Air-Sea Gas Exchange and CO_2 Fluxes in a Tropical Coral Reef Lagoon

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Abstract Coral reefs are found predominantly in tropical and subtropical areas and are sites of active carbon cycling. Knowledge of gas transfer velocities is necessary for carbon cycle studies in coral reef environments, and past studies in these environments have used wind speed/gas exchange parameterizations intended for the open ocean. In order to determine the relationship between wind speed and gas exchange, and to assess the suitability of open ocean wind speed/gas exchange parameterizations for this environment, two $^3He/SF_6$ tracer release experiments were conducted during two separate years in a tropical coral reef lagoon in Kaneohe Bay, Hawaii. The results show that because water depth is relatively deep in much of Kaneohe Bay, some parameterizations intended for the open ocean can be used to predict gas transfer velocities in that environment. The bay was a source of CO_2 to the atmosphere during both studies, and the residence times of water in the bay during the two studies differed by a factor of two.

Plain Language Summary In order to study carbon cycling in coral reef ecosystems, scientist need to know the rate at which gases move between the ocean and the atmosphere, called the gas transfer velocity. Geochemical tracers are used to investigate the relationship between wind speed and gas transfer velocity in Kaneohe Bay in Hawaii, a tropical coral reef lagoon. The study determined that relationships between wind speed and gas transfer velocity developed for the open ocean could be applied in coral reef ecosystems, if the water is sufficiently deep.

1. Introduction

Coral reefs are important ecosystems in tropical and subtropical areas (e.g., Moberg & Folke, 1999) and are sites of active carbon transformation via photosynthesis/respiration and calcification/dissolution (e.g., Eyre et al., 2018). Coral reefs are typically a source of CO_2 to the atmosphere since calcification releases CO_2 into the water, which is then emitted into the atmosphere via air-sea gas exchange (e.g., Bates, 2002). Hence, in studies aimed at examining carbon cycling and balance in coral reef ecosystems (e.g., Andersson et al., 2013), or those employing oxygen mass balance to estimate primary productivity (e.g., Long et al., 2013), there is considerable interest in the rates of air-sea gas exchange since it is necessary for determining biogeochemically relevant gas budgets.

For the open ocean, it is convenient to parameterize air-sea gas exchange using wind speed, and over the years, a number of wind speed/gas exchange parameterizations have been proposed for the ocean. The early parameterizations yielded results that differed by a factor of 2 (e.g., Liss & Merlivat, 1986; Wanninkhof, 1992). However, in the last two decades, the $^3He/SF_6$ dual-tracer technique (Wanninkhof et al., 1993; Watson et al., 1991) has provided robust measurements of gas transfer velocities in the coastal and open oceans (see Ho & Wanninkhof, 2016, and references therein), and two widely used wind speed/gas exchange parameterizations derived for the coastal ocean (Nightingale et al., 2000) and open ocean (Ho et al., 2006) using the $^3He/SF_6$ dual-tracer technique yield similar results.

Despite the fact that there might be major differences between coral reef ecosystems and the open ocean with respect to factors that influence air-sea gas exchange, such as differences in wind fetch and the potential of increased turbulence due to water flow over reefs, past studies that examined inorganic carbon dynamics in coral reef ecosystems have used a number of wind speed/gas exchange parameterizations typically used for the open ocean to determine CO_2 fluxes (see Table 1). These parameterizations have different origins. The parameterization of Liss and Merlivat (1986) was based on SF_6 additions in a small lake and on wind tunnel

Table 1
Some Carbon Cycling Studies Conducted in Coral Reef Ecosystems Requiring Knowledge of the Gas Transfer Velocity

Study site	Citation	Mean depth (m)	Parameterizations[a]
Tiahura barrier reef, Moorea, French Polynesia	Gattuso et al. (1993)	1.4	LM86
Moorea, French Polynesia	Frankignoulle et al. (1996)	1.3	LM86, W92
Yonge Reef, Great Barrier Reef, Australia		1.7	
Bermuda Platform, Bermuda	Bates et al. (2001)	6	W92
Hog Reef Flat, Bermuda		8.5	
Kaneohe Bay, Hawaii, USA	Fagan and Mackenzie (2007)	4 to 6	LM86, W92, WM99, N00
Kaneohe Bay, Hawaii, USA	Drupp et al. (2013)	2 to 9.5	H06
Great Barrier Reef, Australia	Shaw and McNeil (2014)	20	H06
Heron Island Lagoon, Great Barrier Reef, Australia	Cyronak et al. (2014)	1.4	RC01
Muri Lagoon, Rarotonga, Cook Islands		1.7	
Coroa Vermelha, Brazil	Longhini et al. (2015)	0.5	LM86
Luhuitou Reef, Sanya, Hainan Island, China	Yan et al. (2016)	4	W92

[a]These are the wind speed/gas exchange parameterizations used in each study; LM86 = Liss and Merlivat (1986); W92 = Wanninkhof (1992); WM99 = Wanninkhof and McGillis (1999); N00 = Nightingale et al. (2000), RC01 = Raymond and Cole (2001); H06 = Ho et al. (2006).

results, the parameterization of Wanninkhof (1992) was based on the bomb radiocarbon inventories of the Red Sea and of the global ocean, the parameterization of Wanninkhof and McGillis (1999) was based on eddy covariance measurements of CO_2 from the North Atlantic Ocean, and the parameterizations of Nightingale et al. (2000) and Ho et al. (2006) were based on $^3He/SF_6$ experiment in the coastal ocean (Georges Bank and North Sea) and the open ocean (Southern Ocean), respectively. A recent publication (Table 1) also used the parameterization of Raymond and Cole (2001), which was based on fitting some transient (i.e., ^{222}Rn and chlorofluorocarbons) and deliberate gas tracer (SF_6 and $^3He/SF_6$) studies in rivers and estuaries.

In order to assess whether these wind speed/gas exchange parameterizations are applicable to coral reef lagoons, gas transfer velocities were measured in Kaneohe Bay, Hawaii, using the $^3He/SF_6$ dual-tracer technique during two field campaigns. In conjunction with these measurements, partial pressures of CO_2 (pCO_2) in the atmosphere and sea surface were also measured to determine the air-sea CO_2 fluxes during these studies.

2. Methods

2.1. Study Site

The $^3He/SF_6$ tracer release experiments were conducted in the southern part of Kaneohe Bay (referred to here as the south bay), on the northeast (i.e., windward) coast of Oahu, Hawaii (Figure 1). Overall, Kaneohe Bay has patch and fringing reefs throughout and is protected from the open ocean by a large barrier reef. Trade winds are persistent from the northeast, and circulation in the bay is mainly driven by flow across the barrier reef and back out through two channels near the northern and southern ends of the bay (Bathen, 1968; Lowe et al., 2009). The south bay has an area of ~13 km^2, has fewer coral reefs than the northern bay, and lacks the large barrier reef of the central bay. The mean depth of the south bay is 7.5 m, although the portion occupied by tracer tagged water is deeper (see below). Overall, the mean depth of central Kaneohe Bay, which includes most of the barrier reef, is ~1.6 m shallower than that of the south bay, and the northern part of Kaneohe Bay is 3.8 m shallower than that of the south bay.

2.2. Kaneohe Bay Tracer Release Experiment

Three separate studies, as part of the Kaneohe Bay Tracer Release Experiment (KBayTREx), were conducted in the south bay between 23 and 29 July 2012 (KBayTREx 1), 12 and 18 June 2013 (KBayTREx 2), and 9 and 16 July 2014 (KBayTREx 3) using a 7.5-m-long outboard motor boat instrumented with underway sampling systems and discrete sampling capabilities (see below). KBayTREx 1 was a pilot experiment, conducted with SF_6 as a tracer, with simultaneous measurements of surface water pCO_2. The experiment yielded information about circulation patterns of the south bay, allowed general sampling strategies to be developed, and will not be discussed further. KBayTREx 2 and 3 were conducted with $^3He/SF_6$ as tracers, along with measurements of pCO_2, and yielded information about gas transfer velocities, CO_2 fluxes, and residence times of the south bay.
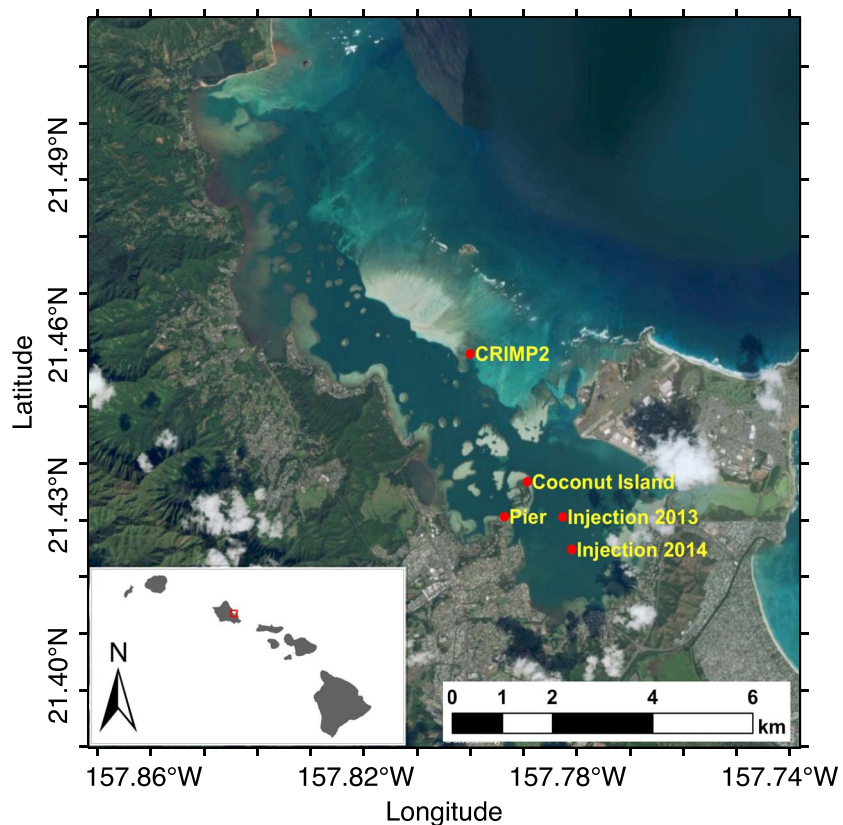
Figure 1. Map of Kaneohe Bay showing the location of the tracer injection in 2013 (KBayTREx 2) and 2014 (KBayTREx 3), the pier and Coconut Island where wind speed measurements were made, and the CRIMP2 buoy. The inset shows the location of Kaneohe Bay on the island of Oahu in Hawaii. KBayTREx = Kaneohe Bay Tracer Release Experiment; CRIMP2 = Coral Reef Instrumented Monitoring Platform 2.

2.3. Tracer Injection

During KBayTREx 2 and 3, a compressed mixture of ^{3}He and SF_6 at a ratio of 1 to 340 was injected on the first day of each experiment as a point source by bubbling the tracer mixture through a length of diffusion tubing at ~11 m depth at locations near the center of the south bay (Figure 1). The injection for KBayTREx 2 took place at 21.42957°N and 157.78070°W on 12 June 2013 over the course of 10 min, and the injection for KBayTREx 3 was further south (i.e., further into the bay) at 21.42385°N and 157.77903°W on 10 July 2014 over the course of 13 min.

2.4. Underway SF_6 and pCO_2 Measurements

After the tracers were injected, underway measurements were performed for 5 and 6 days during KBayTREx 2 and 3, respectively (Figure 2; also see the supporting information). For these measurements, a flexible impeller pump connected to a water intake mounted on the side of the boat delivered surface water from ~1-m depth to the underway instruments, which included a thermosalinograph (TSG; Sea-Bird SBE-45) to measure temperature and salinity at a frequency of one sample every 5 s, an underway SF_6 system, and an underway pCO_2 system.

An underway SF_6 analysis system (Ho et al., 2002) measured surface SF_6 concentrations at a frequency of approximately one sample every 45 s. The system consists of a gas extraction unit that uses a membrane contactor to continuously remove SF_6 from the water stream for measurement and an analytical unit that consists of a gas chromatograph equipped with an electron capture detector (GC/ECD). The system has a detection limit of 1×10^{-14} mol L^{-1} and an analytical precision of ±1%, based on repeated measurements of an SF_6 standard during the experiments.
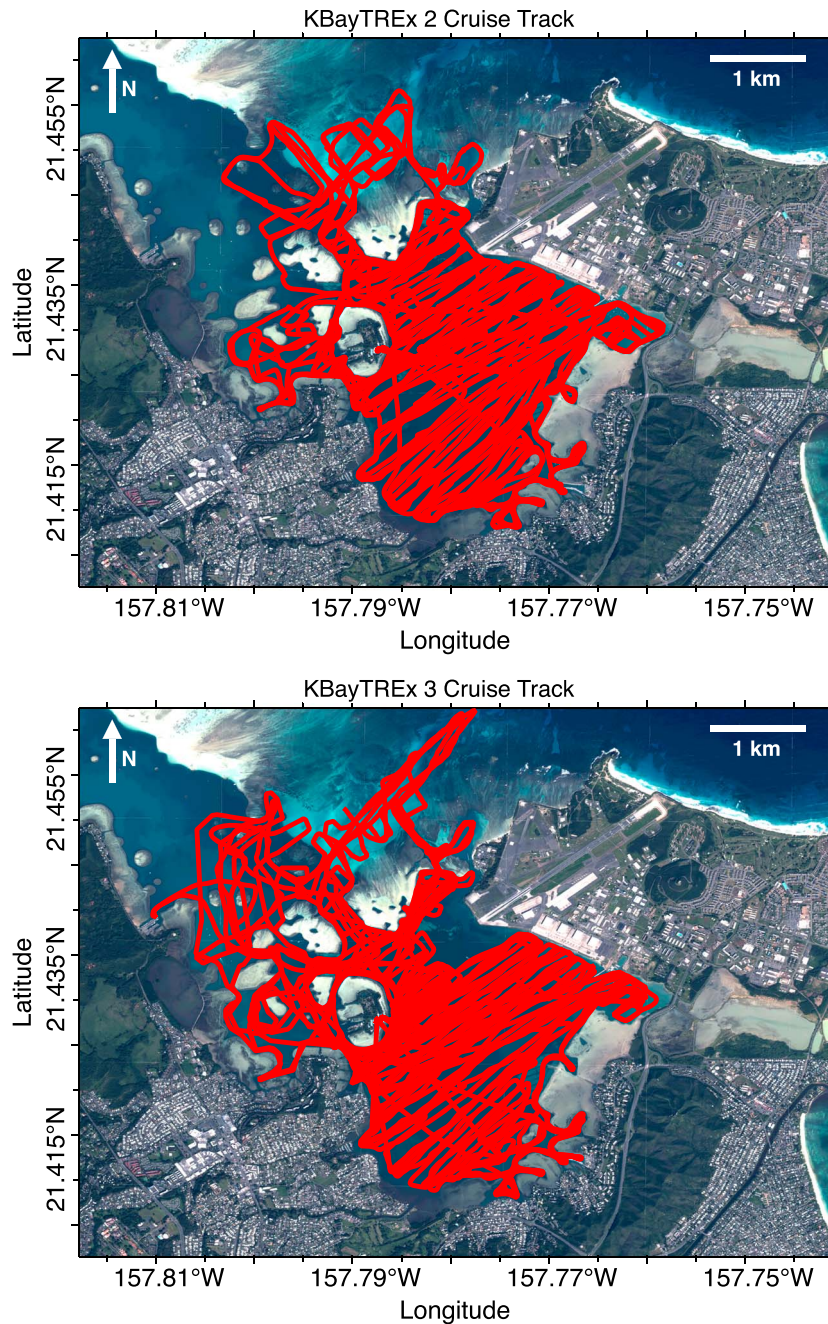
Figure 2. Cumulative cruise tracks from KBayTREx 2 and 3, showing where underway measurements for temperature, salinity, SF_6, and pCO_2 were made. KBayTREx = Kaneohe Bay Tracer Release Experiment.

The SF_6 measurements were displayed in real time on a personal computer. This provided an areal distribution of the tracer patch, which guided the boat navigation, allowed the tracer patch boundaries to be defined, and helped locate the center of the patch for discrete [3]He and SF_6 sampling (see below).

An underway pCO_2 system measured atmospheric and sea surface pCO_2 at a frequency of approximately one sample every 40 s. The system was constructed based on the design of Ho et al. (1997), consisted of a showerhead equilibrator to equilibrate the CO_2 in the water with a headspace, and a diaphragm pump to sample atmospheric air through a series of particle filters. A nondispersive infrared analyzer (LI-COR LI-840A) measured the mole fraction of CO_2 (xCO_2) of the equilibrator headspace, the atmosphere, or the

standard. The CO_2 measurements were calibrated with zero air (i.e., air that has been stripped of CO_2 using soda lime) and a compressed CO_2 standard (507 ppm) referenced to a primary standard from National Oceanic and Atmospheric Administration (NOAA)/Earth System Research Laboratory/Global Monitoring Division.

2.5. Discrete ^{3}He and SF_6 Measurements

Discrete samples for ^{3}He and SF_6 were collected for 6 days each during KBayTREx 2 and 3. Each day, underway SF_6 measurements were used to locate the center of the tracer patch, and three stations were sampled using a 5-L Niskin bottle. On the last day of KBayTREx 2, underway SF_6 measurements were not available due to mechanical issues with the boat, and discrete samples were taken from a smaller boat at two locations in the bay where high SF_6 concentrations were observed the previous day.

At each station, samples were taken at two different depths in the water column, 1 m above the bottom and 1 m below the surface. In addition, samples were taken before the tracer injection to determine the background concentrations of ^{3}He and SF_6.

For each ^{3}He sample, about 40 ml of water was taken in copper tubes mounted in aluminum channels and sealed at the ends with stainless steel clamps. These samples were transported back to the Lamont-Doherty Earth Observatory Noble Gas Laboratory at the end of the experiment, where the gases were extracted from the water samples into glass ampules and measured on a dedicated He isotope mass spectrometer (Ludin et al., 1998).

SF_6 samples were taken in 50-ml glass syringes and submerged in water in a cooler until measurement back in the laboratory at the end of each day. SF_6 was extracted using a headspace technique and measured on a GC/ECD as described by Wanninkhof et al. (1987).

At each of the discrete sample stations, vertical profiles of temperature and salinity were obtained with a conductivity, temperature, and depth sonde (CTD).

2.6. Bathymetry Measurements

The water depths were measured at an interval of 2 s during the underway surveys with a 500-W dual-frequency (50/200 kHz) sonar transducer mounted on the stern of the boat. The data are gridded (5-m resolution) such that multiple measurements in the same grid cells are averaged.

The water depth data collected during KBayTREx 2 and 3 were then compared to the published bathymetry of Kaneohe Bay determined using multibeam sonar and LiDAR surveys, which have vertical and horizontal resolutions of 0.01 and 4 m, respectively (Pacific Islands Benthic Habitat Mapping Center, 2011).

2.7. Wind Speed Measurements

During both KBayTREx 2 and 3, wind speeds were measured with a sonic anemometer (at 6.5-m height), and a propeller anemometer (at 6.0-m height) deployed at the end of a pier protruding about 120 m into the south bay (Figure 1). The data were acquired every 10 s, averaged every 1 min, and scaled to 10 m assuming a log profile for the wind speed. Wind speeds were also measured every 6 min at 10-m height by NOAA/National Ocean Service on Moku o Lo'e Island (also called Coconut Island) (NOAA/National Data Buoy Center, 2014) in the south bay, which is the site of the Hawaii Institute of Marine Biology. In the analysis presented below, the NOAA wind speed data were used because they compared well with the wind speed measurements made at the pier, the measurements were made at 10 m and thus did not require scaling to a standard height, and the data are publicly available.

2.8. Gas Transfer Velocity Measurements

Gas transfer velocities (k) were determined using the ^{3}He/SF_6 dual-tracer method. The method relies on injecting ^{3}He and SF_6 into the water at a constant ratio and then measuring the change in the ^{3}He/SF_6 ratio over time to determine k. The well-tested assumption is that advection and dispersion by turbulent exchange are first-order processes that do not affect the ^{3}He/SF_6 ratio and gas exchange is the only process that will alter the ^{3}He/SF_6 ratio. The gas transfer velocity for ^{3}He ($k_{^3He}$) can be determined by

$$k_{^3\text{He}} = -h\frac{d}{dt}\left(\ln(^3\text{He}_{exc}/\text{SF}_6)/1 - \left(Sc_{\text{SF}_6}/Sc_{^3\text{He}}\right)^{-1/2}\right),\tag{1}$$

where h is the measured water depth in Kaneohe Bay, adjusted for tidal variation; $^3\text{He}_{exc}$ is the ^3He in excess of solubility equilibrium with the atmosphere (used interchangeably with ^3He here); and Sc_{SF_6} and $Sc_{^3\text{He}}$ are the Schmidt numbers (i.e., kinematic viscosity of water divided by diffusion coefficient of the gas in water) for SF_6 and ^3He, respectively (Jähne, Heinz, et al., 1987; King & Saltzman, 1995; Wanninkhof, 2014).

$k_{^3\text{He}}$ is then normalized to $k(600)$, where 600 is Sc for CO_2 in freshwater at 20 °C, as follows:

$$k(600) = k_{^3\text{He}}\left(600/Sc_{^3\text{He}}\right)^{-1/2}.\tag{2}$$

The Sc exponent of $-1/2$ is for a wavy surface without bubble entrainment (Jähne, Munnich, et al., 1987; Ledwell, 1984).

In order to evaluate the appropriateness of different wind speed/gas exchange parameterizations for Kaneohe Bay, measured wind speeds are used in conjunction with the various parameterizations to produce time series of $k_{^3\text{He}}$ during KBayTREx 2 and 3. These $k_{^3\text{He}}$ time series are used to model the time evolution of $^3\text{He}/\text{SF}_6$ during the two experiments using the analytical solution to equation (1):

$$\left(^3\text{He}/\text{SF}_6\right)_t = \left(^3\text{He}/\text{SF}_6\right)_{t-1}\exp\left(-\frac{k_{^3\text{He}}\Delta t}{h}\left(1 - \left(Sc_{\text{SF}_6}/Sc_{^3\text{He}}\right)^{-1/2}\right)\right).\tag{3}$$

The model is run at the same temporal resolution as the wind speed measurements, which is 6 min during KBayTREx 2 and 3. The skill of the models to predict the measured $^3\text{He}/\text{SF}_6$ during KBayTREx 2 and 3 is evaluated in terms of the coefficient of variation of the root mean square error (cvRMSE):

$$\text{cvRMSE} = \sqrt{\frac{\Sigma_{n=1}^{N}\left(R_{model}^n - R_{obs}^n\right)^2}{\overline{R_{obs}}}},\tag{4}$$

where R_{model} and R_{obs} are the modeled and observed $^3\text{He}/\text{SF}_6$ ratios, respectively. The cvRMSE is an indicator of how appropriate it is to apply these wind speed/gas exchange parameterizations to Kaneohe Bay and to similar coral reef ecosystems.

2.9. Air-Sea CO$_2$ Fluxes

To determine the air-sea CO_2 fluxes (F_{CO_2}; mmol·m^{-2}·day^{-1}), the gas transfer velocity for CO_2, k_{CO_2}, was first determined from $k(600)$:

$$k_{CO_2} = k(600)\left(Sc_{CO_2}/600\right)^{-1/2}.\tag{5}$$

Then, F_{CO_2} was calculated as follows:

$$F_{CO_2} = k_{CO_2}K_0\Delta p CO_2,\tag{6}$$

where K_0 (mol·atm^{-1}·m^{-3}) is the solubility of CO_2 in seawater (Weiss, 1974), and $\Delta p CO_2$ (μatm) is the difference between the measured pCO$_2$ in the water and atmospheric pCO$_2$.

2.10. Residence Time Calculations

The residence times of SF_6-tagged water, and hence any point source released into the south bay, were evaluated with respect to flushing of the bay and gas exchange.

To determine the residence time with respect to both flushing and gas exchange, the change in total SF_6 inventory with time was examined. SF_6 inventory for each day was determined by dividing the bay into 0.0001 × 0.0001° grids (roughly 11 × 10 m), averaging the SF_6 concentration in each grid cell, and filling

the empty cells using ordinary kriging. Then, the total inventory of SF_6 in Kaneohe Bay each day (ΣSF_{6t}) was found by summing up the mass of SF_6 in each grid:

$$\Sigma SF_{6t} = \Sigma_{i=1}^{N} [SF_6]_i h_i A_i, \qquad (7)$$

where $[SF_6]_i$, h_i, and A_i are the concentration of SF_6, mean depth, and area, respectively, of each grid, and N is the total number of grids.

The time constant for SF_6 decrease due to both flushing and gas exchange (λ) was determined from the change of SF_6 inventory over time:

$$\lambda = -\frac{\Delta \ln(\Sigma SF_{6t})}{\Delta t}. \qquad (8)$$

To determine the residence time with respect to air-sea gas exchange, the gas transfer velocity for SF_6 (k_{SF_6}) was determined using an expression similar to equation (2), and then the e-folding residence time for SF_6 (i.e., the time it takes the mass of SF_6 in the bay to decrease to $1/e$, or 36.8%, of its initial amount) with respect to gas exchange (τ_k) was calculated according to:

$$\tau_k = \frac{1}{\lambda_k} = \frac{h}{k_{SF_6}}, \qquad (9)$$

where λ_k is the time constant for exponential decrease in SF_6 due to gas exchange, h is the mean depth of the experimental domain, and k_{SF_6} is expressed here in $m\ d^{-1}$ (as opposed to $cm\ h^{-1}$) to match the units of h and τ_k.

The e-folding residence time for SF_6 with respect to flushing (i.e., time it takes for $1/e$ of the SF_6-tagged water to be transported out of the bay; τ_f) was determined by correcting the residence time due to the combined effect of flushing and gas exchange by the residence time due to gas exchange alone, determined by equation (9):

$$\tau_f = -\frac{1}{(\lambda - \lambda_k)}. \qquad (10)$$

The residence times determined using equation (10) represent the e-folding flushing times for point source releases near the center of the south bay during KBayTREx 2 and 3.

3. Results and Discussion

3.1. Water Temperature, Salinity, Wind Speeds, and Water Depths

In the center of the tracer patches, the mean sea surface temperatures were 26.0 and 27.5 °C, respectively, during KBayTREx 2 and 3, and the corresponding mean sea surface salinities were 35.1 and 35.0, respectively. The salinity was lower along the southern coast of the south bay, where mountain streams discharge into the bay, with measured salinity as low as 25. During both experiments, the water column was well mixed for temperature and salinity at all the $^3He/SF_6$ stations.

Mean wind speeds (u_{10}) were higher during KBayTREx 2 (6.9 ± 1.1 m s^{-1}) than during KBayTREx 3 (5.2 ± 1.1 m s^{-1}; also see Table 2 and Figure 3). Wind speeds were relatively constant during each experiment and mainly from the east. There was slightly greater variability in wind speeds during KBayTREx 3, as revealed by the relative standard deviations (16% versus 21% for KBayTREx 2 and 3, respectively) and by examining enhancement in $k(600)$ that would result due to variability in u_{10} assuming a quadratic functional form, $\varepsilon = \overline{u_{10}^2}/\overline{u_{10}}^2$ (Wanninkhof et al., 2004). For KBayTREx 2 and 3, ε ranged from 1.02 to 1.03 and 1.04 to 1.05, respectively (Table 2).

The depth of the south bay with tracer-tagged water ranged from ~1 to 16 m, with a mean of 10.8 m (Figure 4). Even though there was a significant (~25%) portion of the bay that was less than 5 m, most of the volume, and hence mass of tracers, was in areas that are deeper than 5 m. To illustrate this point,

Table 2
Summary of Wind Speeds and Gas Transfer Velocities During KBayTREx 2 and 3

Date and time (local)		Wind speeds u_{10} (m s^{-1})						Sc		
Start	End	Mean	Range	ε^a	n	Temp (°C)	Sal	^{3}He	SF$_6$	$k(600)$ (cm h^{-1})
13 Jun 2013 14:25	15 Jun 2013 12:56	7.1 ± 1.3	3.3–11.2	1.03	465	26.0	35.1	116	803	10.7 ± 2.0
14 Jun 2013 12:40	16 Jun 2013 12:18	6.3 ± 1.0	3.3–8.9	1.02	478	26.0	35.1	116	800	11.2 ± 2.1
15 Jun 2013 12:56	17 Jun 2013 12:35	6.7 ± 1.0	3.0–10.6	1.02	477	26.1	35.1	116	799	10.7 ± 2.4
16 Jun 2013 12:18	18 Jun 2013 11:19	7.0 ± 1.0	3.0–10.6	1.02	471	26.0	35.2	116	801	11.8 ± 3.1
11 Jul 2014 13:21	14 Jul 2014 12:36	5.1 ± 1.0	2.4–9.3	1.04	473	27.5	35.0	109	720	8.8 ± 0.2
12 Jul 2014 11:54	14 Jul 2014 11:03	4.8 ± 1.0	2.4–9.3	1.04	472	27.4	35.0	109	721	7.7 ± 0.9
13 Jul 2014 12:36	15 Jul 2014 11:17	5.1 ± 1.2	2.4–8.4	1.05	465	27.5	35.0	109	720	6.1 ± 0.0
14 Jul 2014 11:03	16 Jul 2014 13:11	5.6 ± 1.2	3.2–8.4	1.05	500	27.5	35.1	109	720	4.4 ± 1.0

$^a \varepsilon = \overline{u_{10}^2}/\overline{u_{10}}^2$.

consider a study area with a mean depth of 10.8 m. If 25% of the study area has a water depth of 5 m, then the water in the shallow areas would make up only 13% of the total volume.

3.2. ^{3}He/SF$_6$ Measurements

^{3}He and SF$_6$ decreased exponentially over the course of the experiments due to gas exchange and mixing. For KBayTREx 2, ^{3}He concentrations decreased 255-fold from ~53,000 × 10^{-16} to 208 × 10^{-16} cm^{3}STP g^{-1} over the course of the experiment, and for KBayTREx 3, ^{3}He concentrations decreased 258-fold from ~48,000 × 10^{-16} to 186 × 10^{-16} cm^{3}STP g^{-1}. The values at the end of both experiments were both well above the background concentration of ~3 × 10^{-16} cm^{2}STP g^{-1}. The highest SF$_6$ values were ~110 and 850 pmol L^{-1} for KBayTREx 2 and 3, respectively, and the lowest on the last day were 3 and 9 pmol L^{-1} for KBayTREx 2 and 3, representing decreases of 37- and 94-fold, respectively. These values are still orders of magnitude above the background SF$_6$ concentrations (~0.04 pmol L^{-1}).

3.3. Gas Transfer Velocities

For both KBayTREx 2 and 3, the decreases in the ^{3}He/SF$_6$ ratio were divided into four periods each to derive the gas transfer velocities, $k(600)$. For KBayTREx 2, the mean u_{10} for these periods ranged from 6.3 to 7.1 m s^{-1}, and $k(600)$ ranged from 10.7 to 11.2 cm h^{-1}. For KBayTREx 3, the mean u_{10} for these periods ranged from 4.8 to 5.6 m s^{-1}, and $k(600)$ ranged from 4.4 to 8.8 cm h^{-1} (Table 2). These values are generally consistent with $k(600)$ from previous ^{3}He/SF$_6$ experiments in the coastal and open oceans (Figure 5).
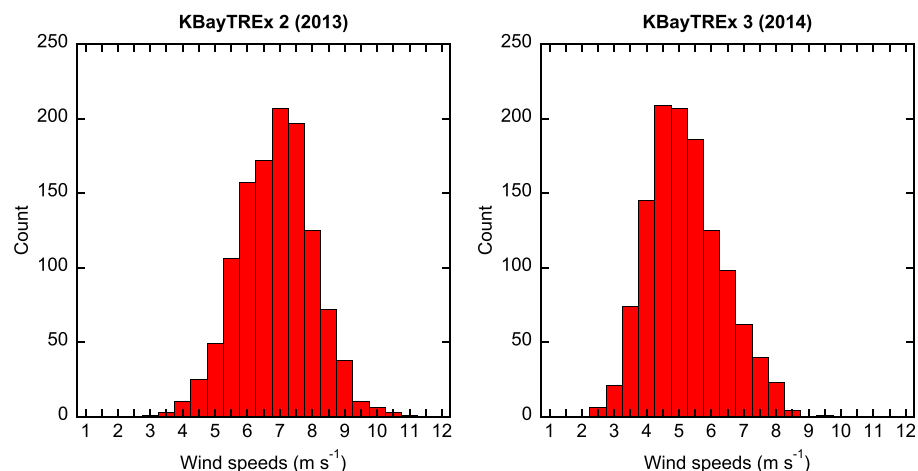

Figure 3. Histograms of wind speed distributions for KBayTREx 2 and 3. The mean wind speeds for KBayTREx 3 were lower by approximately 2 m s^{-1}. KBayTREx = Kaneohe Bay Tracer Release Experiment.
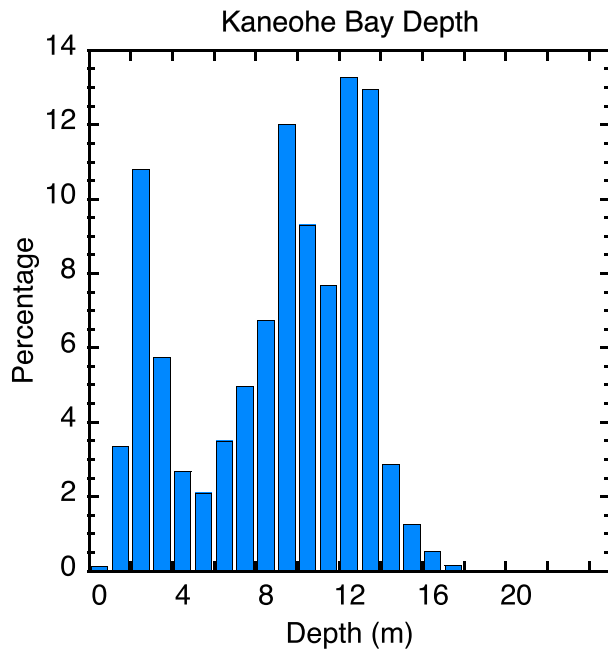
Figure 4. Histogram of water depths measured in the tracer patch.

3.4. Wind Speed/Gas Exchange Parameterizations

When the wind speed/gas exchange parameterizations that have been used in coral reef ecosystems are used to predict $^3He/SF_6$ ratios for KBayTREx 2 and 3, it can be seen that some of them deviate significantly from the measurements (i.e., Liss & Merlivat, 1986; Wanninkhof, 1992; Wanninkhof & McGillis, 1999) (Table 3 and Figure 6). These parameterizations also perform poorly in predicting evolution of $^3He/SF_6$ during open ocean $^3He/SF_6$ experiments (Ho, Wanninkhof, et al., 2011; Ho & Wanninkhof, 2016).

For KBayTREx 2 and 3, the parameterizations of Nightingale et al. (2000), Raymond and Cole (2001), Ho et al. (2006), and Wanninkhof et al. (2009) are the most suitable.

From the results here and in past experiments (e.g., Ho, Schlosser, et al., 2011), it seems that if the mean depth of the water body is greater than 10 m, an ocean wind speed/gas exchange parameterization could be used in such environments. In Ho, Schlosser, et al. (2011), measurements show that bottom-generated turbulent kinetic energy is dissipated by an order of magnitude over a distance of 5 m, so it is possible that these gas exchange parameterizations are also applicable in water depths between 5 and 10 m, but this will have to be confirmed with further experiments.

For study sites that are shallower than 5 to 10 m, parameterizations that take into account the influence of the bottom-generated turbulence will likely be needed (e.g., Ho et al., 2016). For example, a parameterization that includes current velocity and depth, along with wind speed, would be more appropriate for such environments. For previous experiments conducted in coral reef ecosystems shallower than 5 to 10 m (e.g., Cyronak et al., 2014; Frankignoulle et al., 1996; Gattuso et al., 1993; Longhini et al., 2015; Yan et al., 2016), using an ocean wind speed/gas exchange parameterization will likely produce $k(600)$ and CO_2 fluxes that are too low (Table 1).
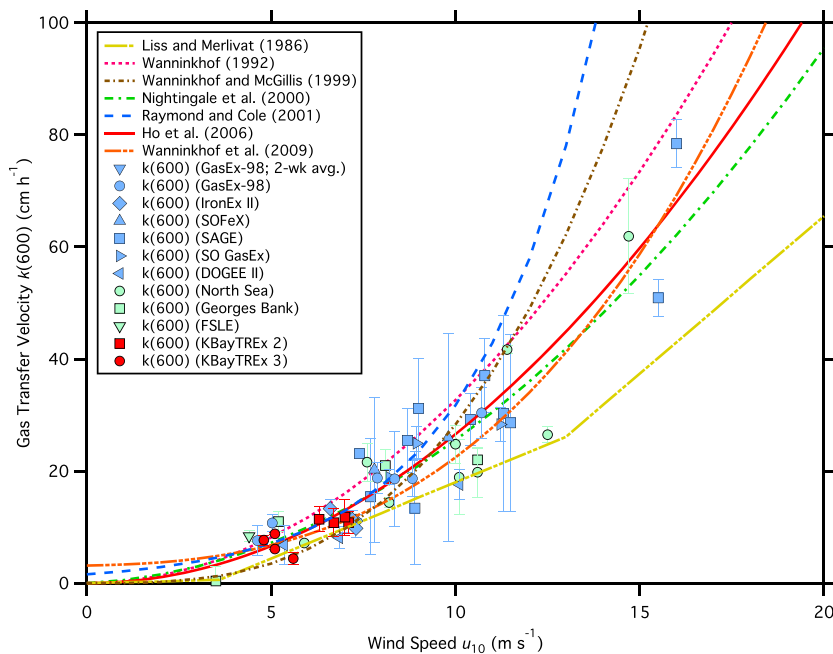

Figure 5. Gas transfer velocities, $k(600)$, measured during KBayTREx 2 and 3, along with results from previous $^3He/SF_6$ experiments conducted in the coastal and open oceans. Also shown are wind speed/gas exchange parameterizations using during carbon cycle experiments conducted in coral reef ecosystems.

Table 3
cvRMSE Between Measured and Modeled ^{3}He/SF$_6$ Decrease for KBayTREx 2 and 3, Shown in Figure 6

	cvRMSE (%)	
Parameterization	KBayTREx 2	KBayTREx 3
Liss and Merlivat (1986)	25	39
Wanninkhof (1992)	32	15
Wanninkhof and McGillis (1999)	19	39
Nightingale et al. (2000)	13	10
Raymond and Cole (2001)	14	10
Ho et al. (2006)	12	11
Wanninkhof et al. (2009)	11	10

Note. cvRMSE = coefficient of variation of the root mean square error; KBayTREx = Kaneohe Bay Tracer Release Experiment.

While it is likely that there are other factors that contribute to gas exchange during KBayTREx 2 and 3, such as differences in wind fetch and current velocities, the fact that ocean wind speed/gas exchange parameterizations are able to predict the change in ^{3}He/SF$_6$ during both experiments suggests that those effects are secondary. Turbulence produced by flow over the coral reefs in shallow waters could be an important driver for gas exchange. Yet, for biogeochemical mass balances in ecosystem with mean depths similar to Kaneohe Bay, air-sea gas exchange in deeper areas will dominate, especially in the absence of significant localized sources in the shallow areas, since most of the mass is contained in areas with greater depths. However, for studies examining local mass balances on a coral reef, where most of the water will be in shallow areas, bottom-generated turbulence will likely play an important role in controlling air-sea gas exchange.

3.5. pCO$_2$ and Air-Sea CO$_2$ Fluxes

The mean sea surface pCO$_2$, pCO$_{2water}$, was lower during KBayTREx 2 than during KBayTREx 3 (489.8 ± 18.8 versus 548.8 ± 30.3 μatm), and ranged from 386.9 to 553.3 μatm and 394.5 to 755.3 μatm, for KBayTREx 2 and 3, respectively. Despite this large range, most of the values (98% and 94% for KBayTREx 2 and 3, respectively) are within 10% of the mean values. The elevated pCO$_2$ in the south bay has been discussed extensively in the literature (e.g., Drupp et al., 2011; Massaro et al., 2012) and derives mainly from net heterotrophy and coral calcification.

The underway surveys were conducted during daylight hours, and the variability in pCO$_2$ represents, to a large extent, the spatial variability in the bay. However, it is known that there is also a substantial diurnal variability in pCO$_2$ on the barrier reef of Kaneohe Bay (Drupp et al., 2013), where the nighttime pCO$_2$ are generally higher than the daytime values mainly due to respiration. Measurements from the Coral Reef Instrumented Platform 2 (CRIMP2) buoy (21.4584°N, 157.7983°W), located near the barrier reef in the central part of Kaneohe Bay, indicate that during KBayTREx 2 and 3, the maximum daily range in pCO$_2$ was 333.4 and 334.6 μatm, respectively, and the maximum range during the sampling periods of KBayTREx 2 and 3 was 263.2 and 313.5 μatm, respectively (Sutton et al., 2016; Table 4).

Because of the higher wind speeds and slightly higher sea surface temperatures (and hence slightly lower Sc_{CO_2}) during KBayTREx 2, k_{CO_2} was substantially higher than during KBayTREx 3. Despite the lower ΔpCO_2, F_{CO_2} was 70% higher during KBayTREx 2 than during KBayTREx 3 (8.9 versus 5.2 mmol·m^{-2}·day^{-1}). From the CRIMP2 data, the F_{CO_2} during KBayTREx 2 and 3 were 5.3 versus 5.0 mmol·m^{-2}·day^{-1}, respectively, a difference of only 6% between the two experiments (Table 4). The differences in F_{CO_2} determined from the underway pCO$_2$ surveys and from the CRIMP2 buoy could be attributable to spatial variability. The CRIMP2 buoy is located in the central bay on the edge of the barrier reef in shallow water (~3 m) and has different pCO$_2$ than observed in the south bay (Table 4; see also Drupp et al., 2013; Massaro et al., 2012). This difference between the KBayTREx surveys and CRIMP2 buoy highlights the caution that needs to be exercised when extrapolating timeseries measurements of pCO$_2$ and sea surface temperature from a single location in a coral reef lagoon to calculate F_{CO_2} of an entire lagoon.
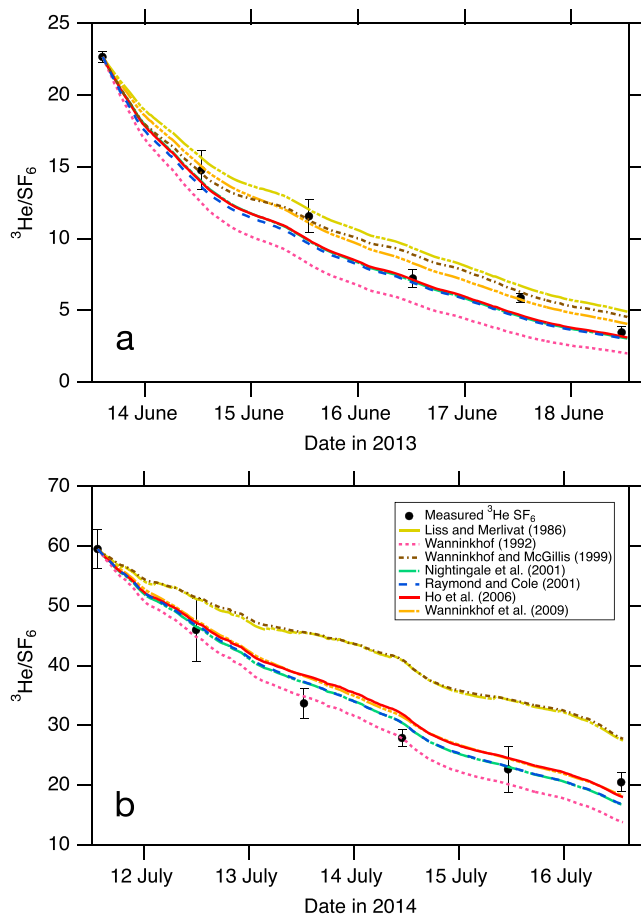

Figure 6. Measured and modeled decline in ^{3}He/SF$_6$ over time in (a) 2013 and (b) 2014 during KBayTREx 2 and 3, respectively. KBayTREx = Kaneohe Bay Tracer Release Experiment.

Table 4
Comparison Between Measurements Made During Underway Surveys and at the CRIMP2 Buoy

Measurement	pCO_{2water} (μatm)	pCO_{2air} (μatm)	ΔpCO_2 (μatm)	Sc_{CO_2}	k_{CO_2} (cm h^{-1})	F_{CO_2} (mmol·m^{-2}·day^{-1})
KBayTREx 2 underway	489.8 ± 18.8	384.7 ± 0.8	105.1 ± 18.6	489 ± 10	13.0 ± 0.7	8.9 ± 1.6
CRIMP2 during KBayTREx 2	452.6 ± 102.0	384.6 ± 1.3	68.0 ± 101.0	510 ± 19	13.9 ± 4.1	5.3 ± 8.3
KBayTREx 3 underway	548.8 ± 30.3	389.7 ± 0.7	159.1 ± 30.2	462 ± 10	7.9 ± 0.7	5.2 ± 0.9
CRIMP2 during KBayTREx 3	478.6 ± 96.8	389.9 ± 1.2	88.7 ± 95.9	474 ± 15	9.0 ± 2.9	5.0 ± 5.5

Note. CRIMP2 = Coral Reef Instrumented Monitoring Platform 2; KBayTREx = Kaneohe Bay Tracer Release Experiment.

3.6. Residence Times

The mean gas transfer velocities for SF$_6$, k_{SF_6}, for KBayTREx 2 and 3 were 10.2 ($\lambda_k = 0.2265$) and 6.3 ($\lambda_k = 0.1398$) cm h^{-1}, respectively, and this leads to τ_k of 4.4 and 7.2 days, respectively. λ calculated from the SF$_6$ inventories (equation (6)) were 0.3271 and 0.3403 for KBayTREx 2 and 3, respectively, which yields similar residence times of 3.1 and 2.9 days for the two experiments. λ_f were 0.1006 and 0.2005 for KBayTREx 2 and 3, respectively, and this yields residence times due to flushing of 9.9 and 5.0 days for KBayTREx 2 and 3, respectively. Since wind speeds were higher during KBayTREx 2, there should have been greater water exchange due to wind and wave forcing (e.g., Lowe et al., 2009). However, the observed difference in residence times likely resulted from differences in tidal forcing on water exchange during the two experiments. KBayTREx 2 was conducted during a period of neap tides, with a maximum tidal range (i.e., between low and high tides) of 0.64 m, whereas KBayTREx 3 was conducted during a period of spring tides, with a maximum tidal range of 1.0 m.

The residence time of an aquatic ecosystem is an important parameter to know because it indicates how effectively the ecosystem is being flushed, and flushing, like air-sea gas exchange, affects biogeochemical mass balances. During KBayTREx 2 and 3, the roles of flushing and gas exchange were of the same order of magnitude, with gas exchange being more important in KBayTREx 2 and flushing being more important in KBayTREx 3.

These residence times for the south bay determined using ^{3}He and SF$_6$ are considerably shorter (by an order of magnitude) than those determined for that part of the bay by Lowe et al. (2009) using a hydrodynamic model. In Lowe et al. (2009), residence times for the south bay, defined as the water export time (i.e., time it takes for a water parcel located inside the bay to move out of the bay), ranged from 20.9 to 49.2 days. As Jouon et al. (2006) showed with a numerical model in New Caledonia, the average water export time can be almost the same as the *e*-folding flushing time, or up to twice as long, depending on the control volume. The residence times from Lowe et al. (2009) would indicate that flushing is secondary to gas exchange in determining geochemical mass balances in the south bay, whereas actual measurements show that they are equally important.

4. Conclusions

Results from ^{3}He/SF$_6$ experiments in the tropical coral reef lagoon of Kaneohe Bay show that the relationship between wind speed and gas exchange there is comparable to other coastal and open ocean regions and that certain wind speed/gas exchange parameterizations derived for the coastal and open ocean can be applied there to predict the gas transfer velocity. These data lend support to the applicability of these wind speed/gas exchange parameterizations in aquatic environments with mean water depth greater than 10 m.

In environments with mean water depth shallower than 10 m, such as those observed on the barrier reef of Kaneohe Bay, the situation is more uncertain and dedicated experiments in shallow environments are needed to determine how surface and bottom-generated turbulence interact to influence air-sea gas exchange.

During the experiment, pCO_2 in Kaneohe Bay was above that of the atmosphere (mean pCO_2 was 489.8 and 548.8 for KBayTREx 2 and 3, respectively), and the bay was a source of CO_2 to the atmosphere (CO_2 flux of 8.9 and 5.2·mmol·m^{-2}·day^{-1} for KBayTREx 2 and 3, respectively). The residence times determined from the tracer release experiments are shorter than previous estimates using hydrodynamic models (4.4 and 7.2 d for KBayTREx 2 and 3, respectively).

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