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ORIGINAL PAPER

Carbon dioxide dynamics in rivers and coastal waters of the "big island" of Hawaii, USA, during baseline and heavy rain conditions

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Abstract The distributions of the partial pressure of carbon dioxide (pCO_2) and total alkalinity (TA) were examined for a 6-month period in the Wailuku and Wailoa rivers and coastal waters of Hilo Bay on the west coast of the Island of Hawaii, USA. Main results for the largest and turbulent Wailuku River show in the watershed an oversaturation in CO_2 with respect to atmospheric equilibrium and a CO_2 undersaturation in the estuary. In the Wailoa river-estuary system, extremely high pCO_2 values ranging from 1500 to 10500 ppm were measured with significant shifts in pCO_2 from drought to flood period. In the two rivers, water residence time, groundwater inputs and occasional flood events are the predominant drivers of the spatial and temporal patterns in the distribution of pCO_2. In Hilo Bay, CO_2 oversaturation dominates and the bay was a source of CO_2 to the atmosphere during the study period. TA is conservative along the salinity gradient, indicating calcification in the bay is not a significant source of CO_2 to the atmosphere.

Keywords Carbon dioxide · Total alkalinity · Big Island of Hawaii · Tropical aquatic systems · Rivers · Estuaries · Coastal waters

1 Introduction

Tropical and subtropical freshwater and coastal marine ecosystems have been largely understudied and ignored in terms of the dynamics of the CO_2-carbonic acid

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system and carbon dioxide exchange across the air–water surface despite the fact that about 60% of global freshwater inputs, 80% of total organic and 45% of total inorganic carbon burial take place at tropical and subtropical latitudes (Ludwig et al. 1996; Mackenzie et al. 2004). At these latitudes, sediment discharge by high-standing islands of the Pacific Ocean is estimated to contribute more than 40% of the total sediment discharge to the global ocean (Milliman et al. 1999). Knowledge of carbon dioxide exchange between the atmosphere and aquatic environments is important considering that up to 461 ± 19 PgC were emitted by fossil-fuel combustion and land-use activities to the atmosphere and an approximate 122 ± 2 PgC were absorbed by the ocean since the start of the Industrial Revolution (Mackenzie et al. 2004; Sabine et al. 2004). The coastal ocean organic and inorganic carbon cycles budgets have been significantly altered by human activities and there is a need for a better understanding of the chemical and biogeochemical processes occurring in coastal areas. In tropical and subtropical latitudes, continental shelf waters (Cai et al. 2003a; Ito et al. 2005; Zhai et al. 2005), mangroves surrounding waters (Borges et al. 2003), coral reefs (Gattuso et al. 1993; Frankignoulle et al. 1996a; Bates et al. 2001), estuaries (Sarma et al. 2001; Mukhopadhyay et al. 2002; Bouillon et al. 2003), and large rivers like the Amazon (Richey et al. 2002) are generally net sources of CO_2 to the atmosphere, as well as the majority of major rivers worldwide at any given latitude (Garrels and Mackenzie 1971; Frankignoulle et al. 1998; Cole and Caraco 2001; Abril and Borges 2004). These emissions of CO_2 to the atmosphere are not always related to highly polluted systems like the Scheldt estuary (Frankignoulle et al. 1996b, 1998) but are also typical of relatively pristine systems such as the Satilla River estuary (Cai and Wang 1998). It is noteworthy to mention that not all coastal waters and rivers are CO_2 sources, but may act as CO_2 sinks, as shown by Cai (2003) for the Mississippi River plume and by Ternon et al. (2000) for the Amazon plume. According to a tentative scaling based on published CO_2 field data, subtropical and tropical coastal ocean waters behave as sources of CO_2 to the atmosphere, as opposed to high and temperate latitude waters acting as sinks of atmospheric CO_2 (Borges 2005; Borges et al. 2005). Importantly, near-shore coastal ecosystems, and in particular, estuaries play a key role in determining whether the coastal ocean behaves as a source or a sink of CO_2 (Borges 2005; Borges et al. 2005). However, available data on the partial pressure of CO_2 (pCO_2) in coastal environments are scarce, and more are needed to assess quantitatively the role of the coastal ocean in the global carbon cycle.

The work discussed here represents a 6-month study of the dynamics of the dissolved inorganic carbon pool (DIC), the pCO_2 and the total alkalinity (TA) distribution in the land–sea margin and coastal areas of Hilo Bay and two river-estuary systems (Wailuku and Wailoa Rivers) on the Big Island of Hawaii, USA. A similar but longer-term research study was carried out, and is still under way biweekly, at Kaneohe Bay on the Island of Oahu, Hawaii (Fagan and Mackenzie 2006).

2 Study area

Hilo Bay area opens up to the North Pacific Ocean on its northeast margin. It is a crescent-shaped bay semi-closed by a 3-km break wall on its eastern margin (Fig. 1). Total surface area of Hilo Bay, including the area south of the break wall, is about 6.4 km^2. Current patterns vary greatly over time due to the break wall and significant

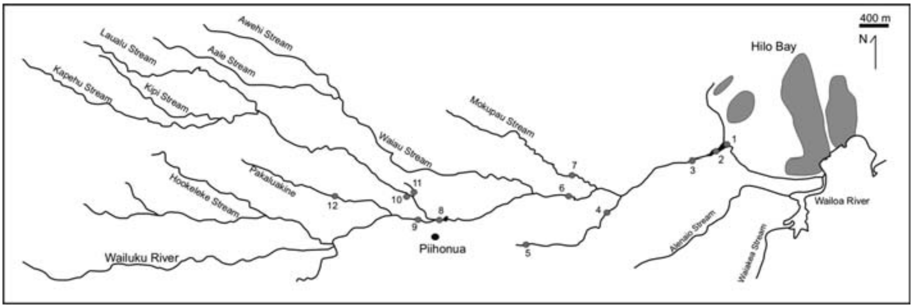


Fig. 1 Map with the locations of the sampling stations in the Wailuku River. The grey areas in Hilo Bay show the locations where freshwater springs emerge from the sea floor

meteorological variability, especially in the winter time. Overall, the bay is a positive estuary with variable salinity values (20–34) depending on the intensity of recent rainfall and freshwater discharge into the bay. Freshwater inputs are from two different sources: Wailuku and Wailoa Rivers, and from numerous basal springs, whose exact numbers and locations are not well known. Coral reefs are scarce in the bay except for a few patches over the ‘‘Blonde Reef’’ near the break wall. The poorly developed reefs are found in an area of high sediment discharge from the Wailuku River, which is the largest river in the State of Hawaii. Its headwater begins at an elevation of approximately 3600 m and its distal end forms a microtidal estuary in Hilo Bay. The Wailuku River drainage area is 590 km^2 and is covered by forest reserve (76%), pasture (20%) and a few urban areas downstream (4%) (Fig. 1). In the upper part of the watershed, the flow alternates from surface to groundwater due to a complex geology consisting of basaltic lava tubes and intrusive dikes. The river is characterized by a series of plunge pools at higher elevations and by numerous waterfalls below 700 m. North of the river and in the Wailuku area itself, the freshwater input to the bay is mainly from surface runoff as a relatively impermeable layer of Recent Pahala ash covers the area. Thirteen main tributaries enter the Wailuku River, mainly small streams 3–4 m wide that are less turbulent than the main river. Based on a 71-year record (1928-present, USGS, http://hi.water.usgs.gov/adrweb/swstations/16704000.html), the average fresh water discharge is 7.56 m^3 s^{-1} at the Piihonua station. However, this value may drop down to less than 0.4 m^3 s^{-1} during dry summers and attain 100–300 m^3 s^{-1} during heavy rains (e. g., on the 11th of August 1940, up to 2140 m^3 s^{-1} of discharge were recorded).

Geologically, the Wailuku River forms the approximate boundary between lava flows from two volcanoes: Mauna Kea to the north and Mauna Loa to the south. The stream channel is cut through lava from Mauna Loa that overlaps older lavas from Mauna Kea. These lava flows consist of tholeitic and alkali basalts. The river substrate is mainly composed of bedrock and large basalt boulders. Soils consist of andisols, which are formed on volcanic ash, and as a result they possess a high-water retention capacity and the ability to fix (and make unavailable for plants) large quantities of phosphorus. Earlier biological and chemical data attest to the Wailuku being a relatively pristine river (Yee et al. 1986).

The Wailoa River lies to the east of Hilo and is located in an area of by high urban density. Its drainage basin covers an area of 0.2 km^2 (Fig. 2). The river is mainly fed by numerous freshwater springs, because the watershed is underlain by highly

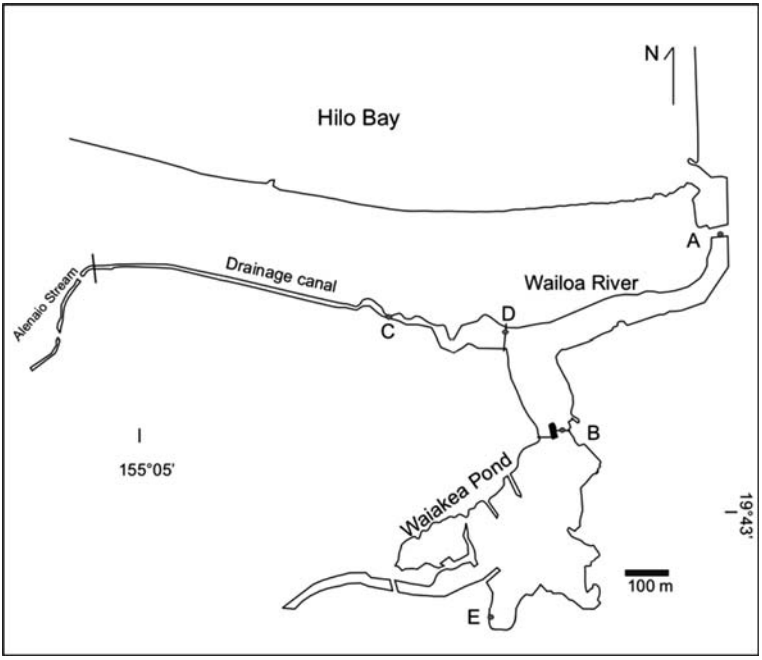


Fig. 2 Map with the locations of the sampling stations in Wailoa River

permeable basalts with little overlying ash. The Wailoa River-estuary system is influenced moderately by tidal mixing and is mainly an impounded brackish water system (salinities range between 0 and 10). The drainage basin area is 410 km^2 on the slopes of Mauna Loa. Several tributaries enter the pond: Waiakea-Kawili Stream, Alenaio Stream and Palai Creek. These tributaries cross wooded areas, sugar cane fields or farmlands. The flow from Palai Creek emerges from the subsurface as a spring in the lower part of the pond. These tributaries are channelized in the city, most of the time dry, poorly defined and flow mainly during major heavy rain events.

3 Materials and methods

Twelve stations were sampled on the Wailuku River and five on the Wailoa River (Figs. 1, 2). Surface water samples were collected where the water was most likely to be vertically well mixed. For some stations, the centers of the bridges satisfied these conditions, and were used as sampling sites because no direct access was available on the banks in the estuarine part of the systems. Additional water sampling was carried out during heavy rain events in order to study the effects of storms on the carbonic acid system and air–water CO_2 exchanges. Sampling took place during the Hawaiian winter, from November 2003 to May 2004, and included both dry and heavy rain conditions.

At every bridge sampling station, surface water was sampled using a 13 l plastic bucket lowered from the bridge into the surface upper 25 cm of the stream. pH was immediately measured to prevent alteration from CO_2 exchange with air, using a portable pH-meter (model Orion 266S). Calibration of the pH electrode was carried out before each survey with pH 4, 7 and 10 ORION buffer solutions with an accuracy of ±0.01 pH units. Temperature and salinity measurements were carried out using a YSI probe (model 85), with an accuracy of ±0.1°C and ±0.1, respectively. Conductivity was calibrated before each survey. TA samples were collected and stored in 250 ml plastic bottles after adding $HgCl_2$ until further analysis in the laboratory, usually within 48 h. Before analysis, water samples for the determination of TA were filtered through 0.7-μm Whatman GF/F filters, and 100 ml were analyzed with the Gran titration method (1952), using an Orion 950 FASTQC^{TM} titrator by addition of small increments of a 0.1 N HCl as titrant. On each sampling day, 2–4 replicates analyses were carried out for each sample, and precision ranged from ±1 to ±4 μmol kg^{-1}. Samples for $\delta^{13}C$ were collected in 50 ml glass bottles to which 100 μl of $HgCl_2$ were added, and the water samples were stored in a cooler with ice. The instrumentation used to measure $\delta^{13}C$ is a ThermoFinnigan Delta plusXP isotope ratio-monitoring mass spectrometer coupled to a ThermoFinnigan GasBenchII autosampler-assisted sample preparation and sample injection interface. The accuracy and precision for $\delta^{13}C$ is ±0.15 ‰. The pCO_2 and DIC values were computed from pH and TA measurements using the carbonic acid dissociation constants given by Mehrbrach et al. (1973) on the National Bureau of Standards scale and the CO_2 solubility coefficient of Weiss (1974). From the precision of the computed pCO_2 analytical technique used and the precision of the pH and TA measurements, the precision of the pCO_2 values was estimated to be about 10 ppm.

4 Results and discussion

4.1 Wailuku River: baseline conditions

During baseline conditions (March 13 and May 1, 2004), the Wailuku watershed waters (station 4 to 12) are characterized by similar TA values for the two dates and lower than those of estuarine waters (Fig. 3). On average for both surveys, freshwater stations show TA values ranging from 0.190 to 0.793 mmol kg^{-1} (mean of 0.362 and 0.390 mmol kg^{-1} for surveys on March 13 and May 1, respectively) and DIC values ranging from 0.206 to 0.837 mmol kg^{-1} (mean of 0.394 and 0.423 mmol kg^{-1} for surveys on March 13 and May 1, respectively). Station 7 (Mokupau Stream) shows during both surveys higher TA (0.792 mmol kg^{-1}) and DIC values (0.825 mmol kg^{-1}) than other freshwater stations. DIC values are higher for the tributaries at stations 4, 7 and 12. In the river and tributaries of the watershed, TA and DIC values are variable. However in the estuary, TA and DIC are conservative because of the very rapid mixing of freshwater and seawater as shown in Fig. 4 during baseline conditions. The freshwater station, Wailuku 3, shows scattered values ranging from 0.131 to 0.497 mmol kg^{-1}. The variations are probably related to changing weather conditions. Increased TA values appear to be related to the warmer periods of drought in the area that probably lead to enhanced chemical weathering rates and longer soil and ground water residence times, during which time TA, DIC and pCO_2 increase in concentration in the subsurface systems. On the other hand, runoff is important during cooler periods of heavy rains and subsurface

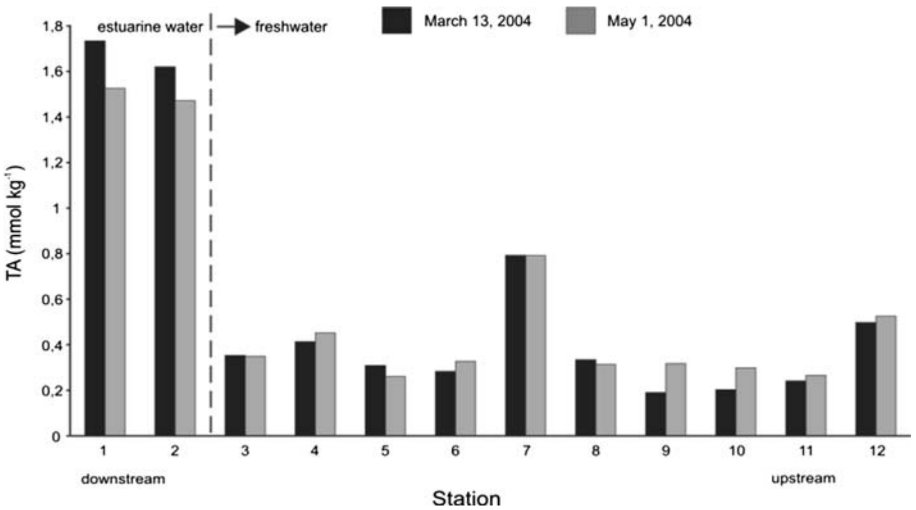


Fig. 3 Longitudinal variations of DIC (mmol kg^{-1}) on two surveys (March 13 and May 1, 2004) in the Wailuku River watershed during drought periods and between two heavy rains events

water residence times are relatively short so that chemical weathering rates may decrease slightly, and the alkalinity signal becomes diluted by the rapid water recharge. Results tend to show that TA values are lower when sampling was carried

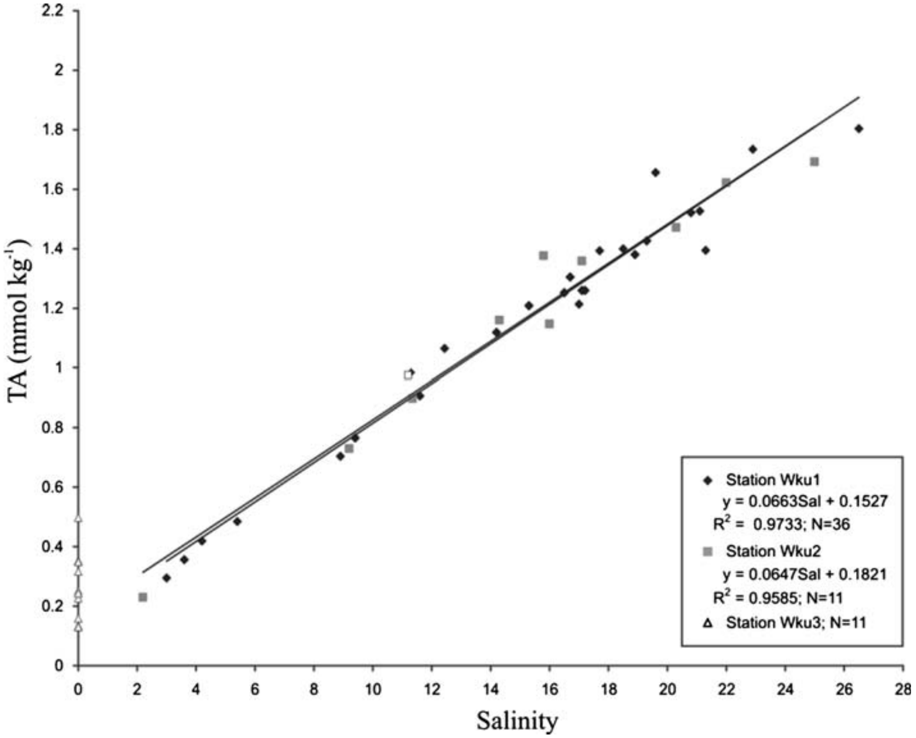


Fig. 4 TA (mmol kg^{-1}) versus salinity at stations Wailuku 1-2-3

out following a heavy rain event, as dilution occurs. Atekwana and Krishnamurthy (1998) reported a negative relationship between DIC and discharge of the Kalamazoo River (southwest Michigan), due to dilution during flood events. Cai (2003) reported a similar relationship for the Mississippi River. Temporal variations of DIC are probably very rapid in the Wailuku River where freshwater discharge can change quickly from one day to another depending on the rainfall.

In the Wailuku watershed, HCO_3^- represents 92% of the DIC, CO_2 about 8%, and CO_3^{2-} is negligible. The average DIC is 0.357 mmol kg^{-1} for a total of 40 samples collected in the Wailuku freshwater watershed. According to a data set from 250 pristine rivers in France (Meybeck and Helmer 1989), HCO_3^- concentration from a monolithologic basin draining volcanic rocks is 0.425 mmol kg^{-1}. Also, HCO_3^- concentrations for waters throughout the Hawaiian Islands compiled by Dessert et al. (2003) range from 0.057 to 1.024 mmol kg^{-1} (average 0.407 mmol kg^{-1}). The variations of HCO_3^- concentrations depend on chemical weathering intensity related to rainfall, rock age, topography, bedrock, soil thickness (Stewart et al. 2001), temperature (Dessert et al. 2003), and presence or absence of lichens (Brady et al. 1999). Lithological differences over a watershed will strongly influence the DIC (Hélie et al. 2002). DIC in rivers can drop to 0.045 mmol kg^{-1} in areas draining purely granitic basin, but reach values up to 3,000 mmol kg^{-1} in carbonate catchments (e.g. Ottawa River, Telmer and Veizer 1999). These latter values are characteristic for pristine to nearly-pristine streams but are higher in highly polluted rivers where twice the HCO_3^- theoretical value may be found as in the Scheldt (Abril et al. 2000). The highest concentration values found in the tributaries at station Wailuku 7 (Mokupau Stream), Wailuku 4 and 12 probably result from different local conditions, for example, more reactive rocks and soils, and are unlikely the result of anthropogenic inputs.

Baseline conditions show CO_2 oversaturation relative to atmospheric equilibrium (375 ppm value for the year 2003 measured at the nearby Mauna Loa Observatory) for the watershed stations (Fig. 5). Average pCO_2 from station Wailuku 3 to 12 was 884 ppm on March 13 and 940 ppm on May 1. These values are within the range typically encountered in rivers worldwide (Raymond et al. 1997; Telmer and Veizer 1999; Cole and Caraco 2001) but they also suggest the likely input of groundwater because of a low instream biotic metabolism (Yee et al. 1986; see also Kempe 1991; Cai et al. 2003b).

Estuarine waters of Wailuku River (station 1, 2 and 3) are close to or below atmospheric CO_2 equilibrium. Average pCO_2 for these stations is 328 ppm on March 13 and 329 ppm on May 1, 2004. Station 3 is undersaturated whereas the upstream station, Wailuku 6, is oversaturated with respect to CO_2 This is due to degassing of CO_2 at the Rainbow Waterfalls, located below station Wailuku 6 (10 m high), and at the 3 m high falls uptstream of station 3. The result of this degassing is that the river waters decrease in pCO_2 to near equilibrium with atmospheric CO_2, and the observed slight CO_2 undersaturation could be due to net autotrophy in the estuary driven by the short residence time of freshwater and absence of a maximum turbidity zone that would promote heterotrophy in long residence time, macrotidal estuaries (Wollast 1988; Herman and Heip 1999; Abril and Borges 2004). Even though the sampling did not cover the summer period, it is suggested that pCO_2 should not vary significantly because of the slight difference between winter and summer temperature at this latitude.

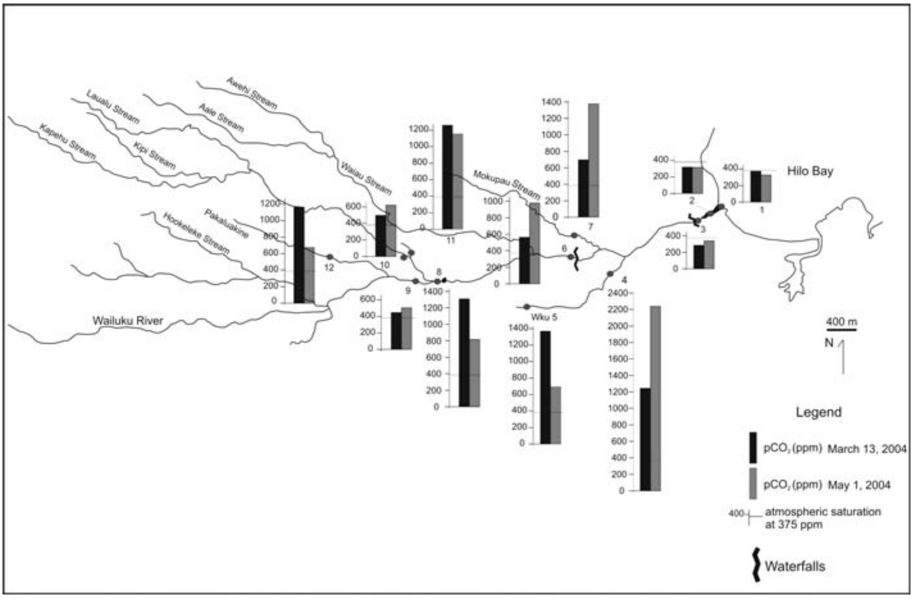


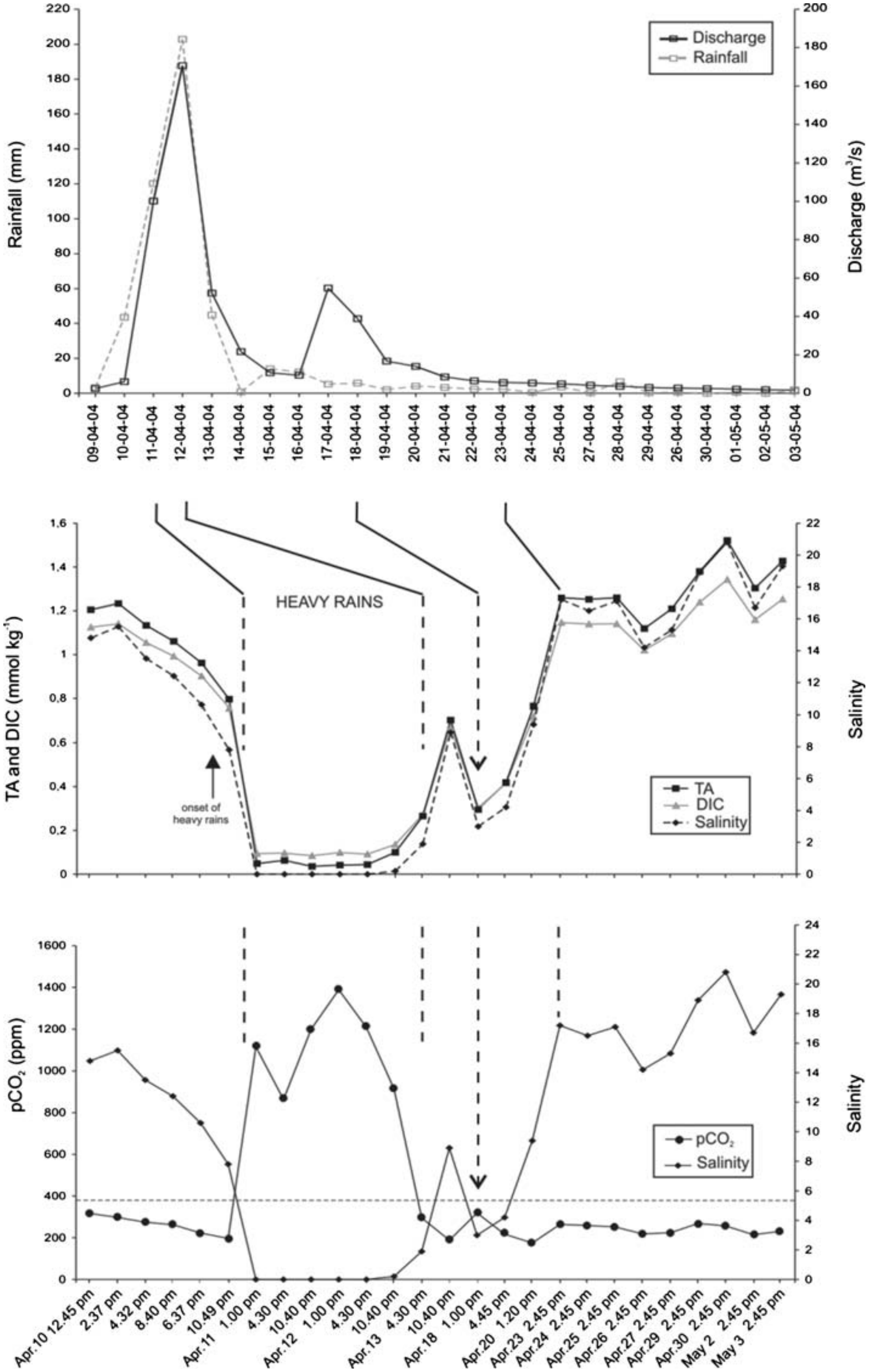
Fig. 5 pCO_2 (ppm) values in the Wailuku watershed on two dates (March 13 and May 1, 2004) corresponding to drought periods

4.2 Wailuku River: heavy rain conditions

The impact of heavy rains on the DIC pool was studied from April 10 to May 3, 2004 at the Wailuku River mouth (station Wailuku 1) considering that it is representative of the changing conditions. Evolution of salinity, TA and DIC show a significant decrease following the onset of heavy rains on the evening of April 10, 2004 (Fig. 6).

The Wailuku mouth is undersaturated with respect to CO_2 during baseline conditions (with a mean pCO_2 of 246 ppm), but at the time of the highest discharge, there is a sharp increase of pCO_2 with values up to 1500 ppm. Following this 48 h event, the Wailuku mouth returns to a state of CO_2 undersaturation from April 13 onwards. The degassing effect caused by the waterfalls is clearly inhibited during the heavy rains. The high pCO_2 values likely reflect inputs of groundwater CO_2 flushed out of the soils by heavy rains, and diverted to the flow of the Wailuku River. Groundwater and soil pCO_2 values are known to be high due to the production of CO_2 by microbial respiration of organic matter in these systems (Kling et al. 1991; Jones and Mulholland 1998; Cole and Caraco 2001; Jones et al. 2003). In Kaneohe Stream, Oahu, Hawaii (Fagan and Mackenzie 2006) have shown that when sampling was performed at appropriate times in stream waters following the peak of a storm event, pCO_2 values were of the same order of magnitude as in the Wailuku River with values up to 1880 ppm. However, in Kaneohe stream the transition from CO_2

Fig. 6 Rainfall (mm) (http://www.ncdc.noaa.gov) over the Hilo area, and influence of the heavy rains event on April 11–12, 2004 on discharge ($m^3 s^{-1}$) (data from the Piihonua station number 16704000, http://www.hi.water.usgs.gov), DIC (mmol kg^{-1}), TA (mmol kg^{-1}), salinity and pCO_2 (ppm) of the Wailuku River. Horizontal dotted line corresponds to the atmospheric CO_2 equilibrium ▶


Discharge
Rainfall
Rainfall (mm)
Discharge (m³/s)
0
20
40
60
80
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120
140
160
180
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11-04-04
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HEAVY RAINS
onset of heavy rains
TA and DIC (mmol kg⁻¹)
Salinity
TA
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Salinity
0
0,2
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0,6
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Salinity
0
200
400
600
800
1000
1200
1400
1600
Apr.10 12.45 pm
2.37 pm
4.32 pm
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6.37 pm
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Apr.11 1.00 pm
4.30 pm
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Apr.27 2.45 pm
Apr.29 2.45 pm
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May 2 2.45 pm
May 3 2.45 pm

oversaturation to undersaturation seems to extend for a larger period of time than in the Wailuku, since storm waters are retained for approximately 2 months in the Kaneohe Stream watershed, preventing waters from returning rapidly to baseline conditions. This significant difference between the Wailuku River and Kaneohe Stream watersheds might be in part a function of the slope of the watershed and the porosity and permeability of the underlying soils and bedrock. The high pCO_2 waters from soils and groundwater appear to be released in one major event in Wailuku whereas the water residence time is longer in Kaneohe watershed. Strong increases in river pCO_2 during strong rain-flood events have also been observed in the St. Lawrence River and estuary (Barth and Veizer 1999; Hélie et al. 2002), and the Garonne (Semhi 1996 in Abril et al. 2000). According to Abril et al. (2000) and their studies of the Scheldt estuary in Belgium and five of its tributaries, the relationships between the fresh water discharge and CO_2 oversaturation were different for each of the five tributaries of the Scheldt estuary. In the case of the Scheldt, the Dender and the Nete, flood events were associated with an increase in CO_2 concentrations. However in the highly polluted Zenne River draining the town of Brussels, a flood event led to a decrease of CO_2. Although relationships between pCO_2 and discharge are not always evident, it is likely that in general the increased pCO_2 at the time of the highest discharge is due to the flushing out of high pCO_2 soil and groundwater. Dynamics of CO_2 in the Wailuku River is not primarily controlled by seasonal variations in biological activity or temperature but more by the variations in rainfall and flushing of carbon and nutrients from soil and subsurface waters into rivers.

The flux of DIC discharged by the Wailuku River into Hilo Bay during baseline and heavy rain conditions was computed according to:

$$\text{Input flux (mmol/d}^{-1}\text{)} = QC_0 \tag{1}$$

where C_0 (mmol kg^{-1}) is the concentration of DIC at zero salinity, Q is the freshwater flow (m^3 d^{-1}) (discharge data collected by the Department of Water Resources of the USGS at the gauging station at Piihonua, West of Hilo, which is an underestimate of the value at the Piihonua station, because some tributaries downstream are not accounted for). The average DIC value for all the freshwater stations during baseline conditions is 0.357 mmol kg^{-1}. The average discharge of the Wailuku River is $6.51 \cdot 10^5$ m^3 d^{-1} according to the mean given by the Department of Water Resources of the USGS. The average flux of DIC to the bay is 19.35 g C d^{-1} to the bay. On the other hand, during heavy rains when freshwater discharge easily reaches values up to 150 m^3 s^{-1} but DIC decreases to 0.090 mmol kg^{-1}, the DIC flux is 7050 g C d^{-1} to the bay. Hence, the DIC export from an ordinary storm is of the same order of magnitude as the average annual export of DIC into the bay during baseline conditions.

4.3 Wailoa River

Figure 7 shows the variations of salinity, temperature, TA, DIC and pCO_2 on nine sampling days for the five stations of the Wailoa River estuary. DIC closely follows TA variations and is in excess of TA; this excess of DIC represents CO_2. The flood event on March 14, 2004 led to a clear decrease in all the parameters. At station Wailoa E, the parameters are affected by the flood event to a lesser extent because waters preferentially flow northward due to the position of the channelized streams.

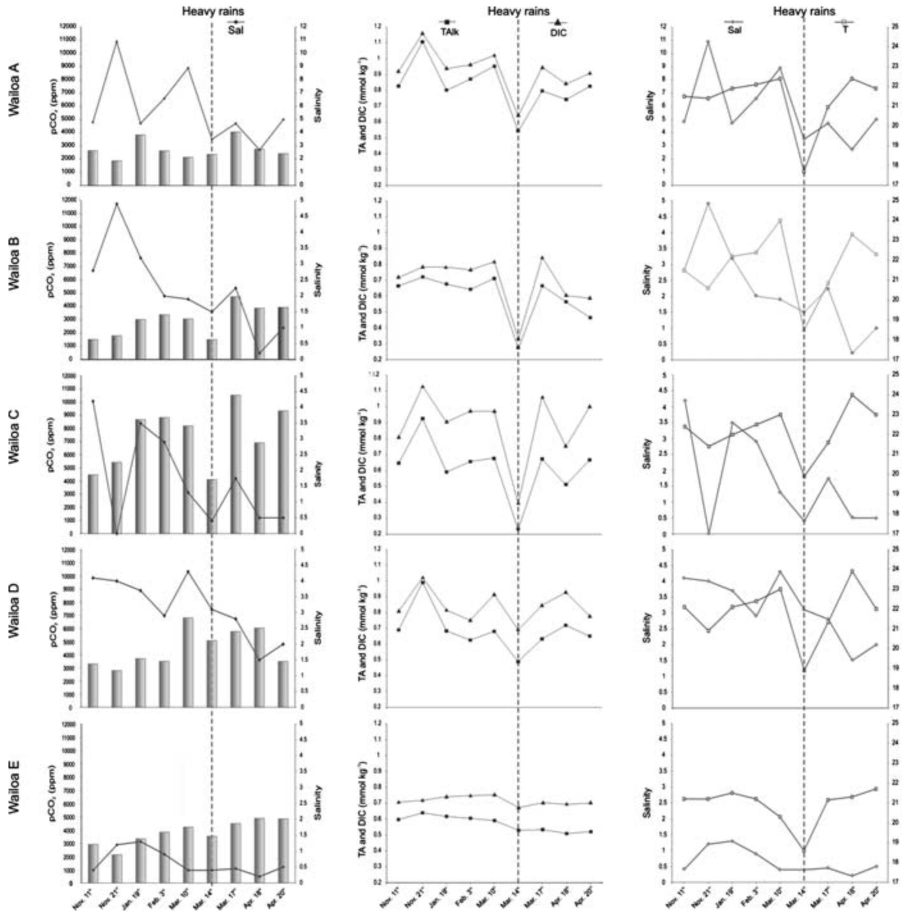


Fig. 7 pCO_2 (ppm), TA (mmol kg^{-1}), DIC (mmol kg^{-1}), temperature (°C) and salinity evolution at 5 stations in the Wailoa River on nine sampling dates. The scale of salinity at station Wailoa A is different from the other stations

Net CO_2 oversaturation with respect to the atmosphere is observed for all stations and for all sampling dates. The pCO_2 values range from a minimum of 1515 ppm at Wailoa B on March 14 during a flood event to a maximum of 10545 ppm at Wailoa C on March 17 following the flood. The mouth of the pond (Wailoa A) was characterized by the lowest pCO_2 values (mean of 2771 ppm) while the extreme west of the pond (Wailoa C) located near Alenaio Stream was characterized by the highest pCO_2 values (mean of 7392 ppm). Variations of salinity were unrelated to those of pCO_2.

The flood event significantly affected station Wailoa C with a pCO_2 decrease from 8206 ppm on March 10 to 4108 ppm on March 14. This contrasts with the Wailuku River where pCO_2 increased during flood events. The origin of this different behavior is unclear but it is most likely related to differences in soil texture and composition and a dilution effect that is stronger in the Wailoa River than in the Wailuku River. The drawdown of pCO_2 values during the March 14 flood event could be due to two different processes: a productivity bloom caused by nutrient loading during the storms or the input of lower TA freshwaters. The first process is unlikely given the stormy weather conditions, cloudiness and turbid waters. The effect of groundwater with high pCO_2's on the system is reduced when the flow of water with lower TA and pCO_2 is re-established. The computations of the pCO_2 at a constant temperature of 21°C (which is an average value for the Wailoa River), using the in-situ values of salinity, DIC, and TA, show no strong deviations from the in situ pCO_2 values. Three days after the storm, pCO_2 increases at all stations to a maximum of 10545 ppm at station Wailoa C. A phytoplankton bloom was not observed and this observation is likely due to the excessive remineralization and respiration of the suspended organic matter and the steep light extinction of the waters because of high turbidity. An additional process accounting for the increased CO_2 is the long residence time allowing CO_2 to build up due to microbial respiration. Cole et al. (1994) concluded that this same process accounts for the total oversaturation in CO_2 found in 1835 lakes at boreal, temperate and tropical latitudes. A cruise carried out on January 29, 2005 showed that Wailoa River waters had negative δ^{13}C DIC values ranging from –11.76 (at station Wailoa A) to –14.88 ‰ (at station Wailoa E). This confirms the intense remineralization of terrestrial organic matter that occurs in soils and in groundwater and possibly in stream waters. The dissolved oxygen data that we were able to collect and analyzed have shown undersaturated values and no relationships between the PO_2 and the pCO_2. We believe that there are complex biogeochemical and physical processes occurring in the Wailoa River that require further data and investigation.

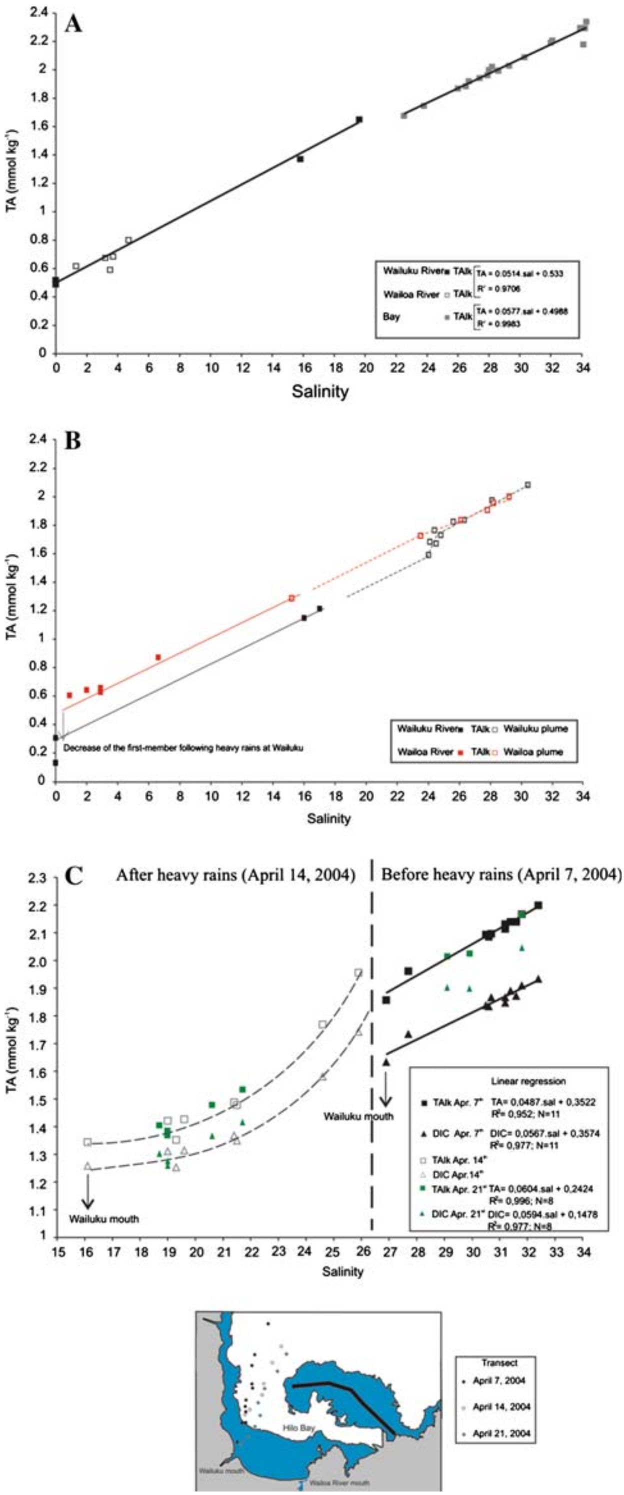
Total respiration probably exceeds gross primary production in the Wailoa River estuarine system, thus we suggest that the system is net heterotrophic, although this conclusion must be considered tentative. Ancillary data are needed to know with certainty which part of the groundwaters of the Wailoa pond account for the high pCO_2. Li (1988) showed that Hawaiian groundwaters are extremely high in pCO_2 (3000 ppm) and have pH values of about 6. Studies of groundwater aquifers in South Carolina (Cai et al. 2003b) and in the Amazon River basin (Richey et al. 2002) have shown that pCO_2 values in groundwaters may vary from 100 up to 300 times greater than the atmospheric concentration. Wailoa waters are thus a mix of groundwater with low pH and high pCO_2 and seawater entering into the pond with higher pH and lower pCO_2.

The high pCO_2 values observed in the oligohaline (stations C, E) and mesohaline (stations B, D, A) regions of Wailoa River estuary are consistent with those reported in temperate (Frankignoulle et al. 1996b, 1998; Raymond et al. 2000; Abril and Borges 2004) and subtropical and tropical estuaries (Cai and Wang 1998; Sarma et al. 2001; Mukhopadhyay et al. 2002; Bouillon et al. 2003).

4.4 Hilo Bay

Figure 8A shows baseline conditions for TA in Hilo Bay (January 21, 2004) combined with data from both the Wailuku and Wailoa River plumes (January 19, 2004).

Fig. 8 **A**: TA (mmol kg^{-1}) versus salinity in Hilo Bay on January 21 including data from Wailuku and Wailoa River from January 19, 2004; **B**: TA (mmol kg^{-1}) versus salinity in the Bay on February 5, 2004 including data from Wailuku and Wailoa River from February 3, 2004; **C**: Changes of parameters TA and DIC (mmol kg^{-1}) variations in Hilo bay along a transect from the Wailuku mouth to the break wall in the bay following heavy rains event on April 11–12, 2004 including a map of the three cruises (April 7–14–21, 2004) ▶


A
TA (mmol kg^{-1})
Salinity
Wailuku River ■ TAlk
Wailoa River □ TAlk
TA = 0.0514.sal + 0.533
R² = 0.9706
Bay ■ TAlk
TA = 0.0577.sal + 0.4988
R² = 0.9983
B
TA (mmol kg^{-1})
Salinity
Decrease of the first-member following heavy rains at Wailuku
Wailuku River ■ TAlk □ Wailuku plume
Wailoa River ■ TAlk □ Wailoa plume
C
After heavy rains (April 14, 2004)
Before heavy rains (April 7, 2004)
TA (mmol kg^{-1})
Salinity
Wailuku mouth
Wailuku mouth
Linear regression
■ TAlk Apr. 7th TA= 0,0487.sal + 0,3522 R²= 0,952; N=11
▲ DIC Apr. 7th DIC= 0,0567.sal + 0,3574 R²= 0,977; N=11
□ TAlk Apr. 14th
△ DIC Apr.14th
■ TAlk Apr. 21st TA= 0,0604.sal + 0,2424 R²= 0,996; N=8
▲ DIC Apr. 21st DIC= 0,0594.sal + 0,1478 R²= 0,977; N=8
Hilo Bay
Wailuku mouth
Wailoa River mouth
Transect
• April 7, 2004
• April 14, 2004
• April 21, 2004

TA behaves conservatively along the salinity range as for other cruises on December 14, January 28, March 4 and April 28, 2004 (not shown). Using a combination of data from both rivers for February 3 and data from the bay on February 5, 2004 (Fig. 8B), significant shifts of different direction in TA and DIC are observed in the two river plumes: the Wailoa River plume shows an increase of TA and DIC at zero salinity, while a decrease of TA and DIC is observed in the Wailuku River plume.

Figure 9 shows the pCO_2 distribution in Hilo Bay, 4 days before and 12 days after the heavy rains on January 25, 2004. pCO_2 values ranged from 300 to 454 ppm on January 21 and from 306 to 1002 ppm on February 5, with this latter representative of the Wailoa plume. The Wailuku plume is characterized by pCO_2 values lower than the rest of the bay, while the Wailoa plume is characterized by pCO_2 values higher than the rest of the bay (Figs. 9, 10). Both plumes have a limited spatial distribution in the bay. North of Hilo Bay, the pCO_2 distribution also suggests the impact from the turbulent Honolii River. The pCO_2 spatial distribution shows that generally the bay is a source of CO_2 to the atmosphere. Changes in parameters following heavy rains are best illustrated along a transect from the Wailuku mouth towards the break water (Fig. 8C). TA and DIC show conservative behavior on April 7, which switches to a curvilinear trend downward after the flood event of April 11–12, 2004. pCO_2 values do not decrease significantly, with an average of 411 ppm on April 7 and 379 ppm on April 14 (not shown). The TA and DIC change to non-linear distribution on April 14 could be a transient phenomenon due to the time lag for the sudden decrease of DIC and TA at zero salinity to propagate along the salinity gradient (e.g. Regnier and Steefel 1999). Indeed, TA and DIC showed a conservative behavior one week later, on April 21. The spatial distribution of pCO_2 in Hilo bay is mainly controlled by the Wailuku inputs. The conservative behavior of TA shows that calcification in the bay is not an important process affecting water column pCO_2 due to the virtual absence of coral reefs, except for small patch reefs along the break wall.

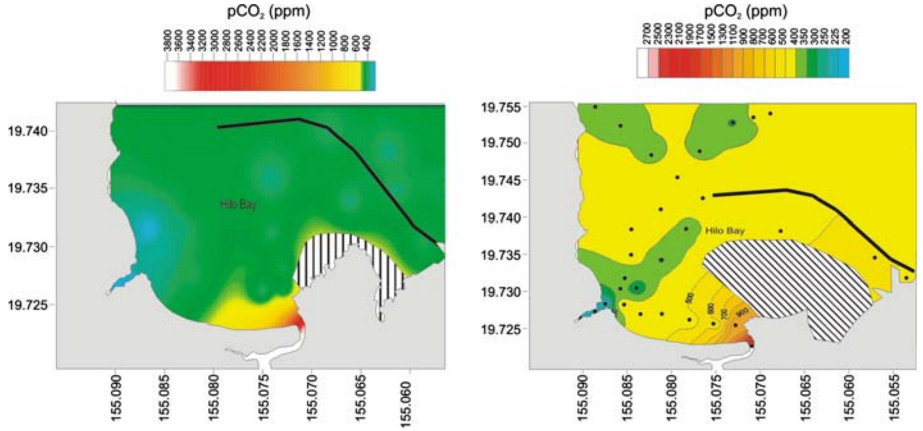


Fig. 9 pCO_2 (ppm) in Hilo Bay on two dates (January 21 and February 5, 2004)

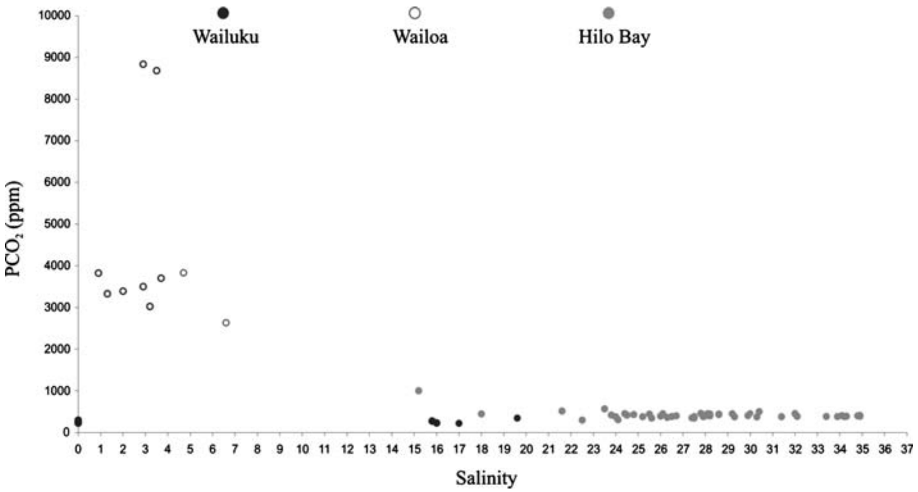


Fig. 10 pCO_2 versus salinity based on the combination of data from the Wailuku, Wailoa Rivers and Hilo Bay on January 21 and February 5, 2004

5 Conclusions

The present study is one of the first concerned with the CO_2-carbonic acid system and the direction, but not the magnitude of flux, of air–sea CO_2 exchange in coastal environments of the Hawaiian Islands. The Wailuku River surface waters with a drainage basin dominated by tropical forests, barren lava rocks, and impermeable ash are oversaturated in CO_2 and pCO_2 values are within the range of values previously reported for other temperate and tropical river systems (Cole and Caraco 2001; Abril and Borges 2004). The Wailuku River estuary with a short water residence time is undersaturated in CO_2 in contrast to CO_2 oversaturation as observed in other tidal estuaries (Cai and Wang 1998; Frankignoulle et al. 1998; Sarma et al. 2001; Mukhopadhyay et al. 2002; Bouillon et al. 2003; Abril and Borges 2004). Waterfalls located on the Wailuku River allow the ventilation of river CO_2 and the freshwater than mixes with seawater in the estuary at near equilibrium with the atmosphere.

The smaller Wailoa River, located in a populated area and one of limited fresh water discharge, exhibits variable CO_2 oversaturation. The difference between the two river-estuarine systems is likely due to their differences in physical characteristics; the Wailuku River is very turbulent, has a short residence time and drains a relatively unpopulated region while the Wailoa River receives freshwater inputs from surface sources sporadically and is relatively calm, has a longer residence and drains mainly a populated area.

In Hilo Bay, the dynamics of DIC, TA and pCO_2 are largely dominated by the carbon inputs from the Wailuku River. The concentrations of DIC and TA in the bay generally follow a conservative mixing line when plotted against salinity, except during transient events following heavy rains, indicating that carbonate mineral formation through the process of calcification is not overly important in bay waters. The Wailuku River plume has higher pCO_2 values than in the rest of the bay and in the less extensive Wailoa River plume. The bay as a whole is slightly oversaturated in CO_2, venting CO_2

to the atmosphere. In the absence of significant calcification, the biogeochemical process maintaining pCO_2 values above atmospheric equilibrium is the imbalance between production and respiration of organic matter, in which the respiration of river-derived total organic carbon and that produced in situ exceeds gross primary production. This conclusion is supported by the dissolved oxygen data obtained from 21 bay-wide cruises from 2001–2005 by the Marine Science Department of the University of Hawaii at Hilo (http://www.kmec.uhh.hawaii.edu). These data show that surface and subsurface waters of the bay and slightly outside the bay are undersaturated with respect to oxygen. Therefore, we suggest that Hilo Bay is likely a net heterotrophic system, recognizing the fact that more CO_2 and O_2 data and calculations of these gas fluxes are needed to substantiate this tentative conclusion.

The widespread groundwater springs in the bay (Fig. 1), whose waters could contain relatively high dissolved CO_2, did not give rise to any observations of anomalously high pCO_2 values for bay surface waters during any of the cruises. The reasons could reside in the strong stratification of the water column due to the freshwater inputs from the Wailuku River and intrusion of open ocean waters on the bottom, combined with the short water residence time of the bay waters (of the order of a few days). This research confirms previous studies that subtropical and tropical continental shelves behave as sources of CO_2 to the atmosphere (Cai et al. 2003a; Ito et al. 2005; Zhai et al. 2005) but also that groundwater can significantly affect the CO_2-carbonic acid system in at least proximal coastal waters. These results should be taken into account in any further studies of the CO_2-carbonic acid system of the numerous high islands of the Pacific that are very important in material fluxes to the ocean.

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