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Assessment of optodes analytical performances in high dissolved oxygen gradient zones

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In the context of ocean deoxygenation and increase of hypoxia events (e.g. in coastal zones), many questions exist about the analytical performances of optodes and electrodes used to measure dissolved oxygen in high gradient zones (lakes, estuaries, Oxygen Minimum Zones in open ocean), i.e. between fully oxygenated environments and hypoxic, or even anoxic, environments. Comparing the performance of commercial sensors has become essential to harmonize their implementation and estimate the overall in situ measurement uncertainty.

Tests were carried out on Lake Pavin (Massif central, France) in June 2024 using optodes commonly used by 10 laboratories for measurements in lakes, groundwater, rivers, estuaries, coastal and oceanic waters. Lake Pavin is a meromictic lake which presents in early summer three zones of interest for dissolved oxygen measurements:
- an oxygenated surface layer between 0 and 25 m (at the top of the mixolimnion) in which is observed a peak of supersaturated oxygen concentrations related to the photosynthetic activity of highly productive phytoplankton.
- a transition zone between 50 and 60 m presenting a strong negative gradient (oxycline within the mesolimnion layer),
- an anoxic zone between 60 and 90 m depth which corresponds to the monimolimnion.

Several dissolved oxygen profiles were carried out using a frame on which were mounted 22 portable meter instruments (multiparameter or dissolved oxygen only) from various manufacturers, including 8 identical ones, in order to:
(1) quantify measurement uncertainties in gradient zones,
(2) identify and quantify the most significant interferences in terms of bias,

(3) estimate the detection limit in anoxic zones,
(4) evaluate the minimum stabilization time in the gradient zones and in the anoxic zone,
(5) compare measurements collected during downcast and upcast,
(6) evaluate the influence of sensors response times on results.

The profiles were carried out with different downcast/upcast speeds and with various stop durations at depths of interest. Continuous measurements were also taken overnight at a fixed point in the anoxic layer. Water samples were collected using a Niskin bottle for dissolved oxygen cross-calibration using the Winkler reference method.

Two statistical treatments were implemented to estimate the standard deviation of reproducibility between optodes (EN ISO 5725-2 standard and algorithm A of the EN ISO 13528 standard). Furthermore, an estimation of the overall measurement uncertainty was carried out for the 8 identical optodes using the RANOVA4 software.

The results showed significantly better performances during upcast, with slow speed and when stops of 5 min are carried out at depths of interest. These results will enable us to propose recommendations (1) for choosing optodes according to measurement objectives and expected dissolved oxygen concentration ranges, and (2) for carrying out profiles under conditions that limit the measurement uncertainties to monitor with confidence trends and extreme events in changing aquatic environments.