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Turbulent mass transfer near gas-liquid interfaces in water and shear-thinning dilute polymer solution

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Abstract

Turbulence is known to enhance gas-liquid mass transfer and mixing of high Schmidt number dissolved gases in water by deforming the concentration boundary layer that develops at the interface. Fundamental mechanisms of surface renewal and injection have been progressively evidenced throughout the last decades, *via* fundamental experiments of low mean shear turbulence interacting with flat interfaces in water. However, and despite the obvious influence of non-Newtonian behaviours on gas liquid mass transfer in industrial and environmental applications, not such study exists (to the best of the author's knowledge) on whether and how these mechanisms apply in shear-thinning dilute polymer solutions (DPS). Following a previous work on near surface hydrodynamics, turbulent mass transfer and mixing is studied in a weakly shear-thinning fluid, and compared to the Newtonian, water case. Stereoscopic Particle Image Velocimetry (SPIV) and Inhibited Planar Laser Induced fluorescence are used simultaneously to measure the local liquid phase velocity and dissolved gas concentration fields respectively. Coupled measurements are used to estimate the turbulent mass fluxes, which are interpreted using a conditional quadrant analysis. Results show that in DPS as well as in water, surface renewal is the most frequent mechanism, but injection events are the most efficient in terms of mass transfer. Even

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at a low concentration, the polymer significantly modifies the signature of those mass transfer events, by enhancing scalar stretching and injection mass transfer outside of the viscous sub-layer, altering classical gradient models.

Keywords: Turbulence, mass transfer, shear-thinning, PIV, PLIF, quadrant analysis

1. Introduction

Turbulence is known to be a highly efficient enhancement mechanism for mixing and mass transfer between phases. In particular, liquid side turbulence has been shown to enhance air-water mass transfer of low diffusive atmospheric gases at interfaces, by locally deforming the liquid side concentration boundary layer [1, 2, 3]. Local, near-surface, mixing mechanisms occur in thin sub-layers under the interface, typically of 1 cm to less than 1 mm. They have been investigated for several decades, but the question of their depiction is arduous to tackle, both numerically and experimentally, because of the small scales involved. Studies have so far focused mostly on air-water interfaces, clean [4, 5, 6, 7, 8] or polluted [9, 10]. Despite the numerous industrial processes involving turbulent gas-liquid mass transfer in complex fluids (see e.g. [11],[12]) local mass transfer events and near-surface turbulence have never been measured in non-Newtonian media. Here, focus is made on the case of a low liquid phase diffusivity atmospheric gas, carbon dioxide, frequently encountered in industrial and environmental applications. Indeed, capture and storage of carbon dioxide is a crucial challenge for industrial and environmental process aiming at an increased sustainability [13, 14, 15], and many of such process involve flows of liquids with complex rheologies [15, 16].

The aim of this work is to provide a first experimental observation of near-surface turbulence-induced mass transfer and mixing in a non-Newtonian, moderately shear-thinning fluid, in the few millimetres underneath a flat gas-liquid interface. The gas is dissolving from an over saturated gaseous phase at rest towards a complex liquid phase, at initially zero concentration, stirred by bulk turbulence. The simplified case of a flat horizontal interface is studied in order to visualize fundamental mass transfer mechanisms at small scales. Spatially and temporally synchronised application of stereoscopic particle image velocimetry (SPIV) and planar laser induced fluorescence (PLIF) allows to measure coupled liquid phase velocity fluctuations and dissolved gas

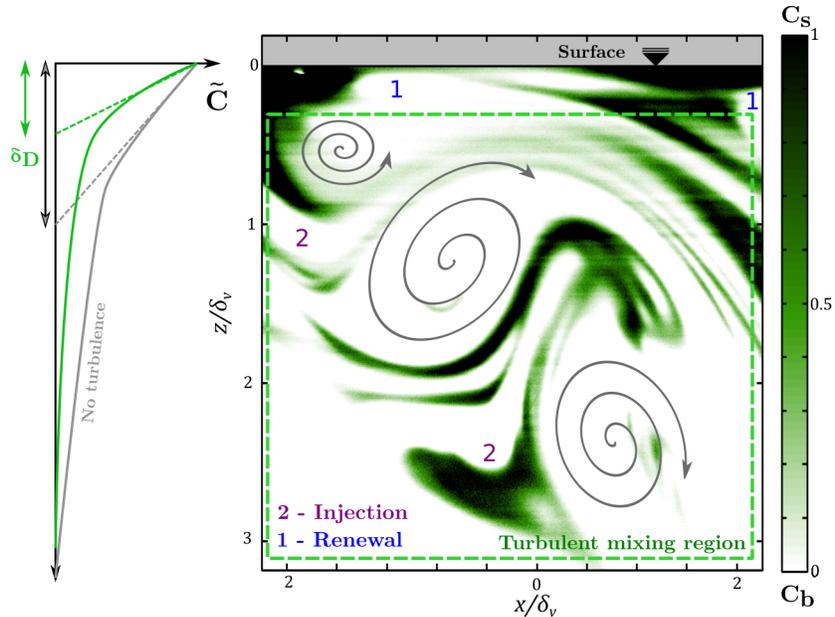


Figure 1: Principles of turbulent mass transfer at a flat interface. Left: contraction effect of the apparent diffusive boundary layer in presence of turbulence. Right: illustration of surface renewal and peeling/injection events and of the typical scalar sub-layers, from PLIF measurements presented hereinafter.

31 concentration fluctuations, and thus access local turbulent mass fluxes. Con-
 32 ditional quadrant analysis of mass fluxes leads to the accurate observation
 33 and description of mass transfer mechanisms near the gas-liquid interface,
 34 and how they are affected by the shear-thinning rheology. First order gradi-
 35 ent modelling is developed in order to obtain values of eddy diffusivity and
 36 characteristic time coefficients.

37 2. Background

38 In a liquid phase in contact with an over-saturated gas phase, the concen-
 39 tration C of a dissolved species varies exponentially between its interfacial
 40 value C_{sat} and the bulk value C_b far from the interface, according to Fick's
 41 laws of diffusion. One may write

$$\tilde{C}(z, t) = \frac{C(z, t) - C_b(t)}{C_{sat}(t) - C_b(t)} = e^{-z/\delta_D} \quad (1)$$

42 where $\tilde{C}(z, t)$ is the concentration normalised by saturation and bulk concen-
 43 trations, t is the time and z the distance from the interface (here the depth
 44 below the flat horizontal interface, see fig 1).

45 Assuming a negligible resistance to mass transfer on the gas side, the
 46 saturation value is fixed by the partial pressure of the same species in the
 47 gaseous phase p^* according to Henry's law $p^* = H_{c,i}C_{sat}$ [17]. Resistance to
 48 mass transfer on the liquid side is expressed by the δ_D parameter: the appar-
 49 ent diffusive layer depth, or liquid film. This sub-layer accounts for diffusion
 50 but also advection mechanisms. In cases with no liquid side motion, this
 51 sub-layer is simply equivalent to a purely diffusive sub-layer. The liquid side
 52 mass transfer efficiency/velocity is defined $k_L = \frac{D}{\delta_D}$ is with D the molecular
 53 diffusion coefficient of the dissolved gas in the aqueous medium considered
 54 [18], with here $D = 1.90 \times 10^{-9} \text{ m}^2.\text{s}^{-1}$ for carbon dioxide in water at 20°C.
 55 The relative effects of momentum diffusion over molecular diffusion are quan-
 56 tified by the Schmidt number $Sc = \nu/D$ with ν the kinematic viscosity of the
 57 fluid.

58 For high Schmidt number (low diffusivity) phenomena, flow structures
 59 may deform, contract or stretch the local diffusive layer δ_D . What is known
 60 of turbulence action on dissolved gas at the interface can thus be summarized
 61 as follows (see figure 1). A turbulent eddy coming from the bulk enters the
 62 surface influenced region and is deformed by surface action [4, 5, 19]. If its
 63 typical size is large compared to the apparent scalar sub-layer depth, it mainly
 64 contracts the scalar sub-layer thus sharpening the concentration gradient
 65 and increasing mass transfer. This is the picture of the film model by [18].
 66 Smaller eddies however have the ability to peel the diffusive film and send
 67 saturated fluid downwards, while replacing it with fresh fluid brought from
 68 the bulk. Under-saturated fluid being brought at the interface, concentration
 69 gradients are increased making the boundary layer δ_D thinner and enhancing
 70 near surface diffusion. This is the principle of surface renewal or film renewal
 71 [20, 21, 6]. This renewal is associated with a complementary mechanism [22,
 72 1, 23, 2]: injection/peeling events of the boundary layer by velocity structures
 73 resulting in the injection of saturated fluid inside the bulk where i) diffusion
 74 is thus enhanced and ii) multi-scale turbulent mixing becomes dominant.
 75 The wide range of turbulent structure sizes and the various ways eddies can
 76 interact with the scalar boundary layer result in an intricate combination
 77 of surface renewal and injection events responsible of global turbulent mass
 78 transfer.

79 The influence of turbulence on gas-liquid mass transfer and the depths at

80 which it is relevant thus needs to be understood in light of the behaviour of
 81 turbulence approaching the interface. In water, the interactions between an
 82 horizontal free surface and upcoming bulk turbulence are usually character-
 83 ized using two "undisturbed" scales of turbulence [24, 5]: the horizontal inte-
 84 gral length scale L_∞ and horizontal velocity fluctuations (root mean square
 85 value) u' . These are the values that would be found at the interface location
 86 if there were no interface, obtained by extrapolation of the bulk turbulence
 87 scaling laws [25]. They thus depend on the bulk turbulence properties only.
 88 The depth at which turbulence begins to "see" the interface is called the
 89 surface-influenced layer, and is assumed to be about the size of one integral
 90 length scale of the upcoming bulk turbulence L_∞ [4, 5, 6]. Velocity dynamics
 91 in the surface-influenced layer is mostly independent of the surface boundary
 92 condition, and the theory of [4] applies equally well to clean, contaminated
 93 and no-slip surfaces up to a certain proximity with the interface [26], which
 94 is in turn defined by another smaller typical depth: the viscous sub-layer
 95 δ_v , scaling as $\delta_v = L_\infty Re_T^{-0.5}$ [5, 27]. Here Re_T is the turbulent Reynolds
 96 number at the interface expressed as $Re_T = \frac{\rho u' L_\infty}{\mu}$, with ρ and μ the density
 97 and dynamic viscosity respectively. This sub-layer is defined as the depth
 98 from which an eddy adjusts to the boundary condition set by the interface by
 99 viscous effects. For turbulent mass transfer of high Schmidt number gases at
 100 non negligible Reynolds number, the characteristic scalar depth δ_{OD} is typi-
 101 cally smaller than the viscous sub-layer depth δ_v : most of the events relevant
 102 for mass transfer occurs within the viscous sub-layer.

103 In a recent work [19], the liquid phase velocity data of the present set
 104 of measurements presented has been used to extend this description to the
 105 case of shear-thinning dilute polymer solutions (DPS). A correlation for the
 106 evolution of the viscous sub-layer depth in the dilute regime of shear-thinning
 107 inelastic xanthan gum (XG) solutions has been derived. The increase of the
 108 viscous sub-layer depth was smaller than what could be expected from the
 109 increase in zero shear rate viscosity, and better correlated to the value of
 110 the infinite-shear viscosity. In what follows, comparison is made between a
 111 Newtonian case and a shear-thinning case with comparable Reynolds number
 112 and viscous sub-layer depth. In that way, scalar and mass transfer events can
 113 be compared between the Newtonian and shear-thinning case for equivalent
 114 hydrodynamic conditions of up-coming turbulence.

115 It should also be mentioned that the influence of non-Newtonian prop-
 116 erties on turbulent or non-turbulent mass transfer can be found addressed

117 from a global, process oriented point of view in the literature, where studies
 118 try to relate the evolution of global mass transfer parameters such as the
 119 volumetric mass transfer coefficient $k_L a$, to dimensionless numbers describ-
 120 ing the non-Newtonian properties of the flow. This has been done on a large
 121 variety of two phase flows, among which aerated stirred tanks [28, 29, 30, 11]
 122 and bubble columns [31, 12, 32], to cite a few. The fundamental limitation in
 123 these configurations is that mass transfer depends on both the mass transfer
 124 velocity k_L but also on the interfacial area a , both of which are modified by
 125 non-Newtonian properties: hydrodynamics of the liquid phase act on the gas
 126 phase properties, that is to say the bubble size, size dispersion, rising velocity,
 127 or residence time [28, 32] making it difficult to disentangle the two effects and
 128 isolate from such studies the effects of turbulence and non-Newtonian fluids
 129 on mass transfer velocity and mixing alone. This is why fundamental, local,
 130 flat surface experiments are essential first steps to the better understanding
 131 of non-Newtonian turbulent mass transfer.

132 3. Materials and methods

133 3.1. Shear-thinning polymer solutions

134 Distilled water and a dilute solution of XG (10 ppm concentration, $M_w =$
 135 3.4×10^6 g.mol⁻¹, polydispersity close to 1.12 [33]) are used as the New-
 136 tonian and shear-thinning fluid, respectively. XG yields clear aqueous non-
 137 Newtonian solutions suitable for the use of optical methods metrology, and
 138 is here chosen for its high resistance to strong shears and extreme pH condi-
 139 tions [34]. Such features are necessary when using it in the oscillating
 140 grid apparatus, in which strong local shear may be experienced by polymer
 141 chains nearby the grid, and when dissolving carbon dioxide in the liquid
 142 phase, a process during which the pH may decrease to acidic values. The
 143 polymer concentration is chosen well inside the dilute regime [35, 25]. It
 144 is assumed that the diffusion coefficient of carbon dioxide in the aqueous
 145 medium is not modified by the presence of the polymer chains in this dilute
 146 concentration limit [36]. The weak shear-thinning behaviour of such a so-
 147 lution is measure on an Anton-Paar MC302 rheometer and modelled by a
 148 Carreau-Yasuda equation $\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = (1 + (t_{CY} \dot{\gamma})^m)^{\frac{n-1}{m}}$ with $\mu_0 = 1.30$ mPa.s
 149 the zero shear rate viscosity, $\mu_\infty = 0.99$ mPa.s the infinite shear rate New-
 150 tonian plateau, $t_{CY} = 0.08$ s the characteristic time scale of the polymer,
 151 $n-1 = -0.4$ the shear-thinning power law exponent, and $m = 2$ the transition
 152 parameter. Viscoelasticity is checked to be negligible at this concentration

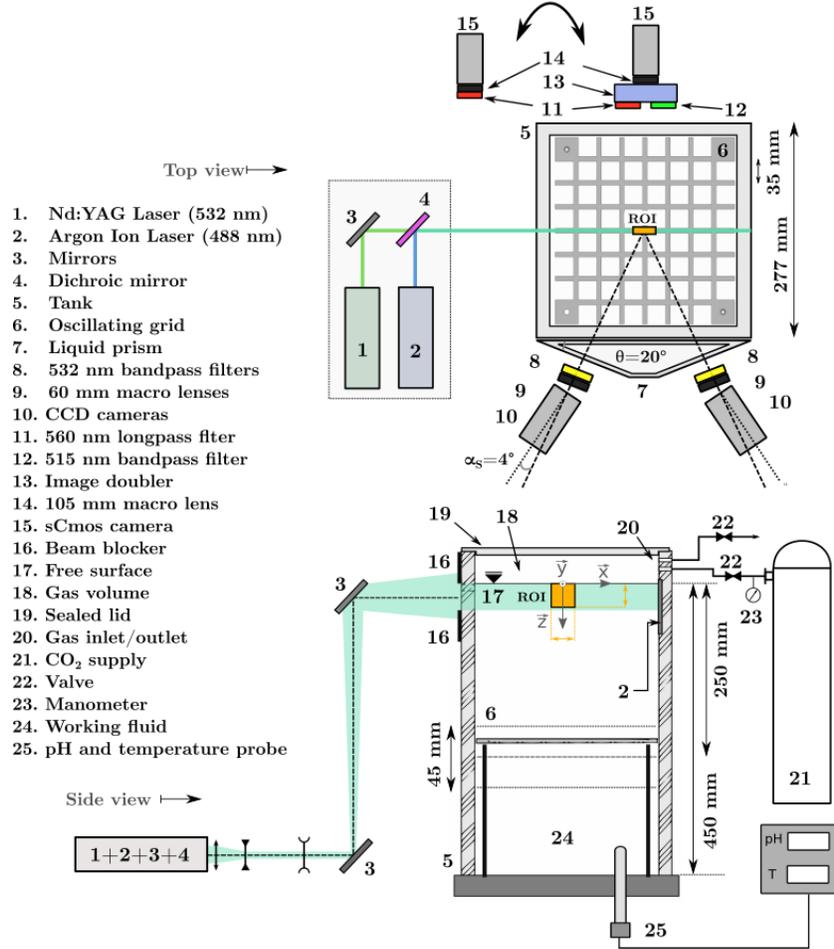


Figure 2: Sketch of the experiment set-up for coupled measurements.

153 [35, 25]). Moreover, in the context of the near surface turbulence results
 154 [19], this low concentration allows for comparable viscous sub-layer depth
 155 and turbulence properties within the viscous sub-layer between water and
 156 XG solution, and hence the mass transfer events are compared in equivalent
 157 hydrodynamic conditions. Here the viscous sub-layer depth is 5.10 mm for
 158 water and 5.64 mm for the DPS case (see table 1).

159 3.2. Turbulence generation

160 Turbulence is generated in the liquid phase by an oscillating grid device
 161 previously described and used in [25, 37, 19, 38, 39], and sketched in figure 2.

162 The transparent tank has a 277 mm by 277 mm inner cross section, the fluid
 163 height is set at $H=450$ mm and the distance between the surface and the
 164 average grid position is 250 mm. The grid oscillations frequency is $f=1$ Hz
 165 and the Stroke (amplitude) is 45 mm. A Cartesian squared-meshed grid is
 166 used, the grid mesh size (distance between the center of two successive grid
 167 bars or holes) being 35 mm (see figure 2). With the very dilute solution
 168 considered here, the mean flow structure and mean flow to turbulence ratio
 169 are close to that achieved in water, and the mean flow is considered weak
 170 enough not to affect our local mass transfer study [25]. When the grid is
 171 oscillated, the flat surface hypothesis is verified up to sub-millimetric vertical
 172 oscillations of the surface (about 1.5 % of the viscous sub-layer depth) caused
 173 by the in and out motion of the grid supporting rods [19]. Special care is
 174 taken to ensure that both the water and DPS experiments are performed in
 175 clean interface conditions (see [19]). The undisturbed velocity and length
 176 scales are estimated from [25, 19] and reported in table 1. The table also
 177 shows the corresponding values of the interface Reynolds number based on
 178 the maximum viscosity, $Re_T = \frac{\rho u' L_\infty}{\mu_0}$. Note that Re_T slightly decreases
 179 in the polymer case, mostly because it is defined on μ_0 , which may not
 180 be a representative viscosity of the flow [19]. The Deborah numbers based
 181 on the shear-thinning time scale t_{CY} and on the grid oscillations period is
 182 $De = t_{CY} f = 0.08$.

183 3.3. Concentration and velocity measurements

184 3.3.1. Methods

185 Dissolved CO_2 concentration fields are measured using fluorescein-based
 186 inhibited fluorescence techniques: $I_{pH} - PLIF$ [40]. For the DPS case, a
 187 ratiometric improvement of the method, $I_{pH}^r - PLIF$, described in [41], was
 188 also applied. This ratiometric method also allows to reduce noise and sys-
 189 tematic error of $I_{pH} - PLIF$ on quantitative measurements at high concen-
 190 tration values, very close to the interface (see [42], appendix G). The spatial
 191 scales and the shape of concentration structures are by no mean dependent
 192 on the method used. Hence for the purpose of the present work where only
 193 a qualitative and conditional analysis of the concentration field is required,
 194 the two methods are equivalent. Hereinafter and if not specified differently,
 195 all water and DPS results presented come from respectively $I_{pH} - PLIF$
 196 and $I_{pH}^r - PLIF$ measurements. In each case, fluorescein sodium concen-
 197 tration in the working fluid is $C_{Fl} = 5 \times 10^{-7}$ mol.L⁻¹. Fluorescence is
 198 triggered by a Stabilite 2017 Argon-Ion Continuous Wave Laser (CWL). The

Parameter	Water	DPS
μ (mPa s)	1.0	1.0-1.3
L_∞ (mm)	24.5	45.6
δ_v (mm)	5.10	5.64
Re_T	110	106-110
Sc	527	527-686
De	0	0.08
δ_D (mm)	0.50	0.20
$\delta_D^e = 2L_\infty Re_T^{-1/2} Sc^{-1/2}$ (mm)	0.25	0.34-0.38
$\delta_B^e = 2L_\infty Re_T^{-3/4} Sc^{-1/2}$ (mm)	0.063	0.11-0.12

Table 1: Hydrodynamic parameters and mass transfer sub-layers of the two working fluids. L_∞ and δ_v were determined in [19], by interpolation of bulk turbulence scaling [25] or directly measured, respectively. The expected apparent diffusive sub-layer δ_D^e and Batchelor sub-layer δ_B^e are computed as $\delta_D^e = 2L_\infty Re_T^{-1/2} Sc^{-1/2}$ and $\delta_B^e = 2L_\infty Re_T^{-3/4} Sc^{-1/2}$ respectively [22]. The experimental apparent diffusive layer δ_D is derived from measured concentration profiles (figure 3). For the DPS, Re_T , Sc , δ_D^e and δ_B^e are viscosity dependent: ranges based on maximum and minimum viscosity values are reported.

199 effective maximum output power is 0.6 W and the laser sheet thickness is
200 $e_{Ar} = 250 \mu\text{m}$. Fluoresced light intensity fields are recorded by a Lavision
201 sCMOS camera (2560 by 2160 pixel sensor) equipped with a 105 mm focal
202 length Macro lens. For $I_{pH} - PLIF$ measurements, the lens is only equipped
203 with a long-pass filter to suppress the PIV and fluorescence excitation wave-
204 lengths from measured intensities. For $I_{pH}^r - PLIF$ measurements, an image
205 doubler is added in front of the lens. One "eye" of the doubler is equipped
206 with a 515 nm bandpass filter, and the other with a 560 nm cut-off long-pass
207 filter. The camera is used in its single frame configuration with an opening
208 time of $dt_f = 10$ ms, and an acquisition frequency of $f_{acq} = 4$ Hz (bounded
209 by that of SPIV, [19]). Calibration procedures described in [40] and [41]
210 are respectively applied when using intensity (I) based $I_{pH} - PLIF$ or ratio
211 (R) based $I_{pH}^r - PLIF$. They both consist in recording sets of fluorescence
212 images at different homogeneous pHs in the region of interest (ROI), and
213 building either pixel by pixel $I=f(\text{pH})$ or unique $R=f(\text{pH})$ calibration curves
214 (available in appendix Appendix A), where I is the total fluoresced light in-
215 tensity and R the intensity ratio of two fluoresced light spectral bands (two
216 colours). Dissolved gas concentration versus pH equilibria in water are solved

217 numerically using Matlab (see [42]). For the small amount of polymer added,
 218 it is checked experimentally that the addition of XG does not modify these
 219 equilibria. The relationship between pH and dissolved gas concentration is
 220 $C = Ae^{-BpH}$ with $A=1.55 \times 10^{11}$ mg/L and $B = 4.63$. Using a method de-
 221 scribed in [41], the relative uncertainty on the ratio in for $I_{pH}^r - PLIF$ is
 222 estimated to be below 1.2%. The maximum relative uncertainty on pH is
 223 close to 1%, relative uncertainties on concentration are below 10% for $pH < 5$
 224 and $pH > 6.5$. As for the 1 color PLIF technique, relative uncertainties still
 225 fall below 5% in the same range, however additional errors due to reflection
 226 and darker stripes are introduced, which can multiply the uncertainty by a
 227 factor of 10.

228 Liquid phase velocity measurements in the vicinity of the interface are
 229 achieved by SPIV and have already been reported in [19], where all the ex-
 230 perimental details can be found. The experimental set-up is sketched in figure
 231 2. In this study, the velocity fields are revisited and analysed in combination
 232 with concentration fields. Spatial calibration of all cameras is performed by
 233 taking separate images of a LaVision standard reference pattern, and simul-
 234 taneous images of a transparent test pattern placed inside the fluid prior to
 235 the experiment. Concentration and velocity fields are coupled using a bin-
 236 ning procedure: the spatial resolution of the scalar field is reduced to that of
 237 the vector field by spatially averaging the concentration value in each SPIV
 238 interrogation window projected on the scalar field. In other words, SPIV
 239 sets the resolution limit the mass transfer study. Note that this "full average
 240 binning" [41] is slightly different from the "binning at center" method used
 241 by [2]: "full average" binning tends to reduce the noise associated to con-
 242 centration measurement by smoothing over a wider span than "binning at
 243 center", and is more consistent in terms of processing with SPIV, which is
 244 also window-based.

245 *3.3.2. Experimental protocol and definition of concentration statistics and* 246 *convergence*

247 The tank is first filled with the working fluid and fluorescein sodium is
 248 added. Dissolved carbon dioxide concentration is increased up to its gas
 249 saturation limit and the first PLIF calibration image (lower pH) is recorded.
 250 This concentration is then gradually decreased by nitrogen stripping, and
 251 calibration images are recorded for decreasing dissolved gas concentrations
 252 (higher pH) until the fluid is cleared from any dissolved carbon dioxide. The
 253 corresponding initial pH and dissolved gas concentration are measured, as the

254 initial condition of the experiment. Grid oscillations are started, followed by
 255 PIV and PLIF recording once the oscillating grid turbulence is established
 256 and stationary, and the volume of gas above the interface is instantly replaced
 257 by pure carbon dioxide (injection time <10 s). Rheological measurements
 258 are performed on the DPS before and after the experiments to check that no
 259 polymer degradation occurs.

260 Concentration fields are inherently transient: at a given point in the
 261 flow, concentration varies with time due to both diffusion acting on \overline{C} and
 262 turbulence causing c' , where \overline{C} denotes the mean concentration field (sta-
 263 tistical average) and c' the turbulent fluctuations. Statistical analysis of
 264 concentration fields would in principle require performing many trial in sim-
 265 ilar conditions, which is impracticable given the time and resource cost of
 266 each mass transfer experiment. The estimation of mean and fluctuating con-
 267 centrations from such transient measurements is thus rather done as in [2].
 268 The instantaneous concentration fields are first averaged over the horizontal
 269 dimension x (operator $[\cdot]_x$) into the quantity $[C(z, t)]_x$ (see figure 3). The
 270 expected concentration values $C_E(z, t)$ are then obtained by exponential fit-
 271 ting time series of $[C(z, t)]_x$ at all z with expressions of type $C_E(z, t) =$
 272 $k_c(z)(1 - e^{-k_{t1}(z)t - k_{t2}(z)t^2})$. $C_E(z, t)$ estimates the concentration that would
 273 be expected without the presence of turbulent scalar structures. It is as-
 274 sumed in the following that $C_E(z, t) \equiv [\overline{C}]_x(z, t)$, or in other words that the
 275 expected concentration is equivalent to a statistical average. Concentration
 276 fluctuations are subsequently defined as $c'(x, z, t) = C(x, z, t) - [\overline{C}]_x(z, t)$.
 277 With this definition, there is no need to demonstrate the statistical conver-
 278 gence of the mean concentration. The computation of second order statistical
 279 properties such as root-mean-square (rms) of concentration fluctuations (or,
 280 later, turbulent mass fluxes) is made on time intervals of 1050 s (between
 281 $t = 200$ s and $t = 1250$ s for water and between $t = 700$ s and $t = 1750$ s
 282 for DPS, see figure 3 c,d). The typical lifetime of a scalar event can be es-
 283 timated from the integral time scale (see section 4.1.4). Here the order of
 284 magnitude of integral time scale of concentration fluctuations is 10 s and so
 285 the time intervals used are at least 100 times greater than the typical scalar
 286 eddy turnover, which is deemed sufficient for statistical convergence.

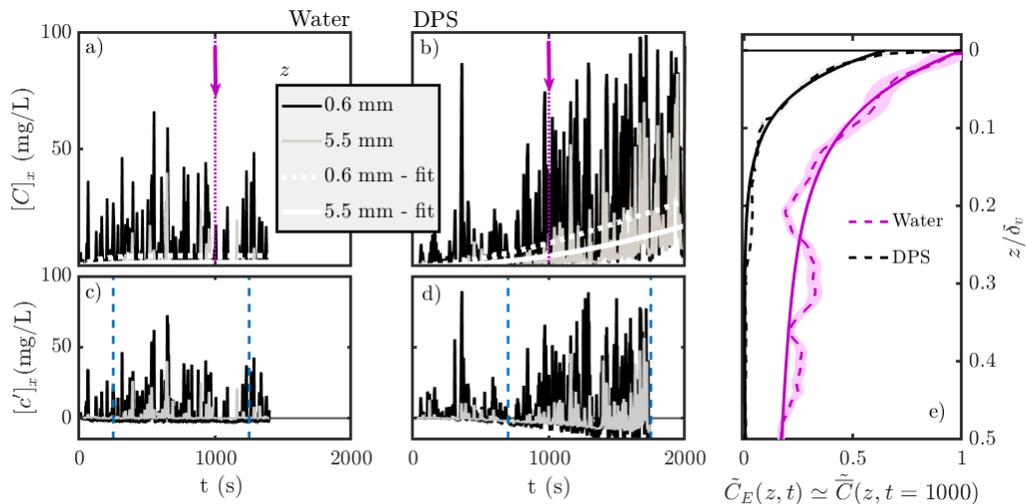


Figure 3: Time series of mean concentration (a,b) and of concentration fluctuations (c,d) for water (a,c) and DPS (b,c) respectively, at two different depths. e) Average concentration profiles at $t=1000$ s, dotted lines representing measured data and full lines the expected concentration fittings C_E .

287 4. Results and discussion

288 4.1. Scalar properties

289 4.1.1. Scalar structures

290 An example of instantaneous concentration field (in water) is shown in
 291 figure 1. The colors scale is for $(C - C_b)/(C_s - C_b)$ with C_b and C_s the
 292 bulk and interfacial values, of order 10^{-2} mg/L and 10^0 mg/L respectively
 293 (note that $C_s \leq C_{sat}$ as discussed below). Concentration is higher close to
 294 $z/\delta_v=0$ (location of the gas liquid interface) and decreases with increasing
 295 z . Between the interface and the bulk, a complex combination of high con-
 296 centration structures exists: these are characteristic of injection events. One
 297 also notices that the concentration near the interface can locally and instan-
 298 taneously be close to C_b , when highly concentrated fluid at the interface is
 299 replaced by fresh one coming from the bulk as part of the renewal mech-
 300 anism. Measurements in the purely diffusive case (no fluid motion) were
 301 not conducted in the present study. Indeed, when dissolved in a fluid at
 302 rest (in equivalent vertical configurations) dissolved carbon dioxide is known
 303 to trigger gravitational instabilities [43], which quickly disrupt the diffusive
 304 boundary layer, and would have made such measurements unsuitable for com-

305 parison. It is worth mentioning that the theoretical saturation concentration
 306 predicted by Henry’s law is here never measured in the ROI. Typical concen-
 307 trations at the smallest measurable depths ($z \simeq 200 \mu\text{m}$) only reach up to
 308 100 mg/L (fluctuating both in time and space for water and DPS), about 10
 309 times lower than the 1394 mg/L value given by Henry’s law. It is likely that
 310 Henry’s law saturated CO_2 concentration value were also not measured in
 311 sub-surface measurements of [2] and bubble-wake measurements of [40] (both
 312 using $I_{pH} - PLIF$) or in the works of [22, 1] on sub-surface oxygen dissolu-
 313 tion. This difference between the maximum measured concentration and the
 314 theoretical C_{sat} may be ascribed to the limited sensitivity PLIF techniques i)
 315 in the high concentration range (concentrations higher than about 100 mg/L,
 316 corresponding to pH lower than 4.5 that cannot be measured efficiently since
 317 fluorescence intensity levels at pH 4 and 4.5 are similar) and ii) the possibility
 318 for surface renewal and injection events to sweep concentration patches away
 319 from the interface before they have time to reach saturation concentration.

320 4.1.2. Concentration boundary layer

321 Example of near-surface ($z < 0.5\delta_v$) expected non-dimensional concentra-
 322 tion profiles $\tilde{C}_E(z, t)$ (see section 3.3.2) at $t=1000$ s are shown in figure 3 e),
 323 and fitted by an exponential function similar to equation 1) where C_{sat} is
 324 replaced by the apparent interfacial concentration $C_s(t)$. Shaded areas are
 325 $\pm 10\%$ uncertainty regions. From this sub-figure it appears that the appar-
 326 ent scalar boundary layer thickness δ_D is close to 0.5 ± 0.1 mm ($z/\delta_v=0.098$)
 327 for the water case, 0.25 ± 0.02 mm ($z/\delta_v=0.036$) for DPS (table 1) (uncer-
 328 tainties estimated from standard deviation over the statistically stationary
 329 range). Measured values are consistent with the range predicted by scaling
 330 laws [22] reported in table 1. However, relying on such "Newtonian" scaling,
 331 one would have expected δ_D to be larger in the DPS case. This is a first
 332 evidence that the non-Newtonian aspect of the fluid, even moderate, makes
 333 the DPS behaviour’s depart from the expected viscous Newtonian one.

334 4.1.3. Spatial scalar scales

335 Now investigating the spatial properties of turbulent scalar structures,
 336 the correlation coefficient of concentration fluctuations between two points
 337 separated by a distance r_i along spatial dimension i ($i = x, y$ or z), at a
 338 given depth z , is defined as $R_c^i(z, r_i) = \left[\frac{c'(r_i^0, z, t)c'(r_i^0+r_i, z, t)}{c'^2} \right]_x$. An example
 339 of correlation coefficients R_c^z plotted versus the separation length r_z along

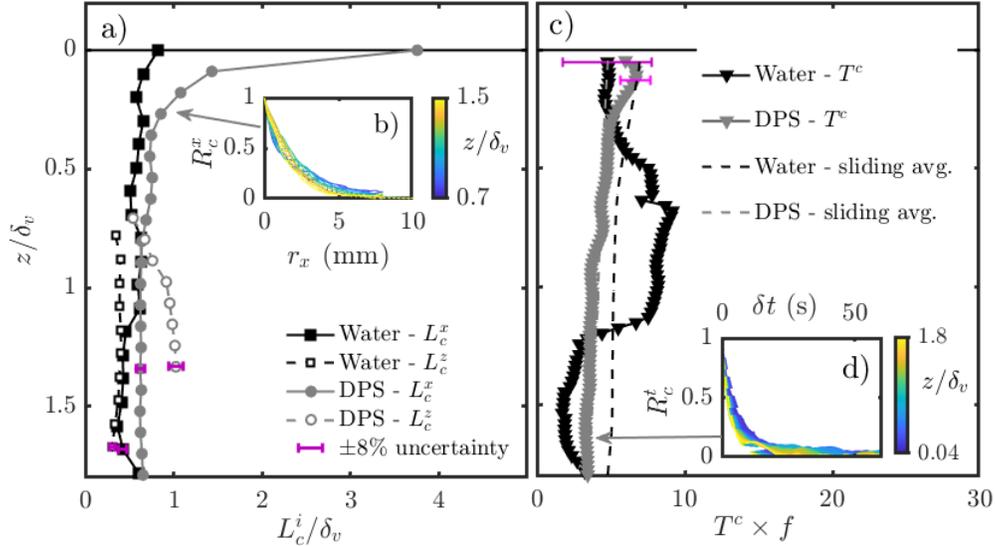


Figure 4: Spatial and temporal concentration integral scales, estimated from the integration of two-points and two-times correlation coefficients of concentration fluctuations, respectively. Spatial: integral length scales for water and DPS (a) and example of corresponding two point concentration correlation coefficient for DPS (b). Full markers are scales along the horizontal dimension, empty markers are scales along the vertical dimension. Full lines in the sub-figure are computed correlation coefficients, dashed lines are exponential fittings. Temporal: integral time scale for water and DPS (c) and example of the corresponding two times correlation coefficient for DPS (d). Time is made non dimensional multiplying by the oscillating grid frequency. Markers in c) are computed scales, dashed lines are sliding average of the computed scales over a 2 mm span ($\simeq 40\%$ of δ_v).

340 dimension z , for the DPS run, at different depths is shown in the insert of
 341 figure 4 b). Correlation curves are fitted by a sum of exponential functions
 342 and the spatial integral length scale for concentration along dimension z
 343 (vertical scale) obtained by integrating from $r_z=0$ mm to infinity. A similar
 344 process is applied to correlation coefficient along the horizontal direction x .
 345 Integral concentration length scale are plotted versus depth in figure 4 a) for
 346 both fluids. Vertical length scales are not computed at the smallest depth
 347 ($z/\delta_v < 0.7$) due to the size of the sampling region. The 5% confidence
 348 interval on exponential fittings is used to estimate a typical uncertainty of
 349 $\pm 8\%$ on length scales, illustrated by an error bar on one marker per curve
 350 (for readability).

351 Horizontal length scales L_c^x for water show scattering due to the single
 352 color LIF method employed. Nevertheless, it appears to be always greater
 353 than the vertical one, L_c^z . The latter stays approximately constant between
 354 $z/\delta_v = 0.8$ and $z/\delta_v = 1.4$ at a value around $L_c^z/\delta_v = 0.40$. In the same
 355 depth range, but also up to $z/\delta_v = 0.20$ the horizontal scale is $L_c^x/\delta_v \simeq 0.5$.
 356 For $z/\delta_v < 0.2$, L_c^x/δ_v increases up to its apparent maximum value of 0.84
 357 at $z/\delta_v = 0$. These trends imply that patches of turbulent concentration
 358 fluctuations are statistically larger in the horizontal dimension than in the
 359 vertical one in water at such depths. The increase of L_c^x near the interface
 360 is an evidence of the development of the scalar boundary layer, of depth
 361 δ_D under the interface. In this sub-layer, concentration patches appear in
 362 this two-dimensional view as large horizontal stripes of high concentration,
 363 partially and randomly broken by renewal events (see figure 1). At larger
 364 depths, concentration structures are stretched and deformed in an isotropic
 365 fashion by turbulence and the length scales in both dimensions tend to similar
 366 values with increasing depths, still with a preferential horizontal dimension
 367 inherited from the peeling process.

368 Similarities with water can be found for the integral length scales of the
 369 DPS: almost constant horizontal scale in most of the ROI, with an abrupt
 370 increase at small z , here for $z/\delta_v < 0.2$. In [19], an increase in the horizontal
 371 length scale of horizontal velocity fluctuations was observed in the near-
 372 interface region for 100 ppm DPS, consistent with the behaviour observed
 373 here. The depth at which L_c^x begins to increase is close to the outer-diffusive
 374 sub-layer depth δ_{OD} estimated from the mean concentration profiles. Both
 375 vertical and horizontal length scales are always higher in DPS than in water.
 376 The value of L_c^x/δ_v at the interface is 3.75, 5 times bigger than the one for
 377 water. A striking difference is yet that the vertical length scale is higher
 378 than the horizontal one at depths higher than $z/\delta_v = 0.80$. While it stayed
 379 quite constant with depth in water, it is here decreasing with decreasing z .
 380 DPS thus generally tends to increase the size of concentration patches in
 381 all dimensions: DPS has an increased viscosity compared to water, hence in-
 382 creased Kolmogorov and Batchelor scales. However, horizontal scalar patches
 383 that can be found in the boundary layer are statistically more horizontally
 384 elongated in DPS than in water: they are less likely to be broken by renewal
 385 events. Renewal rather takes the form of a contraction of the scalar bound-
 386 ary layer with partial replacement of the saturated fluid from the bottom of
 387 the boundary layer. Strong sweeping events locally replacing saturated fluid
 388 up to $z=0$, and leading to a split of the boundary layer are seemingly less

389 frequent in DPS than in water. Outside of the scalar boundary layer, the
 390 presence of polymer promotes vertical elongation of concentration structures.
 391 This behaviour is consistent with the modification, upon polymer addition, of
 392 near-surface hydrodynamics: vertical elongation of turbulent eddies [19, 42],
 393 and modification of inter-component energy transfers, with an enhancement
 394 of down-going vertical momentum fluxes, as depicted in [42].

395 4.1.4. Temporal scalar scales

396 The temporal concentration correlation coefficient is defined for a given lo-
 397 cation (x, z) as the correlation between concentration fluctuations at instants
 398 t and $t + \delta t$, with δt a small time increment. The correlation coefficient at
 399 a given depth z is then $R_c^t(z, \delta t) = \left[\frac{c'(x, z, t)c'(x, z, t + \delta t)}{c'^2} \right]_x$ as defined by [1]. An
 400 example of correlation coefficients R_c^t plotted versus the separation time
 401 δt , for DPS, at different depths is shown in the insert of figure 4 d) (the
 402 blue curve being the closest to the interface and the yellow curve the fur-
 403 thest). Time correlation curves are non Gaussian and can be fitted by a sum
 404 of exponential functions, the numerical integration of which from zero to in-
 405 finity yields an integral concentration time scale T_c (inasmuch as R_c^t curves
 406 fall to zero within the time of measurement). The higher the integral time
 407 scale the longer the time available for diffusion. Error bars on T_c profiles in
 408 figure 4 c) are estimated as the maximum, among all curves, of the difference
 409 between numerical integration of R_c^t at a given depth and analytic integra-
 410 tion of its exponential fitting. Uncertainties are typically of ± 3 s for water
 411 and ± 1 s for the DPS case (purple and pink error bars). They are shown at
 412 a single depth for each curve for clarity reasons.

413 Integral time scales globally increase with decreasing z , which is consistent
 414 with the establishment of a scalar boundary layer close to the interface where
 415 turbulent stretching of scalar patches is less intense and diffusion has time
 416 to occur. The concentration time scales are quite close for water and DPS:
 417 about 3.5 s and 4.1 s at $z/\delta_v = 1.50$ and 5.7 s and 6.8 s at $z/\delta_v = 0.20$
 418 respectively. However, profile for water shows significant scattering, possibly
 419 due to the single color method noise being amplified by high order statistical
 420 analysis, or to poor convergence of the integral time scale. The temporal
 421 resolution of scalar fields is indeed quite low: typical persistence times for
 422 concentration are of the order of a few seconds, the exponential fitting of
 423 correlation curves is thus done with a limited number of points. In order to
 424 estimate the uncertainty of integral time scale measurement, the time scale

425 for a given fluid and a given depth is additionally computed as the numerical
 426 integral of the measured R_c^t curve, using a trapezoidal method and this value
 427 is compared to the one obtained by integration of the exponential fitting.
 428 The maximum differences found are of about 1 s for the DPS measurement,
 429 and 3 s for water.

430 4.2. Velocity / concentration correlations

431 Coupled measurements of concentration and velocity fields bring an inter-
 432 esting added value to the concentration field by showing some of the flow
 433 structures at the origin of the scalar patches' shapes, and allow to compute
 434 local mass fluxes [2]. Figure 5 shows examples of coupled instantaneous (a,b)
 435 and fluctuating (c,d) fields for water and DPS. While injection events seem
 436 obvious from instantaneous fields (e.g in figure 5 b)), fluctuating fields allow
 437 to better visualize surface renewal occurring, for example at $z/\delta_v < 0.35$,
 438 $x/\delta_v < 0$ on sub-figure d1)). The 3D views bring additional evidence of
 439 the out-of-plane motion. With instantaneous information about velocity and
 440 concentration fluctuations, it is possible to compute the ensemble average
 441 of velocity-concentration correlations $\overline{u'_i c'}$ and the ensemble rms $\langle u'_i c' \rangle_{rms}$,
 442 and plot their width averaged profiles along depth $[\overline{u'_i c'}]_x$ and $[\langle u'_i c' \rangle_{rms}]_x$
 443 (see figure 6). A $\pm 15\%$ uncertainty is expected, derived from the $\pm 10\%$ and
 444 $\pm 5\%$ uncertainties on concentration and velocity measurements respectively
 445 [41, 19]. Vertical mass fluxes $\overline{u'_z c'}$ are found to be always positive: turbulence
 446 tends to enhance mass transfer. Horizontal turbulent mass fluxes are also sig-
 447 nificant. They contribute to horizontal turbulent mixing of the dissolved gas,
 448 and do not tend to zero here given the narrow ROI considered. Horizontal
 449 mass fluxes do not appear isotropic in the x and y direction from figure 6 a),
 450 especially for the DPS case. Anisotropy increases for decreasing z in water
 451 and stays approximately constant with z in DPS. However, 6 b) shows that
 452 in terms of rms, horizontal mass fluxes along x and y are equivalent.

453 4.3. Conditional analysis of turbulent mass fluxes

454 Further insight on the mass transfer mechanisms is brought by performing
 455 conditional analysis of the coupled velocity and mass fluxes [2]. It consists in
 456 sorting local flow events according to the sign of their fluctuation, and per-
 457 forming a conditional analysis of turbulent mass or momentum fluxes based
 458 on this sorting [44, 45, 46, 2, 47]. A turbulent event is defined using u'_z and
 459 c' instantaneous fluctuations. The joint probability density function (PDF
 460 or covariance) $P(u'_z, c')$ represents the occurring probability of a turbulent

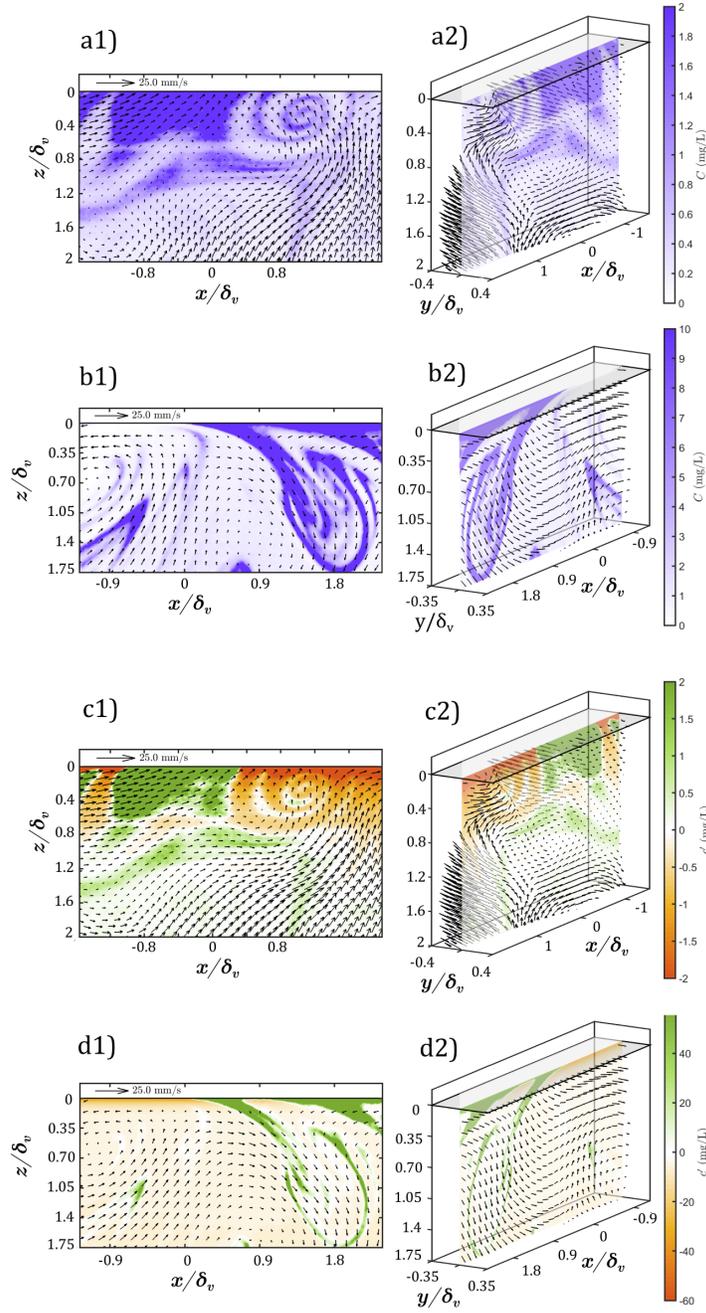


Figure 5: Example of coupled instantaneous (a,b) and fluctuating (c,d) velocity and dissolved gas concentration fields in water (a,c, $t=123.5$ s) and DPS (b,d, $t=1075.25$ s). (1) sub-figures are projected 2D views of the (2) plots.

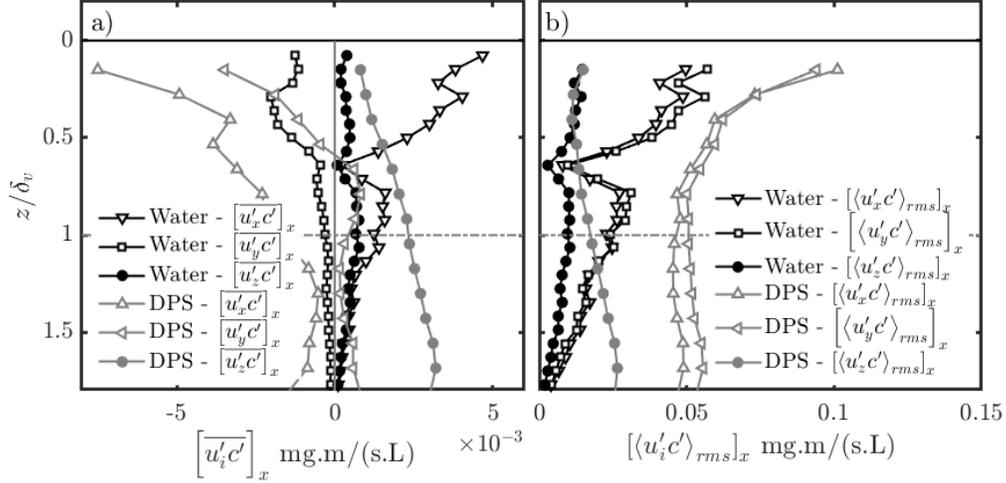


Figure 6: Width averaged profiles of $u'_i c'$ correlations (a) and their rms (b) for water and DPS.

461 event with fluctuation values equal simultaneously to u'_z and c' at a given
 462 location of the flow or in a ROI. The joint PDF is decomposed into four
 463 quadrants based on the sign of each fluctuation, according to figure 7. The
 464 relative strength of each quadrant can be quantified by the covariance inte-
 465 grand $u'_z c' P(u'_z, c')$. The higher this product the most probable and intense
 466 are the event of the associated quadrant. The type of event described by
 467 each quadrant is the following:

- 468 • **Q1:** Up-going patch of fluid carrying higher dissolved gas concentra-
 469 tion. The concentration fluctuation is positive, meaning that the local
 470 concentration at the point of interest is higher than the mean concentra-
 471 tion at this depth. This higher concentration patch is moved upwards
 472 where it merges into an area of higher (equivalent) mean concentration.
 473 Q1 events are thus expected to reduce diffusion efficiency.
- 474 • **Q2:** Up-going patch of fluid carrying lower dissolved gas concentra-
 475 tion. If this low concentration patch enters high mean concentration bound-
 476 ary layer close to the interface, the event can be qualified as a surface
 477 renewal event [2].
- 478 • **Q3:** Down-going patch of fluid carrying lower dissolved gas concentra-
 479 tion. The concentration fluctuation is negative, meaning that the local

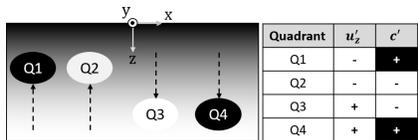


Figure 7: Principle of quadrant analysis

480 concentration is lower than mean concentration at this depth. Mov-
 481 ing downwards, the scalar patch meets an area of lower dissolved gas
 482 concentration. As for Q1 events, Q3 events are expected to reduce
 483 diffusion efficiency.

- 484 • **Q4:** Down-going patch of fluid carrying higher dissolved gas concentra-
 485 tion. The patch of positive concentration fluctuation is moved down-
 486 wards, towards an area of event lower mean concentration. Diffusion
 487 is thus greatly increased. Q4 events correspond to peeling/injection
 488 events.

489 Conditional average of the turbulent mass fluxes can be performed in each
 490 quadrant. For example the overall vertical mass flux $\overline{u'_z c'}$ can be decomposed
 491 into $\overline{u'_z c'} = \sum (P(u'_z, c') \overline{u'_z c'})_{Q_i}$ where $\overline{u'_z c'}_{Q_i}$ is the contribution of quadrant
 492 i to the total flux.

493 4.3.1. Probability of events

494 Sub-figures 8 a) show joint PDFs of $P(u'_z, c')$ for water and DPS in the
 495 ranges $[-8 \ 8]$ mm/s for u'_z and $[-25 \ 25]$ mg/L for c' . The same representation
 496 is adopted for the covariance integrand in sub-figures 8 b). Close to the
 497 surface, a higher probability of negative c' events (Q2,Q3, renewal) is visible.
 498 A balancing towards $c' = 0$ with increasing depth is evidenced for water but
 499 not so much for DPS. Water PDF figures compare qualitatively well to the
 500 results of [2]: a high probability peak at moderate negative c' and a long
 501 tail of low probability events at low u'_z and positive c' , reducing with depth.
 502 Covariance integrand, are also quite similar (keeping in mind that $u'_z > 0$ here
 503 corresponds to $u'_z < 0$ in [2]). The major difference with [2] experiments that
 504 can be observed in both PDF and covariance integrand plots is that sufficient
 505 depths to observe an even balance between quadrants is not attained here.
 506 In DPS, a persistence of large amplitude negative c' events with increasing
 507 depth is visualized. From the covariance integrand plot of figure 8 b), it

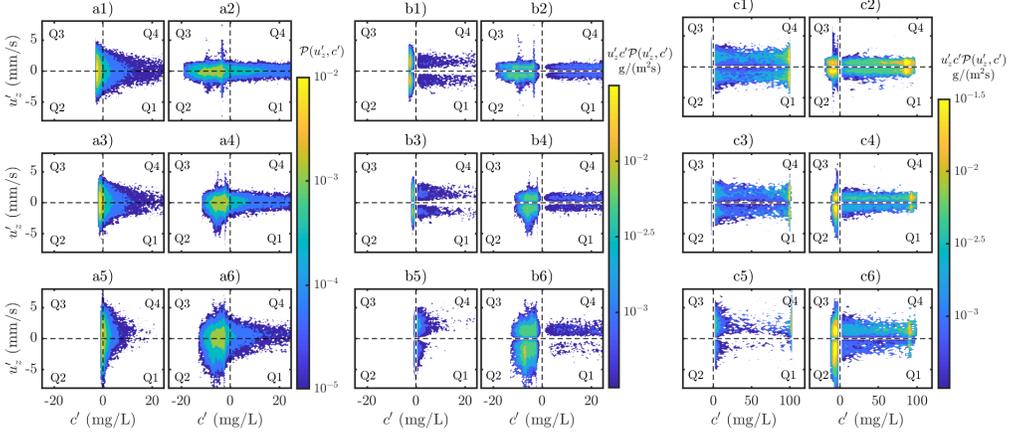


Figure 8: Joint PDF (a) and covariance integrand (b,c) of u'_z and c' for $c' \in [-25 \ 25]$ mg/L (a,b) and $c' \in [-25 \ 125]$ mg/L (c), for water (abc, odds) and DPS (abc, evens). Results are shown at three sample depths: $z/\delta_v = [0.15, 0.35, 1.10]$ for water, $z/\delta_v = [0.15, 0.41, 0.92]$ for DPS (sub-plots 1 and 2, 3 and 4, 5 and 6 respectively). The variable space is divided in 101 bins in both dimensions. Contour plots of are shown at values regularly distributed along a log scale indicated by the color bars.

508 appears that injection events are also significant. As in water, the tail of low
 509 u'_z and positive c' events reduces with increasing depth.

510 Covariance integrand plots show that even if the quadrants are quite
 511 balanced at larger depths, Q4 events are more probable than Q1 and Q2
 512 than Q3. We thus here evidence the existence of surface renewal (Q2) and
 513 injection (Q4) mechanisms in DPS. In order to get access to the high c'
 514 injection events, covariance integrand plots are plotted this time expanding to
 515 $c' \in [-25 \ 125]$ mg/L (sub-figures 8 c). This new representation confirms what
 516 was visible of injection events: the tail at large positive c' values progressively
 517 disappears with increasing z for both water [2] and DPS. The existence of
 518 two covariance integrand peaks at high positive c' , characteristic of strong
 519 injection events in the Q4 case is observed.

520 The peak at c' value close to 100 mg/L is explained by the limitations of
 521 the PLIF measurements, which saturates concentration fields at this value
 522 due to reduced pH sensitivity at pHs lower than 4. We infer that a similar
 523 feature would have been present in the results of [2] if a broader concentra-
 524 tion fluctuation range had been considered for result display (as in figure
 525 8 sub-plots c). With a sufficient measurement accuracy at lower pHs, the
 526 peak would likely spread over a wider range of high c' values. On this new

527 representation of the covariance integrand, Q2 and Q3 events completely dis-
 528 appear from the water balance at high depths, for which a combination of
 529 high and low c' , Q1 and Q4 events dominate. In DPS, Q2 and Q3 events still
 530 persist at high depths. The balance between Q1 and Q4 events, which was
 531 at equilibrium at small z , is shifted towards Q4 for increasing concentration.

532 Joint PDF and covariance integrand plots thus bring several information
 533 on vertical turbulent concentration events:

- 534 • The most probable events are those at moderate negative c' , for water
 535 and DPS. Positive c' events are displayed over a wider range of c' values.
- 536 • At small depths for water and DPS, joint PDF and covariance plots are
 537 symmetric with respect to the $u'_z = 0$ axis. With increasing depths, the
 538 dominance of Q2 over Q3 and Q4 over Q1 begins to emerge, especially
 539 in DPS. Injection (Q4) and renewal (Q2) events are thus confirmed to
 540 contribute to mass transfer in both water and DPS.
- 541 • From covariance integrand plots, one clearly sees that even if they are
 542 less probable than renewal events, injection events are associated to
 543 stronger fluctuations.

544 The probability of each type of events is plotted as a function of depth in
 545 figure 9. To do so, the probability of each quadrant type \mathcal{P}_{Q_i} is evaluated at
 546 each point of the ROI by counting the number of occurrence N_{Q_i} of each type
 547 of event at this location and dividing by the total number of instantaneous
 548 fields N_{tot} such that $\mathcal{P}_{Q_i} = N_{Q_i}/N_{tot}$. $[\mathcal{P}_{Q_i}]_x$ is then simply the width-averaged
 549 profile of \mathcal{P}_{Q_i} . Q2 and Q3 probabilities are higher than Q1 and Q4 ones close
 550 to the $z=0$ interface in both water and DPS. This corresponds to the shift of
 551 c' PDF's towards negative fluctuations observed in 8 a). In DPS, quadrants
 552 with $c' < 0$ are more probable than those associated to $c' > 0$ at all depths,
 553 which is another evidence of the preserved dominance of concentration re-
 554 newal with increasing depth. For water Q1 and Q4 quadrants show higher
 555 probability at depths $z/\delta_v > 1.40$. The main difference between water and
 556 DPS is found in the evolution of probabilities with depth. In water, the
 557 probability of Q2 and Q3 events increases with decreasing z , and the proba-
 558 bility of Q1 and Q4 events decreases. For water, the probability of injection
 559 (Q4) and renewal (Q2) events are equivalent at moderate depths, leading to
 560 symmetrical c' PDFs. When approaching the interface however, the proba-
 561 bility of injection events (Q4) decreases versus that of renewal events (Q2),

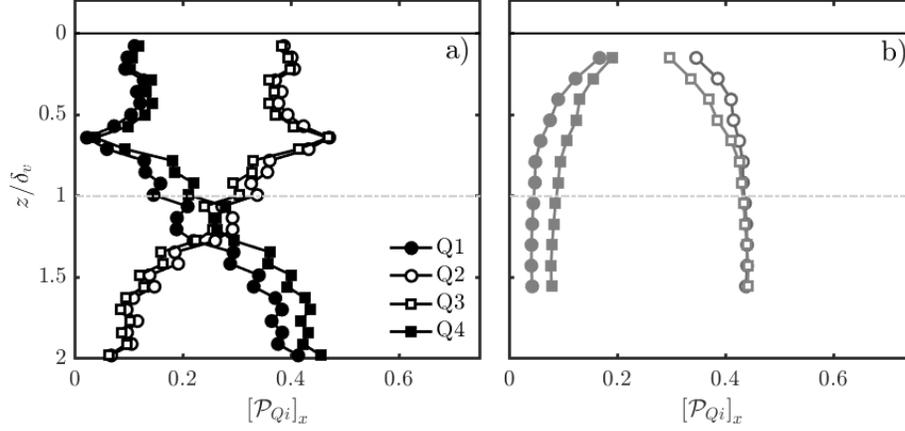


Figure 9: Width averaged probability profile of each quadrant in water (a) and DPS (b). The horizontal line marks the viscous sub-layer depth $z=\delta_v$.

562 leading to a shift in concentration PDFs towards negative values. In DPS,
 563 renewal events (Q2) are always more probable than injection ones. Yet, the
 564 probability of these renewal events decreases when approaching the interface,
 565 while that of injection events increases. This probability only indicates the
 566 likeliness of each type of events to occur, but not the strength of the related
 567 mass transfer.

568 4.3.2. Quadrant analysis of vertical mass fluxes

569 To tell which events are the most relevant in terms of turbulent mass
 570 fluxes, quadrant averaged vertical mass fluxes $\overline{u'_z c'^j}_{Q_i}$ are computed for each
 571 point of the ROI, and the absolute value of their width averaged profile are
 572 plotted as a function of depth on figure 10 a) and b) for water and DPS.
 573 The $\pm 15\%$ uncertainty error bars are shown for only one curve per sub-plot
 574 for clarity. For water, Q1 and Q4 quadrant corresponding to positive con-
 575 centration fluctuations yield higher turbulent mass fluxes than quadrants
 576 Q2 and Q3, especially at $z < \delta_v$. Turbulent mass fluxes of all quadrants in-
 577 crease with decreasing z , but Q1 and Q4 increase faster than Q2 and Q3,
 578 thus increasing their share in the total turbulent mass flux when approach-
 579 ing the interface. Values of Q1 and Q4 and Q2 and Q3 are respectively
 580 close, but at all depths though, $\overline{u'_z c'^j}_{Q_4} > \overline{u'_z c'^j}_{Q_1}$ and $\overline{u'_z c'^j}_{Q_2} \geq \overline{u'_z c'^j}_{Q_3}$, thus
 581 confirming that both renewal and injection events tend to create positive
 582 turbulent mass fluxes and enhance mass transfer. Injection events are the

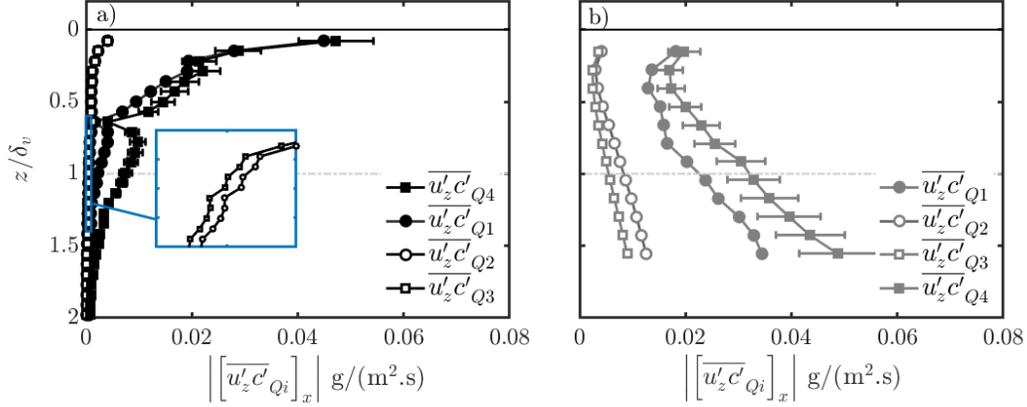


Figure 10: Quadrant sorted vertical turbulent mass fluxes $\overline{u'_z c'}$ as a function of depth, in water (a) and DPS (b). The horizontal dashed-dotted line marks the viscous sub-layer depth $z=\delta_v$. $\pm 15\%$ error bars are shown for only one curve per sub-plot for clarity. Inset in a) provides a close up for Q2 and Q3 events in water.

583 major contributor to the turbulent mass transfer. The same order of impor-
 584 tance $\overline{u'_z c'_{Q4}} > \overline{u'_z c'_{Q1}} > \overline{u'_z c'_{Q2}} > \overline{u'_z c'_{Q3}}$ can be observed at all depth for
 585 the 10 ppm DPS run. There, all quadrant sorted turbulent mass fluxes decrease
 586 with decreasing z , both inside and outside of δ_v except at very small
 587 depths (top two depths of measurement). The difference between renewal
 588 and injection events does not seem to depend on depth z . For both water
 589 and DPS, turbulent events opposed to the mass transfer direction are not
 590 negligible, but the overall turbulence tends to promote mass transfer. In-
 591 jection events are the main contributor to mass transfer in the two fluids.
 592 The mechanisms of turbulent mass transfer are yet quite different: in water,
 593 turbulence mostly acts close to the interface and less outside of the viscous
 594 sub-layer, while in DPS, the renewal and injection actions is spread over the
 595 full depth of the ROI, well outside the viscous sub-layer δ_v . Turbulent mass
 596 fluxes are quite intense in the bulk, reach a minimum at $z/\delta_v \simeq 0.27$ before
 597 further increasing.

598 4.4. Modelling of turbulent mass fluxes

599 A first approach modelling of turbulent mass flux at the interface is typi-
 600 cally achieved by first order eddy-diffusivity or gradient models. The eddy
 601 diffusivity can be derived from the turbulent mass flux and expected concen-

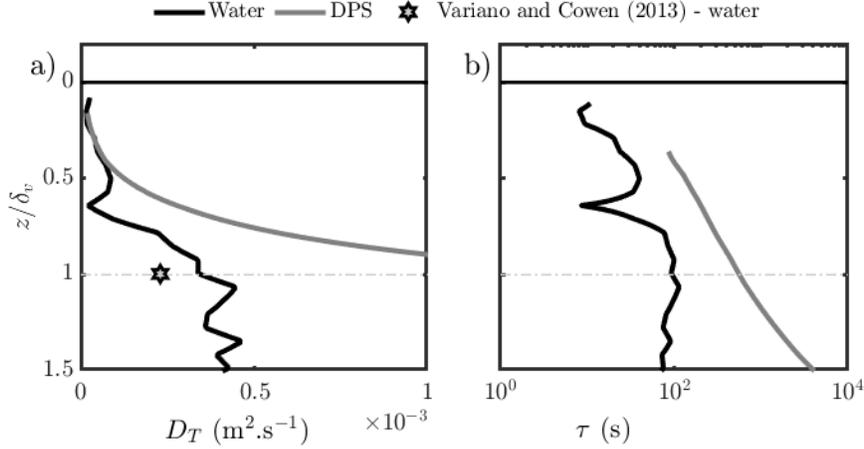


Figure 11: Profiles of D_T (a) and τ as a function of z/δ_v for water and DPS. The star in a) is the value reported in [2] for $z \simeq \delta_v$.

602 tration profile by using a gradient diffusion analogy [2, 45, 46]:

$$\overline{u'_z c'} \simeq -D_T \times \frac{\partial C}{\partial z} \quad (2)$$

603 Profiles for D_T for water and DPS are shown in figure 11 a). D_T increases
604 with depth, as previously observed in water for $z > \delta_v$ by [2]. The value of
605 D_T reported in the latter study for water at $z = \delta_v$ (star symbol in figure 11
606 a)) is in good agreement with the present data. In DPS, the increasing trend
607 is much more pronounced and D_T values, which were close to that of water
608 for $z \ll \delta_v$, increase by an order of magnitude when $z/\delta_v \rightarrow 1$. Non constant
609 values broadly suggest that the Eddy-diffusivity model is not the best suited
610 to describe near surface mass transfer from a modelling perspective conversely
611 to case of classical boundary layers. A more elaborate mean gradient models
612 described in [45, 46] is thus applied, in which the vertical turbulent mass flux
613 is written as

$$\overline{u'_z c'} \simeq \tau \overline{u'_z{}^2} \times \frac{\partial C}{\partial z} \quad (3)$$

614 with τ a model parameter homogeneous to a diffusion time. Profiles of τ are
615 shown in figure 11 b). The value of τ also increases with depth, in a more
616 pronounced fashion for DPS as compared to water. Indeed, in DPS, the
617 expected concentration profiles quickly tend to asymptotic values and zero

618 gradients when moving outwards the viscous sub-layer (figure 3 e), while
 619 strong injection events and thus non negligible turbulent mass fluxes are still
 620 observed (figure 10), thus leading to larger τ values. This last figure illustrate
 621 the need to account for strong intermittent injection events in the modelling
 622 of mass transfer in DPS. Moreover, the way turbulence approaches the sur-
 623 face has to be questioned in regards to the different hypothesis necessary to
 624 obtain equation 3 from complete scalar transport equations. In particular,
 625 the nature of large eddies responsible for large instantaneous mass fluxes
 626 events may be significantly different here as compared to a classical bound-
 627 ary layer. In the case of classical boundary layers for which a mean flow,
 628 parallel to the surface exists, large scale events are intrinsically aligned in
 629 the flow direction, along the surface. In the present case, large structures are
 630 related to bulk turbulence properties and possibly grid oscillation making
 631 them more likely vertically oriented (perpendicular to the interface) in the
 632 bulk, and only constrained in their orientation and shape in the surface in-
 633 fluenced layer, in which the dynamics is known to be affected by the presence
 634 of polymers [19]. In case of water the last modelling (equation 3, figure 11
 635 b) could be acceptable if defining two distinct zones, inside δ_v and outside
 636 δ_v . For DPS however, the difference between such zones doesn't exists ques-
 637 tioning the very use of δ_v , such as defined here, as a relevant boundary layer
 638 for modelling near-surface mass transfer. Future experiments performed on
 639 a larger ROI could allow to investigate deeper asymptotic behaviours and
 640 possibly define a more suitable characteristic depth for turbulent mass fluxes
 641 in non-Newtonian media.

642 5. Conclusion

643 In this work, turbulent dissolution and mass transfer of carbon dioxide
 644 into water and a moderately shear-thinning liquid phase was studied experi-
 645 mentally coupling SPIV and $I_{pH}^{(r)}$ - *PLIF*. In both water and low concentra-
 646 tion DPS, scalar fields in the sub-surface ROI consist in a complex combina-
 647 tion of injection and renewal events. In the first 1 or 2 mm underneath the
 648 interface, a statistical concentration boundary layer establishes and takes the
 649 form of a long horizontal saturated patch, randomly broken or made thinner
 650 by renewal events. Below this scalar boundary layer, injection-type struc-
 651 tures prevail. At the highest depths of the ROI, these patches are eventually
 652 broken and mixed. The presence of polymer promotes horizontal or vertical
 653 elongation of scalar structures, inside or outside the viscous sub-layer respec-

654 tively. Conditional analysis confirms that all four types of events relevant to
655 vertical turbulent mass transfer (as defined by the quadrant decomposition)
656 have non negligible probability of occurrence at all depths. Events in favour
657 of downward mass fluxes (Q2 and Q4) are yet always respectively stronger,
658 and mass transfer is effectively enhanced.

659 The physical mechanisms behind turbulent mass transfer are thus broadly
660 similar in water and DPS: negative concentration fluctuation events have
661 moderate c' amplitude but high probability, while positive concentration
662 fluctuation occur at a larger range of c' but with lower probability. Renewal
663 events are the most probable but only weakly contributing to mass transfer,
664 while injection events are less probable but associated to higher concentra-
665 tion fluctuations and thus the major contributors to vertical turbulent mass
666 transfer. The major difference between water and DPS, lays in the signa-
667 ture of those mechanisms, *i.e* the distribution of mass transfer events along
668 depth. In water, most of the mass transfer events are concentrated inside
669 the hydrodynamic viscous sub-layer, whereas in DPS, strong turbulent mass
670 fluxes are observed at depth higher than δ_v , and a minimum value is found
671 inside the viscous sub-layer.

672 Local measurement of turbulent mass fluxes such as those reported here
673 are highly desirable in the context of mass transfer modelling, for which first
674 order gradient model appear insufficient. Extensive effort has been and is
675 still being made to relate mass transfer velocity k_L to local turbulence prop-
676 erties [20, 48] and our experimental contribution can be used to power this
677 modelling effort, that is now facing the challenge of complex fluid rheology
678 encountered in many industrial applications [49]. Three-component informa-
679 tion brought by SPIV, or other more elaborate three-dimensional methods
680 such as PTV [38] applied near-surface, could be useful in the context of sur-
681 face divergence modelling [50, 48]. As for experiments, a natural next step
682 further would be to investigate more shear-thinning fluids (higher polymer
683 concentration) [25, 19] for which the hydrodynamic behaviour in the viscous
684 sub-layer significantly differs from the Newtonian one. Classical boundary
685 layer modelling tested here seems to fail, and this failure is even more re-
686 markable with DPS, raising questions on the hypothesis at the origin of
687 those models and the choice of the relevant length scales. Further study
688 on the effect of the largest scales which are at the origin of the turbulence
689 generation seems to be needed, both in water and DPS.

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694 *Conflicts of interest*

695 The authors declare no conflicts of interest.

696 **References**

- 697 [1] J. G. Janzen, H. Herlina, G. H. Jirka, H. E. Schulz, J. S. Gulliver,
698 Estimation of mass transfer velocity based on measured turbulence pa-
699 rameters, *AIChE Journal* 56 (8) (2010) 2005–2017.
- 700 [2] E. A. Variano, E. A. Cowen, Turbulent transport of a high-Schmidt-
701 number scalar near an air–water interface, *Journal of Fluid Mechanics*
702 731 (2013) 259–287.
- 703 [3] T. Lacassagne, M. EL Hajem, F. Morge, S. Simoens, J.-Y. Champagne,
704 Study of Gas Liquid Mass Transfer in a Grid Stirred Tank, *Oil & Gas*
705 *Science and Technology – Revue d’IFP Energies nouvelles* 72 (1) (2017)
706 7.
- 707 [4] J. C. R. Hunt, Turbulence Structure and Turbulent Diffusion Near Gas-
708 Liquid Interfaces, in: W. Brutsaert, G. H. Jirka (Eds.), *Gas Transfer at*
709 *Water Surfaces*, no. 2 in *Water Science and Technology Library*, Springer
710 Netherlands, 1984, pp. 67–82.
- 711 [5] B. H. Brumley, G. H. Jirka, Near-surface turbulence in a grid-stirred
712 tank, *Journal of Fluid Mechanics* 183 (1987) 235–263.
- 713 [6] C. R. Chu, G. H. Jirka, Turbulent gas flux measurements below the air-
714 water interface of a grid-stirred tank, *International Journal of Heat and*
715 *Mass Transfer* 35 (8) (1992) 1957–1968.
- 716 [7] J. Magnaudet, I. Calmet, Turbulent mass transfer through a flat shear-
717 free surface, *Journal of Fluid Mechanics* 553 (2006) 155–185.
- 718 [8] O. Flores, J. J. Riley, A. R. Horner-Devine, On the dynamics of turbu-
719 lence near a free surface, *Journal of Fluid Mechanics* 821 (2017) 248–265.

- 720 [9] H. Herlina, J. G. Wissink, Isotropic-turbulence-induced mass transfer
721 across a severely contaminated water surface, *Journal of Fluid Mechanics*
722 797 (2016) 665–682.
- 723 [10] J. G. Wissink, H. Herlina, Y. Akar, M. Uhlmann, Effect of surface con-
724 tamination on interfacial mass transfer rate, *Journal of Fluid Mechanics*
725 830 (2017) 5–34.
- 726 [11] J.-C. Gabelle, F. Augier, A. Carvalho, R. Rousset, J. Morchain, Effect
727 of tank size on kLa and mixing time in aerated stirred reactors with
728 non-newtonian fluids, *The Canadian Journal of Chemical Engineering*
729 89 (5) (2011) 1139–1153.
- 730 [12] Y. Kawase, N. Hashiguchi, Gas—liquid mass transfer in external-loop
731 airlift columns with newtonian and non-newtonian fluids, *The Chemical*
732 *Engineering Journal and the Biochemical Engineering Journal* 62 (1)
733 (1996) 35–42.
- 734 [13] A. A. Olajire, CO₂ capture and separation technologies for end-of-pipe
735 applications – A review, *Energy* 35 (6) (2010) 2610–2628.
- 736 [14] H. E. Huppert, J. A. Neufeld, The Fluid Mechanics of Carbon Dioxide
737 Sequestration, *Annual Review of Fluid Mechanics* 46 (1) (2014) 255–272.
- 738 [15] N. Seyed Hosseini, H. Shang, J. A. Scott, Biosequestration of industrial
739 off-gas CO₂ for enhanced lipid productivity in open microalgae culti-
740 vation systems, *Renewable and Sustainable Energy Reviews* 92 (2018)
741 458–469.
- 742 [16] L. Li, H. S. Lim, Y. T. Kang, Mass transfer characteristics for CO₂
743 absorption in nanoabsorbents, *International Journal of Heat and Mass*
744 *Transfer* 129 (2019) 650–659.
- 745 [17] W. Henry, Experiments on the Quantity of Gases Absorbed by Water,
746 at Different Temperatures, and under Different Pressures, *Philosophical*
747 *Transactions of the Royal Society of London* 93 (1803) 29–276.
- 748 [18] W. K. Lewis, W. G. Whitman, Principles of Gas Absorption., *Industrial*
749 *& Engineering Chemistry* 16 (12) (1924) 1215–1220.

- 750 [19] T. Lacassagne, S. Simoëns, M. EL Hajem, J.-Y. Champagne, Oscillating
751 grid generating turbulence near gas-liquid interfaces in shear-thinning
752 dilute polymer solutions, *Physical Review Fluids* 5 (3) (2020) 033301,
753 publisher: American Physical Society.
- 754 [20] R. Higbie, *The rate of absorption of a pure gas into still liquid during
755 short periods of exposure,*, New York, 1935.
- 756 [21] P. V. Danckwerts, Significance of Liquid-Film Coefficients in Gas Ab-
757 sorption, *Industrial & Engineering Chemistry* 43 (6) (1951) 1460–1467.
- 758 [22] H. Herlina, G. H. Jirka, Experiments on gas transfer at the air–water
759 interface induced by oscillating grid turbulence, *Journal of Fluid Me-
760 chanics* 594 (2008) 183–208.
- 761 [23] W. E. Asher, H. Liang, C. J. Zappa, M. R. Loewen, M. A. Mukto,
762 T. M. Litchendorf, A. T. Jessup, Statistics of surface divergence and
763 their relation to air-water gas transfer velocity, *Journal of Geophysical
764 Research: Oceans* 117 (C5) (2012) C05035.
- 765 [24] J. C. R. Hunt, J. M. R. Graham, Free-stream turbulence near plane
766 boundaries, *Journal of Fluid Mechanics* 84 (02) (1978) 209–235.
- 767 [25] T. Lacassagne, S. Simoëns, M. EL Hajem, A. Lyon, J.-Y. Champagne,
768 Oscillating grid turbulence in shear-thinning polymer solutions, *Physics
769 of Fluids* 31 (8) (2019) 083102.
- 770 [26] J. Bodart, J.-B. Cazalbou, L. Joly, Direct numerical simulation of un-
771 sheared turbulence diffusing towards a free-slip or no-slip surface, *Jour-
772 nal of Turbulence* 11 (2010) N48.
- 773 [27] J. Magnaudet, High-Reynolds-number turbulence in a shear-free bound-
774 ary layer: revisiting the Hunt-Graham theory, *Journal of Fluid Mechan-
775 ics* 484 (2003) 167–196.
- 776 [28] V. R. Ranade, J. J. Ulbrecht, Influence of polymer additives on the
777 gas-liquid mass transfer in stirred tanks, *AIChE Journal* 24 (5) (1978)
778 796–803.
- 779 [29] M. S. Puthli, V. K. Rathod, A. B. Pandit, Gas–liquid mass transfer
780 studies with triple impeller system on a laboratory scale bioreactor,
781 *Biochemical Engineering Journal* 23 (1) (2005) 25–30.

- 782 [30] F. Cabaret, L. Fradette, P. A. Tanguy, Gas-liquid mass transfer in un-
783 baffled dual-impeller mixers, *Chemical Engineering Science* 63 (6) (2008)
784 1636–1647.
- 785 [31] Y. Kawase, A. De, Turbulent heat and mass transfer in newtonian
786 and dilute polymer solutions flowing through rough pipes, *International*
787 *Journal of Heat and Mass Transfer* 27 (1) (1984) 140–142.
- 788 [32] M. Han, G. González, M. Vauhkonen, A. Laari, T. Koiranen, Local gas
789 distribution and mass transfer characteristics in an annulus-rising airlift
790 reactor with non-Newtonian fluid, *Chemical Engineering Journal* 308
791 (2017) 929–939.
- 792 [33] A. B. Rodd, D. E. Dunstan, D. V. Boger, Characterisation of xanthan
793 gum solutions using dynamic light scattering and rheology, *Carbohydrate*
794 *Polymers* 42 (2) (2000) 159–174.
- 795 [34] F. Garcia-Ochoa, V. E. Santos, J. A. Casas, E. Gomez, Xanthan gum:
796 production, recovery, and properties, *Biotechnology Advances* 18 (7)
797 (2000) 549–579.
- 798 [35] N. B. Wyatt, M. W. Liberatore, Rheology and viscosity scaling of
799 the polyelectrolyte xanthan gum, *Journal of Applied Polymer Science*
800 114 (6) (2009) 4076–4084.
- 801 [36] M. Lohse, E. Alper, G. Quicker, W.-D. Deckwer, Diffusivity and solubil-
802 ity of carbondioxide in diluted polymer solutions, *AIChE Journal* 27 (4)
803 (1981) 626–631.
- 804 [37] T. Lacassagne, A. Lyon, S. Simoëns, M. E. Hajem, J.-Y. Champagne,
805 Flow around an oscillating grid in water and shear-thinning polymer
806 solution at low Reynolds number, *Experiments in Fluids* 61 (1) (2019)
807 15.
- 808 [38] T. Lacassagne, J. Vatteville, C. Degouet, M. El Hajem, S. Simoëns,
809 PTV measurements of oscillating grid turbulence in water and polymer
810 solutions, *Experiments in Fluids* 61 (7) (2020) 165.
- 811 [39] T. Lacassagne, S. Simoëns, M. EL Hajem, J.-Y. Champagne, POD anal-
812 ysis of oscillating grid turbulence in water and shear thinning polymer
813 solution, *AIChE Journal* 67 (1) (2020) e17044.

- 814 [40] P. Valiorgue, N. Souzy, M. EL Hajem, H. Ben Hadid, S. Simoëns, Con-
815 centration measurement in the wake of a free rising bubble using planar
816 laser-induced fluorescence (PLIF) with a calibration taking into account
817 fluorescence extinction variations, *Experiments in Fluids* 54 (4) (2013)
818 1–10.
- 819 [41] T. Lacassagne, S. Simoëns, M. E. Hajem, J.-Y. Champagne, Ratiomet-
820 ric, single-dye, pH-sensitive inhibited laser-induced fluorescence for the
821 characterization of mixing and mass transfer, *Experiments in Fluids*
822 59 (1) (2018) 21.
- 823 [42] T. Lacassagne, Oscillating grid turbulence and its influence on gas liq-
824 uid mass transfer and mixing in non-Newtonian media, PhD Thesis,
825 University of Lyon, INSA Lyon (2018).
- 826 [43] A. Vreme, F. Nadal, B. Pouligny, P. Jeandet, G. Liger-Belair, P. Meu-
827 nier, Gravitational instability due to the dissolution of carbon dioxide
828 in a Hele-Shaw cell, *Physical Review Fluids* 1 (6) (2016) 064301.
- 829 [44] J. M. Wallace, H. Eckelmann, R. S. Brodkey, The wall region in turbu-
830 lent shear flow, *Journal of Fluid Mechanics* 54 (1) (1972) 39–48.
- 831 [45] J.-Y. Vinçont, S. Simoëns, M. Ayrault, J. M. Wallace, Passive scalar
832 dispersion in a turbulent boundary layer from a line source at the wall
833 and downstream of an obstacle, *Journal of Fluid Mechanics* 424 (2000)
834 127–167.
- 835 [46] S. Simoëns, J. Wallace, The flow across a street canyon of variable width
836 - part 2: Scalar dispersion from a street level line source, *Atmos. Envi-
837 ron.* 42 (2008) 2489–2503.
- 838 [47] J. M. Wallace, Quadrant Analysis in Turbulence Research: History and
839 Evolution, *Annual Review of Fluid Mechanics* 48 (1) (2016) 131–158.
- 840 [48] D. E. Turney, S. Banerjee, Air–water gas transfer and near-surface mo-
841 tions, *Journal of Fluid Mechanics* 733 (2013) 588–624.
- 842 [49] R. Petříček, T. Moucha, F. J. Rejl, L. Valenz, J. Haidl, Volumetric
843 mass transfer coefficient in the fermenter agitated by Rushton turbines
844 of various diameters in viscous batch, *International Journal of Heat and
845 Mass Transfer* 115 (2017) 856–866.

846 [50] S. P. McKenna, W. R. McGillis, The role of free-surface turbulence and
 847 surfactants in air–water gas transfer, International Journal of Heat and
 848 Mass Transfer 47 (3) (2004) 539–553.

849 **Appendix A. $I_{pH}^{(r)}$ – *PLIF* calibrations**

850 The $R = f(pH)$ and $I^* = f(pH)$ for $I_{pH}^{(r)}$ – *PLIF* (DPS) and I_{pH} –
 851 *PLIF* (water) are shown in figure A.12. I^* is the single color fluoresced light
 852 intensity normalized by its maximum value at pH=7. The processing steps
 853 on a given instantaneous fluoresced light signal for the $I_{pH}^{(r)}$ – *PLIF* method
 854 are illustrated in figure A.13. The intensity from color 1 (a) and color 2 (b)
 855 are used to compute the ratio R (c), which is then converted into ratio using
 856 the calibration curve from fig A.12. The pH (d) is then used to estimate the
 857 dissolved gas concentration (e,f) by numerical solving of dissolved carbon
 dioxide acid-base equilibria (see [42]).

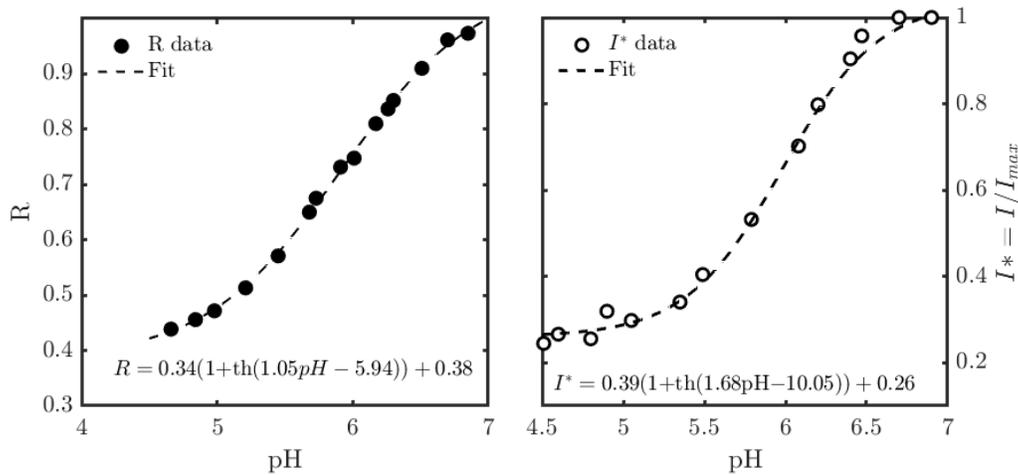


Figure A.12: Calibration curves for $R = f(pH)$ (left) and $I^* = f(pH)$ (right)

858 When a single color method is used, a "shortcut" from a single color
 859 intensity to the pH value is taken, as illustrated by the arrow on figure A.13,
 860 using the single color calibration curve from figure A.12.

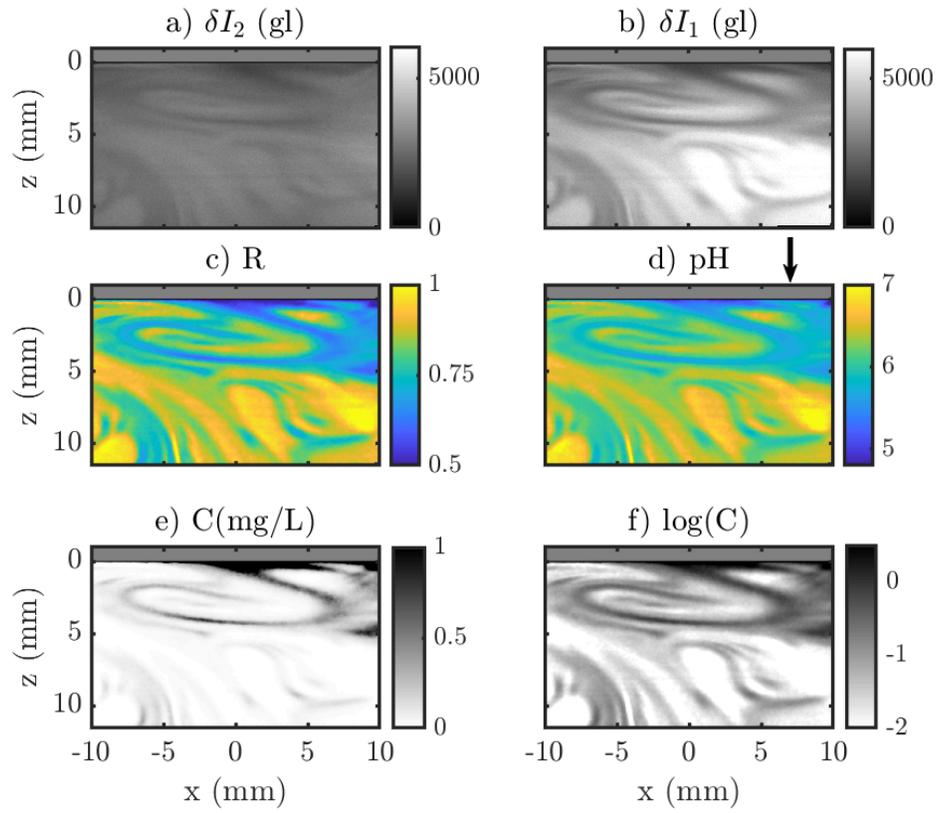


Figure A.13: Processing step of the $I_{pH}^{(r)}$ - PLIF method from the two color intensities (a,b) in gray level (gl) to Ratio (c), pH (d) and concentration fields in linear scale (e) and log scale (f).