

February 17, 2016

Dear Editors,

In the following, we answered point-by-point to the comments raised by S. Konovalov and the second anonymous reviewer. We copied the reviewer's comments in their totality. Our answers to the reviewers first comment are given in blue (2 Feb 2016). The additional changes operated after the editorial reply appears in red (17 Feb 2016). In addition to the present document we join the revised version of the manuscript, as well as a version underlying the changes operated to the former version. We'd like to express our gratitude towards the reviewers for their constructive comments and to the editorial staff for their work.

Arthur Capet, on behalf of coauthors.

1 Reviewer 1: S.Konovalov

1.1 General Comments

C: *This manuscript is addressed to an extremely important issue of decline in the oxygen inventory in marine systems. This decline has been traced in many marine systems, but it is crucially important for oxygen deprived oxic/anoxic marine systems, like the Black Sea, for example. Indeed, the thickness of oxygenated waters in the Black Sea does not exceed upper 200 meters. Thus, even minor variations in the distribution of oxygen are important for this marine system. For all these reasons, the manuscript suggests valuable information and it is worth publishing in Biogeosciences.*

C: *The authors analyze data from 1955 to 2014. They split all these data in several individual periods of specific trophic- and/or climate-driven changes in the Black Sea. Except for the most recent period of 1999-2013, and specifically for the period after 2010, all results and conclusions look good and well-justified.*

C: *The major problem is in DIVA analysis of highly limited and spatially located data in 1999-2013. While DIVA analysis is explained briefly for this major tool of this work, any kind of interpolation cannot fill spatial gaps of about 80-90% of the basin area (Fig. 2, lower panel).*

A: We agree that the scarcity of the data challenges the computation of meaningful diagnostics and the production of gridded fields. Given the importance of this topic, the question is what best analysis can be made out of scarce data. Studies of the long term evolution of the Black Sea oxycline or chemocline usually make the hypothesis that these characteristics when expressed on a density scale are independent of the spatial location and of the season. Diagnostics are then obtained by averaging the information derived from punctual profiles expressed on a density scale even if they are scarcely distributed throughout the basin. Our approach to remedy to this data deficiency and to strengthen the meaning of our diagnostics is (1) to exploit at best the information that can be gathered from an extended dataset and (2) to complement the analysis with independent estimates from Argo, acknowledging the issue of their comparability. Regarding (1), our working hypothesis is that recurrent spatial structure, that can be evidenced from data-rich period, could and should be exploited to enhance the analysis of data from the data-poor period. To be clear : Spatial analyses are made gathering data for the whole period. Temporal trends are then identified as the average misfit between data of a given year and the climatological spatial analyses. We understand that our succinct description of the DIVA analysis tool led to confusion. For better clarity we now included an appendix to describe the method, in addition to the previous reference to Capet et al. (2014) where the method is detailed and applied on synthetic and real (Black Sea CIL) case studies.

C: *This problem seems even more serious, when DIVA analysis is applied to the position of 20 μM of oxygen, while the authors suggest that it varies versus depth and density.*

A: The position of 20 μM of oxygen is expressed in terms of depth and density and derived for every profile. Reducing the dimensionality of the problem by extracting scalar diagnostics from vertical profiles simplifies both the analysis (2D interpolation of specific diagnostics instead of diagnostic derivation from 3D interpolation) and the presentation/discussion of the results. We considered three different diagnostics to show that the overall

conclusion (deoxygenation of Black Sea) does not strictly depend on the choice of a specific diagnostic. In particular the temporal artifacts induced by horizontal variability of these diagnostics is addressed by considering both depth and density coordinates for the oxygen penetration depth, and through the DIVA detrending procedure.

C: *It is absolutely important to show that DIVA analyses is correct when it is applied to highly limited and spatially irregular distribution of data in 1999-2013.*

A:

1. In fact, the situation is worse than previously thought, as we noticed that some Argo data were reported in the WOD database and erroneously mistaken for ship-based data. We now carefully checked the WOD set to dissociate ship-based data (analyzed using DIVA) from Argo data.
2. The DIVA detrending analysis is applied on the ship-based data set as a whole, not period by period. This procedure aims at identifying both spatial variability and temporal trends from the whole dataset. Spatial climatology are constructed for the entire period and from the whole data set. For the spatial analyses, the detrending consists in considering the anomaly associated to each data due to its location in time (ie. the trend associated with the year containing the data). Temporal trends are assessed for each particular year. For these temporal analyses, the detrending consists in considering the anomalies associated with the spatial location of each data. The procedure is iterative ie. guess for spatial and temporal trends are re-estimated together and updated until reaching convergence.
3. We hope the equations provided in the extended description of the algorithm would make it clearer (the additional Appendix is given below).
4. The influence of data from the latest period on the spatial climatology is of minor importance given the low amount of data compared to data from previous periods.
5. The main and remaining question therefore regards the temporal trend given for 2001, 2003, 2005. The basic estimates for these trends would be the average of the diagnostic obtained from the profiles of those year. The DIVA estimates are based on those average values but apply a correction considering the spatial and seasonal distribution of the data. This correction stems from the spatial variability, which are identified from the whole dataset and are therefore not tainted from the scarcity of data for these years. In other words, the basis estimates are weakened by the lack of data, but the DIVA corrections are not.

C: *Another problem is that the major part of observational oxygen data are from Winkler titration of water from Niskin samplers, while data for 2012-2013 are from Argo floats. I do support Argo floats, but the authors have to demonstrate that these two types of oxygen data are precisely comparable.*

A:

1. Argo data erroneously introduced in the “ship-based” dataset have been removed.
2. The calibration and error of Argo oxygen profiles data for the two Argo floats presented in the former version of the manuscript are discussed in Stanev et al. (2013) (see paragraphs 8 and 10, hereafter). “[8] *The sensor for temperature and salinity was CTD SBE 41, and the one for oxygen was Aanderaa Oxygen Optode 3830. Oxygen sensors show little or no drift and high accuracy [Johnson et al., 2009; Riser and Johnson, 2008]. In the Black Sea, there is a “natural calibration” every time when the float produces a new profile because there is a “solid zero” at depth. Analysis of data in the anoxic layers never showed values higher than 1 μ M, which can roughly be taken as an error estimate for the analyses presented in this paper. Furthermore, comparisons with historical observations (see next section) demonstrated that the sensors used provide credible results*” “[10] *The comparison between profiling float data and historical observations demonstrates the consistence of the new measurements. Furthermore, it enables to objectively decipher oxic conditions and changes in the Black Sea hydro-chemistry in the area of suboxic zone. In the following, the advantages of the two data sets (long-term sampling in the historical data and continuous sampling in the profiling float data) are put together in a complementary manner.*”
3. Additional Argo profiles are considered in the revised manuscript. Those were collected, checked and made freely available by the International Argo Program, part of the Global Ocean Observing System, and the national programs that contribute to it (<http://www.argo.ucsd.edu>, <http://argo.jcommops.org>). Only good quality-checked data were considered (see Argo user-manual, <http://archimer.ifremer.fr/doc/00187/29825/40575.pdf>).

- Several studies address the error of Argo real-time oxygen data (e.g., Bittig and Körtzinger, 2015; Takeshita et al., 2013; Johnson et al., 2015). Demonstrating that the Black Sea real-time Argo data are precisely (ie, at fine scales) comparable with historical Winkler data, or identifying the relevant correction, is beyond the scope of the present study which addresses monthly to decadal time scales. Evenly distributed small scales error (eg., difference between ascending and descending profiles due to sensor time response) were thus filtered by the temporal smoothing. However, a systematic error is not strictly excluded which could reach an underestimation of 10 μM (Virginie Thierry, IFREMER, personal communication, January 2016). Therefore, we evaluated a “worst-case” scenario in the analysis of Argo data by considering a systematic underestimation of oxygen concentration by 10 μM .

C: *I know, for example, that Winkler titration data for 2013 reveal $\sigma_t = 15.60\text{--}15.65$ for 20 μM of oxygen and a rather isopycnal spatial distribution (look for the attached figure), while the authors suggest about 15.40 and a spatially variable distribution.*

A:

- A confusion occurred in the former manuscript regarding the computation of the potential density scale for the different data sources. In the revised manuscript, the density scale used is the potential density anomaly, σ_θ , computed from the different data sources following TEOS-10 standards and scripts (<http://www.teos-10.org/>).
- The value derived from the Argo are now presented separately on additional Fig. 5. Ignorant of the spatial distribution of the data presented by the reviewer we are unable to comment on the spatial variability.
- As commented previously, we acknowledge an inherent uncertainty on the Argo real-time data. As we lack Winkler data within the Argo years, our approach is to consider a possible large error on the Argo data (10 μM) when discussing the results.

C: *I recommend an in-depth analysis of that patchiness in Fig. 3c and data for 2012–2013.*

A: We thank the reviewer for pointing us two mistakes in our previous submission (already addressed above): (1) Data reported in the WOD database for 2012-2013 (also 2010) were indeed Argo data and were therefore removed from the DIVA analysis. (2) Miscomputation of density anomaly from different data sets resulted in the patchiness of figure 3c. This figure has been updated and reveals interesting features **now shortly described in the discussion**.

1.2 Specific Comments

C: *Title. The discussed decline is not that “recent”. I would suggest to drop “recent” and to limit to “Decline of the Black Sea oxygen inventory”.*

A: The title has been changed accordingly.

C: *Page 16235, line 5. Consider “the surface layer of a lower salinity”.*

A: The sentence has been changed to “... *that separates the surface layer (of low salinity due to river inflow) from the deeper layer (of high salinity due to inflowing Mediterranean seawater), restraining ventilation to the upper layer*”.

C: *Page 16235, line 9. Murray et al. (1989) considered 10 μM of oxygen and the first appearance of sulfide because they analyzed high quality oxygen data from the KNORR cruise. 20 μM of oxygen were applied later to analyze historical oxygen data of lower quality*

A: We mainly referred to Murray et al. (1989) for introducing the suboxic layer. The choice of 20 μM as a threshold for analysis is presented later in the result section 2.2. We added the precision suggested by the reviewer in the manuscript

C: Page 16239. A better description of DIVA analysis is needed.

A: We added a description of the DIVA software and DIVA detrending algorithm in a dedicated appendix, although a full description and skill assessment on synthetic and real cases can be found in Capet et al. (2014).

C: Page 16239. What are the trends in original data?

A: If this concerns the sentence “A new data set is constructed by subtracting the trends from the original data.”, it is a misunderstanding. The sentence should read “A new data set is reconstructed out of the original dataset by subtracting the trends” or “New Set = Original Set - Trends”. This is clarified in the appendix.

C: Page 16239. What is “detrended” spatial climatology?

A: A spatial climatology constructed out of the entire dataset but removing from each data the anomaly associated with its location in time, using the temporal trends identified in the iterative process. As the same remarks was raised by reviewer #2, we avoided this confusing expression in the revised manuscript.

C: Page 16239. If a spatial climatology is applied to every specific year, it is hardly correct for both depth and density data.

A: The three spatial climatologies (one per diagnostic) are computed from the entire dataset (see above comments). Ignoring the spatial variability also constitutes a strong assumption, if only a simpler one. Here we consider that a statistically recurrent spatial structure of the diagnostics can (and should) be exploited to enhance the interpretation of the temporal variability depicted by the data. In the case where there would be no such recurrent spatial structure, either because spatial variations are low, either because spatial variations canceled when they are averaged in time (ie. they are not “recurrent”), the spatial climatology would be flat (ie., small compared to temporal variations) and bear low impact on the analyzed temporal trends (which would then be close to the average value for given years).

C: Page 16240, line 2. Are these spatial variations? What are trends?

A: We changed the titles of section 3.1 and 3.2 to “Spatial variability“ and “Temporal variability“.

C: Page 16240, line 17. I would discuss a decline in oxygen penetration depth for a period, rather than an average rate because it definitely varies in time (Fig. 4).

A: The linear trends were not given because we consider the decrease to be linear, but to provide a long-term “averaged” decreasing rate. However the discussion can be extended considering the different periods.

A: We included in the discussion : *Using σ_θ coordinates depicts clearer temporal variations (Fig. ?? and Fig. ??). The shoaling rate varies in time and was more intense during 1970–1985 and from 1996 onwards.*

C: Page 16244, line 14. It does not illustrate any decoupling because it is not discussed and/or analyzed in this work.

A: We removed the last paragraph.

2 Reviewer 2: Anonymous

2.1 General Comments

C: This paper aims to reassess estimates of trends oxygen content in the Baltic taking into accounts the past 60 years, split into periods of different physical and biological dynamics.

A: It is not clear to which extent the repeated mistake “Baltic Sea“ instead of “Black Sea“ affects the reviewing comments. We considered that it was just a word mistake and addressed most of the comments reading “Black Sea“ instead of “Baltic Sea“.

C: The authors interpolate data using an interpolation scheme which attempts to account for variable data

density in the hopes of being able to compare more data sparse periods to the rest of the dataset. Overall, I agree fully with and would reinforce the comments made by S. Konovalov (C7404–C7407, 5/11/2015). There is what I consider to be a significant flaw with the paper in that they base the bulk of their conclusions on a severely under sampled time-period.

A: In answer to this general comment (also raised by the first reviewer), we considered additional Argo floats extending the study period to the end of 2015.

C: The interpolation that the authors perform for the majority of the basin between 1999-2013 (and to a lesser extent, 1986-1998) is difficult to trust due to the paucity of data coverage. Even the best interpolation scheme in the world is only as good as the input data.

A: No spatial interpolations are done for restricted periods. The spatial climatologies presented in Fig. 4 are constructed considering the entire WOD dataset.

C: I'm also left wondering how sensitive the analysis is to changes in selected oxygen threshold of 20 μM . The latter will greatly impact oxygen penetration depth estimates as the oxycline not only experiences vertical migration but also strong changes in gradient over the past 50 years.

A: In this precise case, we could not decide whether the remark on strong gradient change was specific to the Baltic Sea. Nevertheless, considering oxygen inventory (the vertical integral) as a diagnostic was specifically intended to answer this question, as this diagnostics is particularly robust against the choice of a particular threshold. A rough computation gives $200 \text{ mmol/m}^3 * 100 \text{ m} = 20.000 \text{ mol/m}^2$ for the upper part (above $20\mu\text{M}$) against $10 \text{ mmol/m}^3 * 30 \text{ m} = 300 \text{ mmol/m}^2$ for the lower part. Extending the vertical integration beyond the threshold would change the oxygen content by a few percent at best.

C: The paper presents interesting results and a novel approach to estimating the variability of the Baltic oxygen content, but the authors need to do more to convince the reader that their study is robust due to the severe lack of data between 1993-2003. Is their method still functional in this context? Much more information needs to be provided on the results of the DIVA analysis for the reader to not dismiss the work as suffering from the issues described above.

A: We extended the description of the DIVA algorithm to avoid any confusion on the analysis procedure.

C: I personally have no issue with the inclusion of Argo data, although the authors should make a statement reminding the reader of the possible accuracy/precision issues inherent to Argo float oxygen measurements..

A: This is now more precisely commented in the data description section

C: .. but agree that a more in-depth study of patchiness is necessary. I suspect there is sufficient data available from the winklers to build empirical variograms and identify scales of variability.

A: The correlation length used in the DIVA analysis was evaluated in Capet et al. (2014). We would prefer to avoid enlarging further the manuscript. Please refer to answer to S. Konovalov regarding the patchiness of Figure 3c.

C: The authors present some good figures, but need more attention to detail in the axis, labels and captions. Many captions would benefit from being fleshed out. I would also consider adding an additional figures; a diagram indicating the relative depth of the surface, bottom and CIL water masses, with a mean oxygen, H_2S and either TSS or density profiles overlaid. I leave this to the author's discretion whether they feel it is necessary or not, but I believe it would complement the introduction well for readers less acquainted with the Baltic region.

A: We added a figure (1) with typical temperature, density and oxygen profiles, and detailing the diagnostics.

C: Although the abstract sounds a bit stilted (I would suggest reworking it very slightly for better legibility), the rest of the manuscript reads wells. The introduction is excellent, and covers the topic well. The methods section relating to the DIVA analysis must be expanded to reassure the reader that the method can cope with the huge variability of data density. The results section is brief, but to the point and highlights the important aspects, but again I would add a section providing technical results from the DIVA analysis (assessment of variability, variability of trends identified).

A: As the trend identified for a given year is the mean of the misfits of this year data with respect to the overall

climatology (Eq. A3 in the appendix), we computed for every year the standard error of this mean (sample standard deviation/ \sqrt{N}). These error bars were added on Figure 6 and described in the caption.

C: *The discussion feels rushed; this does not impact the quality of the conclusion, rather it is my opinion that the reader would benefit from being guided through the logic and argument a bit more, particularly when relating conclusions in text to Figure 5. Finally, the conclusions were surprisingly disconnected from the rest of the paper: the last paragraph seems to bear little relation to the actual results or conclusions.*

A:

- We developed the line of discussion related to Fig 5 (now 7) "The positive correlations between CIL cold content and oxygen inventory observed for all the periods illustrate the ventilation of intermediate layers by CIL formation and advection (Fig. 7b). In the early 90s, the transient recovery of the three oxygenation diagnostics (Figs. 6a, b, c, 7a) provided arguments supporting the stability of the oxic interface (Tugrul et al., 1992; Buesseler et al., 1994). This stabilization matched the convenient perception of a general recovery of the Black Sea ecosystem after the reduction of nutrient load around 1990 (Kroiss et al., 2006). However, Fig. 7 indicates that the oxygenation diagnostics obtained for the period 1986–1998 were associated with much higher ventilation rates (ie, higher CIL cold content) than during the previous periods. If, in response to nutrient reduction, the biogeochemical oxygen consumption terms had been lower during the period 1986–1998 than previously, the increased ventilation during that period would have resulted in higher oxygen inventories. Instead, oxygen inventories observed during 1986–1998 are lower than those observed in the previous decade for similar levels of CIL cold content. We conclude that high CIL formation rates during this period (Piotukh et al., 2011; Capet et al., 2014) provided enough ventilation to mask ongoing high oxygen consumption."
- We removed the last paragraph.

2.2 Minor Comments

C: /8: *originated -> originating*

A: Corrected

C: 16238/8: *went drifting -> drifted*

A: Corrected

C: 16239 and onwards: *climatology cannot be detrended. Please correct the language throughout and provide a better explanation of what you mean.*

A: Ok for avoiding the terms "detrended climatology". Please refer to the new appendix for the description of the method.

C: 16240/13: *the spatial variability needs further explaining; I feel at the moment there is insufficient information to fully understand what the authors are saying.*

A: The clarification on the DIVA methods should make it clearer now. The results description has been extended and the spatial variability is discussed a bit more extensively at the beginning of the discussion section.

C: 16242/1-5: *I'm struggling to follow the logic, please detail further.*

A: These lines now reads : *Considering spatial variability revealed a clear shoaling trend for oxygen penetration depth. This shoaling can be seen on both depth and density scales (Fig. 6a,b). This confirms the hypothesis that the shoaling of oxygen penetration depth is not due to a general shoaling of the main halocline, but is associated with a shifted biogeochemical balance in the oxygen budget (Codispoti et al., 1991; Konovalov and Murray, 2001; Tugrul et al., 2014).*

C: 16242/6-8: *What is the importance of solubility in this analysis? Does the same trend show in % saturation?*

A: This is a very pertinent remark. However we did not consider oxygen in terms of saturation but in absolute value. We would prefer to defer this analysis to a further extended work identifying more precisely the mechanisms underlying the deoxygenation trend depicted here.

A: The conclusions was completed with the following sentences : "Further works are urgently required to

assess how actual nutrient emission policies adequately prevents, in the context of fore-casted warming, the ecological and economical damages that would arise from a further shoaling of the oxic interface. Spatially-resolved biogeochemical models are needed to integrate explicitly the interacting processes affecting the Black Sea oxycline. For instance, in addition to biogeochemical processes and ventilation mechanisms, the decrease of oxygen solubility in warming waters might have had a significant role in the deoxygenation trends depicted here. “

C: 16244/1: arose -> arise

A: Corrected

2.3 FIGURES

C: Figure 1 caption could do with more details, mainly repeating the source and criteria for the profiles being kept so that it can stand independently.

A: The Caption has been extended accordingly.

C: Figure 2: Please expand axis labels to full words.

A: lon and lat have been considered obvious and removed.

C: Figure 3 caption also needs rephrasing. For example, what trends were removed (instead of saying simply detrended). The oxygen threshold needs to be stated. Also, if I understand correctly “oxygen penetration density anomaly” is incorrect; it’s not an anomaly but rather the “oxygen density penetration” or “mean density at the upper oxic boundary”? Units should be written correction (kg m⁻³, rather than kg/m³). Also... how can climatology be detrended?

A: Done

C: Figure 4: units need to be described correctly for each linear trend: decades⁻¹ needs to be added for each. This isn’t a nature paper, you have the space now. Units should be written correction (kg m⁻³, rather than kg/m³).

A: Done

C: Figure 5: Units should be written correction (mol m⁻², rather than mol/m²). I would say “Frequency distribution” rather than “Distribution density” to avoid confusion with physical density and, in my opinion, the term is more accurate.

A: Done

References

- Bittig, H. C. and Körtzinger, A.: Tackling oxygen optode drift: Near-surface and in-air oxygen optode measurements on a float provide an accurate in-situ reference, *Journal of Atmospheric and Oceanic Technology*, p. 150310071431006, 2015.
- Buesseler, K., Livingston, H., Ivanov, L., and Romanov, A.: Stability of the oxic-anoxic interface in the Black Sea, *Deep-Sea Research Part I : Oceanographic Research Papers*, 41, 283–296, 1994.
- Capet, A., Troupin, C., Carstensen, J., Grégoire, M., and Beckers, J.-M.: Untangling spatial and temporal trends in the variability of the Black Sea Cold Intermediate Layer and mixed Layer Depth using the DIVA detrending procedure, *Ocean Dynamics*, 64, 315–324, 2014.
- Codispoti, L., Friederich, G., Murray, J., and Sakamoto, C.: Chemical variability in the Black Sea: implications of continuous vertical profiles that penetrated the oxic/anoxic interface, *Deep-Sea Research Part I : Oceanographic Research Papers*, 38, S691–S710, 1991.
- Johnson, K. S., Plant, J. N., Riser, S. C., and Gilbert, D.: Air Oxygen Calibration of Oxygen Optodes on a Profiling Float Array, *Journal of Atmospheric and Oceanic Technology*, 32, 2160–2172, 2015.
- Konovalov, S. K. and Murray, J. W.: Variations in the chemistry of the Black Sea on a time scale of decades (1960–1995), *Journal of Marine Systems*, 31, 217–243, URL <http://www.sciencedirect.com/science/article/pii/S0924796301000549>, 2001.

- Kroiss, H., Zessner, M., and Lampert, C.: daNUbs: lessons learned for nutrient management in the Danube Basin and its relation to Black Sea eutrophication, *Chemistry and Ecology*, 22, 347–357, 2006.
- Piotukh, V., Zatsepin, A. G., Kazmin, A., and Yakubenko, V.: Impact of the Winter Cooling on the Variability of the Thermohaline Characteristics of the Active Layer in the Black Sea, *Oceanology*, 51, 221–230, 2011.
- Stanev, E., He, Y., Grayek, S., and Boetius, A.: Oxygen dynamics in the Black Sea as seen by Argo profiling floats, *Geophysical Research Letters*, 2013.
- Takeshita, Y., Martz, T. R., Johnson, K. S., Plant, J. N., Gilbert, D., Riser, S. C., Neill, C., and Tilbrook, B.: A climatology-based quality control procedure for profiling float oxygen data, *Journal of Geophysical Research: Oceans*, 118, 5640–5650, 2013.
- Tugrul, S., Basturk, O., Saydam, C., and Yilmaz, A.: Changes in the hydrochemistry of the Black Sea inferred from water density profiles, *Nature*, 359, 137–139, 1992.
- Tugrul, S., Murray, J. W., Friederich, G. E., and Salihoğlu, İ.: Spatial and temporal variability in the chemical properties of the oxic and suboxic layers of the Black Sea, *Journal of Marine Systems*, 135, 29–43, 2014.

Recent Decline of the Black Sea Oxygen Inventory

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Abstract.

We show that from 1955 to ~~2013~~2015, the inventory of oxygen in the Black Sea has decreased by ~~36~~44% and the basin-averaged oxygen penetration depth has decreased from 140m in 1955 to 90m in ~~2013~~2015, which is the shallowest annual value recorded during that period.

5 The oxygenated Black Sea surface layer separates the world's largest reservoir of toxic hydrogen sulphide from the atmosphere. The threat of chemocline excursion events led to hot debates in the past decades arguing on the vertical stability of the Black Sea oxic/suboxic interface. In the 1970s and 1980s, when the Black Sea faced severe eutrophication, ~~Enhanced~~, enhanced respiration rates reduced the thickness of the oxygenated layer. ~~The consecutive increase of~~ Re-increasing oxygen
10 inventory in 1985–1995 supported arguments in favor of the stability of the oxic layer. Concomitant with a reduction of nutrient loads, ~~this increase~~ it also supported the perception of a Black Sea recovering from eutrophication. More recently, atmospheric warming was shown to reduce the ventilation of the lower oxic layer by lowering Cold Intermediate Layer (CIL) formation rates.

The debate on the vertical migration of the oxic interface also addressed the natural spatial variability affecting Black Sea properties when expressed in terms of depth. Here we show that using isopycnal coordinates does not free from a significant spatial variability of oxygen penetration
15 ~~depths~~. Considering depth. By considering this spatial variability, the analysis of a composite historical set of oxygen profiles evidenced a significant shoaling of the oxic layer, and showed that the transient “recovery” of the 1990s was mainly a result of increased CIL formation rates during that
20 period.

As both atmospheric warming and eutrophication are expected to increase in the near future, monitoring the dynamics of the Black Sea oxic layer is urgently required to assess the threat of further shoaling.

1 Introduction

25 The Black Sea deep waters constitutes the world's largest reservoir of toxic hydrogen sulphide.
100 meters of ventilated surface waters are all that separate this reservoir from the atmosphere.
This situation results from the permanent halocline (Özsoy and Ünlüata, 1997) that separates ~~a low~~
~~salinity~~ the surface layer (of low salinity due to river inflow) ~~and a higher salinity from the~~
layer (of high salinity due to inflowing Mediterranean seawater), restraining ventilation to the upper
30 layer (Fig. 1).

~~Around~~ In the lower part of the halocline, a permanent suboxic layer separates the Black Sea sur-
face oxygenated waters ($[O_2] > 20 \mu M$) from the deep sulphidic waters ($[H_2S] > 20 \mu M$) (Murray
et al., 1989; Tugrul et al., 1992; Murray et al., 1995). More precisely, Murray et al. (1989) considered
a threshold of $10 \mu M$ of oxygen because they analyzed high quality oxygen data. The threshold of
35 $20 \mu M$ of oxygen was applied later to analyze historical oxygen data of lower quality. The upper
(O_2 disappearance) and lower (H_2S onset) interfaces of this suboxic layer are controlled by differ-
ent biogeochemical and physical processes (Konovalov et al., 2006; Stanev et al., 2014), and undergo
uncorrelated vertical migrations (Konovalov and Murray, 2001). Sinking organic matter is mainly
respired aerobically within the oxycline, i.e. the lower part of the oxygenated layer where oxy-
40 gen concentration decreases ~~to~~ $> 20 \mu M$ downwards to $20 \mu M$. Increasing flux of organic matter,
induced by a period of high nutrient load from the 70s to the late 80s, resulted in higher oxygen
consumption above the suboxic layer and a shoaling of the upper suboxic interface (Codispoti et al.,
1991; Konovalov and Murray, 2001; Tugrul et al., 2014).

After reduction of nutrient inputs around 1990 (Kroiss et al., 2006), the Black Sea was described
45 as a recovering ecosystem (Mee et al., 2005; Oguz et al., 2006). This perspective was supported by
improved eutrophication indices in the open sea (Kideys, 2002) as well as the stabilization of the
upper suboxic interface in the 90s (Konovalov and Murray, 2001). However, the time scale of the
expected recovery, i.e. the time scale associated with the chain of biogeochemical mechanisms re-
lating oxycline penetration depth to riverine nutrient loads, is not quantitatively understood. Several
50 processes cause the oxycline depth to respond with a time lag to the reduction of riverine nutrient
inputs. First, nutrients are mainly delivered to the northwestern shelf, where the accumulation of
organic matter in the sediments buffers the riverine inputs, with slow diagenetic processes control-
ling and delaying the nutrient outflow across the seaward boundary (Capet et al., 2013). Second,
the intermediate oxidation–reduction cycling of nitrogen, sulfur, manganese, iron and phosphorus
55 that separates oxygen from hydrogen sulphide (Shaffer, 1986; Codispoti et al., 1991; Konovalov
et al., 2006; Yakushev et al., 2007) can delay the response of the lower suboxic interface to changing
nutrient fluxes by several years (Konovalov et al., 2006).

In addition to these biogeochemical factors, the dynamics of the upper and lower interfaces of the
suboxic layer are controlled by physical processes (Konovalov et al., 2006; Stanev et al., 2014). In
60 the Black Sea, dense waters formed by winter cooling and mixing Staneva and Stanev (2002) do

not sink to the deepest layer, as in the Mediterranean sea, but accumulate on top of the permanent halocline, ~~playing a major role in the vertical structure by forming the~~ (Fig. 1). The resulting Cold Intermediate Layer (CIL) is a major feature of the Black Sea vertical structure. Cold intermediate ~~waters-water~~ formation and advection by the cyclonic basin-wide Rim Current (Öszoy and Ünlüata, 65 1997; Capet et al., 2012) ventilate the oxycline and thereby influence variability in the depth of the upper suboxic interface (Konovalov et al., 2006). Recently, atmospheric warming (Oguz et al., 2006) was shown to reduce the ventilation of the lower oxyc layer (Tugrul et al., 2014; Pakhomova et al., 2014). At deeper levels, the dense sinking plume formed by the Mediterranean inflow through the Bosphorus, which entrains water from the overlying CIL, injects fingers of oxygenated water directly 70 into the deeper part of the suboxic layer and upper sulphidic layer and thus acts to control the depth of the lower suboxic interface (Konovalov and Murray, 2001; Konovalov et al., 2003; Glazer et al., 2006; Konovalov et al., 2006).

Previous long-term analyses of the vertical migration of the suboxic interfaces either ended (1955–1995 (Konovalov and Murray, 2001)) or started (1985–2015 (Pakhomova et al., 2014)) with 75 the eutrophication period, excluding the large-scale overview required to grasp the interactions of eutrophication and climate factors. Those analyses lacked a comprehensive consideration of the natural spatial and seasonal variability of the vertical distribution of oxygen.

In the presence of large gradients, uneven data distribution may induce artificial signals when inter-annual trends are assessed from direct annual averages. In the stratified Black Sea, properties 80 expressed in terms of depth coordinates (m) present a high spatial variability due to mesoscale features (Kempe et al., 1990) and to the general curvature of Black Sea isopycnals (Öszoy and Ünlüata, 1997; Stanev et al., 2014). As an alternative, using density (isopycnal levels, σ_θ) as vertical coordinate is generally considered a stable solution to assess the vertical migration of the chemocline on a decadal scale (Tugrul et al., 1992; Saydam et al., 1993; Murray et al., 1995). However, the spatial 85 confinement of the lateral oxygen injections associated with the Bosphorus plume, as well as the spatial variability of diapycnal ventilating processes (Zatsepin et al., 2007), imposes an horizontal structure to the oxygen penetration depth when expressed in terms of density (Stanev et al., 2004; Glazer et al., 2006). As this spatial gradient might scale with the temporal variations (a range of 0.17 kg m^{-3} was observed during the Knorr2003 campaign, Glazer et al. (2006)), it has to be considered 90 when deriving interannual trends.

The present study describes the application of the DIVA (Data-Interpolating Variational Analysis) detrending procedure (Troupin et al., 2012; Capet et al., 2014) to untangle the temporal and spatial ~~trends-variability~~ of three indices related to the Black Sea oxygenation status: the depth and density level of oxygen penetration and the oxygen inventory. These values were diagnosed from a composite 95 historical dataset of oxygen vertical profiles. We reviewed the evolution of those indices through the past 60 years and discuss the respective controls of eutrophication and climate factors.

2 Material and methods

2.1 Data

We gathered a composite set of ~~4467–4385~~ ship-based vertical profiles (oxygen, temperature and salinity) obtained between 1955 and ~~2013–2005~~ in the Black Sea using CTD rosette bottles, continuous pumping profilers (Codispoti et al., 1991) and in situ analyzers (Glazer et al., 2006) from the World Ocean Database (<http://www.nodc.noaa.gov/OC5/SELECT/dbsearch/dbsearch.html>), R/V Knorr 2003 and R/V Endeavor 2005 campaigns (<http://www.ocean.washington.edu/cruises/Knorr2003/>, <http://www.ocean.washington.edu/cruises/Endeavor2005/>). Only the profiles containing at least 5 observation depths, one observation above 30 m depth and one record with $[O_2] < 20 \mu\text{M}$ were retained for analysis. The temporal and spatial distribution of the selected ship-based profiles are displayed in Figs. 2 and 3, respectively.

~~In addition To complement the analysis of ship-based casts, we considered data originated from two profiles originating from ten Argo autonomous profilers (ARGO) released in May 2010 southwest of the Crimean peninsula (Stanev et al., 2013). These provided recent independent estimates (119 and 187 profiles, 2010–2012) used to complement May 2010–December 2015). Only good quality-checked real-time data were considered (Carval et al., 2014). Two of these floats (Argo ID 7900465 and 7900466) have been presented and discussed by Stanev et al. (2013), where the consistence and comparability of Argo and historical profiles is asserted within a $1 \mu\text{M}$ error range.~~

~~Several studies address the error of Argo real-time oxygen data (e.g., Bittig and Körtzinger, 2015; Takeshita et al., 2013; Johnson et al., 2015). Demonstrating that the Black Sea real-time Argo data are precisely (ie, at fine scales) comparable with historical Winkler data, or identifying the relevant correction, is beyond the scope of the present study which addresses monthly to decadal time scales. Evenly distributed small scales error (eg., difference between ascending and descending profiles due to sensor time response) were thus filtered by the temporal smoothing. However, a systematic error is not strictly excluded which could reach an underestimation of $10 \mu\text{M}$ (Virginie Thierry, IFREMER, personal communication, January 2016). Therefore, we evaluated a “worst-case” scenario in the analysis of ship-based casts. One Argo data by considering a systematic underestimation of oxygen concentration by $10 \mu\text{M}$.~~

~~Although most of the floats went drifting in the central basin while the other approximately followed the shelf break drifted along the basin periphery, some were also advected in the central part (Fig. 3). Thanks to these trajectories, the difference between the two floats also provided ranges. These trajectories highlight the range of spatial variability for the diagnostics described in Sect. 2.2.~~

The investigation time frame was divided into periods according to data availability and to dissociate known phases of eutrophication (Oguz, 2008; Kroiss et al., 2006) and CIL dynamics (Piotukh et al., 2011; Capet et al., 2014) (see also Oguz et al. (2006) for decadal cycles in the Black Sea): 1955–1975 (1575 ship-based profiles), 1976–1985 (1350 ship-based profiles), 1986–1998 (1324

ship-based profiles) and ~~1999–2013 (218~~ 1999–2015 (136 ship-based profiles ~~+306 ARGO and~~ 1393 Argo profiles).

2.2 Profile analysis

135 From each profile we derived (1) the depth and (2) the ~~density-level~~ potential density anomaly σ_θ
where oxygen concentration went below 20 μM and (3) the oxygen inventory, integrated above
this limit (Fig. 1). The threshold value of 20 μM used to define the upper interface of the suboxic
layer was suggested to compare oxygen observations issued from sensors with different detection
limits (Konovalov and Murray, 2001). To evaluate how a 10 μM underestimation by Argo profilers
140 would affect the main conclusions, oxygen penetration depths and density levels for Argo were also
computed using a threshold of 10 μM .

The ~~Cold water inventory, or~~ CIL cold content ~~(Fig. 1)~~ was diagnosed from corresponding salin-
ity and temperature profiles following (Piotukh et al., 2011; Capet et al., 2014) Capet et al. (2014).
It indicates on the intensity of CIL formation smoothed over 4-5 years, i.e. the residence time of cold
145 intermediate waters (Staneva and Stanev, 2002; Piotukh et al., 2011; Capet et al., 2014).

$$\text{CIL cold content} = c\rho \int_{\text{CIL}} [T(z) - T_{\text{CIL}}] dz, \quad (1)$$

where ρ is the density and c the heat capacity and $T_{\text{CIL}} = 8.35$ °C (Stanev et al., 2013).

2.3 DIVA analysis

~~Annual climatologies~~ Climatologies for the whole period and interannual trends were identified for
150 the three oxygen diagnostics ~~using by applying~~ the DIVA detrending algorithm ~~, to account for the~~
~~sampling error associated with spatial/temporal variability~~ on the ship-based data set (see details in
Appendix A).

In short, the DIVA interpolation software (<http://modb.oce.ulg.ac.be/mediawiki/index.php/DIVA>
Troupin et al. (2012)) computes a gridded climatology obtained by minimizing a cost function which
155 penalize gradients and misfits with observations (~~see Troupin et al. (2012) for more details~~). The
DIVA detrending algorithm (Capet et al., 2014) ~~then~~ computes trends for ~~subsets of data~~ each year,
i.e. the average difference between data pertaining to this subset year and the spatial analysis at these
data locations. ~~Here, two classes of subset were considered: the data grouped per year and per month~~
~~(all year included). A new data set is constructed by subtracting the trends from the original data.~~
160 ~~This new set is used to compute a new “detrended” spatial climatology. Refined trends are computed~~
~~iteratively with respect to detrended spatial analyses, until reaching convergence (~10 iterations).~~
~~The temporal trend identified for one variable thus corresponds to a time evolving average bias~~
~~adding homogeneously to the climatological spatial structure.~~ This procedure allows one to account
for the sampling error associated with spatial/temporal variability.

165 3 Results

3.1 Spatial Trends ~~variability~~

The spatial distribution of the oxygen penetration depth (Fig. 4a) reflects the general curvature of the Black Sea vertical structure. A range of approximately 70 m was observed between oxygen penetration depth in the periphery (150 m) and in the central part (80 m).

170 ~~The spatial distribution of the oxygen inventory (Fig. 4b) follows that of the oxygen penetration depth. The range of spatial variability reaches 12, ie. between 17 and 29.~~

A significant spatial variability remains when expressing oxygen penetration in terms of ~~density levels~~ potential density anomaly, σ_θ , (Fig. 4e). ~~A-b). While the central part bears typical values of 15.75 kg m⁻³, a deeper anomaly (in terms of density) can be seen in the area of the Bosphorus~~ 175 plume (16.1 kg m⁻³), which then decreases along the ~~Anatolian coast. This anomaly results southern~~ (15.85-15.9 kg m⁻³) and eastern periphery (15.85 kg m⁻³). ~~These result~~ in a range of spatial variability of ~~0.3-0.35~~ kg m⁻³.

The ~~spatial distribution of the oxygen inventory (Fig. 4c) follows that of the oxygen penetration depth. The range of spatial variability reaches 12 mol O m⁻², ie. between 17 mol O m⁻² in the~~ 180 ~~central part and 29 mol O m⁻² in the periphery.~~

~~The~~ ranges of spatial variability derived from these spatial analysis agreed with those depicted by the ~~difference between the two ARGO-Argo~~ profilers (Fig. 6)5), ~~bearing in mind the different time scales under consideration.~~

3.2 Temporal trends ~~variability~~

185 ~~Since 1955~~ ~~Between 1955-2005~~, the oxygen penetration depth rose by an average rate of ~~8.2-7.9~~ m per decade, ~~from a basin average (Fig. 6a). The basin average was of 140 m in 1955 to (ship-based),~~ 100 m in 2005 (ship-based) and 90 m in ~~2013-2015 (Argo). Considering a systematic underestimation~~ by 10 μM in the Argo data would result in an oxygen penetration depth around 95 m for 2015 (Argo).

190 This shoaling was also observed on ~~a vertical~~ the potential density scale (~~-0.085-0.074~~ kg m⁻³ per ~~decades~~ decade, Fig. 6b). ~~The basin average was of 16.05 kg m⁻³ in 1955 (ship-based), 15.6 kg m⁻³ in 2005 (ship-based) and around 15.3 kg m⁻³ in 2015 (Argo). Considering a systematic underestimation by 10 μM in the Argo data would result in values of 15.5 m for 2015 (Argo).~~

The oxygen inventory, integrated from the surface down to the suboxic upper interface, decreased 195 by ~~3644%~~ during ~~those 58 years~~ the last 60 years (Fig. 6c), considering the ship-based estimate for 1955 (27 mol O m⁻²) and the Argo estimate for 2015 (15 mol O m⁻²). The few ship-based profiles available after the mid 90s revealed the lowest oxygen inventories recorded during the time frame covered by the present study (Fig. 6c). ~~These low values were confirmed by the two ARGO profilers (Fig. 6).~~

200 The temporal signals departed from these linear trends between 1988 and 1996, during which deeper oxygen penetration (both in terms of depth and density) and higher oxygen content were observed.

3.3 Oxygen inventory and CIL cold content

205 Positive relationships between oxygen ~~and Cold Intermediate Water inventories~~ inventory and CIL cold content were obtained for all periods (Fig. 7). ~~The oxygen inventories corresponding to a given~~ Considering a given level of CIL cold content, the corresponding oxygen inventory decreased significantly from period 1955–1975 to period 1986–1998 (Fig. 7b).

~~Fewer oxygen profiles were available for the period 1999–2013, even when including profiles from the ARGO floats. The combined data set depicts a~~ The relationship between oxygen ~~and cold waters inventories during 1999–2013 which~~ inventory and CIL cold content for the period 1999–2015 does not differ significantly from that obtained ~~during for the period~~ during for the period 1986–1998 (Fig. 7b). This comparison should be considered with caution, however, as ~~ARGO sampling rates differs strongly from those of ship-based casts (ARGO oxygen profiles for the period 1999–2015 originate mainly from Argo floats whose~~ Argo floats whose sampling rate is much higher ~~)than ship-based casts.~~

215 ~~Observed CIL cold contents were generally higher~~ High CIL cold content are much more frequent during the period 1986–1998, while ~~more low cold contents are observed~~ low CIL cold content are more frequent during 1999–2013.

4 Discussion

220 The spatial analysis of oxygen penetration depth showed that the use of density coordinates does not eliminate the sampling error associated with uneven spatial coverage ~~. Rather, the~~ (Fig. 4). Deeper pycnal oxygen penetration in the Bosphorus area were expected, in relation with the intermediate lateral injections associated with the Bosphorus plume. In addition, deeper pycnal oxygen penetration in the southern and eastern periphery suggests the occurrence of diapycnal ventilation along the steep bathymetry (Zatsepin et al., 2007). The aggregation of the most recent ship-based profiles ~~in the Bosphorus area and along the north eastern coast in the southeastern region~~ (Fig. 3), where deeper penetration occurs (Fig. 4), might have led to an overestimation of the basin-average oxygen penetration depth in the last decade, hence to an underestimation of the shoaling trend of the Black Sea oxic layer.

230 Considering spatial variability revealed a clear shoaling trend for oxygen penetration depth. This shoaling can be seen on both depth and density scales (Fig. 6a,b). This confirms the hypothesis that ~~higher oxygen consumption associated with eutrophication, rather than a~~ the shoaling of oxygen penetration depth is not due to a general shoaling of the main halocline, ~~caused the vertical migration of the oxycline (Codispoti et al., 1991; Konovalov and Murray, 2001; Tugrul et al., 2014)~~ but is associated

with a shifted biogeochemical balance in the oxygen budget (Codispoti et al., 1991; Kononov and Murray, 2001; Tugrul et al., 2014)

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Using σ_θ coordinates depicts clearer temporal variations (Fig. 5 and Fig. 6). The shoaling rate varies in time and was more intense during 1970–1985 and from 1996 onwards. Argo diagnostics using different oxygen threshold show a larger discrepancy in the case of pycnal coordinates. The co-occurrence of density and oxygen gradients (Fig. ??) results in a higher sensitivity to the sensor accuracy for the σ_θ diagnostic for oxygen penetration. However, even a systematic underestimation by 10 μM of oxygen concentration by Argo profilers does not invalidate our results.

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The positive correlations ~~observed~~ between CIL cold content and oxygen inventory ~~observed~~ for all the periods illustrate the ventilation of intermediate layers by CIL formation and advection (Fig. 7b) ~~illustrate how CIL formation and advection ventilates the intermediate layers. The transient stabilization of the oxygen penetration depth in the~~. In the early 90s (Tugrul et al., 1992; Buesseler et al., 1994) (Fig. 6, the transient recovery of the three oxygenation diagnostics (Figs. 6a, b, c, 7a) provided arguments supporting the stability of the oxic interface (Tugrul et al., 1992; Buesseler et al., 1994). This stabilization matched the convenient perception of a general recovery of the Black Sea ecosystem after the reduction of nutrient load around 1990 (Kroiss et al., 2006). However, Fig. 7 indicates that ~~this stabilization was mainly induced by a decade of high CIL formation (1985–1995, Piotukh et al. (2011); Capet et al. (2014))~~, which provided enough ventilation to mask ongoing high oxygen consumption. ~~If the oxygenation diagnostics obtained for the period 1986–1998 were associated with much higher ventilation rates (ie, higher CIL cold content) than during the previous periods. If, in response to nutrient reduction,~~ the biogeochemical oxygen consumption terms had been lower during the period 1986–1998 ~~in response to nutrient reduction than previously~~, the increased ventilation during that period ~~should would~~ have resulted in higher oxygen inventories. Instead, oxygen inventories observed during 1986–1998 are lower than those observed in the previous decade for similar levels of CIL cold content. ~~We conclude that high CIL formation rates during this period (Piotukh et al., 2011; Capet et al., 2014) provided enough ventilation to mask ongoing high oxygen consumption.~~

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The fact that the relationship between oxygen inventories and CIL content ~~after 1999 for the last period 1999-2015~~ is similar to that of 1986–1998 indicates a stabilization in the biogeochemical oxygen consumption terms. Higher air temperature in ~~these last years this last period~~ (Oguz and Cokacar, 2003; Oguz et al., 2006; Pakhomova et al., 2014), by limiting winter convective ventilation events (Capet et al., 2014), ~~led to the lower oxygen inventories ever recorded for the Black Sea (Fig. 6c).~~

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Fore-casted global warming, without excluding transient high ventilation periods, will limit CIL water formation (Capet et al., 2014) and reduce the oxygenation of the Black Sea intermediate layers. At the same time, uncertainties remain regarding the capacity of ~~reflourishing re-flourishing~~ economies of the lower Danube watershed to recover their productivity in a more sustainable, less

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polluting form. Economic development in the Danube Basin could reverse the improving situation of eutrophication if nutrients are not managed properly (Kroiss et al., 2006). Under these conditions, there is no reason to expect that the oxycline shoaling observed over the past 60 years will stabilize.

275 There are reasons to worry about a rising oxycline in the Black Sea. First, biological activity is distributed vertically on the whole oxygenated layer, as indicated by zooplankton ~~diel~~diel migration Ostrovskii and Zatsepin (2011). The ~~36~~reduction of the oxygenated volume described in this study could therefore have impacted on Black Sea living stocks by reducing carrying capacity and increasing predation encounter rates. It would come in timely to estimate now the impact that a further shoaling of the oxic interfaces would bear on the Black Sea resources for the fishing industry.

280 Second, under present conditions, a massive atmospheric release of hydrogen sulphide caused by a sudden outcropping of anoxic waters remains unlikely, due to the stability of the Black Sea pycnal structure. Such outcropping event of sulphidic waters would have dramatic ecological and economical consequences (Mee, 1992). On the 27th October 2005, an anomalous quasi-tropical cyclone was observed over the western Black Sea that led, in a few days, to the outcropping of waters initially
285 located at 30 m depth (Efimov et al., 2008). Two years earlier, sulphide was measured in the same area (western central gyre) around 80 m (Glazer et al., 2006). Because global warming is expected to increase the occurrence of extreme meteorological events (Beniston et al., 2007), every meter of oxycline shoaling would bring the Black Sea chemocline excursion events closer to the ~~realms of possible~~realm of possibility.

290 5 Conclusions

The ~~results presented in this study demonstrated~~present study evidenced the decline of the Black Sea oxygen inventory during the second half of the XXth century and first decade of XXIth and highlighted the threat that further atmospheric warming casts upon the vertical stability of the Black Sea oxygenated layer. ~~To~~

295 Further works are urgently required to assess how actual nutrient ~~emissions~~emission policies adequately prevents, in the context of fore-casted warming, the ecological and economical damages that would ~~arose~~arise from a further shoaling of the oxic interface ~~it is~~.

Spatially-resolved biogeochemical models are needed to integrate explicitly the interacting processes affecting the Black Sea oxycline. here.

300 It is also essential (1) to determine to which extent the shoaling of the oxygen penetration depth entrains a shoaling of the the sulphidic onset depth; (2) to set up a continuous monitoring of the Black Sea oxygen inventory and the intensity of winter convective ventilation (through CIL cold content); and (3) to clarify and quantify the interplays of diapycnal and isopycnal ventilation mechanisms and, in particular, the role played by the peripheral permanent/semi-permanent mesoscale
305 structures and how this relates to the intensity of the Rim Current (Stanev et al., 2014; Kubryakov

and Stanichny, 2015). We propose that these objectives might be answered by maintaining in the Black Sea a minimum population of both moored and drifting autonomous profilers equipped with oxygen and sulphidic sensors.

~~Deoxygenation is currently affecting a growing number of sites in the world Diaz (2001); Diaz and Rosenberg (2008).~~

310 ~~While the present study does not extend on the description of mechanisms balancing the deoxygenation budget, it does illustrate how the biogeochemical terms of this budget can be largely decoupled from~~

Appendix A: The DIVA detrending algorithm

DIVA (Data-Interpolating Variational Analysis) is a method for spatial interpolation. Its principle is to construct an analyzed field φ that satisfies a set of constraints expressed in the form of a cost function over a spatial domain Ω . The cost function is made up of (1) an *observation constraint*, which penalizes the misfit between data and analysis, and (2) a *smoothness constraint*, which penalizes the irregularity of the ~~changes in nutrient loads by inertial mechanisms. It highlights the importance of considering spatial variability in assessing long term trends~~ analyzed field (gradients, Laplacian etc).

320 REFER TO REVISION MANUSCRIPT FOR THE EQUATION APPEARING HERE

The first term of (??) measures the spatial variability (curvature, gradient and value) of the analyzed field and is identified as the smoothness constraint. The second term is a weighted sum of data-analysis misfits and is identified as the observation constraint: it tends to pull the analyzed field towards the observations. The coefficients of (??) can be determined from: (1) the relative weights w_i attributed to each observation d_i , (2) the correlation length L and (3) the signal-to-noise ratio λ (Troupin et al., 2012). The analyses presented in this study were achieved with equal weights $w_i = 1$, $L = 0.8^\circ$ and $\lambda = 0.5$. The minimization of ?? is solved over Ω with a finite-element technique (Brasseur et al., 1996) which excludes data influence across land points Troupin et al. (2010).

330 The detrending algorithm, presented in (Capet et al., 2014) with synthetic and real case studies, proceeds as follows. Input data can be classified amongst the different classes C_j (e.g. 1990, 1991, ...) of a given group C (e.g. the year). The observation constraint of the functional (??) can then be rewritten by including an unknown trend value for each class (d_{C_1}, d_{C_2}, \dots):

$$\begin{aligned} J_{\text{obs}}[\varphi] &\equiv \sum_{i \in C_1} \mu_i [d_i - d_{C_1} - \varphi(x_i, y_i)]^2 \\ &\quad \pm \sum_{i \in C_2} \mu_i [d_i - d_{C_2} - \varphi(x_i, y_i)]^2 + \dots \end{aligned} \quad (\text{A1})$$

335 If the function $\varphi(x, y)$ were known, minimization with respect to each of the unknowns d_{C_j} would yield

$$d_{C_1} = \frac{\sum_{i \in C_1} \mu_i [d_i - \varphi(x_i, y_i)]}{\sum_{i \in C_1} \mu_i} \quad (\text{A2})$$

and similarly for the other classes: the trend for each class is the weighted misfit of the class with respect to the overall analysis.

340 Using an analysis without detrending as a first guess for φ , trends are computed for each classes in each group and subtracted from the original data. Following this, a new analysis is performed, the trends are recalculated, and the iterations continue until a specified convergence criterion is fulfilled. The procedure can be generalized with several groups of classes. The present study considered years and months.

345 The DIVA software and up-to-date related informations can be found on <http://modb.oce.ulg.ac.be/mediawiki/index.php/DIVA>.

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350 Argo data were collected, checked and made freely available by the International Argo Program, part of the Global Ocean Observing System, and the national programs that contribute to it (<http://www.argo.ucsd.edu>, <http://argo.jcommops.org>).

355 **References**

- Beniston, M., Stephenson, D. B., Christensen, O. B., Ferro, C. A., Frei, C., Goyette, S., Halsnaes, K., Holt, T., Jylhä, K., Koffi, B., et al.: Future extreme events in European climate: an exploration of regional climate model projections, *Climatic Change*, 81, 71–95, 2007.
- 360 Bittig, H. C. and Körtzinger, A.: Tackling oxygen optode drift: Near-surface and in-air oxygen optode measurements on a float provide an accurate in-situ reference, *Journal of Atmospheric and Oceanic Technology*, p. 150310071431006, 2015.
- Brasseur, P., Beckers, J.-M., Brankart, J.-M., and Schoenauen, R.: Seasonal temperature and salinity fields in the Mediterranean Sea: Climatological analyses of a historical data set, *Deep-Sea Research Part I : Oceanographic Research Papers*, 43, 159–192, doi:10.1016/0967-0637(96)00012-X, 1996.
- 365 Buesseler, K., Livingston, H., Ivanov, L., and Romanov, A.: Stability of the oxic-anoxic interface in the Black Sea, *Deep-Sea Research Part I : Oceanographic Research Papers*, 41, 283–296, 1994.
- Capet, A., Barth, A., Beckers, J.-M., and Grégoire, M.: Interannual variability of Black Sea’s hydrodynamics and connection to atmospheric patterns, *Deep-Sea Research Part II : Topical Studies in Oceanography*, 77-80, 128–142, doi:10.1016/j.dsr2.2012.04.010, <http://www.sciencedirect.com/science/article/pii/S0967064512000586>, *satellite Oceanography and Climate Change*, 2012.
- 370 Capet, A., Beckers, J.-M., and Grégoire, M.: Drivers, mechanisms and long-term variability of seasonal hypoxia on the Black Sea northwestern shelf — is there any recovery after eutrophication?, *Biogeoscience*, 10, 3943–3962, 2013.
- Capet, A., Troupin, C., Carstensen, J., Grégoire, M., and Beckers, J.-M.: Untangling spatial and temporal trends in the variability of the Black Sea Cold Intermediate Layer and mixed Layer Depth using the DIVA detrending procedure, *Ocean Dynamics*, 64, 315–324, 2014.
- 375 Carval, T., Keeley, B., Takatsuki, Y., Yoshida, T., Stephen, L., Schmid, C., Goldsmith, R., Wong, A., McCreadie, R., Thresher, A., and Tran, A.: *Argo User’s manual*, 2014.
- Cleveland, W. S., Grosse, E., and Shyu, W. M.: Local regression models, in: *Statistical models in S*, edited by Chambers, J. and Hastie, T., Wadsworth & Brooks/Cole, 1992.
- 380 Codispoti, L., Friederich, G., Murray, J., and Sakamoto, C.: Chemical variability in the Black Sea: implications of continuous vertical profiles that penetrated the oxic/anoxic interface, *Deep-Sea Research Part I : Oceanographic Research Papers*, 38, S691–S710, 1991.
- Diaz, R. J.: Overview of hypoxia around the world, *JEQ*, 30, 275–281, 2001.
- 385 Diaz, R. J. and Rosenberg, R.: Spreading Dead Zones and Consequences for Marine Ecosystems, *Science*, 321, 926–929, doi:10.1126/science.1156401, <http://www.sciencemag.org/content/321/5891/926.abstract>, 2008.
- Efimov, V., Stanichnyi, S., Shokurov, M., and Yarovaya, D.: Observations of a quasi-tropical cyclone over the Black Sea, *Russian Meteorology and Hydrology*, 33, 233–239, 2008.
- Glazer, B. T., Luther, G. W., Kononov, S. K., Friederich, G. E., Trouwborst, R. E., and Romanov, A. S.: Spatial and temporal variability of the Black Sea suboxic zone, *Deep-Sea Research Part II : Topical Studies in Oceanography*, 53, 1756–1768, 2006.
- 390 Johnson, K. S., Plant, J. N., Riser, S. C., and Gilbert, D.: Air Oxygen Calibration of Oxygen Optodes on a Profiling Float Array, *Journal of Atmospheric and Oceanic Technology*, 32, 2160–2172, 2015.
- Kempe, S., Liebezett, G., and Diercks, A.-R.: Water balance in the Black Sea, *Nature*, 346, 419, 1990.

- 395 Kideys, A. E.: Fall and rise of the Black Sea ecosystem, *Science*, 297, 1482–1484, 2002.
- Konovalov, S., Murray, J. W., Luther, G., and Tebo, B.: Processes controlling the redox budget for the oxic/anoxic water column of the Black Sea, *Deep-Sea Research Part II : Topical Studies in Oceanography*, 53, 1817–1841, doi:10.1016/j.dsr2.2006.03.013, <http://www.sciencedirect.com/science/article/B6VGC-4KSSW7D-1/2/f04cc2994d928a16eacb1af3868b9b08>, *Black Sea Oceanography*, 2006.
- 400 Konovalov, S. K. and Murray, J. W.: Variations in the chemistry of the Black Sea on a time scale of decades (1960–1995), *Journal of Marine Systems*, 31, 217–243, <http://www.sciencedirect.com/science/article/pii/S0924796301000549>, 2001.
- Konovalov, S. K., Luther III, G., Friederich, G. E., Nuzzio, D. B., Tebo, B. M., Murray, J. W., Oguz, T., Glazer, B., Trouwborst, R. E., Clement, B., et al.: Lateral injection of oxygen with the Bosphorus plume—fingers of oxidizing potential in the Black Sea, *Limnology and Oceanography*, 48, 2369–2376, 2003.
- 405 Kroiss, H., Zessner, M., and Lampert, C.: daNUbs: lessons learned for nutrient management in the Danube Basin and its relation to Black Sea eutrophication, *Chemistry and Ecology*, 22, 347–357, 2006.
- Kubryakov, A. and Stanichny, S.: Seasonal and interannual variability of the Black Sea eddies and its dependence on characteristics of the large-scale circulation, *Deep-Sea Research Part I : Oceanographic Research Papers*, 97, 80–91, 2015.
- 410 Mee, L., Friedrich, J., and Gomoiu, M.-T.: Restoring the Black Sea in times of uncertainty., *Oceanography*, 18, 32–43, 2005.
- Mee, L. D.: The Black Sea in crisis: a need for concerted international action., *Ambio*, 21, 278–86, 1992.
- Murray, J., Jannasch, H., Honjo, S., Anderson, R., Reeburgh, W., Top, Z., Friederich, G., Codispoti, L., and Izdar, E.: Unexpected changes in the oxic/anoxic interface in the Black Sea, *Nature*, 338, 411–413, 1989.
- 415 Murray, J. W., Codispoti, L. A., and Friederich, G. E.: Oxidation/reduction environments, *Aquatic Chemistry*, pp. 157–176, 1995.
- Oguz, T., ed.: State of the Environment of the Black Sea (2001 - 2006/7), Publications of the Commission on the Protection of the Black Sea Against Pollution (BSC), http://www.blacksea-commission.org/_publ-SOE2009.asp, 2008.
- 420 Oguz, T. and Cokacar, T.: Climatic warming and accompanying changes in the ecological regime of the Black Sea during 1990s, *Global Biogeochemical Cycles*, 17, doi:10.1029/2003GB002031, 2003.
- Oguz, T., Dippner, J. W., and Kaymaz, Z.: Climatic regulation of the Black Sea hydro-meteorological and ecological properties at interannual-to-decadal time scales, *Journal of Marine Systems*, 60, 235–254, doi:10.1016/j.jmarsys.2005.11.011, <http://www.sciencedirect.com/science/article/pii/S092479630500206X>, 2006.
- 425 Ostrovskii, A. and Zatsepin, A.: Short-term hydrophysical and biological variability over the northeastern Black Sea continental slope as inferred from multiparametric tethered profiler surveys, *Ocean Dynamics*, 61, 797–806, 2011.
- 430 Öszo, E. and Ünlüata, Ü.: Oceanography of the Black Sea: a review of some recent results., *Earth-Science Reviews*, 42, 231–272, 1997.
- Pakhomova, S., Vinogradova, E., Yakushev, E., Zatsepin, A., Shtereva, G., Chasovnikov, V., and Podymov, O.: Interannual variability of the Black Sea Proper oxygen and nutrients regime: The role of climatic and anthropogenic forcing, *Estuarine, Coastal and Shelf Science*, 140, 134–145, 2014.

- 435 Piotukh, V., Zatsepin, A. G., Kazmin, A., and Yakubenko, V.: Impact of the Winter Cooling on the Variability of the Thermohaline Characteristics of the Active Layer in the Black Sea, *Oceanology*, 51, 221–230, 2011.
- Saydam, C., Tugrul, S., Basturk, O., and Oguz, T.: Identification of the oxic/anoxic interface by isopycnal surfaces in the Black Sea, *Deep-Sea Research Part I : Oceanographic Research Papers*, 40, 1405–1412, 1993.
- 440 Shaffer, G.: Phosphate pumps and shuttles in the Black Sea, *Nature*, 321, 515–517, 1986.
- Stanev, E., Staneva, J., Bullister, J., and Murray, J. W.: Ventilation of the Black Sea pycnocline. Parameterization of convection, numerical simulations and validations against observed chlorofluorocarbon data, *Deep-Sea Research Part I : Oceanographic Research Papers*, 51, 2137–2169, doi:10.1016/j.dsr.2004.07.018, <http://www.sciencedirect.com/science/article/B6VGB-4DN17DM-1/2/c889c55405c12a02e8d7c3e725814eef>, 2004.
- 445 Stanev, E., He, Y., Grayek, S., and Boetius, A.: Oxygen dynamics in the Black Sea as seen by Argo profiling floats, *Geophysical Research Letters*, 2013.
- Stanev, E. V., He, Y., Staneva, J., and Yakushev, E.: Mixing in the Black Sea detected from the temporal and spatial variability of oxygen and sulfide – Argo float observations and numerical modelling, *Biogeosciences*, 11, 5707–5732, doi:10.5194/bg-11-5707-2014, <http://www.biogeosciences.net/11/5707/2014>, 2014.
- 450 Staneva, J. and Stanev, E.: Water mass formation in the Black Sea during 1991–1995, *Journal of Marine Systems*, 32, 199–218, doi:10.1016/S0924-7963(02)00038-6, <http://www.sciencedirect.com/science/article/pii/S0924796302000386>, 2002.
- Takeshita, Y., Martz, T. R., Johnson, K. S., Plant, J. N., Gilbert, D., Riser, S. C., Neill, C., and Tilbrook, B.: A climatology-based quality control procedure for profiling float oxygen data, *Journal of Geophysical Research: Oceans*, 118, 5640–5650, 2013.
- 455 Troupin, C., Machín, F., Ouberdous, M., Sirjacobs, D., Barth, A., and Beckers, J.-M.: High-resolution climatology of the North-East Atlantic using Data-Interpolating Variational Analysis (DIVA), *Journal of Geophysical Research*, 115, C08 005, doi:10.1029/2009JC005512, <http://www.agu.org/pubs/crossref/2010/2009JC005512.shtml>, 2010.
- 460 Troupin, C., Sirjacobs, D., Rixen, M., Brasseur, P., Brankart, J.-M., Barth, A., Alvera-Azcárate, A., Capet, A., Ouberdous, M., Lenartz, F., Toussaint, M.-E., and Beckers, J.-M.: Generation of analysis and consistent error fields using the Data Interpolating Variational Analysis (DIVA), *Ocean Modelling*, 52-53, 90–101, doi:10.1016/j.ocemod.2012.05.002, <http://www.sciencedirect.com/science/article/pii/S1463500312000790>, 2012.
- 465 Tugrul, S., Basturk, O., Saydam, C., and Yilmaz, A.: Changes in the hydrochemistry of the Black Sea inferred from water density profiles, *Nature*, 359, 137–139, 1992.
- Tugrul, S., Murray, J. W., Friederich, G. E., and Salihoğlu, İ.: Spatial and temporal variability in the chemical properties of the oxic and suboxic layers of the Black Sea, *Journal of Marine Systems*, 135, 29–43, 2014.
- 470 Yakushev, E., Pollehne, F., Jost, G., Kuznetsov, I., Schneider, B., and Umlauf, L.: Analysis of the water column oxic/anoxic interface in the Black and Baltic seas with a numerical model, *Marine Chemistry*, 107, 388–410, 2007.

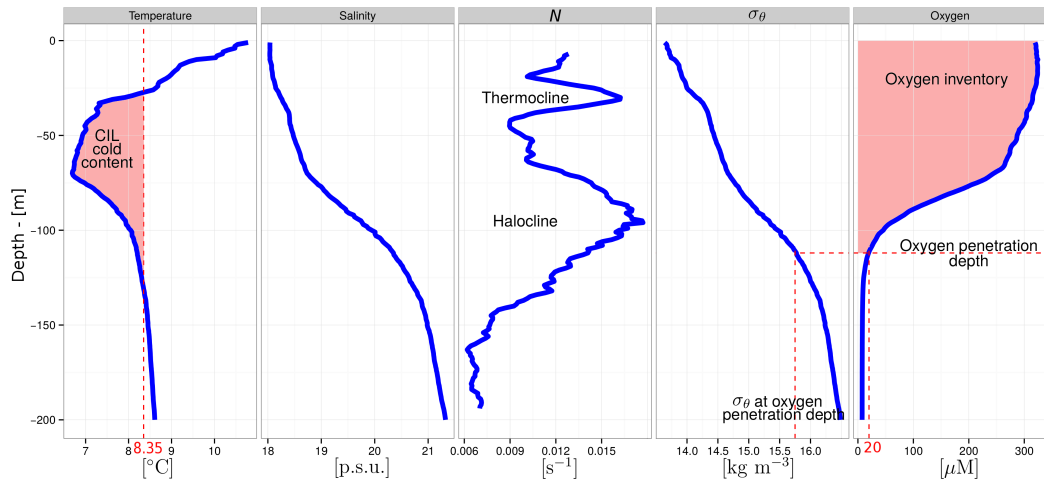


Figure 1. Typical profiles of temperature, salinity, Brunt-Väisälä frequency (N), potential density anomaly (σ_θ) and oxygen concentration in the central Black Sea (May). Note the two peaks in the vertical stratification: the thermocline, which is seasonal and corresponds roughly to the upper limit of the Cold Intermediate layer and the halocline, which is permanent, and correspond roughly to the lower limit of the Cold Intermediate layer and the upper boundary of the suboxic zone. Red dotted lines and shaded areas illustrate the diagnostic values derived from each profiles (Sect. 2.2).

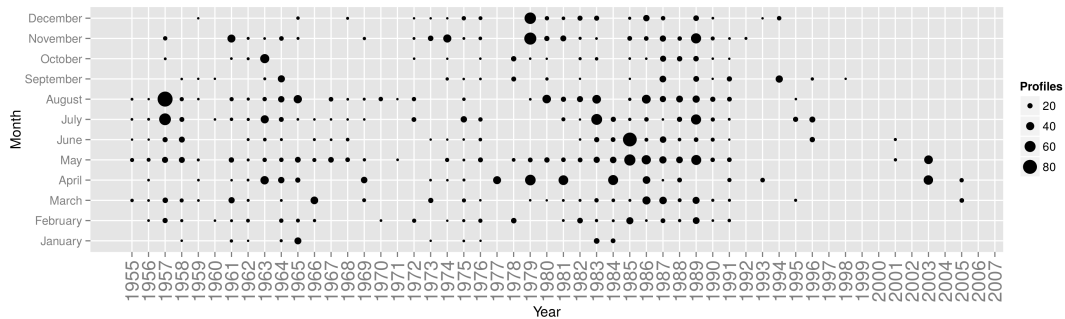


Figure 2. Temporal distribution of the ship-based oxygen profiles merged from the World Ocean Database, R/V Knorr 2003 and R/V Endeavor 2005 campaigns. Only the profiles containing at least 5 observation depths, one observation above 30 m depth and one record with $[O_2] < 20 \mu\text{M}$ were considered.

Zatsepin, A., Golenko, N., Korzh, A., Kremenetskii, V., Paka, V., Poyarkov, S., and Stunzhas, P.: Influence of the dynamics of currents on the hydrophysical structure of the waters and the vertical exchange in the active layer of the Black Sea, *Oceanology*, 47, 301–312, 2007.

Temporal distribution of the ship-based oxygen profiles.

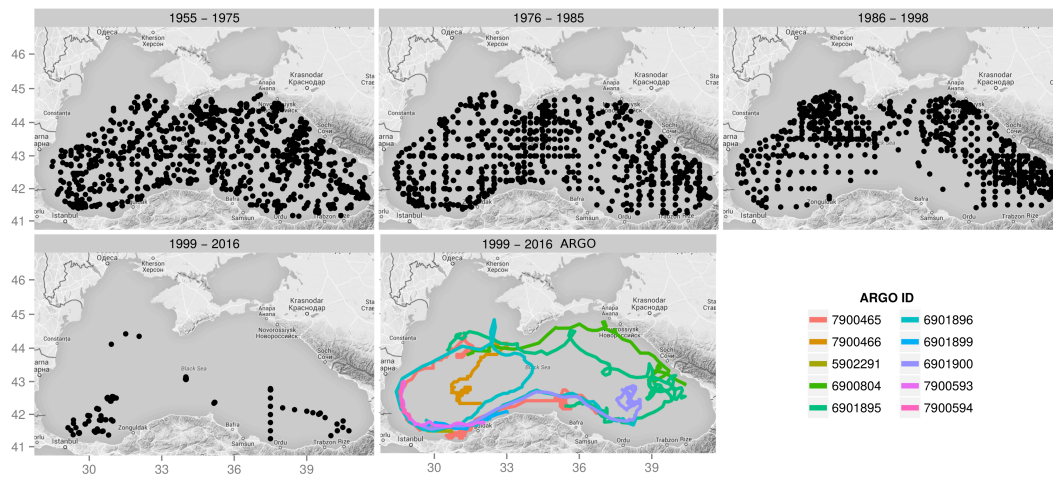
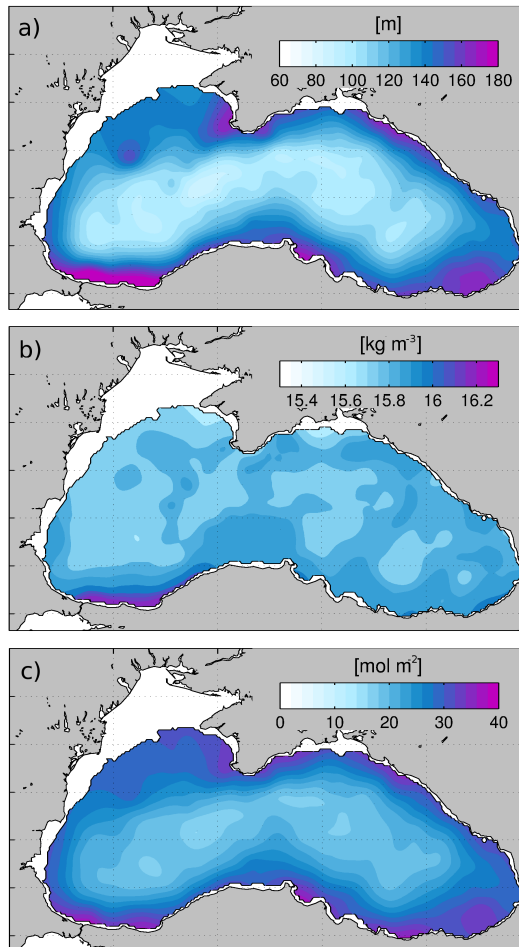


Figure 3. Distribution of the ship-based oxygen profiles (Fig. 2) available for each period (black dots). The lower-last panel also displays the trajectories of the two ARGO profilers (dark and light grey lines) floats. Number of profiles for each period are given in the text (map, Map data: ©Google 2015)-2015.

Detrended-annual climatology for (a) oxygen penetration depth, (b) oxygen inventory and (c) oxygen



penetration-density-anomaly (σ_T).

Figure 4. Annual climatologies of (a) oxygen penetration depth (where $[O_2] = 20 \mu\text{M}$), (b) potential anomaly at oxygen penetration depth and (c) oxygen inventory. These spatial climatologies were constructed from the ship-based dataset (1955–2005), accounting for the temporal variability of these diagnostics and the uneven distribution of data (see Sect. 2.3).

Modern trends for three indices of the Black Sea oxygenation status: (a) oxygen penetration depth, (b) oxygen penetration density level (σ_T) and (c) oxygen inventory. Dots: trends deduced from the detrended analysis of ship-based casts. Colored contours: the same indices derived from the coastal (red) and central (blue) ARGO profilers. Red lines: the linear trends are -8.2 m, -0.085 kg m^{-3} and -1.4 mol O m^{-2} per decades for (a), (b) and (c), respectively.

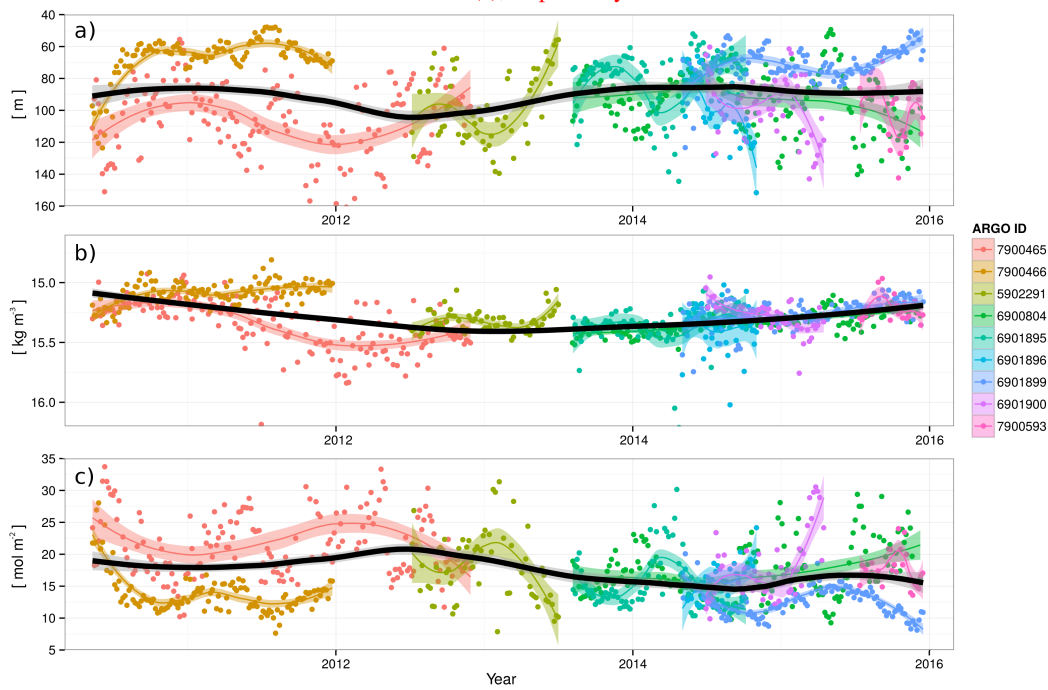


Figure 5. (a) Oxygen penetration depth, (b) Oxygen penetration density levels and (c) oxygen inventory derived from Argo profiles. The color legend gives the unique Argo identification number of the floats. Colored lines and color-filled areas indicate smoothed time series for each float (second degree loess smoother, span=0.5, 0.95 confidence intervals). The black line and gray shaded area are the smoothed time series obtained when considering all floats (reported on Fig. 6).

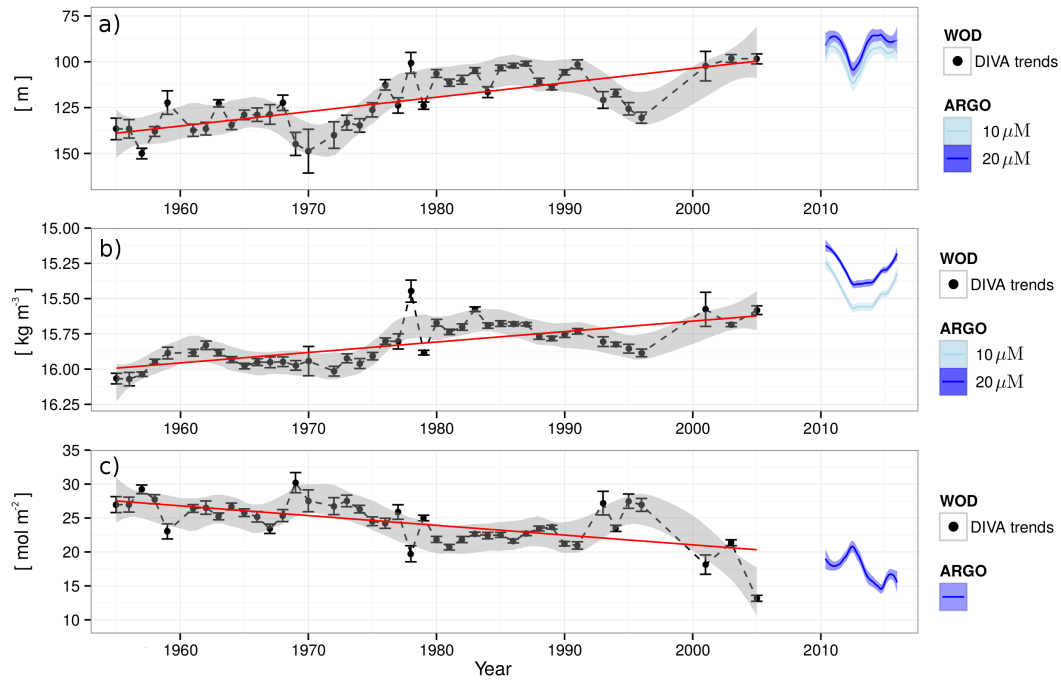


Figure 6. Trends of (a) oxygen penetration depth, (b) oxygen penetration density level (σ_θ) and (c) oxygen inventory deduced from (dots) DIVA analysis of ship-based casts and (blue) ARGO floats. On (a) and (b), the diagnostics from ARGO are also shown for the lower threshold of $10 \mu\text{M}$ to acknowledge a potential bias between Winkler and Argo data. Red lines: the linear trends assessed from the ship-based data set are $-7.9 \text{ m decades}^{-1}$, $-0.074 \text{ kg m}^{-3} \text{ decades}^{-1}$ and $-1.44 \text{ mol O m}^{-2} \text{ decades}^{-1}$ for (a), (b) and (c), respectively. Error bars on DIVA estimated trends indicate the standard error associated with the estimation of the mean misfit for each year (see Appendix A).

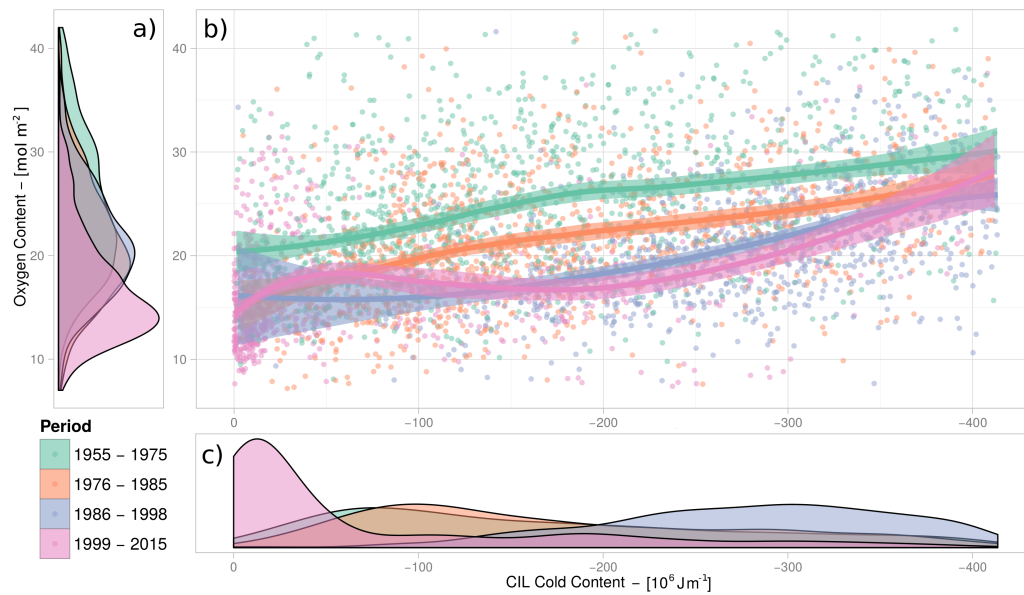


Figure 7. Impact of convective ventilation on oxygen inventory. [Distribution densities](#) [Frequency distributions](#) of [\(a\)](#) [\(a\)](#) oxygen inventory and [\(e\)](#) [\(c\)](#) Cold Intermediate Layer (CIL) cold content diagnosed from ship-based and [ARGO profilers](#) [Argo profiles](#) for different periods (color legend). [\(b\)](#) [\(b\)](#) Loess regressions (second degree polynomials, span=0.75, [Cleveland et al. \(1992\)](#) [Cleveland et al. \(1992\)](#)) between oxygen inventory and CIL cold content for the different periods (confidence interval $\alpha = 0.99$). The positive relationships observed during each period illustrate the ventilating action of CIL formation as a source of oxygen to the intermediate levels. The shift of these relationships towards lower oxygen inventories indicates shift in the oxygen budgets (higher consumption) that are independent of the intensity of CIL formation.