Response to the reviewer #2

We would like to thank the reviewer for comments and for valuable and constructive suggestions for improving the paper.

Comment #1

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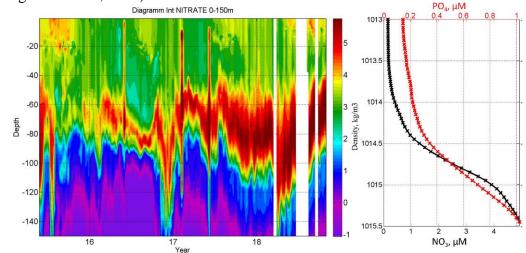
"The role of nitrates is widely discussed though data have not been presented. The role of NO3 is discussed using literature and MLD differences between 2016 and 2017. However, from Figure 4, MLDs look very similar. To support conclusions, NO3 profiles must be analysed. These profiles exist and have been acquired by the float 6901866. Other NO3 profiles have also been acquired in the same area by the float 6903240".

Answer. Unfortunately, there is no direct information about newly entrained nitrates in the upper layers in the winter season. There are some important reasons for it.

The entrained nutrients are usually rapidly consumed and then are transformed into organic form 15 – i.e. phytoplankton, zooplankton, dissolved organic matter, etc. To account for these entrained nutrients we need to know all the compounds where e.g. nitrogen is situated, which is almost impossible nowadays. Particularly, in our institute, we made several surveys with nitrates measurements included in 2016 and 2017 in the summer and autumn periods. However, this is certainly not enough to estimate nitrates coming in the euphotic layer continuously in short-period events of winter mixing throughout 20 all autumn-winter season.

The regular optical-based nitrates measurements of Bio-Argo buoys could be a good alternative for this task. Unfortunately, in the Black Sea data of Bio-Argo buoys is poorly consistent with information of nitrates distribution known from numerous in-situ studies. In particular, Bio-Argo buoys show the persistent presence of more than 3 μ M nitrates in the upper layer of the Black Sea throughout the year (see diagram in Fig. R1-left in the attached file), which is not consistent with 0.5 μ M

25 the year (see diagram in Fig. R1-left in the attached file), which is not consistent with 0.5 μ M documented in many previous studies (Konovalov, Murray, 2001; Turgul et al., 2015). A possible reason for this is the complex optical characteristics of the Black Sea with a lot of dissolved organic matter, etc. (see e.g. Organelle et al., 2017).



30 **Fig. R1**: left – Interannual diagram of NO₃ (μ M) measured by buoy Bio-Argo; right – multiannual averaged vertical profiles of NO₃ (μ M, black line) and PO₄ (μ M, red line) for October shown in σ -coordinates.

Therefore, we use indirect estimates of newly entrained nitrates.

In colder winters, convection will be stronger and more nutrients will be entrained in the upper
layer, than in warm winter. Please see the review by Williams & Follows (2003). For the Black Sea this is proven by the strong relationship between winter temperature and interannual variability of winter-early spring bloom of diatoms (Mashtakova, 1985; Sorokin 2002; Mikayelyan et al., 2018) and following the early-summer bloom of coccolithophores (Mikaelyan et al., 2015; Silkin et al., 2014, 2019), the variability of surface chlorophyll-a (Chl-a) (Oguz et al., 2006; Finenko et al., 2014). In the strongly

- 40 stratified Black Sea, the depth location of nutricline is tightly related to certain isopycnals as it is shown in many chemical studies by Tugrul et al. (1992), Konovalov et al. (2005). That is why nutricline variations in σ -coordinates are significantly less than in-depth coordinates (Tugrul et al., 1992; Konovalov et al., 2005). The multi-annual vertical profiles of nitrate (NO₃) and phosphate (PO₄) presented in σ -coordinates for October, the month preceding the onset of intense winter convection, are
- 45 shown in Fig. R1 (right) (in the attached file). For example, the concentration of nitrates begins to gradually increase below the isopycnal of 1014.0 kg/m³, and increases more sharply below the isopycnal of 1014.4 kg/m³ where the upper part of nutricline is located (Konovalov, Murray, 2001). The deeper isopycnals the winter convection reaches, the more new nutrients will be entrained into the euphotic layer. The tight relation between density and the position of chemical elements (see Konovalov et al., 2005) suggests that the density of the upper mixed layer in winter can be used as a proxy, showing from
- which layers nutrients were entrained to the surface layer (Kubryakova et al., 2018).

At the same time, the mixed layer depth in the cold period of a year may vary significantly due to the dynamical forcing, such as eddies, large-scale circulation, etc (see in detail (Kubryakov et al., 2019)). This is related to the deepening of the density barrier – the main halocline. For example, in anticyclones, it can reach 100 m. However, if the density of the mixed layer remains low, then no new nitrates will entrain from deep isopycnals layers.

The density of the mixed layer depends partly on the vertical uplift of isopycnals during the intensification of cyclonic circulation. The rise of cyclonic circulation on the opposite decreases mixed layer depth. Therefore, in the Black Sea the MLD is not correlated with sea surface temperature (Titov, 2004), but strongly depends on dynamic forcing (Kubryakov, Belokopytov, et al., 2019).

That is why the density rather than the depth of the mixed layer is a more robust indicator of the vertical entrainment of nutrients in winter. We use this indicator to show that in cold 2017 more nutrients are entrained in the euphotic layer than in warm 2016.

We extended the explanation in the revised version of the manuscript.

- 65 Also, Chl-a is one of the widely-used indicators of the phytoplankton biomass, which directly depends on nutrient concentration. In 2017 Chl-a in winter and spring was higher than in 2016, which is consistent with the fact, that the winter convection and related vertical entrainment of nutrients was more intense in 2017.
- We also want to underline that we are not basing on the quantitative values of nitrates, but use the above indicators to argue that in the cold winter of 2017 the vertical entrainment of nitrates was higher than in the warm winter of 2016. The increase of nutrient concentration in the Black Sea in the cold years was documented in the chemical study of (Tugrul et al., 2015).

Comment #2

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- ⁷⁵ "The difference between winters seems more related to mesoscale circulation than to a severe winter. In Figure 1, red squares clearly show that in winter 2017 the floats were entrapped within eddies, which would help explain also density features in Figure 2d. To support conclusion, the impact of mesoscale should be addressed and, if any, excluded".
- Answer. The winter of 2017 was one of the most severe in the Black Sea and this fact was already documented in several recent studies by Stanev et al. (2019), Capet et al. (2020). It was significantly colder than in warm 2016 and cause significantly stronger vertical mixing than in 2016 (Stanev et al., 2019; Capet et al., 2020). It is worth noting, that in colder winters, convection will be stronger and more nutrients will be entrained in the upper layer, than in warm winter.
- The investigation of the impact of small scale structures such as fronts, eddies on Chl-a is a very interesting and important problem. However, in this study, we are focused on the annual time scales. Particularly, Fig. 5 shows that in cold 2017 Chl-a in upper layers was higher in all seasons, while in warm 2016 it was higher in deeper layers in all seasons. This fact was observed during all investigated periods of both buoys measurements. Please see Fig. 5a, which is the main figure for this manuscript. That is, yearly average profiles of Chl-a are of main interest and they depend on the intensity of winter
- 90 convection (see Fig. R2 and R3 in the attached file).

The short-period variability of the Chl-a is out of the scope of this paper, but we briefly discuss it in the discussion part. Short period variability of the Chl-a in the summer period is related to the occasional entrainment of nutrients from nitroclyne in the euphotic zone caused by storms or dynamical forcing (studied in the Black Sea by Kubryakov, Zatsepin et al. (2019)), such as eddies horizontal and vertical advection (see e.g. Oguz et al., 2002; Shapiro et al., 2010; Kubryakov et al., 2016). After warm winters with higher water transparency, the euphotic layer is deeper and closer to the nitroclyne. Therefore, we might expect that the impact of dynamics features in summer will be more effective in years with weak winter convection.

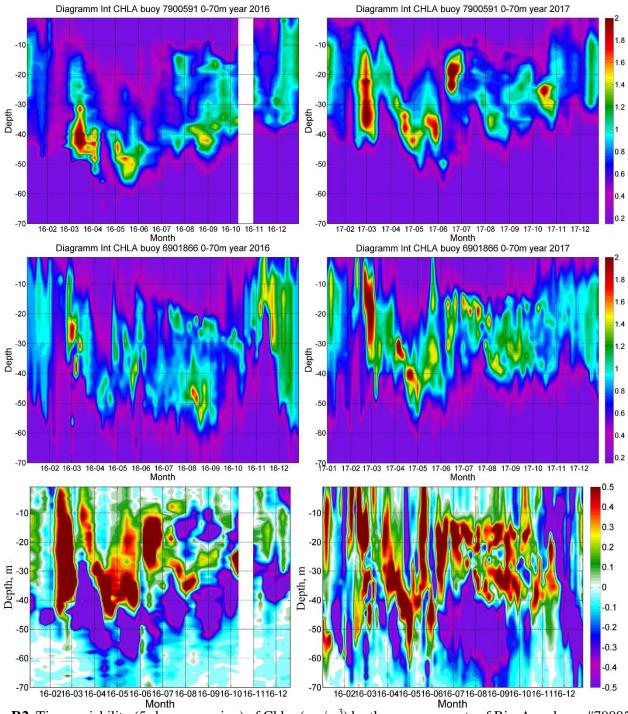
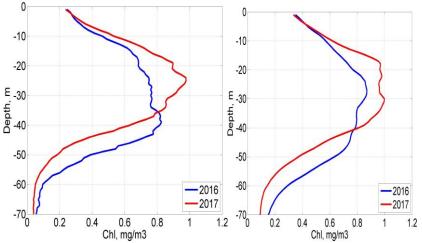


Fig. R2. Time variability (5-days averaging) of Chl-a (mg/m³) by the measurements of Bio-Argo buoy #7900591 (top panel) and buoy #6901866 (central panel) in 2016 (left) and 2017 (right). Bottom panel – the differences between 2017 and 2016 by buoy #6901866 (left) and buoy #7900591 (right).

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- 105 In Fig. R2 (in the attached file) we show a diagram of 5-days averaged profiles of Chl-a for both buoys in 2016 and 2017 to demonstrate that in both years the short-period variability takes place. It is also well-seen that these two buoys were situated in different dynamic features and the Chl-a variability differs among the buoys in both years. At the same time, it is visually seen that both buoys show that in warm 2016 Chl-a subsurface maximum was deeper than in cold 2017, which is the main conclusion of 110 the study. It is also well seen that Chl-a was higher in 2017 in the winter-spring period in upper layers
- and higher in summer of 2016 in deep layers (35-55 m depth) (see Fig. R2 bottom). We will add this information in the revised version of the manuscript.



115 Fig. R3. Average profile of Chl-a in 2016 and 2017 by the measurements of the buoy #6901866 (left) and buoy #7900591(center) and both buoy measurements (right).

Comment #3

"Self-shading is interpreted only as a change in chlorophyll concentration (derived from 120 fluorescence measurements) which is used as a proxy of algal biomass or at least to indicate productive layers. Using only chlorophyll makes hard to establish if changes in the magnitude of DCM are due to actual changes in productive biomass because the same modifications could be due to photoacclimation. Optical measurements such as the optical backscattering coefficient could help decipher what changes in chlorophyll are due to actual modifications in algal biomass. Backscattering measurements are available for all the floats in the Black Sea". 125

Answer. Chl-a is the main absorbing pigments, which significantly stronger impact on the light attenuation that the backscattering by particles. Absorption is usually more than 10 times higher backscattering (see e.g. Jerlov N. G. Optical oceanography. - Elsevier, 2014). Backscattering in the Black Sea significantly depends on the intense coccolithophore blooms (nanoplankton), which despite

- their very strong scattering plays a minor role in the light attenuation in the sea, as well as on 130 phytoplankton biomass (Balch, W. M., Holligan, P. M., Ackleson, S. G., & Voss, K. J. (1991). Biological and optical properties of mesoscale coccolithophore blooms in the Gulf of Maine. Limnology and Oceanography, 36(4), 629-643). The variability of backscattering in the Black Sea and its relation to coccolithophore blooms was studied in detail in our previous paper on the base of Bio-Argo data in
- 135 (Kubryakov, Mikaelyan et al., 2019). In particular, in the winter-early spring season during the strongest diatom bloom, b_{bp} does not exceed 0.002, which is only 2% of the total attenuation of PAR. During extremely strong coccolithophore blooms b_{bp} does not exceed 0.02, which is less than 20% of attenuation coefficient. The above suggestions demonstrate that b_{bp} is not a reliable parameter for accessing the biomass of the Black Sea phytoplankton. In our paper, we focus on the chlorophyll, which significantly 140 control the primary productivity in the ocean.

Comment #4

"Argo data analysis lacks of details, applied protocols and procedures and this makes difficult to evaluate its appropriateness. For example, for chlorophyll, it is unclear if NPQ at the surface and CDOM 145 influence at depth have been corrected. How chl has been calibrated? Radiometry has been quality controlled before Kd computation?"

Answer. We use the standard product downloaded from ftp://ftp.ifremer.fr/ifremer/argo. The description of the used protocol is given at http://www.argodatamgt.org/Documentation. The nonphotochemical quenching was not corrected. We can expect that this effect will not alter the obtained

result, as we focus on the differences of Chl-a between two years. NPQ is important in the most upper 150 layers (0-15 m), while the differences in this study were observed in all 10-70 m layer (see Fig. 5 and Fig. R2, R3). Also, NPQ depends primarily on the irradiance conditions on the surface, in which seasonal variability (change from summer to winter) is significantly larger than intraseasonal variations. Therefore, we believe the correction of NPQ will not generally change the main results of the paper.

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Additional comments (AC)

AC1: "Line 15: 0.2-0.6 mg m3 is a large range of variability". Answer. We exclude these numbers from the abstract.

160 AC2: "Lines 17-18: to rephrase as it looks contracditory".

Answer. Thank You. We rephrased it as: "These results demonstrate that the increase of light availability in warm years causes the deepening of Chl subsurface maximum and partly compensate the impact of weaker convective entrainment of nutrients on the decrease of biological productivity".

AC3: "Line 42: remove "in" before references". 165 Answer. Removed.

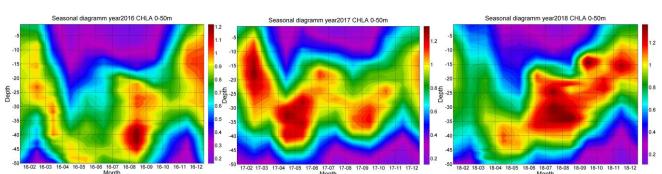
> AC4: "Line 59: why only these floats? More floats are available in the Black Sea". Answer. Only these floats give synchronous information on Chl-a and PAR in the study period.

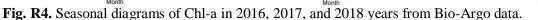
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AC5: "Line 60: the floats sampled a longer period. It would be interesting to see what's happened during winter in other years".

Answer. To answer the question, we are sending the Chl-a variability in 3 consecutive years – warm 2016, cold 2017, and moderately warm 2018 (see Fig. R4 in the attached file). As it is seen the main differences between 2017 and 2018 are similar. In 2018 high values of Chl-a were situated deeper 175 (up to 55 m) than in 2017 (see Fig. R4, R5, R6 in the attached file). They are smaller in the upper 0-25 m at least in the first half of the year (before the start of convection in autumn). In this paper, we are focused on the difference between consecutive cold and warm years. To avoid confusion of the reader we demonstrate these differences on the base of two contrasting years 2016 and 2017. We note, that here we use all the buoys for the analysis.

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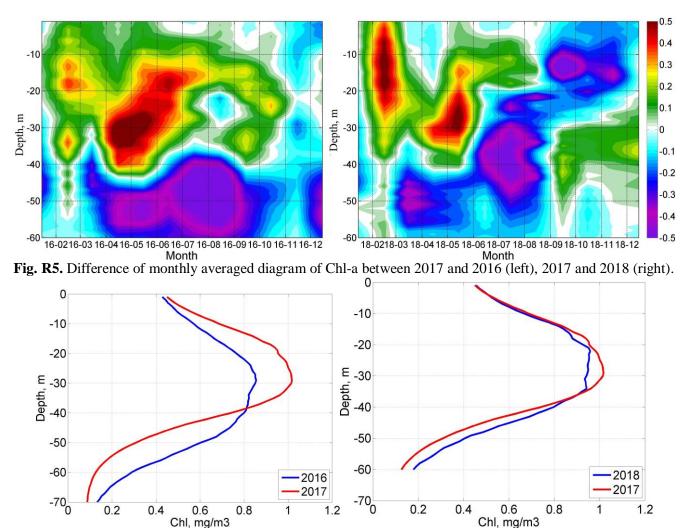


Fig. R6. Average profile of Chl in 2016 and 2017 (left), 2017 and 2018 (right) by Bio-Argo buoy measurements (right).

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The investigation of longer Chl-a variability in 2014-2020 was made in our submitted manuscript to Progress in Oceanography. Unfortunately, it is now in the revision phase. We are sending a draft to You.

AC6: "Line 69: which equation in Xing 2011 has been used? Have you calibrated Chl with Xing procedure? In this case, I suppose you have calibrated Chl using Ed(490). Ed(490) and derived Kd are quite correlated with PAR (see Morel et al., 2007 Remote Sensing of Environment) thus making analysis of the relationships between Chl and PAR as presented in this study not fully independent".

Answer. Thank You for this question. We use the standard product downloaded from 200 <u>ftp://ftp.ifremer.fr/ifremer/argo (Schmeichtig et al., 2015)</u>. The description of the used protocol is given at <u>http://www.argodatamgt.org/Documentation</u> We corrected the data description.

AC7: "Line 69: how have you taken into account spikes and other source of errors in Chl profiles?"

205 **Answer.** There were no spikes in Chl-a profiles during the study period for these two buoys. We show in Fig. R2 (in the attached file) 5-days average variability of Chl-a for both buoys in 2016-2017. The instruments work well for all the study period.

AC8: "Line 70: please give the reference for 5 umol photons".

210 **Answer.** We corrected it to 2.5 μmol and provided a reference on OCR-500 documentation <u>https://www.seabird.com/ocr-504-irradiance-cosine-response-in-water/product-</u> <u>downloads?id=54627923874.</u>

AC9: "Line 73: have PAR profiles been quality controlled? Have you taken into account also clouds when computing Kd? Could it be possible to see Kd profiles? I imagine that they should be noisy as a 1 m window is very narrow".

Answer. All the profiles were visually quality controlled for consistency and absence of outliers. This information was added to the text. Clouds were not taking into account. Clouds should not significantly impact on the Kd as it depends on the gradient of PAR. The Kd profiles are noisy in fact. In this study, we are focusing on monthly or even annual time scales. The statistical averaging allows us to obtain smooth results on Kd distribution. Additionally, for Fig. 2 we use smoothing by moving-average with 5 m vertical bin size. We added this information to the text. We attached below unsmoothed monthly-averaged diagrams of Kd in 2016-2017 to show the unsmoothed monthly variability and their yearly-averaged distribution (see Fig. R7 in the attached file).

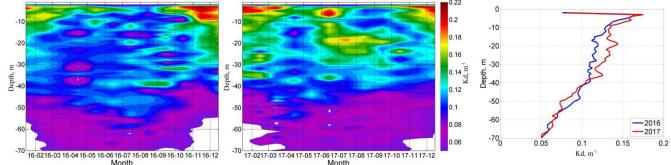


Fig. R7. Monthly-averaged vertical distribution of Kd (PAR) in 2016 (left) and 2017(center), Kd yearly-averaged profile in 2016 and 2017 (right) in the Black Sea from Bio-Argo data.

AC10: "Line 77: Claustre et al 2010 is not the right reference for the public database. Argo data are available at http://doi.org/10.17882/42182 or can be downloaded from the DAC (such as Coriolis)". **Answer.** Thank you, it is corrected.

AC11: "Line 77: Temperature and salinity have been quality-controlled?" Answer. All the data was visually quality-controlled for consistency with known T, S distribution

in the Black Sea. We added the information in the text.

AC12: "Figures 2, 4, 6: profiles have been monthly averaged? Details are missing to understand how single profiles have been managed before drawing the figures".

Answer. Yes, they were monthly-averaged. We added this information to the text.

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AC13: "Line 81: replace "large" with "high". **Answer.** Thank You. Corrected.

AC14: "Figures 2 and 3: add MLD".

Answer. We added MLD to Fig. 3 (see Fig. R8 in the attached file). Despite MLD in 2017 was higher than in 2016, as it is described in the answer on comment #1 the MLD is not a proper indicator for the estimates of the intensity of entrainment of nutrients. The proper indicator is density, as nutrients are tightly related to the certain isopycnals layers.

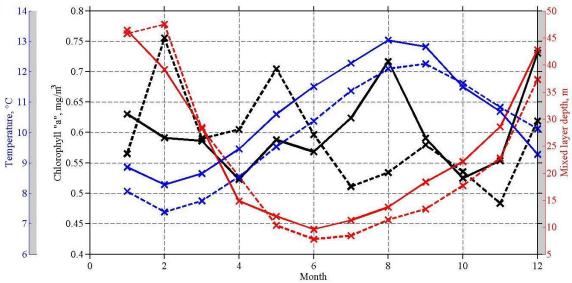


Fig. R8. Average seasonal variability of Chl, temperature and mixed layer depth in 2016 (solid line) and 2017 (dashed) in the 0-70 m layer.

AC15: "Line 105: to prove with data".

Answer. Please, see the answer on comment #1. We extended the explanation in this part of the

AC16: "Line 109: why average instead of integration over depth?" Answer. This is generally similar. The use of average just seems to be more convenient for us.

AC17: "Figures 4c and d: add MLD and euphotic depth **Answer.** Added.

AC18: "Line 124: remove "yin yang sign". **Answer.** Removed.

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text.

AC19: "Line 133: add reference for isolume 3 umol photons, why not using the 1% of irradiance just below the surface?"

Answer. There is growing that the usage of the classic definition of the euphotic layer can lead to significant errors in defining productive zone (see Cullen, 2015). Euphotic layer depth is determined 270 as the depth at which 1 % of surface PAR penetrates. Therefore, it does not take into account the impact of the strong seasonal variability of surface PAR, which can lead to significant errors in defining the depth of the productive zone (Banse, 2004). PAR at z=1 m in the Black Sea changed from 1200 to 300 µmole photons m⁻² s⁻¹. Therefore 1% of this irradiance will correspond to Ed of 12 and 3 µmole photons m^{-2} s⁻¹ in summer and winter, respectively. Photosynthesis efficiency depends on the absolute values of Ed (Jassby, Platt, 1976). Phytoplankton is often observed in the layers which are significantly deeper 275 than the depth corresponding to 1% of surface PAR (Letilier et al., 2004; Marra et al., 2014). In our submitted study (Kubryakov et al., 2020, PROOCE, submitted) we show that in the Black Sea isoline Ed of 3 μ mole photons m⁻² s⁻¹ (or Qs=0.08 mole photons m⁻² d⁻¹) in all seasons correspond well to the bottom boundary of relatively high Chl-a values. Other authors often use other definitions, e.g. (Mayot et al., 2017) use 0.415 mol photons m⁻² d⁻¹. Therefore, the usage of the value of Ed=3 μ mole photons m⁻ 280 ² s⁻¹ for the definition of the lower border of the productive zone in the Black Sea intuitively is less robust. We are sending Your submitted manuscript (Kubryakov et al., 2020, PROOCE, submitted) for more details.

285 AC20: "Line 134: shallower instead of higher?" Answer. Corrected.

AC21: "Figures 5 and 6: I suggest to show PAR and Kd time series on the same figure". Answer. We agree and corrected the text.

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AC22: "Caption figure 6: explain the choice of 25 umol photons". **Answer.** We deleted this isolume to avoid confusion.

AC23: "Figure 6: show MLD, DCM, euphotic depth".

Answer. We added euphotic depth to this figure. MLD is shown in Fig. 2a,b. It is not clear how 295 to show DCM in this figure. Instead, we show isolumes in Fig. 2a, b.

AC24: "Figure 7 does not sum up your case study as in the figure MLDs are different. In this study the MLDs in winter look very similar".

Answer. We agree with this comment. As it is stated in the answer on comment #1: "At the same 300 time, the mixed layer depth in the cold period of a year may vary significantly due to the dynamical forcing, such as eddies, large-scale circulation e.t.c. (see in details in Kubrykov et al., 2019). This is related to the deepening of the density barrier - the main halocline. For example, in anticyclones, it can reach 100 m. However, if the density of the mixed layer remains low, then no new nitrates will be 305 entrained from deep isopycnals layers.

The density of the mixed layer depends partly on the vertical uplift of isopycnals during the intensification of cyclonic circulation. Rise of cyclonic circulation on opposite decrease mixed layer depth. Therefore, in the Black Sea the MLD is not correlated with sea surface temperature (Titov, 2004), but strongly depends on dynamic forcing (Kubryakov, Belokopytov, et al., 2019). That is why the density rather than the depth of the mixed layer is a more robust indicator of the vertical entrainment of nutrients 310 in winter". To account for this fact, we change the label of the figure to "winter mixing".

AC25: "Paragraph at Line 208: the influence of CDOM is less detectable from PAR as PAR integrates irradiance between 400 and 700 nm while the highest CDOM influence is in the UV range. As irradiance profiles at 380 nm are measured by BGC floats, Kd(380) should be computed to 315 corroborate or not your statements".

Answer. The detailed investigation of the variability of Kd(380), as well as DOM on the base of its measurements, were made in our previous study (Kubryakov, Mikaelyan, et al., 2019). We have extended the explanation in this part of the text:

- 320 "Another strong source of light attenuation, which is nutrient-dependent, is autochthonous DOM formed due to the release of lipids during lysis of phytoplankton cells. In (Kubryakov, Mikaeyan et al., 2019) based on the Bio-Argo data on diffuse attenuation at 390 nm and backscattering measurement authors shows that one the most significant source of DOM is related to the lysis of coccolithophores cells during the termination of their early-summer bloom. As it is shown in (Burenkov et al., 2011;
- Mikaelyan et al., 2011, 2015) the intensity of coccolithophore blooms in the Black Sea are significantly 325 related to winter temperature and amount of entrained nutrients. Particularly, the extremely strong coccolithophore bloom was observed in the Black Sea after cold 2017, which results in the observed maximum light attenuation in July-August in 2017 at 10-30 m depth (Fig. 5b). Such DOM release in cold years additionally increases the light attenuation, which plays a role in equalizing the total productivity in warm and cold years". 330

AC26: "Line 213: please give some explanations". Answer. We corrected this phrase.

335 AC27: "Line 214: Are lipids colored?"

> Answer. This depends on the lipids content. The one discussed here causes strong light attenuation at 390 nm, as it is in detail investigated by Kubryakov, Mikaelyan, et al. (2019), i.e. are partly colored. We extended the explanation in this part of the text (see the answer to the AC25).

AC28: "Line 237: with no nutrient data this statement cannot be proved by this study".

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Answer. We agree and excluded this phrase from the text. As it is explained in the answer on comment #1, in this paper we can use only indirect estimates of the intensity of the vertical entrainment of nutrients. Previously, the increase of nutrient concentration in the Black Sea in the cold period was documented in the chemical study by Tugrul et al. (2015).