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# Systematic error and correction of intensity based I-PLIF for local pH and concentration measurements in unsteady boundary layers

Tom Lacassagne<sup>1\*</sup>, Mahmoud EL Hajem<sup>2</sup>, Jean-Yves Champagne<sup>2</sup> and Serge Simoëns<sup>2</sup>

<sup>1\*</sup>IMT Nord Europe, Institut Mines-Télécom, Univ. Lille, Centre for Energy and Environment, F-59000 Lille, France.

<sup>2</sup>Laboratoire de Mécanique des Fluides et d'Acoustique, UMR CNRS 5509, Univ. Lyon, INSA Lyon, Ecole Centrale de Lyon, Université Claude Bernard Lyon I, 20 avenue Albert Einstein, F-69621, Villeurbanne, France.

\*Corresponding author(s). E-mail(s):  
[tom.lacassagne@imt-nord-europe.fr](mailto:tom.lacassagne@imt-nord-europe.fr);

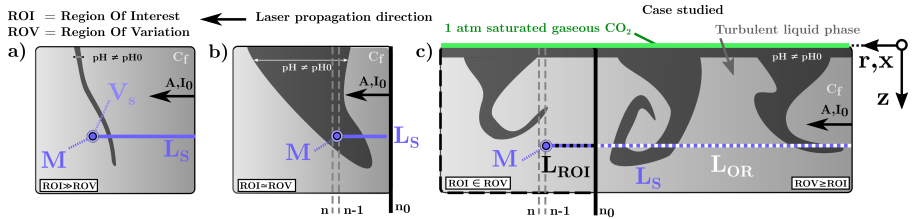
## Abstract

Planar Laser Induced Fluorescence methods, in particular in their Inhibited version (I-PLIF) are powerful tools to measure local scalar values in various types of flows. The most commonly used LIF methods are intensity-based: scalar value is extracted from fluoresced light intensity information. However such methods are prone to error when used in challenging configurations (multiphase flows, non-optically-thin systems, *etc*). In this short paper, the systematic error on concentration measurement in a dissolved gas boundary layer caused by scalar-dependency of the extinction coefficient is discussed, in the context of a non optically thin system with significant out-of-field absorption. Results of single color  $I_{pH} - PLIF$  measurements are compared to  $I_{pH}^r - PLIF$  (ratiometric) measurements for which the out-of-field absorption is intrinsically accounted for. An empirical correction based on first order concentration statistics derived from ratiometric measurements is proposed. It is used to demonstrate that the oversight of out-of-field absorption in intensity-based methods can lead to significant error on the scalar measurements inside the boundary layer.

**Keywords:** Planar Laser Induced Fluorescence, Calibration, Concentration, pH

## 1 Introduction

Achieving accurate, time resolved, and local measurement of scalar properties in complex liquid flows is a challenge in experimental fluid mechanics. Such measurements are highly desirable in heat and mass transfer studies, where they can be used to investigate mixing fundamentals (Bouche et al., 2013; Lacassagne et al., 2018). Planar Laser Induced Fluorescence (PLIF) methods are a powerful tool in that context. In their "classical" version, the local concentration of a fluorescent dye is related to its fluoresced light intensity triggered in a plane by a laser source, and the dye's dispersion and mixing is monitored by recording fluoresced light intensity using cameras (Papanicolaou and List, 1988). As an extension, the inhibited version of PLIF, I-PLIF, uses the scalar-dependency of well-mixed dye's fluorescence to "make visible" an intrinsic scalar quantity transported in the flow, and measure its local value, under some assumptions that are precisely discussed in the present work. Depending on the chosen dye, various flow scalars can be measured, such as temperature (Chaze et al., 2016; Mishra et al., 2019), pH (Asher and Pankow, 1986; Variano and Cowen, 2013; Valiorgue et al., 2013; Lacassagne et al., 2018; Kong et al., 2018) or dissolved gas concentration (Jimenez et al., 2014; Butler et al., 2016; Xu et al., 2020). PLIF methods yet face several limitations due to the fact that the local fluoresced light intensity also depends on the local laser excitation intensity mapping, which may not be homogeneous, especially in non optically thin systems. It may also be disturbed by unsteady phenomena such as reflections at gas liquid interfaces (Bouche et al., 2013; Butler et al., 2016), making all optical calibration steps performed in steady excitation condition non applicable. To account for such limitations, ratiometric methods have been developed (Coppeta and Rogers, 1998; Bouche et al., 2013; Chaze et al., 2016; Lacassagne et al., 2018; Kong et al., 2018). They no longer rely on fluoresced light intensity, but on the ratio of two fluoresced light intensities (colors, coming from one or multiple dyes) the value of which also depends on the scalar quantity to be measured. Ratiometric versions exist for "classical" (Bouche et al., 2013) or inhibited PLIF (Chaze et al., 2016; Lacassagne et al., 2018; Kong et al., 2018), and have been applied to mixing characterisation (Bouche et al., 2013), mass transfer measurements (Lacassagne et al., 2018; Kong et al., 2018), or temperature measurements (Chaze et al., 2016). In particular, pH sensitive techniques (Asher and Pankow, 1986; Valiorgue et al., 2013; Variano and Cowen, 2013; Lacassagne et al., 2018) are useful tools for fundamental and applied chemical engineering and process research in that they allow to quantify micro-mixing in presence of chemical reaction. They are nevertheless associated to an additional limitation inherent to the dyes used



**Figure 1** Configurations of high laser attenuation with scalar-dependent absorption coefficient a) easily correctable b) Correctable using a pixel-by-pixel method (Valiorgue et al., 2013), c) Non correctable with a single color method. The illustration is based on measurements reported in Lacassagne et al. (2022) used hereinafter.

40 (fluorescein sodium or others (Kong et al., 2018)): the scalar (pH) dependency  
 41 of the absorption coefficient, which, in turn, affects the absorption of excitation  
 42 intensity and makes the limitations of single color, intensity based PLIF  
 43 even more critical. The constraints associated to scalar dependency of the absorp-  
 44 tion coefficient can be illustrated with figure 1, inspired and completed  
 45 from Lacassagne et al. (2018).

46 In figure 1 a, the scalar’s region of variation (ROV) is small compared  
 47 to the region of homogeneous scalar, hence the absorption coefficient is only  
 48 locally modified, and it can be assumed that the overall absorption as seen  
 49 by a point  $M$  of the region of interest (ROI) ”after” the scalar patch (in the  
 50 laser propagation direction) is similar to what would have been without the  
 51 scalar structure. Hence, a simple normalisation of the incident light intensity  
 52 accounting for Beer-Lambert absorption is sufficient, and no further correction  
 53 is required after calibration. In figure 1 b however, the scalar patch occupies  
 54 a significant portion of the ROI, and thus the laser attenuation on its way  
 55 through the ROI is significantly altered. This has an influence on the incident  
 56 light effectively reaching the far side of the ROI. Progressive pixel-by-pixel  
 57 calibration and processing as described in Valiorgue et al. (2013) are required  
 58 to estimate the actual excitation intensity reaching each point of the ROI, which  
 59 depends on the scalar structure encountered. Finally, figure 1 c corresponds to  
 60 the critical case where most of the scalar structure encountered are outside of  
 61 the ROI, in the so called outer region (OR). The laser path history on its way  
 62 to the ROI is not known: it is not possible to account for out of field absorp-  
 63 tion (OFA) in the OR using elaborate pixel by pixel correction, and ratiometric  
 64 methods are required. The above picture is a textbook example of challenges in  
 65 unsteady scalar boundary layer measurements, where the size of the boundary  
 66 layer in the liquid phase is often small compared to typical flow scales, forcing  
 67 experimentalists to zoom the ROI well into the ROV, making optical access  
 68 challenging, and measurement accuracy questionable (Valiorgue et al., 2013).

69 The objectives of this paper are twofold: firstly, understand and estimate  
 70 the errors one makes when using single color PLIF in situations where the  
 71 ratiometric method is *a priori* required; secondly, suggest a correction of single  
 72 color concentration measurements in unsteady boundary layers based on the  
 73 prior knowledge of the mean, steady, concentration profiles. For that purpose, a

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74 data set presented in Lacassagne et al. (2022) is used. It corresponds to carbon  
 75 dioxide dissolution and mass transfer at a flat horizontal gas liquid interface  
 76 enhanced by bottom shear turbulence. pH sensitive laser induced fluorescence  
 77 was applied in both its intensity-based ( $I_{pH} - PLIF$ ) and ratiometric form  
 78 ( $I_{pH}^r - PLIF$ ), the pH decreasing with increasing dissolved gas concentration.  
 79 Such measurements are well suited to the aims of this paper: they are targeting  
 80 sub-millimetric scalar boundary layers in a flow of much larger scale, and thus  
 81 focus on a ROI much smaller than the ROV and the OR, which is bound to  
 82 be associated to significant, concentration dependent, and unsteady OFA.

83 All notations used throughout the present article (coordinates and param-  
 84 eters) are similar to those used in Lacassagne et al. (2022) (or Lacassagne et al.  
 85 (2018)), unless stated otherwise. In what follows, the theoretical backgrounds  
 86 of single color and ratiometric methods are recalled in section 2 (additional  
 87 details available in Valiorgue et al. (2013) and Lacassagne et al. (2018), re-  
 88 spectively). The experimental conditions reported in Lacassagne et al. (2022)  
 89 are then briefly summarized in section 3. In section 4, the calibration strate-  
 90 gies and data processing steps are first detailed, and the concentration results  
 91 obtained with both methods are compared. The proposed correction is also  
 92 assessed. As a conclusion, the origin of systematic error on single color mea-  
 93 surement and its implications for the interpretation of literature measurements  
 94 (including Lacassagne et al. (2018)) are discussed.

95 **2 Theory**

96 In Lacassagne et al. (2018), The recorded fluoresced light intensity coming  
 97 from point  $M$  of the ROI for a given excitation wavelength  $\lambda_e$  is derived as

$$I_r(M) = I_0 A C_f \phi(M) \epsilon(\lambda_e, M) V_s \cdot e^{-C_f \int_0^{L_s(M)} \epsilon(\lambda_e, r) dr} \quad (1)$$

98 where  $I_0$  is the output laser intensity,  $A$  is a constant which depends on the  
 99 optical set-up used to format the laser sheet,  $V_s$  is a small volume centred  
 100 around  $M$ ,  $L_s(M)$  is the length crossed by a laser beam before reaching point  
 101  $M$  (see figure 1),  $C_f$  is the concentration of fluorescent dye in the fluid assumed  
 102 identical at any point and  $\phi$  and  $\epsilon$  are the fluorescence quantum yield and  
 103 extinction coefficient of the dye respectively. These last two quantities vary  
 104 inside the fluid since they depend on local pH values. The above equation as-  
 105 sumes that fluoresced light re-absorption on the way to the sensor is negligible  
 106 (Lacassagne et al., 2018), and the present work is restricted to this assumption.

107 In single color methods a reference intensity field  $I_{r,ref}$  measured at an ho-  
 108 mogeneous and known pH,  $pH_{ref}$ , is used to normalize recorded intensity fields,  
 109 in order to account for non-homogeneity of  $I_0$  and Beer-Lambert absorption.  
 110 The non dimensional intensity at point  $M$  is then written

$$I^*(M) = \frac{I_r(M)}{I_{r,ref}(M)} = \frac{\phi(M) \cdot \epsilon(\lambda_e, M)}{\phi_{ref} \cdot \epsilon_{ref}} \cdot e^{-C_f \int_0^{L_s(M)} (\epsilon(\lambda_e, pH(r)) - \epsilon_{ref}) dr} \quad (2)$$

111 With  $\phi_{ref} = \phi(pH_{ref})$  and  $\epsilon_{ref} = \epsilon(\lambda_e, pH_{ref})$  the normalized quantum yield  
 112 and extinction coefficients respectively. For the sake of simplicity, the  $\lambda_e$  de-  
 113 pendency in the equations is dropped, as the laser source wavelength is most  
 114 of the time known, unique and fixed in PLIF applications. The equations for  
 115 the full fluoresced light spectrum are derived hereinafter, but similar equations  
 116 can easily be written for specific fluorescence wavelengths  $\lambda$  or spectral band.  
 117 One simply needs to replace  $\phi$  by  $S_\phi(\lambda)$  and if needed integrate the ex-  
 118 pressions over the chosen spectral band. It appears that in equation 2, laser  
 119 reference intensity  $I_0$  and the geometrical constant  $A$  have disappeared. How-  
 120 ever, the Beer-Lambert absorption term cannot *a priori* be cancelled out, since  
 121  $\epsilon(\lambda_e, pH)$  generally differs from  $\epsilon_{ref}$ . The expression of the received intensity  
 122 thus still depends on laser absorption conditions.

In the ratiometric case however, bands of polychromatic fluoresced light  
 are used instead of the full spectrum. The ratio  $R$  for fluoresced intensity  
 integrated over two spectral bands  $(\lambda_1^{inf}, \lambda_1^{sup})$  and  $(\lambda_2^{inf}, \lambda_2^{sup})$  is

$$R(\lambda_1^{inf}, \lambda_1^{sup}, \lambda_2^{inf}, \lambda_2^{sup}, M) = \frac{\int_{\lambda_1^{inf}}^{\lambda_1^{sup}} S_\phi(\Lambda, M) d\Lambda}{\int_{\lambda_2^{inf}}^{\lambda_2^{sup}} S_\phi(\Lambda, M) d\Lambda} \quad (3)$$

123 with  $S_\phi$  the "spectral" quantum yield of fluorescence. Demonstration of  
 124 equation 3 can be found in Lacassagne et al. (2018), where it is shown that the  
 125 ratio depends only on the pH (and thus on  $M$ ), and this ratio is monotonous  
 126 for well chosen spectral bands. In the present situation,  $L_s$  can be divided into  
 127 two parts:  $L_{ROI}$  which corresponds to the laser path inside the ROI, accessi-  
 128 ble to measurement, and  $L_{OR}$  which is the path in the outer region. Assuming  
 129 that laser beams are horizontal (weak laser sheet divergence) and the location  
 130 of the ROI kept constant, the path crossed in the OR does not depend on  $M$ .  
 131 The exponential terms in equation 2 can thus be separated and the equation  
 132 becomes:

$$I^*(M) = \frac{\phi(M) \cdot \epsilon(M)}{\phi_{ref} \cdot \epsilon_{ref}} \cdot e^{-C_f \int_0^{L_{OR}} (\epsilon(pH(r)) - \epsilon_{ref}) dr} \cdot e^{-C_f \int_{L_{OR}}^{L_{OR} + L_{ROI}(M)} (\epsilon(pH(r)) - \epsilon_{ref}) dr} \quad (4)$$

133 In conventional single color methods, both exponential terms of this  
 134 equation are neglected as a first approach. For non-optically thin systems,  
 135 it comes to assuming that the extinction coefficient stays close to its refer-  
 136 ence value during both calibration and the measurement steps. However in the  
 137 present case, the variations of  $\epsilon$  in the studied pH range are important, thus  
 138 this simplification leads, as will be shown below, to substantial errors.

139 When  $L_{OR} = 0$ , or  $L_{OR} \ll L_{ROI}$  with comparable absorption levels in the  
 140 OR and ROI, the first exponential term of equation 4 approaches unity. This  
 141 is the case where pixel-by-pixel calibration method as proposed by Valiorgue  
 142 et al. (2013) can be applied. The principle is to no longer use the measured  
 143 intensity but the normalized  $(\phi\epsilon)^* = \frac{\phi\epsilon}{\phi_{ref}\epsilon_{ref}}$  as an indicator of pH. Contrary

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144 to  $I^*$ , which depends on Beer-Lambert extinction of the laser intensity, the  
 145 normalized ( $\phi\epsilon$ ) quantity only varies according to the local pH.

146 In cases where  $L_{OR} \gg L_{ROI}$ , the pixel-by-pixel calibration fails at ac-  
 147 counting for absorption coefficient variation, as most of the laser absorption  
 148 occurs outside of the ROI, beyond the experimental reach. On the other hand,  
 149 one may assume that the absorption inside the ROI is negligible *versus* that  
 150 in the OR. This applies for example for experiments where  $L_{OR}$  is of the or-  
 151 der of 10 cm or 1 m, and  $L_{ROI}$  of the order of 1 cm, with similar phenomena  
 152 occurring in OR and ROI regions. The first exponential term of equations 4 is  
 153 no longer close to unity, but the second exponential term is, and the correc-  
 154 tion method proposed below applies in that case. Indeed, in order to account  
 155 for OR variations of extinction coefficient, one needs information on the local  
 156 value of pH in the OR, which is precisely the quantity that is measured in the  
 157 ROI. A way of getting around this problem is to rewrite the exponential term  
 158 of equation 2 as

$$e^{C_f \int_0^{L_{OR}} (\epsilon(r) - \epsilon_{ref}) dr} = e^{C_f L_{OR} (\bar{\epsilon} - \epsilon_{ref})} \quad (5)$$

159 where  $\bar{\epsilon}$  is the average extinction coefficient along  $L_{OR}$ . Its value depends on  
 160 the concentration statistics. In the case depicted in figure 1 (as in Lacassagne  
 161 et al. (2022)), the beams propagation and thus the  $r$  direction is horizontal,  
 162 noted  $r \equiv x$ , and scalar quantities vary along the vertical direction  $z$ . As a  
 163 first order approximation, one may write that

$$\bar{\epsilon}(z, t) = f(\bar{C}(z, t)) \quad (6)$$

164 where  $C$  is the pH dependent scalar quantity, in that case dissolved carbon  
 165 dioxide concentration, which itself influences the local  $\epsilon$  values. The over-bar  
 166 symbol denotes a width averaged profile of the extinction coefficient (along  
 167 the laser path-line), leaving only a depth ( $z$ ) and time ( $t$ ) dependency. All  
 168 that is needed is then an information on the (instantaneous) mean concen-  
 169 tration profile in the boundary layer, as  $\epsilon$  directly depends on  $C$ . In what  
 170 follows, instantaneous concentration profiles obtained from ratiometric mea-  
 171 surements will be used to try and correct single color measurements of the  
 172 same experiment.

### 173 3 Experiments

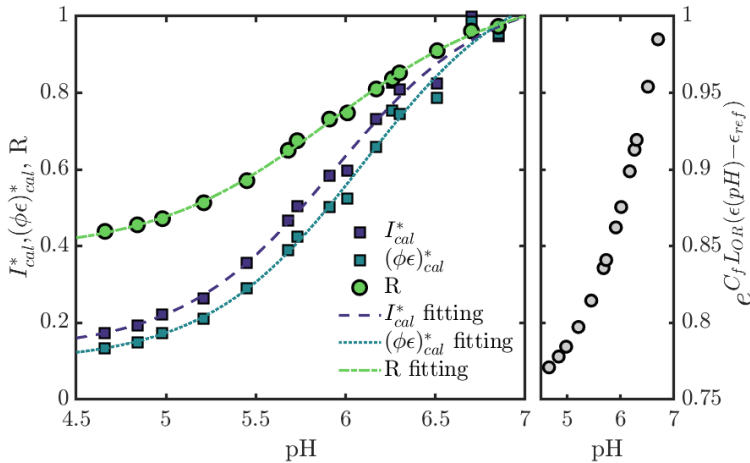
174 The experiments reported in Lacassagne et al. (2022) consisted in pure gaseous  
 175 carbon dioxide dissolving in a liquid phase from a flat horizontal interface,  
 176 under the action of turbulence in the liquid phase (figure 1 c, schematic rep-  
 177 resentation, not to scale). The ROI was located at the center of a large tank,  
 178 and the ROV was wide as the surface of exchanges. An empirical correla-  
 179 tion between dissolved gas concentration and pH was  $C = Ae^{-BpH}$  with  
 180  $A=1.55 \times 10^{11}$  mg/L and  $B = 4.63$  (from Lacassagne (2018); Lacassagne et al.  
 181 (2022)).

182  $I_{pH} - PLIF$  (using the full fluorescence spectrum) and  $I_{pH}^r - PLIF$ , with  
 183 the same spectral bands as used in Lacassagne et al. (2018) were used to collect  
 184 fluoresced light intensity fields. The fluorescent dye was fluorescein disodium  
 185 salt at a concentration of  $C_f = 5.10^{-7}$  M. Fluorescence was triggered by a  
 186 Stabilite 2017 Argon-Ion Continuous Wave Laser (CWL) and recorded by a  
 187 Lavisision 2560 by 2160 sCMOS sensor equipped with a 105 mm focal length  
 188 Macro lens. For  $I_{pH} - PLIF$  measurements, the lens was only equipped with  
 189 a long-pass filter to suppress the fluorescence excitation wavelength. For  $I_{pH}^r -$   
 190  $PLIF$  measurements, an image doubler was added in front of the lens. One  
 191 "eye" of the doubler was equipped with a 515 nm bandpass filter (band 1:  
 192  $\lambda_1^{inf} = 510$  nm,  $\lambda_1^{sup} = 520$  nm), and the other with a 560 nm cut-off long-  
 193 pass filter (band 2:  $\lambda_2^{inf} = 560$  nm,  $\lambda_2^{sup} \rightarrow +\infty$ ). The shutter time was  
 194  $dt_f = 10$  ms.

195 Due to the central location and small size of the ROI with respect to the  
 196 tank in the experiments, PLIF measurements were performed in the situation  
 197 described in figure 1 c:  $L_{OR} = 12$  cm and  $L_{ROI} = 2$  cm: the system cannot  
 198 be considered optically thin, and laser excitation intensity received by a given  
 199 point of the ROI was conditioned by Beer-Lambert absorption. This absorption  
 200 depended on dissolved gas structures encountered by the laser on its path,  
 201 inside and outside of the ROI, because the absorption coefficient on fluorescein  
 202 sodium depends itself on the pH, which in turn depends on the dissolved  
 203 gas concentration to be measured. Concentrations measured by the two-color  
 204 method and their statistics will be used as reference values, keeping in mind  
 205 that  $I_{pH}^r - PLIF$  is also subject to measurement errors as discussed extensively  
 206 in Lacassagne et al. (2018).

207 Hereinafter, two single color procedures are applied. Firstly the Standard  
 208 procedure **S** assumes that  $e^{C_f L_s (\epsilon(pH) - \epsilon_{ref})} = 1$  during both the calibration and  
 209 measurement steps. It is the fastest single color method in terms of processing  
 210 time, since it only requires the normalization of calibration and measurement  
 211 images by a unique reference image recorded at an homogeneous and known  
 212 pH. It is also the most frequently encountered in the literature. It is however  
 213 expected to lead to significant errors, since the variations of extinction coeffi-  
 214 cient are neglected. Single-color PLIF is applied using that of the two available  
 215 fluorescence signals with the best signal-to-noise ratio. Similar results have  
 216 been obtained using the lower intensity spectral band, with yet a higher noise  
 217 level. Secondly, the Standard procedure accounting for absorption in the outer  
 218 region, labelled **Sa**, consists in applying equations 4 and 5, neglecting absorp-  
 219 tion inside the ROI, and using the mean concentration profile obtained from  
 220 ratiometric measurement as an input data (equation 6). In doing so, one as-  
 221 sumes that scalar fields in the ROI and OR are comparable, and that the ROI  
 222 is large enough with respect to the scalar structure so that it provides first  
 223 order concentration statistics that are representative of the whole ROV and  
 224 thus of the OR. In other words, the hypothesis is that the concentration field  
 225 is statistically homogeneous along the beam penetration direction, and in so,  
 226 the mean concentration values have to be the same along this direction. These





**Figure 2** Calibration curves for single color methods S and Sa, and for the ratiometric method R. Markers are points measured from calibration images for respectively  $I_{cal}^*$ ,  $(\phi\epsilon)_{cal}^*$  and R. Dashed and dotted lines are hyperbolic tangent fittings. The exponential corrective factor  $e^{C_f L_{OR}(\epsilon(pH) - \epsilon_{ref})}$  is plotted versus pH in subfigure b.

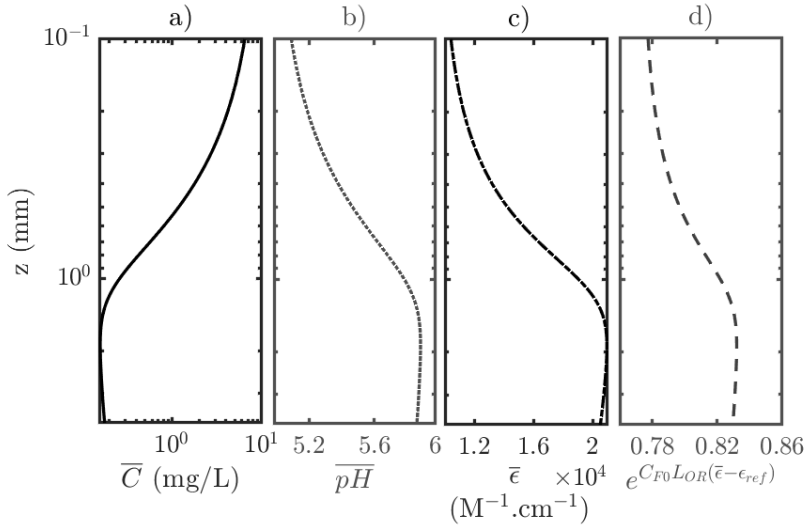
227 two procedures are tested on one single arbitrarily chosen instantaneous field  
 228 ( $t=200$  s), and compared to the ratiometric procedure **R**, also performed on  
 229 the same instantaneous data. A similar analysis has been performed for the S  
 230 and Sa procedures on other instantaneous fields and led to the same conclu-  
 231 sions. Calibration images were recorded at several homogeneous pH values (see  
 232 figure 2). The same processing (S, Sa or R) was applied to calibration images  
 233 to derive the intensity or ratio *versus* pH calibration relationships.

## 234 4 Results

235 Figure 2 shows calibration curves for the S, Sa and R methods. Markers are  
 236 measured points and lines are hyperbolic tangent fittings. It appears that the  
 237  $(\phi\epsilon)_{cal}^*$  relative values are lower than  $I_{cal}^*$  values, especially at low pH. Indeed,  
 238 taking  $\epsilon_{ref} = \epsilon(7)$ , the difference  $\epsilon(pH) - \epsilon_{ref}$  is negative since the absorp-  
 239 tion coefficient decreases with decreasing pH (see figure 2, Klonis and Sawyer  
 240 (1996)). The OR exponential correction term computed from equation 4 here  
 241 ranges from about 0.75 to unity at pH=7 (figure 2 b).

242 Absorption in the outer region is predicted from ratiometric concentration  
 243 measurements. The mean concentration profile  $\bar{C}(z,)$  obtained is turned into  
 244  $\bar{pH}(z)$  using the previously established pH-C calibration.  $\bar{pH}(z)$  is translated  
 245 into  $\bar{\epsilon}(z)$  thanks to hyperbolic tangent fitting of the literature data for epsilon  
 246 (Lacassagne et al., 2018), and the exponential factor  $e^{C_f L_{OR}(\bar{\epsilon}(z) - \epsilon_{ref})}$  can be  
 247 computed as a function of z.

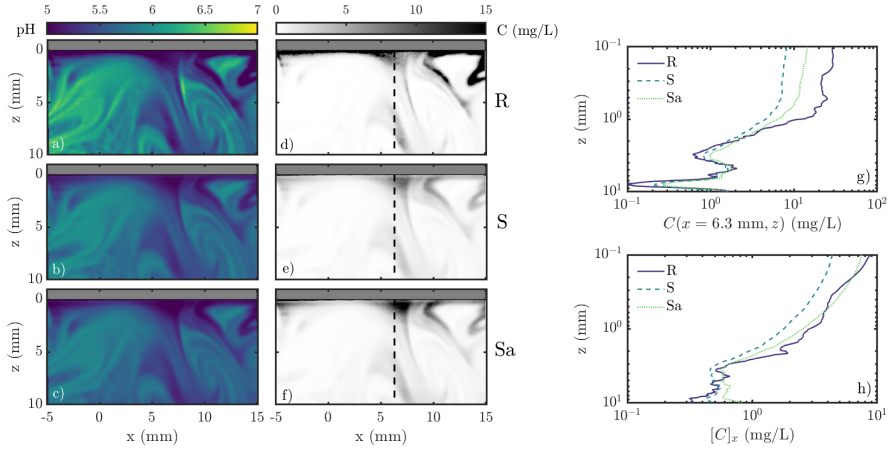
248 All these profiles are shown respectively in figure 3 a), b), c) and d), in  
 249 log scale z axis and log scale concentration values for sub-figure a). Dissolved



**Figure 3** Correction of the outer region absorption based on ratiometric measurement of  $\bar{C}(z, t)$ , with  $t=200$  s. a) is  $\bar{C}$  profile in log-log scale. b)c)d) are profiles for  $\overline{pH}$ ,  $\bar{\epsilon}$  and  $e^{C_{F0}L_{OR}(\bar{\epsilon}-\epsilon_{ref})}$  respectively,  $z$  in log scale.

250 gas concentration in the OR leads to correction factors between 0.75 and 0.85,  
 251 even at the greatest depths where concentration is minimum. In other words,  
 252 accounting for OFA leads to downgrade by up to 25% the measured fluoresced  
 253 light intensity values. It should yet be noted that this correction factor has to be  
 254 considered together with the one on calibration curves: during the calibration  
 255 process, pH is homogeneous in the tank so no such profile exists, however,  
 256 the OR absorption for the lowest calibrated pH values is smaller than the OR  
 257 absorption for the higher ones. This explains the difference in the  $I_{cal}^*$  and  
 258  $(\phi\epsilon)_{cal}^*$  curves in figure 2.

259 Looking now at instantaneous in-flow measurements, the concentration and  
 260 pH fields in figure 4 are visually very similar. This shows that scalar fields  
 261 are qualitatively well captured by all methods. However, it appears that the  
 262 S method underestimates concentration levels, especially at high concentra-  
 263 tions. Correction of outer region absorption makes Sa fields more similar to R  
 264 fields even if some scalar structures still seem of lower concentration in the Sa  
 265 picture than in the R one. pH fields from single color methods never display  
 266 values higher than 6.5 while the reference pH=7 is reached at some regions  
 267 of the field obtained from ratiometric measurement. This however does not  
 268 impact much concentration levels since pH between 6.5 and 7 correspond to  
 269 low concentration values (lower than  $10^{-1}$  mg/L here). pH fields S and Sa  
 270 are visually difficult to compare: variations are of about 0.1 to 0.2 pH units. Yet  
 271 because of the exponential link between pH and concentration this leads to  
 272 important differences in terms of local concentration values.



**Figure 4** Comparison of pH (a,b,c) and concentration (d,e,f) fields obtained by R (a,d), S (b,e) and Sa (c,f) methods, and comparison of g) local ( $x=6.3$  mm, vertical dashed lines) and h) width averaged concentration profiles along depth, obtained by all three methods, in log-log scale.

273 The final comparison is made by extracting concentration profiles along  
 274 depth at a given  $x$  value, here  $x=6.3$  mm (figure 4 g)), and by computing the  
 275 width averaged concentration profile over the ROI (figure 4 h)). Local profiles  
 276 at  $x=6.3$  mm confirm that single color measurements yield lower concentration  
 277 values than the ratiometric one. Correction of the OR absorption allows to in-  
 278 crease the measured concentration values but not exactly up to those measured  
 279 by the R method. However when averaging over the ROI's width, it appears  
 280 than the  $[C]_x$  values obtained by the Sa method are similar to those obtained  
 281 by the R method. Last but not least, the shape of the concentration profiles  
 282 are unaffected by the method used to estimate them. Concentration values  
 283 vary, but not their evolution with depth. It is of great interest since it implies  
 284 that single color measurements can still be used for qualitative comparison of  
 285 concentration structures and profiles with ratiometric measurements.

## 286 5 Conclusions

287 The use of single color PLIF without any specific correction in a condition  
 288 where absorption occurs outside of the ROI globally leads to slightly over  
 289 estimate pH values and ultimately to a significant under estimation of concen-  
 290 tration values. This can be explained in the following way. During calibration,  
 291 images are recorded in conditions that are somehow different from the mea-  
 292 surement conditions: with a pH homogeneous over the full laser path in the  
 293 fluid. During the experiment, the laser beam at a given depth  $z$  sees an aver-  
 294 age absorption value  $\bar{\epsilon}$  defined by the mean concentration profile, hence by the  
 295 measured phenomena. Because of the presence of the boundary layer and of  
 296 high concentration scalar patches (figure 4), this average absorption is always

297 smaller than the reference one, if the reference is chosen constant at higher pH,  
 298 and excitation beams reach the ROI at a higher intensity level than expected  
 299 from the intensity calibration images  $I_{cal}^*$ . Neglecting extinction coefficient  
 300 variations in the OR thus comes to interpret higher recorded intensity levels  
 301 as being caused by higher local pHs (and lower dissolved gas concentrations,  
 302 here), whereas they are in fact due to an increased local excitation intensity.

303 A notable result is yet that this under-estimation does not affect the spa-  
 304 tial distribution of concentration structures or profiles along depth. It only  
 305 changes the magnitude of the concentration. To that extend, while the accu-  
 306 racy of single color methods for quantitative measurements can be questioned,  
 307 they can still be used for analysing of the shape of scalar structures, and of  
 308 qualitative evolution of scalar and mass flux statistics in space.

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