

## ***Interactive comment on “The suspended small-particles layer in the suboxic Black Sea: a proxy for delineating the effective N<sub>2</sub>-yielding section” by Rafael Rasse et al.***

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In “The suspended small-particles layer in the suboxic Black Sea: a proxy for delineating the effective N<sub>2</sub>-yielding section” by Rasse et al, the authors analyze particle back scattering, oxygen, HS- and nitrate float data from the Black Sea. The authors can thus delineate the suboxic zone of the Black Sea with the float, and see productivity and export events. The authors assume that the particle back scattering data in the suboxic zone indicates the presence of anammox and heterotrophic denitrifying bacteria. This assumption may be problematic in the Black Sea where it is known that there are high manganese oxide concentrations in the suboxic zone, and it is known

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that there is an organic matter maximum at the top of the sulfidic zone composed of S oxidizers. However, the data in this paper is useful. The writing just needs to be shifted.

#### Large Issues:

The introduction needs a section at the beginning describing the Black Sea. This is particularly important because the Black Sea differs from oxygen deficient zones in several important ways. The Black Sea has a sulfidic zone. There are fluxes of reduced species out of the sulfidic zone: reduced S, ammonium, reduced manganese, and methane among other reduced species. Additionally, the zone above the sulfide is suboxic rather than anoxic. Oxygen deficient zones, on the other hand, are mid-water zones that have oxygenated water below them. They are truly anoxic (Revsbech et al., 2009). They don't have fluxes of reduced species entering them. In fact, ammonium is usually below detection (Widner, Fuchsman, et al., 2018; Widner, Mordy, et al., 2018). In the Black Sea, the flux of ammonium from the sulfidic zone determines the importance of anammox and its place in the water column. A comparison of depth profiles of anammox bacteria, ammonium flux and N<sub>2</sub> gas can be seen in Fuchsman et al 2012a. Linkage between aerobic ammonium oxidation of the upward flux of ammonium and anammox can be found in (Lam et al., 2007) Additionally, the Black Sea is known to have an organic matter maximum in the redoxcline and quite a bit of information is known about this maximum. (see below) The authors have data from the Black Sea and they need to be more focused on understanding that unique system.

What can this float data tell us about the Black Sea? Are the particle maxima larger on the edges than in the middle of the Sea? Is there a correlation between euphotic zone particles and size of the suboxic zone particle max? Are particle flux events correlated to a season? Not that these particular questions need to be answered. At the moment, this paper tells us things that we already know (there is a particle maximum between 3  $\mu$ M oxygen and 10  $\mu$ M sulfide), but I think it could easily tell us more.

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I think it is important to note that manganese oxides are quite abundant in the Black Sea and that manganese oxides are also particles in the 0.2-20  $\mu\text{m}$  size range. Particle backscattering detects particles of all kinds. In the Black Sea, both ammonium and  $\text{Mn}^{2+}$  have an upward flux from the sulfide zone. Anammox bacteria use the ammonium flux to produce  $\text{N}_2$  gas (Fuchsman et al 2012a) and the  $\text{Mn}^{2+}$  is oxidized to manganese oxides under very low oxygen levels in the same zone (Clement et al., 2009). Thus excess  $\text{N}_2$  gas and manganese oxides are correlated. That correlation is not due to causation however. The authors need to consider how the manganese oxides affect their results. See (Clement et al., 2009; Dellwig et al., 2010; Yakushev et al., 2009) for more information about manganese oxides in the Black Sea.

The ability to detect particles in the water is not a measurement that only exists on floats, but is also present on CTD packages. Thus let us look at a station in the Black Sea where we have all the relevant data—the Western Gyre station in 2005. Here the maximum in organic C associated with microbes is found at sigma theta 16.3 (Figure 1 Fuchsman et al 2011). The maximum in anammox bacteria at the same cruise/station is at sigma theta 16.0-16.1 and the maximum in biologically produced  $\text{N}_2$  gas is at sigma theta 15.9-16.3 (Fuchsman et al 2012a Figure 1d). The maximum in  $\text{MnO}_2$  is at sigma theta 15.85 (Fuchsman et al 2011 Figure 6c). There is a small minimum in transmission from 15.8-15.85. The transmission signal corresponds to the manganese oxide peak not the peak in anammox bacteria or organic matter.

However, that particular station didn't have a large organic matter signal in the redoxycline. From looking at the authors' data, I would guess that they often see the organic matter maximum in the redoxycline. The organic matter maximum in the Black Sea redoxycline is from S oxidizing bacteria, which may or may not be autotrophic denitrifiers (Glaubitz et al., 2010; Kirkpatrick et al., 2018). These organic matter maxima can be dominated by S utilizing autotrophic denitrifiers of the genus *Sulfurimonas* (Kirkpatrick et al., 2018 Figure 7). And thus they could be involved in  $\text{N}_2$  production, but it has not been proven. Some useful papers about the organic matter maximum in the redoxy-

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cline of the Black Sea (Coban-Yildiz et al., 2006; Ediger et al., 2019; Glaubitz et al., 2010; Yilmaz et al., 2006).

Though anammox and denitrification are very important biogeochemically, they aren't actually the most abundant bacteria found in the Black Sea or oxygen deficient zones. In the ETNP oxygen deficient zone, anammox bacteria reached 10% of the community and complete denitrifiers reach ~5% in the water and 14% of the community on particles (Fuchsman et al., 2017). The most abundant bacteria in oxygen deficient zones, by far, are nitrate reducing SAR11, reaching 60% of the community (Fuchsman et al., 2017; Tsementzi et al., 2016). In the Black Sea, once again SAR11 are the most abundant bacteria (Fuchsman et al., 2011 Figure 2). The SAR11 cannot make N<sub>2</sub> gas. They just reduce nitrate to nitrite. I am just trying to note that for heterotrophic denitrifiers and anammox, the authors are using a bulk measurement to look for changes in bacteria that are rarely more than 10% of the community.

Thus, in the Black Sea, I think the assumption that the particle layer represents anammox and heterotrophic denitrifiers is not ideal. First, there are high concentrations of particulate metals in the Black Sea, particularly manganese oxides. Second, the organic matter maximum in the redoxcline is from S oxidizers. Some of these S-oxidizers may be autotrophic denitrifiers. Some aren't. Thus I think the way the particle maximum is talked about in the paper needs to be shifted. Additionally all this information should be in the introduction and discussion.

Specific Comments:

Was the oxygen data from the floats calibrated? See the work of Seth M. Bushinsky to understand the importance of calibration. This information is glossed over in the methods. I think that in previous float work in the Black Sea, scientists used the sulfide zone as a zero to at least track the drift of the oxygen optode over time. Also, it would be good to have a detection limit for all the different float sensors. Bushinsky et al 2016 *Limnology and Oceanography Methods*

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Line 8: This sentence is not accurate as written.

Line 22-23: I am confused what this sentence is trying to say. I note that N<sub>2</sub> gas concentrations can be between 400 and 500 microM in the water due to abiotic gas exchange of N<sub>2</sub> from the atmosphere. So the authors really mean to say N<sub>2</sub> production not concentration. The use of the word respectively in line 23 implies that denitrification is 20% of N<sub>2</sub> production and anammox is 40%. Rather, I think the authors are talking about how 20-40% of N<sub>2</sub> production occurs in the water column as opposed to in the sediments. The best citation for this is (DeVries et al., 2013).

Line 25: perhaps “where the bacteria that mediate the process mainly reside”

Line 26-27: I am confused as to the meaning of this sentence? Are the authors trying to say that 90% of the N<sub>2</sub> production occurred in the upper ODZ? Perhaps it would be better to say that 90% of N<sub>2</sub> production occurred in the upper 50 meters of the ODZ. Additionally, one should either say N<sub>2</sub> production or N loss. N loss refers to the loss of nutrients. The N<sub>2</sub> is produced not lost. I also note that anammox rates are not always highest at the top of the ODZ. See (De Brabandere et al., 2014)

Paragraph 1: I am having issues with oxygen deficient zones being called suboxic. The deficient part of oxygen deficient zone implies that the system is anoxic. No oxygen. The word was coined to differentiate these anoxic systems from suboxic systems which are called oxygen minimum zones.

Line 93: The best citation is (Dalsgaard et al., 2014). The authors do cite this paper later. To be consistent it should be noted here as well.

Line 121-122: This sentence needs clarification for two reasons. The authors are comparing depth and density. The Black Sea is much more consistent in density space than depth. It would be good to give the density range as well as the depth in line 121. Additionally, the authors compare a depth where sulfide is 11 μM to a depth where it is 10 nM. It is not surprising that the 11 μM depth is deeper than the 10 nM depth. That's

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an order of magnitude different in concentration. What is the HS- detection limit of the float?

Lines 133-148: The particle layer is between 3  $\mu\text{M}$  oxygen and 11  $\mu\text{M}$  sulfide. Both manganese oxides, and S oxidizers are also found in this range as well as methane oxidizers (Kirkpatrick et al 2018 Figure 6D)– not just anammox and denitrifiers. It is true however, that lots of microbial activity is occurring in this zone. These processes also could all affected by intrusions of oxygen. Lines 142-144: This is interesting.

Line 150-151: This sentence is confusing. I am glad that the authors acknowledge manganese oxides existence. However, manganese oxides are formed by manganese oxidizing bacteria not by denitrifiers. Perhaps autotrophic denitrifiers and manganese oxides, as concepts, should be separated into two sentences.

Line 171: Are the authors that confident in their oxygen concentrations? This would only be true if the sensors are calibrated. Can the optode see the difference between 0.2  $\mu\text{M}$  and 0  $\mu\text{M}$ ??

Line 190: Can you actually differentiate correlations with temperature from correlations with density in these deep layers? There is no biological reason that a change  $< 0.1$  in temperature should matter. However, I think many things, such as sulfide, correlate with temperature in this basin.

Line 235: (Cavan et al., 2018) Line 237: (Margolskee et al., 2019)

3.4 New perspectives for studying  $\text{N}_2$  losses in suboxic ODZs : This section would be more compelling if the floats measured  $\text{N}_2$  gas. There is such a device—Reed et al 2018 Deep Sea Research Part I 139: 68-78.

## References

Cavan, E. L., Giering, S. L. C., Wolff, G. A., Trimmer, M., & Sanders, R. (2018). Alternative Particle Formation Pathways in the Eastern Tropical North Pacific 's Biological Carbon Pump. *Journal of Geophysical Research: Biogeosciences*, 123, 2198–2211.

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<https://doi.org/10.1029/2018JG004392>

Clement, B. G., Luther, G. W., & Tebo, B. M. (2009). Rapid, oxygen-dependent microbial Mn (II) oxidation kinetics at sub-micromolar oxygen concentrations in the Black Sea suboxic zone. *Geochimica et Cosmochimica Acta*, 73(7), 1878–1889. <https://doi.org/10.1016/j.gca.2008.12.023>

Coban-Yildiz, Y., Altabet, M. A., Yilmaz, A., & Tugrul, S. (2006). Carbon and nitrogen isotopic ratios of suspended particulate organic matter (SPOM) in the Black Sea water column. *Deep Sea Research Part II: Topical Studies in Oceanography*, 53(17–19), 1875–1892. <https://doi.org/10.1016/j.dsr2.2006.03.021>

Dalsgaard, T., Stewart, F. J., Thamdrup, B., Brabandere, L. De, Revsbech, P., & Ulloa, O. (2014). Oxygen at Nanomolar Levels Reversibly Suppresses Process Rates and Gene Expression in Anammox and Denitrification in the Oxygen Minimum Zone off Northern Chile. *MBio*, 5(6), e01966-14. <https://doi.org/10.1128/mBio.01966-14>. Editor

De Brabandere, L., Canfield, D. E., Dalsgaard, T., Friederich, G. E., Revsbech, N. P., Ulloa, O., & Thamdrup, B. (2014). Vertical partitioning of nitrogen-loss processes across the oxic-anoxic interface of an oceanic oxygen minimum zone. *Environmental Microbiology*, 16, 3041–3054. <https://doi.org/10.1111/1462-2920.12255>

Dellwig, O., Leipe, T., Ma, C., Glockzin, M., Pollehne, F., Schnetger, B., Yakushev, E. V., & Bo, M. E. (2010). A new particulate Mn – Fe – P-shuttle at the redoxcline of anoxic basins. *Geochimica et Cosmochimica Acta*, 74, 7100–7115. <https://doi.org/10.1016/j.gca.2010.09.017>

DeVries, T., Deutsch, C., Rafter, P. A., & Primeau, F. (2013). Marine denitrification rates determined from a global 3-D inverse model. *Biogeosciences*, 10(4), 2481–2496. <https://doi.org/10.5194/bg-10-2481-2013>

Ediger, D., Murray, J. W., & Yılmaz, A. (2019). Phytoplankton biomass, primary production and chemoautotrophic production of the Western Black

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Sea in April 2003. *Journal of Marine Systems*, 198(January), 103183. <https://doi.org/10.1016/j.jmarsys.2019.103183>

Fuchsman, C. A., Devol, A. H., Saunders, J. K., McKay, C., & Rocap, G. (2017). Niche Partitioning of the N cycling microbial community of an offshore Oxygen Deficient Zone. *Frontiers in Microbiology*, 8, 2384.

Fuchsman, C. A., Kirkpatrick, J. B., Brazelton, W. J., Murray, J. W., & Staley, J. T. (2011). Metabolic strategies of free-living and aggregate-associated bacterial communities inferred from biologic and chemical profiles in the Black Sea suboxic zone. *FEMS Microbiology Ecology*, 78, 586–603. <https://doi.org/10.1111/j.1574-6941.2011.01189.x>

Glaubitz, S., Labrenz, M., Jost, G., & Jürgens, K. (2010). Diversity of active chemolithoautotrophic prokaryotes in the sulfidic zone of a Black Sea pelagic redoxcline as determined by rRNA-based stable isotope probing. *FEMS Microbiology Ecology*, 74(1), 32–41. <https://doi.org/10.1111/j.1574-6941.2010.00944.x>

Kirkpatrick, J. B., Fuchsman, C. A., Yakushev, E. V., Egorov, A. V., Staley, J. T., & Murray, J. W. (2018). Dark N<sub>2</sub> fixation: nifH expression in the redoxcline of the Black Sea. *Aquatic Microbial Ecology*, 82, 43–58. <https://doi.org/10.3354/ame01882>

Lam, P., Jensen, M. M., Lavik, G., McGinnis, D. F., Muller, B., Schubert, C. J., Amann, R., Thamdrup, B., & Kuypers, M. M. M. (2007). Linking crenarchaeal and bacterial nitrification to anammox in the Black Sea. *Proceedings of the National Academy of Sciences*, 104(17), 7104–7109. <https://doi.org/10.1073/pnas.0611081104>

Margolskee, A., Frenzel, H., Emerson, S., & Deutsch, C. (2019). Ventilation Pathways for the North Pacific Oxygen Deficient Zone. *Global Biogeochemical Cycles*, 33(7), 875–890. <https://doi.org/10.1029/2018GB006149>

Revsbech, N. P., Larsen, L. H., Gundersen, J., Dalsgaard, T., Ulloa, O., & Thamdrup, B. (2009). Determination of ultra-low oxygen concentrations in oxygen minimum zones by the STOX sensor. *Limnology and Oceanography:Methods*, 7, 371–381.

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Tsementzi, D., Wu, J., Deutsch, S., Nath, S., Rodriguez-r, L. M., Burns, A. S., Ranjan, P., Sarode, N., Malmstrom, R. R., Padilla, C. C., Stone, B. K., Bristow, L. A., Larsen, M., & Glass, J. B. (2016). SAR11 bacteria linked to ocean anoxia and nitrogen loss. *Nature*, 536, 179–183. <https://doi.org/10.1038/nature19068>

Widner, B., Fuchsman, C. A., Chang, B. X., Rocap, G., & Mulholland, M. R. (2018). Utilization of urea and cyanate in waters overlying and within the eastern tropical north Pacific oxygen deficient zone. *FEMS Microbiology Ecology*, 94(September 2017), fiy138. <https://doi.org/10.1093/femsec/fiy138>

Widner, B., Mordy, C. W., & Mulholland, M. R. (2018). Cyanate distribution and uptake above and within the Eastern Tropical South Pacific oxygen deficient zone. *Limnology and Oceanography*, 63, S177–S192. <https://doi.org/10.1002/lno.10730>

Yakushev, E., Pakhomova, S., Sørensen, K., & Skei, J. (2009). Importance of the different manganese species in the formation of water column redox zones: Observations and modeling. *Marine Chemistry*, 117(1–4), 59–70. <https://doi.org/10.1016/j.marchem.2009.09.007>

Yilmaz, A., Coban-Yildiz, Y., Tellikarakoc, F., & Bologa, A. (2006). Surface and mid-water sources of organic carbon by photoautotrophic and chemoautotrophic production in the Black Sea. *Deep Sea Research Part II: Topical Studies in Oceanography*, 53(17–19), 1988–2004. <https://doi.org/10.1016/j.dsr2.2006.03.015>

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