

1 **Water column poly-aromatic hydrocarbon anomalies measured with** 2 **submersible gliders in the Angolan natural oil seepage province**

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14 **Key Points:**

- 15 • We combined satellites and an underwater glider to monitor natural hydrocarbon seepage in the Lower Congo
16 basin.
- 17 • The detection performance of an underwater glider is evaluated for the detection of natural oil seeps.
- 18 • Hydrocarbon presence in the water column is well expressed in the pyrene channel as vertical high-amplitude
19 signals.
- 20 • Fluorescence measurements suggest a trapped plume of hydrocarbon in the oxygen minimum zone.

21

22 **Keywords:** Glider, Fluorescence, Polycyclic aromatic hydrocarbons, Seeps, Oxygen Minimum Zone.

23 **Abstract.**

24 Fluorescence sensors mounted on unmanned underwater gliders open new ways of investigation to detect dissolved
25 hydrocarbons in seawater. A glider was deployed for 20 days to monitor biogeochemical and physical signals associated
26 with natural hydrocarbon seepages within the first 700 m in the Angolan waters. The glider was equipped with fluorometers
27 (MiniFluo-UV) to measure the concentrations of polycyclic aromatic hydrocarbons (PAH) of interest, i.e. naphthalene,
28 phenanthrene, fluorene and pyrene. A continuous PAH-like signal detected within the 70 m layer below the sea surface is
29 associated with high chlorophyll concentration in the deep chlorophyll maximum. Vertical PAH-like anomalies forming
30 either strong spikes or diffuse columns down to 700 m are observed at the exact location of oil seep sites identified on
31 Synthetic Aperture Radar satellite images. An ~200 m thick layer of enhanced PAH-like concentration, topped by a
32 thermo/pycnocline identified at 280-300 m water depth, is measured in concomitance with the decrease in oxygen
33 concentration. The concomitance of these signals suggests that lower oxygen concentrations induce a preservation of
34 hydrocarbons within the eastern Atlantic oxygen minimum zone. Even if the absence of in-situ measurements limits the
35 understanding of physical and biogeochemical processes affecting PAH concentrations, the measurements conducted at the
36 edges of the OMZ suggests a relationship with microbial activity and organic matter dynamics in this layer. The results
37 presented here show that gliders equipped with PAH sensors represent a promising means for monitoring hydrocarbons in
38 the oceans, especially when they are coupled with other systems (i.e. Synthetic Aperture Radar).

39 **1. Introduction**

40 The volume of hydrocarbons expelled in the marine environment from natural processes (Wilson et al., 1973) is estimated to
41 be equivalent to man-made pollutions (c.f. Deep-Water Horizon, Gulf of Mexico; Prince et al., 2003). Among the different
42 compounds, the polycyclic aromatic hydrocarbons (PAH) in the ocean are mainly sourced from the atmosphere with a
43 monthly amount of four times the total volume released from the Deep-Water Horizon blowout (González-Gaya et al.,
44 2016), which suggests that natural hydrocarbon seepage represents only about 2% of this volume. In the case of natural
45 seepage, hydrocarbons are released from the seafloor as bubbles of oil and/or gas in the water column (Macdonald et al.,
46 2002; Greinert et al., 2006; McGinnis et al., 2006; Korotenko et al., 2016; Jatiault et al., 2018a). Synthetic Aperture Radar

47 (SAR) systems aboard satellites are commonly used to detect oil films at the sea surface (e.g. Bern, 1992; Espedal and
48 Johannessen, 2000; Brekke and Solberg, 2005; Leifer et al., 2012). While the oil seepage mechanism is discontinuous
49 (Garcia-Pineda et al., 2010; Jatiault et al., 2017), the redundancy of seepage slicks on a stack of multi-temporal satellite
50 images enables discrimination with mono-temporal man-made pollutions (MacDonald et al., 2015) and other false positives
51 (i.e. algal bloom; Espedal and Wahl, 1999). Seabed coring and imaging with remotely operated vehicles provide a direct
52 investigation method for seafloor seep activity (Abrams, 2005), while investigation of the hydrocarbons in the water column
53 is limited to bubble-related acoustic anomalies (Greinert et al., 2006; Dupré et al., 2014; Loranger et al., 2018).

54 Hydrocarbons are composed of three main families, i.e. saturated hydrocarbons (e.g. alkanes), unsaturated hydrocarbons
55 (e.g. alkenes), monocyclic (e.g. benzene) and poly-aromatic hydrocarbons (e.g. PAH) consisting of two or more fused
56 benzene rings. PAH have toxic (carcinogenic and mutagenic) effects on marine organisms and can bio-accumulate in the
57 food chains (Hylland, 2006). Some of them are listed among priority contaminants (European Union, United States FWPCA
58 and EPA; Alexander et al., 2008). Under oil spill conditions, low molecular weight petrogenic compounds, such as
59 naphthalene (Naph), phenanthrene (Phe), fluorene (Flu) and their alkylated derivatives, become preponderant within the
60 accumulation of dissolved PAH in seawater (González et al., 2006; Zhou et al., 2013).

61 While most of the released hydrocarbons reach the surface and are detectable with space-borne sensors (Fingas and Brown,
62 2014; Jatiault et al., 2017), a consistent volume potentially remain stored in intermediate waters (Camilli et al., 2010;
63 Adalsteinsson et al., 2011; Wade et al., 2011; Camassa et al., 2013; Landeau et al., 2014). Among the variety of autonomous
64 underwater platforms that are used for submarine applications (e.g. Nicholson and Healey, 2008), buoyancy-driven
65 underwater gliders are particularly useful for understanding hydrocarbon patterns in the water column (e.g., Wood, 2009;
66 Testor et al., 2010; Jenkins and D'Spain, 2016, Dhont et al., 2019). Indeed, underwater gliders or 'gliders' are characterized
67 by low energy consumption, which permits multiple weeks of autonomy without any human intervention and therefore long-
68 term observations without reconditioning (Rudnik and Zerres, 2004; Meyer, 2016).

69 Numerous and varied sensors can be mounted on the glider platform to measure physical and biogeochemical parameters of
70 the oceans, such as dissolved oxygen, chlorophyll-*a*/pigments, turbidity and dissolved organic matter (Mortier et al., 2012,
71 GROOM report, 2014). PAH are highly fluorescent in the ultraviolet (UV) /blue spectral domains owing to their aromatic

72 structure (Dabestani and Ivanov, 1999; Ferretto et al., 2014) whereas light absorption by water increases with wavelength
73 (Clarke and James, 19³⁹; Buiteveld et al., 1994; Pope and Fry, 1997; Wozniak and Dera, 2007). Hence, several submersible
74 fluorometers have been proposed in recent years for the in-situ detection of PAH in seawater in the UV domain (Zielinski et
75 al., 2009, 2018; Tedetti et al., 2010; Conmy et al., 2014; Ferdinand et al., 2017). Recently, MiniFluo-UV fluorometers were
76 installed on a glider to monitor polyaromatic hydrocarbons in marine waters (Cyr et al., 2017, 2019). The combination of
77 gliders and submersible fluorometers therefore opens new fields of investigation to monitor the leakage of hydrocarbons, as
78 already performed during the Deep-Water Horizon event (Camilli et al., 2010).

79 In this study, we report on the first deployment of a glider equipped with dedicated hydrocarbon fluorometers (MiniFluo-
80 UV) to evaluate the effectiveness of PAH sensors mounted on unmanned platforms to assess the fate of naturally expelled
81 hydrocarbons in the water column. The fluorescence signals of dissolved natural hydrocarbon seeps in the ocean will be
82 compared with seepage slicks observed at the sea surface from SAR satellite data acquired simultaneously. The chosen area
83 of study is the Lower Congo Basin, offshore Angola, which is recognized as a prolific oil seepage site in the Atlantic Ocean.
84 These combined observations will be used to discuss the benefits and limitations of hydrocarbon detection using
85 fluorescence sensors on board gliders.

86 **2. The Lower Congo Basin: Regional setting**

87 *2.1. Petroleum systems and hydrocarbon seepage manifestations*

88 The deep-water province of the Lower Congo Basin is one of the most active areas in the world regarding the manifestation
89 of natural oil seepage (Jatiault et al., 2017). The oil source rocks correspond to the Early Cretaceous (145 – 125 Ma)
90 Bucomazi Fm (5 to 20% TOC; Burwood, 1999; Schoellkopf and Patterson, 2000) and Late Cretaceous (99 - 65 Ma) Iabe Fm
91 (~10 % TOC; Burwood, 1999; Cole, 2000). The Paleogene (65 - 45 Ma) Landana Fm shows high potential (~4% TOC) but
92 remains thermally immature for hydrocarbon generation (Cole et al., 2000, Schoelkopf and Patterson, 2000). In the Lower
93 Congo Basin, gravitational deformation associated with salt tectonics inhibits the cap rock efficiency of Tertiary series by
94 deforming the overburden, which eases the dismigration of hydrocarbons towards the seafloor (Marton et al., 2000, 2004;
95 Hudec and Jackson, 2004; Guiraud et al., 2010).

96 Seafloor circular depressions referred to as pockmarks correspond to expulsion sites of hydrocarbons generated in the deeper
97 Cretaceous series (Gay et al., 2007; Andresen et al., 2010; Andresen and Huuse, 2011; Jones et al., 2014, Jatiault et al.,
98 2019a, b). Ultimately, hydrocarbons migrate in the water column before reaching the sea surface (William and Lawrence,
99 2002; Jatiault et al., 2017, 2018). In the Lower Congo Basin, more than a hundred active oil seep sites have been detected
100 using multi-temporal series of satellite SAR images, for water depths ranging from 1000 to 3000 m (Jatiault et al., 2017; Fig.
101 1a).

102 *2.2. Hydrographic conditions*

103 *2.2.1. Water masses*

104 The surficial water masses of the Lower Congo Basin are strongly influenced by the Congo River, the world's second largest
105 river in terms of the discharge volume of water (average 41 200 m³/s; Ukwe et al., 2006; Dupont, 2013). The Congo Plume
106 brings fresh water to the basin at a shallow depth (0-10 m; Hopkins et al., 2013; estuary at 6°S, to the north of the map in
107 Fig. 1a). Multiple currents are reported in the Lower Congo Basin depending on the water depth (Fig. 1a). In the 0-300 m
108 layer, the main reported current is the Angolan current, which transports equatorial waters towards the south (Moroshkin et
109 al., 1970; Hardman-Mountford et al., 2003), even if the seasonal intrusions of the northward Benguela current modifies the
110 displacement of water masses in the area (Jatiault et al., 2018). The Angolan current is steady, narrow and fast (20 to 50
111 cm/s), with water temperatures greater than 24 °C and with a salinity of more than 36.4 in the upper mixed layer (Lass et al.,
112 2000). The 300-500 m layer corresponds to a transition to deeper water masses and no prominent current is reported in the
113 literature. The intermediate water circulation (500-1000 m) is controlled by the southward-flowing Southern Intermediate
114 Counter Current, transporting the South Atlantic Central Water (Stramma and England, 1999; Stramma and Scott, 1999;
115 Shannon, 2001). The Angolan gyre is a retroflection loop centred further south of our study area (10°S, 8°E) that seasonally
116 impacts the circulation of surface, sub-surface and intermediate water masses (Mazeika, 1967; Moroshkin et al., 1970;
117 Peterson and Stramma, 1999; Doi et al., 2007). Deep-water circulation along the Angolan coast is influenced by the North
118 Atlantic Deep Water flowing slowly (~2cm/s; Lynn, 1971) to the south at 2000 m depth (Stramma and England, 1999; Arhan
119 et al., 2003). It also corresponds to the eastern retroflection of the Deep Western Boundary Current (Garzoli et al., 2015).

120

121 **2.2.2. Oxygen Minimum Zone**

122 The study area lies in the South Atlantic Oxygen Minimum Zone (OMZ) in relation with the Northern Benguela Upwelling
123 System (Schmidt and Eggert, 2016). OMZs are defined as volumes of interior oceans characterized by low Dissolved
124 Oxygen (DO) concentration. A restrictive threshold value of 45 $\mu\text{mol/kg}$ is commonly considered, even though a more
125 relaxed DO concentration of 90 $\mu\text{mol/kg}$ has also been reported (Karstensen et al., 2008). OMZs are mostly distributed at the
126 eastern edges of tropical oceans for water depths ranging from 100 to 900 m (Karstensen et al., 2008). The threshold of 45
127 $\mu\text{mol/kg}$ is located between 300 and 500 m in the South Atlantic (Mercier et al., 2003; Karstensen et al., 2008; Mashifane et
128 al., 2016; Schmidt and Eggert, 2016), while a suboxic water layer ($\text{DO} < 90 \mu\text{mol/kg}$) is reported to be 600 m thick (Mercier
129 et al., 2003; Karstensen et al., 2008; Schmidt and Eggert, 2016). Oceanic gyres correspond to hydrologic isolation areas. The
130 presence of the Angolan gyre in the area significantly modifies the spatiotemporal distribution of DO in the Angolan OMZ
131 (Teuber et al., 2013) and, indirectly, the biological processes (Stramma et al., 2012; Wright et al., 2012; Schmidt and Eggert,
132 2016).

133 **2.2.3. Oceanic conditions during the glider mission**

134 Maps of geostrophic currents were produced to assess large and mesoscale circulation over the studied area. The water
135 velocity was derived from sea level altimeter anomalies using satellite products (Jason-3, Sentinel-3A, HY-2A, Saral/AltiKa,
136 Cryosat-2, Jason-2, Jason-1, T/P, ENVISAT, GFO, ERS1/2) with daily temporal resolution and 0.25×0.25 degree spatial
137 resolution (<http://duacs.cls.fr>).

138 The mission lasted 20 days from the deployment of the glider on 29 October to its recovery on 18 November 2017. We
139 extracted geostrophic surface currents (the balance between the pressure gradient force and the Coriolis force) from altimeter
140 satellite measurements (Fig. 1b). The main large-scale geostrophic currents identified during the mission are (i) a strong
141 coastal surface current (30-40 cm/s) that flowed to the east at the beginning of the mission and turned progressively
142 northwards at its end (Fig. 1b), and (ii) the clockwise Angolan gyre loop located in the south (centred on 8.5°S , 10.5°E). At
143 the beginning of the mission, the northern edge of the Angolan gyre impacted the southern limit of the study area. The
144 Congo Plume is not observed on the sea surface currents maps. To sum up, the glider remained isolated from large-scale
145 hydro-dynamic structures during the mission (Fig. 1b) with surface currents lower than 0.10 m/s.

146 **3. Data and methods**

147 *3.1. Satellite data*

148 During the mission, natural oil seepages were monitored with the acquisition of 49 satellite Synthetic Aperture Radar (SAR)
149 scenes combining free-access Sentinel-1 (ESA) and commercial Radarsat, Cosmo-Skymed and TerraSAR-X data (**Fig. 2a, b**).
150 The temporal distribution of SAR data is homogeneous, with generally one image every 12 hours. Oil slicks at the sea
151 surface were detected with the SAR system because of the contrast in roughness with free water (e.g. Alpers and Espedal,
152 2004).

153 *3.2. Glider data*

154 *3.2.1. Acquisition strategy*

155 The navigation mode of underwater gliders is driven by buoyancy changes controlled by the successive inflation/deflation of
156 an external bladder (Davis et al., 2002). This results in alternating upward and downward movements that create a
157 synergistic forward movement along V-shaped acquisition profiles commonly called ‘yos’. The glider can rely on its rudder
158 at the rear of the hull to keep to the planned trajectory despite possible drifting due to the ocean currents.

159 During the mission, the SeaExplorer glider was limited to a investigation depth of 700 m. The GPS position of the glider was
160 remotely monitored by Iridium satellite and the data collected by the sensors were transmitted in near-real time at each
161 surfacing. The underwater currents were estimated from the horizontal distance between the measured versus expected
162 surfacing area of the glider (Kim et al., 2014). Estimated underwater positions or dead reckoning can be derived from
163 navigation data including the pitch (α), heading, depth and vertical speed (Davis et al., 2002). The acquisition frequency is
164 20 s for navigation data and 5 s for sensor measurements.

165 The strategy employed for piloting the glider included parallel transects and virtual moorings (**Fig. 2b**). Virtual moorings
166 consist in a succession of yos at different depths (typically between 100 and 700 m) centred on the location of oil seep sites
167 with a progressive variation of the orientation of profile direction. This navigation style results in rosette patterns with a
168 radius of a few kilometres.

169 Large transects with a maximum depth amplitude (700 m) were carried out to connect the different seep sites investigated
170 during the mission. The glider survey was designed to target the largest number of active hydrocarbon seepage areas (**Fig.**

171 2c). Acquisition phase 1 of the mission was planned to fly above three oil seep sites numbered 1, 2 and 3 (Fig. 2c) and
172 characterized by a high percentage of seepage slick occurrence (Jatiaux et al., 2017). The strategy adopted during the second
173 phase of acquisition was to follow a pseudo-regular grid consisting in ~50 km profiles along the west-east direction for the
174 investigation of seep sites of lower frequency emission (seeps 4 to 7). To enhance the visualization of the data collected, the
175 section displayed in this paper gathers the data along a 1.5 km wide strip that follows the acquisition direction of the glider
176 (see section distance markers in Fig. 2b). The distance between measurement points is typically one metre; an interpolation
177 was used to link discrete measurements in order to produce two-dimensional isocontour maps.

178 3.2.2. Sensors and data processing

179 PAH detection using the MiniFluo-UV sensors

180 A miniaturized (MiniFluo-UV) fluorometer sensor was mounted on the glider for in-situ measurements of polyaromatic
181 hydrocarbons (PAH) and dissolved organic matter descriptors (Tedetti et al., 2013; Cyr et al., 2017, 2019). The MiniFluo-
182 UV has two optical channels, enabling the simultaneous detection of two fluorescent compounds (fluorophores) of interest
183 according to their excitation/emission wavelength ($\lambda_{Ex}/\lambda_{Em}$) couple. Overlaps may occur between the fluorescence of
184 dissolved PAH and that of protein- and humic-like compounds of marine organic matter (Nieke et al., 1997; Parlanti, 2000;
185 Para et al., 2010; Conmy et al., 2014; Zhao et al., 2017). Therefore, the MiniFluo-UV highlights fluorescence signatures
186 having a high probability of being PAHs (PAH-like). The petroleum origin of PAH-like is estimated by comparing the
187 distribution patterns of PAH-like fluorophores with the distribution patterns of physical and biogeochemical parameters of
188 the investigated environment. The more the properties of the 4 PAH-like fluorophores are decoupled from those of
189 chlorophyll-a and humic-like, the more likely it is that they correspond to PAH responses and not to protein-like
190 fluorophores.

191

192 The sensor can operate in two configurations:

193 1) MiniFluo-UV-1 for the simultaneous detection of phenanthrene-like (Phe-like) and naphthalene- (Naph-like) or
194 tryptophan-like (Trp-like) compounds, with fluorescence measurements at $\lambda_{Ex}/\lambda_{Em}$ of 255/360 nm (Phe-like) and 275/340 nm
195 (Naph-like and Trp-like).

196 2) MiniFluo-UV-2 for the simultaneous detection of fluorene-like (Flu-like) and pyrene-like (Pyr-like) compounds, with
197 fluorescence measurements at $\lambda_{Ex}/\lambda_{Em}$ of 260/315 nm (Flu-like) and 270/380 nm (Pyr-like).

198 While Naph (2-rings), Phe and Flu (3-rings) are low molecular weight PAH of petrogenic origin (i.e. issued from crude
199 oil/petroleum or its derivatives), Pyr (4-rings) is a medium molecular weight PAH of pyrogenic origin (i.e. issued from the
200 combustion of fossil fuels; Alexander et al., 2008). Trp is an aromatic amino acid associated with microbial processes
201 (bacteria and phytoplankton) in marine waters. The exact superimposition between the fluorescence spectral domains of
202 Naph and Trp compounds (Tedetti et al., 2010; Xu et al., 2011) prevent their discrimination based on steady-state
203 fluorescence measurements (Tedetti et al., 2010, 2012; Stedmon and Cory, 2014).

204 The raw fluorescence data of the MiniFluo-UV are provided in electronic counts. We followed the method exposed by Cyr et
205 al. (2017, 2019) to normalize and convert the fluorescence electronic counts into fluorophore mass concentrations (g/L) by
206 using appropriate calibration parameters. As recommended by Cyr et al. (2017), the MiniFluo-UV-1 and -2 were calibrated
207 in the laboratory before the cruise using individual PAH (Phe, Naph, Flu, Pyr), as well as Trp standards (Supelco, Sigma-
208 Aldrich) diluted in ultrapure (Milli-Q) water at final concentrations ranging from 0.1 to 10 $\mu\text{g/L}$. The limits of detection of
209 each PAH and Trp are reported in Table 1. For all these compounds, the MiniFluo-UV measurement precision was $\leq 2\%$,
210 meaning that a signal modification $> 2\%$ can be considered as indicative of environmental changes.

211 The calibration of the MiniFluo-UV was performed using individual standard (parent) PAH, which assumes that all
212 dissolved PAH present in seawater are in the non-alkylated form. As alkylated homologues generally have the same
213 fluorescence maxima positions as their parent compounds (Nijegorodov et al., 2009; Ferretto et al., 2014), the MiniFluo-UV
214 sensors actually record the fluorescence signals of alkylated and non-alkylated Naph, Phe, Flu and Pyr, albeit they are not
215 taken into consideration in the calibration procedure. This may lead to overestimations of true PAH concentrations in marine
216 waters (Cyr et al., 2019). Fluorescence quenching refers to any process that decreases the fluorescence intensity of a
217 fluorophore through molecular interactions with a quencher molecule. In seawater, the fluorescence intensity of PAH-like
218 fluorophores may be quenched (reduced) by interactions with oxygen (collisional/dynamic quenching at excited state) or
219 dissolved organic matter (contact/static quenching, i.e., formation of a non-fluorescent complex at the ground state), leading
220 to potential underestimation of the real concentrations of these fluorophores (Cullen and Lewis, 1995; Gauthier et al., 1996).

221 Although PAH-like measurements provide estimated values of PAH-like concentrations, the coherency of PAH patterns
222 observed in the water column validates the detection of anomalous signals by the sensor.

223 **Other sensors**

224 **Conductivity Temperature Depth sensor**

225 The Glider Pumped Conductivity Temperature Depth sensor developed by Seabird provides physical measurements of the
226 seawater such as Potential Temperature (θ), Practical Salinity (Sp), Absolute Pressure (P) and Potential Density Anomaly
227 (σ_θ) according to conversion equations in the TEOS-10 manual (IOC et al., 2010). The practical salinity was derived from
228 raw conductivity and absolute pressure measurements and the potential density anomaly was derived from potential
229 temperature, practical salinity and absolute pressure. The resolution of the sensor is 10^{-5} S/m for Conductivity, 0.001 °C for
230 temperature and 0.002 for pressure.

231 **Oxygen sensor**

232 The glider was also equipped with an oxygen sensor (SBE-43F) to measure concentrations of dissolved oxygen (DO;
233 $\mu\text{mol/kg}$). Computation of oxygen concentrations in physical units was performed according to the Seabird SBE43
234 recommendations (Owens and Millard, 1985) and by using calibration coefficients specific to the sensor. The initial accuracy
235 is 2% of concentration.

236 **FLBBCD sensor**

237 The Wetlabs ECO fluorometer and backscattering (FLBBCD) sensor provides fluorescence measurements of chlorophyll-*a*
238 and dissolved humic substances (humic-like) together with the raw backscattering signal at 700 nm (BB700) used for
239 particle concentration and turbidity (Table 1). Following manufacturer recommendations (Dall'Olmo et al., 2009), raw
240 counts of the sensor were converted into concentrations of fluorophores expressed in mg/m^3 for chlorophyll-*a* and in Quinine
241 Sulphate Units (1 QSU = fluorescence of 1 $\mu\text{g/L}$ of quinine sulphate) for humic-like concentrations. The raw backscattering
242 value for BB700 is expressed in $1/\text{m}\cdot\text{sr}$ (volume scattering function at a centroid angle of 140°), from which we derived the
243 particulate backscattering ($b_{\text{bp}700}$) that is a proxy of the particulate organic carbon concentration in the open sea (Stramski
244 and Morel, 1990). The instrument resolution is 1.3 counts.

245 4. Results

246 4.1. Sea surface manifestations of hydrocarbon seeps during the glider mission

247 The analysis of the 49 available Synthetic Aperture Radar (SAR) scenes (see the temporal distribution in **Fig. 3**) identified a
248 total of 675 slicks during the 20 days of the glider survey, thus confirming the high activity of oil leakages at the location of
249 natural oil seep sites (**Fig. 3a**). Oil slicks were mostly deflected towards the northeast in the southern portion of the survey
250 area and towards the north in the northern area (**Fig. 2** and **Fig. 3a**). A large majority of oil seep sites identified between 1994
251 and 2016 (Jatiaux et al., 2017) were active during the glider mission, whereas some others remained dormant. The 7 seep
252 sites investigated were intermittent with a percentage of slick occurrence varying from 7% to 70%.

253

254 4.2. Water masses

255 Underwater currents were estimated from the glider position and averaged through the 0-700 m layer. Currents flowed
256 westward during phase 1 and north-westward during phase 2 with relative velocities of 20 to 30 cm/s (**Fig. 4a**).

257 The conductivity-temperature-depth sensor showed distinct water masses that remained consistent throughout the glider
258 survey. A homogeneous shallow (first 25 m) buoyant water mass characterized by a high temperature (27°C), low salinity
259 (35.2), low density ($\sim 23 \text{ kg/m}^3$) and high dissolved oxygen (DO) values ($\sim 200 \text{ } \mu\text{mol/kg}$) was present throughout the mission
260 (**Fig. 4b, c**). Between 25 and 50 m, a transition zone is marked by strong gradients of temperature (from 27 to 21 °C), salinity
261 (35.2 to 36) and density ($23 \text{ to } 25.5 \text{ kg/m}^3$) that can be compared to a thermocline or seasonal pycnocline. Maximum salinity
262 values of S_p (36.5) occurred at the base of this pycnocline. Between 50 to 280 m, a homogeneous subsurface layer was
263 identified with a classic depth-dependent decrease in θ (from 18 to 13 °C), S_p (35.3-36) and σ_θ ($26\text{-}26.5 \text{ kg/m}^3$). The DO
264 progressively decreases to reach suboxic levels ($\text{DO} < 90 \text{ } \mu\text{mol/kg}$) at $\sim 150 \text{ m}$. Between 280 and 300 m, a second high
265 thermal gradient develops but is less pronounced than the thermocline. It is observed in association with a decrease in S_p
266 (35.3 to ~ 35) and an increase in θ ($15 \text{ to } 12^\circ\text{C}$), thus generating a higher σ_θ contrast (**Fig. 4d**). This second pycnocline,
267 namely the permanent pycnocline, marks the transition towards a depleted DO layer (**Fig. 4e**). Concentrations of DO reach
268 suboxic values (DO from 45 to 60 $\mu\text{mol/kg}$) consistent with that of the oxygen minimum zone (OMZ) for water depths

269 ranging between 280 to 350 m in the southern area and between 280 to 500 m in the north. DO concentrations in the core of
270 the OMZ drop to $\sim 30 \mu\text{mol/kg}$, giving incoherent values because they are below the detection threshold of the sensor. Below
271 the depleted DO layer, concentrations progressively increase up to $100 \mu\text{mol/kg}$ at 700 m depth, while θ , Sp and σ_θ vary
272 linearly with the water depth.

273 To sum up, the water column remained rather well stratified during the glider survey, yet a relatively strong density gradient
274 is observed at ~ 280 m (**Fig. 4d**). Isopycnal levels are slightly shifted upwards starting from the 60 km mark on the section
275 distance. This area is also characterized by a thickness variation of the OMZ from roughly 150 m in the south to 50 m in the
276 north.

277

278 *4.3. Biogeochemical parameters*

279 High concentrations of chlorophyll-*a*-like occur below the fresh water layer for depths between 20 and 60 m with a
280 fluorescence maximum of 6 mg/m^3 at ~ 50 m (**Fig. 5a**). The minimum chlorophyll-*a* -like concentrations are situated right
281 below the photic zone at 60 m. To a more moderate extent, a slight increase in concentration is observed in the ~ 300 - 500 m
282 depth range corresponding to the OMZ and suboxic layers.

283 Humic-like concentrations are relatively high, generally greater than 0.8 QSU, with a progressive increase in the values
284 along the section distance (**Fig. 5b**). There is a good correspondence between maximal humic-like and chlorophyll-*a* -like
285 concentrations, particularly along the seasonal thermocline (~ 1.60 QSU). The OMZ layer (350-400 m) also emphasizes a
286 slight increase in humic-like values (~ 1.30 QSU), especially in the northern area (~ 50 km north of the seep 1, **Fig. 2c**).

287 As for humic-like records, the total particle concentration (b_{bp700}) progressively increases with time. High concentrations in
288 b_{bp700} are observed in the first 100 m ($0.0004/\text{m.sr}$), which is followed by a strong decrease with depth (**Fig. 5c**). Patches of
289 relatively higher b_{bp700} values (twice the background) also appear in suboxic and anoxic water layers ($0.0007/\text{m.sr}$; **Fig. 5c**).

290 **4.4. PAH-like fluorophores**

291 Four polyaromatic hydrocarbon (PAH-like) concentrations (Phe-, Naph-, Flu- and Pyr-like) were measured with the two
292 MiniFluo-UV sensors (**Fig. 5**). Background concentrations were close to 0 for the Phe-like channel, ranged from 0.01 to 0.02

293 $\mu\text{g/L}$ for the Flu-like channel, varied from 0.1 to 0.2 $\mu\text{g/L}$ for the Naph-like channel and were greater than 1.4 $\mu\text{g/L}$ for the
294 Pyr-like channel. During the mission, significant increases in concentration occurred on the Pyr- and Flu-like optical
295 channels in comparison to the Phe- and Naph-like channels. A slight decrease of the concentrations of Phe- and Naph-like
296 channels over time should be noted, which can be attributed to a drift of the MiniFluo-UV-1 sensor (**Fig. 6a, b**).

297 **4.4.1. PAH-like vertical anomalies**

298 PAH-like anomalies in Pyr- and Flu-like optical channels either extend vertically over a few hundred metres or are stratified
299 horizontally in the water column. Vertical anomalies correspond either to spikes, where the PAH-like concentration is
300 several times greater than the regional background for only a few yos, or columnar anomalies, which record a few percent of
301 PAH-like variations during a succession of several yos.

302 Spikes of fluorescence occurred independently from one PAH-like optical channel to another. The Phe-, Pyr- and Flu-like
303 channels display rapid and strong fluctuations of the signal (coloured dots on the vertical profiles of **Fig. 6a, c, d**) while the
304 Naph-like channel does not show anomalous concentrations compared with the background (**Fig. 6b**). The increase in
305 concentration reaches up to 200 times the background for the Pyr-like ($< 200 \mu\text{g/L}$), 50 times for the Flu-like (1 $\mu\text{g/L}$) and 3
306 times for the Phe-like (0.4 $\mu\text{g/L}$) channels. Even though spikes of fluorescence remained occasional throughout the mission,
307 the percentage of spikes recorded by the Pyr-like channel (7.5%) is higher compared with the Flu-like (0.7%) and Phe-like
308 (1%) channels.

309 Vertical spikes of fluorescence are observed on different PAH-like channels from shallow waters down to 500-700 m depths
310 (seep sites 2, 6 and 7). At oil seep site 3, the spikes observed for the Pyr- and Flu-like fluorophores reach only 250 m depth
311 because the glider did not dive deeper at this location. It is worth noting that the spikes mostly occur at the location of oil
312 seep sites observed on satellite images (**Fig. 7**). No specific signal was detected at seep site 5.

313 Four large columnar anomalies are observed in deep layers (350 to 700 m) on the Flu-like channel at distances of 14 to 18,
314 32 to 45, 52 to 56 and 66 to 75 km (**Fig. 6d**) along the section. Each vertical column is delimited upward by the OMZ layer.
315 Flu-like concentrations associated with these anomalies are weak, with only $\sim 3\%$ variation with respect to the regional
316 background. Three out of the four columnar anomalies correspond to the location of oil seep sites as observed on SAR
317 images (1, 2, and 3; **Fig. 7**), while the remaining one is associated with a pockmark on the seafloor (Jatiault et al., 2019b).

318 4.4.2. PAH-like horizontal anomalies

319 We identified two different types of horizontal signals regarding the PAH-like distribution. First, a strong and continuous
320 signal of all the PAH-like channels in the sub-surface water where concentrations of the four PAH-like channels reach their
321 maximum values at ~50-70 m depth (**Fig. 6**). Then, a moderate signal in the intermediate water layers (250 to 450 m) is only
322 detected for the Pyr- and Flu-like channels (**Fig. 6**). This signal is mostly visible through acquisition phase 2 for section
323 distances between the 55 km mark and the end of the mission. The Pyr- and Flu-like responses are rather concordant and
324 show concentration variations of 10% with maximal values at 350 m (1.8 and 0.025 µg/L for the Pyr- and Flu-like channels,
325 respectively). Another moderate PAH-like increase occurs at deeper depths (550-650 m), where the concentration reached
326 1.6 and 0.02 µg/L for the Pyr- and Flu-like channels, respectively. It is worth noting that the b_{bp700} signal is located in the
327 suboxic waters just above and below the Pyr-/Flu-like horizontal plume anomaly (*Fig. 5c* and *Fig. 6c, d*).

328 5. Discussion

329 5.1. Significance of polyaromatic hydrocarbon (PAH-like) concentration anomalies

330 The MiniFluo-UV measurements showed multiple PAH-like concentration anomalies characterized by:

- 331 • A consistent strong signal in the subsurface for the four PAH-like channels,
- 332 • Spike anomalies detected on Flu- and Pyr-like concentrations at the exact location of oil seep sites,
- 333 • An increase of the Pyr- and Flu-like concentrations within the Oxygen Minimum Zone (OMZ) core (250-450 m) in
334 the northern half of the study area,
- 335 • Vertical columnar anomalies of the Flu-like channel at the location of oil seep sites.

336 Despite being well visible both on the scattered plots and along the 2D sections, in-situ fluorescence measurements can be
337 influenced by various environmental factors that modify quenching processes (Gauthier et al., 1986; Danielsen et al., 1995;
338 Osburn et al., 2014), among which are temperature (thermal quenching), metal cations and humic substances (static
339 quenching; Danielsen et al., 1995), and molecular oxygen (collisional quenching). Absolute values of PAH-like
340 concentrations reported here shall also be taken with caution since they are directly dependent on the calibration method

341 employed. Nevertheless, the PAH patterns observed in the water column and the detection of concentration anomalies
342 remain fully relevant.

343 Two main hypotheses can be envisioned to explain the Flu- and Pyr-like field: (i) protein- and humic-like materials display
344 the same fluorescence signature ($\lambda_{ex}/\lambda_{em}$ couple) couple as PAH and can therefore be misinterpreted as such (PAH look-
345 alike fluorophores; Stedmon et al., 2003), and/or (ii) the effective presence of dissolved hydrocarbons in the water column.
346 The absence of signal variation for both the Naph- and Phe-like channels mounted on the same MiniFluo-UV-1 sensor can
347 be attributed either to sensitivity issues, to lower fluorescence intensity or to a contamination by environmental parameters
348 (i.e. quenching). The background values of Naph-like concentrations recorded during the mission (i.e. ~20 ng/L) are higher
349 than the PAH concentrations usually recorded in ocean waters that range between 1 to 10 ng/L. The strong expression of the
350 Pyr-like signals compared with other PAH is remarkable considering that this pyrogenic component is not expected in
351 natural oil seep systems. The few traces of Pyr reported in some crudes (Pampanin and Sydnes, 2013) combined with a much
352 lower bioremediation efficiency may explain this signal (Stedmon et al., 2003; Ekperusi and Aigbodion, 2015).

353 **5.2. Deep Chlorophyll Maximum in the sub-surface water**

354 In the subsurface water, a consistent layer is enriched in chlorophyll-*a* (**Fig. 5a**), particulate matter (b_{bp700} ; **Fig. 5c**) and to a
355 more moderate extent in the humic-like component (**Fig. 5b**). The chlorophyll-*a* -like fluorescence shows a classical shape of
356 a deep chlorophyll maximum (Cullen, 1982) at ~50 m. This corresponds fairly well to depth values of the deep chlorophyll
357 maximum reported closer to the coast (Jourdin et al., 2006; Erickson et al., 2016), where the transition between photic and
358 aphotic zones is shallower (Wasmund et al., 2005). High chlorophyll-*a*-like values suggest intense photosynthetic activity by
359 the phytoplankton at the top of the first pycnocline (Zeng et al., 2017). Enrichment in phytoplankton concentrations is also
360 coherent with high backscattering values in the first 100 m. The humic-like concentrations we observe (> 0.8 QSU) are
361 rather high but remain coherent with similar coastal/upwelling systems (Nelson and Siegel, 2013), while low values detected
362 near the surface can be associated with photobleaching (Del Vecchio and Blough, 2002; Miranda et al., 2018). This layer
363 commonly hosts abundant biological processes, whose by-products have a similar fluorescence spectra signature to that of
364 PAH (Tedetti et al., 2010; Jocis et al., 2014). For instance, heterotrophic bacteria (Tedetti et al., 2012) and phototrophic
365 cyanobacteria reported in the sub-surface (within the deep chlorophyll maximum, below 75 m depth; *Synechococcus* and

366 *Prochlorococcus*; Zhao et al., 2017) have similar spectral signatures ($\lambda_{ex}/\lambda_{em}$ couple) compared to the PAH-like channel
367 (Ulloa et al., 2013; Gonzalez-Garcia et al., 2018). In these conditions, very high PAH-like concentrations detected in shallow
368 depths (~30 m; **Fig. 6**) would more likely be associated with biological processes than with a shallow hydrocarbon storage
369 layer.

370 **5.3. Horizontal anomaly in the oxygen minimum zone and interactions with biogeochemical parameters**

371 The intermediate layer of the Angolan waters corresponds to the South Atlantic oxygen minimum zone (OMZ) area (Mercier
372 et al., 2003; Karstensen et al., 2008; Mashifane et al., 2016; Schmidt and Eggert, 2016). In the northern half of the area (i.e.
373 after ~50 km in section distance), the core of the OMZ (300-500 m; **Fig. 4e**) is associated both with an increase in the Pyr-
374 (**Fig. 7c**), Flu- (**Fig. 7d**), humic-like and chlorophyll-*a*-like channels (**Fig. 5a, b**), and with a decrease in particulate matter load
375 and dissolved oxygen (DO) concentration (**Fig. 5c**). The layer between 250-350 m (i.e. above the Pyr-/Flu-like anomalies) is
376 characterized by slightly higher gradients of temperature and salinity, which is interpreted as the second thermo/pycnocline
377 (**Fig. 4a, b**).

378 The hypothesis of a layer of enhanced hydrocarbon content related to PAH-like concentrations in the intermediate layer is
379 supported by the density gradient modification (**Fig. 4c**). In these conditions, hydrocarbons released from the seafloor remain
380 stored and accumulate below the second thermo/pycnocline (**Fig. 6d**; Adalsteinsson et al., 2011; Camassa et al., 2013;
381 Landeau et al., 2014). The accumulation of PAH in the pycnocline vicinity has been already pointed out by Cyr et al. (2017).
382 Interactions between gas and water are inhibited in the gas hydrate stability zone in the water column, the depth of the upper
383 limit of these conditions depends on temperature, pressure, salinity and gas composition (**Fig. 8a**) but is usually estimated to
384 be 430 m below the sea surface (Kvenvolden and Barnard, 1983; Dholabhai et al., 1991; Rehder et al., 2002; McGinnis et al.,
385 2006; Sloan, 2003). Above this, hydrates dissociate and gases are rapidly oxidized ($2\text{CH}_4 + 4\text{O}_2 \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O}$). While the
386 top of the intermediate PAH-like anomaly corresponds to higher temperature gradients (**Fig. 8a, b**), the base correlates with
387 the dissociation depth of a classic mix of thermogenic gases (Tissot et Welte, 2012; Floodgate and Judd, 1992). In these
388 conditions, gas removal in the ascending hydrocarbon plume leads to a relative weighting of hydrocarbon mixing and to
389 dissolved oxygen (DO) depletion (**Fig. 8b**). This could support the hypothesis of a storage of heavier hydrocarbon
390 components above the top of the gas hydrate stability zone. In the deep waters of the Gulf of Mexico, Camilli et al. (2010)

391 made similar observations of a Naph trapped in a depleted DO layer after the Deep-Water Horizon blowout. In our case, the
392 correlation between both the location and thickness of the PAH-like horizontal plume and the depths of the second
393 thermocline, as well as the calculated hydrate-free transition layer forming physical boundaries suggests that PAH are
394 entrapped in the OMZ.

395 The depleted DO layer is concomitant with an increase in humic-like and particle concentrations. The respiration of
396 heterotrophic bacteria leads to an oxygen depletion linked with the oxidation/mineralization of particulate and dissolved
397 organic matter (Joye et al., 2011; Kowalczyk et al., 2013). In parallel, oxidation is reported as a major removal process of
398 PAH in the environment. Conversely, anoxic water enhances PAH preservation in the OMZ, which can support the
399 hypothesis of horizontal PAH-like fluorescence anomalies in the 350-450 m intermediate water layer (*Fig. 6 c, d*).
400 Collisional quenching effects can also contribute to increase the fluorescence signal. Even if the anti-correlation is not
401 systematic, PAH-like signals coincide with a layer of lower DO concentrations and lower temperatures at these depths (*Fig.*
402 *4a, d*).

403 In the eastern South Pacific, the OMZ core at 300-400 m water depths is characterized by a humic-like and chlorophyll-*a*-
404 like signal potentially related to the presence of microbial biomass (Whitmire et al., 2009) and by a b_{bp700} signal that can be
405 associated with the presence of denitrifying and ammonium oxidizing bacteria (Garfield et al., 1983). In the northern half of
406 our study area, apart from shallow waters, the highest particle concentrations occur at the upper and lower edges of the OMZ
407 (*Fig. 5c*), which would reflect the maximal activity of bacteria at these depths.

408 Cyanobacteria (*Synechococcus* and *Prochlorococcus*) and sulphate reducers (prokaryotes: *Thioploca*, *Beggiatoa*) are
409 involved in nitrogen recycling ($NH_4^+ + NO_2^- = N_2 + 2H_2O$; Fariás et al., 2007) and sulphate reduction ($SO_4^{2-} + H_2O = H_2S +$
410 $2H_2O$; Gibson et al., 2003; Schunck et al., 2013), both biochemical processes occurring in OMZ conditions (Ulloa et al.,
411 2012). These organisms and their biological by-products comprising humic-like organic matter have similar fluorescence
412 properties compared with PAH, making it difficult to discriminate between biological products and dissolved hydrocarbons
413 in the OMZ. Cyanobacteria are also reported to consume hydrocarbons (Cerniglia et al., 1980; Narro et al., 1992; Heider et
414 al., 1998; Abed and Köster, 2005; Hazen et al., 2016), suggesting that both signals might be concomitant (Zhang et al.,
415 2012). In our case, the increase of the b_{bp700} signal above and below the PAH-like horizontal anomaly that occurs alongside a

416 transition towards suboxic layers ($DO > 45 \mu\text{mol/kg}$) suggests the activity of an oxygen-dependent, hydrocarbon-consuming
417 bacteria consortium (hydrocarbon oxidizing bacteria; Rosenberg and Gutnik, 1981).
418 In addition to hydrocarbon seepage, the intrusion of the Congo Plume waters in the study area can potentially have strong
419 implications on organic matter and pollutant distribution. Congo waters show a particularly high content in dissolved organic
420 matter (Nelson et al., 2010; Andrew et al., 2013), with concentrations up to 10.7 mg/L (Spencer et al., 2009). This significant
421 river input of dissolved organic matter could thus also contribute to the humic- and chlorophyll-*a*-like anomalies observed in
422 the OMZ core (Fig. 5).

423 **5.4. Significance of spikes and columnar vertical anomalies**

424 Columnar anomalies detected on Flu-like patterns of higher intensity occur at depths between 400 and 700 m. The signal
425 remains low compared with the regional background, but with only a 3% concentration increase it is greater than the sensor
426 precision (2%) and might therefore be related to environmental modifications. PAH-like vertical pipes are superimposed on
427 the location of active oil seep areas, supporting the fact that the MiniFluo-UV sensors was detecting hydrocarbons. The
428 maximum depth of investigation of the glider is 700 m while the water depths of the investigated area range between 1500
429 and 2100 m. It is possible that the dispersion of the oil during the ascent in the water may be at the origin of the low
430 amplitudes of the PAH anomalies observed.

431 The detailed review of fluorescence data acquired during the mission reveals spike anomalies associated with important
432 concentration increases in the PAH signal, either on the Phe-, Flu- or Pyr-like channels, which are usually considered as
433 acquisition artifacts. Spikes appear locally as isolated spots or through a few adjacent glider profiles acquired during virtual
434 mooring phases. Except for seep sites 1 and 5, PAH-like anomalies are all in close proximity to oil seep sites, suggesting a
435 correlation between the recorded PAH signal and the presence of hydrocarbons (Fig. 7). As mentioned before, spikes mostly
436 appear in one PAH optical channel, except at the location of seep site 3 where concomitant peaks are recorded for both the
437 Flu- and Pyr-like channels (Fig. 7c, d). While the absence of PAH signals remains difficult to explain at site 1, the non-
438 detection at seep site 5 can be explained by the fact that the glider only flew once over the seep area, therefore decreasing the
439 probability of the glider to cross the hydrocarbon plume.

440 Considering that the MiniFluo-UV sensors can detect the dissolved portion of hydrocarbons only, their response to a contact
441 with the non-aqueous liquid phase remains unknown. Sea surface slicks detected on SAR images testify to the presence of a
442 liquid phase throughout the ascent in the water column. The MiniFluo-UV response to the presence of a liquid oil phase on
443 the sensor measurement cells is unknown and yet plausible to explain spike signals. Optical paths being physically isolated
444 by the sensor design, both UV channels might therefore be affected differently by the presence of oily-coated bubbles, thus
445 explaining the independent response of the optical channels. In these conditions, spikes of the PAH signal would constitute a
446 proxy for the presence of hydrocarbons in the water column.

447 **6. Conclusions**

448 This paper aimed to evaluate the effectiveness of fluorescence sensors in combination with biogeochemical and physical
449 sensors mounted on submersible vehicles (gliders) to detect hydrocarbons in the natural oil seeping province of the Lower
450 Congo basin. The mission was planned to monitor active natural oil seep sites during 20 days in conjunction with the
451 acquisition of satellite images. The glider mission significantly improved our knowledge regarding hydro-physical
452 conditions in the Lower Congo Basin, especially for the lateral and horizontal distribution of biogeochemical parameters and
453 the evolution of the oxygen minimum zone in the area. Multiple polyaromatic (PAH-like) concentration anomalies were
454 detected in relation with specific anomalous levels of dissolved oxygen and/or biogeochemical parameter responses. In the
455 shallow waters, consistent PAH-like anomalies occurred in strict relationship with the Deep Chlorophyll Maximum, which is
456 likely associated with microbial processes. Between 250 and 450 m, a PAH-like signal reveals the most interesting patterns.
457 Here, the depletion of dissolved oxygen is associated with a horizontal plume characterized by increased concentrations of
458 both pyrene and fluorene. The most conservative hypothesis concerning the origin of this fluorescence anomaly is the effect
459 of bacterial processes. Another possibility is that this horizontal plume corresponds to dissolved hydrocarbons entrapped
460 within stratified intermediate waters limited by the second thermo/pycnocline at the top and the hydrate dissociation layer at
461 the bottom. Most conclusive observations refer to spike anomalies associated with a strong concentration variation of
462 individual PAH-like fluorophores showing a good spatial correlation with oil seep sites evidenced by satellites. Deeper (400-

463 700 m water depth) columnar PAH-like anomalies associated with more moderate concentration changes could also
464 correspond to vertical plumes of hydrocarbons.

465 **Author contributions.**

466 RJ, DD, FB designed the research. RJ, FB and OPdF analyzed the data. MT and MG guided the interpretation of the
467 fluorescence signals. RJ prepared the manuscript with contributions of DD, MT, OPdF, LL, FB, MG and XDdM.

468 **Competing interests.**

469 The authors declare that they have no conflict of interest.

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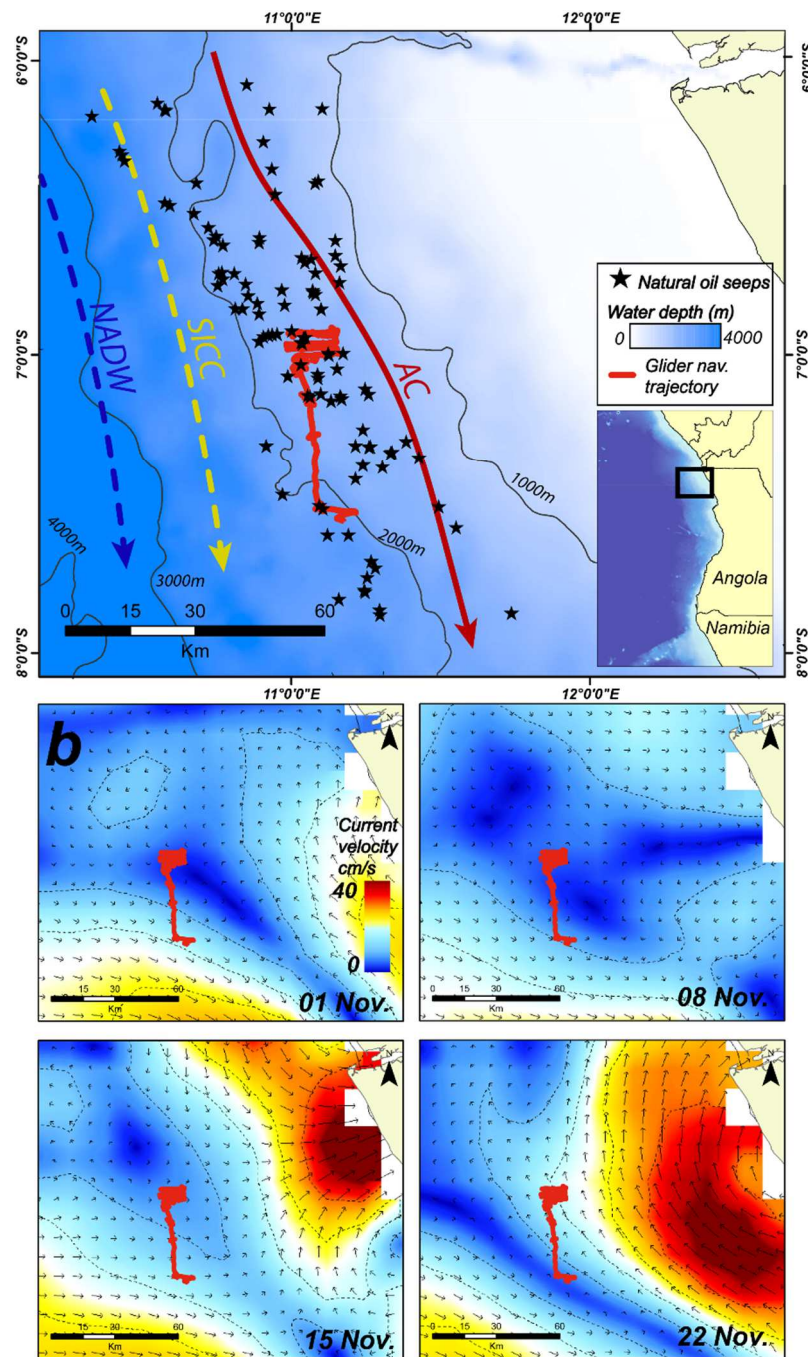
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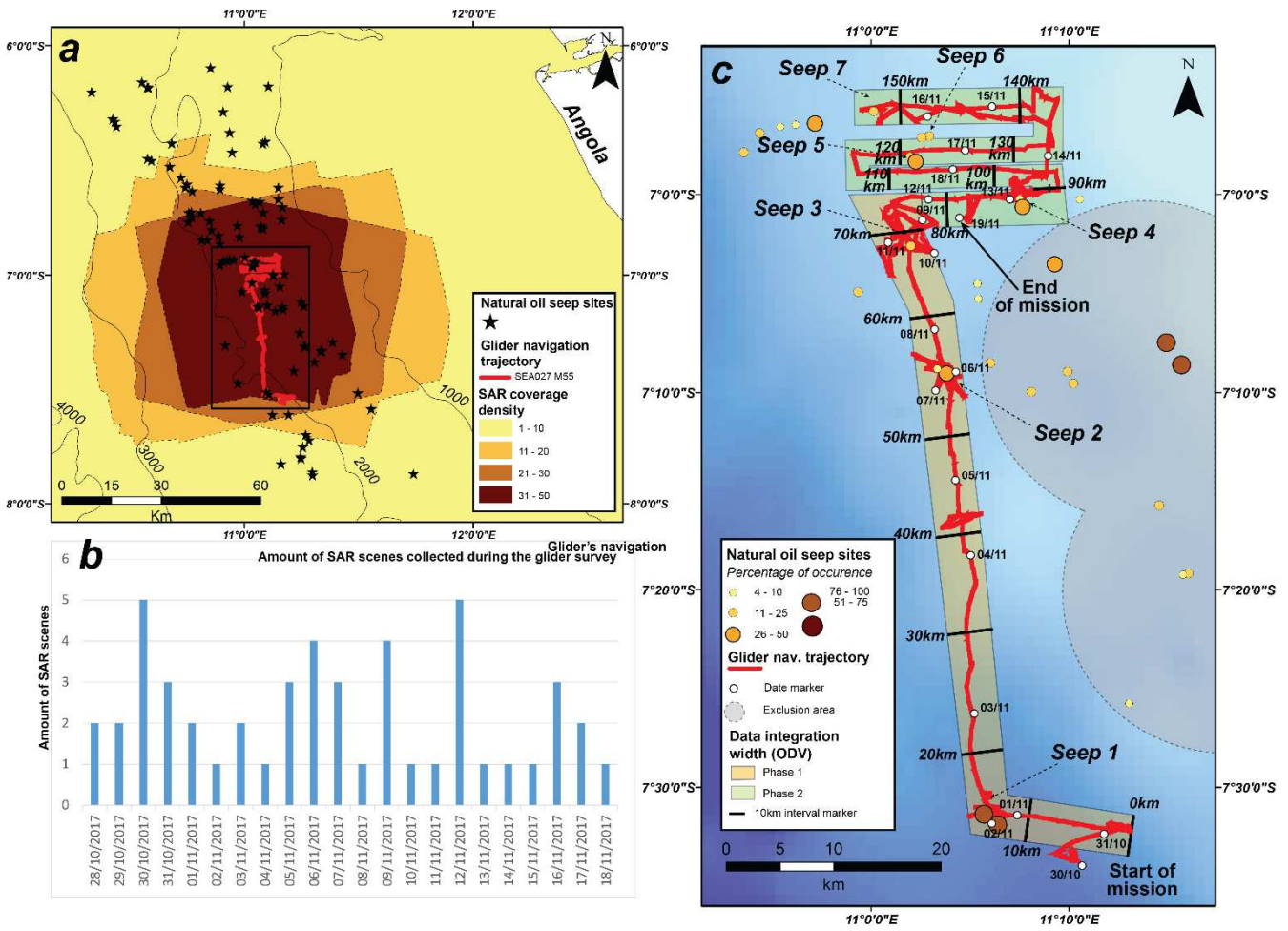
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822 Fig. 1: a. Map of the study area showing the location of natural oil seep sites (black stars) identified on SAR satellite images
 823 (Jatiault et al., 2017). b. Map of weekly averaged geostrophic surface currents of the observed ocean physics (Copernicus
 824 MULTIOBS ARMOR3D dataset; www.marine.copernicus.eu) superimposed with the glider route in red. From top left to bottom
 825 right: 01/11, 08/11, 15/11 and 22/11/2017.

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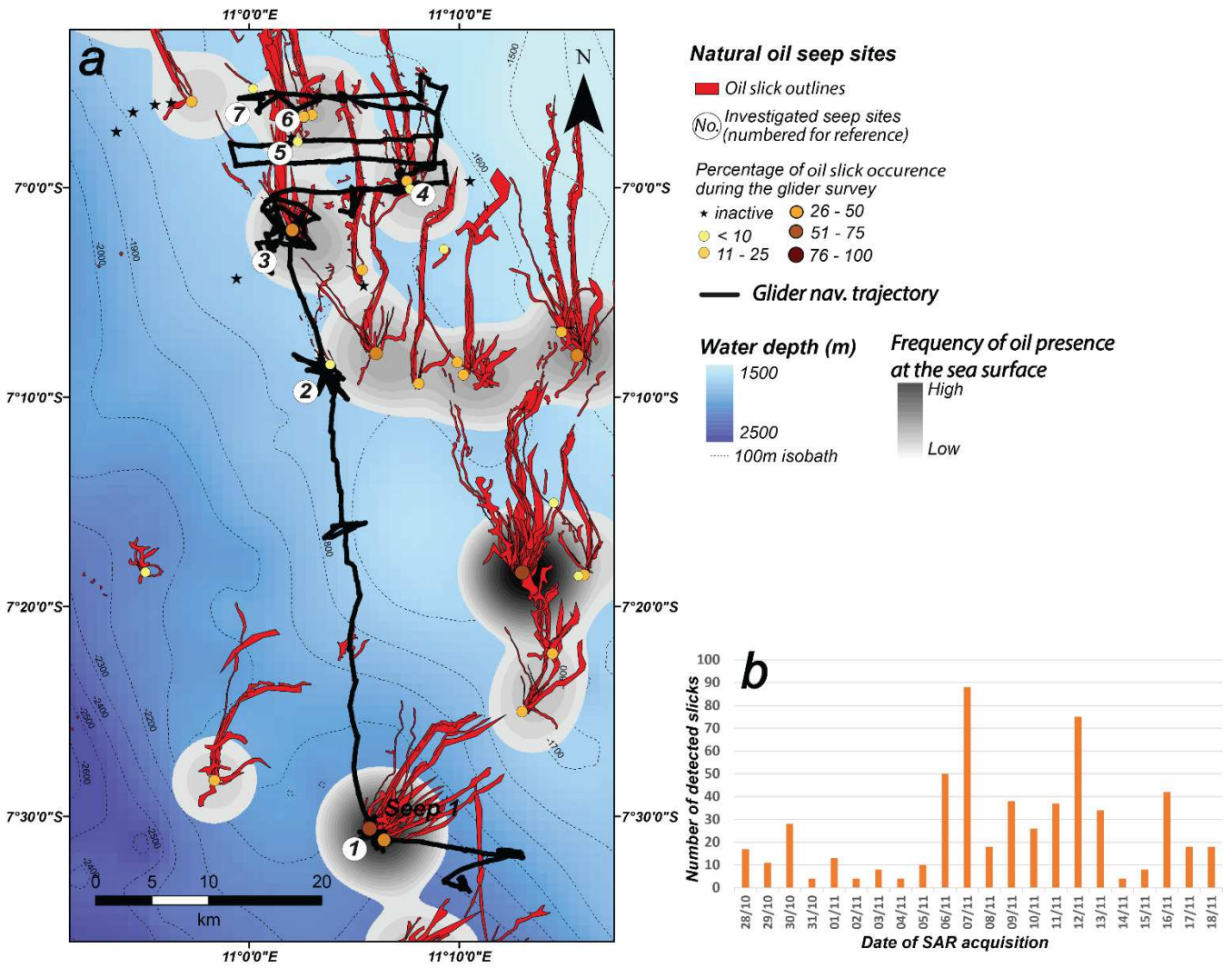


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828 **Fig. 2: a. Density coverage of satellite scenes collected during the glider mission. Black stars correspond to the location of oil seep**
 829 **sites detected during a 1994 - 2016 SAR monitoring (Jatiaux et al., 2017) superimposed with the navigation trajectory of the glider.**

830 **b. Temporal distribution of SAR scenes collected during the 20 days of mission (from 29 October to 18 November 2017). c. Zoom**
 831 **on the glider mission acquisition plan. White dots correspond to the temporal location of the glider. Glider data have been stacked**
 832 **within a 1.5 wide strip (orange and green polygons) for the generation of 2D profiles using Ocean Data View (ODV) software.**

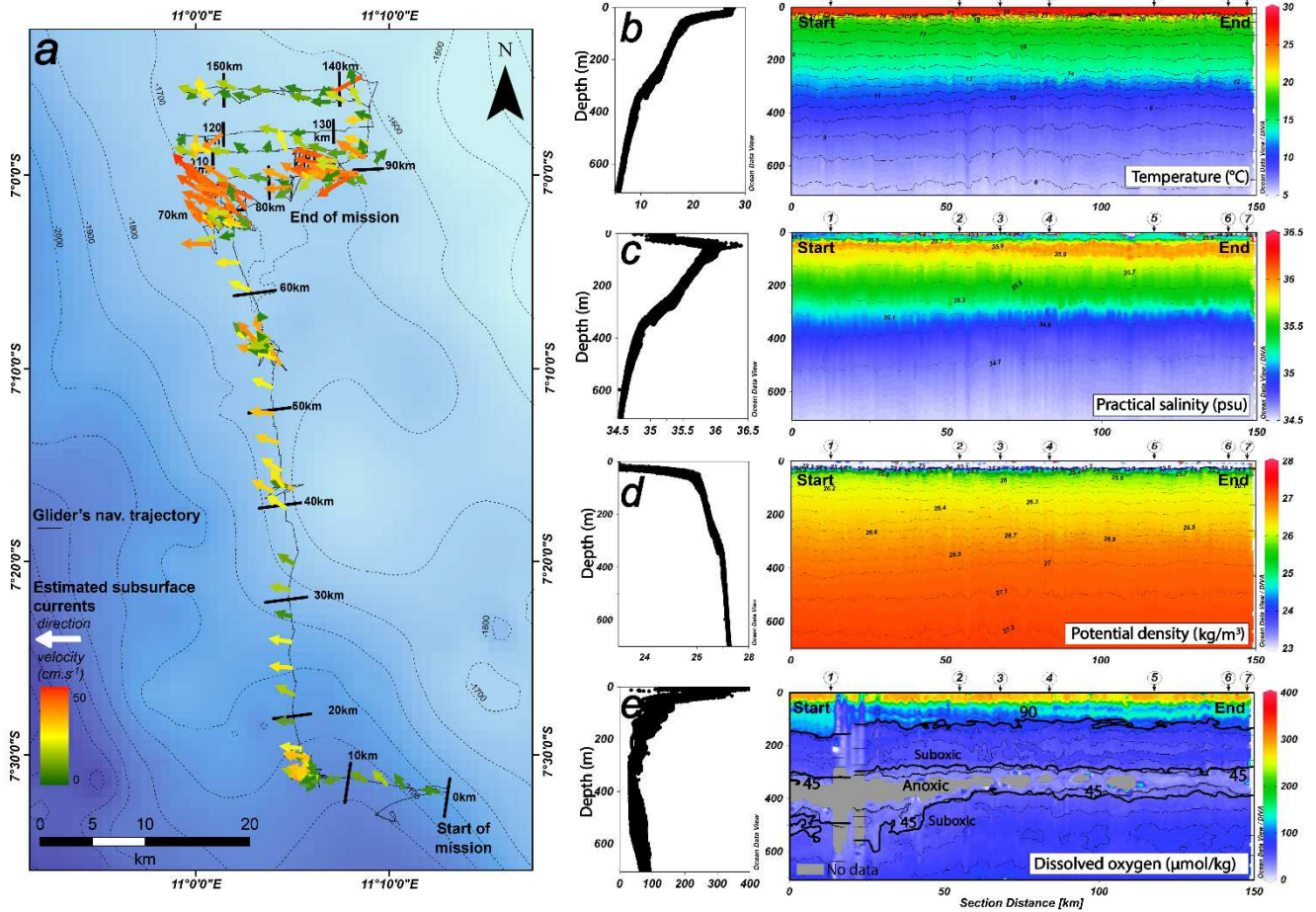
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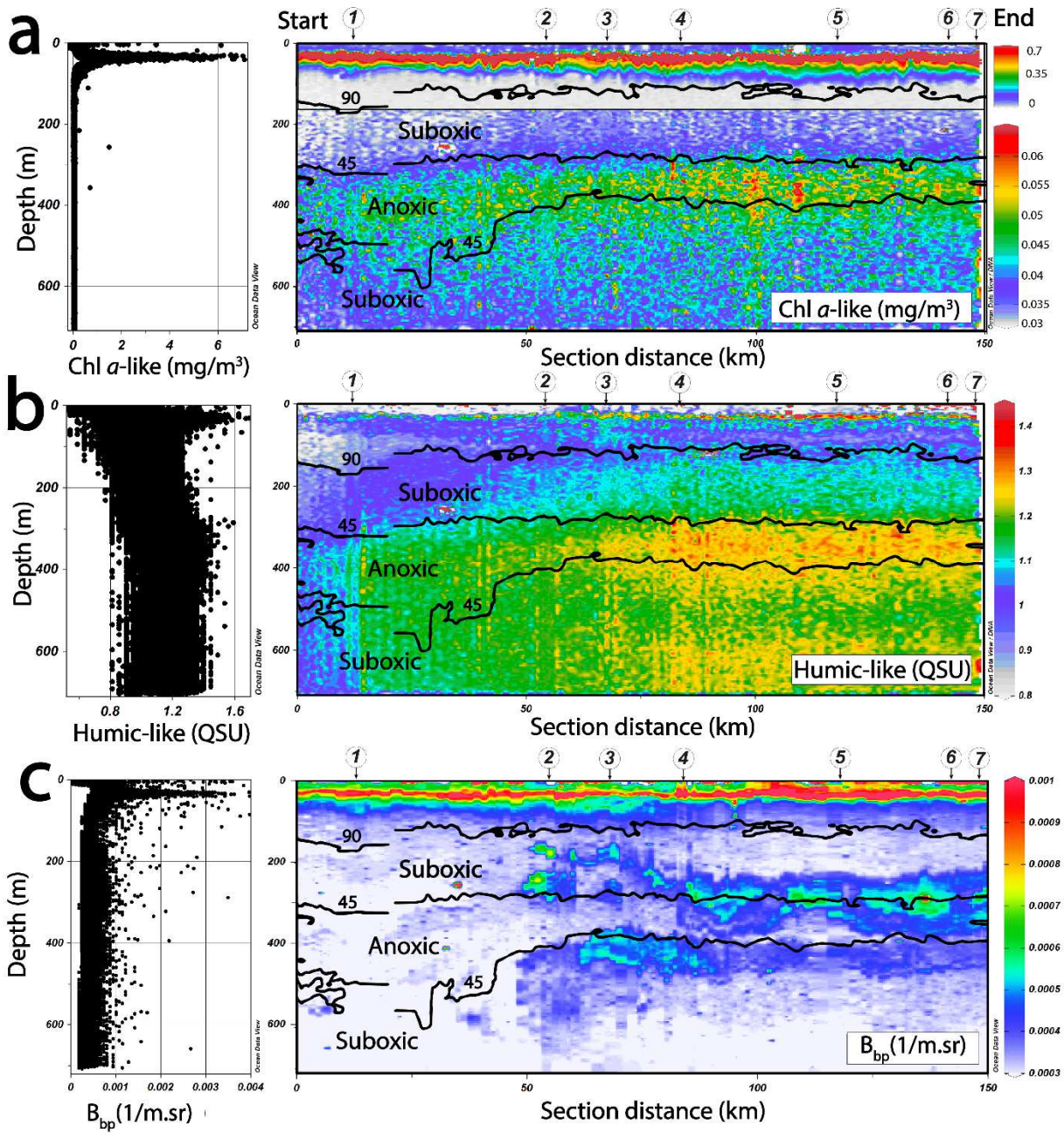
835 **Fig. 3: Glider trajectory (black line) superimposed with oil slicks detected on SAR images during the glider mission (20 days from**
 836 **29 October 2017 to 18 November 2017). During the mission, previous oil seep sites identified between 1994 and 2016 (Jatiaux et al.,**
 837 **2017) were either active (coloured dots correspond to occurrence rates, i.e. the ratio between the number of slicks detected and the**
 838 **SAR scene coverage density) or inactive (black stars).**

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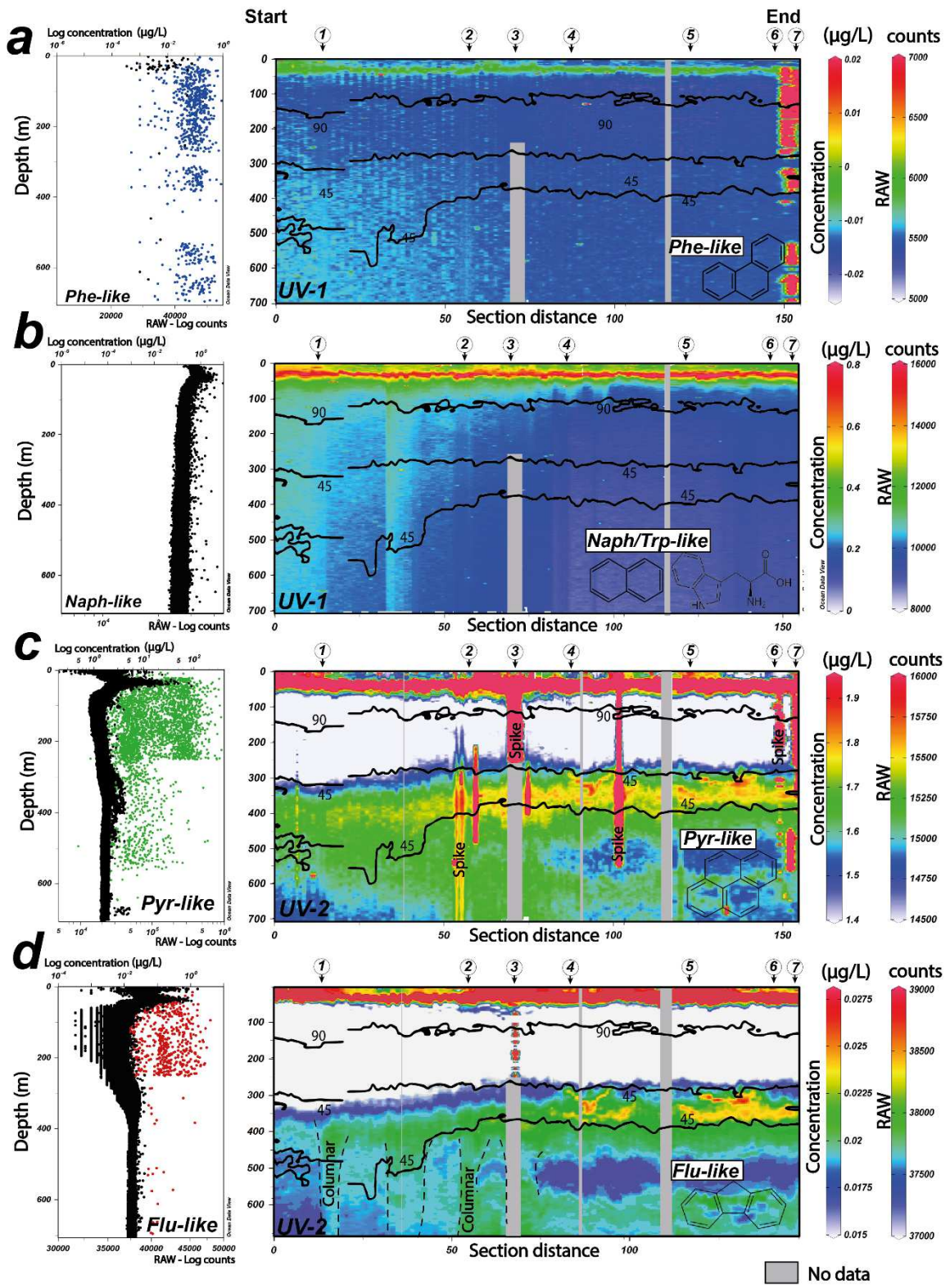
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841 **Fig. 4: Hydrological measurements acquired with the glider. Oil seep positions are reported on top of section distance profiles. a.**
 842 **Map of the estimation of underwater current (Depth Averaged Current) between the estimated and real surfacing location of the**
 843 **glider. The estimated currents are superimposed with the water depth, the glider trajectory and landmarks along the glider**
 844 **trajectory. b. Potential Temperature (θ). c. Practical salinity (S_p). d. Potential density (σ_θ). e. DO concentration. Each physical**
 845 **parameter is displayed on a scatterplot (on the left) and on a 2D section (on the right) where measurements have been stacked**
 846 **along a 1.5 km wide strip following the glider trajectory (see Fig. 2).**

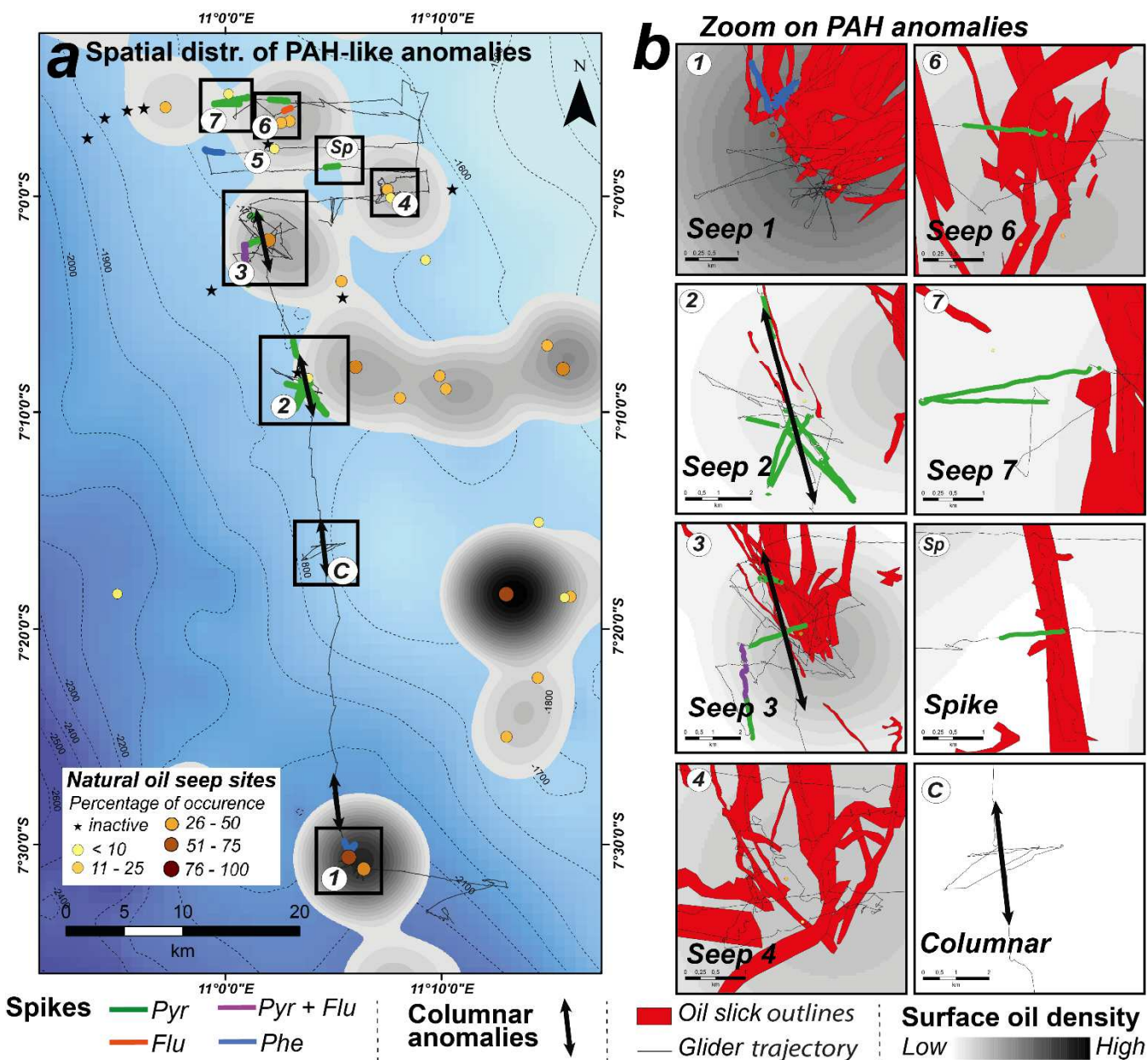


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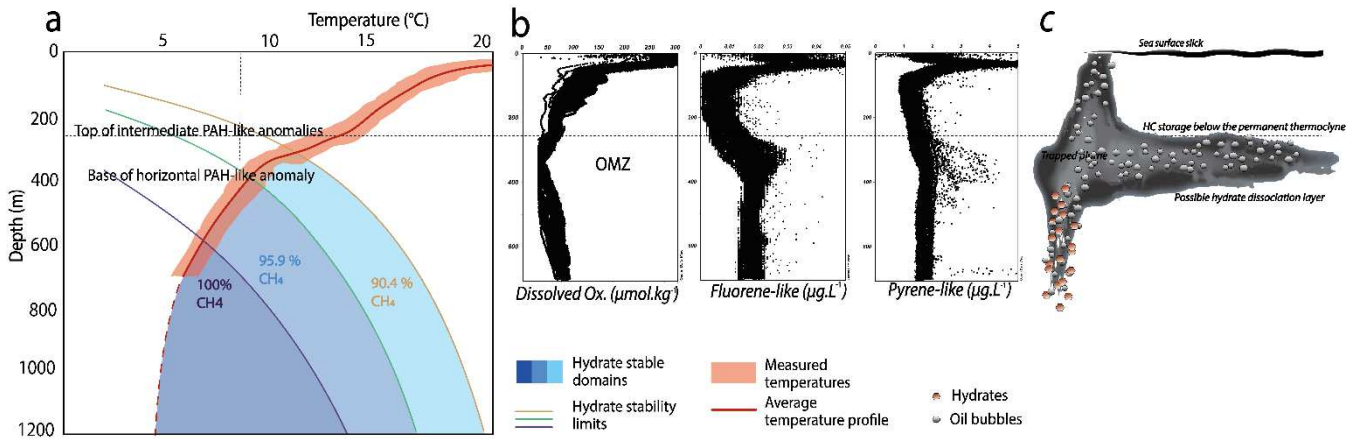
848 Fig. 5: Distribution of (a) Chlorophyll-a-like concentration, (b) humic-like content and (c) the particle backscattering signal at 700
 849 nm (bbp700). Biogeochemical parameter concentrations are superimposed with dissolved oxygen isocontours (thick black contour
 850 lines) marking the limits between the suboxic layers and the oxygen minimum zone. Measures are displayed in scatterplots (left)
 851 and section profiles (right).



853 **Fig. 6: General overview of dissolved PAH-like concentrations detected during the 20 days of acquisition by the glider. Left: PAH**
854 **concentrations compared with the water depth (m) in log scale. Coloured dots correspond to spike anomalies with respect to**
855 **classic profiles (black dots). Right: 2D sections displaying PAH-like measurements (raw counts and concentrations) along the**
856 **glider trajectory. Colour scales were stretched in order to highlight fine-scale modification in depth compared with the prominent**
857 **~50 m anomaly. Numbers at the top of each section correspond to the location of oil seep sites identified from SAR slick analysis.**
858 **Thick black contour lines correspond to DO isocontours.**



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861 Fig. 7: a. Geographical distribution of PAH-like anomalies observed on the optical channels of the MiniFluo-UV sensors
862 superimposed with the location of oil slick impact areas and oil seep sites. Black boxes correspond to extracts displayed in Fig. 7b.
863 b. Zooms of PAH anomalies at frequent oil emission sites with the outlines of natural oil slicks.



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865 **Fig. 8: a. Hydrate stability domains in the water column reported as a function of the water depth, the gas composition and in-situ**
 866 **temperature (Sassen et al., 1999; Milkov et al., 2000). b. Dissolved oxygen, Flu- and Pyr-like component distribution measured**
 867 **during the glider mission. c. Interpretative sketch of the interactions between the oil plume and physical properties of the ocean.**

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870 **Table 1: Main characteristics ($\lambda_{Ex}/\lambda_{Em}$ couples and limits of detection) of the different polyaromatic hydrocarbon (PAH-like) and**
 871 **biochemical parameters.**

PAH-like	Excitation λ_{Ex} (nm)	Emission λ_{Em} (nm)	Limit of detection ($\mu\text{g L}^{-1}$)	Sensor
Phenanthrene	255	360	0.01	MiniFluo-UV1
Naphthalene/ Tryptophan	275	340	~0.074	MiniFluo-UV1
Pyrene	270	380	0.08	MiniFluo-UV2
Fluorene	260	315	0.03	MiniFluo-UV2
Biogeochemical parameters			Limit of detection	
Humic-like	370	460	0.28 QSU	FLBBCD
Chlorophyll- <i>a</i>	470	695	0.015 mg.m ⁻³	FLBBCD
Particle backscattering b_{bp700}	700		0.0015 m ⁻¹ .sr ⁻¹	FLBBCD

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