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Recent decline of the Black Sea oxygen inventory

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Abstract

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

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 the Black Sea faced severe eutrophication. Enhanced respiration rates reduced the thickness of the oxygenated layer. The consecutive increase of oxygen inventory in 1985–1995 supported arguments in favor of the stability of the oxic layer. Concomitant with a reduction of nutrient loads, this increase 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 depths. 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 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 required to assess the threat of further shoaling.

1 Introduction

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

Around the halocline, a permanent suboxic layer separates the Black Sea surface oxygenated waters ($[O_2] > 20\,\mu M$) from the deep sulphidic waters ($[H_2S] > 20\,\mu M$) (Murray et al., 1989, 1995; Tugrul et al., 1992). The upper (O_2 disappearance) and lower (H_2S onset) interfaces of this suboxic layer are controlled by different 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 respirated aerobically within the oxycline, i.e. the lower part of the oxygenated layer where oxygen concentration decreases to 20 µM. 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 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 relating oxycline penetration depth to riverine nutrient loads, is not quantitatively understood. Several processes delay the response of oxycline depth 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 controlling 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 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 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 Cold Intermediate Layer (CIL). Cold intermediate waters formation and advection by the cyclonic basin-wide Rim Current (Öszoy and Ünlüata, 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 oxic layer (Tugrul et al., 2014; Pakhomova et al., 2014). At deeper levels, the dense sinking plume formed by the Mediterranean inflow through the Bosporus, which entrains water from the overlying CIL, injects fingers of oxygenated water directly 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, 2006; Glazer et al., 2006).

Previous long-term analyses of the vertical migration of the suboxic interfaces either ended (1955–1995 in Konovalov and Murray, 2001) or started (1985–2015 in Pakhomova et al., 2014) with 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.

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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 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_T) 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 confinement of the lateral oxygen injections associated with the Bosporus plume imprints 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 $0.17\,\mathrm{kg\,m^{-3}}$ was observed during the *Knorr* 2003 campaign, Glazer et al., 2006), it has to be considered 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 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 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 ship-based vertical profiles (oxygen, temperature and salinity) obtained between 1955 and 2013 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 $[O_2] < 20\,\mu M$ were retained for analysis. The temporal and spatial distribution of the selected ship-based profiles are displayed in Figs. 1 and 2, respectively.

In addition, we considered data originated from two 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 the analysis of ship-based casts. One of the floats went drifting in the central basin while the other approximately followed the shelf break (Fig. 2). Thanks to these trajectories, the difference between the two floats also provided ranges 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 ship-based profiles + 306 ARGO profiles).

2.2 Profile analysis

From each profile we derived (1) the depth and (2) the density level where oxygen concentration went below 20 µM and (3) the oxygen inventory, integrated above this limit. 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).

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

$$\text{CIL cold content} = c\rho \int_{\text{CIL}} \left[T(z) - T_{\text{CIL}}\right] \mathrm{d}z, \tag{1}$$

where ρ is the density, c the heat capacity, $T(z)$ the temperature at depth z and T_{CIL} = 8.35 °C (Stanev et al., 2013).

2.3 DIVA analysis

Annual climatologies and interannual trends were identified for the three oxygen diagnostics using the DIVA detrending algorithm, to account for the sampling error associated with spatial/temporal variability.

In short, the DIVA interpolation software (http://modb.oce.ulg.ac.be/mediawiki/index.php/DIVA) computes a gridded climatology obtained by minimizing a cost function which 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, i.e. the average difference between data pertaining to this subset 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. 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.

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3 Results

3.1 Spatial trends

The spatial distribution of the oxygen penetration depth (Fig. 3a) 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).

The spatial distribution of the oxygen inventory (Fig. 3b) follows that of the oxygen penetration depth. The range of spatial variability reaches 12 mol O m^{-2}, i.e. between 17 and 29 mol O m^{-2}.

A significant spatial variability remains when expressing oxygen penetration in terms of density levels (Fig. 3c). A deeper anomaly (in terms of density) can be seen in the area of the Bosporus plume, which then decreases along the Anatolian coast. This anomaly results in a range of spatial variability of 0.3 kg m^{-3}.

The ranges of spatial variability derived from theses spatial analysis agreed with those depicted by the difference between the two ARGO profilers (Fig. 4).

3.2 Temporal trends

Since 1955, the oxygen penetration depth rose by an average rate of 8.2 m per decade, from a basin average of 140 m in 1955 to 90 m in 2013. This shoaling was also observed on a vertical density scale (−0.085 kg m^{-3} decades^{-1}, Fig. 4b).

The oxygen inventory, integrated from the surface down to the suboxic upper interface, decreased by 36 % during those 58 years. 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. 4c). These low values were confirmed by the two ARGO profilers (Fig. 4).

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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

Positive relationships between oxygen and Cold Intermediate Water inventories were obtained for all periods (Fig. 5). The oxygen inventories corresponding to a given CIL cold content decreased significantly from period 1955–1975 to period 1986–1998 (Fig. 5b).

Fewer oxygen profiles were available for the period 1999–2013, even when including profiles from the ARGO floats. The combined data set depicts a relationship between oxygen and cold waters inventories during 1999–2013 which does not differ significantly from that obtained during 1986–1998 (Fig. 5b), This comparison should be considered with caution, however, as ARGO sampling rates differs strongly from those of ship-based casts (ARGO sampling rate is much higher).

Observed CIL cold contents were generally higher during the period 1986–1998, while more low cold contents are observed during 1999–2013.

4 Discussion

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 aggregation of the most recent ship-based profiles in the Bosporus area and along the north eastern coast (Fig. 2), where deeper penetration occurs (Fig. 3), 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.

Considering spatial variability revealed a clear shoaling trend on both depth and density scales (Fig. 4a and b). This confirms the hypothesis that higher oxygen consumption associated with eutrophication, rather than a shoaling of the main halocline, caused the vertical migration of the oxycline (Codispoti et al., 1991; Konovalov and Murray, 2001; Tugrul et al., 2014).

The positive correlations observed between CIL cold content and oxygen inventory for all the periods (Fig. 5b) illustrate how CIL formation and advection ventilate the intermediate layers. The transient stabilization of the oxygen penetration depth in the 90s (Tugrul et al., 1992; Buesseler et al., 1994) (Figs. 4 and 5a) provided arguments supporting the stability of the oxic interface. 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. 5 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 biogeochemical oxygen consumption terms had been lower during the period 1986–1998 in response to nutrient reduction, the increased ventilation during that period should 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.

The fact that the relationship between oxygen inventories and CIL content after 1999 is similar to that of 1986–1998 indicates a stabilization in the biogeochemical oxygen consumption terms. Higher air temperature in these last years (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. 4c).

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 economies of the lower Danube watershed to recover their productivity

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in a more sustainable, less 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.

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 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.

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 27 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 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.

5 Conclusions

The results presented in this study demonstrated the decline of the Black Sea oxygen inventory during the second half of the XXth century and highlighted the threat that further atmospheric warming casts upon the vertical stability of the Black Sea oxygenated layer. To assess how actual nutrient emissions policies adequately prevents, in the context of fore-casted warming, the ecological and economical damages that would arose from a further shoaling of the oxic interface it is 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 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 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). 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 the changes in nutrient loads by inertial mechanisms. It highlights the importance of considering spatial variability in assessing long term trends and stresses the threat that atmospheric warming casts upon ecosystems recovering after nutrient reduction policies.

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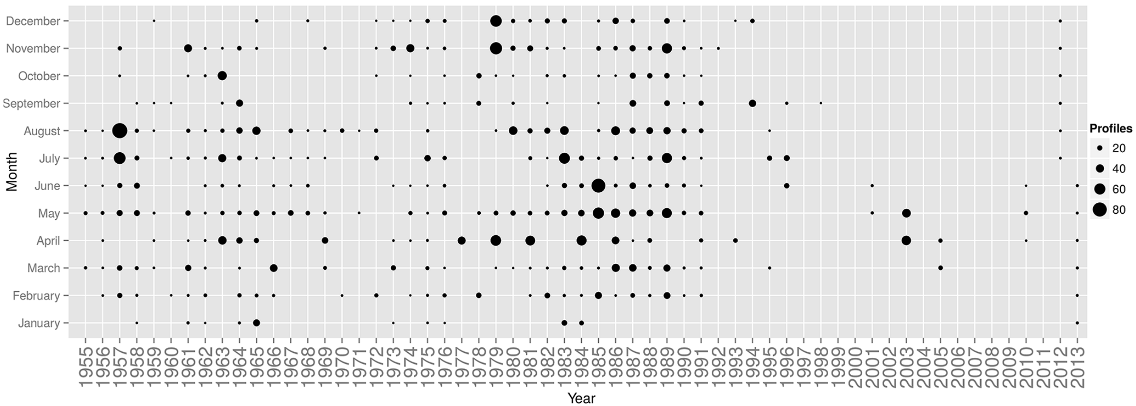

Figure 1. Temporal distribution of the ship-based oxygen profiles.

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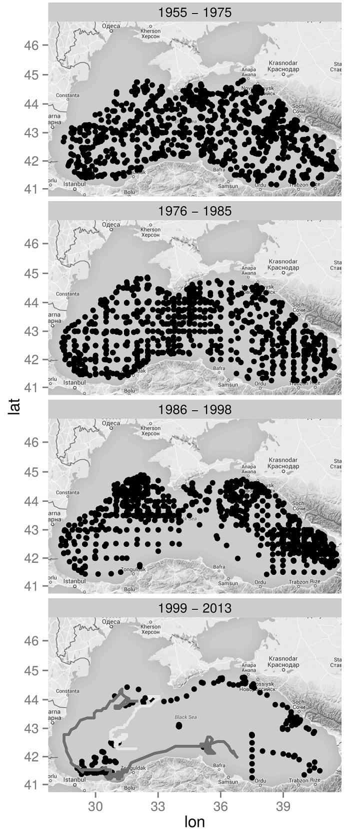

Figure 2. Distribution of the ship-based oxygen profiles available for each period (black dots). The lower panel also displays the trajectories of the two ARGO profilers (dark and light grey lines). Number of profiles for each period are given in the text (map data © Google 2015).

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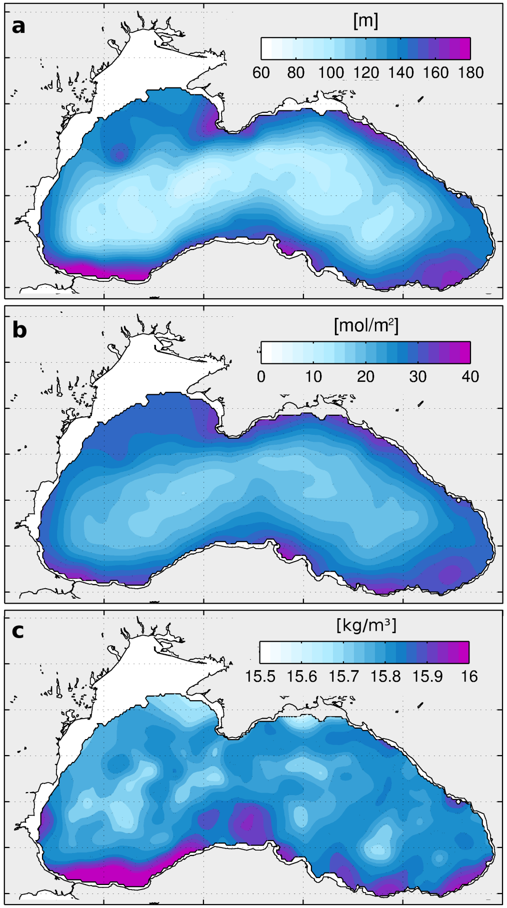

Figure 3. Detrended annual climatology for **(a)** oxygen penetration depth, **(b)** oxygen inventory and **(c)** oxygen penetration density anomaly (σ_T).

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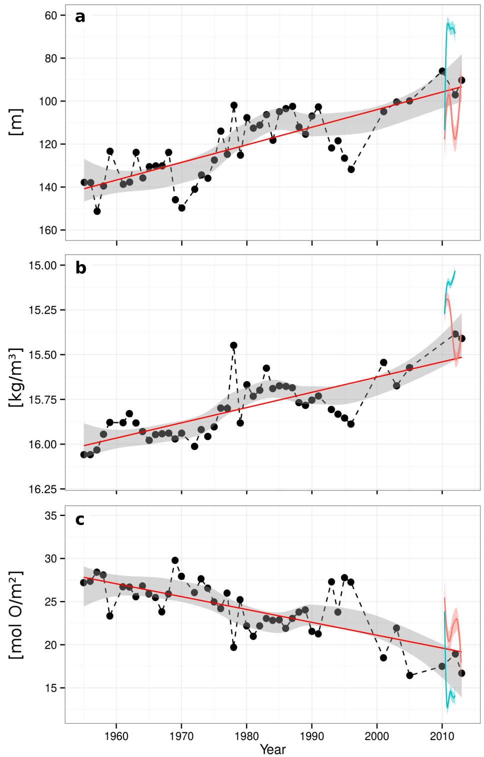

Figure 4. Modern trends for three indices of the Black Sea oxygenation status: **(a)** oxygen penetration depth, **(b)** oxygen penetration density level (σ_T) and **(c)** oxygen inventory. Dots: trends deduced from the detrending analysis of ship-based casts. Colored contours: the same indices derived from the coastal (red) and central (blue) ARGO profilers. Red lines: the linear trends are $-8.2\,\mathrm{m}$, $-0.085\,\mathrm{kg\,m^{-3}}$ and $-1.4\,\mathrm{mol\,O\,m^{-2}}$ decades^{-1} for **(a)**, **(b)** and **(c)**, respectively.

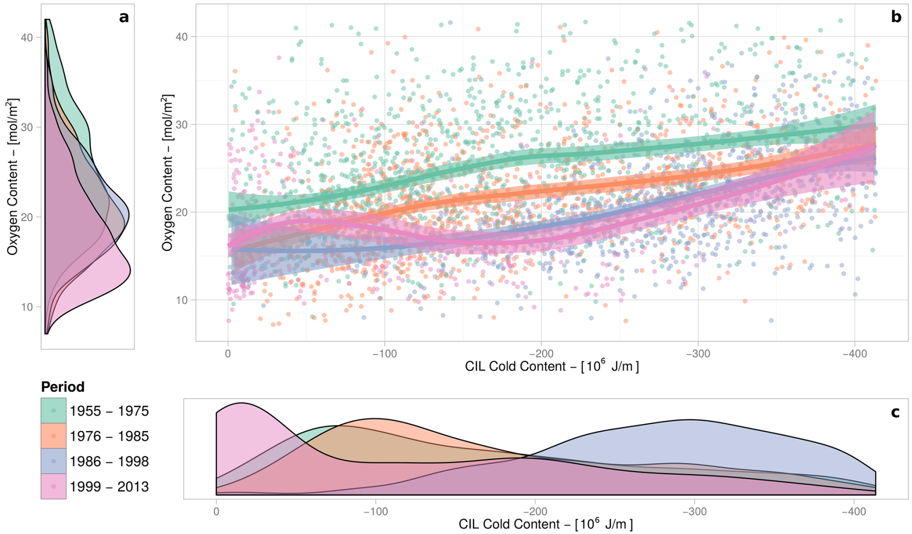

Figure 5. Impact of convective ventilation on oxygen inventory. Distribution densities of **(a)** oxygen inventory and **(c)** Cold Intermediate Layer (CIL) cold content diagnosed from ship-based and ARGO profilers for different periods (color legend). **(b)** Loess regressions (second degree polynomials, span = 0.75, 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.

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