

In the context of ocean deoxygenation and increase of hypoxia events in response to climate change and anthropogenic releases, 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). In those gradients, 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.

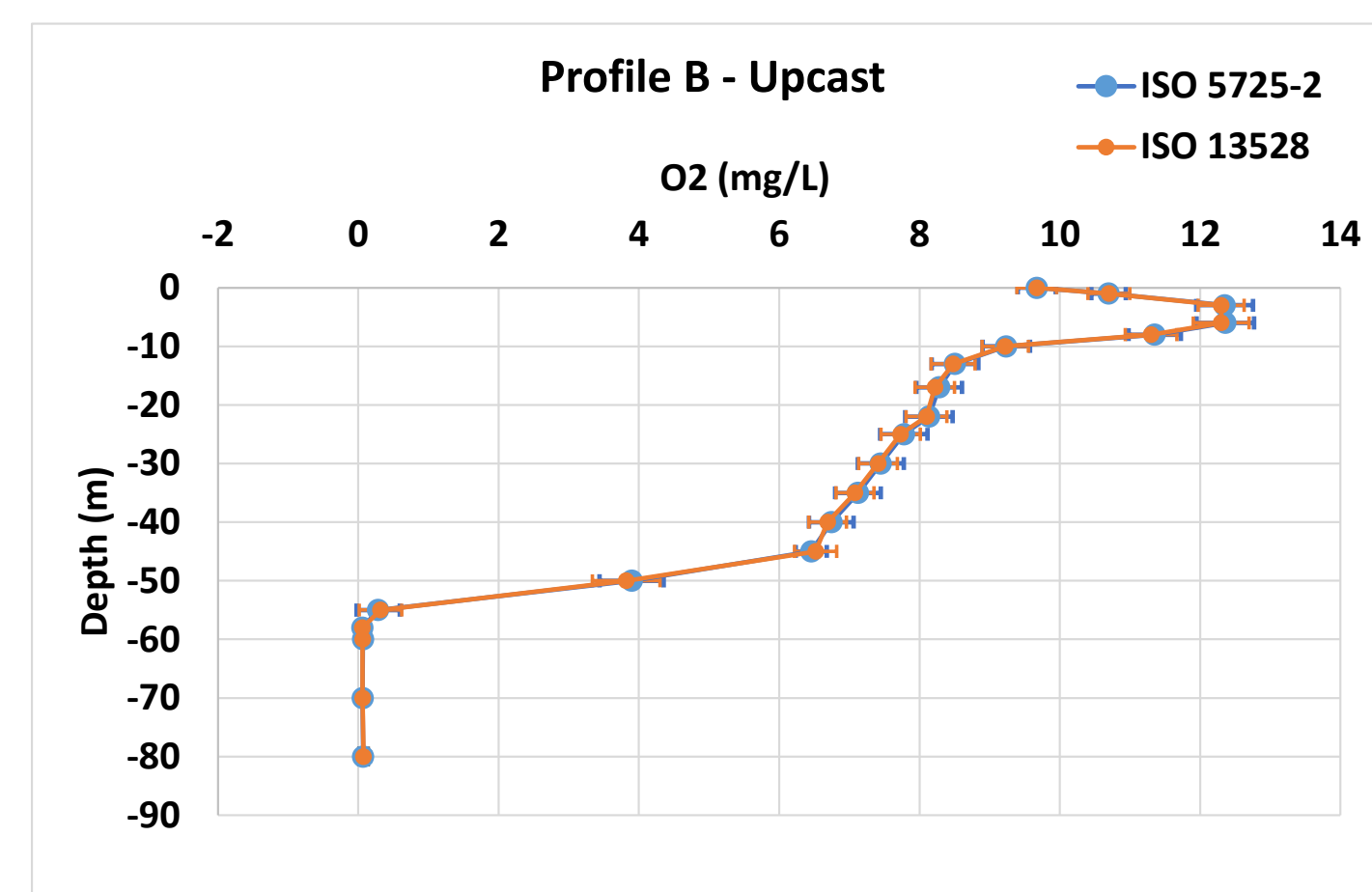
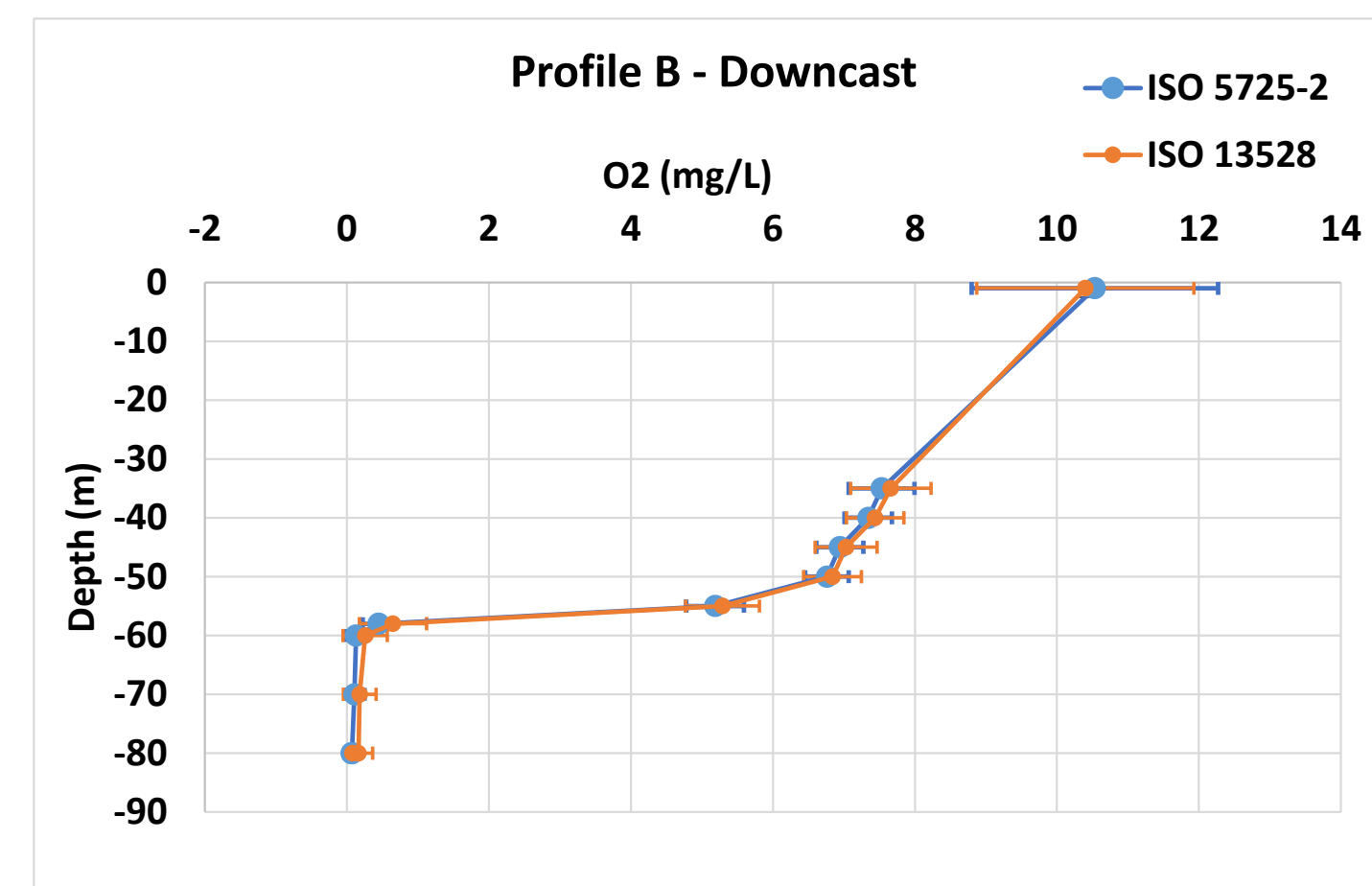
Optodes



- 20 optodes for profile testing
- Reference measurement at selected depths (WINKLER method on samples collected with Niskin bottle)

Manufacturer	Model	Number of optodes
YSI	EXO 2	2
YSI	ProDSS	1
IDRONAUT	Idro 310	1
RBR	Maestro3	1
Pyroscience	AquapHOX-LX-O2	1
NKE	WIMO PLUS	1
NKE	Wisens DO	1
NKE	MP6	1
Seabird	SBE 37 IMP ODO	1
PME	miniDOT	9
ONSET	HOBO U26	1

Interlaboratory comparison performances



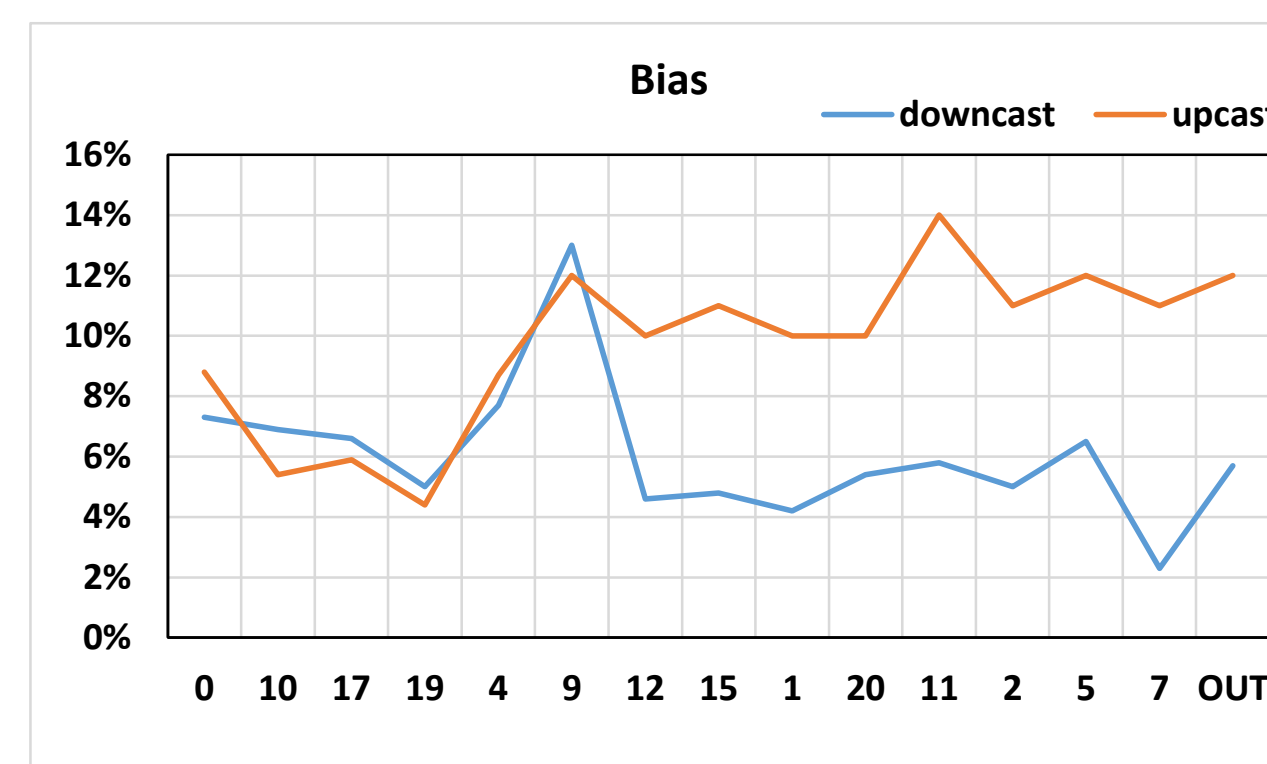
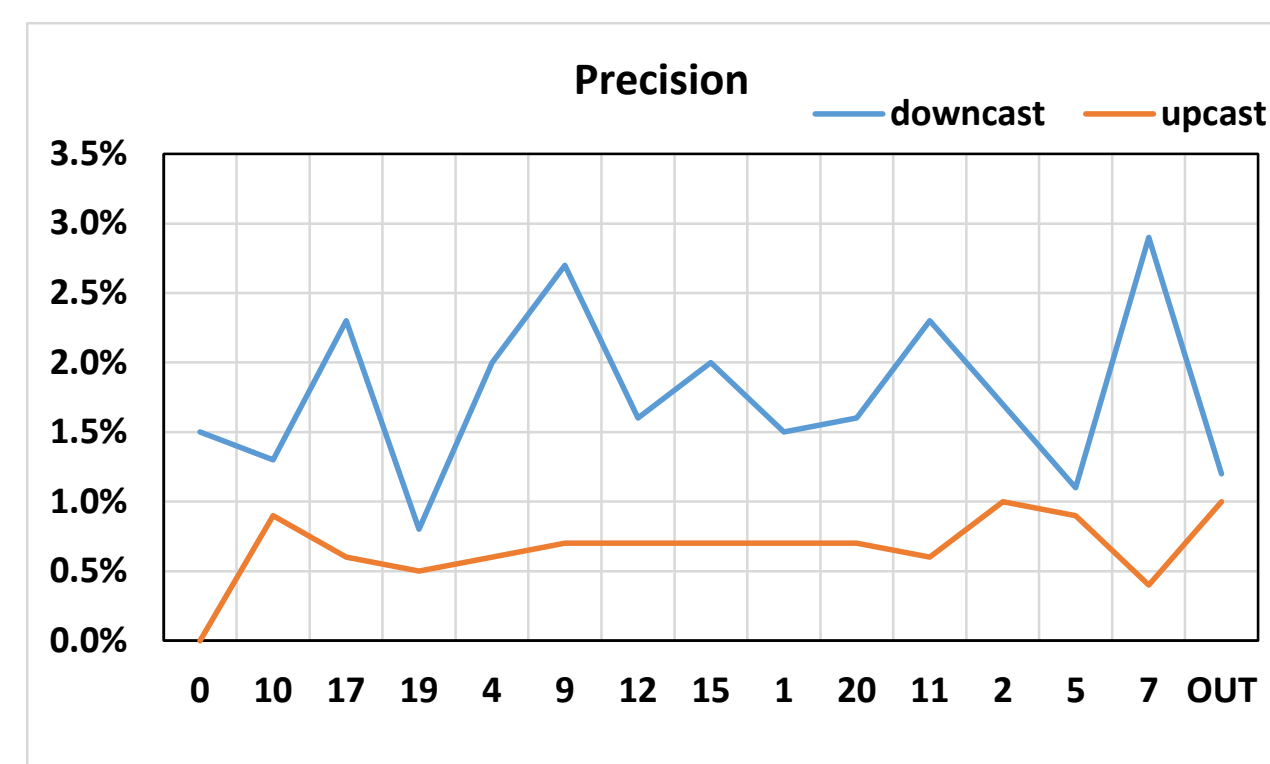
- Interlaboratory repeatability (S_r) and reproducibility (S_R) was assessed considering all probes at each depth of each profile based on ISO 5725-2.
- a robust standard deviation using Algorithm A from ISO 13528 was also calculated
- Results between the 2 approaches gives similar results as illustrated for profile B

Measurement uncertainty

Precision was estimated as the root mean square of the standard deviations calculated using triplicate (1min-consecutive measurement) at each depth

Bias was evaluated as the root mean square of each bias using the Winkler measurements (reference method) at a selection of depths

- Precision is found much better for upcast than downcast profiles (see example for B profiles): < 1%
- Bias between upcast and downcast profiles is similar for probes 6 probes, whereas for the other, an hysteresis exists after spending an overnight at 80 m (anoxic zone)
- U (k=2) is in between 6% and 10% for downcast profile B (except 1 probe at 16%)



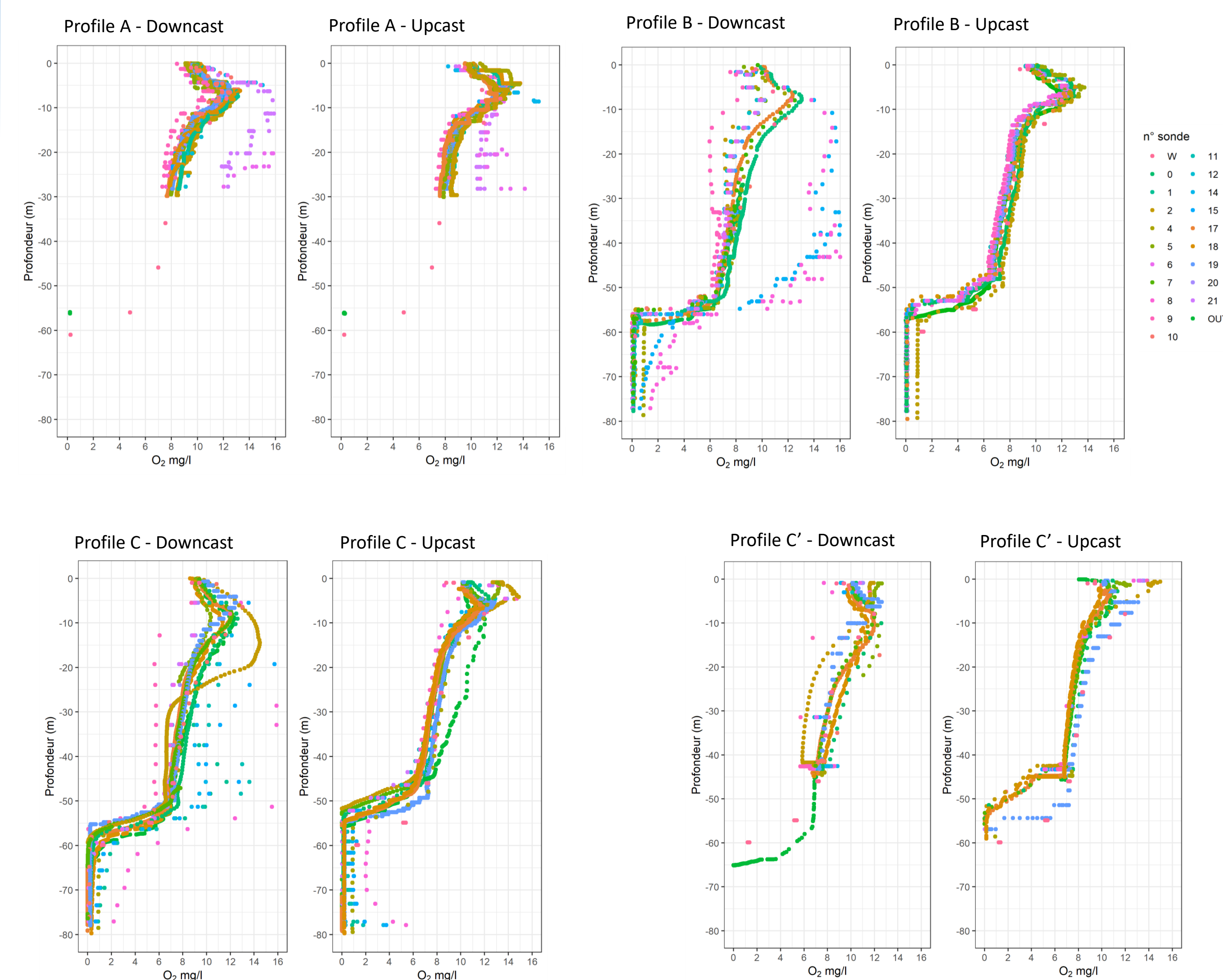
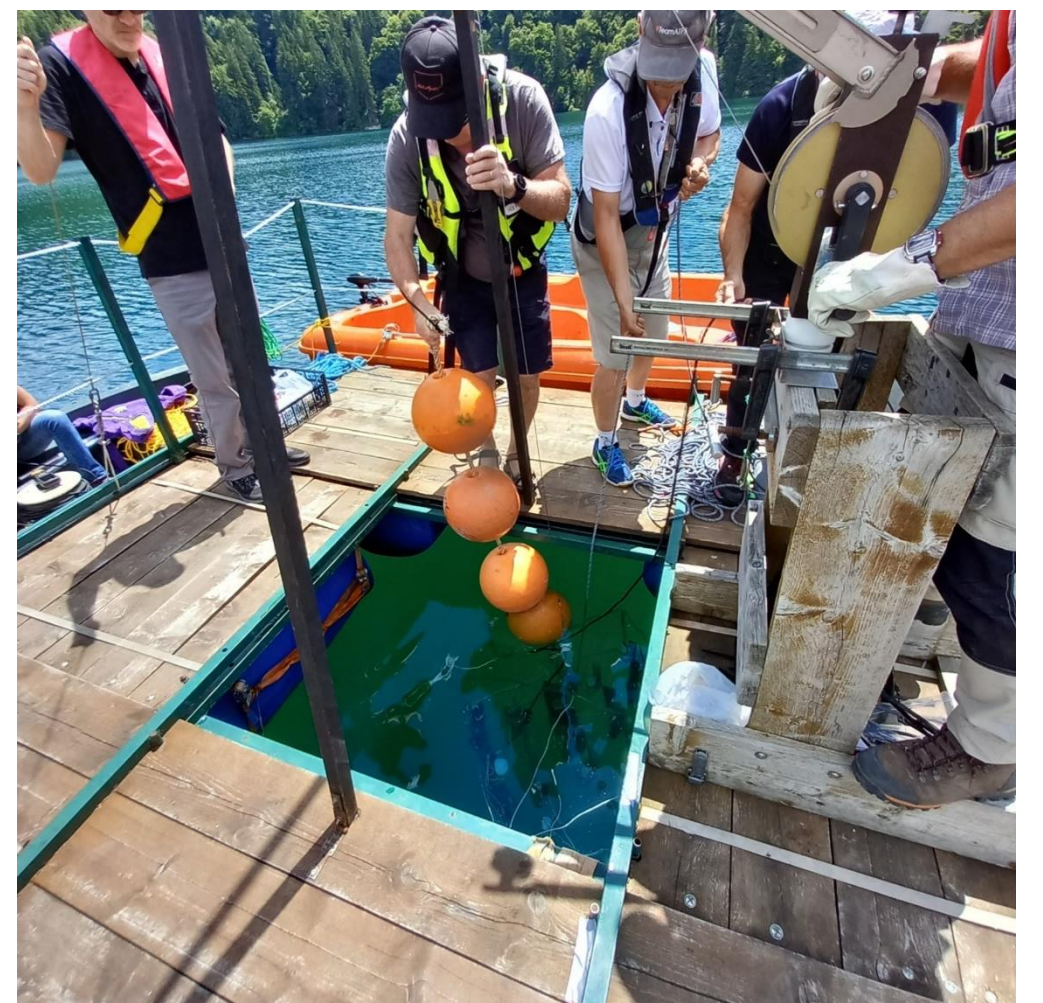
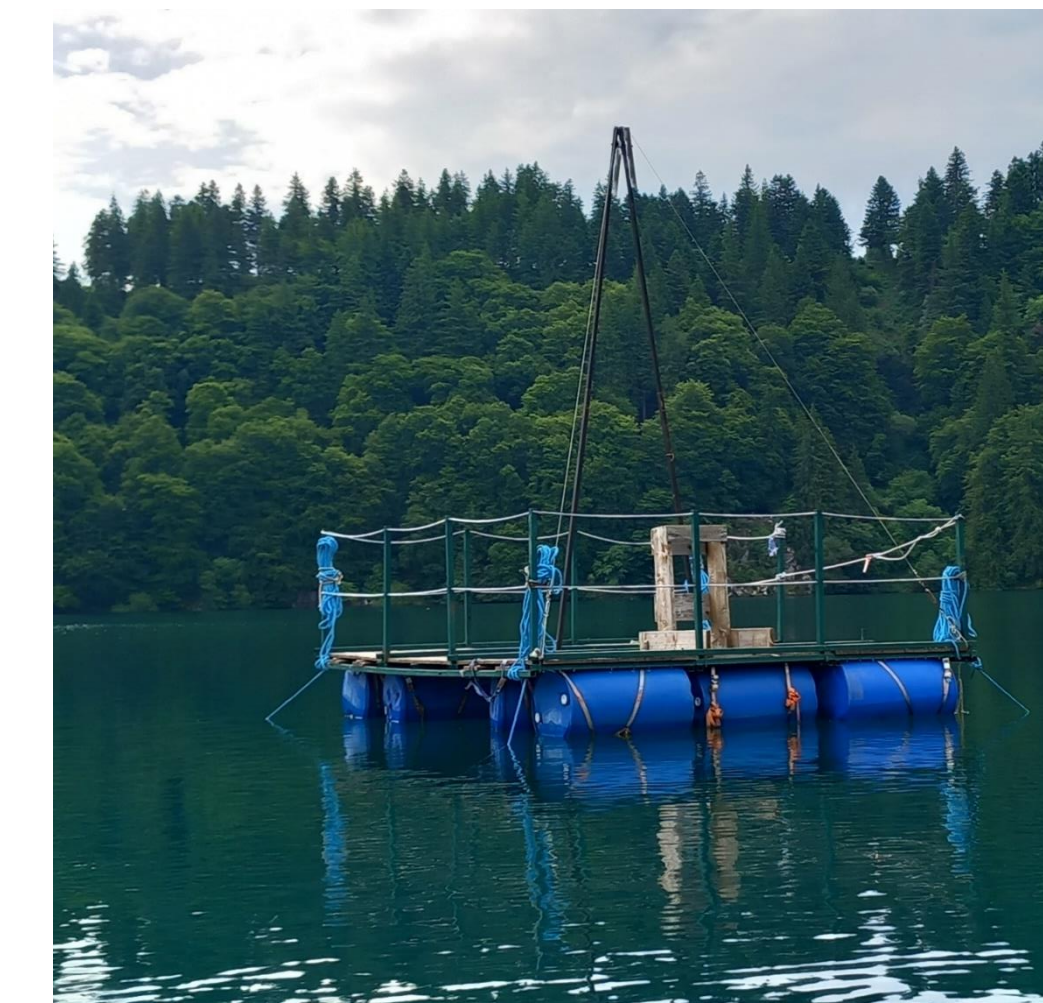
- Robust analysis of variance (RANOVA4, AMC Software) was used to assess the measurement uncertainty of the 8 Minidot probes. Results showed that the best measurement uncertainty is obtained for upcast profiles after an overnight at 80 m (profile B and profile D) with U (k=2) = 5.6% and 7.4%. For upcast profiles A and C, U (k=2) is around 12-13%.

in situ oxygen profiles

Lake Pavin is a meromictic lake, which presents in early summer three zones of interest for dissolved oxygen measurements:

1. An oxygenated surface layer between 0 and 25 m (at the top of the mixolimnion)
2. A transition zone between 50 and 60 m presenting a strong negative gradient (oxycline within the mesolimnion layer)
3. An anoxic zone between 60 and 90 m depth, which corresponds to the monimolimnion

Profile	Depth range	Speed	Stops
A	Down: 1 m – 30 m Up: 30 m – 1 m	<2 cm/s	5 min at selected depths (down & up)
B	Down: 30 – 80 m Up: 80 m – 1 m	<2 cm/s	5 min at selected depths (down & up) 1 night at 80 m
C	Down: 1 – 80 m Up: 80 m – 1 m	5 cm/s	15 min at 1 m and 80 m (down)
C'	Down: 3 – 62.5 m Up: 62.5 m – 1 m	25-30 cm/s	60 min at 45 m and 62.5 m (down & up)
D	Down: 1 – 80 m Up: 80 m – 1 m	25-30 cm/s (down) 60-70 cm/s (up)	1 night at 80 m 15 min at 45 m (up)



In general, upcast profiles showed less dispersion between optodes than downcast profiles.

For some Minidot optodes (e.g. at position 6, 8 and 14), air bubbles stuck to the sensing membrane induced a large bias mainly during downcast profile. However, after an overnight at 80 m depth (see profile B upcast), the bias due to air bubble is eliminated.

Some hysteresis have been observed for some probes between downcast and upcast profiles

CONCLUSION

The results showed significantly better performances during upward profiles at slow speed and when stops of 5 min are carried out at depths of interest.

These results will be used 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.