Turbulent transport of a high-Schmidt-number scalar near an air-water interface
Evan A. Variano and Edwin A. Cowen

Abstract

We measure solute transport near a turbulent air-water interface at which there is zero mean shear. The interface is stirred by high-Reynolds-number homogeneous isotropic turbulence generated far below the surface, and solute transport into the water is driven by a Dirichlet boundary condition at the interface. We measure velocity and concentration fluctuations below the air-water interface, from the viscous sublayer to the middle of the “source region” where the effects of the surface are first felt. Our laboratory measurement technique uses quantitative imaging to collect simultaneous concentration and velocity fields, which are measured at a resolution that reveals the dynamics in the turbulent inertial subrange. Two-point statistics reveal the spatial structure of velocity and concentration fluctuations, and are examined as a function of depth beneath the air-water interface. There is a clear dominance of large scales at all depths for all quantities, but the relative importance of scales changes markedly with proximity to the interface. Quadrant analysis of the turbulent scalar flux shows a four-way balance of flux components far from the interface, which near the interface evolves into a two-way balance between motions that are raising and lowering parcels of low-concentration fluid.

1. Introduction

Many processes in the earth sciences and engineering are sensitive to the dynamics of mass transport at fluid interfaces. Predicting interfacial fluxes depends on our ability to model stirring near the interface. In aquatic environments, stirring typically comes from thermal convection, Langmuir circulation, waves, turbulence generated by shear at the interface, and turbulence generated elsewhere and transported to the interface. The stirring near the air-water interface is sensitive to the details of the driving flow, thus each case of stirring is typically considered individually (Banerjee and MacIntyre, 2004; Jähne et al., 1987).

Here we focus on the case in which turbulence is generated far from an interface and then transported towards it, i.e. a turbulent boundary layer with zero mean shear. We study this primarily for its application at water surfaces under calm wind, including estuaries, the oceanic surface mixed layer, rivers, and wetlands (see e.g. Brutsaert and Jirka, 1984; Komori et al., 2011). The results of this work can also be applied in canopies such as forests and wetlands (Finnigan, 2000), in benthic coastal habitats such as coral reefs (Monismith, 2007), in industrial processes such as thin-film deposition (Delbos et al., 2009), and where separated boundary layers reattach (Perot and Moin, 1995). All of these cases will have unique features due to the exact nature of how the turbulence is generated. For example, hairpin vortices created in the bottom boundary layer are a major feature of near-surface turbulence in open channel flow (Komori et al., 1989; Nagaosa and Handler, 2003; Rashidi et al., 1991). Here, we consider the general case of high-Reynolds-number homogeneous and isotropic turbulence beneath the surface.
Previous studies of scalar transport in zero-mean-shear boundary layers have focused primarily on the viscous sublayer, and for good reason. Dynamics in this layer are of central importance in setting the interfacial flux rate (Jähne and Haußeker, 1998). A number of models for predicting this flux have been used over the past century (reviewed in (Asher and Wanninkhof, 1998)). The majority of recent work agrees that interfacial flux can be reliably predicted from the divergence of the surface velocity field (Asher and Litchendorf, 2004; Calmet and Magnaudet, 1998; Csanady, 1990; Kermani and Shen, 2009; Law and Khoo, 2002; McCready and Hanratty, 1984; McKenna and McGillis, 2004; Turney et al., 2005). A picture is also emerging that large scales affect interfacial flux more than small scales (Calmet and Magnaudet, 1997; Chu and Jirka, 1992; Magnaudet and Calmet, 2006; Tamburrino and Gulliver, 2002), and that large scale motions are more directly connected to the subsurface flow than small scale motions (Savelsberg and van de Water, 2008; Turney and Banerjee, 2011). The questions now remaining are primarily about the effects of surface chemistry, specifically surfactants, on surface divergence statistics (Frew et al., 1990; Handler et al., 2003; Khakpour et al., 2011; McKenna and McGillis, 2004).

In this work, we shift the focus from scalar transport at an interface to scalar transport near an interface. In this region, unique biological and chemical reactions occur in response to the interfacial flux occurring nearby. That is, the surface acts as a source or sink of mass which enables near-surface biogeochemical processes to function differently than those in the “bulk” fluid far from the interface. These near-surface processes depend on the details of near-surface mixing and transport, which are the subject of this paper. Three near-surface biogeochemical processes that are of great importance to environmental engineering are sequestration of atmospheric CO₂, weathering of oil droplets, and plankton population dynamics. Considering the latter example, near-surface transport governs the occurrence of phytoplankton blooms, which can impact ocean ecology, global climate, and public health. Two effects of near-surface transport on bloom dynamics are described in the review by (Ibelings and Maberly, 1998). First, phytoplankton blooms can support themselves by elevating pH near the surface, thereby enhancing the availability of inorganic carbon obtained through interfacial CO₂ flux. Their ability to maintain such a “chemical pump” is sensitive to the amount of near-surface stirring. Second, some phytoplankton gain an advantage over competitive species by forming high-density layers, thus blocking light availability to organisms below them. Their ability to form and hold such layers is sensitive to the amount of near-surface stirring.

The goal of this paper is to better quantify the near-surface mixing and transport of aqueous solutes. Section 2 reviews the most relevant literature, section 3 contains the details of our laboratory experiment, and section 4 includes both the experimental results and their discussion.

2. Background

The case of a shear-free boundary layer was investigated in laboratory experiments by (Uzkan and Reynolds, 1967). They found that the lengthscale over which a wall influences shear-free turbulence (δS) is an order of magnitude smaller than the thickness of a sheared boundary layer. They also found that the lengthscale of turbulent motions decreases slightly near the wall, while the timescale increases greatly there. (Hunt and Graham, 1978) termed the region within δS of the surface the “source layer” (it is also
called the blocking layer or outer layer) and argued that \( \delta_S \approx 1.0L \) where \( L \) is the integral lengthscale in the “bulk” flow (i.e. far from the interface). This behavior has been confirmed by a variety of laboratory and numerical studies (e.g. Brumley and Jirka, 1987; Perot and Moin, 1995; Walker et al., 1996). Two other length scales of relevance have been identified, namely the viscous sub layer \( \delta_v \), in which surface parallel vorticity declines to zero at the interface, and the Kolmogorov sublayer \( \delta_K \), in which surface-normal velocity declines linearly to zero at the interface. Scaling laws for the thickness of these regions are given by (Brumley and Jirka, 1987) and (Calmet and Magnaudet, 2003) respectively, in terms of \( U \) (the turbulent velocity scale in the bulk flow), \( L \), and \( R_e_T \); these are \( \delta_v \approx 2.0L R_e_T^{-1/2} \) for the viscous sublayer and \( \delta_K \approx 4.0L R_e_T^{3/4} \) for the Kolmogorov sublayer. Campagne et al. (2009) offer alternative predictions of \( \delta_S \) in terms of surface, rather than bulk, quantities. The potential advantage of doing this is that surface-based predictions may be more universal than those that implicitly include a specific relationship between bulk flow and surface flow. However, Savelberg and van de Water (2008) warn that the surface of a turbulent flow can be a misleading predictor of subsurface dynamics (including those responsible for interfacial flux) because of capillary motions on the surface that are almost completely independent of subsurface processes.

A major contribution of (Hunt and Graham, 1978) is a method to predict the behavior of turbulent velocity statistics within \( \delta_S \). They show, quantitatively, how kinetic energy is redistributed from surface-normal to surface-parallel velocity fluctuations, and how the power spectra of surface-normal velocity fluctuations is damped at low frequencies and wavenumbers. Confirmation of these predictions were first provided by (Thomas and Hancock, 1977) using a wind tunnel with moving wall, (Brumley and Jirka, 1987) using a stirred tank, and (Perot and Moin, 1995) using direct numerical simulation. Later, (Magnaudet, 2003) showed that Hunt and Graham’s predictions, which utilize rapid-distortion theory, should hold even for long times and steady flows (if Reynolds number is sufficiently high). Other models add viscous effects to the rapid-distortion result (Magnaudet and Calmet, 2006; Teixeira and Belcher, 2000). Banerjee et al. (2004) used the results of rapid-distortion to develop one of the models predicting interfacial flux from for surface divergence.

To further advance the understanding of momentum transport within \( \delta_S \), numerical simulations have been used to investigate the details of intercomponent energy transfer (i.e. energy redistribution from surface-normal to surface-parallel motions). Perot and Moin (1995) consider a range of simplified boundary conditions that are not possible in the physical world, and conclude that intercomponent energy transfer depends on the balance of upwelling and downwelling structures. They also conclude that this balance is mediated by viscosity. Walker et al. (1996) emphasize the role of the local stress anisotropy in setting the balance between upwelling and downwelling structures, while Calmet and Magnaudet (2003) argue that large-scale anisotropy is also extremely influential. Bodart et al. (2010) point out a strong connection between intercomponent energy transfer and skewness in the surface-normal velocity fluctuations. They also observe that velocity dynamics in the source layer are mostly independent of the surface boundary condition, which suggests that the results of Hunt and Graham’s theory will apply equally well to clean, contaminated, and no-slip surfaces (Bodart et al., 2010).
This collection of studies thoroughly describes momentum transport, but says very little about mass transport within the source layer. For many solutes of importance in an aquatic environment, the Schmidt number \( \text{Sc} \equiv \frac{\nu}{D_m} \gg 1 \). This presents a further challenge for numerical studies, as it implies that scalar structures will exist at considerably smaller scales than momentum structures. However, we can infer a basic 'cartoon' of scalar transport by considering the effects of large-scale momentum structures. Upwelling structures (also called “splits”) carry bulk fluid towards the surface, where they spread out and displace a large amount of near-surface fluid. Such “renewal” events can be clearly seen in surface imaging (e.g. Asher and Litchendorf, 2009; Garbe et al., 2004; Tamburrino and Gulliver, 2002). Khakpour et al. (2011) describe the distribution of near-surface residence times for fluid parcels after upwelling. At the edges of upwelling structures, downwelling motions carry displaced fluid into the bulk. Two main types of downwelling structures have been observed: subductions and surface-attached vortices (e.g. Kumar et al., 1998). When near-surface fluid is rich in solute, these downwelling motions inject scalar “sheets” and “needles” into the bulk, as observed by (Herlina and Jirka, 2004, 2008; Woodrow and Duke, 2002).

Considering scalar transport in a Reynolds-averaged sense, the vertical (surface-normal) flux of expected concentration \( \langle c \rangle \) is \( J = -D_m \frac{\partial \langle c \rangle}{\partial z} + \langle w'c' \rangle \), where primes represent fluctuations relative to the expectation value, denoted \( \langle \rangle \). Thus the vertical profile of \( \langle c \rangle \) is determined by boundary conditions and the profile of turbulent flux \( \langle w'c' \rangle \). One way to estimate \( \langle w'c' \rangle \) is to use two gradient diffusion hypotheses and Reynolds’ analogy:

\[
\langle w'c' \rangle \approx -D_T \frac{\partial \langle c \rangle}{\partial z} \quad (1)
\]

\[
D_T \approx \nu_T \quad (2)
\]

\[
\nu_T \approx -\langle w'u' \rangle \left( \frac{\partial \langle u \rangle}{\partial z} \right)^{-1} \quad (3)
\]

This method is commonly used in the sheared boundary layer, in which \( \nu_T \approx \kappa u_* z \). However, in the zero-mean-shear boundary layer, equation (3) becomes

\[
\nu_T \approx \frac{0}{0}, \quad (4)
\]

and the method for predicting \( \langle w'c' \rangle \) fails. Instead, \( \langle w'c' \rangle \) must be studied directly, without using Reynolds’ analogy.

Magnaudet and Calmet (2006) measured some key features of \( \langle w'c' \rangle \) at a shear-free interface using large eddy simulation (LES). They observed that fluctuations of \( w' \) and \( c' \) persist all the way to the surface, which means that although the uppermost region of the flow is dominated by viscosity, dynamics there are stochastic. Similar results were measured in the laboratory by Asher and Litchendorf (2009), using an imaging technique in which light absorption is tuned so that measurements show only the behavior in a very thin near-surface region.

By computing two-point statistics from their LES, Magnaudet and Calmet (2006) measure the distribution of variance (\( \langle w'^2 \rangle \) and \( \langle c'^2 \rangle \)) and covariance (\( \langle w'c' \rangle \)) across large
and medium spatial scales (to a minimum scale of approximately $L/2$). Spectral analysis of the covariance $\langle w'c' \rangle$ shows a dominance of large scales, specifically those larger than $2L$. Autocorrelation curves of $w'$ and $c'$ are identical at medium scales, indicating that the same motions control both $w'$ and $c'$. This is in agreement with the cartoon described above, but neither the cartoon nor the LES describes the small-scale dynamics of solute transport. Such small scale features are important when analyzing processes such as chemical reactions or plankton behavior. Thus in the current work we focus on the spatial structure of turbulent transport at fine scales, i.e. within the inertial subrange.

The two-point statistics reported by Magnaudet and Calmet (2006) are measured in a region very close to the surface, namely the Batchelor sublayer. This sublayer, $\delta_B$, is defined as the region in which $\langle c \rangle$ varies linearly from the interface towards the bulk. Magnaudet and Calmet (2006) show that $\delta_B$ is smaller than the viscous and Kolmogorov sublayers, and argue that $\delta_B = \delta_K S c^{-1/2}$. This scale is extremely small, and thus to study fluid dynamics in this region requires numerical simulation or specialty imaging techniques such as that of Asher and Litchendorf (2009). Herein, we are interested in the entirety of the near-surface region. With increasing distance from the interface, scale separation increases, which makes numerical measurements challenging (e.g. concentration filaments can be both long and extremely thin). For this reason, we use laboratory experiments to further investigate the dynamics of turbulent scalar transport near an air-water interface.

3. Laboratory Experiment

In a stirred tank, we simultaneously measure velocity and dissolved gas concentration fields in the top 3 cm of the water. Velocity fields are collected using particle image velocimetry (PIV) to track neutrally buoyant tracer particles (e.g. Cowen and Monismith, 1997), and concentration fields are collected by using a pH-sensitive laser induced fluorescence technique (e.g. Cowen et al., 2001). The velocity and concentration fields cover a region of 3 cm by 4 cm, and are collected at a data rate of 25 Hz. Our imaging setup uses a single camera and laser light sheet to collect both velocity and concentration measurements, thus ensuring that they are exactly collocated. A second camera tracks the surface location, using the method of Banner and Peirson (1998). The surface fluctuates in response to forcing by subsurface turbulence, with a surface elevation variance of 0.0029 mm$^2$. We define $z = 0$ in our coordinate system as the instantaneous (time-varying) location of the air-water interface, averaged over the image width in $x$. This definition simplifies calculation of mass and momentum fluxes.

The stirred tank (Figure 1) is 80 cm x 80 cm x 91.5 cm deep. The headspace above the water surface ($z = 0$ to $z = 10$ cm) is full of pure CO$_2$ gas bounded by a ceiling at $z = 10$ cm. This headspace is at atmospheric pressure, with CO$_2$ supplied through a diffuser designed to keep the headspace CO$_2$ concentration constant in space and time. The initial condition of the water is 1.9 $\mu$mol L$^{-1}$ of total dissolved carbon (commonly denoted $C_T$, here denoted simply $C$). Throughout this work, we calculate $C$ from pH measurements using the electroneutrality equation and the well-known rate constants for carbonate system dynamics (details given in Variano, 2007). The initial low value of $C$ is achieved by bubbling the tank with Helium through an aquarium diffuser stone for

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approximately 12 hours. The experiment begins when the headspace is filled with CO₂, after which C increases in the tank via molecular and turbulent transport.

Turbulent flow in the water tank is driven by the Randomly Actuated Synthetic Jet Array (RASJA) located at \( z = -80 \) cm. The RASJA is an \( 8 \times 8 \) array of upward-pointing synthetic jets that fire in a spatiotemporally random pattern. This driving flow is stochastic and multi-scaled, but in regions close to the RASJA is not homogeneous turbulence. With increasing distance from the RASJA, the shear caused by the individual jets evolves into a horizontally homogeneous turbulent flow which has lost any signature of the generating mechanism (Variano and Cowen, 2008). The turbulent kinetic energy (TKE) in the flow decays with increasing \( z \) (similar to the streamwise decay seen in a turbulent wind tunnel) until the influence of the air-water interface is felt. The flow statistics in this stirred tank are investigated at length in Variano and Cowen [2008], including a thorough characterization at \( z = -20 \) cm, where the flow is neither influenced by the details of the driving mechanism nor the air-water interface. At \( z = -20 \) cm, the Reynolds number based on the Taylor microscale is \( R_{\lambda} = 314 \), the dissipation rate is \( \varepsilon = 5.20 \) cm\(^2\)s\(^{-3}\), the horizontal longitudinal integral lengthscale is \( L = 7.57 \) cm, and the characteristic magnitude of velocity fluctuations is \( \bar{U} = 4.30 \) cm s\(^{-1}\) (Variano and Cowen, 2008).

The imaging technique used to measure dissolved gas concentration leverages the fact that carbon dioxide gas, when dissolved in water, lowers the pH. A pH-sensitive dye is dissolved in the fluid, and responds to changes in gas concentration by modulating its fluorescence intensity. This technique is discussed at length in Munsterer and Jähne (1998). An important consideration when applying this is that the optical signal relies on a series of chemical reactions, not all of which are instantaneous. Thus the technique is
not valid very close to the gas-water interface, where a method based on quenching is preferred (Falkenroth et al., 2007). However, in our case, even the fastest travel times from the interface to the measurement volume provide adequate time for the entire series of reactions to reach equilibrium (Asher and Litchendorf, 2009; Munsterer and Jähne, 1998; Variano, 2007). For scalar transport measured in this way, the relevant Schmidt number is $Sc = 2045$, calculated from the molecular diffusivity of the fluorescent dye, 2',7'-dichlorofluorescein (DCF). At the water temperature used in our experiments (26.3 Celsius), the diffusivity of DCF is $D_m = 4.24 \times 10^{-10} \text{m}^2\text{s}^{-1}$. We calculate this from the value for standard fluorescein at 22.5 Celsius ($D_m = 4.36 \times 10^{-10} \text{m}^2\text{s}^{-1}$) as measured by Petrášek and Schwille (2008), which we then scale to a value for DCF using the Wilkie-Change model. In this model, diffusivity scales with molar volume to the power $-0.6$ and absolute temperature to the power $1$ (Bird et al., 2006). In doing this, we use the method of Abraham and McGowan (1987) to estimate that the molar volume of DCF is $6.8\%$ larger than standard fluorescein.

Experiments are conducted in a solution made of distilled water, the pH-sensitive fluorescent dye at a concentration of $12.15 \text{mg/L}$, NaCl at $2.925 \text{g L}^{-1}$ (which simplifies the use of pH to predict C), and neutrally buoyant hollow glass spheres (Sphericel, manufactured by Potters Industries) to serve as optical tracers. For the data reported here, the water solution temperature was 26.3 Celsius, thus kinematic viscosity in the fluid was $\nu = 8.67 \times 10^{-7} \text{m}^2\text{s}^{-1}$. Temperature and pH of the bulk fluid are measured with a pH electrode (Thermo Scientific/Corning) at $z = -5 \text{cm}$.

Each image is illuminated by sweeping a 1.4 Watt Argon-ion laser beam (488 nm, delivered by a Coherent Innova 90-6 operating in single-line mode) across the image area for a duration of 4.5 ms. Image pairs are separated by 6.0 ms, and subsequent pairs by 40.0 ms. A useful feature of the pH-sensitive dye is that dissolved CO$_2$ gas makes the image darker, while fluid tracer particles make the image brighter. This allows us to use a simple intensity threshold to separate the data used for concentration calculations and the data used for velocity calculations (this is a key enabling factor for the single-laser, single-camera setup).

Concentration measurements are calibrated using an experimentally generated curve that relates the intensity at a single pixel to the pH, and thus to the concentration $C$. By using a unique nonlinear calibration curve for each pixel, we eliminate the effects of optical variations across the image area, such as the along-beam decay of illumination intensity. Calibration curves are built from a series of measurements in which pH is set at known values and homogeneous throughout the tank.

Uncertainty in $C$ is dominated by spatiotemporally random fluctuations in pixel intensity. These are caused by variations in local delivered light intensity, e.g. when a particle casts a shadow in the laser light sheet. We measure these fluctuations using timeseries recorded at constant pH, and find that they are normally distributed and uncorrelated, i.e. essentially white noise. In addition, data gaps in $C$ appear at spatiotemporally random locations due to interference by PIV tracer particles. Because of their random nature, neither the noise nor the data gaps influence the statistics reported below, with one exception. This exception is our calculation of concentration fluctuation magnitude, in which the imaging noise causes a positive bias. Examination of the spatial autocorrelation curve $\rho_{cc}(r)$ in section 4 indicates that the magnitude of this bias is negligible, for it does not cause a discontinuous jump at $r = 0$. 

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Velocities are calculated at the nodes of a square grid spaced at 1.2 mm, and each velocity measurement is a weighted average of the flow over a finite area. The weighting function used here is a symmetric 2D Gaussian window with $\sigma = 1.16$ mm = 15 pixels, whose radius at $1/e^2$ of the peak amplitude is $r_v = 2.325$ mm $\approx$ 30 pixels and area at this radius is 17 mm$^2$. Velocities are calculated using the commercial software DaVis (LaVision Inc). The dominant source of bias in velocity measurements is data gaps caused by local failure of the PIV cross-correlation algorithm. These gaps cause bias when they occur systematically, e.g. at large velocities. Examining the probability distribution of velocities $U$ and $W$ and the joint probability distribution of $w'$ and $c'$ (example seen in Figure 7 in section 4) showed no bias due to data gaps.

Concentration measurements are made at a much finer spatial resolution than velocity measurements, because concentration values are measured at every pixel in the image, each of which corresponds to an area of 77 $\mu$m by 77 $\mu$m. In this paper, we work only with those concentration measurements that are located at the nodes of the velocity measurement grid. At each node in the velocity measurement grid, we compute a concentration value from the median of a 3x3 pixel region centered on the node. This 3x3 pixel smoothing reduces the magnitude of random noise, and results in a concentration measurement length scale $r_c = 116$ $\mu$m. The ratio $r_c = \frac{\eta_B}{\eta} = \sqrt{Sc}$, where $\eta_B$ is the Batchelor lengthscale. This near equality of ratios implies that our velocity and concentration measurements both include a very similar amount of smoothing relative to the smallest velocity and concentration lengthscales.

An example measurement is seen in Figure 2. Simultaneous velocity and concentration fields in this sample image show two upwelling and two downwelling structures. These motions are evident both from the subsurface velocity patterns and the variable thickness of the concentration boundary layer (thin, dark-colored region above the top row of vectors). The two sources of concentration uncertainty are also evident. Data gaps caused by the presence of PIV tracer particles are visible as white points (especially within the high-concentration regions), and noise is evident in the presence of a dark vertical line at $x \approx 4.1$ cm. This is a shadow caused by temporary obstruction of the laser light sheet, which occurs randomly in $x$ and $t$. Data gaps can also been seen in the velocity field, e.g. at $(x,z) \approx (1.8,0.3)$ cm.
Figure 2 [color online]. Simultaneous velocity and concentration field, number 7,500 of 15,000 analyzed here. The z-axis is labeled in a fixed coordinate system, while most data analysis is referenced to the instantaneous free surface location, shown here in a white line slightly above z=0.

4. Results
4.1 One-point statistics
4.1.1 Velocity profiles
Profiles of velocity statistics near the interface are seen in Figure 3. Across all depths, mean velocities $\langle U \rangle$ and $\langle W \rangle$ are small compared to the magnitude of fluctuating velocities $u' = U - \langle U \rangle$. This small mean flow simplifies experiments and allows us to independently measure the spatial and temporal characteristics of turbulent transport. The fluctuating velocity magnitudes are expressed as $U_{rms} = \sqrt{\langle u'^2 \rangle}$. Figure 3 shows that $W_{rms}$ declines as the interface is approached, with some energy redistributed to $U_{rms}$ by the free surface “blocking” effect as discussed extensively in the literature. Despite the redistribution, the turbulent kinetic energy (TKE) is nearly constant over this region, which we use to define the characteristic magnitude of velocity fluctuations

$U = \sqrt{\frac{2}{3} TKE} = \sqrt{\frac{1}{3} \left( 2U_{rms}^2 + W_{rms}^2 \right)}$ (Tennekes and Lumley, 1972). The vertical average of this velocity scale, computed over the near-constant region, is $U_a=3.6$ cm/s.

There is a noticeable change in the turbulent velocity profiles for $z \lesssim 3$ mm. This corresponds with the beginning of the viscous sublayer, as predicted by the formula of Calmet and Magnaudet (2003) $\delta_v \approx 2.0 L \left( \frac{2U_L}{\nu} \right)^{-1/2} = 1.9$ mm. This demarcates the near-surface boundary of the source layer and corresponding theory from Hunt and Graham (1978).
Behavior in the viscous sublayer indicates the presence of surfactant, evidenced by the decline in $U_{\text{rms}}$ with proximity to the interface. This is to be expected, because although we skim the air-water interface prior to experiments, some surfactant always remains. Our skimming method uses a custom sharp-crested weir whose depth is set via a fine-threaded screw such that only the uppermost layer of water in the apparatus is removed into the skimmer. The skimmed fluid cascades down a plate and accumulates on the surface of a collection reservoir. Water is removed from the collection reservoir at depth and returned to the experimental apparatus, allowing this scheme to run steadily for long periods of time. For the experiment considered here, 2 hours of skimming at a flowrate of 100 mL/min are conducted before the gas transfer experiments. Without such treatment, the effect of surfactant will be much greater than that observed here. Despite the caution to remove surfactant, we note that dynamics in the blocking layer may be quite independent of the surface boundary condition, as suggested by (Bodart et al., 2010).

![Figure 3: Vertical profiles of mean and fluctuating velocity magnitudes near the air-water interface](image)

4.1.2 Scalar profiles

By design, mean concentration timeseries are unsteady in this experiment. We calculate time-varying expectation values $\langle C(z,t) \rangle$ by polynomial fits to horizontally-averaged timeseries $C(z,t)$. By inspection, we determine that concentration fluctuations $c' = C - \langle C \rangle$ are statistically stationary for times between 200 and 600 seconds (see Figure 4, particularly Figure 4d). We use this 400-second interval to calculate the concentration statistics reported herein. 400 seconds corresponds to 247 large-eddy
turnover times in the bulk flow, and we perform convergence tests for each statistical value to confirm that there is adequate data.

We calculate the fluctuation magnitude as $C_{rms} \equiv \langle c^2 \rangle^{1/2}$. The vertical profile seen in Figure 4e shows $C_{rms}$ increasing with proximity to the interface, as expected due to the boundary conditions. Results from (Magnaudet and Calmet, 2006) allow us to predict that $C_{rms}(z)$ will reach a maximum of roughly 10,000 $\mu$mol L$^{-1}$ at $z \approx 20$ micron, which is not resolved in our measurements. To our knowledge, there is no prediction for the shape of the $C_{rms}$ profile in the absence of mean shear; we investigate the profile shape measured here and find that it is not well described by polynomial, logarithmic, power law, or error functions.

Figure 4: Concentration timeseries at three depths: (A) 0.616 mm (B) 3.080 mm (C) 27.720 mm. White lines show the expectation value, which is determined by a polynomial fit to filtered data. (D) shows the timeseries at 0.616 mm depth after the expectation value has been subtracted; dashed lines show the concentration fluctuation magnitude (+/- $C_{rms}$) calculated from a 400-second subset of the data. (E) shows how this 400-second $C_{rms}$ value varies with depth; circles denote the location of timeseries shown in the previous plots. 95% Confidence intervals on $C_{rms}$ are shown for the two points nearest the air-water interface; for all other locations, the uncertainty is smaller than the data markers.
As expected for a flow with nonzero mass flux, the scalar fluctuations show a clear positive skewness (third standardized moment). This statistic is not as well converged as the second moment, but falls within the bounds [3,7] and increases with $z$. Typical values are 4 (at $z = 3 \text{ cm}$) and 6 (at $z = 1 \text{ cm}$).

### 4.1.3 Turbulent scalar transport

Turbulent mass flux in the vertical direction is the covariance $\langle w'c' \rangle$; the ability to directly measure this is a major goal of our simultaneous concentration and velocity imaging setup. This flux is negative in our experiment because the net movement of solute is from the interface towards the bulk fluid. We compute local mass balances from the 2D velocity and concentration fields, and these budgets close as well as can be expected given the lack of 3D information. These 2D mass balances also indicate that, despite the remarkably small mean flow in the experimental facility (Variano and Cowen, 2008) and the intense mixing, the mean advective fluxes make a non-negligible contribution to transport.

A quantitative demonstration of mass balance can be obtained by considering that vertical gradients decrease with depth, and thus the deepest measured value of $\langle w'c' \rangle$ (at $z = 3 \text{ cm}$), can be used to predict the approximate timeseries of concentration in the bulk fluid. By considering this turbulent flux as the only source of mass transfer to the lower $h = 77 \text{ cm}$ of the tank, mass conservation gives $\frac{\partial \langle C \rangle}{\partial t} = \frac{\langle w'c' \rangle}{h}$. Using our measurement $\langle w'c' \rangle = -43.2 \text{ } \mu\text{mol L}^{-1} \text{ cm s}^{-1}$ at $z = 3.02 \text{ cm}$, which is statistically steady from $t=200$ to $600$ seconds, we predict a linear timeseries with a slope of $0.56 \text{ } \mu\text{mol L}^{-1} \text{ s}^{-1}$. Table 1 shows that this prediction agrees reasonably well with the slope of $\langle C(t) \rangle$ measured with our imaging technique at $z = 3.02 \text{ cm}$, and also with the slightly more independent measurement of $\langle C(t) \rangle$ from a submerged pH probe at $z = 5 \text{ cm}$.

<table>
<thead>
<tr>
<th></th>
<th>$\frac{\partial \langle C_{\text{bulk}} \rangle}{\partial t}$ (μmol L$^{-1}$ s$^{-1}$)</th>
<th>95%CI (μmol L$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prediction from $\langle w'c' \rangle$</td>
<td>0.56</td>
<td>+/- 0.01 based on standard error of $\langle w'c' \rangle$ and extreme values of gradient</td>
</tr>
<tr>
<td>Timeseries from image</td>
<td>0.49</td>
<td>+/- 0.01 based on parameter uncertainty from fit</td>
</tr>
<tr>
<td>Timeseries from pH probe</td>
<td>0.63</td>
<td>+/- 0.01 based on parameter uncertainty from fit</td>
</tr>
</tbody>
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Table 1. Evaluation of mass balance using bulk-flow approximations.

From the turbulent flux $\langle w'c' \rangle$ we can calculate the eddy diffusivity by re-casting the approximate model in equation (1) as a definition:

$$D_T = -\langle w'c' \rangle \left( \frac{\partial \langle C \rangle}{\partial z} \right)^{-1}.$$  \hspace{1cm} (5)

The resulting measurements, seen in Figure 5, are consistent with both linear and quadratic forms for $D_T(z)$. The data and fits reach zero between $z = \delta_v$ and $z = 2\delta_v$, and neither fitting function works well when constrained so that $D_T(0)=0$. This is consistent with the definition of the viscous-dominated sublayer $\delta_v$. The results of the linear fit can be directly compared to the commonly used model for sheared boundary layers, namely...
$D_T \approx \nu_T \approx 0.41u_* z$, where $u_*$ is the shear velocity. Our results for the unsheared boundary suggest that $D_T \approx a U_0 (z - 2\delta_v)$, where $U_0 = 3.6 \text{ cm s}^{-1}$ is the characteristic scale of near-surface velocity fluctuations discussed above. The fit shown in Figure 5a gives $\alpha = 0.84$ with a 95% confidence interval of [0.76, 0.92]. The fact that $\alpha$ is greater than 0.41 in the unsheared boundary layer could be interpreted to mean that turbulent interfacial transport is more efficient than in an equivalent sheared boundary layer.

![Figure 5](image)

*Figure 5*: Eddy diffusivity calculated from turbulent flux and vertical gradient in expected concentration. (A) shows linear fit (adjusted $R^2 = 0.958$) and (B) quadratic fit (adjusted $R^2 = 0.970$).

Our next investigation of covariance is to examine the nondimensional cross-correlation

$\varepsilon_{wc}$ defined as $\varepsilon_{wc} = \frac{\langle w'c' \rangle}{w_{rms}c_{rms}}$, seen in Figure 6. The value of $\varepsilon_{wc}$ increases with depth, indicating that the efficiency of turbulent transport increases with depth, rapidly at first and then more slowly. The cross-correlation value $\varepsilon_{wc}$ is set by the frequency and strength of those coherent motions discussed in the 'cartoon' above. The motions can be identified using a standard quadrant analysis as follows: Quadrant 1 (Q1) events carry high-$c'$ fluid towards the surface; Q2 events carry low-$c'$ fluid towards the surface; Q3 events carry low-$c'$ fluid away from the surface; and Q4 events carry high-$c'$ fluid away from the surface. We expect that Q2 and Q4 will dominate near-surface mass transport, as they represent the upwelling and downwelling events in the 'cartoon.'

To determine the total strength of events in each of the four quadrants, we calculate $\varepsilon_{wc}$ conditioned on the sign of $w'$ and $c'$. The results, seen in Figure 6, indicate that the mechanism behind turbulent flux changes with proximity to the interface. Throughout most of the measurement region, Q2 and Q4 events are of nearly equal strength, but near the surface Q2 events (renewal) become much stronger than Q4 (injection) events. This shift indicates why surface-renewal models, which focus on Q2 events, have been successful at predicting interfacial flux. The increased magnitude of Q2 events near the surface is overwhelmed by the decrease in Q4 events, such that $\varepsilon_{wc}$ trends towards zero at the surface. This trend in Q4 events can be interpreted as follows: high-$c'$ filaments in the bulk are much more likely to be on a downward trajectory than high-$c'$ filaments.
near the surface. A related conclusion can be drawn by comparing Q3 and Q4 events: downward motions near the surface are more likely to oppose downward mass transport than to cause it, while downward motions in the bulk behave as expected, contributing substantially to downward mass transport.

![Figure 6: Cross-correlation of fluctuating concentration and vertical velocity, including conditional values from each quadrant: — Net value $\rho_{wc}$; ▲ Quadrant I ($w' > 0, c' > 0$); △ Quadrant II ($w' > 0, c' < 0$); ▽ Quadrant III ($w' < 0, c' < 0$); ▼ Quadrant IV ($w' < 0, c' > 0$). 95% confidence intervals are shown for $\rho_{wc}$, and are roughly twice the size of those for the individual quadrant values (not shown). Another view of these quadrant dynamics can be seen in the joint probability density functions in Figure 7, which show the distribution of events within each quadrant. Weighting this joint PDF by the magnitude of flux at each point in $w' - c'$space, we obtain the distributions in Figure 8. As in Figure 6, this shows that the 4-way balance of events found in the bulk shifts near the interface, eventually becoming a 2-way balance between motions that are raising and lowering parcels of low-concentration fluid.}
Figure 7: Joint probability density function of $w'$ and $c'$. Plot A is at depth 0.616 mm; Plot B is at depth 3.080 mm; and Plot C is at a depth of 27.720 mm. Contour lines are drawn at multiples of 2, beginning with a probability of 0.001, and each region is shaded according to the value of its lower bounding contour.
Figure 8: Probability-weighted turbulent flux magnitude, showing the shift from a 2-quadrant balance to a 4-quadrant balance with depth. Plot A is at depth 0.616 mm; Plot B is at depth 3.080 mm; and Plot C is at a depth of 27.720 mm. Contour lines are drawn at multiples of 2, beginning with a probability-weighted flux magnitude of 0.01. Contour lines are drawn at multiples of 2, beginning with a probability of 0.001, and each region is shaded according to the value of its lower bounding contour.
4.2 Two-point statistics

Our approach to two-point statistics is to calculate covariances, correlations, and structure functions directly from the definitions:

\[ R_{ab}(r) = \langle a'(x)b'(x+r) \rangle \]  \hspace{1cm} (6)

\[ \rho_{ab}(r) = R_{ab}(r) \left( \frac{a_{rms}^{-1}b_{rms}^{-1}}{r} \right) \]  \hspace{1cm} (7)

\[ \rho_{x'}(r) = R_{ab}(r) \left( \frac{a'b'}{r} \right)^{-1} \]  \hspace{1cm} (8)

\[ D_{ab}(r) = \langle (a'(x) - a'(x+r))^2 \rangle \]  \hspace{1cm} (9)

By using equation (6) to calculate covariance instead of the more common Fourier transform method, we avoid having to fill data gaps or assume the data to be cyclical in space. Four different covariances can be calculated from our data: \( R_{uu}(r) \), \( R_{ww}(r) \), \( R_{cc}(r) \), and \( R_{wc}(r) \). We calculate these using a separation vector \( r \) that is aligned with \( x \), because the flow statistics are homogeneous in this direction. The four covariances, nondimensionalized via equations (7) and (8), are shown in Figure 9 at three representative depths. All of these show the same trend with respect to depth: as the interface is approached, the curves shift leftwards and downwards. This indicates that the length scales of turbulent motion and scalar transport are smaller closer to the interface.

Structure functions, shown in Figure 10, show the same trend as the covariance curves. At separations \( r \) corresponding to the inertial subrange, Kolmogorov theory predicts a power-law slope in the structure function of velocity fluctuations, such that \( D \sim r^{2/3} \) for homogeneous isotropic turbulence. We see this behavior for \( D_{uu} \) and \( D_{ww} \) far from the interface, but as the interface is approached, the slope flattens. This shift indicates a decline in the size of turbulent motions close to the interface. Comparing \( D_{ww} \) and \( D_{uu} \), we see that the surface has a much stronger effect on the surface-normal velocity component (\( w \)). In contrast, the slope of the scalar structure function \( D_{cc} \) does not appear to change at all as the interface is approached. At all depths, the slope of \( D_{cc} \) is flatter than \( D \sim r^{2/3} \). The behavior appears to be close to \( D_{cc} \sim r^{1/5} \), based on the qualitative fit shown in Figure 10.

The most familiar way to examine the spatial structure of turbulence is through power spectra, although the results are equivalent to (and interchangeable with) the covariance and structure function. We compute power spectra from the Fourier transform of covariances \( R_{ab}(r) \), and consider the spectra for velocity (\( E_{uu} \) and \( E_{ww} \)), concentration (\( E_{cc} \)), and scalar flux (\( E_{wc} \)) in the following subsections.
Figure 9: Two-point auto- and cross-correlation curves showing the spatial structure of velocity and concentration fluctuations. Symbols correspond to depth beneath air-water interface (\(\ast = 0.616\) mm, \(\bigcirc = 5.544\) mm, \(\bigtriangledown = 27.720\) mm) and worst-case error bars are shown on the right hand side, indicating the 95% confidence interval.
Figure 10: Structure functions (second order) of velocity and concentration fluctuations. Symbols correspond to depth beneath air-water interface ($\star = 0.616$ mm, $O = 5.544$ mm, $\forall = 27.720$ mm). Solid lines indicate the power law $r^{2/3}$, and the dashed line indicates a power law $r^{4/5}$.

4.2.1 Velocity Spectra

The distribution of velocity variance across spatial scales follows the Kolmogorov predictions far from the interface, with both horizontal and vertical velocities exhibiting a power law spectrum in the inertial subrange with slope $\kappa^{-5/3}$, as seen in Figure 11. The vertical velocity spectrum $E_{ww}(\kappa)$ shows a spectral shift near the surface, with small-scale motions becoming relatively more important there. The horizontal velocity spectrum $E_{uu}(\kappa)$ shows evidence of a very weak spectral shift towards larger scales, i.e. in the opposite direction of the shift in $E_{ww}(\kappa)$. Because vertical and horizontal motions are linked by continuity, it is interesting to note how different in magnitude these two opposing spectral shifts are.

Figure 11: Power spectra showing how velocity variance is distributed across horizontal length scales, for (A) horizontal velocity variance and (B) vertical velocity variance. Symbols correspond to depth beneath air-water interface: $\star = 0.616$ mm, $O = 5.544$ mm, and $\forall = 27.720$ mm. Solid lines show a power law $E_{aa} \sim \kappa^{-5/3}$.
4.2.2 Concentration Spectra

The spectrum of concentration fluctuations, $E_{cc}$, shows a flatter slope than $\kappa^{-5/3}$ at all depths. The slope appears to be close to $\kappa^{-6/5}$, which is consistent with the slope of $r^{4/5}$ observed for the structure function $D_{cc}$ in Figure 10. Evident in $E_{cc}$ is a spectral shift emphasizing larger scales near the surface. Notably, this shift is in the opposite direction to that seen in $E_{ww}$. We interpret such behavior to follow from the dynamics of the concentration boundary layer, which is thick and mostly unbroken near the surface, but is stretched and folded into fine-scale filaments in the bulk. As a result, small scales are emphasized at depth, even though large-scale motions are also stronger at depth.

Our results offer a significant counterpoint to the results of Magnaudet and Calmet (2006). While they showed the spectra of $c'$ and $w'$ to be identical, we find $E_{cc}$ is flatter than $E_{ww}$ in the bulk, and that $E_{cc}$ becomes steeper near the surface while $E_{ww}$ becomes flatter there. The difference is easily explained by noting that their measurements were within the energy-containing range, while ours are within the inertial subrange. The behavior we observe in $c'$ and $w'$ emphasizes that small scale fluctuations make a greater contribution to total concentration variance than they do for velocity variance.

![Figure 12: Power spectra showing how concentration variance is distributed across horizontal lengthscales. The spectrum is shown in dimensional form (integrates to $C_{rms}$) in plot (A) and nondimensional form (integrates to one) in plot (B). Symbols correspond to depth beneath air-water interface: $\star = 0.616$ mm, $\bigcirc = 5.544$ mm, and $\triangleright = 27.720$ mm. In plot A, the solid line shows a power law $5/3 \sim \kappa$ and the dashed line shows $6/5 \sim \kappa$. Plot B emphasizes the spectral shift towards larger scales near the surface.

4.2.3 Cospectrum of turbulent scalar flux

The covariance $\langle w'c' \rangle$ is the vertical turbulent mass flux, and the normalized cospectrum $E_{wc}$ shows how this flux is distributed across horizontal spatial scales. We compute the cospectrum by Fourier transform of $\rho_r = \rho_{wc}(r)/\rho(0) = \langle w'(x)c'(x+r) \rangle \langle w'c' \rangle^{-1}$.

Cospectra are typically noisier than spectra calculated from autocovariances such as $E_{ww}$ and $E_{cc}$, and our data is no exception. Despite the noise, three important observations can be made from $E_{wc}$, seen in Figure 13. First, the cospectra display power law behavior. Second, larger motions dominate the turbulent flux within the
inertial subrange. Third, the curves become steeper with depth, indicating a spectral shift emphasizing smaller motions closer to the interface.

To extract more information about the cospectra, we perform a Bessel function fit to the cross-correlation curves $\rho_f$. This model is preferable to the simpler exponential model, because its equivalent spectra and structure functions follow power laws (Pope, 2000). The two fitting parameters in this model are the spectral slope $p$ and the integral scale $\Lambda$. The model is:

$$\rho_f(r) = \frac{2}{\Gamma((p-1)/2)} \left( \frac{\sqrt{\pi} \Gamma(p/2) r}{2 \Gamma((p-1)/2) \Lambda} \right)^{(p-1)/2} \frac{K_{(p-1)/2} \left( \frac{\sqrt{\pi} \Gamma(p/2) r}{\Gamma((p-1)/2) \Lambda} \right)}{1 \pm \int_0^\infty \rho_f(r) dr},$$ (10)

where $K_{(p-1)/2}$ is the modified Bessel function of the second kind. The fitted values are seen in table 2, and the fitted curves shown in Figure 14. This model is only expected to match the data in the turbulent inertial subrange, i.e., for $r \approx 50 \eta \approx 5$mm in our case. Thus we perform the fit using data in the range 5mm < $r$ < 40mm. Results of the fit are statistically converged, in the sense that adding more data beyond $r = 30$mm does not result in a statistically significant change in fit parameters. The fit parameters, i.e., the spectral slope and integral scale, are seen in table 2 and Figure 15 over a range of depths. The spectral slope reaches a value of –2 in the bulk fluid, which agrees with the measurements of Chu and Jirka (1992) in a stirred tank, Mydlarski and Warhaft (1998) in a wind tunnel, and O’Gorman and Pullin (2005) via DNS. All of these experiments, and our result, fall short of the theoretical value of –7/3 predicted by Lumley (1967) and O’Gorman and Pullin (2005), suggesting that this prediction may be limited to extremely high wavenumbers.

Figure 13. Cospectra showing the distribution of turbulent flux across spatial scales. The spectrum is shown in dimensional form (integrates to flux) in plot (A) and nondimensional form (integrates to one) in plot (B). Symbols correspond to depth beneath air-water interface: * = 0.616 mm, O = 5.544 mm, and V = 27.720 mm. Lines show the results of the autocorrelation model fit, transformed to wavenumber space.
Figure 14. Spatially-lagged cross-correlation, including fits to Bessel function model. Symbols correspond to depth beneath air-water interface: $*$ = 0.616 mm, $O$ = 5.544 mm, and $\triangledown$ = 27.720 mm. 95% confidence intervals are shown on the experimentally measured values and on the predictions from each fitted curve.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Spectral slope</th>
<th>95% Confidence Interval (cm)</th>
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<tbody>
<tr>
<td>0.0616</td>
<td>-1.35</td>
<td>-1.24, -1.47</td>
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<tr>
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<td>-1.92</td>
<td>-1.83, -2.02</td>
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<tr>
<td>2.7720</td>
<td>-2.02</td>
<td>-1.94, -2.09</td>
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</table>

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Integral scale (cm)</th>
<th>95% Confidence Interval (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0616</td>
<td>2.93</td>
<td>2.20, 3.67</td>
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<tr>
<td>0.5544</td>
<td>3.16</td>
<td>3.03, 3.29</td>
</tr>
<tr>
<td>2.7720</td>
<td>14.91</td>
<td>13.59, 16.23</td>
</tr>
</tbody>
</table>

Table 2. Fit parameters for the model curves shown in Figure 13. The two parameters are the spectral slope and integral scale for the turbulent scalar flux $\langle w'c' \rangle$. These results are also shown in the context of a complete depth profile in Figure 14, indicated with symbols $*$, $O$, and $\triangledown$. 
Spectral slope and integral scale for the turbulent scalar flux \( \langle w'c' \rangle \), as determined by Bessel function fits similar to those seen in Figure 14. Symbols *, O, and ▼ indicate the three sample depths that are examined in previous plots.

6. Conclusion

We consider those turbulent air-water interfaces in which there is zero mean shear and focus on the spatial structure of turbulent mass transport below the interface. We design a laboratory measurement technique to provide simultaneous concentration and velocity fields under a surface. The resolution of the measurements are optimized to reveal dynamics within the turbulent inertial subrange. We use these techniques to observe 3D homogeneous isotropic turbulence with high Reynolds number and low mean flow as it interacts with a clean air-water interface at which a constant concentration of solute drives mass flux into the water.

From the spatial measurements of turbulent fields, we calculate the spatial spectra, structure functions, and autocovariance curves for velocity and concentration fluctuations. These show that the presence of the air-water interface emphasizes small scales for the surface-normal velocity component, and emphasizes large scales for the surface-parallel velocity component and concentration fluctuations. From the covariance of velocity and concentration fluctuations we calculate the turbulent mass flux. A quadrant analysis reveals that there is a four-way balance between coherent structures far from the interface, and near the interface this evolves into a two-way balance between motions that are raising and lowering parcels of low-concentration fluid.

Cospectra reveal how the turbulent mass flux is distributed over scales within the inertial subrange. Far from the interface, this spectrum follows a power law with an exponent of \(-2\), and the slope flattens as the interface is approached, reaching a value close to \(-4/3\) at the edge of the viscous sublayer. This result indicates that at all depths, large-scale motions dominate scalar flux within the inertial subrange. This result complements the spectral dynamics observed in the energy-containing regime using large-eddy simulation.
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References


Asher, W., and R. Wanninkhof 1998  Transient tracers and air-sea gas transfer, J. Geophys. Res., 103(C8), 958.


