Published in final edited form as:

IEEE Sens J. 2020 February ; 20(3): 1509–1526. doi:10.1109/jsen.2019.2946968.

A Multi-Function Sensor for Eddy Correlation Measurements of Benthic Flux

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Abstract

Eddy Correlation (EC) is a technique that can be used to measure transport of substances in aquatic ecosystems between bottom sediments and the overlying water (i.e. benthic fluxes). Based on high-speed, simultaneous, and co-located velocity and concentration measurements, EC has been successfully used in a variety of freshwater and marine settings to determine benthic fluxes of dissolved oxygen. Application to a larger range of compounds is limited, however, by the lack of suitable chemical sensors. Here, we describe FACT, a novel, high-speed, multi-function sensor created to expand the range of benthic fluxes that can be measured with EC. An optical fiber spectrofluorometer with a proximally located conductivity cell and thermistor, FACT enables benthic flux measurements of fluorescing compounds, such as fluorescent dissolved organic matter, as well as of heat and salinity which can be used as tracers for submarine groundwater discharge. The high bandwidth and open-beam geometry of the fluorescence sensor are particularly beneficial for EC measurements.

FACT was integrated with a velocity sensor into a full EC system capable of simultaneous benthic flux measurements of fluorescing compounds, heat, and salinity. Tested in a laboratory tank, fluxes measured by all three sensors were found to track each other as well as compare favorably with expected values. Furthermore, the ability to measure fluxes of multiple substances both extends the applicability of EC to a wider range of natural sites, and can provide insight into issues of sensing volume and time responses as they affect the application of EC to natural waters.

Index Terms—

chemical sensors; eddy correlation; geoscience; optical sensors; benthic fluxes

I. Introduction

Quantifying chemical fluxes between natural waters and their benthic sediments is a central problem in biogeochemistry. Examples of benthic fluxes of interest include contaminants

such as polycyclic aromatic hydrocarbons (PAHs), whose release to the water can affect human and ecosystem health [1]; dissolved organic material (DOM), an important part of carbon cycling in aquatic ecosystems with a significant role in many biogeochemical processes [2]–[6]; and nutrients, which can cause harmful algal blooms. Knowledge of these and other fluxes at the sediment-water interface is important not only for understanding ecosystem functions, but also for remediating hazards, maintaining water quality, and improving the health of aquatic environments.

However, the current capability to measure benthic fluxes is severely limited. Traditional techniques include benthic chambers placed on the sediment, sediment core incubation techniques, and diffusion calculations based on in-sediment concentration profiles [2]. These methods often disturb and/or fail to recreate the environments they are measuring. In addition, their ability to capture benthic flux varies depending on the mechanism of transport (e.g. molecular diffusion, advection, bioturbation, or bioirrigation) as well as on sediment properties. The accuracy of these flux estimation techniques is very difficult to quantify, and it is not surprising that side-by-side comparisons of different techniques often produce vastly different results [7]–[9]. The small footprint and limited temporal resolution of these techniques also limit their use in many studies, as benthic fluxes are often spatially heterogeneous [10] and temporally variable [5], [11].

Eddy Correlation (EC) is a technique for measuring vertical fluxes that originated in the field of micrometeorology, where it has been widely used for decades to determine fluxes (of e.g. gases, vapors, and heat) to or from the earth's surface. It has also been used in a variety of aquatic settings to estimate heat, momentum, and buoyancy fluxes [12]–[16]. Only more recently has it been applied to benthic fluxes of solutes [7], but it is especially promising as a minimally invasive and in situ technique that addresses many of the challenges faced by traditional methods of benthic flux measurement.

EC provides an estimate of flux by measuring the covariance of the concentration of the target substance and the vertical component of fluid velocity. Such covariance is traditionally considered to represent vertical transport by eddy (turbulent) diffusion, which is typically the dominant mechanism of vertical solute transport in the water column above the sediment-water interface [17]. The name 'eddy correlation' is thus widely and appropriately used. However, we note that, with appropriate data processing choices, the technique can and does measure any solute transport that is mediated by motions of water, whether or not those motions are technically considered turbulence.

Unlike other methods, EC is by nature rapid and non-invasive, and can measure fluxes regardless of the exact mechanism by which substances are released from the sediment or the nature of the benthic substrate; once in the boundary layer, net vertical transport is almost always dominated by eddy diffusion. It has been successfully used in a range of freshwater and marine settings, including sites where traditional methods are unusable, uncertain, or challenging (e.g. permeable sediments [11], [18], [19], hard bottom substrates [20], and various benthic ecosystems [10], [21], [22]). Typically, EC has been used to measure benthic fluxes of dissolved oxygen (DO), using an Acoustic Doppler Velocimeter (ADV) to measure water velocity and either a fast Clark-type microelectrode (e.g. [7], [11],

[23]–[27]) or a fluorescence-based oxygen optode (e.g. [8], [19], [28]) to measure dissolved oxygen concentration.

However, EC can in principle be used to measure the flux of any substance, as long as a suitable sensor exists for that substance. For example, using a temperature sensor, heat flux has been measured in several studies, often alongside oxygen fluxes [8], [29]–[31]. Benthic fluxes of salinity have also been measured using fast conductivity sensors, and EC-measured fluxes of conductivity and temperature have been used to infer submarine groundwater discharge [17]. Other sensors used with EC have included: a bisulfide microelectrode used to measure H_2S fluxes [32]; an In Situ Ultraviolet Spectrophotometer (ISUS) used to measure nitrate fluxes [33]; an H^+ Ion-Selective Field Effect Transistor (ISFET) used to measure hydrogen ion fluxes [19]; and a single-channel Colored Dissolved Organic Material (CDOM) fluorescence probe used to measure DOM fluxes [34].

Nevertheless, application of the EC technique to a larger range of compounds remains limited by the lack of chemical sensors with adequate sensitivity, selectivity, speed, and resolution for eddy correlation.

Here, we describe the FACT (Fluorescence And Conductivity / Temperature) sensor, an optical fiber spectrofluorometer with a built-in conductivity cell and fast thermistor designed with the EC application in mind. Used in an EC system, FACT enables simultaneous quantification of benthic fluxes of fluorescent compounds (e.g. fluorescent dissolved organic material (FDOM)), salinity, and heat content, thus expanding the range of entities whose fluxes can be measured with EC. Additionally, the ability to measure three simultaneous fluxes enables cross-checking of flux measurements, and presents a unique opportunity to explore the impact of factors such as sensor speed, sensing volume size, and sensing volume location on eddy flux calculations.

In the present manuscript, we first review, in Section II, the mathematics underlying the EC technique and the sensor requirements that follow. In Section III, we provide system descriptions of the FACT sensors, and in Section IV we characterize them individually and relate them to the EC requirements. In Section V we compare the sensing volumes and bandwidths of the three FACT sensors in an actual flow field. In Section VI, we describe FACT's integration with an Acoustic Doppler Velocimeter (ADV) to form a complete EC flux measurement instrument. In Sections VII and VIII, we examine the FACT EC system's ability to measure a benthic flux in a laboratory tank. Additional detailed information is available in [35].

II. EC theory and sensor requirements

A. Basic theory of EC flux measurement

Eddy correlation measurements of benthic flux in aquatic systems involve simultaneously measuring the chemical concentration, $c(t)$, and vertical velocity, $w(t)$, of water in a small control volume above the sediment [7]. Although commonly used to measure fluxes of chemical compounds, it can also apply to other scalar properties such as salinity, heat, or

momentum. In the present paper, we use the term ‘concentration’ in a general sense to refer to any scalar measurand whose flux is of interest.

The product of concentration and velocity is the instantaneous vertical flux, which is then integrated over a period of time significantly longer than the time scale of the turbulent eddies to obtain a mean flux, as given by (1):

$$\overline{Flux(t)} = \overline{c(t) \times w(t)} \quad (1)$$

where the overbars represent an average over time. This relationship and its applicability to eddy correlation measurements can be derived from mass (or energy) conservation equations [36].

In EC measurements, prior to calculation of the covariance, a Reynolds’ decomposition is used to break down the instantaneous values $c(t)$ and $w(t)$ into mean values ($\bar{c}(t)$ and $\bar{w}(t)$) and fluctuations around the mean ($c'(t)$ and $w'(t)$), as in (2):

$$\begin{aligned} c(t) &= \bar{c}(t) + c'(t) \\ w(t) &= \bar{w}(t) + w'(t) \end{aligned} \quad (2)$$

The mean flux can then be expressed as in (3):

$$\begin{aligned} \overline{Flux} &= \overline{\bar{w}\bar{c}} \\ &= \overline{\bar{w}\bar{c}} + \overline{\bar{w}c'} + \overline{w'\bar{c}} + \overline{w'c'} \end{aligned} \quad (3)$$

Two distinct and different averaging operations are represented by the overbars in (3). The flux is averaged over a measuring period (flux window) T , so that one period T produces one flux data point. Averaging over some flux window is intrinsically necessary due to the stochastic nature of turbulence, and T is generally chosen such that a representative flux value can be arrived at given the turbulence characteristics of a particular site. For example, systems characterized by larger, slower eddies would require longer flux windows, as one major excursion can have a significant impact on the mean, and the system is not stationary over shorter windows [13].

The averaging of the individual $w(t)$ and $c(t)$ time series for the Reynolds’ decomposition, on the other hand, is used to remove low-frequency components that are not part of turbulent flux. Low-frequency components can arise from e.g. instrument drift, or vertical advection events that do not contribute to flux to/from the interface but instead balance out unmeasured transient horizontal advection or changes in the storage term (assumed in the mathematics behind the technique to be negligible) [26], [36]. When included in calculations over shorter time periods, these processes can bias the statistical techniques used to analyze turbulence. Thus, a mean removal process such as a detrending or filtering operation is often used in the Reynolds’ decomposition, in an attempt to remove the effects of these slower processes from the calculation of turbulent flux [37].

If the averaging operator obeys the Reynolds averaging properties, then the $\overline{w'c'}$ and $\overline{w'\bar{c}}$ terms in (3) disappear [37]. The mean vertical velocity $\bar{w}(t)$ is also assumed to be 0, which is generally true if the measurements are expressed in streamline coordinates, as can often be accomplished by an appropriate coordinate transformation of the velocity data [38], [39].

Thus, given proper mean removal and coordinate rotation, (3) can be simplified and the flux can be calculated from the correlation between the fluctuating components of velocity and concentration, as in (4):

$$\overline{Flux} = \overline{w'c'} \quad (4)$$

The final result is an estimate over the (temporal) averaging period of the (spatial) average flux from an upstream contributing area of the sediment surface (often called the ‘footprint’) whose size, shape and location depends on deployment conditions [40].

Eddy correlation can be used to measure heat or salt fluxes by using temperature or conductivity as the scalar ‘concentration’. Such fluxes can arise when groundwater seeps into a water body of different temperature or conductivity via the bottom sediments; the heat and/or salt flux can then be used to infer the rate of groundwater discharge. Submarine groundwater discharge (SGD) into coastal ecosystems can serve as a significant source of solutes to the coastal ocean, and knowledge of its rates, although difficult to obtain, can be used to directly inform management decisions [41].

It should be noted that, although groundwater seepage into a surface water body is in fact advective, the velocities are usually low relative to surface water velocities, and vertical transport becomes dominated by eddy fluxes more than a few cm above the sediment.

Using control volume analysis, the groundwater flow rate can be found from temperature flux, as given by (5) [17]:

$$q_g = \frac{\overline{w'T'_{\omega}s_{\omega}\rho_{\omega}}}{\rho_g(T_g s_g - T_{\omega}s_{\omega})} \quad (5)$$

where q_g is the groundwater flow, $\overline{w'T'_{\omega}}$ is the EC-measured heat flux, T is the mean temperature ($^{\circ}\text{C}$), s is the specific heat ($\text{J/g}\cdot^{\circ}\text{C}$), ρ is the density (g/cm^3), and the subscripts g and ω denote properties of the groundwater or surface water column. Similarly, groundwater flow can be found from salinity flux, as given by (6):

$$q_g = \frac{\overline{w'S'_{\omega}\rho_{\omega}}}{\rho_g(S_g - S_{\omega})} \quad (6)$$

where $\overline{w'S'_{\omega}}$ is the EC-measured salt flux and S is the mean salinity. Notably, using temperature and/or salinity flux to derive groundwater discharge rates also requires measurements of the mean temperature and/or salinity of the groundwater seeping from the bottom sediments.

EC is a promising technique with many advantages, but successful application requires recognition of the challenges that complicate its usage. Errors that affect the quality of the measurements generally result from 1) sensor limitations, or 2) deviations from assumptions about hydrodynamic settings behind the derivation of (4) [36].

Sensor limitations are often specific to the sensors used; for example, oxygen microelectrodes are known to be sensitive to the velocity of the surrounding fluid [42], [43]. Sensor limitations can also occur when sensors do not meet the performance requirements for EC, described below in Section B.

On the other hand, errors arising from complex hydrodynamic conditions complicate the usage of EC at certain sites, and necessitate careful consideration in data processing and interpretation [26]. Errors can arise from e.g. spatial heterogeneities in the flux footprint [44], transient processes in the water column [45], or complex topography including sloped sediment beds [39]. Systems with waves also present a unique set of challenges [26], [43], [46]. A more complete treatment of these considerations is presented in [35].

B. Requirements of an EC sensor

Eddy correlation measurements require simultaneous and collocated measurements of velocity and concentration. The sensors for these measurements must meet certain requirements in order to produce reliable flux estimates. Some typical parameters are given by Table I, following the analysis presented by Lorrai et al [25]. The major requirements, which guide the development of an EC concentration sensor, are described below.

1) Sensor speed—EC sensors must be fast enough to capture the smallest turbulent fluctuations (eddies) that contribute significantly to the flux. In Table I, the timescale for the fastest (and smallest) eddies is given by the Kolmogorov scale, which represents the end of the turbulence cascade at which kinetic energy is dissipated by viscosity, and in typical waters ranges from 0.2 s to 7.4 s (corresponding to 5 Hz to 0.1 Hz). Commercial ADVs used to measure water velocity generally meet this requirement; the Nortek Vector used in this study, for example, is capable of measuring at up to 64 Hz, though data are less noisy for slower measurements.

Speed requirements are usually more difficult to meet for the concentration sensor. In EC studies thus far, a 90% response time (τ_{90}) of 0.2 s has generally been deemed sufficient [47]. Although this response time is slower than the fastest eddies in some settings (Table I), the ‘flux-relevant frequency ranges’ identified by many EC studies based on cospectra (which give contribution to flux by frequency) have generally not exceeded 1 Hz [25], i.e. the turbulent flux is considered to be carried predominantly by fluctuations slower than 1 Hz [7], although contributions as fast as 4 Hz have been found at some sites [11]. Larger eddies in general carry a greater proportion of the flux, so it is possible that the small, fast eddies that a sensor is unable to observe contribute minimally.

However, definitive conclusions regarding the importance of cospectral contributions at higher frequencies require sensors capable of capturing those frequencies. One laboratory study estimated a 15% loss in measured flux when a sensor with $\tau_{90} = 0.1$ s was used in

flow velocities of 7.4 cm/s [47]. Frequency corrections are sometimes used to account for a slower response time in faster flow, but these corrections can degrade signal quality by amplifying high-frequency noise [25], [47]. Accordingly, a concentration sensor with a response time shorter than 0.1 s would have value both for making more accurate EC measurements in certain settings, and for providing more definitive answers to questions regarding loss of accuracy when using slower sensors.

2) Sensing volume size—The sensing volume ideally should be small enough to distinguish the smallest eddies contributing significantly to flux. For velocity, the ADV sensing volume is often approximated as a vertical cylinder with length and diameter of the order of a cm, which is larger than some of the fluctuations as given in Table I. Thus, in practice the sensing volume of the concentration sensor is likely not a limitation on accuracy as long as it is no larger than that of the ADV's.

In contrast to the requirements set by the *smallest* eddies described above, the length and time scales of the *largest* eddies do not in general impose further requirements on the sensors. However, the time scale of the largest eddies plays an important role in data processing, specifically in the mean removal process, as an averaging time scale must be chosen that is long (low frequency) enough to adequately sample all flux-contributing eddies [23].

The eddy scales given in Table I are typical, order-of-magnitude quantities. Measurements at a fixed point (Eulerian reference frame) do not track the water particles moving within an eddy (Lagrangian frame), but rather measure the turbulence structures as they drift past the sensor [25].

3) Precision and sensitivity—Sensors for EC must be sensitive (precise) enough to measure the turbulence-driven fluctuations in the measurands of interest. For velocity, the size of the fluctuations depends on the level of turbulence; under well-developed turbulence, the friction velocity u_* is generally considered a good proxy for the size of the vertical fluctuations w' .

For concentration, the magnitude of the fluctuations also depends on the local concentration gradient. For a given flux value and velocity scale, the anticipated fluctuations can be estimated using (7) [25]:

$$c'_{\text{estimated}} \approx \frac{\overline{w'c'}}{u_*} \quad (7)$$

Table I gives typical fluctuation magnitudes for a range of dissolved organic material (DOM) fluxes and submarine groundwater discharge (SGD) rates. The magnitude of the expected fluctuations dictates the necessary resolution for the corresponding sensors, whether limited by digitization or by electronic noise.

Although sensor noise is ideally less than the actual concentration fluctuations in the water, the effects of random (white) noise on the final flux number are mitigated to some degree by

the temporal averaging that is an intrinsic part of EC; evenly distributed noise is uncorrelated and averages to zero [24], [32]. Nevertheless, sensor noise degrades measurement quality and may necessitate longer averaging periods to obtain adequate flux measurements.

For the velocity sensor, the sensitivity requirements can also be restrictive, especially in low-flow settings. For ADVs, which function by scattering sonar pulses off particles, low background particle count of a water can also limit the accuracy and precision of velocity measurements [27], [30]. It is therefore generally recommended not to use eddy correlation in quiescent and/or low-turbidity settings. Low-flow settings intrinsically present a challenge for EC anyway, since if there is no turbulence then there is no turbulent diffusion.

4) Physical interference and sensing volume location—The most common velocity sensor used for EC measurements of benthic flux is the Acoustic Doppler Velocimeter (ADV). ADVs measure 3-dimensional velocity by transmitting a short pulse of sound ('ping'), and detecting backscatter from suspended particles, which are typically present in natural waters and move passively with the water. As the sound pulse scatters off particles moving relative to the transmitter, the water velocity is calculated from the Doppler shift between the ping sent and the echo received [48].

ADVs generally have a central transducer that emits the ultrasonic pulses, and two to four receiving transducers spaced around the emitter that detect the reflected pulses. The sensing volume is defined by the intersection of the transmission and receive paths, typically 5 to 18 cm away from the central transducer [49].

For EC measurements, the velocity and concentration sensing volumes are ideally collocated. However, all chemical sensors used with EC to date have measured concentration in the volume of water essentially in contact with their physical structure, and the presence of a probe in or close to the ADV's sensing volume can interfere with its acoustic-based measurements. Thus, the concentration probe is generally located some distance (mm to cm) away from the ADV sensing volume. The resulting displacement in sensing volumes creates an error that can be partially corrected, in some settings, with a time shift; however, the flux estimate is still degraded if the velocity and concentration measurements are too far apart to reliably sample the same eddies, or if the chemical sensor cannot be positioned downstream of the velocity sensing volume with adequate certainty [47]. In addition, at sites with more complicated flow patterns (e.g. waves), improper application of the time shift correction can actually bias the calculated fluxes [46]. Larger sensor probes especially, which are easier to work with and often more robust, require greater displacement from the ADV's sensing volume and thus can only be used under certain field conditions [8]. Thus, one additional motivation for the present study is to explore concentration sensors that intrinsically provide a spatial offset between their physical sensor location and their sensing volume, which can then be positioned to coincide with the velocity sensing volume with minimal interference.

5) Other requirements—A benthic flux sensor system is subject to the usual constraints of portable, field-operable instrumentation, including size, weight, and power (SWaP) limitations as well as the need to be waterproof and rugged. To be economically

practicable for widespread use, the instrument should be built of standard, available, low-cost components to the extent possible.

III. System description of FACT sensors

A. Spectrofluorometer

The primary chemical sensor in FACT is an optical fiber spectrofluorometer capable of high-speed, high-resolution, in situ measurements [50]. A block diagram of the driving electronics is shown in Fig. 1.

The instrument utilizes a light-emitting diode (LED) to excite fluorescence. The 375 ± 10 nm wavelength LED (ThorLabs 370E) is suitable for detecting compounds such as humic substances (dissolved organic material) and dyes such as fluorescein and rhodamine. The LED is housed in a lens tube, which enables coupling with an optical fiber as well as easy exchange for a different wavelength LED to target other compounds. The light source can be modulated to reject ambient light.

To carry light to and from the sensing volume, the system uses a pair of 1000 μm silica optical fibers (Thor Labs FT1000UMT), enabling efficient transmission over much of the visible and UV spectrum. The sensing end of each optical fiber is polished bare fiber, with the final 15 cm encased with 316 stainless steel tubing for stiffness and protection. The optical fibers are held at a 20° angle by a custom stainless steel holder. The fibers are encased for mechanical protection in 3 mm PVC furcation tube, which is further encased in 6.35 mm flexible PVC (Tygon) tubing.

The optical fiber carrying light from the sensing volume terminates in a tunable monochromator (Spectral Products CM110) coupled to a fast photomultiplier tube (PMT; ET Enterprises 9111WB). The monochromator's output wavelength can be adjusted via software within the range of ~ 185 to 650 nm. Thus, the instrument can also be used to target a variety of compounds that fluoresce at different wavelengths, as well as to characterize the fluorescent chemical composition of the environment by scanning the emission spectrum.

The use of optical fibers allows the spectrofluorometer's sensing volume to be separated from the bulkier electronics package, minimizing disturbances to the flow field while allowing the sensing volume to be aligned to that of the ADV. However, as the optical fibers also restrict the amount of light that can be collected from the sensing volume, a maximum sensitivity detector was designed that utilizes photon counting. Circuitry was developed that includes the PMT's high-voltage supply and voltage divider, a proximally located amplifier circuit, a comparator, and two chained 8-bit counters to count pulses directly on the board. The photon pulses have on average a full width half maximum duration of 1–2 ns and can be as small as a few mV (into a 50 Ω load). Thus, special attention was given to minimize ringing and optimize for high-speed data transmission, as well as to minimize susceptibility to radio frequency interference, which proved to be particularly problematic in our laboratory given the proximity of FM broadcast stations.

B. Temperature and conductivity

FACT measures conductivity and temperature in close proximity to the fluorescence sensing volume. Temperature is measured by a miniature NTC thermistor (U.S. Sensor GP104L8F), which has a 1 mm diameter glass body. The thermistor is packaged at the tip of a gauge 18 stainless steel needle (1.27 mm outer diameter) filled with epoxy resin and encased by dual-wall heat shrink tubing. The entire probe (2 mm diameter) is fixed to the sensing end of one of the optical fibers. As in the case of an oxygen sensor, the probe must be offset from the ADV sensing volume.

A Wheatstone bridge converts the temperature-dependent resistance of the thermistor to a voltage. The thermistor's R-T curve is considered locally linear, and the circuitry is designed to operate between 7 °C and 26 °C. The range can be adjusted by changing resistor values, with smaller ranges corresponding to greater temperature resolution.

The conductivity cell is formed directly from the 15 cm stainless steel tubings protecting the sensing ends of the optical fibers. Both tubings (each housing a fiber) are exposed for 1~2 mm at the tip, with their inside-facing edges coated with insulating epoxy. The remainder of each tubing is encased in dual-wall moisture-seal heat shrink tubing.

The conductivity cell is driven by a sine wave voltage produced by a Wien bridge, at a frequency of 72 kHz, chosen to minimize electrode polarization issues [51], [52]. This signal excites the probes through a transformer, which galvanically isolates the probes to prevent current from shunting to other unknown potentials in the external water body. The current of the transformer primary and voltage of the secondary are measured independently to calculate conductivity ($g \sim I/V$). A transformer model was used to select components to reduce the effect of transformer non-idealities on circuit behavior.

C. Microcomputer

The instrument is controlled by a Raspberry Pi 3 Model B microcomputer (1.2 GHz Broadcom BCM2837 64 bit CPU). The Raspberry Pi can communicate with a user-controlled computer via remote login through an underwater Ethernet cable; this connection is used to initiate measurements and read data, but can be disconnected during data collection.

The Raspberry Pi handles all spectrofluorometer functions, including reading in photon counts, processing and storing the data, and controlling the monochromator and LED. Thus, through the command-line user interface, the instrument can be instructed to take a spectral scan (by stepping the monochromator in user-selectable increments), take a specified number of measurements at a fixed monochromator wavelength, or take a time series at some specified frequency. The integration time, as well as the frequency of the optional LED modulation, are also adjustable.

The temperature and conductivity sensors are managed by a front-end microcontroller, a Teensy 3.2 (PJRC), which then transmits its measurements to the main Raspberry Pi microcomputer. This structure enables the Teensy to continue to read temperature and/or

conductivity measurements even as the Raspberry Pi is counting photons for fluorescence measurements, enabling simultaneous measurement.

IV. Performance of individual sensors

A. Performance of spectrofluorometer

1) Precision / Accuracy—Because the arrivals of individual photons at the photocathode of the PMT can be treated as independent events, photon counting can be modeled with a Poisson distribution [53]. Thus, the theoretical standard deviation is given by the square root of the number of counts, i.e. (8).

$$Error (std)\% = \sqrt{N}/N \quad (8)$$

where N is the number of observed counts. Note that N depends on the amount of time the instrument spends counting for any one data point and is thus inversely proportional to measuring speed, although all counts are normalized to counts/s before outputting.

The error performance of the instrument is shown in Fig. 2. The extremely close fit of observed standard deviation to the $\sqrt{N}$ line indicates that the instrument is operating close to the theoretical minimum level of variance (shot-noise limited), with little excess noise introduced by the circuitry, data processing, or PMT dark count. The error performance of the instrument thus depends almost purely on the amount of light passing through the monochromator, which in turn depends on the fluorescence of the compound (e.g. its concentration and quantum efficiency) and the measurement speed.

2) Performance with humic acids; calibration curve—The spectrofluorometer was tested using solutions of various fluorescent substances, including laboratory humic acid (Sigma Aldrich). Humic substances, comprising much of the dissolved organic material in many natural waters, are complex mixtures of naturally occurring organic compounds derived from partial decomposition of (primarily) plant detritus. While their composition varies both spatially and temporally [54], their optical properties remain broadly similar across a useful range of different sources and compositions. FDOM fluorescence cannot always provide definitive information on actual organic material concentration, but it can often be used to infer DOM concentration through site-specific ratios [55], [56].

A piece-wise calibration curve for lower concentrations of humic substances (corresponding to relatively clear natural waters) is shown in Fig. 3. The calibration curve is necessarily somewhat nonlinear due to inner filtering; however, local linear fits, such as those shown in Fig. 3, provide extremely good approximations for the concentration fluctuations that are used in EC measurements. The spectrofluorometer's useful range extends to higher concentrations of humics as well (e.g. tens of ppm), recognizing that the calibration curve flattens due to inner filtering [50].

The x error bars in Fig. 3 represent the observed standard deviation and correspond well to the theoretical minimum given by (8), given the integration time of 50 ms. The y error bars represent the corresponding error in DOM concentration calculated using the fit equations in Fig. 3, and can be compared to the estimated DOM fluctuations given in Table I (6×10^{-7}

ppm to 0.02 ppm). It can be seen that, with an integration time of 50 ms, the sensitivity requirements for the spectrofluorometer are challenging, as even fluctuations on the larger end of expected values (high fluxes, low turbulence) are of the same order of magnitude as the measurement noise.

As the noise is primarily statistical (from photon counting), it can be reduced by measuring longer. In general, the integration time can be adjusted to trade off accuracy and speed, depending on the fluorescence strength, turbulence, and other characteristics of the site. In addition, evenly distributed white noise will also average out to some degree in the flux calculation [24], [32], as described in Section II. Nevertheless, the sensitivity requirements represent a continuing challenge for application of fluorometry-based EC to field conditions, as will be discussed further in the conclusion.

3) Spectral scans—The instrument is capable of taking spectral scans by stepping through detection wavelengths with the monochromator and measuring the light level at each wavelength. Spectral scans are generally useful for characterizing the environment and determining which classes of fluorophores are present, as well as identifying site-specific optimal wavelengths for EC measurements of FDOM. An example of a spectral scan is shown in Fig. 4, which shows the emission spectra of humic acid and fluorescein dye solutions (taken separately), as well as the LED and water Raman scattering signals.

4) Sensor speed—Given the high bandwidth of the photon counting circuitry, the speed of the fluorescence sensor is, practically speaking, limited only by the desired counting statistics given the available light. As an example of typical speeds achieved with the fluorescence sensor, the measurements in Fig. 3 used integration times of 50 ms (corresponding to 20 Hz; processing time is minimal). Further discussion of sensor speed is provided in Section V-D.

B. Performance of temperature sensor

1) Calibration curve—The range and resolution of the temperature sensor are determined by the gain resistor of the amplifier and the resistors of the Wheatstone bridge, and thus can be adjusted depending on the environmental setting. As an example of typical values, a calibration curve over the relatively large range of 7 °C to 28 °C had a slope of 0.0056 °C per least significant bit (LSB) of the analog to digital converter (ADC) (Fig. S2). When measured for 100 ms, repeated measurements of roughly constant temperatures had standard deviations of the order of 1–2 LSB, indicating that the precision of the instrument is in general limited by the ADC resolution.

From Table I, this degree of resolution is likely sufficient for capturing the temperature fluctuations relevant to eddy transport of heat in some but not all environmental settings. However, as described, the resolution can be readily increased by increasing the gain resistor of the amplifier.

2) Time response—The time response of the temperature sensor was estimated by moving it quickly between two beakers of water at different temperatures (Fig. S3). The 90% response time (τ_{90}) was estimated to be between 0.5 and 1 s, likely limited by the

thermal mass of the thermistor. For future work, the faster but more expensive FP07 (GE) thermistor, used in other EC tests [17], [30], will replace the current GP104L8F model.

C. Performance of conductivity sensor

1) Calibration curve—A calibration curve of the conductivity sensor was obtained using NaCl solutions of various concentrations as well as various dilutions of brackish water collected from Boston Harbor. The resulting conductivities ranged from 1 uS/cm to 26 mS/cm. Conductivities were measured independently using a commercial conductivity meter (Amber Science Model 604). The calibration curve (Fig. S4) was broken into two pieces to accommodate the wide range of target conductivities, ranging from dilute freshwaters to waters of typical estuarine salinity.

For lower conductivities (<4000 uS/cm), standard deviations of repeated 100 ms measurements were generally 0.9 uS/cm or less. For higher conductivities, absolute standard deviations over repeated 100 ms measurements were larger, e.g. 17 uS/cm for a 26 mS/cm baseline. Comparison to Table I shows that additional resolution may be necessary for certain low-turbulence, high-salinity settings; this can be achieved with higher gain and/or a higher resolution ADC.

2) Time response—The time response of the conductivity sensor could not be accurately measured by simply transferring the electrodes quickly between beakers containing different solutions, because of the large perturbation in conductivity every time the sensing head was lifted out of the water. However, the electronic response time of the circuit was tested separately using a switched resistor and the 90% response time (τ_{90}) of the electronics was found to be on the order of 2 ms.

V. Sensing volumes and covariance among sensors

The ability of FACT to measure fluorescence, conductivity, and temperature simultaneously and in approximately the same location was evaluated in a series of experiments in a racetrack flume. A warm, salty, fluorescent tracer mix was injected into the flow such that it was carried into and past the instrument's sensing volume. The heat, salinity, and fluorescein dye were assumed to travel together, as their turbulent diffusivities were considered to be nearly equal in this setting.

A. Sensing volumes

Estimates of the sensing volumes for the three FACT sensors, shown in Fig. 5, were used to assess if, when, and to what extent any differences between their measurements could be explained by differences in the location, size, or shape of their sensing volumes.

1) Fluorescence—The sensing volume of the fluorescence sensor lies at the intersection of the cones of emission and acceptance of the two optical fibers. It was verified empirically by assembling a composite of video frames of the sensor head during injections of fluorescein dye, in which the beam of the LED was visualized by the emission of fluorescein within its cone. The cone of acceptance was taken as identical to that of emission, but tilted by 20° in the horizontal plane (the angle between the optical fibers as fixed by their rigid

mounting). Their overlap was marked as the sensing volume, with heavier shading to indicate weighting toward the area of the sensing volume closer to the optical fibers.

2) Temperature—Similar to many chemical probes, including the oxygen microelectrodes traditionally used in EC measurements, the thermistor measures its target property (temperature) in the volume of water in contact with, or within diffusion length scales of, its physical body. The temperature sensing volume can thus be considered to be the thin layer of water surrounding the body of the thermistor (e.g. a diffusive boundary layer) that is almost always near thermal equilibrium with the thermistor body.

This sensing volume is considerably smaller than those of the other two FACT sensors (fluorescence and conductivity), being not much larger than the size of the thermistor itself (a cylinder of 1 mm diameter and 2.8 mm length). It is also collocated with the sensor's physical body. The thermistor is mounted beneath one of the fibers as shown in Fig. 5b, slightly offset from the other sensors to avoid interference with the other measurements.

3) Conductivity—To map the conductivity sensing volume, a 4X scale model of the electrodes was constructed and placed in a 40 L aquarium filled with tap water. A 5 V sine wave voltage was applied across the electrodes at the same 72 kHz frequency as the FACT conductivity sensors, and the resulting potential field was measured using a single wire probe connected to a multimeter. Measurements were made in, and are displayed for, the horizontal plane of the electrodes. The measured potentials were used to inform the construction of a flow net [57] (Fig. 5c), whereby the bodies of the electrodes are modeled as equipotential surfaces of different electrical potential (i.e. the voltage difference across the probes), and perpendicular streamtubes show the path of current between the two electrodes.

The current density is higher where streamtubes have smaller cross-section, and the effective sensing volume is thus weighted toward the water closest to the electrodes. In contrast, the streamtubes in regions further from the electrodes cover much larger volumes over which the potential gradient and therefore the current density are low, and in which small changes in conductivity have less effect on the conductance seen by the electrodes. Five of the nine streamtubes in Fig. 5c are therefore shown only to radiate outward, as conductivity fluctuations in the more distal regions (not shown) are considered to have little impact on the sensor response.

B. Evaluation in a racetrack flume

Tests were conducted in a flume having a channel width of 16 cm, a height of 20 cm, and a straight channel length of 6 m, filled to 17 cm depth with tap water circulated at a velocity of approximately 3 cm/s. The FACT sensing head was mounted at 8.6 cm depth near the end of the channel and oriented to face into the flow. A tracer solution was prepared with an approximate concentration of 5 ppm fluorescein, 20 mS/cm conductivity, and between 40 and 60 °C temperature. The flume started with no fluorescein, a conductivity of 950 to 1050 uS, and a temperature of approximately 17 °C. The tracer was injected 2 to 10 cm upstream of the sensing head. Pulse injections were made with a 5 mL micropipette, while continuous injections were made using a syringe pump connected to a 1.4 mm ID stainless steel tubing outlet. FACT measurements were made at 32 Hz using 30 ms integration times.

Videos of the injections were recorded by a downward-facing camera mounted above the flume, and a side-facing camera mounted on a tripod next to the flume. A 405 nm 'black light' fluorescent tube was positioned nearby to excite sufficient fluorescence in the dye for the cameras to image its flow. Fluorescence excited by the black light was rejected from the FACT fluorescence sensor's signal by the instrument's excitation modulation feature.

C. Results of flume experiments

Tracer pulses injected with the micropipette generally travelled past the FACT sensor head with the appearance of turbulent eddies, and were observed in the sensors' signals as burst events. Tracer injected with the syringe pump generally travelled past the sensor head in the form of distinct, narrow jets. The nature of the resulting signals depended on the location, angle, and speed of the injection relative to the sensor head.

Fig. 6 gives an example of a time series covering four micropipette injections, showing turbulent features of the dye that were picked up by all three FACT sensors. Some differences between the three signals can be attributed to differences in sensor response times, with faster response times leading to sharper peaks and steeper tail-offs. As expected, the temperature response was the slowest, while the fluorescence response was by comparison essentially instantaneous.

A second source of variation among the three time series was the difference in sensing volumes (in location as well as in size, shape, and weighting, as shown in Fig. 5). These differences caused the sensors to sample different parts of the same eddies and to different extents, resulting in somewhat different features being detected. This interpretation is consistent with visualizations provided by comparing the sensor signals with video recordings and estimates of the sensing volumes (see Supplementary Information).

The impact of these differences in sensing volume on flux estimates is unclear, but likely depends on how energetic the environment is, and the extent to which a time shift can be used to correct for sensing volume offsets. However, the sensor configuration provided by FACT provides a means for further examining this question in different environments.

It should also be noted that the effects of differing time responses and sensing volumes are intertwined, and the effects of spatial and temporal averaging can in practice be indistinguishable. For example, the passage of two parcels of water with elevated concentrations might be detected as one event by a sensor with either a slower response time (which cannot adjust quickly enough to reflect the timespan between the two parcels) or a large sensing volume (which simultaneously samples both parcels of water at once).

D. Power spectra from flume experiments

Fig. 7 shows variance-preserving power spectra (frequency multiplied by power spectral density, reflecting the distribution of power by frequency when viewed on a log(f) scale [14], [23]) for each of the three FACT sensors, composited from 31 separate time series taken in the flume under a variety of flow and tracer injection conditions. All spectra were normalized by total variance before being averaged.

The higher bandwidth of the fluorescence sensor is evident, especially above several Hz. The temperature sensor, which as described previously is limited by the thermal mass of the thermistor, is somewhat slower; its power spectrum tails off above 2 or 3 Hz, consistent with its 90% response time of 0.5 to 1 second. The conductivity sensor is shown to have a generally higher bandwidth than the temperature sensor, but is not as fast as the fluorescence sensor, with negligible contributions higher than 7 or 8 Hz.

VI. ADV integration and assessment of interference

To form an eddy correlation flux sensor, the FACT sensor was integrated with a Nortek Vector ADV (velocity sensor). The Vector has three receiving transducers, and a sensing volume approximated as a 1.4 cm diameter cylinder, 1.4 cm in height, located 15.7 cm from the central transducer [48]. The FACT sensing head was mounted to the ADV's transducer stem using a custom holder, which fixed the relative positions of the concentration and velocity sensing volumes to a user-adjustable offset.

To synchronize velocity and concentration measurements, the Raspberry Pi microcomputer was programmed to send TTL synchronization pulses to the ADV, which was in turn configured to initiate a velocity measurement on each pulse. The Raspberry Pi also interacts with the ADV through a serial connection to enable functionalities such as verifying configuration information and interacting with the ADV's recorder. All velocity data are stored on the ADV's recorder and transmitted to the Raspberry Pi at the end of each eddy correlation experiment.

The Vector is equipped with a noise-reducing harness designed by the manufacturer (Nortek AS). In its absence, electromagnetic interference (EMI) radiated by the ADV was found to interfere with the electronics of the FACT sensors, though mitigated as well by thorough EMI reduction measures on the part of the FACT electronics.

A. ADV-FACT acoustic interference

Eddy correlation theoretically requires concentration and velocity to be measured in the exact same location. However, this has not been possible with any EC instrumentation described to date [46], [47], because the chemical sensors currently used (as well as the thermistor in FACT) measure concentrations in actual contact with, or within diffusion length scales of, the physical sensor itself. The probe tips of oxygen microelectrodes, for example, must be positioned outside the ADV's sensing volume to avoid interference, e.g. a few mm away [10], [58] for the traditional microelectrodes, or up to 2.5 cm for a more robust but slightly larger oxygen optode [8], [46]. The offset in sensing volumes can be somewhat adjusted for with a relative time shift, but this technique is only applicable in some settings [46], [47].

For an open-beam fluorescence sensor, however, the physical structure of the sensor can be separate from the actual sensing volume, allowing the chemical and velocity sensing volumes to overlap without any physical interference. To test this potential with FACT, we first assessed the acceptable distance between the optical fiber tips and the ADV's sensing volume. In a test similar to that of Berg et al [8], the fibers were mounted at different

distances from the ADV's sensing volume in stagnant, unseeded water, and the ADV's signal was examined for quality for at least 5 minutes at each distance.

Interference was assessed using the ADV's 'amplitude' output, which represents the strength of the backscatter signal in units of dB (converted from the instrument's output unit of 'counts', also a log-scale measure). In natural environments, higher amplitudes generally indicate more natural backscatter from suspended particles moving with the water (used to infer velocity from the Doppler shift), and thus correspond to more reliable ADV measurements. However, stationary objects or surfaces within the ADV's acoustic field can interfere with measurements by providing a scattering surface for the ping pairs, creating 'artificial' amplitude which does not provide useful Doppler shift information. In particle-free, stagnant water (as used for interference tests), velocity measurements are generally unreliable due to low natural backscatter. However, such conditions can be used to test for the presence of interference from nearby surfaces, which would artificially elevate the amplitudes.

The sensor head was initially aligned to the edge of the ADV sensing volume (representing 0 mm offset). After each measurement, the sensor was offset 1.3 mm further from the sensing volume. Results are given in Fig 8, which shows interference that drops rapidly past 5 mm offset but is still measurable beyond 10 mm offset. Based on the estimated sensing volume (Fig. 5), the FACT fluorescence sensing volume overlaps maximally with the velocity sensing volume at offsets of 3 to 4 mm, but continues to have some direct overlap at offsets of 10 mm or greater. Berg et al [8] considered ADV measurements to be reliable if the additional 'artificial' backscatter from interference is less than 15 dB above the natural backscatter. The offset should therefore be chosen to balance the need for collocation with an acceptable level of acoustic interference, within the context of the environmental setting.

In practice, the level of acoustic interference created by FACT was found to also depend on the rotation and tilt of the holder. We thus checked prior to each experiment that interference was adequately low, by measuring ADV amplitude signals before and after the FACT sensor head was attached to the ADV stem. Separations of 5 to 8 mm were generally chosen as a reasonable tradeoff between acoustic interference and sensing volume collocation, which in our seeded tank typically caused ADV backscatter to increase from around 55 dB without the sensing head attached, to around 60 to 65 dB with the FACT sensor in place.

VII. Flux-sensing experiments: Materials and methods

A. Experimental setup

Tank experiments of flux sensing were conducted in a rectangular $0.6 \times 1.2 \times 0.6$ m glass tank, filled to approximately 46 cm depth with tap water (Fig. 9). A wooden frame was constructed to hold a turbulence-generating mechanism, which caused four plungers at the corners of the tank to oscillate between 33 cm and 39 cm above the tank floor. The plungers were shifted in phase by 45° from each other, and oscillated at a frequency of approximately 0.9 Hz. While the tank was not entirely representative of a typical natural lake or river site, due to the absence of an average horizontal velocity as well as the presence of some secondary circulations, the apparatus did generate vertical fluxes of a tracer solution that

were amenable to measurement by the correlation of vertical velocity and concentration. During operation of the fluorescence sensor, the tank was draped in blackout cloths to minimize the amount of ambient light which would otherwise increase the noise level of the sensor.

The ADV was mounted directly to the tank, to minimize coupling to mechanical vibrations from the turbulence-generating mechanism as well as the building's air handling blowers. In the present experiment, the FACT sensor head was mounted with a separation distance of 6 mm between the optical fiber tips and the ADV sensing volume. The sensing volumes were positioned at a height of 14 cm above the tank floor, approximately over a circular plate that released a controlled flux of a tracer solution from its surface. The plate was designed to create a uniform release across its 30 cm diameter through a 0.1-mm polypropylene mesh stretched over a shallow surface reservoir.

The tracer consisted of 2 ppm fluorescein dye, prepared using distilled water for a conductivity of approximately 25 uS/cm. To create a conductivity contrast, the tank was salted with aquarium salt (Instant Ocean) to a conductivity of approximately 3,500 uS/cm. The salt was stirred into the tank, and left overnight under agitation to ensure dissolution.

For temperature contrast, the dye was chilled in a cold room overnight to 8 °C, while the tank was warmed to a temperature of 26 °C using two aquarium heaters that were removed prior to the experiments. During experiments, the carboy holding the dye was kept in an ice bath, and the tubing leading to the tank was insulated with foam tube insulation. However, absent active thermal regulation of the tracer release plate, the temperature of tracer exiting the plate was certainly higher than 8 °C due to sensible heat gain through the tubing and the surface of the plate. The dye temperature at the location of release was estimated to be 15 °C, with recognition of consequent uncertainties in flux values calculated from thermal data.

Dye releases were visualized using a Nikon D5300 camera under illumination by 405 nm black light (Fig. 10).

To obtain adequate ADV data quality, the floor and most of the walls of the tank were lined with neoprene rubber sheets to reduce reflections of the ADV pings. The tank was seeded with polyamide seed particles with a density of 1.01 g/mL (Ubertone). These measures resulted in adequate SNR, and the Vector ADV was set to measure at LOW power to minimize potential effects of acoustic streaming [49].

B. Experimental procedure for flux measurements

With the equipment configured as above, tracer solution was pumped into the plate beginning at minute 40, at rates of 35 mL/min for $t = [40, 80]$ min; 57 mL/min for $t = [80, 120]$ min; and 35 mL/min for $t = [120, 160]$ min. This schedule thus imposed an upper bound of 40 minutes on the length of periods over which fluxes could be integrated. Measurements were made at 48 Hz, with a 20 ms integration time.

For making intercomparisons among the measured fluorescein, heat, and salt fluxes, as well as with the known tracer input rate, all fluxes were converted to units equivalent to volume of tracer inflow per unit area per unit time, using a calculation similar to that for submarine

groundwater discharge ((5) and (6)). Conductivity measurements (uS/cm) were converted to salinity (parts per thousand) using a local linearization of a conductivity-salinity curve for seawater (1,250 uS/cm per ppt).

The measured and converted inflow rates were compared to the controlled input (pumping) rates of the tracer, as normalized from a volume flux of tracer solution (m^3/day) to a per-area inflow flux density ($\text{m}^3/\text{m}^2/\text{day}$). Because the tracer release plate had a substantially (10X) smaller area than the tank floor, tracer could be transported both sideways and upwards, resulting in uncertainty as to the appropriate area to use for normalization. Thus, a lower bound on input tracer flux density was calculated using the area of the entire interior tank floor (0.675 m^2), while an upper bound was calculated using the release area of the plate (0.07 m^2). The lower and upper bounds were then scaled to account for tracer mass that remained below the sensor height in the tank. As the tank appeared (based on the time series and cospectra) to be well-mixed at the end of all experiments, input tracer flux densities were scaled by a factor of 0.7 (equal to $(d-h)/d$, where d is the water depth of 46 cm and h is the measuring height of 14 cm).

C. Data processing

Data processing for EC was done in MATLAB, following the steps below:

- 1) Data conditioning**—Velocity data from the ADV were screened for quality, resulting in <0.004% of data removed with SNR < 5 and/or correlation < 70%. Data were averaged from 48 Hz to 16 Hz using bin averaging. The velocity data were despiked using the acceleration method of Goring and Nikora [59], using a 0.3 m/s^2 acceleration threshold and 100 iterations. Despiking resulted in different values for 0.2% of the velocity data, which were then replaced using linear interpolation.
- 2) Coordinate rotation**—Velocity data were rotated using fixed angle rotation based on the ADV's internal sensors. Fixed angle rotation was chosen because the tank floor was relatively flat and level relative to true vertical; in addition, the flow patterns in the tank and the possibility of acoustic streaming meant that a non-zero average z velocity ($\bar{w}$) may actually have existed, and forcing it to 0 could be incorrect. Both the double rotation and planar fit calculations yielded unrealistic angles of rotation (e.g. 170° and 66° for double rotation vs 0.1° and 2.3° using fixed angle rotation).
- 3) Mean removal (Reynolds' decomposition)**—Linear detrending was used to isolate the fluctuating components of velocity and concentration. This mean removal technique was chosen due to slow drift in background concentrations, i.e. average concentrations in the tank increasing as tracer was added, a consistent downward trend in average temperature as heat was lost to the surrounding air, and slow drift of the conductivity sensor due to component heating. A linear detrend calculated using a 10-minute window was chosen as the most straightforward way to remove the effects of these processes.

4) Flux calculation—Fluxes were calculated by multiplying the fluctuating components of velocity and concentration, and were converted to inflow rates of tracer solution ($\text{m}^3/\text{m}^2/\text{day}$).

5) Spectral calculations—Power spectra (PSDs) of the velocity and concentrations were used to visualize the frequency components in each time series. For velocity, spectra were calculated after removal of a fixed mean value to avoid sidelobes in the discrete Fourier transform calculation. For the concentrations of fluorescein, salt, and heat, a 40-minute linear trend was first removed prior to spectral calculations to aid in visualization.

Cospectra between vertical velocity and concentration were calculated from the fluctuations identified by the Reynolds' decomposition, and summed in reverse to arrive at cumulative cospectra (ogive plots). Cospectra were calculated separately for each 40 minute segment of the data. While they could be calculated on shorter segments as well, to identify spectral contributions to flux in more granular time windows, doing so generally produced noisier cospectra that did not always converge, possibly due to the presence of phenomena at a time scale larger than the flux window, or lack of stationarity due to too few events.

VIII. Flux-sensing experiments: Results and discussion

A. Turbulence regime

Z velocity at the point of flux measurement was -0.16 cm/s , with a standard deviation (turbulence scale) of 0.20 cm/s . The net negative z velocity was similar to a separate measurement in stagnant water in the same tank and is presumably due to acoustic streaming induced by the ADV, a phenomenon which is only prominent in situations of relatively low turbulence [49].

The modest level of turbulence at the level of the sensing volume indicates that the turbulence created by the plungers, located at a height of 30 to 40 cm above the tank bottom, was not conveyed efficiently to the level of the sensing volumes. Supporting this interpretation, turbulence profiles measured just 5 cm above the sensing volumes showed a z velocity standard deviation of 0.45 cm/s .

B. FACT concentration measurements

Time series measured by the three FACT sensors (Fig. 11) exhibited similar features, with positive spikes in fluorescence corresponding to negative excursions in temperature and conductivity (the tracer was positively fluorescent but had lower temperature and conductivity than the bulk water in the tank). Consistent with previous observations from the flume experiments, the signal from the fluorescence sensor contained features that reflected its faster response time relative the other two sensors.

For the temperature sensor, some degree of temporal averaging was expected due to its slower response time. The temperature response was also affected by discretization, especially visible in the original 48 Hz data, suggesting that its resolution of $0.007 \text{ }^\circ\text{C}$ per LSB (as calibrated for the operating region of 24 to $27 \text{ }^\circ\text{C}$) was limiting. As noted earlier, this resolution can be improved by increasing the gain of the amplifier.

The conductivity sensor signal, which tracked closely with the temperature signal, was also characterized by less high frequency content than the fluorescence signal. Given the intrinsic speed of the conductivity sensor observed in flume tests (Fig. 7), this lower frequency observation may be due in part to its larger sensing volume.

With a 5s running mean low pass filter applied to the three time series, measurements from all three FACT sensors were found to match reasonably well (Fig. 11). The sensors were thus likely detecting the same eddy features, within the limitations of the spatiotemporal averaging inherent to each sensor.

C. Spectral analysis

Variance-preserving spectra for all three concentrations and z velocity are given in Fig. 12. The features observed in all four spectra are consistent with the relatively low frequencies of the turbulence regime in the experimental tank. The fluorescence sensor did, however, detect significant contributions between approximately 0.1 and 1.5 Hz, reflecting its higher bandwidth. The 4 Hz peak in the temperature PSD is due to electromagnetic interference from the building's 60 Hz power lines (aliased to 4 Hz when measured at 16 Hz), and had already been significantly reduced by the use of standard EMI shielding and filtering techniques.

The frequency of the plungers, slightly less than 1 Hz, is observable in the velocity spectrum. However, most of the velocity signal occurred at frequencies below 0.3 Hz (corresponding to velocity fluctuations with durations of > 3 s), while values above 1 Hz were not significantly different from the noise floor.

Spectra calculated separately for sections of the dataset with and without tracer release (not shown) showed that tracer input had no discernable effect on the velocity frequency distribution. In contrast, for the concentration signals, significant components at all frequencies were generally only present during tracer input.

Cumulative cospectra of fluctuations in velocity and concentration (ogive plots) are shown in Fig. 13. Most contributions to flux were at frequencies below 0.1 Hz (10 s), consistent with the low turbulence of the experimental tank environment which resulted in flux being carried by larger, slower events.

D. Calculated fluxes

Fluxes calculated over 5 minute windows are shown in Fig. 14, along with the lower bound flux values calculated from the tracer pumping rate. Given the fundamentally statistical nature of EC flux measurement and the low-energy nature of this particular environment, fluxes calculated over such short windows were expected to exhibit considerable variability (i.e. deviate from a statistically representative temporal average). However, on average the fluxes measured by all three sensors were similar to, albeit somewhat lower than, those estimated from the input (pumping) rates. Fluxes were especially low for all three sensors during the first 20 minutes after an increase in the pumping rate (from 0 to 35 mL/min at $t = 40$ min, and from 35 mL/min to 57 mL/min at $t = 80$ min). This pattern possibly reflected an

expected time lag between the change in flux at the tank bottom and the change at the sensor level.

Further differences between the measured fluxes and the input rates were also expected given the nature of the testing environment. For example, video imagery showed tracer distribution within the tank to be horizontally heterogeneous, implying that the vertical flux of tracer at the sensing volume, measured by the instrumentation, may not have been completely representative of the average vertical flux across the tank bed. Given such limitations of a low-energy, small-tank experiment, the broad general agreement of the input rates to the magnitudes of heat, salinity, and fluorescence fluxes are considered to support the concept and present implementation of the FACT sensor. In addition, given the large uncertainty typically associated with benthic flux measurements—using traditional methods, large variability is commonly observed among replicate measurements and especially between different techniques [2], [7]–[10]—the performance observed in these tests is considered to be quite good.

A small apparently downward flux of heat (which would correspond to a positive tracer flux) was also observed in the $t = [5, 25]$ range, during which time there was no tracer input. The flux likely arose from passive heat loss due to unavoidable temperature differences between the heated tank and its cooler surroundings.

E. Flux comparison among FACT sensors

With some exceptions, fluxes measured by the three FACT sensors generally exhibited similar trends and were of roughly similar magnitude, with fluorescence generally producing somewhat higher values that more closely matched the input (pumping) rates. More notably, Fig. 14 also shows that, even over smaller flux windows for which significant variability can be expected in the measured fluxes (due to the dominance of events of duration comparable to the flux window), the three sensors still produced tracking fluxes, indicating that they were likely responding to the same eddy events. The correlation among sensors is also apparent in Fig. 15, which plots the fluxes shown in Fig. 14 on a scatter plot (see also Fig. S6). Despite some outliers, the linear regressions, correlation coefficients and p values all demonstrate a strong correspondence between the measurements from the three sensors. Scatter was greater for the temperature flux, as expected due to conductive and advective heat flux at the tank wall.

When averaged over 5 min periods (Figs. 14 and 15), the largest discrepancies between the three sensors occurred in the $t = [105, 115]$ min range, including the outliers observed in Fig. 15 and reflected as well in the cumulative cospectra (Fig. 13). Some differences between the three sensors were indeed expected due to differences in their bandwidths and sensing volumes. Fluxes appeared to be especially sensitive to the degree of overlap between the velocity and concentration sensing volumes (in location, size, shape, and weighting). The role of sensing volume overlap can be seen qualitatively in the time series of the individual signals (e.g. Fig. 11), in which individual eddy events can be identified that mathematically give rise to many of the larger observed fluxes. It was often observed that large spikes detected by the fluorescence sensor closely coincided with spikes in vertical velocity w' , whereas the temperature and conductivity sensors appeared to pick up the same events but

with slightly different waveforms. For example, concurrent spikes in velocity and fluorescence were observed at $t = 112$ min in Fig. 11, whereas both the temperature and conductivity sensors sampled a small spike coincident with this feature but did not sample a large excursion until ~ 30 s later. These signals are consistent with the interpretation that the different sensing volumes of the sensors, and especially their different locations (offsets), caused them to sample different parts of the same eddy and/or the same eddy at different times.

Given the size and duration of these features compared to the 5 minute flux windows shown in Figs. 14 and 15, single incidents like this can dominate the calculated flux for entire periods. In this case, this single event was responsible for the large discrepancy observed in flux measurements for the $t = [105, 115]$ min range, corresponding to the outliers in Fig. 15.

The fluorescence sensor's sensing volume more nearly overlaps that of the ADV than do the temperature or conductivity sensing volumes, and is therefore expected to show closer correspondance between concentration and velocity fluctuations. This factor likely accounts for much of the somewhat higher covariance, and therefore somewhat higher fluxes, measured by the fluorescence sensor (and corresponding slopes < 1 in the linear regressions of Fig. 15)

F. Turbulence vs. larger flux-carrying features

The time series of FACT measurements observed in this experiment showed some features that lasted for several minutes, which is too slow to be properly described as turbulence. Even taking into account the relatively low level of turbulence ($w' \sim 0.2$ cm/s), the largest timescale expected for our measuring height of $h = 14$ cm would be $\tau_{LE} = h / w' \approx 70$ s. However, some of the features observed by the system were even slower. The temperature and conductivity sensors in particular appeared to detect larger sub-turbulent phenomena that were specific to the tank environment.

Although these features were larger than typical scales of turbulence, they appeared to correlate with z velocity and thus to carry flux: higher concentrations were brought upward by positive w , and lower concentrations were brought downward with negative w . Thus, the same correlation methodology was still applicable, with the understanding that longer-term averages could only be obtained with long enough flux periods that the system could be considered stationary.

To estimate the flux mediated by faster eddies, we also calculated flux using fluctuations around a 30 s running mean (i.e. using a 30 second running mean as the mean removal algorithm in the Reynolds' decomposition). The resulting fluxes (data not shown) accounted for approximately 1% of the total flux. Fluxes mediated by turbulent eddies would represent a much larger proportion of total flux in many natural waters.

IX. Conclusion

To expand the range of benthic fluxes that can be measured with eddy correlation, we have developed FACT, a high-speed multi-function sensor that combines an open-beam optical

fiber spectrofluorometer with a built-in conductivity cell and fast thermistor. FACT was designed to be used in an EC system to simultaneously measure benthic fluxes of fluorescent material, salinity, and heat.

The fluorescence sensor was demonstrated to be intrinsically fast, recognizing however that speed represents a tradeoff with precision (sensitivity) as set by the choice of integration time. Sensitivity is in fact an important consideration for the spectrofluorometer, given the extremely small concentration fluctuations that must be resolved for field measurements of benthic DOC fluxes at many sites. As built, the sensor may still be immediately usable in some high-flux field settings, such as shallow macrophyte habitats, especially during summer daytimes [5], as well as anoxic conditions in dimictic freshwater habitats where reducing conditions have been linked to large DOC efflux from sediment [6]. Natural fluctuations should also be larger closer to the sediment, where concentration gradients are larger (with correspondingly smaller velocity fluctuations). Thus, smaller measuring heights should be used, with proper recognition of the impact on footprint size [40] and the ability of natural hydrodynamics to blend benthic heterogeneities [44].

However, the principle focus for further improvements to the spectrofluorometer would be an increase in sensitivity. As the optical detector already operates at close to theoretical maximum precision, improved sensitivity and precision will require increasing the amount of fluoresced light reaching the photomultiplier tube, such as by use of a stronger light source (e.g. a laser) or increasing the optical throughput of the detector optics (e.g. larger optical fibers, replacing single fibers with bundles, increasing throughput of the monochromator, or switching in a filter in place of the monochromator when measuring flux). A significant increase in light does, however, require attention to possible saturation of the photon counter; pulse pile-up losses are a known feature of photon counting at high counting rates, and the light levels at which they become significant depend on the bandwidth of the electronics and/or PMT pulse width (and resulting dead time). As an example, using the current photon counter (capable of maximum counts of the order of 3×10^7 photons/s), a reasonable target to achieve (through increases in excitation intensity and optical throughput) is a signal of 10^6 fluoresced photons/s for a 1 ppm humic background. The relative standard deviation by (8) for 100 ms measurements (i.e. 10^5 photons) would then be 0.3%, corresponding to 0.003 ppm. Such a level of (statistical) noise is of similar magnitude to expected natural fluctuations in many natural environments (Table I). However, it should be noted that the challenge of measuring small fluctuations against a high background is inherent to the EC technique, and sensor noise can be limiting for DO and other sensors as well. Fortunately, good results can often be obtained even with sensor noise levels that exceed environmental fluctuations, due to the averaging that is intrinsic to the technique [24]. Given the high bandwidth, ability to achieve high overlap between velocity and concentration sensing volumes, and ability to obtain information about the composition of a natural water, the application of spectrofluorometric sensors in EC appears to have considerable potential.

For the temperature sensor, both the speed and precision are sufficient for eddy correlation in some settings, but will benefit from the planned substitution of a faster thermistor and

appropriate adjustment of amplification. The conductivity sensor as tested also appears to be sufficiently fast and precise for many environmental settings.

Integrated with an Acoustic Doppler Velocimeter, FACT was used in a tank experiment to measure simultaneous and co-located benthic fluxes of a fluorescing substance, salt, and heat. Flux estimates produced by all three FACT sensors were in reasonable agreement with the tracer input rate and with each other. Differences between the three sensors were explainable and often expected on the basis of differences in response time and the exact sensing volumes of each sensor.

The experiment highlighted the merits of a sensing volume that is displaced from the actual sensor head; the improved overlap of sensing volumes afforded by the open-beam fluorescence sensor was found to yield increased covariance between the concentration and velocity signals. Further work is needed to determine an optimum geometry for all three FACT sensors that results in the best coincidence of velocity and concentration sampling volumes that is consistent with acceptably low levels of interference to the ADV by the chemical sensor probes.

Finally, this study demonstrated that the ability of the FACT sensor to measure three properties independently and simultaneously provides an opportunity to explore issues of sensing volume and time responses as they affect the EC technique. The ability to examine EC implementations for internal consistency was also proven to be useful, and will be of further benefit as a sense check on measurements in field studies at sites where benthic fluxes of fluorescent material, heat, and/or salinity are simultaneously present. On the other hand, the ability to measure fluxes of multiple substances expands the range of natural sites where benthic flux measurements can be made, even if one or two of the analytes are not present at significant levels. Finally, combining of the FACT sensor with an oxygen microelectrode could further enhance the value of EC-based benthic flux measurements, whether for studying geochemical processes or for more applied efforts such as localizing benthic chemical releases to improve remediation efforts.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

The authors would like to thank three anonymous reviewers for their helpful comments.

This work was partially supported by the National Institute of Environmental Health Sciences Superfund Basic Research Program, National Institute of Health, P42 ES027707; the MIT Sea Grant College Program, under NOAA Grant Number NA10OAR4170086, MIT SG Project Number 2015-R/RCM-42; the National Research Foundation Singapore through the Singapore MIT Alliance for Research and Technology's Center for Environmental Sensing and Modeling interdisciplinary research program; and MIT CEHS under a core center grant P30-ES002109 from the National Institute of Environmental Health Sciences, National Institutes of Health.

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Fig. 1. Block diagram and (inset) photograph of optical fiber spectrofluorometer created for eddy correlation measurements of fluorescing compounds.

Fig. 2.

Observed error performance of spectrofluorometer. Standard deviation of counts is plotted against the average (N), over 300 measurements per data point. Each point in the figure represents the average and standard deviation over repeated measurements at a fixed light level. To achieve different average counts, measurements were taken at different integration times. The dashed line represents the theoretical $\sqrt{N}$ standard deviation.

Fig. 3.

Calibration curves of spectrofluorometer for low concentrations of humic acid, measured at 460 nm; piece-wise calibration was used due to inherent non-linearity arising from inner filtering. Measurements represent averages and standard deviations over 600 measurements at each concentration, each of 50 ms counting time with 50 ms dark counts subtracted. Fits (dashed lines) were used to scale standard deviations of photon counts to concentration error bars, which ideally should be of same order of magnitude or lower than expected fluctuations in concentration. Humic acid concentration was measured as total organic carbon of dissolved (0.4 μ m filtered) humic acid solutions by a Shimadzu TOC 5000.

Fig. 4.

Spectral scan of solutions of distilled ('DI') water, humic acid ('HA') and fluorescein ('fluor') dye. For these tests, the LED scattering peaked at 377 nm, and the water Raman peak appeared at 432 nm. The emission spectra of humic acid (450 to 500 nm) and fluorescein (~510 nm) are also apparent.

Fig. 5.

Estimated sensing volumes of FACT sensors from (a) top and (b) side views, with conductivity shown separately in (c) on a larger scale model for clarity (scalebar corresponds to true electrodes and not electrode model). Thirteen isopotentials are shown in (c), of which five are labelled, along with two half-potentials. Temperature sensing volume is not visible in top view (a). See text for derivation.

Fig. 6.

FACT sensor signals from flume experiments, corresponding to a series of micropipette injections of a warm, salty, fluorescent tracer into the flow in front of the sensing volumes. All three sensors captured similar features but were not exactly the same, likely due to differences in their response times and sensing volumes.

Fig. 7. Variance-preserving spectra of FACT measurements composited from 31 separate experiments in the flume. The higher bandwidth of the fluorescence sensor is evident.

Fig. 8.

Amplitude (backscatter strength) of ADV measurements, averaged over 5 min, as a function of the distance between the optical fiber tips and the edge of the ADV's cylindrical sensing volume. As measurements were conducted in unseeded, stagnant water, higher amplitudes signify interference with the ADV's measurements by the FACT sensing head.

Fig. 9.
Experimental setup in tank showing ADV head, optical fibers, and tracer release plate.

Fig. 10. Typical release of tracer from plate. Fluorescence under a 405 nm black light is shown; image is processed to enhance visibility of the fluorescein dye.

Fig. 11.

Time series of fluctuations in velocity and concentration during EC experiments in tank, corresponding to 57 mL/min tracer release. Blue line shows data with a 5 s running mean applied. Upward flux of tracer is indicated by positive excursions in velocity that coincide with positive excursions in fluorescence and/or negative excursions in temperature and conductivity (note flipped axes for temperature and conductivity). The extent of agreement between the three filtered concentration time series implies that the sensors were detecting the same features but with differing amounts of spatiotemporal averaging.

Fig. 12. Variance-preserving spectra of vertical velocity, fluorescein, temperature, and conductivity, normalized by total variance, for EC experiments in tank.

Fig. 13.

Cumulative cospectra (ogive plots) for fluorescein (top), temperature (middle), and conductivity (bottom), shown separately for different 40 minute segments of tank test sequence. Upward flux of tracer is indicated by positive covariance for fluorescence and negative covariance for temperature and conductivity (note flipped axes).

Fig. 14.

Tracer inflow rates calculated from EC measurements made by each FACT sensor. Dashed red line shows lower bound (calculated using entire tank floor as area of release) of expected inflow based on pumping rate.

Fig. 15.

Tracer inflow rates calculated from conductivity and temperature measurements plotted against those calculated from fluorescence, for 5 min flux periods. Statistically significant correlations demonstrate that flux measurements from the three sensors were generally tracking each other. Linear regression and p values of correlations were calculated with outlying

TABLE I

SCALE ANALYSIS OF TWO TURBULENCE LEVELS TYPICAL OF THE BBL OF NATURAL WATERS

Property	Symbol	Value	
		Low turbulence	High turbulence
Horizontal velocity (by definition)	u_{1m}	2 cm/s	20 cm/s
Friction velocity	$u_* = (C_{1m})^{1/2} u_{1m}$	0.1 cm/s	1 cm/s
Energy dissipation	$\epsilon = u_*^3 / \kappa h$	2.4×10^{-8} W/kg	2.4×10^{-5} W/kg
Horizontal velocity at $h = 10$ cm	$u_{0.1m} = u_{1m} - \frac{u_*}{\kappa} \ln \frac{1m}{h}$	1.4 cm/s	14 cm/s
Length and time scales of eddies			
Largest eddies			
Length scale = height above sediment	$l_{LE} = h$	10 cm	10 cm
Time scale	$\tau_{LE} = h / u_*$	100 s	10 s
Smallest eddies			
Length scale = Kolmogorov scale	$l_K = 2\pi(\nu^3/\epsilon)^{1/4}$	2 cm	0.3 cm
Time scale	$\tau_K = (L_K^2/\epsilon)^{1/3}$	7.4 s	0.2 s
Example scales of fluctuations			
Vertical velocity - use u_*		0.1 cm/s	1 cm/s
Dissolved organic material: flux = 0.5 – 1500 mg C/(m ² ·d)		$6 \times 10^{-6} - 0.02$ mg/L	$6 \times 10^{-7} - 0.002$ mg/L
Temperature: SGD = 2 – 400 cm/d, $T = 7$ °C		0.002 – 0.3 °C	0.0002 – 0.03 °C
Conductivity: SGD = 2 – 400 cm/d, $S = 29$ (PSU)		8 – 2000 uS/cm	0.8 – 200 uS/cm

All values assume a measurement height $h = 10$ cm, bottom drag coefficient $C_{1m} = 0.0025$, and a kinematic viscosity $\nu = 1.3 \times 10^{-6}$ m²/s corresponding to a temperature of 10 °C.

^aThe hydrodynamic values are from Lorrai et al [25], who used a similar table to estimate order of magnitude for DO fluxes. DOM and SGD fluxes were chosen to represent several orders of magnitude as represented in the literature, e.g. [2], [5], [6], [60] for DOM and [17], [61], [62] for SGD. Temperature and conductivity fluctuations were estimated from SGD values using (5) and (6), respectively. Temperature and salinity differences between surface and groundwater were chosen based on the values found by Crusius et al [17] for a small estuary, with $T = 7$ °C and $S = 29$ (PSU). Salinity fluctuations were converted to conductivity using a linearization around $S = 29$ at $T = 20$ °C from a conductivity-salinity lookup table, which yielded a slope of 1250 uS/cm per unit of salinity (PSU or ppt).