66° S to 74° S).

z_{mix} based on curvature as proposed by Lorbacher et al. (2006) showed a similar overestimation of $z_{\text{mix}}(O_2)$ as the density and temperature criteria. Although the L06 criterion does not require a common vertical resolution between analysed profiles, this criterion was created from monthly means data and may therefore not work for single profiles as in our case. The L06 criterion however has the advantage of being independent of the actual value of the variable in question. This is also true for the $z_{\text{mix}}(O_2)$ which uses a relative difference of 0.5 % independent of the oxygen concentrations.

The 95 % O_2 saturation criterion proposed by Talley (1999) gives mostly lower z_{mix} values than $z_{\text{mix}}(O_2)$ as defined here. It is not suitable as a general criterion because the physical and biogeochemical processes would not appear to be comparable enough from place to place and time to time to allow using such an "absolute" horizon.

The nighttime convection and overturning have a daily effect on the z_{mix} with higher values as the wind speed increases during the night. This effect might also yield a differential response of gas fluxes due to diurnal thermocline variations. From the total CTD profiles evaluated here in the continental shelf of the Bellingshausen Sea, 17 % (43 stations) were sampled during the period of darkness (about 5 h; from 23:00 to 04:00 LT). From the observations in Fig. 7, there is no clear difference between z_{mix} during the night and day either using O_2 or the potential density criterion (i.e. $\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}}$). This may be expected because nighttime convection is likely to be limited during summer (and early autumn). In order to evaluate in detail the effect of nighttime convection on $z_{\mathrm{mix}}(O_2)$, in situ measurements of the vertical profile of O_2 in a daily time series at the same geographical location are needed. High variability due to diurnal effects has been investigated before for oxygen isotopes in dissolved water from Sagami Bay, Japan (Sarma et al., 2006). The authors found that the distribution of oxygen isotopes is strongly influenced by diurnal variability. This effect would also influence of production calculations, but can be neglected for our study.

The accuracy of z_{mix} depends on the resolution of the instrumental parameter used in the criterion to define it. By using CTD observations, the resolution is sufficiently high to identify the vertical distribution of O_2 in the upper water column, and therefore define an adequate z_{mix} in a less coarse vertical resolution than the integrated observations by z_{mix} climatologies and WOA data. The low abundance of O_2 profiles in the WOA record for the Southern Ocean make z_{mix} obtained from these data sets unreliable when compared to the in situ z_{mix} values based on CTD-O_2 profiles. Moreover, the difference between $z_{\mathrm{mix}}(\Delta\sigma_\theta)$ and the $z_{\mathrm{mix}}(O_2)$ for CTD profiles and WOA05-profiles are mainly due to the interpolation method used to construct the temperature, salinity and O_2 fields in WOA05.

Finally, despite in this work the O_2 concentrations from the CTD profiles were previously calibrated against results from Winkler method, the z_{mix} obtained after the $z_{\text{mix}}(O_2)$ criterion can be also applied directly to non-calibrated vertical profiles, provided bad data such as spikes are removed from the O_2 profiles.

5 Conclusions

The O_2 concentration in the coastal Southern Ocean is a better parameter to define z_{mix} for gas exchange studies. For profiles in the Bellingshausen Sea collected during late summer and autumn in 2007, the z_{mix} was well defined by the depth where the absolute difference in the concentration of O_2 was higher than 0.5 % of the concentration at 10 dbar depth. The criterion was validated by further visual inspection with 94 % of the total working profiles agreeing well with the proposed criterion.

In coastal waters of the Southern Ocean, the vertical stratification of salinity is a delimiting factor for the upper water dynamics due to the strong ice-melting water signal. After validation of the z_{mix} obtained from O_2 against the z_{mix} obtained from traditional potential density and temperature criteria, it was found a best agreement with the $\Delta\sigma_\theta = 0.03\,\text{kg}\,\text{m}^{-3}$ criterion, applied to the CTD profiles and with the corresponding z_{mix} extracted from the monthly climatology (BM04) (de Boyer Montégut et al., 2004).

Thus, in the absence of O_2 profiles, the $z_{\text{mix}}(\Delta\sigma_\theta = 0.03\,\text{kg}\,\text{m}^{-3})$ criterion might be used. Furthermore, in the absence of CTD stations at all, the public monthly climatology BM04 (de Boyer Montégut et al., 2004), based on the same $\Delta\sigma_\theta$-criterion, is encouraged to be used for determination of z_{mix} in the coastal areas of the Southern Ocean.

For gas exchange studies, $z_{\text{mix}}(O_2)$ has the advantage of being directly related to a species of interested. Moreover, the relative nature of $z_{\text{mix}}(O_2)$ criterion means that it should be applicable in many other parts of the worlds' oceans, including during other times of the year. Therefore, for gas exchange studies, dissolved gas budget or determination of marine production using dissolved gases as proxy in the coastal Southern Ocean, the use of the $z_{\mathrm{mix}}(O_2)$ criterion is suggested. The proposed criterion is more sensitive to reflect better upper mixed layer air-sea dynamics and influence of biological and physical processes, rather than the traditional criteria based on potential temperature or density, particularly in regions where weak vertical gradients of temperature and density in the upper waters are suspected.

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Table 1. Climatologies used in this work to compare with the mixed layer depths extracted from O_2 profiles.

Abbreviation	Authors	Description	Data source[2]	Profiles	Resolution	Criteria	Reference depth
ML97	Monterey and Levitus (1997)	z_{mix} climatology	WOA94 (1900–1992)	averaged, interpolated	1° × 1° monthly	$\Delta\sigma_\theta = 0.5\,\text{g}\,\text{m}^{-3}$ and $\Delta\theta = 0.5\,^\circ\text{C}$	0 m
K03	Kara et al. (2003)	z_{mix} climatology	WOA94 (1900–1992)	averaged, interpolated	1° × 1° monthly	$\Delta\sigma_\theta$ corresponding to $\Delta\theta = 0.8\,^\circ\text{C}$	0 m
BM04	de Boyer Montégut et al. (2004) and LOCEAN-IPSL[1] (2008)	z_{mix} climatology	NODC/WOCE/Argo (1941–2008)	individual	2° × 2° monthly	$\Delta\sigma_\theta = 0.03\,\text{kg}\,\text{m}^{-3}$ and $\Delta\theta = 0.2\,^\circ\text{C}$	10 m
WOA05-σ_θ	This work	T and S climatology	WOA (1965–2005)	averaged, interpolated	1° × 1° monthly	$\Delta\sigma_\theta = 0.03\,\text{kg}\,\text{m}^{-3}$	10 m
WOA05-O_2	This work	$c(O_2)$ climatology	WOA (1965–2005)	averaged, interpolated	1° × 1° monthly	$\Delta_s\,(O_2) = 0.5\,\%$	10 m

[1] Laboratoire d'Océanographie et de Climatologie par l'Expérimentation et l'Analyse Numérique – Institut Pierre Simon Laplace (updated version from the previously published by de Boyer Montégut et al., 2004).

[2] WOA: World Ocean Atlas; NODC: National Oceanographic Data Center; WOCE: World Ocean Circulation Experiment

Table 2. Mean (± 1σ) difference from $z_{\mathrm{mix}}(O_2)$ in CTD and World Ocean Atlas 2005 (WOA05) profiles to data from climatologies and WOA05 based on $\Delta\sigma_\theta$.

Differences in z_{mix} to climatological and data from WOA05	Mean ± 1σ (m)	Number of profiles compared
$z_{\mathrm{mix}}(O_2) - z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}}$, BM04)	-6 ± 11	160
$z_{\mathrm{mix}}(O_2) - z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.125\,\mathrm{kg\,m^{-3}}$, ML97)	1 ± 11	160
$z_{\mathrm{mix}}(O_2) - z_{\mathrm{mix}}(\Delta\sigma_\theta$ (0.8 °C), K03)	15 ± 14	160
$z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}}$, CTD) – $z_{\mathrm{mix}}(\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}}$, WOA05)	17 ± 17	120
$z_{\mathrm{mix}}(O_2$, CTD) – $z_{\mathrm{mix}}(O_2$, WOA05)	8 ± 12	120

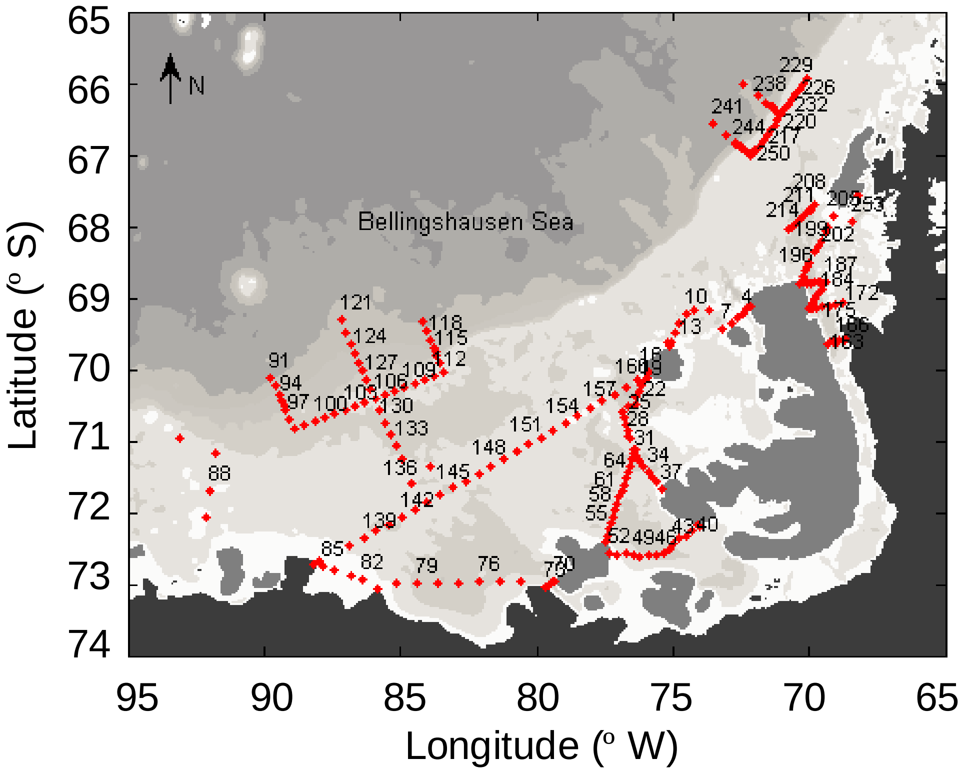

Fig. 1. CTD stations occupied by RRS *James Clark Ross* cruise JR165 in the Bellingshausen Sea during late summer and early autumn 2007 (3 March to 9 April 2007). Labels indicate station numbers. Black corresponds to the Antarctic mainland, dark grey to island of the coast. Shading corresponds to the depth intervals from 0–200 m, 200–600 m, 600–1000 m, 1000–2000 m, 2000–3000 m and deeper than 3000 m.

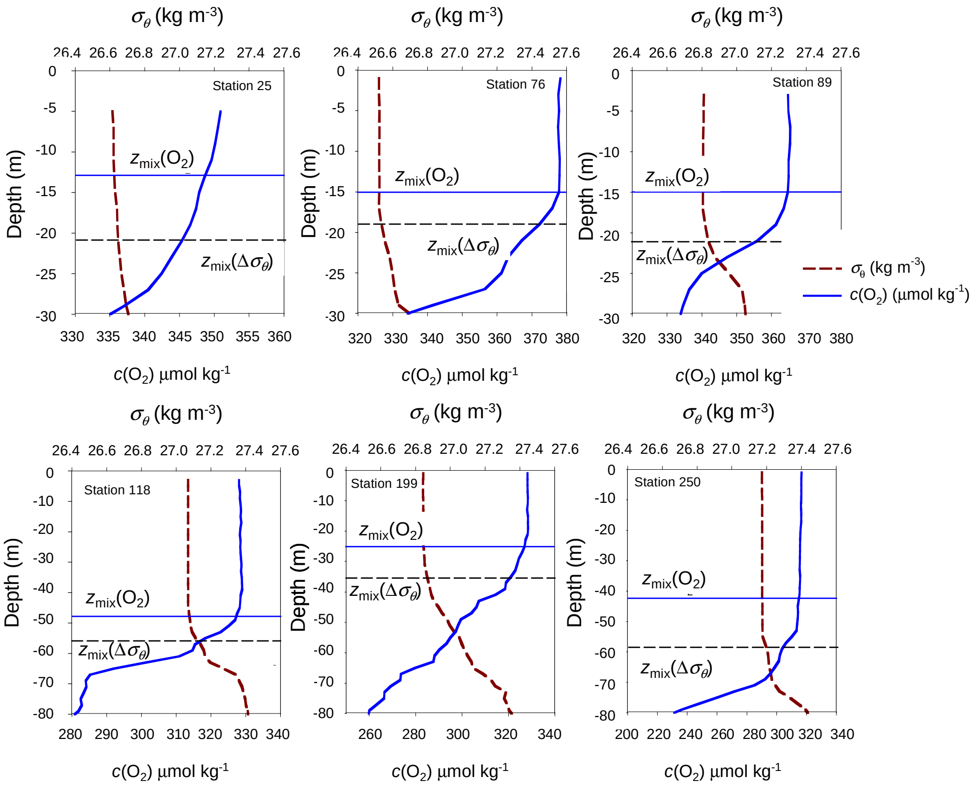

Fig. 2. Vertical profiles of O_2 concentration, $c(O_2)$, and potential density (dashed line, σ_θ). Horizontal lines indicate the location of the z_{mix} defined by $c(O_2)$ and σ_θ after the criterion $\Delta\sigma_\theta = 0.03\,\text{kg}\,\text{m}^{-3}$.

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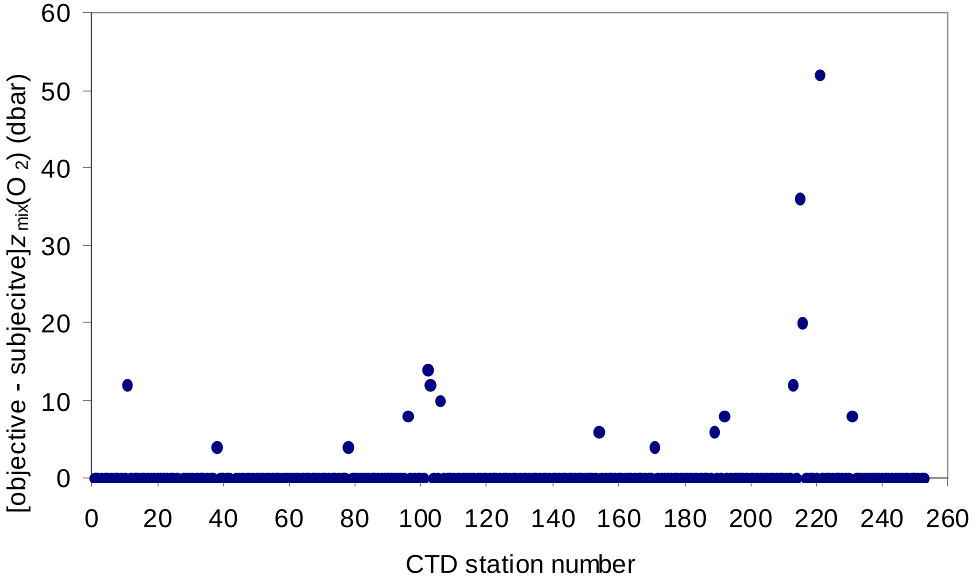

Fig. 3. Difference between $z_{\mathrm{mix}}(O_2)$ from numerical algorithms (objective result) and visual inspection (subjective result).

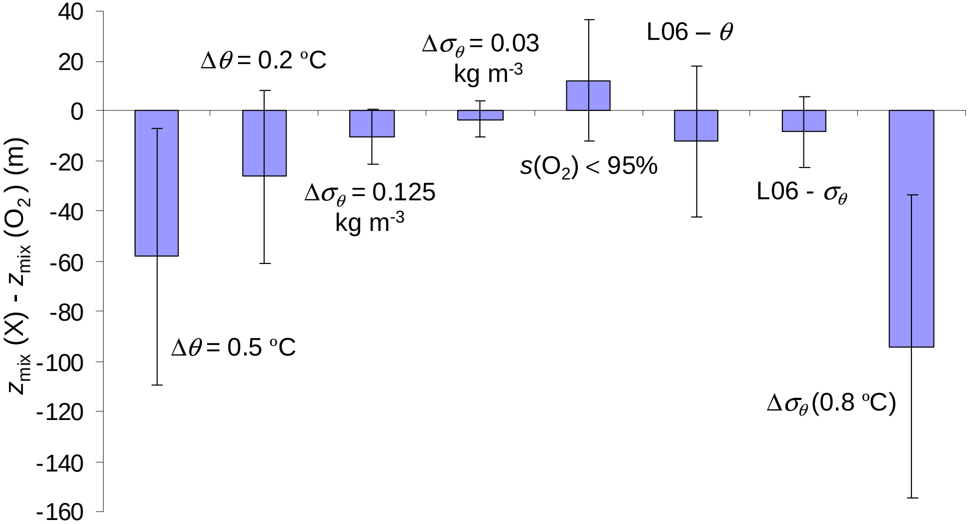

Fig. 4. Mean difference between z_{mix} based on potential temperature and salinity differences or oxygen saturation state (z_{mix}(X)) to $z_{mix}(O_2)$. Lorbacher et al. (2006) is the algorithm used by Lorbacher et al. (2006) to define z_{mix} based on potential temperature (L06-θ) and potential density (L06-σ_θ). The $\Delta\sigma_\theta$(0.8 °C) criterion is based on the difference in density given by a temperature difference of 0.8 °C.

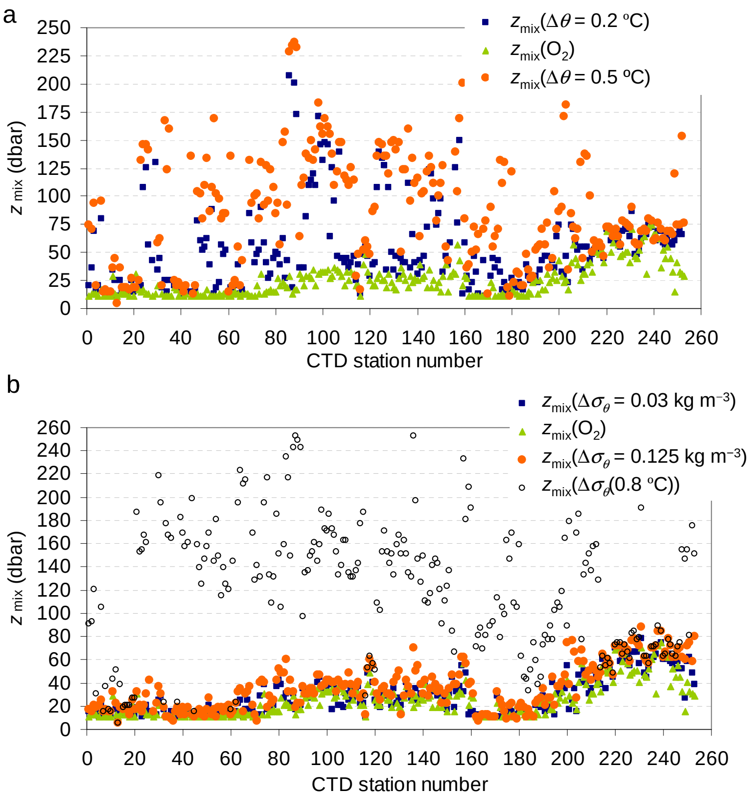

Fig. 5. Comparison between z_{mix} from the $z_{mix}(O_2)$ criterion (green triangles) and from typical other z_{mix} criteria: **(a)** z_{mix}-θ (squares: $\Delta\theta = 0.2\,^\circ$C; circles: $\Delta\theta = 0.5\,^\circ$C), and **(b)** z_{mix}-σ_θ (squares: $\Delta\sigma_\theta = 0.03\,\mathrm{kg\,m^{-3}}$; orange circles: $\Delta\sigma_\theta = 0.125\,\mathrm{kg\,m^{-3}}$.

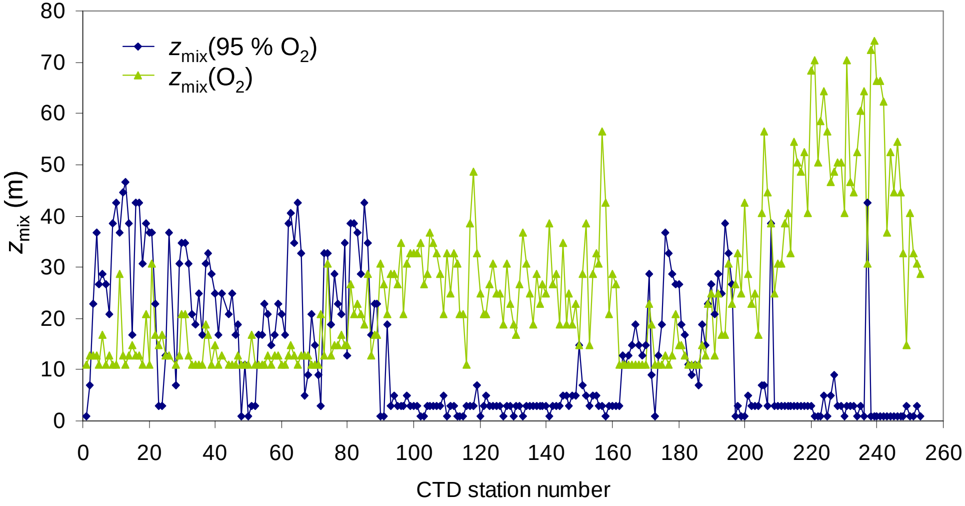

Fig. 6. Comparison between $z_{mix}(O_2)$ criterion against $z_{mix}(95\,\%\ O_2)$ using the criterion proposed by Talley (1999) (i.e. 95 % O_2 saturation-horizon, corresponding to $c(O_2) = 0.95\ c_{sat}(O_2)$, where $c_{sat}(O_2)$ is the O_2 concentration at saturation).

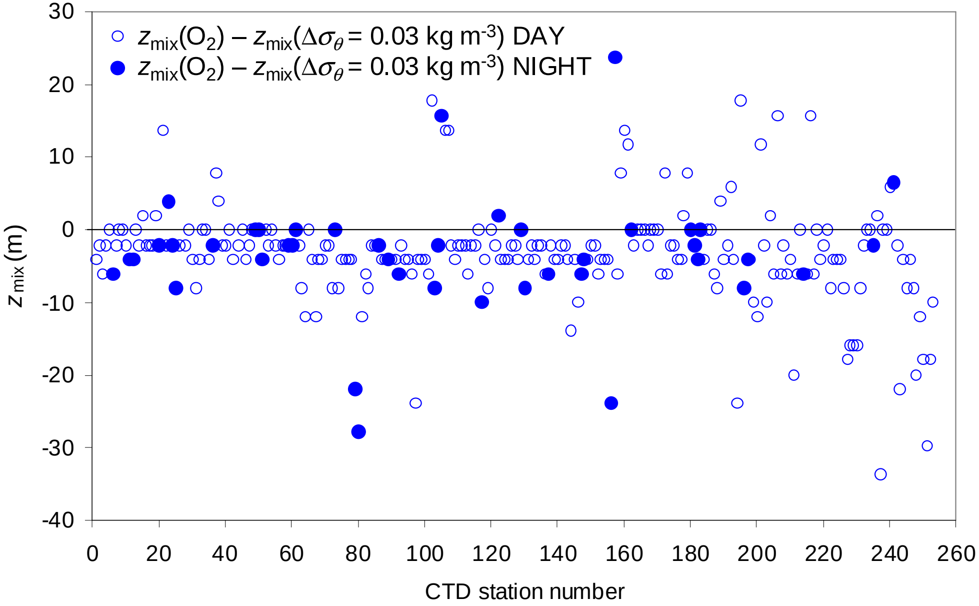

Fig. 7. Comparison between $z_{mix}(O_2) - z_{mix}(\Delta\sigma_\theta = 0.03\,kg\,m^{-3})$ during day (empty symbols) and night (filled symbols).