

Twists in estimating O₂ changes in oxygen minimum zones from old O₂ data

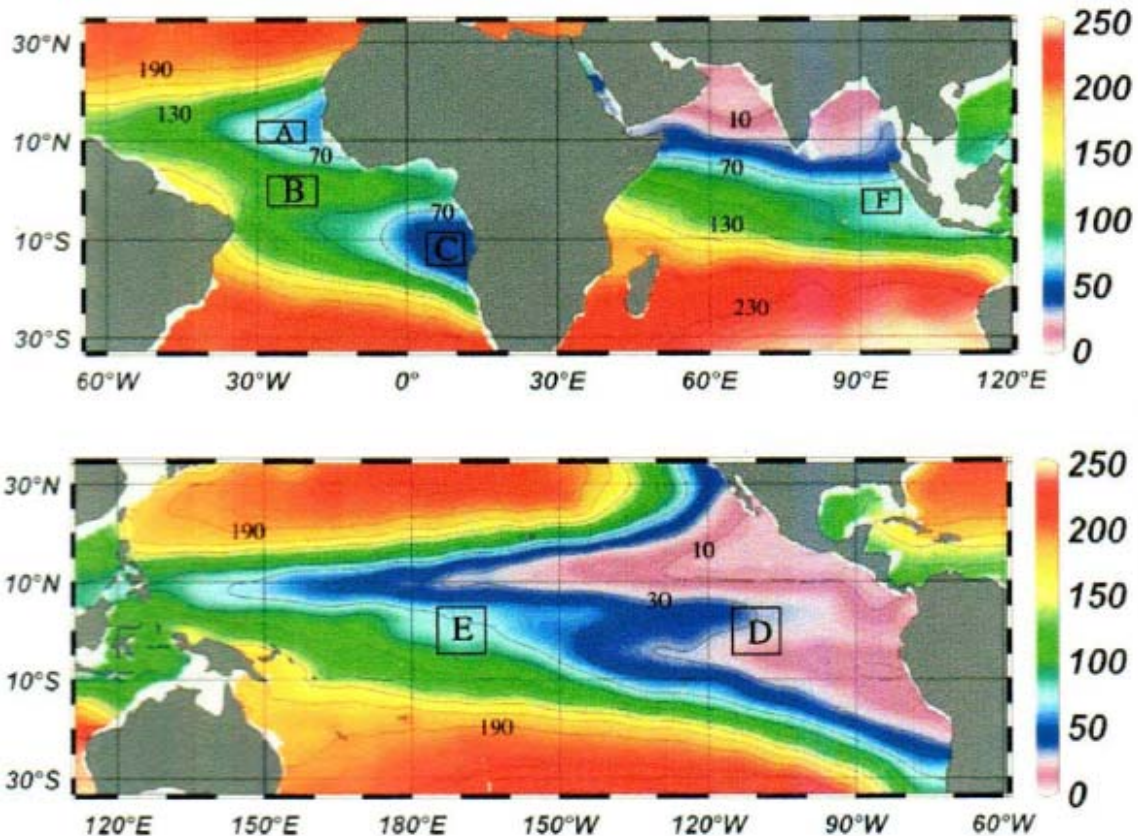
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The present PICES session concerns the 50 years since the first edition of ***A Practical Handbook of Seawater Analysis*** by Strickland and Parsons appeared. We show for published very low O₂ concentrations that one has to distinguish two sets of Winkler O₂ values owing to the change in the methods of titration end point detection in the mid-1970s / early 1980s.

Tempora mutantur, et nos mutamur in illis
Times change, and we change with them
(Attributed to Emperor Lothar I, son of Charlemagne, ~ 850)

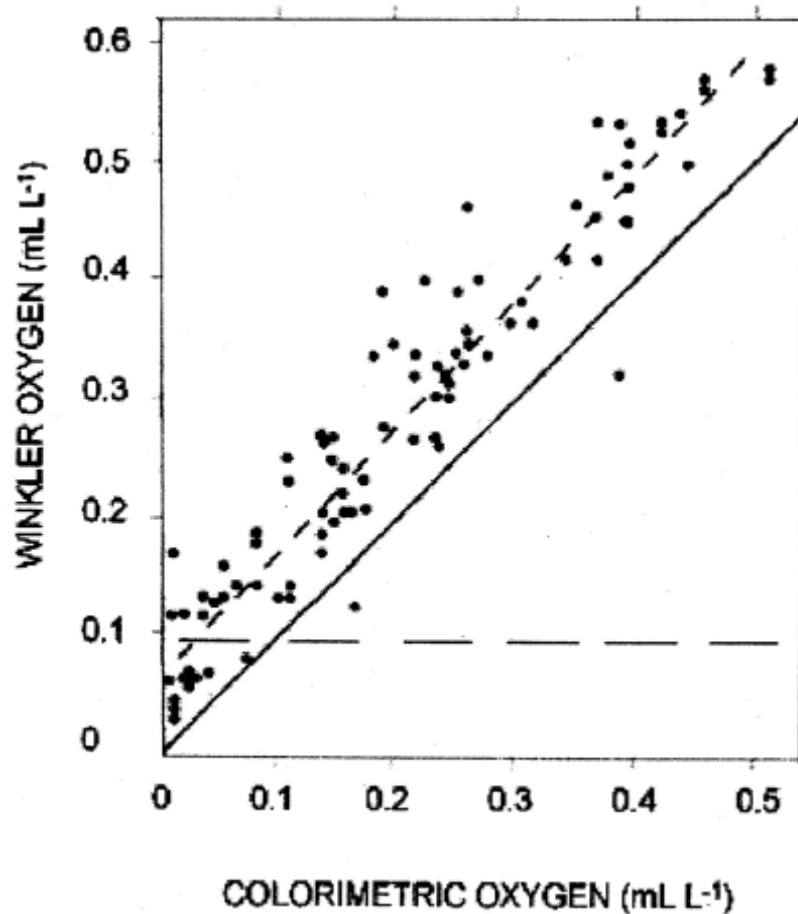


Dissolved O_2 in $\mu\text{mol kg}^{-1}$ at 400 m depth (Stramma et al., Science 320: 655, 2008). The oxygen minimum zones (OMZs) are shown in pink and extend few hundred meters above and below.

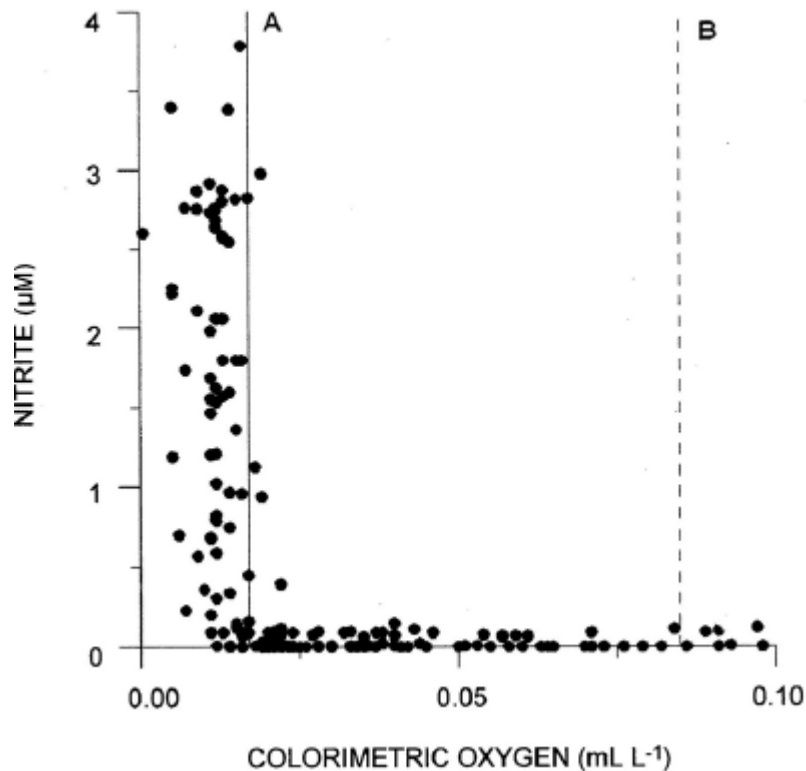
Most of the bound N below the upper layers is NO_3^- , which is perpetually supplied to the ocean from weathering, lightning at sea, N_2 fixation by some phytoplankton, and lately from runoff of fertilizers. About half of it is reduced at $\sim \leq 2 \mu\text{M O}_2$ to N_2 by the two OMZs in the eastern tropical Pacific and the third, largest one in the central Arabian Sea; the other half is reduced in the sediments. The powerful green house gas N_2O is a by-product.

While the ocean overall is changing, do the OMZs intensify and expand and affect the world's nitrogen balance, as well as N_2O production? Accurate O_2 time series are required but the few series going back to 1960 are biased toward OMZ intensification because of a change from visual (starch addition) to automated

endpoint detection (VED and AED) in the Winkler titration since the mid-1970s / early 1980s.

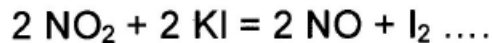
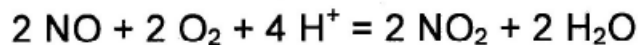
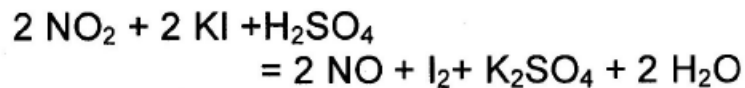


O_2 from VED on O_2 from an AED method (Broenkow and Cline, *Limnol Oceanogr.* 14: 541, 1969). The O_2 from VED reaches zero while O_2 is still present (the broken line suggests an average error). All VED data are affected to variable but significant degrees. When plotted in a time series together with the new AED data, a decadal-scale decrease of O_2 may falsely be suggested. Oceanographic data centers do not flag the old measurements.

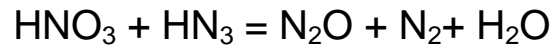


Nitrite on dissolved O_2 in the ventral Arabian Sea (Naqvi, original). Denitrification sets in well below the lower limit of the VED, as indicated by the appearance of NO_2^- , an intermediate of NO_3^- reduction. The offset (bias, broken line) varies unpredictably among institutions and operators, usually by 0.05-0.10 $mL L^{-1}$ ($\sim 2-4 \mu M$).

The bias in part depends on the speed of titration because of the reaction of iodide with NO_2^- , which in the acidic solution is catalyzed by O_2 continually dissolving from the air, and on NO_2^- .



The NO_2^- can be eliminated by adding azide to the NaOH / KI Winkler reagent ($2\text{-}4 \text{ g L}^{-1} \text{ NaN}_3$).



The VED bias cannot be corrected *post hoc*, but erroneously high O_2 values accompanied by high NO_2^- can be recognized and removed. For example, from an Arabian Sea OMZ set of 694 VED data between about 200 and 500 m depth by 13 ships of 7 countries we rejected 215 with $\text{O}_2 > 0.10 \text{ mL L}^{-1}$, which were accompanied by $\text{NO}_2^- > 0.20 \text{ }\mu\text{M}$.

In conclusion about the errors, the published O_2 means and distributions for sub-oxic O_2 horizons and OMZs in atlases bear checking.

The data centers should at least flag and, preferably, annotate each original data set, and future authors will have to specify their methods in detail in their papers.

(From the Discussion of the talk: Even with the now wide use of electric O_2 recorders attached to CTDs, the Winkler method remains for calibrating the probes. However, the standardization of the $\text{Na}_2\text{S}_2\text{O}_3$ for titration continues to be a troubling variable. Like for nutrients, could not a Certified Reference Material of K_2IO_3 be introduced?)

Finally, judging from about three decades of AED measurements, is the intensity of O_2 minimum zones changing?

Yes, it might: For three sub-areas of the Pacific TAO region east of the date line between 3°N and 3°S from 200 to 700 m depth, Stramma et al. (J. Geophys. Res. Ocean 115. 2010) estimated for the last 30 years that O_2 decreased significantly by 0.32 , 0.38 , and $0.55 \text{ }\mu\text{mol kg}^{-1}\text{yr}^{-1}$, or roughly

0.4 $\mu\text{mol kg}^{-1}\text{yr}^{-1}$. After accounting for advection and eddy diffusion of O_2 the bulk consumption rate turned out to be $\sim 4 \mu\text{mol kg}^{-1}\text{yr}^{-1}$. We suggest that the latter rate is the biogeochemically more important estimate.

Because of the context of this PICES session, we cannot refrain from noting that in 1960, the same year Strickland and Parsons' ***Practical Handbook of Seawater Analysis*** appeared, their entire group in Nanaimo followed a plankton bloom for 22 days without the disturbance by the bane of plankton studies in the sea, the ever-present advection and diffusion, because the water was enclosed in a 125 m^3 plastic sphere floating near-shore. They actually *measured* bulk parameters of growth and decay.

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