1 # *In situ* measurement of trace sulfide concentrations in marine coastal
2 waters using diffusive gradient in thin film passive samplers

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14

15 ## Abstract

16 The diffusive gradient in thin film technique (DGT) represents an *in situ* passive sampling
17 method designed to preconcentrate various compounds, including sulfides, for detection
18 at low concentrations. While DGT applications for sulfides have been studied in
19 freshwater, this research extends its use to marine environments. A detailed methodology
20 is presented for synthesizing, assembling, calibrating, and field-deploying DGT samplers
21 to measure sulfides in the low micromolar range in marine waters. The in-house DGT
22 samplers developed in this study demonstrated improved performance, with more
23 homogeneous binding gels and smaller silver iodide particles (0.51 ± 0.34 µm) compared
24 to commercial alternatives. Grayscale imaging enabled accurate quantification of sulfide
25 accumulation in the gels, confirming the method's reliability for detecting trace-level
26 sulfides in marine environments. Comparative analysis showed in-house and commercial
27 samplers performed similarly in estimating sulfide concentrations. Field deployments
28 along the Peruvian coast revealed significant vertical and spatial sulfide gradients. In the
29 Callao coastal area (July–August 2022), concentrations ranged from 0.03 to 0.45 µM
30 across a 35 m depth profile. In Paracas (March–April 2023), a shallower coastal station,
31 concentrations ranged from 1.17 to 6.46 µM, reflecting increased benthic production.
32 These results highlight the utility of DGT samplers as cost-effective tools for
33 biogeochemical monitoring, enabling studies of the ocean sulfur cycle. The findings
34 emphasize the growing application of DGTs in marine and coastal water column research.

35 ## Keywords

36 Diffusive gradient in thin film (DGT); sulfides; trace concentration levels; low-cost
37 marine observatory.

38

39 ## 1. Introduction

40 The sulfur cycle in the ocean is a key biogeochemical process, with sulfate serving as a
41 significant reservoir (Sievert et al., 2007). In low oxygen zones, primary production and
42 export of organic matter drive the sulfur cycle. The oxidation of organic matter, together

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43 with sulfate reduction and sulfidogenesis, mainly generates sulfides (HS^-) and other
44 reduced sulfur intermediates such as hydrogen sulfide (H_2S), thiosulfate ($S_2O_3^{2-}$) and
45 sulfite (SO_3^{2-}) (Callbeck et al., 2021). The transformation of inorganic sulfur, through the
46 reductive and oxidative pathways of the marine sulfur cycle, produces nitrite and
47 ammonium, which are critical substrates for anammox and nitrification processes
48 (Canfield et al., 2010; Callbeck et al., 2021). This process influences the fixation of
49 carbon (Fike et al., 2015) and nitrogen (Callbeck et al., 2021) in anoxic zones, reinforcing
50 the formation of sulfur plumes and potentially enhancing phosphate release from
51 sediments (Heijs et al., 2000; Lomnitz et al., 2016; Wu et al., 2019). Furthermore, in
52 anoxic sediments, dissolved sulfide significantly affects the distribution and mobility of
53 trace metals like iron by forming stable metal sulfide complexes (Di Toro et al., 1990;
54 Gao et al., 2015; Wu et al., 2019).

55 Recent studies indicate that sulfur cycle activity intensifies in highly productive, low-
56 oxygen areas (Dugdale et al., 1977; Callbeck et al., 2021). The Humboldt Current
57 ecosystem is one of the most productive ocean regions in the world due to nutrient-rich
58 upwelling. It features a shallow oxygen minimum zone, resulting from high primary
59 production, carbon export, and organic matter remineralization (Wooster and Gilmartin,
60 1961; Codispoti and Packard, 1980). Organic matter degradation through sulfate
61 reduction leads to hydrogen sulfide (H_2S) formation, which accumulates in anoxic
62 sediments and can occasionally diffuse into the oxic layer (Jørgensen, 1982; Chauca,
63 2018; Callbeck et al., 2021). Large sulfide plumes along the Peruvian coast cause fish and
64 invertebrate migrations and mortality, due to H_2S toxicity even at low concentrations
65 (Copenhagen, 1953; Levin et al., 2009; Bagarinao, 1992; APHA, 1995; Wang and
66 Chapman, 1999). Therefore, monitoring sulfide concentrations (H_2S + HS^- + S^{2-}) is
67 crucial for environmental protection, as well as for oceanographic, and biotoxicological
68 research (Radford-Knoery and Cutter, 1993; Li et al., 2022).

69 Various analytical methods have been developed to quantify sulfide concentrations,
70 including spectrophotometry (Cline, 1969; Shanthi and Balasubramanian, 1996;
71 Grasshoff et al., 1999; Bowles et al., 2003; Čmelík et al., 2010), fluorescence (Toda et
72 al., 2011, 2012; Wu and Tong, 2019; Leal et al., 2021), chemiluminescence (Huang, 2007;
73 Du et al., 2001; Liu Han, 2016), chromatography (Tang and Santschi, 2000; Mylon and
74 Benoit, 2001; Small and Hintelman, 2007), and atomic fluorescence spectroscopy (Jin et
75 al., 2007). However, these methods often require complicated handling, which can lead
76 to oxidation, volatilization, and loss of sulfides (Toda et al., 2011; Li et al., 2022). To
77 overcome these challenges, various *in situ* methods have been developed, each presenting
78 advantages and limitations (Tang and Santschi, 2000). For example, *in situ* detection
79 techniques such as cathodic stripping voltammetry (Ciglenečki and Ćosović, 1996;
80 Ciglenečki et al., 2005) are susceptible to electrode fouling, causing anomalous readings
81 (Mylon and Benoit, 2001). Sensitive sulfide microsensors with *in situ* pumps and profilers
82 have also been developed (Kuhl et al., 1998; Meyer et al., 2018; Schunck et al., 2013),
83 but they require constant calibration to compensate for oxide formation on the sensor
84 surface (Kuhl et al., 1998). These challenges emphasize the difficulty of accurately
85 measuring trace levels of sulfides in oceanic waters.

86 The diffusive gradients in thin film technique (DGT) (Davison and Zhang, 1994)
87 represents an alternative and promising technique for *in situ* measurement of dissolved

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88 sulfide which has been successfully applied across various environments, mostly in fresh
89 waters, soils (Zhang et al., 2001), and sediments (Zhang and Davison, 1995; Harper et
90 al., 2000; Twiss and Moffett, 2002; Degryse et al., 2003; Dunn et al., 2003; Gimpel et al.,
91 2003; Winderlund and Davison, 2007; Li et al., 2019). Validation and application of DGT
92 technique for marine waters is mostly undocumented. Passive DGT samplers used for
93 sulfide preconcentration include a binding gel containing silver iodide (AgI) particles that
94 react with sulfides in the medium (Teasdale et al., 1999; Devries and Wang, 2003), and a
95 diffusive gel made of agarose or polyacrylamide. Sulfides accumulate in the binding gel
96 depending on exposure time, DGT surface area, sulfide concentration, and their diffusion
97 properties according to Fick law through the diffusive gel. In the presence of sulfides,
98 AgI reacts with them to become Ag_2S, leading to a color change from white to dark brown
99 in the binding gel as a function of sulfide amounts, which can be analyzed by computer
100 densitometry to estimate sulfide concentration (Teasdale et al., 1999; Devries and Wang,
101 2003; Motelica-Heino et al., 2003). DGT samplers are easy to use and provide advantages
102 such as capturing dissolved sulfide (Teasdale et al., 1999) and stabilizing the silver sulfide
103 (Ag_2S) complex to prevent further reoxidation and volatilization losses (Teasdale et al.,
104 1999; Rearick, 2004). The detection limit can be increased with longer deployment times
105 and/or thinner diffusion layers (Zhang and Davison, 1995; Teasdale et al., 1999). DGT
106 samplers are also efficient across a wide range of pH values (Zhang and Davison, 1995,
107 1999; Gimpel et al., 2001; Rearick, 2004). Despite of these advantages, most DGT
108 calibration and accuracy studies have mostly focused on freshwaters, with limited
109 research on measurement validation and application for marine environments (Vrana et
110 al., 2005).

111 In this study, we present the synthesis procedure and characterization of AgI particles in
112 agarose binding gels, as well as the preparation of agarose diffusive gels. In-house DGT
113 samplers were prepared, calibrated in the laboratory using both fresh and marine waters
114 and deployed in the field to measure diluted sulfide concentrations (within the low
115 micromolar range) in coastal marine waters depth profiles. Finally, we conducted a
116 comparative study between in-house DGT samplers and commercial DGT® Research
117 samplers (Zhang and Davison, 1995), evaluating their performance both in the laboratory
118 and in the field in two different areas of the Peruvian coast.

119

120 2. Material and methods

121

122 2.1. Reagents

123

124 Agarose (BioReagent, for molecular biology, under EEO A9539), Silver nitrate ($AgNO_3$,
125 EMSURE ACS, ISO, Reag. Ph Eur.), Potassium Iodide (KI, >99% EMSURE, ISO, Reag.
126 Ph Eur.), Sodium sulfide ($Na_2S.9H_2O$ ⩾98% ACS Reagent – Sigma, Aldrich), Sodium
127 chloride (NaCl, 99.99% Suprapur EMSURE, ISO, Reag. Ph Eur.), Potassium nitrate
128 (KNO_3, > 99.0 % EMSURE, ISO, Reag. Ph Eur), Phosphate buffer (0.1 M – pH: 7.00)

129

130 2.2. DGT gels fabrication and assemblage

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132 The diffusive gels were prepared using 1.5% (m/v) agarose (Wang et al., 2016). First,
133 0.525g of agarose was added to 35 ml of MilliQ water in a 40 ml transparent glass vial
134 with a stir bar and stirred at 100 rpm for 10 minutes at room temperature. The vial was
135 then placed in a 75°C water bath on a magnetic stirrer for 35 min at 100 rpm to achieve
136 complete dissolution of the agarose. The temperature of the water bath was reduced to
137 70°C prior to pipette the warm agarose solution using a preheated tip covered by
138 aluminum foil (70°C). The solution was immediately cast between two glass plates of
139 200x60 mm and 2 mm thick, also preheated at 70°C and separated by a 0.75 mm Teflon
140 spacer and held by clamps (See supplementary information Fig.S01). The plates were
141 allowed to cool for 60 minutes at room temperature. The plates were then immersed in a
142 flat container with 500 ml of MilliQ water and separated gently to remove the gel sheet,
143 which was cut using a 24 mm circular punch. The diffusive binding gels were placed in
144 a Falcon tube filled with MilliQ water at 4°C for 24 h before use.

145 The optimized procedure for the synthesis of AgI binding gels was adapted from Ren et
146 al., 2021. Briefly, the formation of AgI particles was carried out through the mixing of a
147 23 mM solution of silver nitrate ($AgNO_3$) and a 28 mM solution of potassium iodide (KI).
148 We dissolved separately in two 40mL amber glass vials 0.056 g of $AgNO_3$ and 0.066 g
149 of KI in 18 and 17 ml of MilliQ water respectively. To complete the synthesis of AgI
150 particles, 0.3 ml aliquots of the KI solution were added every 30 seconds to the $AgNO_3$
151 solution under low stirring conditions at room temperature. Once the final volume
152 reached 35 ml, 0.525 g of agarose was added and allowed to stir for 10 minutes. The vial
153 was then placed in a 75°C water bath on a magnetic stirrer for 35 min at 100 rpm to
154 achieve complete dissolution of the agarose. A glass ball was placed on top of the EPA
155 vial during this step, to minimize water loss. The temperature in the water bath system
156 was reduced to 70 °C (See supplementary information Fig.S02). Then the AgI solution
157 with melted agarose was pipetted with a tip preheated to 70 °C (covered with aluminum
158 foil), between two glass plates also preheated at 70°C and separated by a 0.5 mm Teflon
159 spacer held with clamps. The same steps as for the diffusive gels were applied for
160 punching out the binding gel disks. Additionally, the binding gels were rinsed 10 times
161 with MilliQ water bin in a Falcon tube and agitated gently by hand to remove reagent
162 impurities. Binging gels were stored in 30mM NaCl at 4°C before use.

163 The DGT were assembled using piston-type plastic holders and caps obtained from DGT®
164 Research (Zhang and Davison, 1995). The samplers were assembled by depositing the
165 binging gel at the surface of the piston first. The diffusive gel was added to the binding
166 gel, followed by a 25 mm Supor® 450 hydrophilic polyethersulfone (PES) filter with a
167 pore size of 0.45 µm. The sampler was then sealed with a plastic cap. In-house DGT
168 samplers were kept in a small zip lock bag filled with a few drops of MQ/30mM NaCl.
169 All samplers were stored at 4°C before use.

170

171 **2.3. Characterization of the binding gel by image microscopy**

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173 The determination AgI particle size distribution in the agarose binding gel was performed
174 using an enhanced dark field microscope (Olympus BX51 Cytoviva). The binding gels
175 were cut in pieces, placed between glass slides and observed in oil immersion (objective
176 x60). Obtained images were processed using the ImageJ software (Fiji version 1.0).
177 Images were converted into grayscale, pixel scaled, and threshold to only account for
178 signals from particles in focus. Particles were automatically detected using the Fiji
179 "analyze particle" function (filtering out the particle touching the edge of the image). The
180 number of particles per mm^2 (particle density) in the images was estimated based on these
181 results. The minimum Ferret's distance was used as a proxy of the tracked particles'
182 diameter for both in-house (n=1628 particles) and commercial samplers (n=690 particles).
183 Average particles' diameter, associated confidence interval and histogram of particle size
184 distribution within the gels were calculated using XLStat (version 2023.3.0).

185

186 **2.4. Calibration of DGT samplers**

187

188 Commercial and in-house DGT samplers were exposed to known sulfide concentrations
189 ranging from 4 to 200 µM for 4 hours in 1L airtight plastic vessels filled with MilliQ
190 waters containing 0.01M KNO_3 previously purged with Argon for 40 min to achieve
191 anoxia in the system, and without headspace and buffered to pH 7.00 with 0.1M
192 phosphate buffer. Both commercial and in-house DGT samplers were implemented in
193 triplicate at each concentration. The vessels were placed on a magnetic stirrer set at 220
194 rpm, throughout the purge and exposure time. The concentration of sulfide in the solution
195 was adjusted to the desired value using a primary standard solution, prepared daily using
196 sodium sulfide (Na_2S) in a 250 ml Nalgene container filled with MilliQ water previously
197 purged with argon for 40 min without headspace. The concentration of the primary
198 standard solution was prepared in way so that the volume of standard solution added to
199 the plastic vessels was less than 1% of the total volume (1L)

200 For the exposure of DGT in seawater, MilliQ water was replaced by filtered seawater
201 purged with argon for 50 min. The same calibration procedure as above was used.

202

203 **2.5. Binding gel imaging**

204

205 After exposure, DGT plastic supports were separated to recover the binding gels with
206 plastic tweezers. The binder gels were placed between two 0.2 mm thick sheets of
207 transparent vinyl. A Xerox Versalink C7025 PCL6 flatbed scanner was used to obtain a
208 JPEG image at 300 dpi. The image files were then transformed into 8-bit grayscale images
209 using ImageJ software, giving a resolution of 256 shades of gray in RGB color ranges;
210 from white (255) to deep black (0). The RGB value of each binding gel obtained with
211 image J was spatially integrated over the binding gel surface area.

212

213 **2.6. Sulfide concentration estimates**

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215 Sulfide concentration estimates in the binding gels were determined by relating the
216 grayscale intensity to the amount of sulfide accumulated in the gel. The accumulated mass
217 of sulfides per unit area (M/A) can be determined in equation 1, based on the known
218 concentration of sulfides exposed in the calibration solution, the exposure time in seconds
219 (t), the thickness of the diffusive layer (diffusive gel and the membrane filter) in cm (Δg)
220 and the diffusion coefficient of the analyte in the diffusive gel in $cm^2\ s^{-1}$(D) (Davison,
221 2016). Finally, M/A is plotted against the grayscale intensity of the binding gels for the
222 different calibration solutions (Figure 4) and fitted using a non-linear function (equation
223 2)

224 $$C_{DGT} = \frac{M\Delta g}{AD\ t} \quad (1)$$

225 $$y = \ln(a) + bln(x) \quad (2)$$

226

227 **2.7. Field deployments**

228

229 For field deployments, both in-house and commercial DGTs were deployed at different
230 depths in the bay of Callao, North of Lima, and in Southern Pisco - Paracas (Figure. 1a)
231 between July - August 2022 and March - April 2023 respectively. In the bay of Callao,
232 DGTs were deployed at station E0 (approximately 35m depth), located on the northern
233 side of San Lorenzo Island (Figure.1b) and at station EM (10m depth), located in the
234 central part of Paracas Bay - Pisco (Figure. 1c) an area located in the South of Lima
235 characterized by sulfides plumes (Callbeck et al., 2021; Ohde 2018; Schunck et al. 2013).

236

237 **3. Results and Discussion**

238

239 **3.1. Characterization of synthesized binding gels**

240

241 The detection of sulfide concentration by DGT is based on the color change of the AgI
242 binding gel from white to dark brown in the presence of dissolved sulfides ($HS^- + H_2S$).
243 It is essential to get a homogeneous distribution of reactive AgI particles in the binding
244 gel to get more precise, reproducible, and accurate sulfide measurements. In this way, the
245 synthesis process is particularly important. In this study, we adapted a procedure for the
246 synthesis of AgI(s) using $AgNO_3$ and KI from Ren et al., 2021, differing from previous
247 methods, where successive immersions of the binding gel were carried out in solutions of
248 $AgNO_3$ and KI (Teasdale et al., 1999). Unlike the method proposed by Devries and Wang
249 (2003), which achieved greater homogeneity of AgI in the binding gel, but required
250 significantly higher amounts of $AgNO_3$ and excessive concentrations of KI, our approach
251 minimizes the need for extensive rinsing while still achieving a uniform distribution of
252 AgI particles.

253 By slowly adding the KI solution at a sufficiently high concentration into a warm and
254 well stirred $AgNO_3$(s) solution, we were able to better control the formation of smaller
255 AgI particles within the low micrometer-upper nanometer range. These particles were

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256 homogeneously dispersed in the binding gel after the addition of 1.5% agarose at 75 °C.
257 Microscopy images of the binding gels are shown in Figure 2. The results confirmed
258 that AgI particles produced by this procedure are distributed relatively homogeneously
259 and that their average diameter is significantly smaller (0.51±0.34 µm) than commercial
260 DGT binding gels (1.0 ±0.8 µm), roughly by a factor 2 (Figure 2a). Furthermore, the AgI
261 particle density (Figure 2c) was twice as high in the in-house gel (7.4×10^{10} particles.mm^2)
262 compared to the commercial binding gels ($3,1 \times 10^{10}$ particles.mm^2). This increase in
263 particle density within the gel results from a different size distribution, closer to the
264 nanometer range in the in-house gel, thus increasing the specific surface area of the
265 particles, and improving their reactivity with sulfides within the gel. The improved
266 synthesis procedure detailed in this study is therefore expected to result in a more
267 sensitive binding gel with greater preconcentration potential, facilitating the measurement
268 of sulfide concentrations at low concentration levels over long deployment periods.

269

270 **3.2. Calibration and performance of in-house DGT samplers in MQ water and**
271 **seawater**

272

273 In-house DGT samplers were exposed in triplicate for 4 hours to 8 different
274 concentrations of sodium sulfide, ranging approximately from 4 to 200 µM, in MilliQ
275 water. Calibration in filtered seawater was also performed for 4 hours with 4 different
276 concentrations of sodium sulfide within the same ranges. The grayscale intensity was
277 measured for each gel using the imaging software as detailed in the Methods section. A
278 calibration curve, similar to those reported by (Teasdale et al., 1999) and (Devries and
279 Wang, 2003) was plotted (Figure 3). The logarithmic relationship between greyscale
280 intensity and accumulated sulfide indicates that the densitometric measurement is more
281 sensitive at low sulfur concentrations and less sensitive at high concentrations, indicating
282 that after 4 h of exposure the AgI in the gels possibly reaches saturation, a hypothesis that
283 could be resolved in subsequent studies.

284 In-house DGT samplers exposed to filtered seawater at four different concentrations fitted
285 on the same trend as those obtained in MilliQ water (Fig. 3) suggesting that our in-house
286 DGT samplers performed identically in both fresh and seawater. The average precision
287 (n=3) was 1.1% in MilliQ water and 3.4% in seawater.

288 Given that the DGT technique is based on a kinetic build-up process, the actual working
289 range of the calibration curve can be optimized by adjusting the exposure time or the
290 thickness of the diffusion gel. A shorter or longer exposure period can be used relative to
291 the expected concentration. In practice, the minimum deployment time should not be less
292 than 1 h, and the maximum deployment time varies from weeks to months depending on
293 the binding capacity of the gel and the limiting biofouling (Zhang and Davison, 1995).

294

295 **3.3. Batch to batch binding gel reproducibility**

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297 To validate the reproducibility of the synthesis procedure, we prepared two different
298 batches on different dates (separated by 36 days). For this purpose, two sets of in-house
299 DGT samplers from each batch were assembled and immersed for 4 hours in Milli-Q
300 water (0.01M ~0.69 Ωcm) and filtered seawater, both enriched with sulfides (average
301 concentration 182 ± 2 μM). The estimated sulfide concentrations determined for the in-
302 house DGT sampler were 182± 2 μM and 180 ± 4 μM for MilliQ water and 177 ± 2 μM
303 and 185 ± 2 μM for filtered seawater, for the two batches respectively.

304 The sulfide concentration estimates by the in-house DGT samplers showed nearly
305 identical results relative to direct measurements performed by spectrophotometry (Figure
306 4). The concentrations of sulfides estimated by DGT for each batch were 179 ± 4μM
307 (batch 1) and 183 ± 3 μM (batch 2) with a difference between them of 3 μM (less than
308 2%). This result suggests again that the in-house DGT samplers performed identically in
309 both MQ and seawater. Moreover, a similar measurement performance is observed
310 between two independent production batches separated by more than a month.
311 Furthermore, even though two groups were estimated for significance measurements
312 showing a slight difference in batch 2. The % variation among batches prepared on
313 different dates (separated by more than a month) was below 3%, providing precise
314 determinations even after several weeks of storage before use. Values obtained among
315 the different batches were nearly identical to direct sulfide measurements, thus providing
316 relatively accurate determinations in both MQ and seawater.

317

318 **3.4. Comparison between in-house and commercial DGT samplers**

319

320 The performance of the commercial samplers obtained from DGT® Research was
321 compared with that of the in-house DGTs by exposing both sets to MilliQ water spiked
322 with sulfides over a concentration range of 4-200 μM. The overlap in the distribution in
323 particular among the two slope values and their associated uncertainty demonstrate that
324 the measurements obtained by both sets of DGTs were in relative good agreement across
325 a wide concentration range. This suggests that our in-house DGT samplers can be used
326 alternatively relative to commercial DGT (Figure 5). The distribution of sulfide values
327 obtained in both cases were very good, within the range of the acceptable limit for
328 experiments involving passive samplers, as pointed out by Teasdale et al., (1999) and
329 Devries and Wang (2003).

330

331 **3.5. Field applications**

332

333 During July–August 2022 and March–April 2023, commercial and in-house DGT
334 samplers were deployed in the coastal areas of Callao and Paracas Bay (Figure 1). These
335 areas are characterized by high organic carbon content and high sulfate reduction rates
336 (Böning et al., 2004) with a permanent oxygen minimum zone (Callbeck et al., 2021;
337 Aguirre-Velarde et al., 2019). This environment occasionally leads to significant sulfur
338 accumulation, which can cause water discoloration, (Schunck et al., 2013; Sommer et al.,
339 2016; Callbeck et al., 2018; Callbeck et al., 2021), locally referred to as "white water

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340 plume" (Ohde et al., 2007; Aguirre-Velarde et al., 2019). Overall, the deployments show
341 that both in-house DGT and commercial DGT samplers detected similar biogeochemical
342 depth gradients of sulfides, showing relatively similar values at both the lower end (0.1-
343 0.2 µM) and the upper end concentrations (6-8 µM).

344 In Paracas Bay, during the months of March and April 2023, DGTs deployed above the
345 sediment surface suggest a benthic production of sulfide. The highest value was observed
346 at two meters from the bottom, reaching values greater than 8.00 µM for the commercial
347 samplers and 6.5 µM for the in-house DGT samplers (Figure 6a). These ranges in sulfide
348 concentrations were similar to those recorded in 2009 during the largest sulfide event off
349 the Peruvian coast (Schunck et al., 2013). Likewise, the increase in sulfides in Paracas
350 Bay may have been subjected to permanent anoxic conditions typical of the season and
351 the regional hydrodynamics of the bay during deployment times (Aguirre-Velarde et al.,
352 2019; Flores et al., 2023), facilitating the diffusion of sulfide from the sediment into the
353 water column.

354 For Callao Bay, samplers deployed between July to August 2022 were exposed for a
355 longer time (27 days) with a full vertical profile, compared to those in Paracas Bay.
356 Despite these differences, a gradient in sulfur concentrations was still evident. Both
357 passive samplers detected sulfide concentrations up to the first six meters of the water
358 column from the bottom, with values reaching 0.11 µM. The in-house samplers recorded
359 concentrations of 0.44 µM, while the commercial samplers detected around 0.52 µM
360 (Figure 6b). Off Callao, sulfide concentrations were lower compared to Paracas bay,
361 probably related to a local ventilation effect on the coast (Ohde, 2018) that causes
362 oxygenation of the water column, inhibiting the formation of sulfide-enriched waters.

363

364 **4. Conclusion**

365

366 This study presents a comprehensive procedure for the synthesis of AgI binding gels
367 which provide sensitive, reproducible, and quantitative measurements of sulfides in both
368 MilliQ and seawater media. Comparison between in-house DGT samplers and
369 commercially available DGT research samplers, conducted both in the laboratory and in
370 the field in coastal marine waters, showed strong agreement between the two. However,
371 synthesis in the procedure for the elaboration of binding gels in in-house DGT samplers
372 allows obtaining gels with a smaller diameter in the AgI particles. This study
373 demonstrates the potential of DGT samplers to quantify, with high precision and accuracy,
374 sulfide at trace levels and also high concentrations in marine environments. It also
375 highlights the advantage and efficiency of this innovative and low-cost *in situ* tool to
376 explore and document the sulfur cycle in the ocean and coastal areas. This tool would be
377 particularly useful to monitor the impact of sulfide compounds, in particular H_2S in
378 eutrophicated coastal environments affected by seaweed production and decomposition.

379

380 **CRediT authorship contribution statement**

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Kevin Diaz: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **David Point:** Experimental design, Writing – review & editing, Supervision, Resources, Validation, Methodology, Investigation, Formal Analysis, Conceptualization. **Wilson Carhuapoma:** Writing – review & editing, Validation, Methodology, Investigation. **Astrid Avellan:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis. **Maricarmen Igarza:** Writing – review & editing. **Jesús Ledesma:** Writing – review & editing, Validation. **Fanny Rioual:** Writing – review & editing, Validation. **Michelle Graco:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

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