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Autonomous Observation of Oxygen Deficient Zone (ODZ) Biogeochemistry

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Open ocean oxygen deficient zones (ODZ's) host unique subsurface biogeochemical processes that have global impacts including fixed nitrogen loss and the cycling of N₂O. They have been predicted to expand geographically in response to global warming though contrary perspectives are available. In addition, biogeochemical activity is highly variable in time and space as associated with coastal upwelling plumes and certain types of mesoscale eddies. Correspondingly, ship based observations are insufficient to both capture relevant scales of variability and provide the sustained time series records required to detect long term (\geq decadal) changes.

While many of the observational requirements of ODZ's overlap with those of the global ocean, the unique subsurface biogeochemistry of ODZ's requires additional sensor capabilities. In the cores of ODZ's, O₂ is often undetectable even with nM sensitivity and key ODZ microbial nitrogen cycle processes now appear to have O₂ sensitivities in the 0 to 3 μ M range. Hence, relatively small changes in O₂ control the buildup of nitrite and the loss of fixed nitrogen to N₂ gas. Up to now, there has been no commercially available, autonomously-deployable O₂ sensor. Here we show field data from float deployments in the Mexican ODZ that the Clark-type SBE43 O₂ sensor is capable of reliable nM measurements. To do so, sufficient exposure to ODZ waters was needed for O₂ to diffuse out of elastomeric parts and for data processing to be geared to the nM range. Working with SeaBird, a prototype NanoSBE43 sensor has been produced and satisfactorily tested.

Measurements of biogenic N₂ production is definitive for N-loss in ODZ's but analytically challenging particularly for autonomous deployment. We have used a gas tension device (GTD) to do so, with which total dissolved gas pressure is measured. In ODZ's, ~99% of the total pressure is from N₂ and its concentration is derived from Henry's law. The biogenic contribution is determined by subtracting atmospheric and physical supersaturation terms. Short term float deployments showed vertical profiles consistent with lab-based measurements made by mass spectrometer determination of N₂/Ar ratio. A GTD-Argo float deployed since Nov. 2016 has continued to operate reliably with an apparent precision of 0.15 μ mol kg⁻¹.

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