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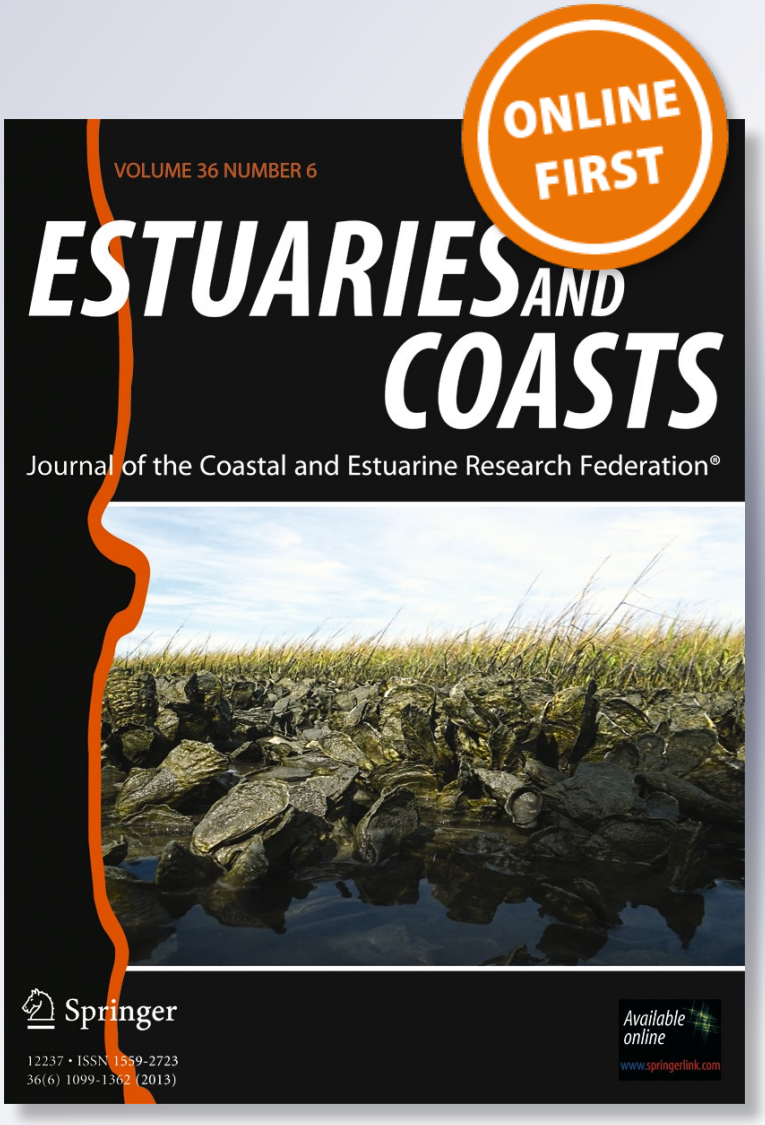

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Surface Water Metabolism Potential in Groundwater-Fed Coastal Waters of Hawaii Island, USA

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Abstract Submarine groundwater discharge (SGD) has become increasingly recognized as an important source of freshwater and nutrients to coastal waters worldwide. Although groundwater nutrients have been found to cause algal blooms in many temperate coastal waters, little is known about the biological response to these nutrients in the tropics. On the leeward coast of Hawaii Island, SGD is the dominant freshwater and nutrient source to coastal waters. Kiholo Bay, HI and Kaloko-Honokohau National Historical Park, HI are two nearshore regions with well-documented SGD with high nutrient concentrations; however, little is known about how biological processes within the surface waters respond to these inputs. This study examined how potential gross primary production (pGPP), respiration (RESP), and potential metabolism (pMET) within surface waters differed inside and outside of groundwater plumes at these two sites and between wet and dry seasons. pGPP and RESP were both significantly higher within groundwater plumes, suggesting that SGD stimulated these biological processes; however, RESP responded to a much greater extent than pGPP, resulting in heterotrophic surface waters. RESP also varied seasonally, with greater rates during the dry season compared to the wet one; pGPP did not vary seasonally. Autotrophic conditions were found within groundwater plumes at Kiholo Bay, while heterotrophic conditions were found within them at Kaloko-Honokohau and were greater during the dry season. Overall, our results show that coastal biological processes respond to SGD and that their responses vary over short spatial and temporal scales.

Keywords Metabolism · Primary production · Respiration · Submarine groundwater discharge · Nutrients

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Introduction

Groundwater discharge has become increasingly recognized as an important freshwater and nutrient source to coastal waters worldwide (Umezawa et al. 2002; Garrison et al. 2003; Slomp and Van Cappellen 2004; Hwang et al. 2005; Paytan et al. 2006). Nutrient loads from groundwater entering the coastal zone have been found to be a significant source of excess nitrogen and phosphorus that can rival or exceed that of riverine inputs in some regions and, in some instances, result in coastal eutrophication in both temperate and tropical coastal regions in the form of nuisance and harmful algal blooms (Gobler and Sañudo-Wilhelmy 2001; Slomp and Van Cappellen 2004; Hu et al. 2006). Quantifying how an ecosystem responds to water quality perturbations is crucial in evaluating the effects of coastal eutrophication. Ecosystem metabolism (MET) is an effective measurement that assesses the biological response of an ecosystem to environmental perturbations, such as excess nutrient and organic matter (OM) inputs (Smith and Hollibaugh 1993). MET measures the difference between gross primary production (GPP) and respiration (RESP) and is often measured to determine the trophic status of a water body. In net autotrophic systems, OM production from GPP exceeds its consumption by RESP, resulting in an increase in pO_2 and a decrease in pCO_2 within the water body. In contrast, net heterotrophic systems have greater OM consumption than production, with a decrease in pO_2 and an increase in pCO_2, and are a net source of CO_2 to atmosphere. Additionally, MET can be used to describe trophic efficiency within a water body. In a tightly

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coupled system, RESP is almost entirely supported by GPP and has a MET near zero. In a less efficient system, RESP may exceed GPP due to consumption of allochthonous OM.

There is high variability in coastal MET which can be attributed to factors influencing primary production and RESP. These factors can be physical, such as light levels (Cotner et al. 2000; Caffrey et al. 2007) and water temperature (Caffrey 2004), chemical, such as nutrient and OM loadings to coastal waters (D'Avanzo et al. 1996; Smith and Hollibaugh 1993, 1997), or biological, such as plankton biomass, plankton community composition, and trophic interactions such as grazing pressure and viral infections (Fuhrman 2000). Of these, the ratio of dissolved organic matter (DOM) to inorganic nutrient concentrations is thought to be one of the most influential parameters affecting MET (Kemp et al. 1997; Eyre and McKee 2002; Delgadillo-Hinojosa et al. 2008). A high ratio of DOM to nutrient concentrations generally promotes RESP over GPP, while a low ratio of DOM to nutrients tends to stimulate GPP over RESP. Allochthonous OM from rivers to estuaries is thought to drive estuarine RESP (Smith and Hollibaugh 1993; Delgadillo-Hinojosa et al. 2008; Thottathil et al. 2008); however, it is not presently known if the same is true for groundwater-fed coastal waters. In these systems, the amount of allochthonous DOM entering the coastal waters is low because it is filtered through the vadose zone before entering the estuary (Slomp and Van Cappellen 2004), possibly leading to a lower DOM to nutrient ratio and potentially resulting in more autotrophic systems. Both groundwater and river inputs have strong seasonal variability, with higher flux of water and nutrient concentrations during wet seasons compared to dry seasons (Medina-Gómez and Herrera-Silveira 2006; Caffrey et al. 2007; Thottathil et al. 2008). Seasonal variations in these freshwater inputs lead to seasonal variation in MET in both temperate (Caffrey 2004) and tropical estuaries (Pradeep Ram et al. 2003; Thottathil et al. 2008), as inorganic nutrients, OM, and many other physiochemical parameters that influence both GPP and RESP vary with freshwater input.

Most studies examining GPP, RESP, and MET to date have focused on temperate estuaries (D'Avanzo et al. 1996; Kemp et al. 1997; Caffrey 2004; Caffrey et al. 2007; Delgadillo-Hinojosa et al. 2008), with few having been conducted in the tropics (Thottathil et al. 2008; Ringuet and Mackenzie 2005; Mead and Wiegner 2010), especially in regions where groundwater is the prevalent freshwater input (Medina-Gómez and Herrera-Silveira 2006). The Hawaiian Islands are an ideal place to study the influence of groundwater inputs on the tropical coastal ocean. Groundwater discharge is especially important on the leeward coast of Hawaii Island, where the relatively young and permeable basalt limits the formation of streams and surface water runoff (Oki 1999). Groundwater discharge has been found to be a significant source of nutrients to coral reefs on Hawaii Island's leeward side (Slomp and Van Cappellen 2004; Paytan et al. 2006; Street et al. 2008). On Maui Island, groundwater nutrients are responsible for large benthic macroalgal blooms, which have overgrown coral reefs and resulted in a considerable amount of ecological damage and economic losses in tourist revenue (Van Beukering and Cesar 2004; Smith et al. 2006). While the effects of groundwater nutrients in Hawaii have been studied on benthic macroalgae, little is known about the effects of these nutrients on microbes within the surface waters, where the less dense groundwater accumulates.

The purpose of this study was to examine the biological response of coastal waters to groundwater nutrients at two sites on the leeward coast of Hawaii Island, where groundwater discharge is well documented (Knee et al. 2008; Peterson et al. 2009). Specifically, the response of GPP, RESP, MET, phytoplankton, and bacterial abundances within the surface waters to groundwater nutrient and OM inputs were examined. This study is novel in that it is one of the few that have examined MET in the tropics and that was conducted in areas where freshwater inputs are dominated by groundwater discharge. This information is important as upland development, climate change, and invasive flora may be impacting the quality and quantity of groundwater discharging into the coastal ocean, especially on the leeward side of Hawaii Island. Additionally, it is essential to understand how submarine groundwater discharge (SGD) affects the balance between GPP and RESP as they primarily control pCO_2 in the coastal ocean and determine whether it is a source or sink for atmospheric CO_2; this is important to understand in the face of a changing climate and an acidifying ocean.

Materials and Methods

Study Site Description

The leeward coast of Hawaii Island is arid (<25 cm year^{-1}); however, high rainfall (>45 cm year^{-1}) on Hualalai, a 2,521-m basalt shield volcano, enters the coastal ocean through groundwater discharge (Peterson et al. 2009). Two coastal regions where groundwater inputs have been well documented are Kiholo Bay and Kaloko-Honokohau National Historical Park (Knee et al. 2008; Peterson et al. 2009; Fig. 1). The Kiholo Bay watershed is 90.9 km^2, which is largely undeveloped, with groundwater discharge rates estimated to be 7,100 m^3 day^{-1} (Peterson et al. 2009). However, the surrounding *Prosopis pallida* (mesquite known as Kiawe in Hawaii) trees, which host N_2-fixing bacteria and are phreatophytic, may increase nitrogen concentrations within the groundwater while they reduce the amount of groundwater entering the nearshore waters. In contrast, the Kaloko-Honokohau National Historical Park watershed is a much smaller area (18.8 km^2), with groundwater discharge rates estimated to be 10–382 m^3 day^{-1} (Knee et al. 2008). Kaloko-Honokohau National Historical Park is

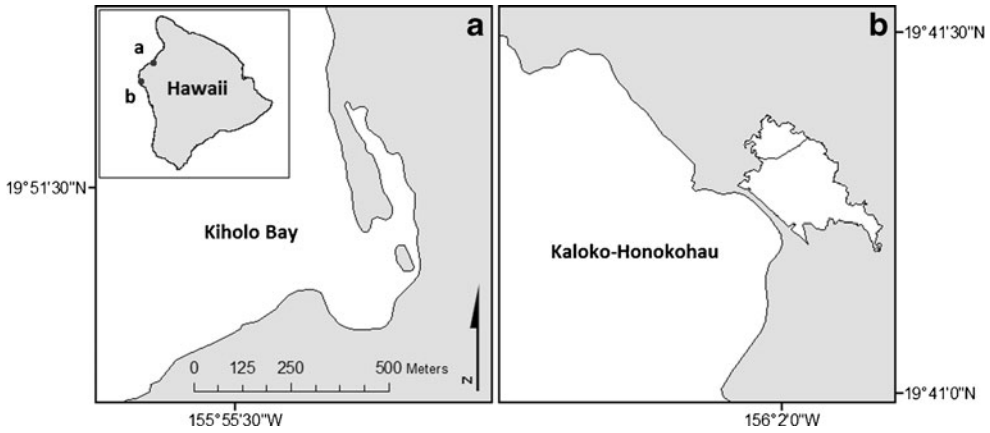

Fig. 1 Kiholo Bay (**a**) and Kaloko-Honokohau National Historical Park (**b**) are two nearshore regions on the leeward coast of Hawaii Island (*inset*), HI, USA, where groundwater enters the coastal ocean

threatened by upland development; its watershed is much more developed than Kiholo Bay's one, containing a wastewater treatment plant injection well, county landfill, and a golf course, as well as rapidly expanding residential and industrial areas (DeVerse 2006). Groundwater entering Kaloko-Honokohau National Historical Park has been characterized as having high nutrient concentrations (Johnson et al. 2008; Knee et al. 2008; Street et al. 2008); in comparison, nutrient inputs to Kiholo Bay are not well characterized.

Salinity Mapping

To delineate and determine extent of groundwater plumes, high-resolution spatial surface water salinity mapping was conducted by continuously pumping surface water (5- to 10-cm-deep) with an 800 L h^{-1} impeller driven bilge pump through a YSI 6600 V2 multiparameter sonde interfaced with a YSI 650 MDS data logger and a Garmin etrex GPS unit. This setup (a modification of Bean et al. 2002) was mounted to a kayak, which was navigated around the coastline and then within that boundary in a grid-like fashion, while surface water salinity and GPS coordinates were recorded every 3 s. Data were uploaded through YSI's Ecowatch® software and imported into Golden Software's SURFER 9. High-resolution maps of surface water salinity for each sampling event were developed using a Krigging interpolation (Fig. 2).

Water Collection and Analyses

To examine the influence of groundwater in the coastal ocean, surface water (<5 cm) samples were collected, as groundwater, and its constituents are separated from ocean water by density stratification in a 0.5- to 2-m-deep halocline. Surface water from each of the two sites was collected once monthly from six stations at both sites, with three stations haphazardly chosen within the groundwater plume and three stations outside of it between March 2011 and February 2012. Groundwater plumes were defined prior to sampling as areas with salinities near the mean value of the salinity range found at that site to ensure that samples contained a mixture of groundwater and seawater. Wet and dry seasons were defined using the Hawaii Department of Health's delineations, where the wet season is from November to April and the dry season is from May to October. In- and out-plume stations were selected during surface water salinity mapping. Samples were collected during morning hours at low tide when groundwater fluxes are most detectable (Peterson et al. 2009) and wind induced mixing was minimal. Water samples were collected in 10 L acid-washed high-density polyethylene carboys, which were insulated with towels, away from direct sunlight to maintain a stable temperature (±0.3 °C) during transport to the laboratory.

Water samples for dissolved organic carbon (DOC), total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP), as well as for $NO_3^-+NO_2^-$, PO_4^{3-}, H_4SiO_4, and NH_4^+, were taken from each carboy, filtered through a combusted (6 h at 500 °C) GF/F (Whatman®) filter, and stored frozen until analysis. DOC and TDN were analyzed on a Shimadzu TOC-V CSH, TNM-1 analyzer following recommendations of Sharp et al. (2002), with detection limits (DL) 10.0 and 5.0 μmol L^{-1}, respectively. Dissolved organic nitrogen (DON) was calculated from the differences between TDN and dissolved inorganic nitrogen (DIN=$NO_3^-+NO_2^-+NH_4^+$). Concentrations of $NO_3^-+NO_2^-$ (USEPA 353.4, DL=0.1 μmol L^{-1}), PO_4^{3-} (USEPA 365.5, DL=0.1 μmol L^{-1}), H_4SiO_4 (USEPA 366, DL=1.0 μmol L^{-1}), NH_4^+ (USGS I-2525, DL=1.0 μmol L^{-1}), and TDP (USGS 4650–03, DL=0.5 μmol L^{-1}) were determined using a Technicon Pulse II AutoAnalyzer. Dissolved organic phosphorous (DOP) was calculated from the difference between TDP and PO_4^{3-}. GF/F filters used here were then flash frozen, stored at −80 °C, and later analyzed for chlorophyll *a* (Chl *a*). Chl *a* was measured on a Turner 10-AU fluorometer following EPA method 445.0. All inorganic and organic nutrient samples were analyzed at the University of Hawaii at Hilo Analytical Laboratory.

To quantify phytoplankton and bacterial abundances, water from each carboy was removed, combined with gluteraldehyde (for a final concentration of 0.5 % gluteraldehyde), and placed

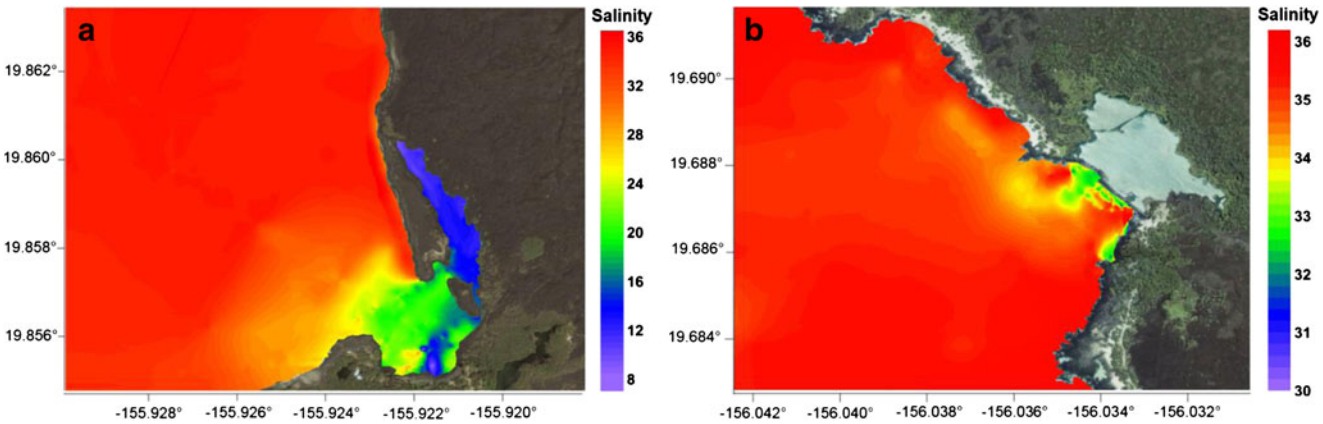

Fig. 2 Surface water salinity (ppt) mapping was used to delineate regions inside and outside of groundwater plumes on each sampling day. Above are examples of maps developed at Kiholo Bay (**a**) on October 23, 2011 and Kaloko-Honokohau (**b**) on July 29, 2011

on ice for 20 min before storage at −80 °C. Thawed samples were analyzed on an Accuri C6 flow cytometer, calibrated with Invitrogen Countbrite® counting beads and Spherotech® 8-peak validation beads. Samples for phytoplankton analysis were analyzed for 2 min with a single wash and agitation between samples. For bacterial analysis, samples were stained with Invitrogen SYTO BC green nucleic acid stain and analyzed for 20 s, with two washes between samples. Estimated spherical volume (ESV) of phytoplankton, calculated from size and abundance measurements derived from flow cytometry, was used as a proxy for phytoplankton biovolume (Li et al. 1993).

Physiochemical parameters were also measured from each carboy including turbidity (Hach 2100P), pH (VWR sympHony SP70P), water temperature, and salinity (YSI 6600 V2 sonde). Photosynthetically active radiation was measured in situ using a Li-Cor LI-250A with a spherical quantum sensor.

O_2 Incubations

Changes in dissolved oxygen (DO) concentration were measured in light/dark bottle incubation experiments to determine GPP, RESP, and MET, following methods modified from Mead and Wiegner (2010). DO concentrations were measured using a Hach® LBOD101 luminescence DO probe (ASTM D888-05 method C), calibrated using the water saturated air method prior to use. Incubations were conducted under controlled laboratory conditions (and are referred to as potential measurements) in order to make comparisons over spatial and temporal scales as natural variations in light intensity and water temperature can strongly influence these processes. Each carboy was mixed and siphoned (overflowing three times) into eight, acid-washed, 60 ml Wheaton® borosilicate biological oxygen demand (BOD) bottles. Initial DO concentration was measured from each BOD bottle using the Hach LDO probe. Four bottles were incubated in the dark, while the remaining four were incubated at a light intensity of 460 μmol photons m^{-2} s^{-1}, the intensity at which the highest rate of photosynthetic activity occurred, as determined through photosynthesis vs. irradiance curves for each site (Johnson 2012). The BOD bottles were incubated at 25°C (±1°C of ambient site temperatures) in a cooler filled with sample water for 14 h to provide a measurable change in DO concentration in both light and dark treatments. The LDO probe provided comparable results to the Winkler titration (R^2=0.993, p<0.001), with a more precise DO measurement (>0.5 μmol O_2 L^{-1}) than the Winkler method (>2.0 μmol O_2 L^{-1}), and substantially reduced processing time and operating costs.

The difference between the initial and light bottle DO concentration divided by incubation time was used to determine potential net primary production (pNPP; Eq. 1), while the difference between initial and dark bottle DO concentration divided by incubation time was used to determine RESP (Eq. 2), which are reported as positive values in this paper. Daily potential gross primary production (pGPP) was calculated as the sum of $pNPP_{Hourly}$ and $RESP_{Hourly}$ multiplied by the average number of daylight hours (12.13 h; Eq. 3). Potential metabolism (pMET) was calculated as the difference between daily pGPP and daily RESP ($RESP_{Hourly}$ multiplied by 24 h; Eq. 4), under the assumption that phytoplankton RESP is similar under light and dark conditions (Bender et al. 1987).

$$pNPP_{Hourly}\left(\text{mmol } O_2 \text{ } m^{-3}h^{-1}\right) = \left([O_2]_{Light} - [O_2]_{Initial}\right)/14 \text{ h} \quad (1)$$

$$RESP_{Hourly}\left(\text{mmol } O_2 m^{-3}h^{-1}\right) = \left([O_2]_{Initial} - [O_2]_{Dark}\right)/14 \text{ h} \quad (2)$$

$$pGPP_{Daily}\left(\text{mmol } O_2 m^{-3}day^{-1}\right) = \left(pNPP_{Hourly} + \left(RESP_{Hourly}\right) \times 12.13 \text{ h}\right) \quad (3)$$

$$\mathrm{pMET_{Daily}}\left(\mathrm{mmol\ O_2 m^{-3} day^{-1}}\right) = \mathrm{pGPP_{Daily}} - \left(\mathrm{RESP_{Hourly}} \times 24\ \mathrm{h}\right) \quad (4)$$

Statistical Analyses

pGPP, RESP, and pMET were compared using individual three-way analysis of variances (ANOVAs) with site (Kiholo Bay vs. Kaloko-Honokohau National Historical Park), plume (inside vs. outside groundwater plume), and season (wet vs. dry season) as factors. Regression analysis was used to evaluate the contribution of pGPP and RESP on pMET; however, we do recognize that these factors are not independent of pMET. Non-normal data were transformed using an arcsine transformation to meet assumptions for parametric tests. Stepwise linear regression models were used to examine how GPP, RESP, and pMET were related to phytoplankton abundance and biovolume, bacterial abundance, inorganic nutrients and DOM concentrations, and other abiotic factors that influence these biological processes. Correlations were used to examine associations between surface water salinity and $NO_3^-+NO_2^-$ at each site. Statistical analyses were conducted using Minitab 14 statistical software.

Results

Salinity

Surface water salinity was significantly lower within groundwater plumes ($p<0.001$), with lower salinity found in-plume at Kiholo Bay (mean±SE=25.81±0.68 ppt) than in-plume at Kaloko-Honokohau National Historical Park (33.85±0.10 ppt). Surface water salinity outside of groundwater plumes was similar at Kiholo Bay (34.64±0.3 ppt) and Kaloko-Honokohau National Historical Park (34.92±0.1 ppt; Table 1). No significant difference was found in surface water salinity within the groundwater plumes between the wet and dry seasons at Kiholo Bay ($p=0.495$) or Kaloko-Honokohau National Historical Park ($p=0.434$). Mixing plots depicting the relationship between surface water salinity and $NO_3^-+NO_2^-$ concentrations show nonconservative mixing at both sites, further suggesting biological uptake of groundwater nutrients (Fig. 3).

Incubation Analyses

pGPP

Across sites, average pGPP was over two times higher within groundwater plumes (7.07±2.63 mmol O_2 m^{-3} day^{-1}) than outside of them (2.81±0.24 mmol O_2 m^{-3} day^{-1}; $p<0.001$). Overall, pGPP was two times higher at Kiholo Bay (9.51±2.3 mmol O_2 m^{-3} day^{-1}) than at Kaloko-Honokohau National

Table 1 Mean (SE) physiochemical and nutrient parameters of surface water samples collected at Kiholo Bay, HI and Kaloko-Honokohau National Historical Park, HI

Site	Location	Season	Temp (°C)	Salinity (ppt)	pH	Turbidity (NTU)	PO_4^{3-} (μmol L^{-1})	$NO_3^-+NO_2^-$ (μmol L^{-1})	DIN (μmol L^{-1})	DON (μmol L^{-1})	DOC (μmol L^{-1})
Kiholo Bay	In-plume	Wet	25.0 (0.2)	25.3 (0.9)	8.13 (0.03)	0.36 (0.09)	0.48 (0.16)	15.99 (1.78)	16.55 (1.83)	25.46 (11.86)	138.02 (35.68)
		Dry	25.4 (0.1)	26.2 (1.0)	8.10 (0.01)	0.37 (0.04)	0.25 (0.07)	11.75 (1.48)	12.89 (1.46)	10.34 (2.54)	202.65 (21.97)
	Out-plume	Wet	25.0 (0.1)	34.0 (0.5)	8.14 (0.01)	0.20 (0.04)	0.01 (0.01)	2.64 (0.76)	4.50 (0.88)	26.47 (11.14)	145.77 (39.12)
		Dry	25.8 (0.1)	35.1 (0.1)	8.14 (0.02)	0.16 (0.01)	0.09 (0.06)	0.85 (0.24)	4.24 (0.78)	6.62 (1.74)	253.10 (51.86)
Kaloko-Honokohau	In-plume	Wet	24.1 (0.2)	33.8 (0.2)	8.24 (0.02)	0.32 (0.11)	ND<0.1	2.65 (0.29)	4.81 (0.82)	28.96 (12.65)	172.37 (47.64)
		Dry	25.9 (0.1)	33.9 (0.1)	8.26 (0.02)	0.24 (0.03)	ND<0.1	1.35 (0.10)	5.51 (0.67)	5.80 (1.38)	220.31 (38.57)
	Out-plume	Wet	24.1 (0.3)	35.1 (0.2)	8.20 (0.01)	0.23 (0.07)	ND<0.1	0.97 (0.19)	2.69 (0.70)	37.30 (17.68)	185.65 (46.39)
		Dry	25.9 (0.1)	34.7 (0.1)	8.20 (0.02)	0.13 (0.01)	ND<0.1	1.12 (0.19)	5.58 (0.65)	5.92 (1.48)	214.11 (28.80)

Measurements of DOP were below DLs of 0.5 μmol L^{-1}

ND nondetectable

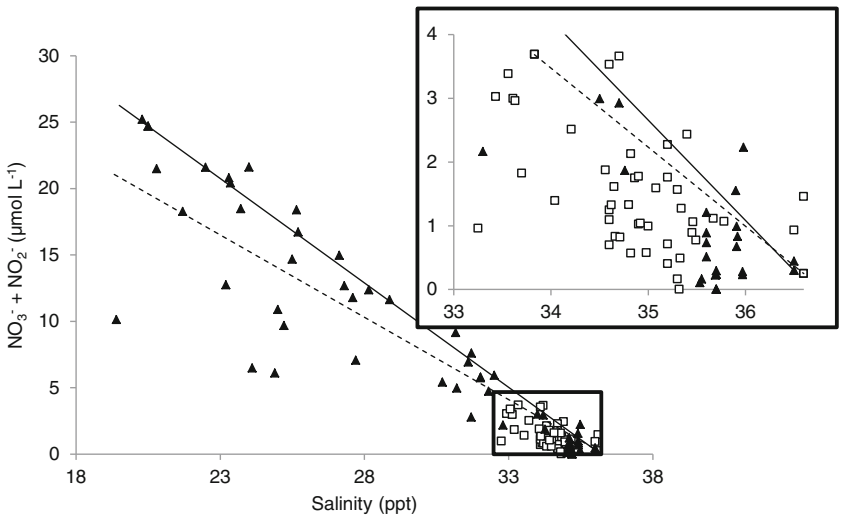

Fig. 3 Mixing plot of NO_3^-+ NO_2^- concentrations with salinity. *Triangles* represent samples collected at Kiholo Bay (*solid conservative mixing line*), while *squares* represent samples collected at Kaloko-Honokohau National Historical Park (*dashed conservative mixing line*). The *enclosed area* is an enlargement of the values found at higher salinities

Historical Park (4.85±0.68 mmol O_2 m^{-3} day^{-1}; $p=0.015$). pGPP between wet (7.34±1.57 mmol O_2 m^{-3} day^{-1}) and dry (7.61±2.13 mmol O_2 m^{-3} day^{-1}) seasons were similar ($p=0.319$) across sites. A stepwise linear regression suggests that ESV and DIN were the best predictors of pGPP at Kiholo Bay ($R^2=0.52$, $p=0.004$), while Chl *a* and ESV were the best predictors at Kaloko-Honokohau National Historical Park ($R^2=0.71$, $p=0.008$).

Respiration

On average across sites, RESP was two times higher within groundwater plumes (12.39±0.82 mmol O_2 m^{-3} day^{-1}) than outside of them (5.44±0.43 mmol O_2 m^{-3} day^{-1}; $p<0.001$). RESP was significantly lower at Kiholo Bay (8.39±0.78 mmol O_2 m^{-3} day^{-1}) than at Kaloko-Honokohau National Historical Park (9.46±0.82 mmol O_2 m^{-3} day^{-1}; $p=0.029$). RESP was significantly different between the wet and dry seasons ($p=0.010$) across sites, with RESP being higher within the dry season (9.80±0.86 mmol O_2 m^{-3} day^{-1}) than during the wet season (7.71±0.68 mmol O_2 m^{-3} day^{-1}). Stepwise linear regressions suggest that NO_3^-+NO_2^- concentration was the most influential parameter affecting RESP at Kiholo Bay ($R^2=0.40$, $p<0.001$), while there were no significant predictors of RESP at Kaloko-Honokohau National Historical Park.

Potential Metabolism

There was no significant difference in surface water pMET between in-plume and out-plume stations across sites ($p=0.132$). However, there was a significant difference in pMET between sites; surface waters at Kiholo Bay (pMET=1.13±2.37 mmol O_2 m^{-3} day^{-1}) were less heterotrophic than those at Kaloko-Honokohau National Historical Park (−4.61±0.89 mmol O_2 m^{-3} day^{-1}; $p=0.003$; Table 2; Fig. 4). Surface waters at Kiholo Bay were frequently heterotrophic; however, they switched twice to highly autotrophic conditions during the year. The elevated RESP within the dry season resulted in more heterotrophic conditions during this season (−2.19±1.50 mmol O_2 m^{-3} day^{-1}) than in the wet season (−0.36±2.4 mmol O_2 m^{-3} day^{-1}) across sites ($p=0.020$). In-plume samples collected at Kiholo Bay during September and November 2011 were outliers with regards to pGPP and pMET, with measurements eight and ten times higher than the mean values, respectively. These values were not removed from the data set as they are supported by nutrient and phytoplankton biovolume measurements and represent the high variability within this system. Linear regressions indicated that pGPP ($R^2=0.892$, $p<0.001$) affected pMET more than RESP ($R^2=0.099$, $p=0.002$) at both sites. The two sites were analyzed separately as pGPP, RESP, and pMET were significantly different between them (Fig. 5). At Kiholo Bay, pGPP explained 89 % of the variation in pMET ($p<0.001$), while RESP only explained 3 % ($p=0.084$). Likewise at Kaloko-Honokohau National Historical Park, pGPP was a significant predictor of pMET ($p=0.001$) and accounted for 21 % of the variability. However at Kaloko-Honokohau National Historical Park, RESP accounted for more of pMET than pGPP, explaining 45 % of the variability ($p<0.001$).

Phytoplankton Biovolume and Bacterial Cell Abundance

Phytoplankton biovolume (estimated through ESV) was two times higher within groundwater plumes ($2.66\times10^5\pm4.39\times10^4$ μm^3 ml^{-1}) than outside of them ($1.10\times10^5\pm6.52\times10^3$ μm^3 ml^{-1}; $p<0.001$). It was also two times higher at Kiholo Bay ($2.30\times10^5\pm3.86\times10^4$ μm^3 ml^{-1}) than at Kaloko-Honokohau National Historical Park ($1.31\times10^5\pm1.29\times10^4$ μm^3 ml^{-1}; $p=0.004$). No difference in phytoplankton biovolume was detected between the wet ($2.02\times10^5\pm4.20\times10^4$ μm^3 ml^{-1}) and dry ($1.77\times10^5\pm2.45\times10^4$ μm^3 ml^{-1}) seasons ($p=0.33$) across sites. ESV was significantly correlated to NO_3^-+NO_2^- concentrations at Kiholo Bay ($r=0.41$, $p=0.001$);

Table 2 Mean (SE) biological parameters of surface water samples collected at Kiholo Bay and Kaloko-Honokohau National Historical Park, HI

Site	Location	Season	Sample size	Bacteria abundance ($\times 10^5$ cells ml^{-1})	Phytoplankton abundance ($\times 10^3$ cells ml^{-1})	Phytoplankton biovolume ($\times 10^5$ μm^3 ml^{-1})	Chl *a* (μg L^{-1})
Kiholo Bay	In-plume	wet	12	6.81 (1.01)	6.14 (0.81)	4.50 (1.45)	0.48 (0.08)
		dry	18	7.46 (0.83)	16.25 (2.83)	2.69 (0.65)	0.30 (0.05)
	Out-plume	wet	12	5.49 (0.34)	8.84 (1.50)	1.15 (0.20)	0.17 (0.05)
		dry	18	6.01 (0.29)	22.92 (2.27)	1.17 (0.07)	0.10 (0.01)
Kaloko-Honokohau	In-plume	wet	12	5.53 (0.38)	7.46 (0.79)	1.57 (0.31)	0.99 (0.28)
		dry	12	4.02 (0.23)	13.13 (2.32)	1.63 (0.36)	0.28 (0.04)
	Out-plume	wet	12	5.62 (0.39)	8.55 (1.16)	0.88 (0.10)	0.27 (0.07)
		dry	12	5.46 (0.24)	13.38 (1.39)	1.21 (0.17)	0.18 (0.03)

however, it was not significantly correlated at Kaloko-Honokohau National Historical Park ($r=0.30$, $p=0.057$). Bacteria cell abundance was significantly higher at Kiholo Bay ($6.51\times10^5\pm3.5\times10^4$ cells ml^{-1}) than Kaloko-Honokohau National Historical Park ($5.22\times10^5\pm1.9\times10^4$ cells ml^{-1}; $p=0.005$). No significant differences in bacterial cell abundance were found between in- and out-plume stations ($p=0.219$) or between wet and dry season ($p=0.994$) across sites (Table 2).

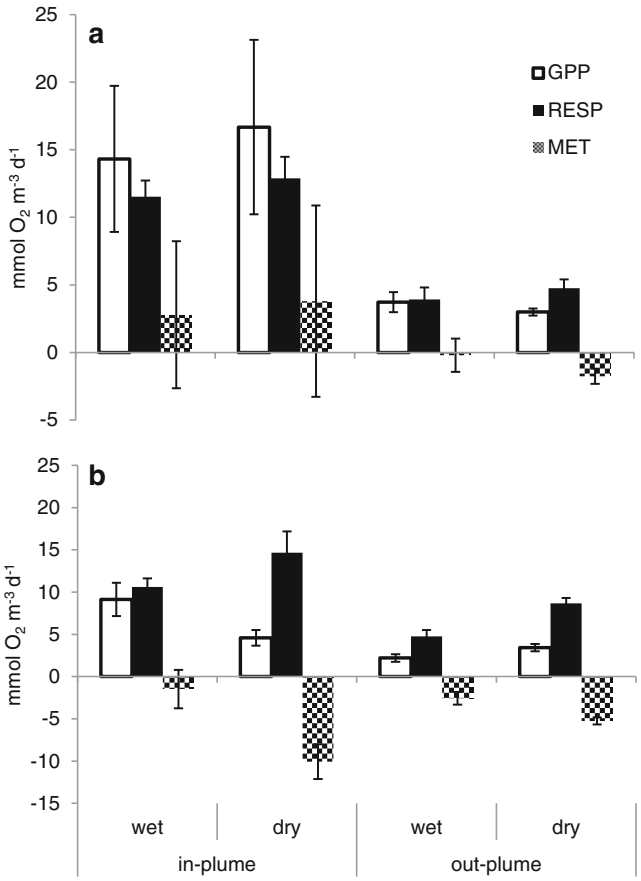

Fig 4 Average (SE) pGPP, RESP, and pMET at Kiholo Bay (**a**) and Kaloko-Honokohau National Historical Park (**b**) observed inside and outside for groundwater plumes during wet and dry seasons (2011–2012)

Bacteria cell abundance was significantly correlated to turbidity ($r=-0.424$, $p=0.003$) and concentrations of TDP ($r=-0.483$, $p<0.001$), TDN ($r=-0.486$, $p<0.001$), and DON ($r=-0.445$, $p<0.001$) at Kiholo Bay; however, it was only significantly correlated to DON concentrations ($r=-0.459$, 0.001) at Kaloko-Honokohau National Historical Park.

Discussion

Effect of Groundwater on pGPP, RESP, and pMET

Increased GPP has been observed in response to freshwater inputs in other tropical (Ringuet and Mackenzie 2005; Mead and Wiegner 2010) and temperate (Gazeau et al. 2005; Azevedo et al. 2006) riverine-dominated coastal systems. In this study, mean pGPP was several times higher within groundwater plumes, with measurements as high as 124.0 mmol O_2 m^{-3} day^{-1}, which was 14 times higher than the maximum pGPP value outside of the groundwater plumes (8.88 mmol O_2 m^{-3} day^{-1}). Increased surface water pGPP within groundwater plumes is likely attributed to utilization of groundwater nutrients by nearshore phytoplankton, as pGPP was positively correlated to phytoplankton biovolume (Fig. 6a) and $NO_3^-+NO_2^-$ concentrations (Fig. 6b). Our findings are consistent with previous studies that have found that inorganic nutrients, particularly nitrogen, stimulate GPP in coastal (D'Avanzo et al. 1996; Kemp et al. 1997; Caffrey 2004; Azevedo et al. 2006; Russell et al. 2006) and pelagic (McAndrew et al. 2007; Viviani et al. 2011) systems. Concentrations of $NO_3^-+NO_2^-$ measured in groundwater entering Kaloko-Honokohau National Historical Park are high (up to 82.6 μmol L^{-1}; Knee et al. 2008; Johnson et al. 2008; Street et al. 2008); however, concentrations measured in this study were much lower (8.36 ± 1.02 μmol L^{-1}) within the nearshore groundwater plumes (Table 1). These low $NO_3^-+NO_2^-$ concentrations, coupled with PO_4^{3-} concentrations below DLs, suggest that nutrient availability may be limiting GPP.

While low nutrient concentrations may be controlling pGPP at Kaloko-Honokohau National Historical Park, it is difficult to

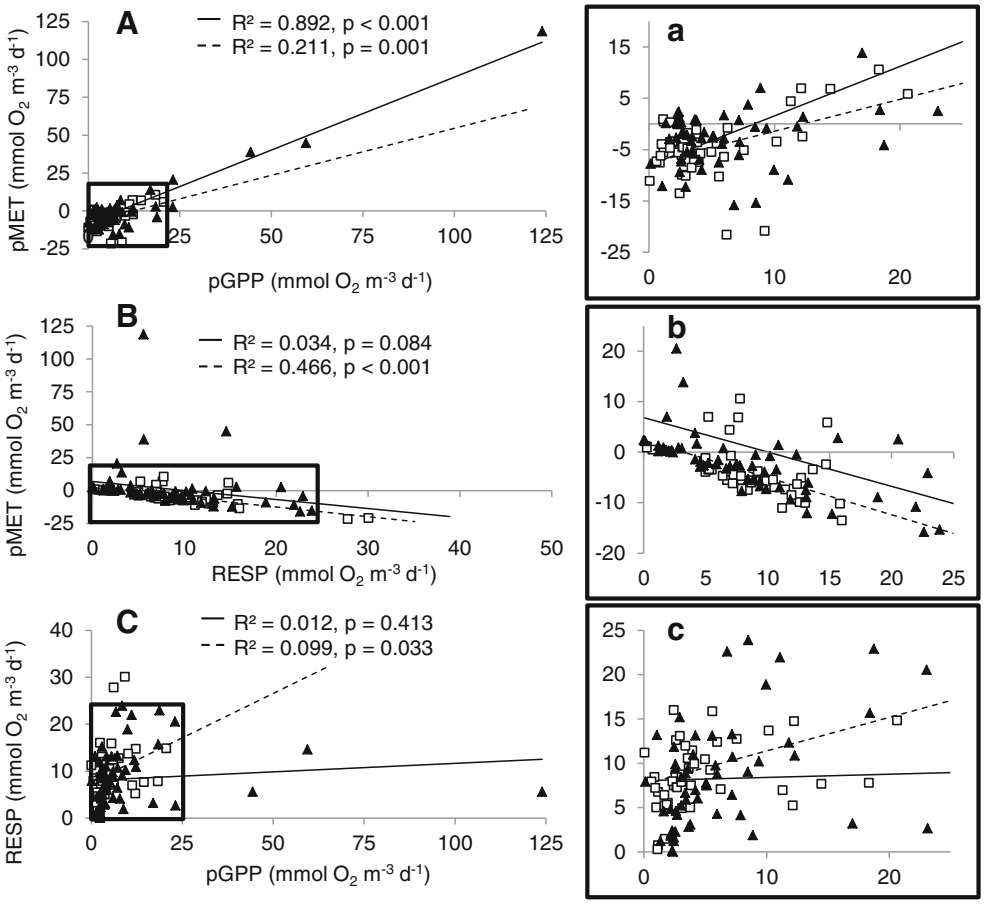

Fig. 5 Regression analyses examining the influence of pGPP on pMET (**A**, **a**), RESP on pMET (**B**, **b**), and pGPP on RESP (**C**, **c**) in surface water samples. *Triangles* represent data collected at Kiholo Bay (*solid trendline*). *Squares* represent data collected at Kaloko-Honokohau National Historical Park (*dashed trendline*). *Enclosed areas* are enlargement of values found at the low-end of the scale

determine what may be controlling productivity at Kiholo Bay, where nearshore nutrient concentrations were high. Increased freshwater inputs have been found to negatively influence GPP in tropical river-dominated (Mead and Wiegner 2010) and groundwater-fed (Medina-Gómez and Herrera-Silveira 2006) coastal waters by reducing residence time of nutrients and autotrophs within the system. Residence time at Kiholo Bay is likely short because of the high freshwater discharge rate (7,100 m^3 day^{-1}, Peterson et al. 2009) in the nearshore waters. Turbidity also strongly influences GPP in many river-dominated estuaries, where suspended particles reduce light availability to photosynthetic organisms, reducing rates of primary production (Iriarte et al. 1996; Cotner et al. 2000; Pradeep Ram et al. 2003; Thottathil et al. 2008). Turbidity at Kiholo Bay was much lower (0.08–0.73 NTU) than that found in river-dominated estuaries in Hawaii (Kaneohe Bay: 1–8 NTU, De Carlo et al. 2007; Hilo Bay: 0.7–6.8 NTU, Mead and Wiegner 2010). While high turbidity may not be inducing light limitation, photosynthesis vs. irradiance curves for each site suggest that high in situ light intensity (as high as 2,025 μmol photons m^{-2} s^{-1}) may lead to photoinhibition, where primary productivity is reduced.

RESP in river-dominated estuaries has been found to increase in response to increased freshwater inputs in some regions (Pradeep Ram et al. 2003; Russell et al. 2006) and decrease in others (Mead and Wiegner 2010). This study found RESP was significantly higher within groundwater plumes, suggesting that groundwater inputs stimulated heterotrophic processes. RESP increases are typically attributed to high OM inputs (Smith and Hollibaugh 1993; Kemp et al. 1997; Gazeau et al. 2005), while decreases in RESP may be due to flushing and displacement of autotrophs and heterotrophs (Iriarte et al. 1996; Mead and Wiegner 2010). Our study found no strong associations between RESP and DOC, DON, or DOP concentrations at both sites; however, concentrations may not be representative of OM loading as cycling efficiency can be high within the microbial loop (Azam et al. 1994). RESP has also been shown to be positively correlated to Chl *a* in a temperate riverine estuary at concentrations above 5 μg L^{-1} (Iriarte et al. 1996). The sites sampled in this study are oligotrophic, with low Chl *a* concentrations (range=0.01–2.57 μg L^{-1}), which may explain why no relationship was found between Chl *a* and RESP. Bacterial cell abundance has also been found to be significantly correlated to RESP (Iriarte et al. 1996); however, it was not in our study, which may be explained by the relatively low bacterial cell abundances measured at Kiholo Bay and Kaloko-Honokohau National Historical Park (2.4×10^5–1.4×10^6 cells ml^{-1}). While $NO_3^-+NO_2^-$ concentrations were found to strongly influenced RESP at Kiholo Bay, the driving

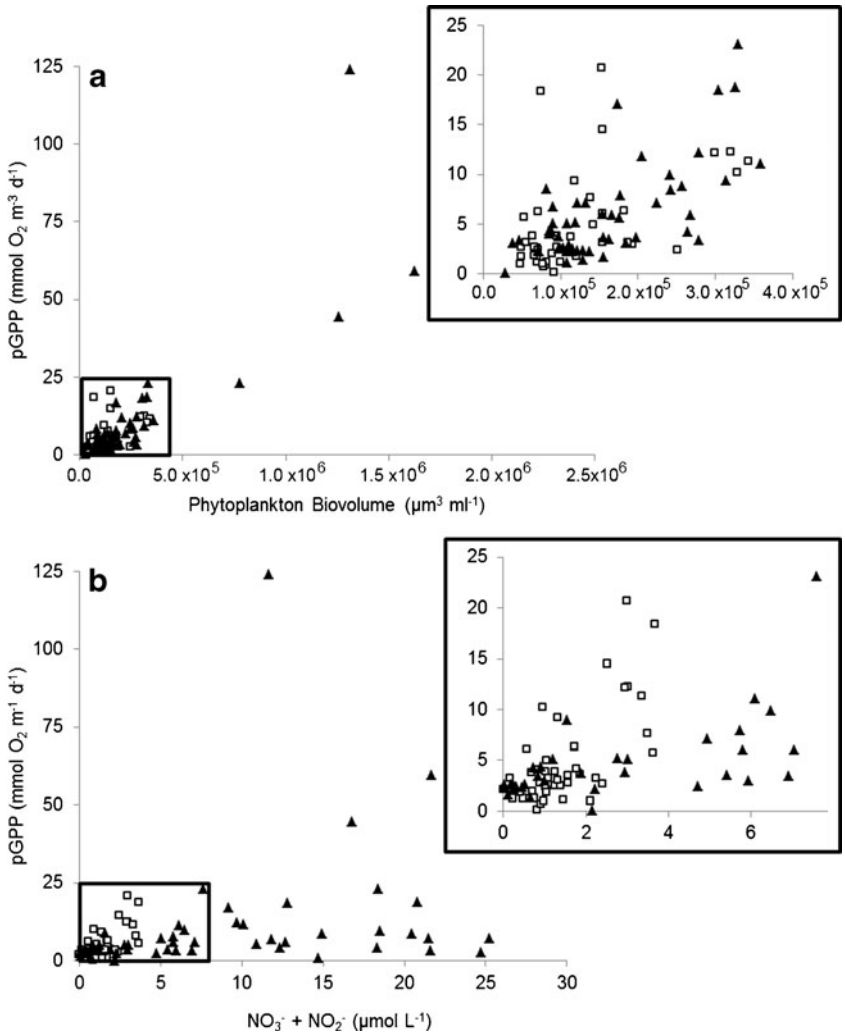

Fig. 6 Correlation between pGPP and phytoplankton biovolume (**A**) at Kiholo Bay (*triangles*; $r=0.679$, $p<0.001$), and Kaloko-Honokohau (*squares*; $r=0.545$, $p<0.001$), and pGPP and $NO_3^-+NO_2^-$ concentrations (**B**) at Kiholo Bay (*triangles*; $r=0.527$, $p<0.001$), and Kaloko-Honokohau National Historical Park (*squares*; $r=0.627$, $p<0.001$), Hawaii Island, USA. Enclosed areas are enlargement of values clustering around the low ends of the axes

force of RESP at Kaloko-Honokohau remains unclear. Kaloko Fishpond is a highly productive (Bulseco et al., unpublished data) coastal brackish pond that enters the nearshore waters at Kaloko-Honokohau National Historical Park through a small inlet. The microbial community and OM that enters the relatively nutrient-poor coastal waters from Kaloko Fishpond, where GPP and RESP were high (Bulseco et al., unpublished data), may be enhancing nearshore RESP.

Trophic conditions have been shown to vary both within and between systems, with net heterotrophy dominating the majority of tropical (Pradeep Ram et al. 2003; Thottathil et al. 2008) and temperate river-dominated estuaries studied to date (Smith and Hollibaugh 1993; Caffrey 2004; Gazeau et al. 2005; Delgadillo-Hinojosa et al. 2008); however, autotrophic conditions have been found in coastal Hawaiian waters (Ringuet and Mackenzie 2005; Mead and Wiegner 2010). When in-plume data from both sites were combined and compared to out-plume data, no significant differences in pMET were observed. However, significant pMET responses to groundwater inputs became more apparent when examining sites individually (Fig. 4). At Kiholo Bay, in-plume pGPP exceeded RESP, resulting in net autotrophic conditions. In contrast, at Kaloko-Honokohau National Historical Park in-plume RESP exceeded pGPP, resulting in net heterotrophic conditions. MET and the trophic status of an estuary depends on the many factors that can influence GPP and RESP. Previous research has suggested that the ratio of DIN to OM loading may control MET (Kemp et al. 1997); however, loading was not measured in this study. While the response within the groundwater plumes varied between sites, the out-plume regions were less variable, with net heterotrophic conditions prevailing. Similarly, oceanic ends of estuaries are generally less variable than their freshwater ends, as they receive less terrestrial derived nutrients and OM than their freshwater ends (Caffrey 2004; Gazeau et al. 2005; Azevedo et al. 2006). Open ocean MET measurements are also much less variable and typically near balance (Smith and Hollibaugh 1993; Viviani et al. 2011). With the exclusion of major outliers, pGPP, RESP, and pMET at Kaloko-Honokohau and Kiholo Bay fall within the range of other comparable surface waters studied (Table 3).

Table 3 Rage of surface water GPP, RESP, and MET (in mmol O_2 m^{-3} day^{-1}) found in this study and comparable studies

Location	Study	GPP	RESP	MET
Kiholo Bay, HI	Present study	0.14–124	0–23.88	−15.82–118.44
Kaloko-Honokohau, HI	Present study	0.07–20.64	0.26–30.08	−21.59–10.56
Hilo Bay, HI	Mead and Wiegner 2010	1.51–67.57	0.78–31.81	−13.09–54.37
Kaneohe Bay, HI	Ringuet and Mackenzie 2005	~8	~3	~7–10
Bay of Blanes, Spain	Duarte et al. 2004	~1–4.5	~1–6.5	~−2.5–0.5
Sagami Bay, Japan	Hashimoto et al. 2006	~1–50	~1–16	N/A
Equatorial Pacific Ocean	Viviani et al. 2011	0.25–4.05	0.31–1.56	−1.31–3

Coupling Between Processes

Coupling between production and consumption of OM can be used to infer trophic efficiency. In tightly coupled, more efficient systems, changes in RESP generally coincide with changes in GPP, as RESP is dependent on in situ production (Smith and Kemp 1995). Decoupling of these processes and low trophic efficiency can occur as allochthonous OM enters a system, increasing RESP, or as autochthonous OM exits, reducing RESP. Coupling between pGPP and RESP was weak at our two sites, with only 1.2 % of RESP explained by pGPP at Kiholo Bay ($p=0.413$) and 9.9 % at Kaloko-Honokohau National Historical Park ($p=0.033$; Fig. 5). Previous studies have suggested that coupling between GPP and RESP may vary as a function of productivity, where in highly autotrophic waters, GPP and RESP are poorly coupled, while in highly heterotrophic waters, coupling between GPP and RESP can be high (Biddanda et al. 1994; Smith and Kemp 1995; Iriarte et al. 1996). While most samples collected in this study exhibited relatively low productivity, decoupling of pGPP and RESP was most apparent in the samples with high pGPP (Fig. 5). The absence of strong coupling shows that RESP was largely independent of pGPP, suggesting that RESP may be supported by allochthonous OM. Groundwater input is likely the dominate source of allochthonous OM as strong density stratification at the halocline limits upwelling and thus the influence of benthic resuspension.

pGPP and RESP can both be significant predictors of pMET. Our findings show that pGPP strongly affected pMET at Kiholo Bay, explaining 89.2 % of the variation in pMET, while RESP explained only 3 % of pMET ($p=0.084$). Our study suggests that pGPP was stimulated by $NO_3^-+NO_2^-$ concentrations at Kiholo Bay, which supports previous research that has found that positive MET estuaries are strongly influenced by nutrients (Kemp et al. 1997; Russell et al. 2006; Delgadillo-Hinojosa et al. 2008). Nutrient concentrations in the nearshore waters of Kaloko-Honokohau National Historical Park were low (Table 1), suggesting that high nutrient concentrations found within groundwater may be consumed by nearshore regions such as the highly productive Kaloko Fishpond (Bulseco et al., unpublished data). These low nutrient concentrations may be responsible for pGPP exerting less influence on pMET ($R^2=0.229$, $p=0.001$), enabling RESP to influence pMET to a larger extent ($R^2=0.466$, $p<0.001$).

Temporal and Spatial Variability

In order to properly assess trophic conditions of a system, temporal and spatial variability must be taken into account. Seasonal variations of MET are found in many coastal systems, where light intensity, day length, water temperature, and other factors that influence GPP and RESP vary temporally. Since seasonal variability increases with latitude, seasonal effects are likely to be higher in temperate regions than in tropical ones. A comprehensive study examining net ecosystem MET in 22 estuaries throughout North America noted that seasonal variations were relatively low in the Caribbean and Gulf of Mexico estuaries compared to more temperate US estuaries, concluding that temperature was more influential than inorganic nutrient concentrations on MET (Caffrey 2004). The incubation method used in this study controlled light and temperature conditions to focus on the impact of groundwater inputs, so seasonal variations measured here can be attributed to changes in inorganic nutrient and OM concentrations, as well as variability of phytoplankton and bacterioplankton communities. Studies have found increases in both GPP and RESP during summer; however, systems typically become more heterotrophic during the dry summer months (Kemp and Boynton 1992; Smith and Hollibaugh 1997; Duarte et al. 2004; Hashimoto et al. 2006). While we did not find a seasonal response in pGPP, RESP was significantly higher within dry seasons, resulting in more heterotrophic conditions (Fig. 4). Other studies have found a reduction in GPP during wet seasons, as increased freshwater inputs can reduce residence time and flush autotrophs from the system (Medina-Gómez and Herrera-Silveira 2006; Mead and Wiegner 2010). While we did not find seasonal differences in pGPP, displacement of microbes or a decrease in residence time may be shifting the geographic extent of the biological response outside of the in-plume region we studied. In our study, variability of pGPP and pMET was profound on shorter temporal scales, with large month-to-month variability that did not fall within a particular season. At Kiholo Bay, high pGPP was observed in September 2011 (54.7±34.7 mmol O_2 m^{-3} day^{-1}) and November 2011 (42.3 ±10.6 mmol O_2 m^{-3} day^{-1}), whereas it was relatively low in

October 2011 (6.44±1.31 mmol O_2 m^{-3} day^{-1}). These pulses in GPP and those found in other studies (Karl et al. 2003) suggest that MET measurements in highly dynamic systems should be taken on short temporal scales in order to accurately assess the true metabolic condition of a system.

High spatial variability in MET has been found in many systems (Smith and Kemp 2001; Russell et al. 2006; Russell and Montagna 2007; Mead and Wiegner 2010), but not in all systems (Caffrey 2003; D'Avanzo et al. 1996). High spatial variability in pGPP, RESP, and pMET were found both between and within sites on the leeward sides of Hawaii Island. Kiholo Bay and Kaloko-Honokohau National Historical Park are both groundwater-fed systems only 25 km apart; however, they had contrasting metabolic conditions. Within sites, pGPP, RESP, and pMET varied considerably between in- and out-plume regions, only 0.5 km apart (Fig. 4). While variability has been noted within river-fed estuaries at scales less than 1 km (D'Avanzo et al. 1996; Caffrey 2003), variability at that spatial scale is typically found to be low in many systems (Smith and Kemp 2001; Russell et al. 2006; Russell and Montagna 2007). In Hilo Bay, a river-fed estuary in East Hawaii, spatial variability was low under base flow conditions; however, it was high during storm events when river discharge was high, suggesting that pulse events that lead to changes in freshwater input can strongly influence variability. In this study high variability was also found at much smaller spatial scales within the groundwater plume region. The largest variation was found at Kiholo Bay in September 2011, where in-plume pGPP varied from 17.0 to 124.0 mmol O_2 m^{-3} day^{-1} in samples collected only 20 m apart, a seemingly unprecedented variability on that spatial scale. Understanding spatial variability within a system is crucial in formulating broad-reaching conclusions from geographically isolated measurements.

Conclusion

This study has shown that groundwater inputs stimulate biological processes within the coastal surface water microbial community. Groundwater nutrients and OM inputs led to increased pGPP and RESP; however, the magnitude of response of these parameters varied between sites and seasons, resulting in contrasting pMET conditions. Understanding the response of coastal waters to groundwater discharge has become increasingly important in leeward Hawaii Island as increasing development, invasive flora, and climate change are projected to degrade the quality and quantity of coastal groundwater inputs. This study also has broader implications elsewhere as global carbon models largely dismiss the coastal ocean due to its relatively small geographic area and highly dynamic and poorly understood carbon contribution (Smith and Hollibaugh 1993). The high temporal and spatial variability found in this study and many others (e.g. Smith and Hollibaugh 1993, 1997; Smith and Hollibaugh 1997; Caffrey 2004) reveal the importance of using repeated measures over short spatial and temporal scales to properly evaluate coastal ocean metabolic conditions.

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