# Anomalies of oxygen measurements performed with Aanderaa optodes

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Four sets of measurements performed between 2005 and 2010 in the deep central Atlantic, the deep north-western Mediterranean Sea, and in the Arctic Ocean revealed strange anomalies in the performance of the Aanderaa optode 3830 sensors mounted on RCM11 current meters in low current regimes (current speeds >10 cm $s^{-1}$). All oxygen datasets collected during these deployments showed significant drops of oxygen (50–100 $\mu$mol) affecting the data stability of the optode sensors in low hydrodynamic conditions.

High correlations between all acquired parameters (temperature, turbidity, speed and direction of currents) verified that no unusual event occurred in the mooring areas during the periods of acquisition, although natural events responsible for such abrupt, short and intense oxygen variations cannot be easily identified. Despite the well-known performance of the Aanderaa optodes, these experiments demonstrate that the data acquired by those installed on RCM11s cannot be always reliable, especially in low energy systems (typical for the deep ocean), and that current speeds should always be considered in order to verify the reliability of the data recorded.

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Nadia Lo Bue has worked at the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in Rome since 2003. Her research interests involve physical oceanographic processes focusing on long-term ocean observations performed though multidisciplinary benthic observatories. Between 2009–2010 she spent one year at the Ifremer Institute working on the analysis of long oceanographic dataset collected in the Mediterranean Sea.

## INTRODUCTION

Although the principle of fluorescence quenching has been known for a long time, it has only been applied to seawater technology within the last few years. There already exists a large amount of literature featuring the use and performance of optical oxygen measurements in seawater achieved through fluorescence quenching-based sensors, like the Aanderaa optode.[1–11] Unfortunately, in most of this literature, complementing data on hydrodynamic conditions are missing.

On the basis of its widely documented efficiency, optodes were used in different scientific programmes carried out by the Ifremer/Laboratoire Environnement Profond and the Deep-Sea Research Group at the Alfred Wegener Institute for Polar and Marine Research from 2005 to 2010 in order to exploit their good performance on long-term measurements monitoring oxygen concentration in deep seawater.[12–15] These programmes reported long-term oxygen data recorded by optodes mounted on RCM11 acoustic current meters moored in various environments, and showed the same kind of doubtful results at comparable hydrodynamic conditions.

# MATERIAL AND METHODS

## Measurement sites and moorings

During the EXOMAR research programme[12] conducted on the Mid-Atlantic Ridge in 2005, four moorings were deployed at increasing distance from the Tour Eiffel chimney of the Lucky Strike hydrothermal vent field (37° 17' N, 32° 16' W), with the main aim to better explore and understand the environment of hydrothermal micro-organisms (Fig 1a). Two moorings were equipped with current meters, one of which (RCM11 s/n 177) carried an Aanderaa optode 3830. This mooring, handled by the Remotely Operated Vehicle (ROV) *Victor 6000*, was deployed 5m southward (in 1700m water depth) from the Tour Eiffel chimney 15m above the bottom. It acquired a series of oxygen data over 25 days with a sampling rate of one sample every 10 minutes.[11]

The ENVAR programme,[13] as part of the European HERMES project, focused on the study of turbidity events in the Var submarine canyon (Fig 1b) and its effects on the deep benthic ecosystems. During two years (2005–2007) several long-term moorings were repeatedly deployed at different depths along the Var canyon axis. Among other instruments, the moorings were equipped with mechanical current meters (Aanderaa RCM8) and turbidity meters. At two sites (VA, 43° 22' N, 7°32' E, 1866m and VC, 43° 29' N, 7°22' E, 1904m; Fig 1b), an additional acoustic current meter (Aanderaa RCM11 s/n 542) was intermittently attached to the moorings (at ~460m and ~260m above bottom, respectively), in order to compare the efficiency of mechanical and acoustic current measurements.

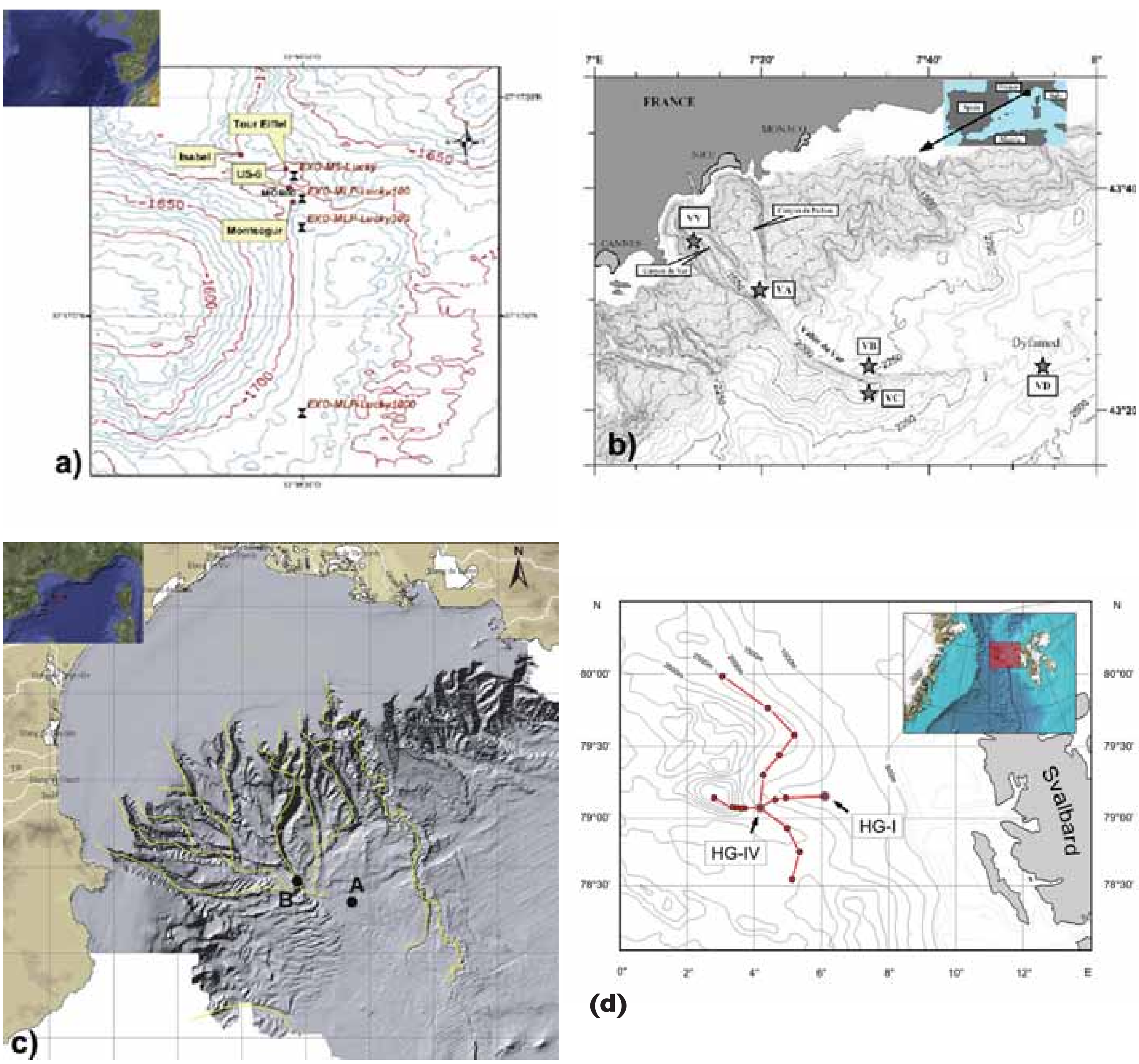


Fig 1: Sites of measurement: a) EXOMAR site in the Mid-Atlantic ridge, b) ENVAR site in the Var Canyon (Mediterranean Sea); c) DEEP site in the canyons system of Gulf of Lion (Mediterranean Sea), d) HAUSGARTEN observatory in the deep eastern Fram Strait (Arctic Ocean)

As for the previous experiment, the RCM11 was equipped with an optode sensor 3830, thus oxygen data were collected by the same sensor during two different time periods (May–August 2006 at VC site, and August–November 2006 at VA site) with a sampling rate of one sample every 30 minutes.[11]

In 2008, the French Agence Nationale de la Recherche (ANR) funded the EXTREMA research programme to study the sedimentary mass transported by the Rhone river into the Gulf of Lions, NW Mediterranean. In this framework, the Ifremer/DEEP activities[14] focused on the particle input at two different stations located at the base of the margin (Station A, 42° 10' N, 4° 33' E, 2256m) and at the confluence of two submarine canyons (Creus and Sète, Station B, 42° 15' N, 4° 20' E, 2197m), respectively (Fig 1c). In total, three moorings were deployed at these sites (one at Station A, and two at the Station B) in order to study the local current regime and to determine the flux of particulate matter to the seafloor. Each of these moorings carried an acoustic current meter (Aanderaa RCM11 s/n 177 s/n 542, and s/n 625) equipped with optode 3830 at 30m above the bottom.

Within the frame of the time-series work at the deep-sea long-term observatory HAUSGARTEN[15] west of Svalbard,[7] two Aanderaa RCM11 meters (s/n 691 and s/n 692) with optode sensors 3830 were deployed at the shallowest and the central HAUSGARTEN site, respectively (HG-I, 79° 08,02' N, 6° 05,59' E, 1282m and HG-IV, 79° 04,83' N, 04°05,41' E, 2467m) (Fig 1d). Both instruments were fixed at about 2m above ground on top of free-falling devices (bottom-lander) and deployed for one year between the summers of 2009 and 2010.

### Calibration

The calibration of optode sensors was performed according to the Aanderaa protocol, consisting of two points of measurements: zero oxygen saturation, adding a small quantity of Thiosulfate at the calibration bath, and 100% oxygen saturation, through the injection of air in the calibration. In both cases oxygen concentrations were calculated as a function of temperature and salinity through the Aanderaa software OXYWIEW 6.

Except for the RCM11 s/n 625 (bought on the occasion of the DEEP research programme) and for the optodes mounted on RCM 11 s/n 691 and 692 (specifically bought and used for the first time in HASGARTEN experiments), the other sensors were repeatedly used throughout all different deployments; however, a complete calibration and foil check was performed only before the DEEP experiment (RCM11 s/n 177 and s/n 542).

## RESULTS

### Data collected during the EXOMAR experiment

During 25 days of deployment several parameters (temperature, current speed, current direction, and oxygen) were acquired by the Aanderaa RCM11 meter close to the hydrothermal Tour Eiffel chimney (Mid-Atlantic Ridge). Among these parameters, oxygen and temperature data showed abrupt variations starting from a quite stable mean value (about 307$\mu$mol and about 4.3°C). Several drops occurred in the oxygen readings (Fig 2a), showing variations between 20 and 100$\mu$mol occurring in a few tens of minutes. At the same time, temperature data readings exhibited many peaks with increasing values of up to 1°C from the mean value.

A comparison between all data recorded revealed that temperature and oxygen variations were not concurrent. In fact, peaks in temperature do not occur simultaneously with oxygen drops but seem to be in completely accordance with variations in current speed. Looking more closely at the data (Fig 2b), it was also possible to observe that all oxygen drops seemed to arise in conjunction with low current speeds and a particular current orientation (>250°).

### Data collected during the ENVAR experiment

Data recorded at two different sites of the Var submarine canyon (VA and VC; Fig 1b) showed generally stable oxygen values of about 230$\mu$mol, episodically interrupted by sudden drops reaching minimum values of ~147$\mu$mol at VC and ~170$\mu$mol at VA (Figs 3a and b). According to the high homogeneity of Mediterranean bottom seawater, no significant temperature variations were found during the ENVAR experiment. Nevertheless, comparisons between oxygen and current data showed a good agreement between drops in oxygen concentrations and periods of comparably weak currents. At higher current velocities oxygen values remained stable and showed no anomalies in the signal. This behaviour is clearly visible in the oxygen series collected at VC site (Fig 3a), but hard to see in the VA series because of a generally more noisy signal. At first sight, the oxygen drops might also be related to a particular current direction, as already observed in EXOMAR data.

### Data collected during DEEP experiment

Three different optode series data collected in the Gulf of Lions showed similar strong anomalies during the first months of the deployment (Figs 4a and b). This noisy period exhibited several drops which corresponded well with minimum current values recorded during the measurements (speed current <5 cm $s^{-1}$) and suddenly disappeared when current speeds increased.

For all oxygen sensors the mean oxygen concentration measured was ~200$\mu$mol. This value remained stable when current velocities exceeded 10 cm $s^{-1}$, showing abrupt decreases in oxygen (in some case >100$\mu$mol) for lower current speeds. Furthermore, drops in oxygen measured during the first months by all optodes mounted on RCM11 s/n 177, s/n 542 and s/n 625, seemed in good agreement with continuous and rapid fluctuations of current direction.

### Data collected at HAUSGARTEN observatory

Optodes at the HAUSGARTEN sites were deployed for almost 12 months recording oxygen values at 1h intervals, and revealed 8613 valid records for the shallower station

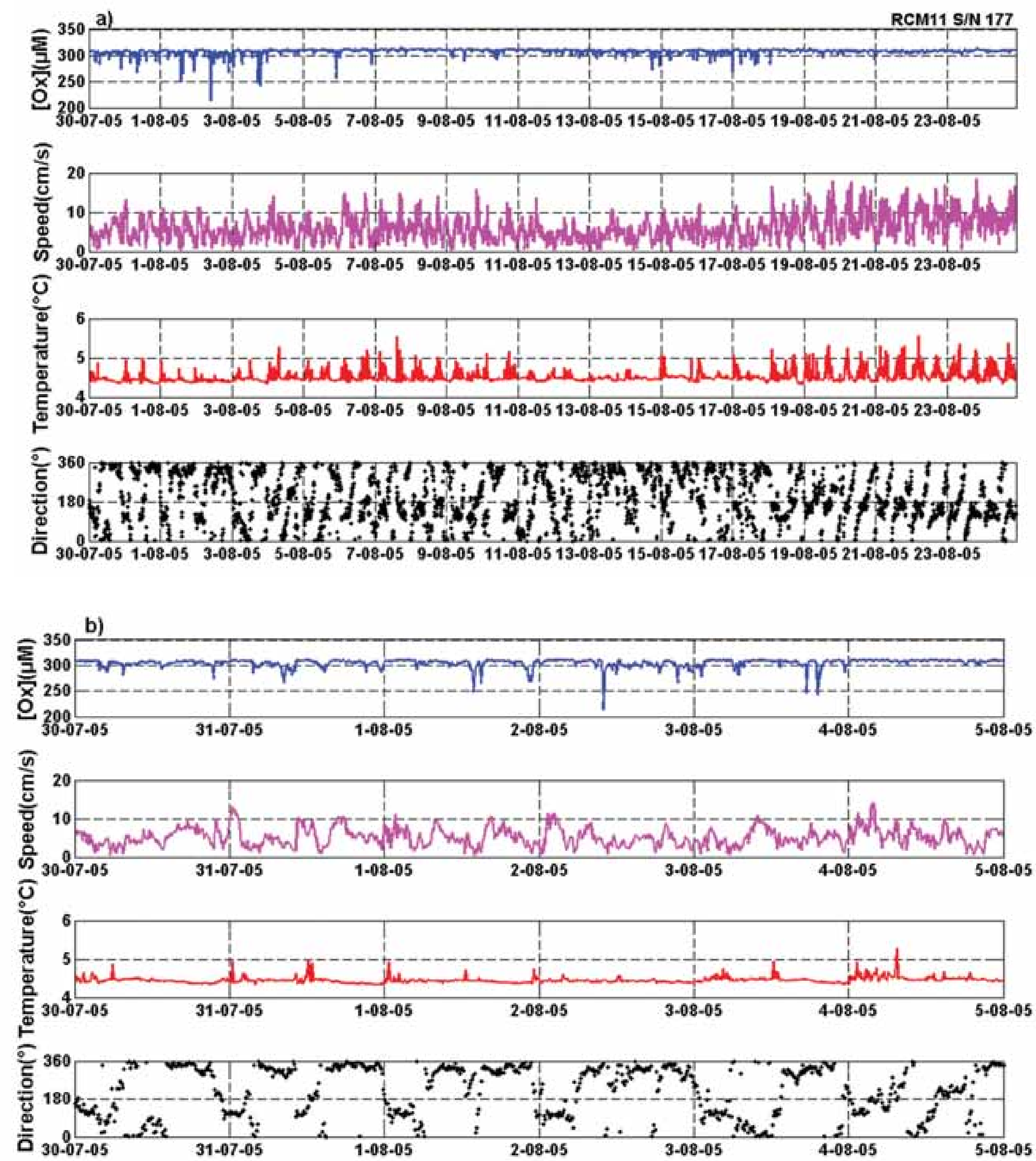


Fig 2: a) EXOMAR dataset 25 days long acquired through RCM11 s/n 177 close to the Tour Eiffel hydrothermal chimney in the Mid-Atlantic ridge at1700m depth; b) zoom of first seven days of measurement

(HG-I) and 8284 records at the deeper site (HG-IV). The instrument deployed at 1282m water depth (HG-I) showed generally much more noise in the data, compared to the oxygen data retrieved at 2467m depth (HG-IV) (Fig 5). As for the previous experiment, optode readings showed strongest anomalies immediately following the deployment of the sensors, in this case covering a time period of 1–2 months. The mean oxygen values at HAUSGARTEN were about 7$\mu$mol higher at HG-I (279.9 ± 14.9$\mu$mol), compared to those obtained at HG-IV (273.1 ± 6.0$\mu$mol).

Both readings showed several significant drops in oxygen (minimum values reached 130.6$\mu$mol at HG-I, and 148.9$\mu$mol at HG-VI) and an overall slight increase in oxygen concentrations between 2009 and 2010. Again, the comparison of optode data with current velocities registered by the RCM11 showed a close correlation between drops in oxygen concentrations and reduced current speeds below 10–12 cm $s^{-1}$. No clear correlations could be found for oxygen values compared to water temperatures and current directions.

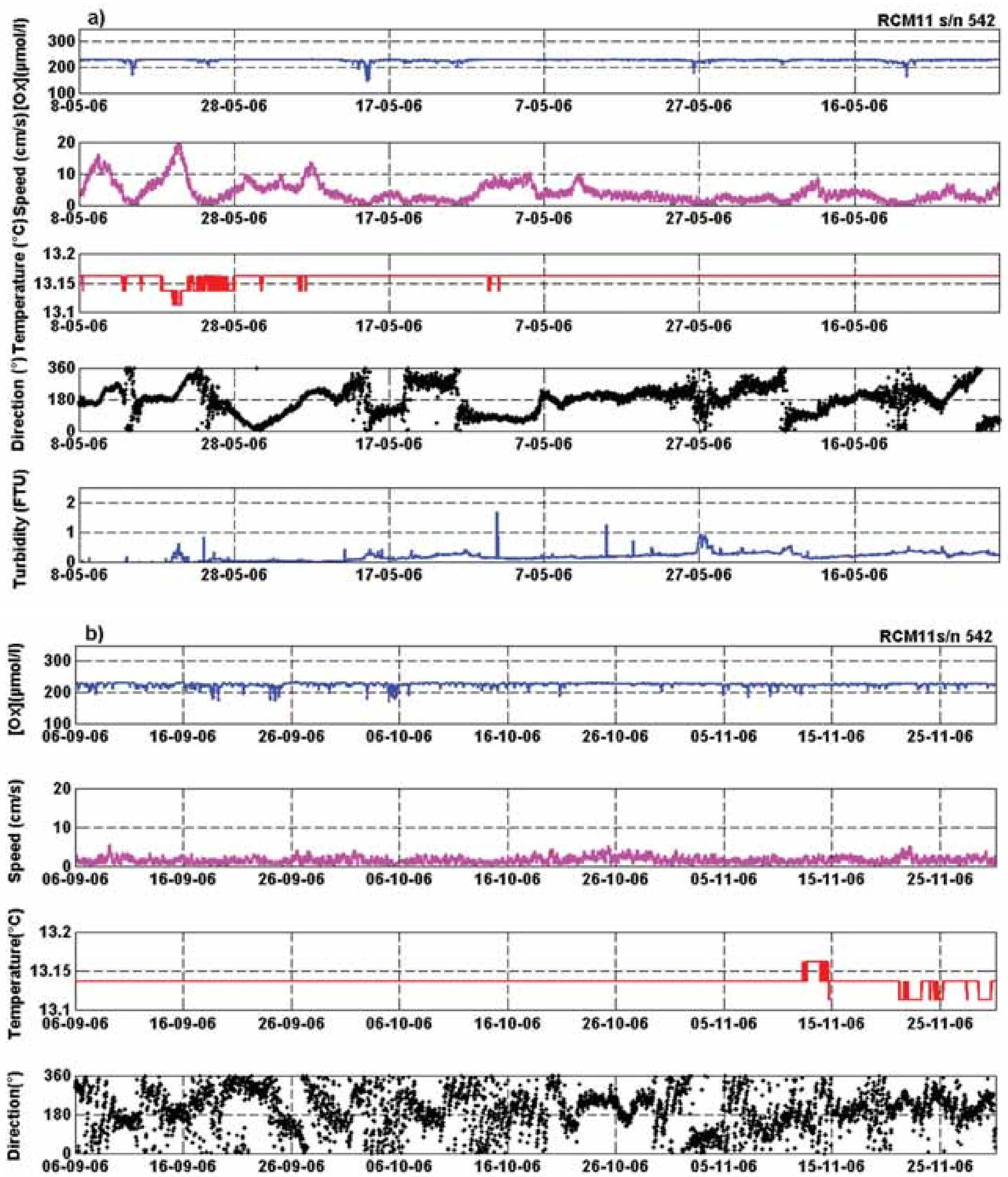


Fig 3: ENVAR series 118 days long collected through the RCM11 s/n 542 at the Var Canyon: a) measurements at sites VC 1904m depth; (b) measurements at sites VA 1866m depth. Record collected at site VA was missing turbidity data

## DISCUSSION AND CONCLUSION

Aanderaa optodes 3830 mounted on RCM11 acoustic current meters deployed at various deepsea sites in the Atlantic Ocean, the north-western Mediterranean Sea, and the Arctic Ocean showed several anomalies in their readings. All oxygen data exhibited episodic drops in oxygen concentrations lasting for varying time periods from minutes to days.

These drops were initially noticed during the EXOMAR experiment, where the good correlation between current speeds and temperature variations reflected the influence of the hydrothermal fluid activity: peaks in temperature occurred when current speeds suddenly increased, corresponding to the escape of warmer water from the vent area. Surprisingly, during these events, oxygen showed unexpected stable values (~307$\mu$mol), while drops in oxygen were observed only during low temperature values (~4.3–4.5°C) confirming a complete independence from possible hydrothermal vent influence (Fig 2). Other oxygen measurements were performed much closer to the hydrothermal vent

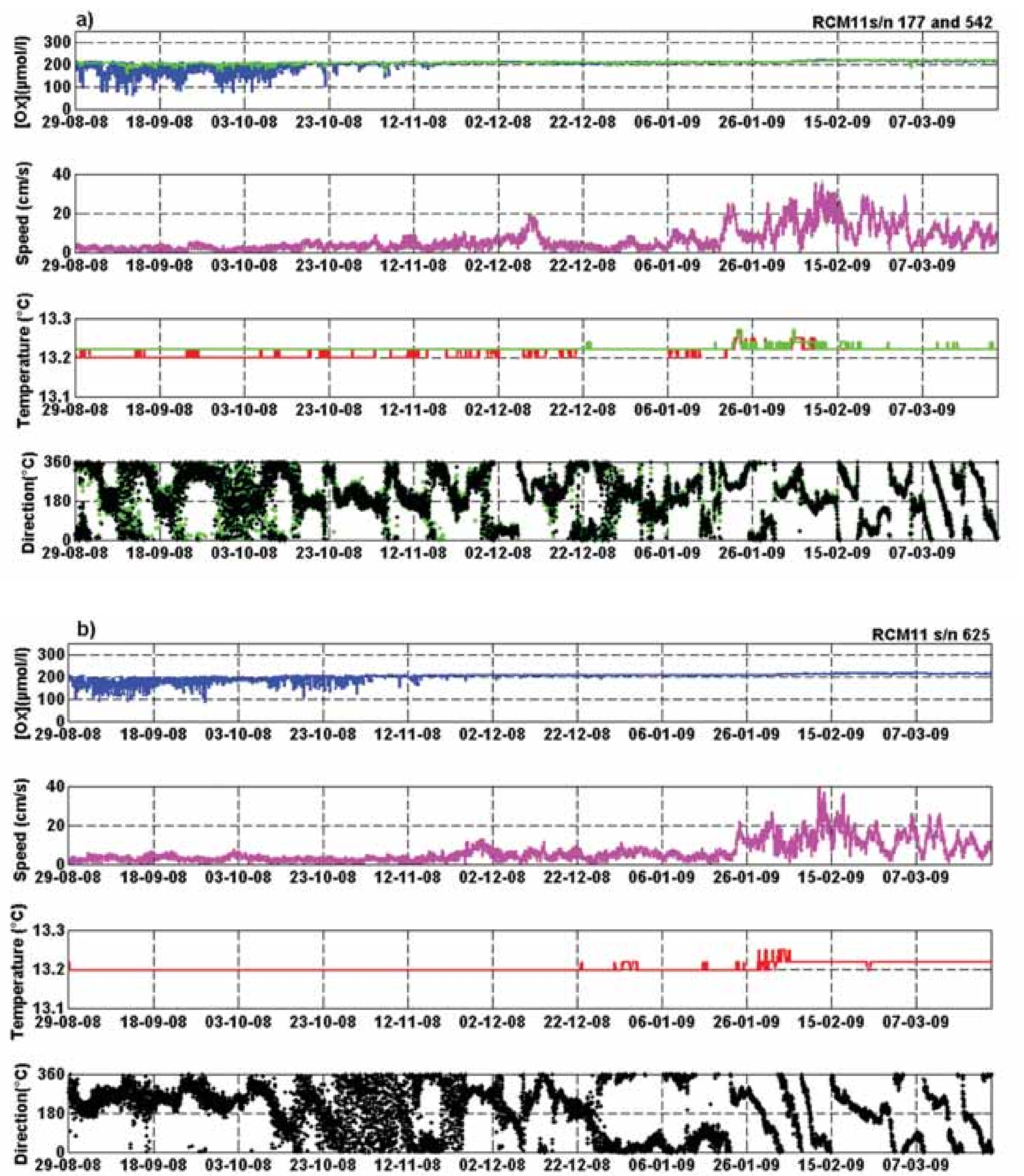


Fig 4: DEEP experiment 219 days long in the Gulf of Lion. Measurements acquired by three independent moorings: a) RCM11s 177 and 542 at station B respectively at 2197m and 2139m depth; b) RCM11 625 deployed at station A at 2256 m depth

using an optode connected to an independent data logger (NKE) with internal temperature sensor but without current speed. They showed the typical inverse correlation between temperature and oxygen under the direct influence of hydrothermal vents,[16] confirming that the drops observed during the EXOMAR experiment cannot be due to natural variations.

In order to exclude possible random peaks, a spectral analysis was performed on all data acquired at the hydrothermal vent site. The same periodicities, related to the tidal effect (~20–26h, ~12h and ~6h), appeared in all time-series recorded, showing that the observed variations were not associated to any instrumental noise.[11]

The same behaviour was observed during the ENVAR, DEEP and HAUSGARTEN series, where drops suddenly reached $\Delta O_2$ values of >80–100$\mu$mol (Figs 3, 4 and 5). Also, the stability of temperature recorded in these time-series excluded any possible correlation or influence of temperature variations on the occurrence of drops in oxygen.

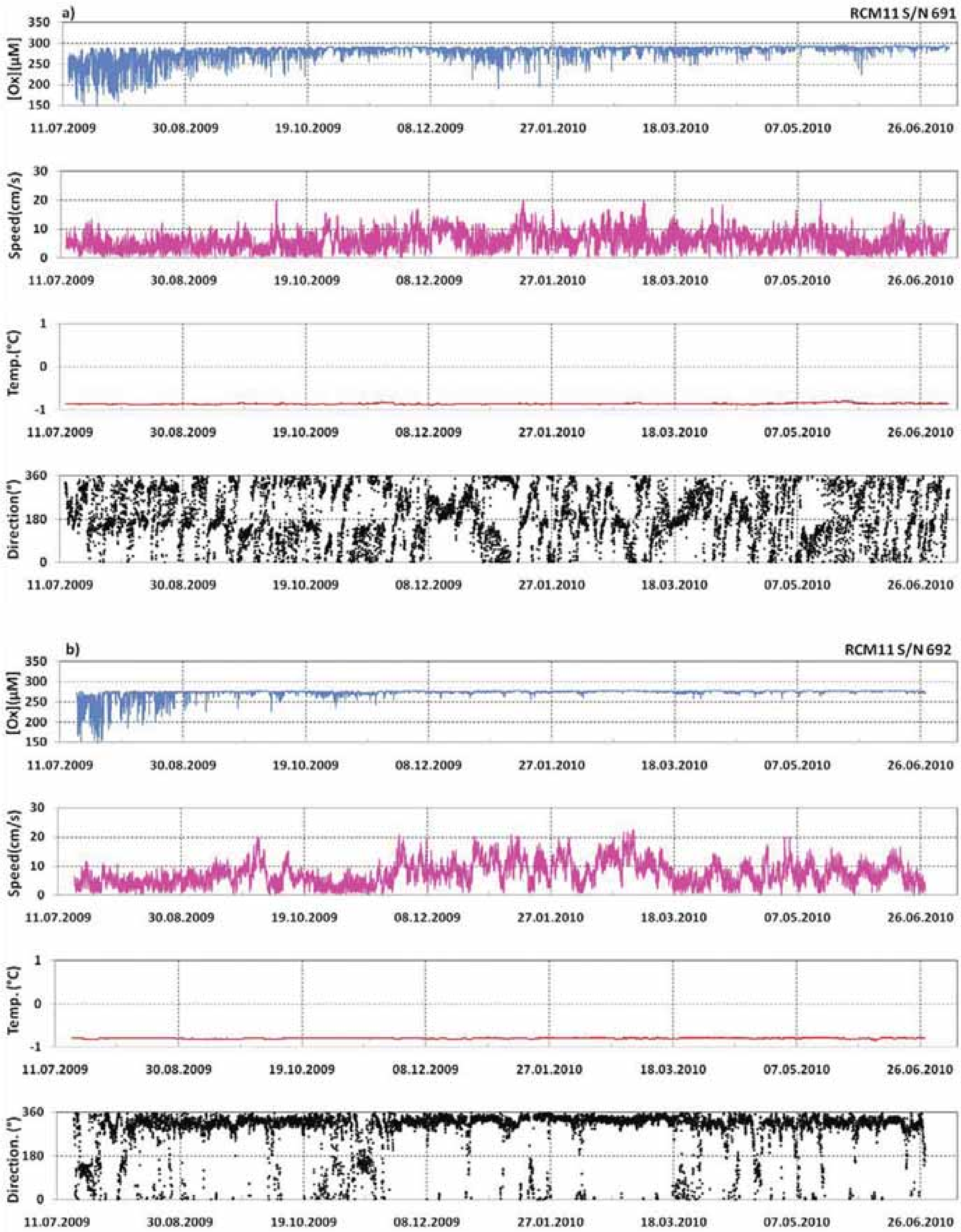


Fig 5: HAUSGARTEN dataset from 12 month deployments between 2009 and 2010 at (a) station HG-I (1282m), and (b) station HG-IV (2467m)

The data collected in the Gulf of Lions (DEEP experiment) gave one of the best comprehensive examples of this correlation, showing once again the presence of oxygen drops occurring mainly in periods of weak and stable currents below 5–10 cm $s^{-1}$, while stable oxygen values occurred in time periods with increased current velocities (Fig 6).

At first sight, the recorded drops in oxygen concentrations seem to be associated with abrupt changes in current direction. In fact, looking at the oxygen readings from the VC site (ENVAR experiment), it seems that the biggest drops recorded are in correspondence with period of minimum speed but also with changes in current orientation (Fig 3a). A similar correlation was found in the HAUSGARTEN and EXOMAR data. In the latter case, drops in oxygen primarily occurred when currents were oriented between 250° and 350° (Figs 2a and b). Fig 7 displays the relationship between current speeds and oxygen values versus current directions, showing that oxygen drops occurred in correspondence with low currents and specific current orientations (blue shaded area).

Looking at the data series in more detail (Figs 2–5), it becomes obvious that when current speeds decreased, current directions became more unstable and therefore mostly affected by sudden changes in direction. Consequently, the change in current orientation is not directly responsible for the drops in oxygen concentrations, but is simply an indirect effect induced by decreasing currents.

The good agreement of data collected by acoustic (RCM11) and mechanical (RCM8) current meters validated the proper functioning of the sensors, confirming the reliability of the current velocity acquired.[11] Moreover, to verify if the low speed values were due to an excess of particles reducing the acoustic signal, a comparison was made between speed and turbidity data during the ENVAR experiment. Turbidity was measured by two indirect means: the backscatter signal recorded by the RCM11 and the turbidity data obtained by a turbidimeter (LSS connected to a NKE data logger) installed close to the RCM11. In both cases, low current speeds were not correlated to increased turbidity, and there was no relationship between drops in oxygen recorded by the optodes and data from the turbidity meter (Fig 3b).

As mentioned at the beginning of this work, the existing literature on the use of the optode technology in marine studies showed that optode data were often obtained with satisfying results. Unfortunately it is not possible to use data presented by other authors for direct comparisons, because they often refer to shallow water environments focussed on high-energy systems or because simultaneous current measurements were missing. Only a recent experiment performed by Ifremer during the European CoralFish project offers a good opportunity of comparison.[17].

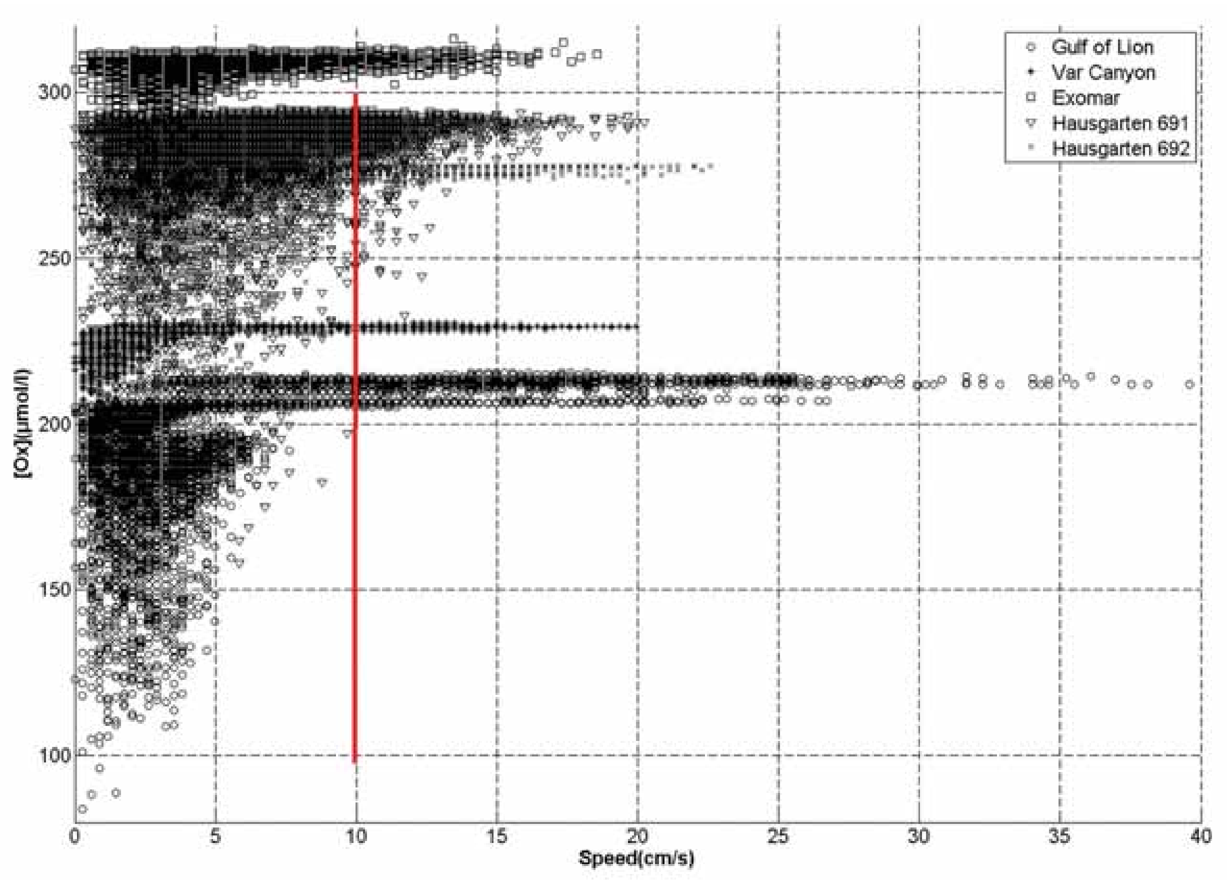


Fig 6: The comparison between all oxygen and speed measurements highlights the presence of a threshold speed below which all minimum measured oxygen values occurred

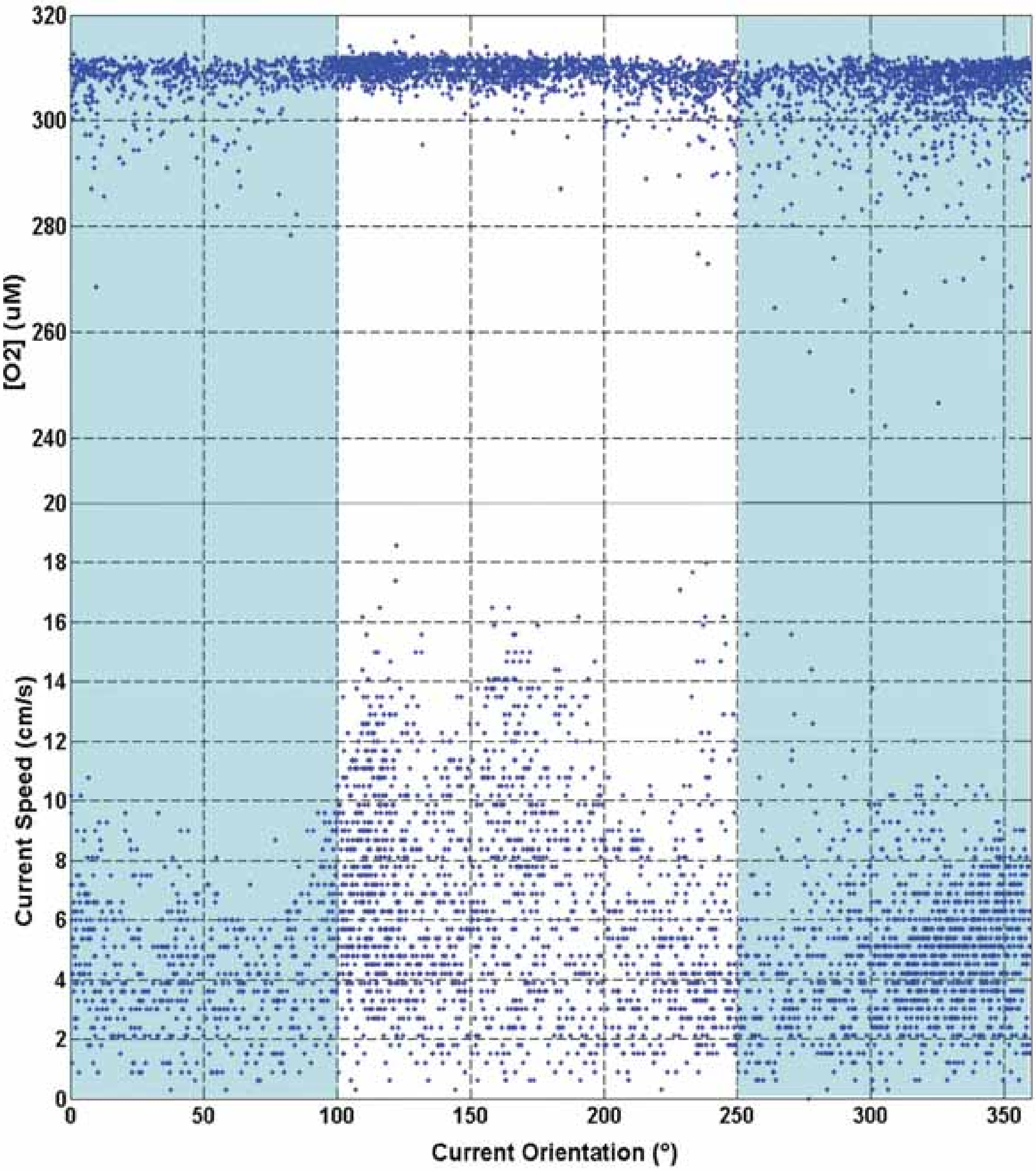


Fig 7: Comparison between current speed and oxygen values versus current direction, confirming that oxygen drops are not definitely associated to current direction, but rather to low speed values

In October 2009, a mooring carrying an Aanderaa RCM 11 (s/n 625) including the same optode mounted in the previous DEEP experiment, was deployed at 30m above the bottom (at 895m depth) for nine months at the head of the Canyon du Guilvinec located in the North of the Bay of Biscay (46° 55'N, 05° 21' W). The data collected showed oxygen values oscillating within the range of natural values (mean oxygen concentration was 212$\mu$mol, with a maximum value of 279$\mu$mol and a minimum value of 180$\mu$mol) not affected by any significant drops in oxygen values (Fig 8). Variations in oxygen concentrations may be correlated to tidal currents affecting vertical movements of water masses accentuated by the local steep topography. Surprisingly, the optode performance is in complete contrast with data collected by the same instrument during the DEEP experiment. The reason for this may be seen in the overall much higher current speeds at the Canyon de Guilvinec (mean current speed of 18 cm $s^{-1}$, varying between 0.2 cm $s^{-1}$ and 70.5 cm $s^{-1}$) as well as to shorter low current periods than during the DEEP experiment. This latter dataset confirms that the problem encountered during previous experiments could depend on low current regime and was not attributable to any natural cause.

A simple hypothesis explaining these anomalies might refer to corrosion related to the sacrificial anode mounted on the current meter vessel. In fact, reduced currents may contribute to stagnation of reduced oxygen concentrations around the sensor head due to ongoing oxygen consumption by the corroding anode. Furthermore, experiments using coupled RCM11-optode systems (protected by an anode) as well as optodes with cable connections to the RCM11 on free-falling systems (bottom-lander) at HAUSGARTEN showed that

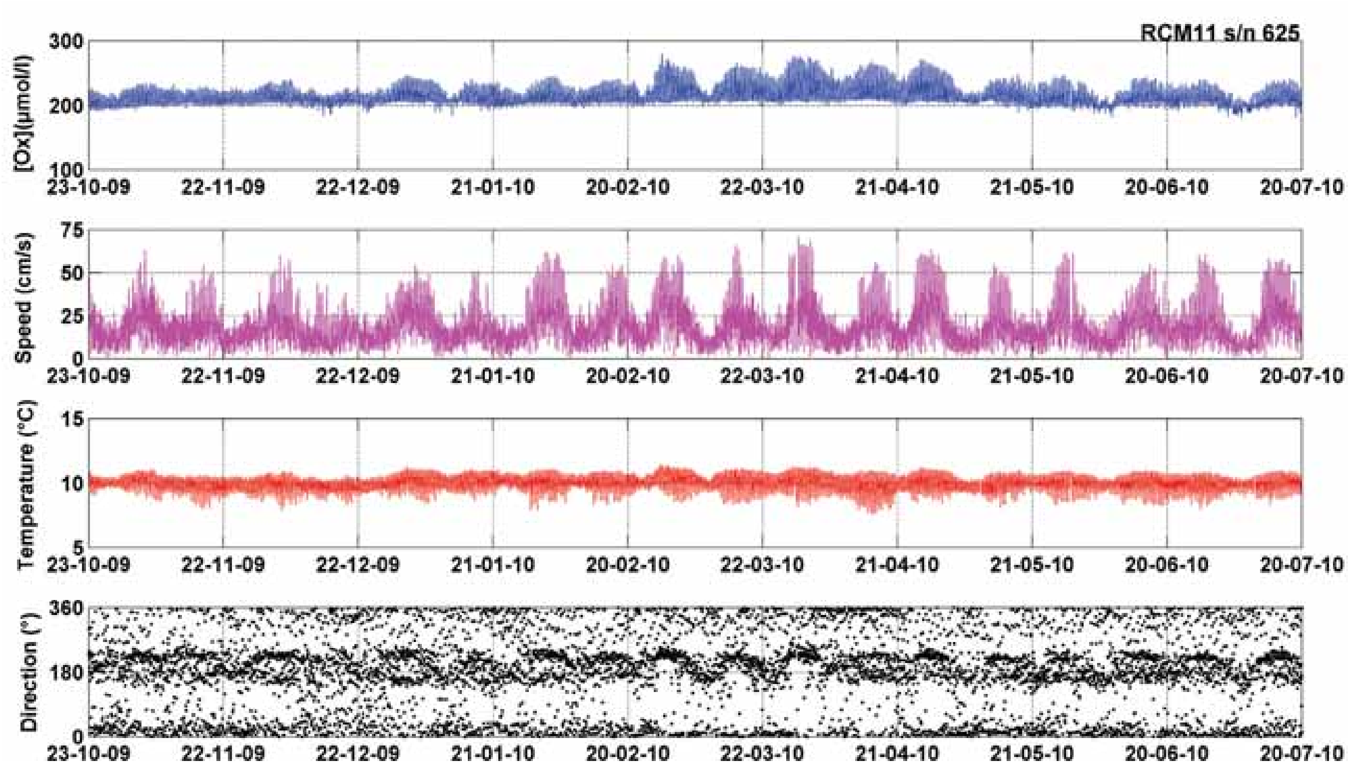


Fig 8: CoralFish dataset collected during nine months of measurements at the head of the Canyon du Guilvinec at 895m depth. It shows the absence of oxygen drops (only a few) in a high hydrodynamic regime

episodic drops in the optode readings were well recorded by all sensors, raising the presumption that corrosion by any metallic part in the vicinity of the optode (including sacrificial anodes, bottom-lander weights and/or the entire lander frame) might disturb the measurement of the optode in low current regimes.

There is no final solution to the encountered problem. If the drops in the oxygen reading are exclusively caused by corrosion effects the use of a pump system flushing the optode sensor might help to clear the readings from the anomalies occurring in low-energy environments. However, drops in oxygen concentrations encountered in all discussed experiments were sometimes extremely high (up to 100$\mu$mol) and there are still doubts whether corrosion in the vicinity of the optode might cause those large effects. Appropriate tests should be carried by the manufacturer to resolve the issue of the optode anomalies as determined in deep water/low-energy environments. In the meantime, for all applications in deep waters or, more generally, in all environments characterised by weak hydrodynamics, it is important to monitor the current intensities, in order to be able to verify optode data reliability.

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