Surface Water Metabolism Potential in a Tropical Estuary, Hilo Bay, Hawai'i, USA, During Storm and Non-storm Conditions

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Abstract Surface water gross primary production potential (pGPP), respiration (RESP), metabolism potential (pMET), and CO_2 fluxes in Hilo Bay, Hawai'i, USA, were examined along two river plumes during storm (high-flow) and non-storm (low-flow) conditions. Significant differences in pGPP, RESP, and pMET were found between low- and high-flow conditions, with lowest rates of all processes occurring during high-flow conditions. CO_2 fluxes were influenced by metabolic processes at all but one site, with the bay's surface waters being autotrophic and a sink for atmospheric CO_2 during low-flow conditions and less autotrophic and a source of atmospheric CO_2 during high-flow conditions. Significant differences in pMET were found between the two river plumes during low-flow conditions at spatial scales of 1.5 km; however, no differences between river plumes were found during high-flow conditions. Our study suggests that an increase in storms associated with global climate change could impact surface water metabolic dynamics of tropical estuaries.

Keywords Estuaries · Metabolism · Primary production · Respiration · CO_2 flux · Storms

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Introduction

An increase in the number and severity of storms is predicted to occur as a result of global warming (UNFCCC 2008). While the sometimes devastating impacts of storms are most apparent when they disrupt human lives, they can have dramatic effects on watersheds as well. Flooding caused by storms can change the physical, chemical, and biological characteristics of a watershed from its headwaters to the coastal oceans and beyond (Burkholder et al. 2004; Davis et al. 2004). These storms can deliver up to 80% of the annual nutrient and particle inputs to estuaries (Eyre 1995; Wiegner et al. 2009). Estuaries, as the initial receivers of fluvial inputs, are some of the most biologically productive ecosystems on Earth (Schlesinger 1997). Biological processes in estuaries, like primary and secondary production, as well as respiration, can quickly respond to changes in the quantity and quality of riverine discharge (Hubertz and Cahoon 1999; Ringuet and Mackenzie 2005; Russell et al. 2006), and in extreme cases, estuaries can become hypoxic or anoxic, leading to ecologically and economically devastating fish and shellfish kills (Laws 2000; Anderson and Taylor 2001; Burkholder et al. 2004).

A commonly used measure to assess the response of estuaries to perturbations, such as storms, is metabolism (MET; e.g., Pradeep Ram et al. 2003; Ringuet and Mackenzie 2005; Russell et al. 2006). MET is a measure of the balance between gross primary production (GPP) and respiration (RESP) in a given area or community and is controlled by both the organisms in the community and the abiotic factors (i.e., temperature, salinity, light) that affect them. When GPP exceeds RESP (MET >0), an estuary is autotrophic and functions as a net producer of organic matter. When RESP exceeds GPP (MET <0), an estuary is heterotrophic and functions as a net consumer of organic

matter. In estuaries, MET can be largely controlled by the ratio of organic to inorganic nutrients, with high ratios supporting heterotrophy and low ratios supporting autotrophy (Kemp et al. 1997). However, intense physical processes, like storms, stratification, and mixing, can also have strong effects on biota, masking the influence of available nutrients (e.g., Alpine and Cloern 1992; Heip et al. 1995; Iriarte et al. 1996; Cotner et al. 2000). Increased freshwater discharge from storms to estuaries can stimulate or reduce rates of GPP and RESP depending on how the nutrient qualities, quantities, or physical properties within the estuary change (e.g., Pradeep Ram et al. 2003; Ringuet and Mackenzie 2005; Azevedo et al. 2006; Russell et al. 2006; Russell and Montagna 2007).

Estuarine MET affects the CO_2 dynamics of the community, with autotrophic estuaries being a sink and heterotrophic estuaries being a source of CO_2 to the atmosphere, respectively. It is generally believed that most estuaries are heterotrophic and thus function as sources of CO_2 to the atmosphere (Smith and Hollibaugh 1993; Caffrey 2003; Borges et al. 2005); however, that paradigm may be changing as atmospheric CO_2 concentrations and inorganic nutrient inputs to estuaries continue to increase (Andersson and Mackenzie 2004). Recent studies suggest that estuarine MET may also be more variable than previously thought; it can vary from heterotrophic to autotrophic on daily and monthly time-scales, as well as among and even within estuaries (Russell and Montagna 2007). Thus, estuarine MET and CO_2 fluxes have the potential to be highly variable. While the MET of many temperate estuaries has been measured (Caffrey 2003), limited data exist on tropical estuaries. Even less understood is how the MET of temperate and tropical estuaries will respond to storms. While several estuarine studies have captured storms during sampling, few have directly examined the MET response to repeated storm perturbations. It is important to understand how MET and CO_2 fluxes vary under different environmental conditions in order to accurately characterize estuaries and predict future responses of estuaries to increased storms due to climate change (Russell and Montagna 2007).

Our study used Hilo Bay, Hawai'i, USA, to examine the impacts of storms on the surface water MET potential (pMET) and CO_2 dynamics of a tropical estuary. Hilo Bay is heavily influenced by pulsed storm events since it drains the windward sides of the largest and most massive mountains in the world and receives on average between 50 and 600 cm of rain per year (Juvik and Juvik 1998). The high slope and relatively small size of Hawaiian watersheds allows for a quick fluvial response to storms (Tomlinson and De Carlo 2003). The high annual rainfall within the Hilo Bay watershed, combined with the quick riverine

response to storms, makes Hilo Bay an ideal location to study the effects of storm inputs on estuarine MET. The goal of the present study was to examine how surface water pMET changes with pulsed fluvial discharge events from storms in a tropical estuary. Here, we examined the surface water pMET and CO_2 dynamics at ~1.5-km resolution at four sites within Hilo Bay during both storm and non-storm conditions. While several studies have examined the effects of discrete storm events on tropical estuaries, to our knowledge, our study is one of the first to quantify the effects of multiple storms at multiple sites on estuarine metabolic processes.

Materials and Methods

Study Site and Design

This study was conducted in Hilo Bay, a salt-wedge estuary located on the northeast side of Hawai'i Island, Hawai'i, USA. Approximately 9 km of the estuary's perimeter is bordered by land, while the outer margin is defined by a 3-km-long breakwater running east to west with a 1.5-km-wide mouth opening to the Pacific Ocean on the northwest corner (Fig. 1). The partially enclosed bay has a nearly 6.4-km^2 surface area (Paquay et al. 2007) and ranges in depth from ~0 to 15 m. Hilo Bay's watershed is the largest in the state of Hawai'i (Juvik and Juvik 1998), and its surface water inputs are dominated by two rivers, the Wailuku and the Wailoa. While the Wailuku and Wailoa watersheds are adjacent to one another, their attributes vary greatly (Table 1). The Wailuku River's watershed is steep, drains permeable basalt overlain by ash, has substantial surface runoff, and is mostly forested (M&E Pacific 1980). In contrast, the Wailoa River's watershed has a gentle relief, drains extremely permeable basalt, has high infiltration and subsurface flow rates, and more of its land is developed. These contrasting attributes of the two rivers may influence the quality of freshwater discharged into Hilo Bay. Additionally, groundwater inputs from the surrounding area also contribute freshwater into the bay (HDOH 2000; Paquay et al. 2007); however, these sources remain generally uncharacterized.

Four sites were chosen within Hilo Bay for this study, two replicate sites each within the Wailuku (sites S2 and S3) and Wailoa (sites S5 and S6) rivers' plumes (Fig. 1). These sites were chosen to capture the variability both within and between the plumes of the two rivers. Within each river plume, one of the two sites was located near the river mouths (S2 and S5), and the other was located ~1 km offshore (S3 and S6). All sites were recorded and located during sampling using a Garmin 2210C global positioning system receiver.
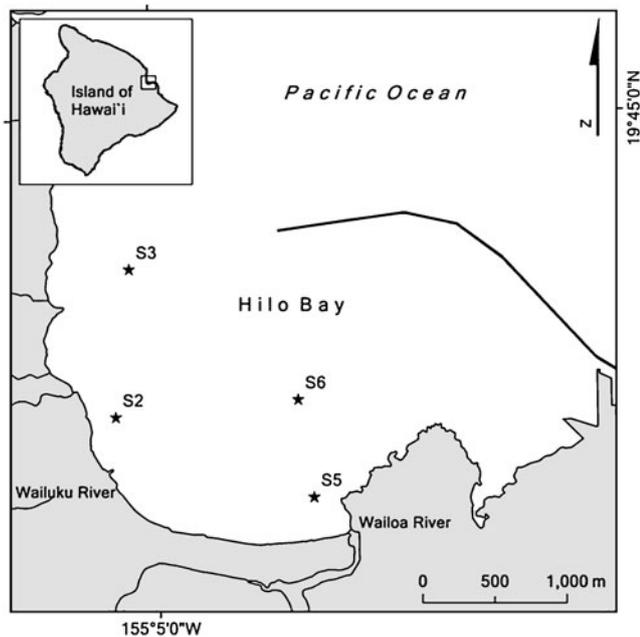
Fig. 1 Map showing the location of the Hilo Bay estuary, Hawai'i, USA, and the four sampling sites, indicated by *stars*, used in this study. Sites S2 and S3 are located within the plume of the Wailuku River, and sites S5 and S6 are located within the plume of the Wailoa River

Nine low-flow and 11 high-flow events were sampled between January 2007 and February 2008 (Table 2). Low- and high-flow categorization was based upon the daily United States Geological Survey (USGS) gauge discharge at Pi'ihonua (USGS station no. 16704000) on the Wailuku River as it is the only gauged source of freshwater into the estuary. For this study, low flow was defined as the Wailuku discharge $<2,500 \text{ L s}^{-1}$, and high flow was defined as the Wailuku discharge $>3,500 \text{ L s}^{-1}$. This designation was chosen because our observations show that the ephemeral portion of the Wailoa River draining the upper watershed connects to the lower perennial portion when the Wailuku discharge is above $\sim3,500 \text{ L s}^{-1}$. Discharge from the Wailuku River tends to increase with rainfall (Table 2); hence, low-flow events occurred during periods of low rainfall and high-flow events occurred during storms.

Surface Water MET

This study concentrated on surface waters as density stratification suspends riverine waters in this region after storms, and we expected the largest biological response to occur in this area of new fluvial nutrient inputs (Smith et al. 1981; Ringuet and Mackenzie 2005; De Carlo et al. 2007). Hilo Bay surface water pMET was quantified through incubations of surface water samples in both light and dark 60-mL borosilicate biological oxygen demand (BOD)

bottles (Wheaton). On each sampling date, 15 L of surface water was collected in acid-cleaned, high-density polyethylene (HDPE) carboys with no headspace from the upper 0.5 m of the water column at each site. Additionally, bottom water samples at sites S2 and S5 were collected during six low-flow events between June and November of 2007. Bottom water was collected 1 m above the water–sediment interface with a hand pump. The pump was rinsed thoroughly with sample water from each site before bottom water samples were collected. Samples were stored on the boat and processed at the laboratory no more than 3 h after collection.

At the laboratory, surface and bottom waters were siphoned into the acid-cleaned BOD bottles, with each bottle's volume being overflowed at least three times. A total of nine bottles were filled with water from each site: three bottles for the light incubation (primary production), three bottles for the dark incubation (respiration), and three bottles for the initial oxygen determination. Bottles for initial oxygen determination had their oxygen precipitated in accordance with the azide modification method 4500-O C (APHA/AWWA/WEF 1995) prior to starting the light and dark incubations. Light and dark bottles for primary production and respiration were incubated in water baths ($\pm3°C$ of Hilo Bay surface waters, see Table 3) for approximately 16 h to allow sufficient time for the production or consumption of oxygen to levels within our limits of detection ($\leq2 \text{ μmol O}_2 \text{ L}^{-1}$). Light bottles were incubated under constant artificial lighting in order to

Table 1 Characteristics of the Wailuku and Wailoa watersheds, Hawai'i, USA

Parameter	Wailuku	Wailoa
Watershed area (km^2)	576	481
Headwater elevation (m)	3,500	762
Riparian land cover (% of each river)		
High-intensity developed	0.1	3.3
Low-intensity developed	0.2	7.7
Cultivated land	0.8	3.9
Grassland	26.0	27.3
Evergreen forest	59.0	40.7
Scrub/shrub	10.7	14.6
Bare land	2.9	0.3
Emergent wetland	0.3	N/A
Water	N/A	2.3

Stream data obtained from http://hawaii.gov/dbedt/gis/streams.htm, land cover data obtained from www.csc.noaa.gov/crs/lca/hawaii.html. Riparian land cover calculated in ArcGIS (ESRI) using land cover extractions from 100-m buffers surrounding each river. Watershed area and headwater elevation were calculated using ArcGIS

N/A no data available for that parameter

Table 2 Daily discharge from the Wailuku River, Hilo, Hawai'i, USA, on low- and high-flow sampling days for this study

Flow	Date	Wailuku River discharge (L s⁻¹)	Σ rain 5days (cm)
Low	3/06/2007	1,841	1.12
	3/14/2007	1,133	0.86
	5/04/2007	1,246	1.57
	6/19/2007	793	4.93
	7/09/2007	708	1.45
	7/31/2007	1,161	2.29
	9/06/2007	2,407	1.14
	10/11/2007	1,642	5.00
	11/08/2007	1,727	5.16
High	1/11/2007	7,504	15.16
	1/13/2007	6,683	8.03
	1/15/2007	4,078	1.98
	3/02/2007	7,872	17.60
	3/04/2007	3,738	12.07
	12/13/2007	15,150	10.82
	12/15/2007	31,149	11.43
	12/17/2007	30,865	7.72
	1/28/2008	12,318	8.66
	1/30/2008	6,485	15.83
	2/01/2008	76,739	25.30

Discharge data from the Wailuku River were obtained from USGS gauge no. 16704000. Σ rain 5 days=sum of daily rainfall 5 days prior to sampling including sampling date, as measured at the Hilo International Airport, Hilo, Hawai'i, USA. Rain data obtained from NOAA National Climatic Data Center

control for the natural irradiance variability in Hilo Bay. Uniform laboratory conditions allowed for the isolation of river flow effects on the production potential of surface waters, as well as the comparison of production measurements made at different times of the year under different weather conditions. Artificial light levels were maintained at ~75 µmol photons s⁻¹ m⁻², a level within the naturally occurring ranges of Hilo Bay [low-flow water column range = 12.2–1823.5 µmol photons s⁻¹ m⁻², average (±SE) = 296.0 (18.9) µmol photons s⁻¹ m⁻²; high-flow water column range = 0.0–1913.9 µmol photons s⁻¹ m⁻², average (±SE) = 143.0 (11.9) µmol photons s⁻¹ m⁻²]. This light level was adequate for primary production to occur, but low enough to inhibit oxygen bubble formation within the bottles, which is a potential source of error associated with the azide modification method. Additionally, nitrification may contribute to our oxygen production measurements; however, we suspect that it is a small component of the signal as ammonium concentrations in both the river waters draining into Hilo Bay and the bay's surface waters are low to below detection limits (0.00–3.24 µM; Wiegner and Mead 2009). Respiration bottles were incubated in the dark. All samples had their dissolved oxygen titrated to their potentiometric endpoint using 3.125 mmol L⁻¹ sodium thio-

sulfate. Titrations were conducted on an Orion 950 auto-titrator using an Orion 960 titrating tower and a Thermo-Orion combination redox/ORP electrode (9678BNWP) that was calibrated daily. Since primary production experiments were conducted under constant artificial lighting, we will refer to these measurements and calculations derived from these measurements as *potential* primary production values.

Net community production potential (pNCP) rates were calculated as the difference between final and average initial oxygen concentrations in light bottles divided by incubation time (*t*, Eq. 1). Daily pNCP rates were calculated by multiplying hourly pNCP rates by the average hours of daylight during this study (11.76 h). RESP rates, reported as positive values in this study, were calculated as the difference between average initial and final oxygen concentrations in dark bottles divided by *t* (Eq. 2). Daily RESP rates were calculated by multiplying hourly RESP rates by 24 h. The three pNCP and RESP replicates were averaged to obtain daily rates for each site. Gross primary production potential (pGPP) was calculated as the sum of daily pNCP and daylight RESP (Eq. 3), assuming light and dark algal RESP rates were similar (Bender et al. 1987). Average daily metabolism potential (pMET) for each site

Table 3 Average (SE) salinity (Sal.), turbidity (Turb.), surface water temperature (Temp.), daily pGPP, daily RESP, and daily pMET for surface water samples during low- and high-flow conditions in Hilo Bay, Hawai'i, USA

Flow	Site	River plume	Sal. (ppt)	Turb. (NTU)	Temp. (°C)	pGPP (mmolO$_2$ m^{-3}day^{-1})	RESP (mmolO$_2$ m^{-3}day^{-1})	pMET (mmolO$_2$ m^{-3}day^{-1})	pGPP/ RESP
Low	S2	Wailuku	27.6 (1.0)	0.8 (0.1)	25.1 (0.4)	11.13 (1.51)	4.86 (0.75)	6.27 (1.20)	2.44 (0.25)
	S3	Wailuku	30.3 (0.8)	0.7 (0.1)	24.8 (0.3)	15.67 (3.54)	6.97 (1.53)	8.70 (2.76)	2.68 (0.50)
	S5	Wailoa	24.4 (1.3)	0.8 (0.1)	25.0 (0.4)	29.44 (7.59)	5.86 (1.95)	23.58 (6.83)	4.57 (0.92)
	S6	Wailoa	26.4 (0.5)	0.7 (0.1)	24.9 (0.3)	30.97 (7.57)	12.52 (3.54)	18.46 (6.57)	3.50 (0.66)
High	S2	Wailuku	21.8 (1.4)	6.8 (2.2)	22.1 (0.4)	3.48 (0.86)	3.04 (0.63)	0.44 (0.70)	1.33 (0.34)
	S3	Wailuku	23.5 (1.0)	4.4 (1.5)	22.1 (0.4)	3.69 (0.53)	2.84 (0.54)	0.85 (0.90)	3.35 (1.25)
	S5	Wailoa	18.4 (1.1)	2.2 (0.5)	22.1 (0.3)	3.90 (0.67)	3.42 (0.73)	0.48 (0.86)	1.24 (0.23)
	S6	Wailoa	21.2 (1.4)	4.1 (1.3)	22.0 (0.3)	4.06 (0.64)	1.89 (0.39)	2.18 (0.51)	3.18 (0.85)

All data were collected between January 2007 and February 2008. For each parameter, $n=9$ for each site during low-flow conditions and $n=11$ for each site during high-flow conditions

was calculated as the difference between daily pGPP and daily RESP (Eq. 4).

$$pNCP_{HOURLY}\left(mmol\ O_2\ m^{-3}\ h^{-1}\right) = \left([O_2]_{LIGHT} - [O_2]_{INITIAL}\right)/t \tag{1}$$

$$RESP_{HOURLY}\left(mmol\ O_2\ m^{-3}\ h^{-1}\right) = \left([O_2]_{INITIAL} - [O_2]_{DARK}\right)/t \tag{2}$$

$$pGPP_{DAILY}\left(mmol\ O_2\ m^{-3}\ d^{-1}\right)$$
$$= \left(pNCP_{HOURLY} \times 11.76\right) + \left(RESP_{HOURLY} \times 11.76\right) \tag{3}$$

$$pMET_{DAILY}\left(mmol\ O_2\ m^{-3}\ d^{-1}\right)$$
$$= pGPP_{DAILY} - \left(RESP_{HOURLY} \times 24.00\right) \tag{4}$$

Total Alkalinity

Between September 2007 and February 2008, total alkalinity (TA) measurements were made at all sites on the same waters collected for primary production and respiration measurements. Three low-flow and three high-flow events were sampled during this time. At the laboratory, water samples from the 15-L carboys were siphoned into triplicate 250-mL acid-washed HDPE bottles, with each bottle's volume being overflowed three times. Samples for TA determination were unaltered and the initial pH of samples were recorded using a calibrated Thermo-Orion pH probe (8172BNWP) accurate to 0.03 pH units using NIST certified buffers (Orion Application Solution, pH buffers). Average precision of pH measurements made in triplicate was 0.002 standard deviations. One hundred milliliters of each sample was titrated to pH 4.5 with 0.1000 N standard HCl (Baker,

CAS no. 7647-01-0) in accordance with USEPA method 310.1. Sample processing began within 1 h of returning to the laboratory. Titrations were conducted on an Orion 950 auto-titrator using an Orion 960 titrating tower and a Thermo-Orion pH probe that was calibrated daily. Average precision of TA titrations made in triplicate using our system was three standard deviations.

CO_2 concentrations in seawater ($[CO_2]_{WATER}$) were calculated using the CO2SYS model developed by Lewis and Wallace (1998) with carbonate dissociation constants K_1 and K_2 from Roy et al. (1993) as these constants encompass the temperature and salinity ranges observed in this study (E. Lewis, personal communication). Input parameters to Lewis and Wallace's (1998) model were TA, pH (National Bureau of Standards, NBS), silicic acid (H_4SiO_4), and phosphate (PO_4^{-3}). Gas exchange coefficients (k) were calculated using the method of Wanninkhof (1992) (Eq. 5), with Schmidt numbers (Sc) calculated from Wanninkhof (1992) and average daily wind speeds (u) obtained from the NOAA National Climatic Data Center (station no. 21504) located at the Hilo International Airport. Atmospheric CO_2 concentrations ($[CO_2]_{AIR}$) were obtained from Cape Kumukahi, Hawai'i Island, Hawai'i (Keeling and Whorf 2005). CO_2 fluxes were calculated as the difference between $[CO_2]_{WATER}$ and $[CO_2]_{AIR}$, multiplied by k (Eq. 6).

$$k = 0.31u^2(Sc/660)^{-1/2} \tag{5}$$

$$CO_2\ flux = k\left([CO_2]_{WATER} - [CO_2]_{AIR}\right) \tag{6}$$

Positive CO_2 fluxes indicated movement of CO_2 from the bay's waters to the atmosphere, while negative CO_2 fluxes indicated movement of CO_2 from the atmosphere to the bay's waters.

Abiotic Measurements

Abiotic parameters of the surface waters were also measured at each site at the time of collection. Surface water temperature and salinity were measured using a YSI model 85 multi-parameter probe calibrated daily for specific conductivity before use. Turbidity was also measured using a Hach model 2100P turbidimeter which was calibrated daily before use. Surface water samples were taken in triplicate 1-L acid-cleaned HDPE bottles at each site for H_4SiO_4 and PO_4^{3-} analyses. Samples were stored on ice after collection and filtered through pre-combusted (6 h at 500°C) GF/F filters (Whatman®) at the laboratory. H_4SiO_4 and PO_4^{-3} concentrations were measured on a Pulse Technicon II autoanalyzer using USEPA methods 365.5 [detection limit (d.l.) 1.0 μM] and 366 (d.l. 0.1 μM), respectively.

Statistical Analyses

Differences in pGPP, RESP, and pMET between river plumes during low- and high-flow conditions were examined using individual nested two-way analysis of variances (ANOVA) and the Fisher LSD test. Factors for the ANOVAs were *flow* and *site* nested within *river*. A regression analysis was used to examine the contribution of pGPP and RESP to overall surface water pMET, even though these two factors are not independent of pMET. Regression analysis was also used to examine the coupling between pGPP and RESP. Additionally, a correlation analysis was conducted between the average CO_2 flux and the average surface water pMET of the bay. Differences in surface and bottom water pGPP, RESP, and pMET during low-flow conditions at sites S2 and S5 were examined using a two-way ANOVA and the Fisher LSD method with the factors being *site* and *depth*. Regression analyses were performed between the abiotic factors known to influence pGPP and RESP and the gauged flow of the Wailuku River to determine how these parameters change from low to high flow. Statistical analyses were conducted using S-PLUS® 8.0 software (Insightful Corporation). Data that did not meet the assumptions for parametric statistics were log-transformed.

Results

Surface waters were more autotrophic and pGPP, RESP, and pMET were significantly higher in Hilo Bay during periods of low flow than high flow ($p<0.001$, Table 3). During low-flow conditions, pGPP rates in the Wailuku River plume ranged from 6.20 to 42.97 and averaged (±SE) 13.40 (1.95) $mmolO_2m^{-3}day^{-1}$. While not significantly different from the Wailuku River plume, pGPP rates in the Wailoa River plume under the same conditions were about twice as high and ranged from 1.51 to 67.57 and averaged 30.21 (5.20) $mmolO_2m^{-3}day^{-1}$. RESP rates in the Wailuku River plume during low-flow conditions ranged from 1.54 to 15.42 and averaged 5.91 (0.86) $mmolO_2m^{-3}day^{-1}$. RESP rates in the Wailoa River plume during low flow were slightly, but not significantly, higher than rates in the Wailuku River plume and ranged from 0.78 to 31.81 and averaged 9.19 (1.96) $mmolO_2m^{-3}day^{-1}$. Average surface water pMET rates in the Wailuku River plume ranged from 0.67 to 29.35 and averaged 7.49 (1.49) $mmolO_2m^{-3}day^{-1}$. Surface waters in the Wailoa River plume during the same conditions were more autotrophic and their pMET rates were nearly three times higher than those in the Wailuku River plume ($p=0.022$), which ranged from −13.09 to 54.37 and averaged 21.02 (4.64) $mmolO_2m^{-3}day^{-1}$. Positive average pMET values in both the Wailuku and Wailoa River plumes during low flow indicate that the surface waters were autotrophic for the majority of the time during the study period (Fig. 2). No statistical differences in pGPP, RESP, or resulting pMET were found between replicate sites (S2 and S3, S5 and S6) within each of the two rivers' plumes ($p>0.05$).

During high-flow conditions, average surface water pGPP, RESP, and pMET were significantly reduced from low-flow conditions and the waters were less autotrophic ($p<0.001$). pGPP rates in the Wailuku River plume ranged from non-detectable (n.d.) to 10.01 and averaged 3.59 (0.50) $mmolO_2m^{-3}day^{-1}$ during high-flow conditions. Under the same conditions, pGPP rates in the Wailoa River plume were almost identical to the Wailuku River plume, which ranged from 0.12 to 8.08 and averaged 3.98 (0.45) $mmolO_2m^{-3}day^{-1}$. High-flow RESP rates in the Wailuku River plume ranged from n.d. to 5.98 and averaged 2.94 (0.41) $mmolO_2m^{-3}day^{-1}$. Similarly, RESP rates in the Wailoa River plume ranged from n.d. to 6.08 and averaged 2.65 (0.44) during these periods. pMET rates during high-flow conditions in the Wailuku River plume ranged from −3.61 to 4.76 and averaged 0.65 (0.56) $mmolO_2m^{-3}day^{-1}$. pMET rates in the Wailoa River plume were higher and the surface waters were more autotrophic, but they were not statistically different from those in the Wailuku River plume and ranged from −5.09 to 5.12 with an average of 1.33 (0.52) $mmolO_2m^{-3}day^{-1}$. Averaged pMET values in both rivers' plumes during high flow were near zero and indicated that surface waters were nearly balanced with respect to primary production and respiration during these times (Fig. 2). The trend toward balanced pMET during high-flow conditions was due mainly to a decrease in pGPP. Daily surface pMET rates were strongly affected by daily surface pGPP rates ($p < 0.001$, $R^2=0.90$) and only weakly affected by surface RESP rates ($p=0.002$, $R^2=0.14$;
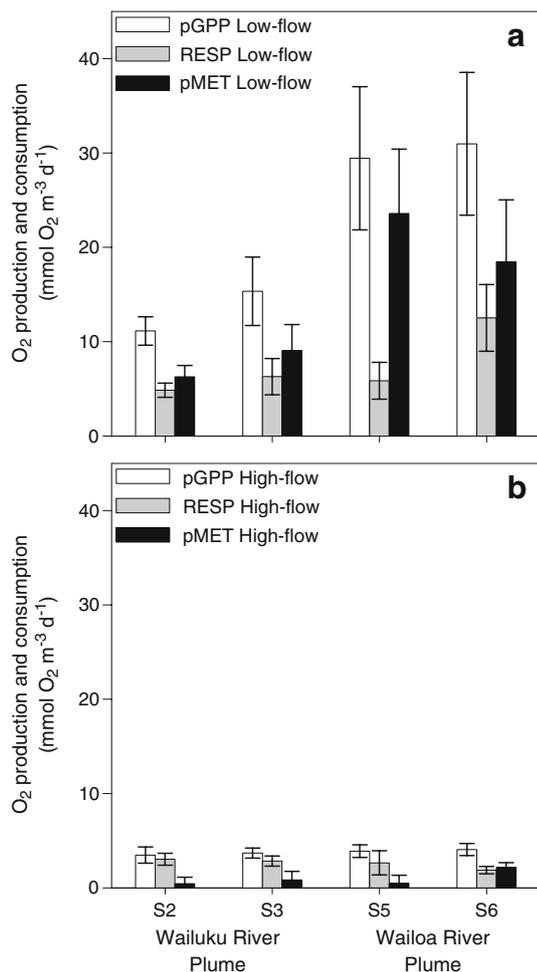
Fig. 2 Average (SE) pGPP, RESP, and pMET at all sites in Hilo Bay, Hawai'i, USA, during low- (**a**) and high-flow (**b**) conditions. Significant differences were observed between low and high flow for all parameters ($p < 0.001$), and significant differences in pMET were observed between the Wailuku and Wailoa River plumes ($p = 0.022$)

Fig. 3a, b). pGPP was found to be a moderate predictor of RESP at all sites in the bay ($p < 0.001$, $R^2 = 0.41$), accounting for 41% of the variability in these measurements (Fig. 3c).

Average daily surface water pMET rates were significantly and negatively correlated with both daily surface water CO_2 concentrations ($p = 0.008$, $r = -0.604$) and daily CO_2 fluxes ($p = 0.010$, $r = -0.587$; Fig. 4). During high-flow periods of slightly autotrophic or heterotrophic conditions, surface waters were generally a source of CO_2 to the atmosphere, whereas during low-flow periods of autotrophic conditions, surface waters were generally a sink for atmospheric CO_2 (Fig. 4). Data from site S5 in the Wailoa River plume were removed from the correlation analysis because the CO_2 fluxes at this site were strongly influenced by the low pH and salinity of the water, making site S5 a

continuous source of CO_2 to the atmosphere during both low- and high-flow conditions.

Bottom waters were less autotrophic and their pMET rates were significantly lower ($p = 0.001$) than surface waters at the same sites (Fig. 5). Additionally, surface and bottom Wailoa River plume waters were more autotrophic and their pMET rates were significantly higher than in the surface and bottom waters within the Wailuku River plume ($p = 0.004$). Average pMET rates in surface waters of the Wailuku River plume were 7.56 (1.50) $mmol O_2 m^{-3} day^{-1}$ and over three times higher when compared to Wailuku River plume bottom waters [-3.26 (3.16) $mmol O_2 m^{-3} day^{-1}$]. Average pMET rates in surface waters of the Wailoa River plume were 31.21 (8.78) $mmol O_2 m^{-3} day^{-1}$ and over six times higher than Wailoa River plume bottom waters [5.02 (2.23) $mmol O_2 m^{-3} day^{-1}$]. While not statistically significant, average surface water pGPP rates were two and three times higher than bottom water pGPP rates in the Wailuku and Wailoa River plumes, respectively. Additionally, while not significant, RESP rates were twice as high in
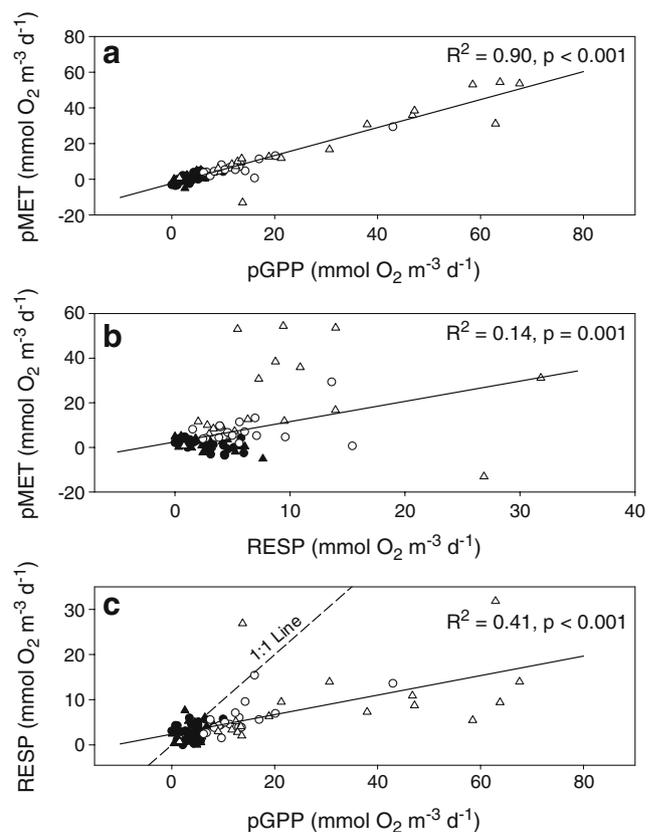

Fig. 3 Regression analyses of pGPP versus pMET (**a**), RESP versus pMET (**b**), and pGPP versus RESP (**c**) for surface waters in Hilo Bay, Hawai'i, USA. *Circles* represent measurements made within the Wailuku River plume, and *triangles* represent measurements made within the Wailoa River plume. *Open symbols* are measurements taken during low-flow conditions, and *filled symbols* are measurements taken during high-flow conditions
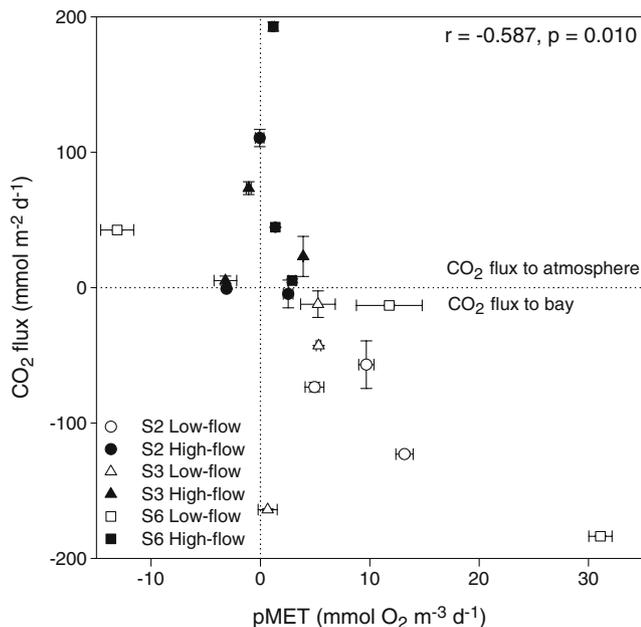
Fig. 4 Correlation between surface water pMET and CO_2 fluxes in Hilo Bay, Hawai'i, USA, from September 2007 to February 2008. Samples were taken during three low-flow and three high-flow conditions. *Dotted lines* represent balanced pMET ($pGPP_{DAILY}$= $RESP_{24H}$) and CO_2 fluxes

bottom versus surface waters in the Wailuku River plume, but nearly identical between depths in the Wailoa River plume (Fig. 5a, b).

A significant negative linear relationship was found between the gauged discharge of the Wailuku River and Hilo Bay surface water pMET ($p<0.001$, $R^2=0.23$; Fig. 6a). Wailuku River discharge was found to be an even better predictor of Hilo Bay surface water temperature, salinity, and turbidity (Fig. 6b–d). As would be predicted, surface water temperature ($p<0.001$, $R^2=0.71$) and salinity ($p<0.001$, $R^2=0.53$) both decreased linearly with increasing river discharge, while turbidity increased linearly with increasing discharge into the bay ($p<0.001$, $R^2=0.58$). The covariance of surface water temperature, salinity, and turbidity to the gauged discharge of the Wailuku River makes it difficult to decipher the degree to which each of these factors individually affects pMET in Hilo Bay.

Discussion

Effects of Flow on pGPP, RESP, and Resulting pMET

While several studies in the tropics have captured pulsed ecosystem perturbations caused by storms within their sampling regime (Ringuet and Mackenzie 2005; Hoover et al. 2006; De Carlo et al. 2007; Paquay et al. 2007), few studies to our knowledge have specifically tested for the

metabolic impact of repeated storm events at multiple sites within a tropical estuary. Therefore, the overall response of surface water MET to storms in the tropics remains largely uncharacterized. Our results show that pGPP, RESP, and pMET are highest during periods of low flow and result in strongly autotrophic surface waters; lower values of these parameters were measured during high-flow conditions and resulted in less autotrophic surface waters (Fig. 6a). When grouped by flow, pGPP, RESP, and pMET rates are also more variable during low- versus high-flow conditions (Fig. 2a, b) as pGPP and RESP followed a seasonal pattern with highest rates occurring in summer (July). This pattern of high biological activity in summer is typical of other tropical (Khan and Siddiqui 1971) and temperate (Gazeau et al. 2005; Hashimoto et al. 2006) estuaries. When
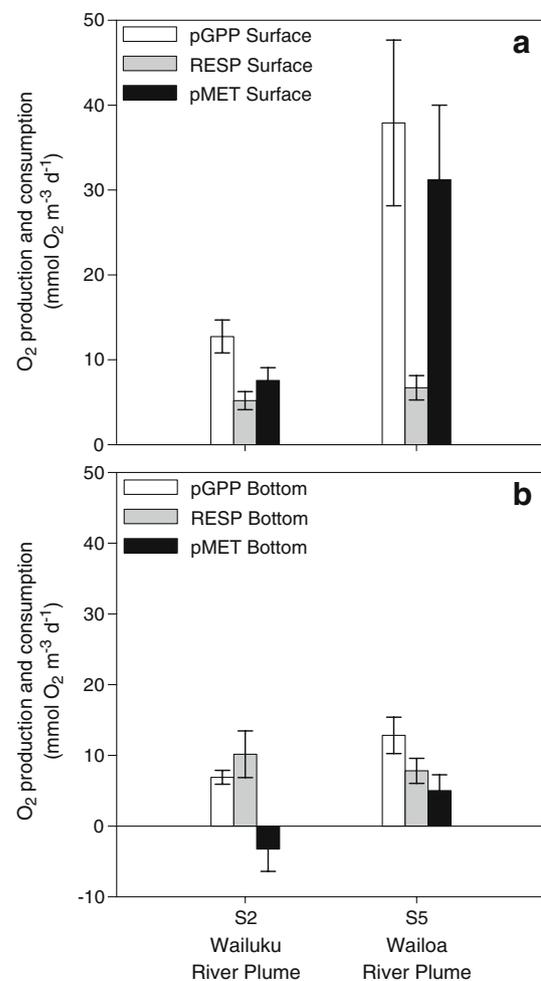

Fig. 5 Average (SE) pGPP, RESP, and pMET of surface (**a**) and bottom (**b**) waters at sites within the Wailuku (S2) and Wailoa (S5) river plumes, Hilo Bay, Hawai'i, USA, respectively. pGPP was only marginally higher in surface waters compared to bottom waters ($p=0.057$) and not different between sites ($p>0.050$). RESP was not different between depths or sites ($p>0.050$). Significant differences in pMET were observed between surface and bottom waters ($p=0.001$) and between sites S2 and S5 ($p=0.004$)
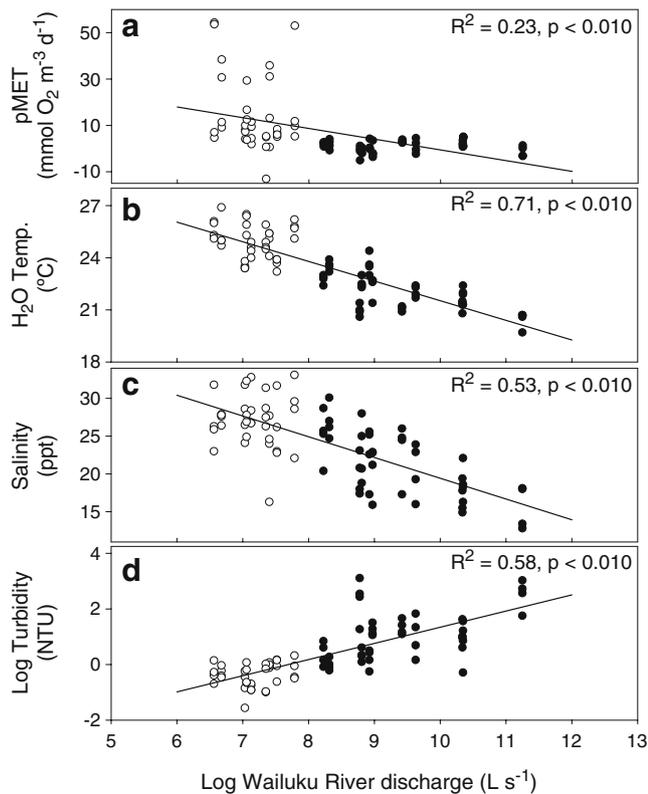
Fig. 6 Regression analyses of the Wailuku River discharge versus surface water pMET (**a**), water temperature (**b**), salinity (**c**), and log-transformed turbidity (**d**) in Hilo Bay, Hawai'i, USA. *Open circles* represent measurements made during low flow (discharge <2,500 L s^{-1}), and *closed circles* represent measurements made during high flow (discharge >3,500 L s^{-1})

compared to other surface water estimates of GPP, RESP, and MET rates during low-flow conditions in estuaries worldwide, Hilo Bay values appear high, but are within the observed ranges (Table 5).

Increases in freshwater discharge to estuaries can significantly affect rates of primary production and respiration, changing the MET of these systems (Pradeep Ram et al. 2003; Ringuet and Mackenzie 2005; Azevedo et al. 2006; Russell et al. 2006; Russell and Montagna 2007). In Hilo Bay, storms significantly reduce pGPP and RESP by about two to eight times and the overall pMET rates between 10 and 49 times from levels observed during low-flow conditions (Table 3 and Fig. 2a, b). Reduced pGPP was most likely a function of increased turbidity, decreased salinity, and decreased water temperature as these factors have been shown to reduce GPP in other systems (Lira et al. 1992; Cotner et al. 2000; Azevedo et al. 2006; Russell and Montagna 2007). Additionally, the decrease in pGPP may be a result of the one third reduction in the concentration of NO_3^- entering Hilo Bay from the Wailuku River during high- versus low-flow conditions (Wiegner et al. 2009) as NO_3^- is an important nutrient for primary

production. The decrease in pMET was due primarily to a reduction in pGPP and not an increase in RESP (Fig. 2a, b). In fact, RESP rates significantly decreased during high-flow conditions, a pattern that contrasts with other studies of tropical and temperate estuaries (Pradeep Ram et al. 2003; Russell et al. 2006).

The reduction in RESP during high-flow conditions is surprising since dissolved and particulate organic matter fluxes from the Wailuku River (plume sites S2 and S3) dramatically increase during storm flow conditions (Wiegner et al. 2009). In fact, storms in the Wailuku River watershed deliver up to 81% and 83% of the annual load of bioavailable dissolved organic carbon (DOC) and nitrogen (DON), respectively, to Hilo Bay (Wiegner et al. 2009). Since inputs of organic matter from streams and rivers to estuaries can stimulate heterotrophy (i.e., Laws et al. 1994; Pradeep Ram et al. 2003), an increase in RESP would be expected in Hilo Bay with increasing riverine discharge. However, our results show the opposite to be true. While the storm fluxes of DOC and DON are high, the lack of RESP stimulation in Hilo Bay could be due to the 50% reduction in the bioavailability of DOC and DON discharged by the Wailuku River during storms (Wiegner et al. 2009). Reduction of RESP during high-flow conditions could also be a result of the displacement of primary producers and heterotrophs from the water column as pulses of freshwater inputs to estuaries have been shown to wash out phytoplankton and bacterial communities (Alpine and Cloern 1992; Iriarte et al. 1996). We estimate that the Wailuku River alone would have been capable of replacing the entire water column of the bay in <15 days during the highest flow rate recorded during this study, making it plausible that some portion of the plankton community was washed out during the periods of high flow. This is further supported by a 93% reduction in surface water chlorophyll *a* (Chl *a*) and a 47% reduction in surface water bacteria between 0.6 and 0.2 μm during high-flow conditions in Hilo Bay (Wiegner and Mead 2009). Reduction of plankton community biomass, combined with the decreased bioavailability of the riverine dissolved organic matter available to them, is likely responsible for the observed decrease in RESP during high flow.

Surface waters in Hilo Bay during low-flow conditions were generally autotrophic based on our estimates of pGPP and RESP rates as well as our CO_2 flux calculations. A review of the Wailuku River discharge data during the study period suggests that autotrophic conditions would have prevailed for ~74% of the study period during low-flow conditions (Wailuku River discharge <2,500 Ls^{-1}), and nearly balanced pMET would have prevailed for ~21% of the study period during high-flow conditions (Wailuku River discharge >3,500 Ls^{-1}). Average ratios of Hilo Bay pGPP/RESP values indicate that primary production

exceeded respiration by 3.3 and 2.3 times during low- and high-flow conditions, respectively (Table 3). With the highest rates of surface water pGPP and RESP occurring during low-flow conditions and lowest rates occurring during high-flow conditions, our results suggest that the surface water pMET of Hilo Bay is greatly affected by biotic processes during the prevailing low-flow conditions and abiotic factors during pulsed high-flow perturbations.

CO$_2$ Fluxes and pMET

CO$_2$ dynamics in coastal waters are driven to varying degrees by both biotic (e.g., MET, nitrification, CaCO$_3$ production/dissolution) and abiotic (e.g., temperature, TA, upwelling, stratification, mixing, residence time) factors occurring near the air–water interface (Frankignoulle et al. 1998; Borges and Frankignoulle 1999; Brasse et al. 2002; Gago et al. 2003; Green et al. 2006). Typically, pCO$_2$ values are highest in low-salinity, river-dominated estuarine waters (Cai and Wang 1998; Borges et al. 2006; Green et al. 2006) and decrease along the salinity gradient due to increasing GPP and mixing with low pCO$_2$ seawater (Brasse et al. 2002; Gazeau et al. 2005; Green et al. 2006). Increasing surface water pCO$_2$ values have been reported during periods of high freshwater discharge from rivers, possibly due to reductions in GPP (Brasse et al. 2002) and the high pCO$_2$ associated with the riverine discharge (Borges et al. 2006; Paquay et al. 2007). Since CO$_2$ fluxes have been shown to reflect the MET of the aquatic community, it is believed that most estuaries are sources of CO$_2$ to the atmosphere as estuarine RESP generally exceeds GPP (Borges et al. 2005). The CO$_2$ flux to the atmosphere may be even greater in the tropics as warm water temperatures should enhance CO$_2$ evasion (Zhai et al. 2005). Our finding that surface waters in Hilo Bay are net autotrophic during low-flow conditions is generally supported by the CO$_2$ concentrations in the surface waters and the calculated CO$_2$ fluxes (Fig. 4) and contrasts the paradigm that tropical estuaries are sources of atmospheric CO$_2$. While small in magnitude when compared to other estuaries, average CO$_2$ fluxes during low flow were approximately -70 $\mu mol m^{-2} day^{-1}$ versus ~50 $\mu mol m^{-2}$ day^{-1} during high-flow conditions at all sites except S5 in Hilo Bay (Tables 4 and 5). pCO$_2$ ranges at all sites in Hilo Bay during both low- and high-flow conditions were 83–695 μatm and within the ranges of other tropical and temperate estuaries worldwide (Borges et al. 2005) (Table 5).

pMET influences CO$_2$ fluxes at all of our study sites, except the one at the mouth of the Wailoa River (site S5, Fig. 4). Net autotrophy in surface waters of Hilo Bay was associated with CO$_2$ fluxes from the atmosphere to the bay, and net surface water heterotrophy was associated with CO$_2$ fluxes from the bay to the atmosphere (Fig. 4). Low-salinity waters at site S5 always had high pCO$_2$ values compared to the rest of the bay (Table 4), which is consistent with previous measurements near that site (Paquay et al. 2007) and other low-salinity waters worldwide (e.g., Frankignoulle et al. 1998; Gazeau et al. 2005). Unlike in Kane'ohe Bay, TA was conservative along the salinity gradient (linear regression, $R^2=0.96$, $p<0.001$) in Hilo Bay in both this and a previous study (Paquay et al. 2007), suggesting calcification is not significantly influencing CO$_2$ dynamics within the bay. While calcification in Kane'ohe Bay supports net CO$_2$ evasion during low-flow conditions, spikes in primary production following storms draw down pCO$_2$ levels to below atmospheric concentrations at some sites (Fagan and Mackenzie 2007). These spikes in primary production in Kane'ohe Bay are comparable to periods of high summer production observed during low-flow conditions in Hilo Bay. Our findings that surface waters in Hilo Bay are autotrophic during low-flow conditions lends support to models predicting that estuaries could increasingly be functioning as sinks for atmospheric CO$_2$ as inorganic nutrient loadings to estuaries increases and atmospheric CO$_2$ concentrations continue to rise (Andersson and Mackenzie 2004; Gypens et al. 2009). However, should climate change increase periods of high-flow conditions, this trend toward autotrophy could in fact be negated.

Coupling Between Metabolic Processes

GPP can be both a positive and negative predictor of MET in estuaries (e.g., Smith and Hollibaugh 1993; Heip et al. 1995; Pradeep Ram et al. 2003; Caffrey 2004). It has been suggested that the strength and direction of this relationship are determined by the ratio of inorganic to organic nutrient inputs into coastal systems (Kemp et al. 1997). In communities with high organic to inorganic nutrient ratios, GPP tends to be a negative predictor of MET, with the opposite being true for communities with low organic to inorganic nutrient ratios (Kemp et al. 1997). While both RESP and pGPP were statistically significant predictors of pMET, pGPP was by far the strongest predictor of the relationship, accounting for 90% of the variability in the data (Fig. 3a) as compared to only 14% for RESP (Fig. 3b). Several studies have shown that inorganic nutrient additions to estuarine waters up to a threshold point stimulate GPP, causing surface waters to become highly autotrophic (Oviatt et al. 1986; Duarte et al. 2004); in other instances, nutrient load reductions to hypereutrophic estuaries have resulted in increased Chl a concentrations (Cox et al. 2009). It is possible then that inorganic nutrients inputs into Hilo Bay are driving the observed surface water autotrophy, especially in the highly productive Wailoa River plume where average NO$_3^-$ concentrations are four times higher

Table 4 Average (SE), TA, pH, surface water temperature (Temp.), salinity (Sal.), phosphate (PO_4^{3-}), silicic acid (H_4SiO_4), and pCO_2 for surface water samples during low- and high-flow conditions in Hilo Bay, Hawai'i, USA

Flow	Site	River plume	TA (mmol kg^{-1})	pH	Temp. (°C)	Sal. (ppt)	PO_4^{3-} (μM)	H_4SiO_4 (μM)	pCO_2 (μatm)
Low	S2	Wailuku	0.853 (0.029)	8.18 (0.01)	25.7 (0.2)	25.1 (1.7)	0.00 (0.00)	53.6 (9.4)	103 (4)
	S3	Wailuku	1.006 (0.044)	8.19 (0.03)	25.2 (0.2)	29.9 (1.6)	0.00 (0.00)	43.5 (9.4)	111 (12)
	S5	Wailoa	0.695 (0.094)	7.69 (0.18)	24.6 (0.3)	16.9 (3.1)	0.08 (0.07)	215 (30.9)	401 (149)
	S6	Wailoa	0.931 (0.033)	8.15 (0.07)	25.4 (0.5)	26.8 (1.5)	0.00 (0.00)	98.5 (22.3)	126 (23)
High	S2	Wailuku	0.704 (0.103)	8.01 (0.05)	20.9 (0.1)	19.7 (3.2)	0.00 (0.00)	56.3 (4.4)	151 (10)
	S3	Wailuku	0.775 (0.083)	8.03 (0.03)	20.5 (0.4)	22.2 (2.3)	0.00 (0.00)	49.0 (3.6)	152 (5)
	S5	Wailoa	0.559 (0.032)	7.53 (0.03)	21.0 (0.2)	12.5 (0.7)	0.05 (0.02)	288 (39.1)	455 (12)
	S6	Wailoa	0.708 (0.083)	7.97 (0.06)	20.9 (0.2)	20.1 (2.5)	0.00 (0.00)	64.7 (4.9)	169 (15)

Data were collected between September 2007 and February 2008. For all parameters, $n=3$ for each site during low-flow conditions and $n=3$ for each site during high-flow conditions

than in the Wailuku River plume (Wiegner and Mead 2009). Average surface water pMET in Hilo Bay during low-flow conditions was ~1.5 times higher than the Kane'ohe Bay estuary on O'ahu, Hawai'i, the geographically closest estuary to Hilo Bay for which primary production and respiration data are available under similar river flow conditions (Ringuet and Mackenzie 2005). pGPP rates were one to three times higher in Hilo Bay than in Kane'ohe Bay during similar conditions, potentially due to NO_3^- concentrations that were over 45 times higher in Hilo Bay than at the site where MET measurements were made in Kane'ohe Bay (Ringuet and Mackenzie 2005; Wiegner and Mead 2009).

Studies have shown coupling of respiration to primary production to be variable at different levels of primary productivity (Heip et al. 1995; Smith and Kemp 1995; Iriarte et al. 1996; Duarte and Agustí 1998). Typically, eutrophic waters experience less coupling than oligotrophic waters (Biddanda et al. 1994; Iriarte et al. 1996), suggesting that dependence of RESP on autochthonous GPP may be less in areas of high production. For example, regions experiencing high net autotrophy in the lower Chesapeake

Bay have no significant coupling between primary production and respiration, while more heterotrophic regions within the bay exhibit significant coupling of these processes (Smith and Kemp 1995). Our study shows a moderate coupling between RESP and pGPP within Hilo Bay surface waters (Fig. 3c), with pGPP accounting for 41% of the variability in RESP; coupling may be greater at the ecosystem level when benthic respiration is considered. The reduction of pGPP and RESP to low levels during high-flow conditions leads to a clustering of these data points near the origin; however, low-flow conditions show the general increase of RESP with increasing pGPP (Fig. 3c). Since the ratio of RESP to pGPP in this study was <1:1 (Fig. 3c and Table 2), increases in pGPP were not equally mirrored by RESP, and the result is a net production of organic matter in Hilo Bay surface waters. Since surface water RESP is only a partial sink of this production, the remaining autochthonous organic matter must be transported to sediments for burial or benthic respiration, exported to adjacent coastal waters, or funneled up to higher trophic levels, those not included in our incubations, within Hilo Bay. It is likely that the excess organic matter is

Table 5 Ranges in GPP, RESP, and MET for unaltered surface/euphotic waters reported in mmol O_2 m^{-3} d^{-1} for this study and comparable studies during low flow, baseline, or similar conditions

Location	Conditions	Sample depth	GPP	RESP	MET	Study
Hilo Bay, HI, USA[a]	Low flow	Surface	1.51–67.57	0.78–31.81	−13.09–54.37	This study
Kane'ohe Bay, HI, USA[a]	Baseline	Surface	~8	~3	~7–10	Ringuet and Mackenzie (2005)
Sagami Bay, Japan[b]	N/A	0–30 m	~1–50	~1–16	N/A	Hashimoto et al. (2006)
Bay of Blanes, Spain[b]	N/A	15 m	~1–4.5	~1–6.5	~−2.5–0.5	Duarte et al. (2004)
Bay of Palma, Spain[b]	N/A	0–8 m	0.14–14.02	0.72–10.45	−9.28–4.84	Navarro et al. (2004)
Menai Straight, GB[b]	N/A	1 m	~0–70	~0–30	~−10–60	Blight et al. (1995)

N/A no data available for that parameter

[a] Tropical waters

[b] Temperate waters

partitioned to various degrees among these fates since there is increased heterotrophy in the bottom waters (Fig. 5b), Hilo Bay exchanges directly with the coastal Pacific Ocean (Fig. 1), and autochthonous organic matter supports ~60% of planktonic consumers' diets in Hilo Bay's food web (Atwood 2009).

Temporal/Spatial Variation of Estuarine pMET

Our understanding of the spatial and temporal variability in primary production and respiration among and within estuaries is improving (see Caffrey 2004; Russell et al. 2006; Russell and Montagna 2007). When studying the rates of these biological processes within estuaries, it is necessary for the sampling regime to have adequate spatial and temporal resolution in order to capture the true variability of the system. It has been shown that MET can vary within an estuary from day to day as a result of freshwater inputs and from month to month due to seasonality (Kemp et al. 1997; Russell and Montagna 2007). While this study was not designed to test for temporal variability, we found moderate seasonal variation during our low-flow sampling, as evidenced by the standard error in the grouped data (Fig. 2a). As is typical of other systems, the highest rates of primary production and respiration were observed in the peak summer months, coinciding with the warm surface water temperatures at these times (Fig. 6b).

In addition to temporal variability, significant intra-estuarine variability has been found at distances of 2–4 km (Russell and Montagna 2007). Our results show that even small estuaries, like Hilo Bay, can have significant variation in rates of MET at spatial scales ~1.5 km. We hypothesize that the significant difference in pMET observed between the Wailuku and Wailoa River plumes in Hilo Bay during low-flow conditions is a reflection of land use within their watersheds. Using a 100-m buffer along each river (http://hawaii.gov/dbedt/gis/streams.htm), land use was characterized from Landsat classified land cover data of the watersheds from the year 2000 (http://www.csc.noaa.gov/crs/lca/hawaii.html; Table 1). Our analysis indicates that ~15% of Wailoa River's buffer runs through high- and low-intensity developed areas and cultivated land compared to only ~1% for the Wailuku River. The river along these developed areas may be subject to higher nutrient inputs (Sliva and Williams 2001), which could be transported by the river to the bay and cause the higher concentrations of NO_3^- and higher levels of production observed in the Wailoa River plume. This hypothesis would support the positive pGPP versus pMET relationship observed in the surface waters of Hilo Bay (Fig. 3a) and their autotrophic status that is predicted by high inorganic nutrient inputs (Kemp et al. 1997). Similarly, rivers in high relief areas, like the Wailuku River watershed,

can experience elevated levels of suspended sediments (Sliva and Williams 2001). The high relief and greater percentage of barren and forested land that the Wailuku River flows through is reflected in the higher turbidity values within its plume (S2 and S3) during high-flow conditions (Tables 1 and 3). While we can only speculate at the cause of the observed spatial variation within Hilo Bay, the dynamic nature of pMET is apparent in our study. Not only does this small estuary vary spatially and temporally, but control of pMET in this estuary shifts from biotic control during low-flow to abiotic control during high-flow conditions, supporting conclusions that pMET is driven by both seasonal and event-driven patterns (Pradeep Ram et al. 2003; Russell and Montagna 2007). Changes in these event-driven patterns, such as increased storm activity due to global change, has the potential to alter how this estuary and others worldwide function locally as producers or consumers of organic matter and globally as sources or sinks of atmospheric CO_2.

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