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Bioavailability and export of dissolved organic matter from a tropical river during base- and stormflow conditions

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Abstract

Concentrations, bioavailability, and export of dissolved organic matter (DOM), particulate organic matter (POM), and nutrients from the Wailuku River, Hawai'i, U.S.A., were examined under base- and stormflow conditions. During storms, DOM and POM concentrations increased approximately by factors of 2 and 11, respectively, whereas NO_3^- concentrations decreased by a third. The organic carbon (OC) pool was dominated by dissolved OC (DOC) during baseflow conditions, whereas DOC and particulate OC contributed equally during storms. The nitrogen (N) pool was dominated by NO_3^- during baseflow conditions and by particulate organic N (PON) during storms. Dissolved organic N (DON) comprised a similar percentage of the N pool under base- and stormflow conditions. DOC and DON bioavailability both decreased by half during storms in the Wailuku River. Differences in DOM concentrations and bioavailability between base- and stormflow conditions suggest that DOM flowpaths to the river changed from deep to shallow, and that DOM sources switched from autochthonous to allochthonous. Although DOM bioavailability decreased during storms, calculations suggest that storms contributed >90% to the annual OC and N yields and >80% to the bioavailable DOM yield from the Wailuku River to coastal waters. Overall, our results suggest that storms are important for delivering bioavailable DOM to coastal waters, where they may stimulate primary and secondary production.

Carbon (C) and nitrogen (N) are important elemental components of the dissolved organic matter (DOM) pool in rivers. Dissolved organic C (DOC) and N (DON) are often the dominant forms of organic C and dissolved N in rivers (Meybeck 1982; Seitzinger and Sanders 1997). Historically, riverine DOM was considered refractory because of its conservative mixing in some estuaries, high C : N ratio, and predominance of humic substances that were previously considered biologically unavailable (Thurman 1985). However, recent studies have shown that riverine DOM is metabolically important. It provides energy (C) and nutrients (i.e., N) to heterotrophic bacteria and some algae (Glibert et al. 2001; Wiegner and Seitzinger 2001), possibly contributing to coastal hypoxia and eutrophication (Seitzinger and Sanders 1997; Paerl et al. 1998).

Sources of organic matter in rivers are an important factor affecting how metabolically reactive, or bioavailable, riverine DOM is to microbes (Wiegner and Seitzinger 2001; Seitzinger et al. 2002). DOM in rivers originates from numerous natural (forests, wetlands) and anthropogenic watershed sources (i.e., runoff from agricultural and urban areas), atmospheric deposition, and autochthonous production, each with varying degrees of bioavailability (Seitzinger and Sanders 1999; Seitzinger et al. 2002; Bertilsson and Jones 2003). Thus, the relative contribution of DOM from these different sources is one factor, in addition to microbial and photochemical transformations, that determines the bioavailability of DOM within rivers.

The hydrologic flowpaths by which DOM is delivered to rivers affect riverine DOM concentrations and chemical characteristics (Frank et al. 2000), of which the latter factor greatly affects its bioavailability. The path by which water and DOM are delivered to rivers changes between base- and stormflow conditions. During baseflow conditions, hydrologic flowpaths are predominantly through lower, mineral-dominated soil horizons, whereas during storms, they are through litter and upper soil horizons (Hornberger et al. 1994; Frank et al. 2000). The consequences of this change in hydrologic flowpaths between base- and stormflow conditions on riverine DOM bioavailability are not well known, and the effect is variable among the systems examined to date (Leff and Meyer 1991; Volk et al. 1997; Buffam et al. 2001). With some regions of the globe becoming drier and others wetter with global climate change, the relative importance of shallow- and deep-water pathways for delivering DOM to rivers must be changing, and the resulting effect on the amount and quality of DOM exported from rivers is presently unknown.

Global models predict that rivers in the humid tropics deliver the greatest amount of DOM to the global ocean, with Oceania having the highest DOM export rate per area (Harrison et al. 2005). However, little is known about DOM dynamics in streams and rivers in Oceania (Resh and deSzalay 1995). In the humid tropics, organic matter sources and hydrologic flowpaths are of particular importance to DOM dynamics. First, high population growth rates and increased development in this region are leading to rapid conversion of forests to agricultural lands and urban areas (Coughanowr 1998), which may be changing the sources of DOM to the rivers, as well as the amount

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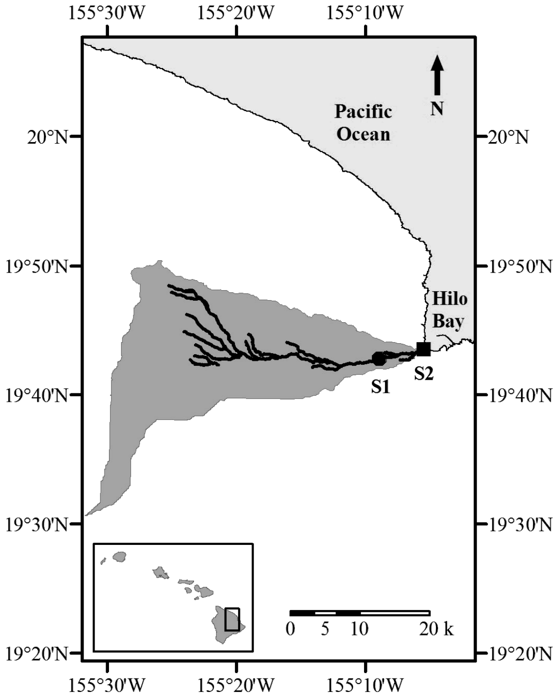

Fig. 1. Map of sites (Site 1 = S1; Site 2 = S2) along the Wailuku River, Hawai'i Island, Hawai'i. Watershed area for the Wailuku River is delineated in gray.

and quality of DOM entering them. Second, water runoff is high in this region and is thought to be the primary factor driving global riverine DOM export (Harrison et al. 2005).

DOM bioavailability in rivers has been extensively examined, with a majority of the studies focusing on DOC, and more recently on DON (Wiegner et al. 2006). Most of these studies have been conducted in temperate systems during baseflow conditions, and only a few studies have examined DOM bioavailability during storms, with DOC as the primary focus. The following study simultaneously compared DOC and DON concentrations, bioavailabilities, and yields, as well as those for particulate organic matter (POM) and nutrients from a river on the Island of Hawai'i during baseflow and storm conditions over 2 yr.

Methods

Site description—The Wailuku River is located on Hawai'i Island and drains both the tallest and the most massive mountains in the world, Mauna Kea and Mauna Loa, respectively. The Wailuku River is the second longest perennial river in the state of Hawai'i and the largest source of surface water to Hilo Bay. For this project, two sites along the Wailuku River were selected to examine spatial variability (Fig. 1). The first site (Site 1, S1) was located 352 m above sea level (asl) at the lower edge of a predominantly native forest comprised of *Acacia koa*, *Metrosideros polymorpha*, *Cheirodendron trigynum*, and *Cibotium glaucum* (Table 1). The second site (Site 2, S2) was located at 55 m elevation asl within the city of Hilo, and the land draining to this site is predominantly forest, with the riparian zone dominated by introduced and invasive trees (*Falcataria moluccana*, *Psidium cattleianum*, *Psidium guajava*, *Syzygium jambos*, and *Mangifera indica*) (Table 1).

Table 1. Characteristics of the two sites along the Wailuku River, Hawai'i Island, Hawai'i. MAP and MAT stand for mean annual precipitation and temperature, respectively. Percentage of land cover in different categories is provided in parentheses.

Attribute	Site 1	Site 2
Latitude	19°42.809′N	19°43.245′N
Longitude	155°08.930′W	155°06.116′W
USGS station	16704000	16713000
Elevation (m)*	352	55
Drainage area (km^2)†	598	659
MAP (mm)‡	5517	3281
MAT (°C)‡	21.7	22.8
Population (individuals)†	240	8916
Forest area (km^2)†	284.85 (48)	329.58 (50)
Grassland area (km^2)†	122.22 (20)	135.92 (21)
Wetland area (km^2)†	0.00 (0)	0.16 (0.02)
Agricultural area (km^2)†	0.03 (0.004)	1.45 (0.22)
Urban area (km^2)†	0.08 (0.01)	1.11 (0.17)
Barren area (km^2)†	190.54 (32)	190.54 (29)

* Elevation measured from a Garmin eTrex Vista GPS.
† Attributes for Wailuku River are taken from J. Michaud unpubl. and from the Hawai'i Department of Health unpubl.
‡ MAT taken from the Western Regional Climate Center website (http://www.wrcc.dri.edu/cgi-bin/clilcd.pl?pi21504).

Water collection—Water was collected from the two sites along the Wailuku River during base- and stormflow conditions from February 2005 to December 2006 (Table 2). Baseflow samples were collected using an acid-cleaned and precombusted (500°C for 6 h) depth-integrated sampler (Rickly Hydrology), transferred into acid-cleaned polypropylene containers, and stored on ice during transport to the laboratory. Stormflow samples were collected using automated storm samplers (model 6712, Isco) programmed to sample when the river's stage height rose by 1 m at United States Geological Survey (USGS) Sta. 16704000, which was located ~50 m upstream from the storm sampler at S1. The trigger height was based on the mode storm stage height from historical USGS records for this station. The trigger height for the storm sampler at S2 was determined by relating stage height data derived from pressure transducers installed on the storm samplers at both sites. Water samples were collected hourly into acid-cleaned 1-liter polypropylene bottles at the two sites while storm conditions were maintained. Storm samples were retrieved within 21 h (range = 3–21 h; average = 13.2 h) following the initiation of sampling and stored on ice during transport to the laboratory. Specific conductivity (model 85, YSI) and pH (model 266 S, Orion) were measured on every sample collected during baseflow and storms, and subsamples were taken from every bottle collected during storms for DOM, POM, and nutrient (NH_4^+, NO_3^- + NO_2^-, and PO_4^{3-}) analyses following the methods described below.

Table 2. Precipitation and discharge measured at the upper site (S1) on the Wailuku River, Hawai'i Island, Hawai'i, during base- and stormflow conditions during 2005–2006. Data for the lower site (S2) are not shown because there is no gauge or weather station at this site. Precipitation amounts for baseflow conditions are the summed total for 5 d prior to sampling. Precipitation amounts for storms are the summed total for the number of rain days prior to collection. Discharge for baseflow is the measured discharge at the time of collection. Discharge for storms is the average (±SE) measured discharge over the period that the storm samplers collected water.

Flow type	Date collected	Rain days prior to storm collection	Precipitation (mm)*	Discharge (L s^{-1})†
Base	15 Feb 2005	—	33.3	747
Base	19 Jul 2005	—	10.9	2939
Base	14 Nov 2005	—	28.7	3803
Base	11 Sep 2006	—	23.4	1419
Base	13 Nov 2006	—	17.5	837
Storm	23 Jun 2005	2	100.1	16,599±1423
Storm	01 Oct 2005	5	116.8	58,092±8548
Storm	21 Jan 2006	5	113.3	69,318±1839
Storm	03 Dec 2006	2	90.2	9798‡

* Precipitation data are from the Pi'ihonua rain gauge (PIIH1) on the island of Hawai'i maintained by the NOAA National Weather Service. Data were obtained from http://www.prh.noaa.gov/hnl/pages/hydrology.php.

† Discharge data are from the Pi'ihonua gauge (USGS Sta. 16704000) on the island of Hawai'i maintained by the USGS. Data were obtained from http://waterdata.usgs.gov/hi/nwis/dv/?referred_module=sw.

‡ Discharge for 03 Dec 2006 is reported as the daily average for 02 Dec 2006 (day of storm) because the storm samplers failed to trigger on this storm. Discharge at the time of collection on 03 Dec 2006, which was during the receding hydrograph, was 2809 L s^{-1}.

Experimental design—DOM bioavailability was determined through nine bioassay experiments carried out in the dark (five baseflow and four stormflow). For each experiment, river water was collected from both sites (*see* above) and a known volume of water was sequentially filtered through 160-μm mesh and precombusted, preweighed GF/F (Whatman) filters to remove particulates, but to leave behind some bacteria to serve as an inoculum for the DOM bioavailability experiments (Kaplan et al. 2006). The GF/F filters were then dried to a constant mass (70°C), reweighed for total suspended solids (TSS), and subsequently analyzed for particulate organic C (POC) and N (PN) on a CHN analyzer (Costech Analytical Technologies; PN is referred to as particulate organic N [PON] from here on). For the storm experiments, the 10 most turbid bottles from the storm sampler were combined for a composite sample that was filtered as described above. Four precombusted 1-liter Erlenmeyer flasks with 600 mL of the filtrate from each site were covered with aluminum foil to ensure dark conditions and prevent atmospheric contamination, placed on a shaker table (3 rotations min^{-1}), and incubated for 4 d at close to in situ temperatures (20–26°C) (Wiegner and Seitzinger 2001). This length of time was chosen because bacterial growth peaks after a period of 3 d and then decreases (Leff and Meyer 1991). Daily measurements of DOM and nutrient concentrations were taken by removing aliquots of water from each flask, filtering the water through precombusted GF/F filters, and immediately freezing the samples until analysis. Chemical analyses were performed within 2 weeks of collection. DOC and DON bioavailability were determined through the maximum measured decreases in DOC and DON concentrations, respectively, over the course of the experiment, and are expressed as percentages (maximum measured decrease in DOC or DON concentration divided by their initial concentrations) (Wiegner et al. 2006).

Analytical measurements—DOC was measured by high-temperature combustion (Shimadzu TOC-V, TNM-1; detection limit [d.l.] 10 μmol L^{-1}). Concentrations of NH_4^+ (USGS method I-2525-89; d.l. 1 μmol L^{-1}), NO_3^- + NO_2^- (USEPA method 353.2; referred to from here on as NO_3^-; d.l. 0.1 μmol L^{-1}), and PO_4^{3-} (USEPA method 365.1; d.l. 0.1 μmol L^{-1}) were measured on a Technicon Autoanalyzer II. Total dissolved N (TDN) was analyzed by high-temperature combustion, followed by chemiluminescent detection of nitric oxide (Shimadzu TOC-V, TNM-1; d.l. 1 μmol L^{-1}). DON was determined from the difference between TDN and dissolved inorganic N (DIN = NH_4^+ + NO_3^- + NO_2^-).

Yield calculations—Annual yields of DOM, POM, and nutrients from the Wailuku River for 2005 and 2006 were calculated by summing the product of concentration and daily average unit-area discharge from S1 (USGS Sta. 16704000). Concentrations used in yield calculations were derived from regressions of concentrations measured across the hydrographs against the instantaneous discharges at the time of sample collection. A total of 48 observations over 2 yr during both base- and stormflow conditions were used for these calculations, including data not presented in this paper (T. Wiegner unpubl.). Annual yields were not calculated for S2 because there is no continuous discharge record for this location.

Statistical analyses—Differences in (1) concentrations for DOM, POM, and nutrients, (2) C and N pools' composition, and (3) DOM bioavailability were examined by two-way analysis of variance (ANOVA) with site (S1 vs. S2) and river flow condition (base- vs. stormflow) as factors. Data that did not satisfy normality and equal variance requirements for ANOVA were transformed (log, arcsin, rank) prior to analyses. Mann–Whitney *U*-tests were performed on data that did not meet the requirements

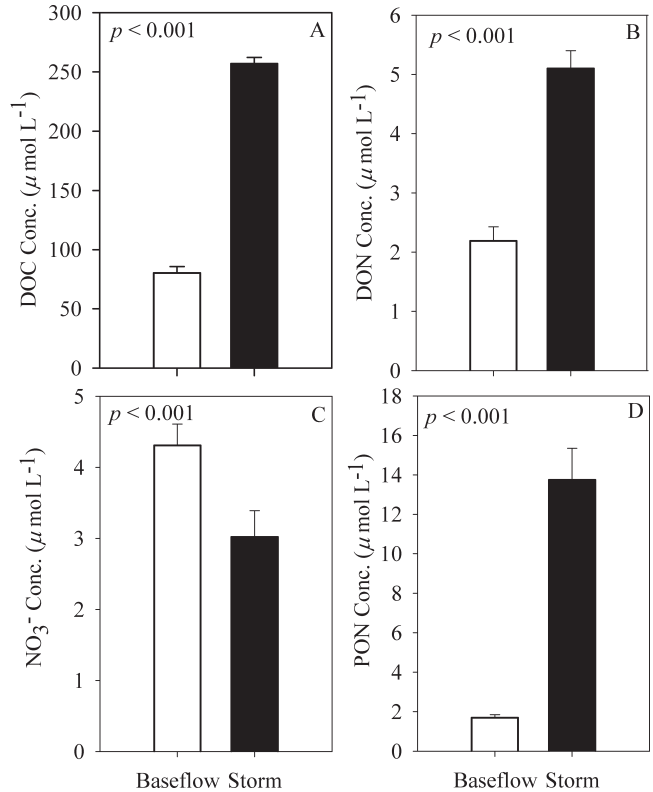

Fig. 2. Average (±SE) concentrations of (A) DOC, (B) DON, (C) NO_3^-, and (D) PON in the Wailuku River, Hawai'i Island, Hawai'i, during base- and stormflow conditions. Data from the two sites were combined because there were no significant differences in concentrations between sites. *p* values indicate results from two-way ANOVAs and Mann–Whitney *U*-tests for flow conditions.

for parametric analyses following transformations. Predictive relationships between DOM, POM, and nutrient concentrations and river discharge were examined using linear regressions. The association between DOC and DON concentrations was examined using a correlation. All statistics were run using Systat 11.

Results

DOC, DON, POC, PON, and NO_3^- concentrations were similar between the two sites ($p \geq 0.110$) and therefore site data were combined in figures and tables (Fig. 2; Table 3). Ammonium and PO_4^{3-} concentrations were generally low or below detection limits at both sites. In contrast, concentrations for DOC, DON, POC, PON, and NO_3^- significantly differed between base- and stormflow conditions ($p < 0.001$). DOC and DON concentrations tripled and doubled, respectively, from base- to stormflow conditions (Fig. 2; Table 3). POC and PON concentrations increased by factors of 13 and 9, respectively, from base- to stormflow conditions ($p < 0.001$; Fig. 2; Table 3). In contrast to these patterns for organic matter, NO_3^- concentrations decreased by a third, and there was a significant interaction term between site and flow condition ($p = 0.032$), where NO_3^- concentrations remained fairly

Table 3. Average (±SE) values for physiochemical parameters and concentrations of dissolved and particulate organic matter, nutrients, and total suspended solids (TSS) in the Wailuku River, Hawai'i Island, Hawai'i, during base- and stormflow conditions. Data from the two sites along the Wailuku River were combined in this table because these measured values were not significantly different between sites ($p \geq 0.110$). PO_4^{3-} concentrations are not reported here, as all measurements were below detection limits.*

Flow type	Date collected	pH	Cond (μS cm^{-1})	DOC (μmol C L^{-1})	POC (μmol C L^{-1})	TDN (μmol N L^{-1})	DON (μmol N L^{-1})	$NO_3^- + NO_2^-$ (μmol N L^{-1})	NH_4^+ (μmol N L^{-1})	PON (μmol N L^{-1})	TSS (mg L^{-1})
Base	15 Feb 2005	7.66±0.12	51.80±4.22	76.80±1.43	23.38±3.15	6.99±0.53	3.16±0.30	3.83±0.30	0.00±0.00	1.80±0.28	1.48±0.41
	19 Jul 2005	7.69±0.41	37.33±0.87	96.21±2.99	15.80±2.51	7.28±0.15	3.68±0.34	3.26±0.27	0.34±0.04	1.44±0.23	0.93±0.23
	14 Nov 2005	7.07±0.01	37.83±2.62	71.17±3.72	14.42±1.23	5.51±0.24	1.80±0.27	3.72±0.11	0.00±0.00	1.35±0.08	0.81±0.18
	11 Sep 2006	7.07±0.17	42.40±2.95	128.30±6.71	14.52±4.97	7.66±0.50	2.57±0.44	4.53±0.17	0.56±0.12	1.94±0.59	1.29±0.40
	13 Nov 2006	7.76±0.08	68.58±7.91	28.82±4.84	16.78±1.58	2.62±0.38	0.00±0.00	6.23±1.23	0.01±0.00	1.88±0.30	0.68±0.20
	Average	7.47±0.26	47.59±2.86	80.26±5.53	17.12±1.47	6.01±0.34	2.19±0.24	4.31±0.30	0.18±0.04	1.70±0.15	1.01±0.14
Storm	23 Jun 2005	6.37±0.02	20.05±0.29	256.45±3.57	85.33±5.93	7.15±0.15	5.62±0.14	1.54±0.04	0.00±0.00	6.37±0.04	2.41±0.19
	01 Oct 2005	NA	NA	277.60±6.78	1135.71±75.62	6.98±0.36	3.73±0.20	1.47±0.02	1.78±0.24	22.30±0.95	17.40±1.10
	21 Jan 2006	6.67±0.04	20.00±2.24	218.51±2.30	167.69±46.97	10.68±0.23	6.80±0.63	2.90±0.49	0.99±0.06	10.12±2.60	10.25±2.67
	03 Dec 2006	6.43±0.09	26.78±0.08	274.95±9.66	208.44±44.91	11.32±0.20	4.92±0.22	6.19±0.18	0.21±0.10	13.71±2.56	8.88±2.92
	Average	6.59±0.04	22.86±1.08	256.88±5.19	409.77±110.94	9.03±0.38	5.10±0.30	3.02±0.37	0.75±0.14	13.75±1.60	10.38±1.60

* Cond, specific conductivity; DOC, dissolved organic carbon; POC, particulate organic carbon; TDN, total dissolved nitrogen; DON, dissolved organic nitrogen; PON, particulate organic nitrogen; NA, data not collected.

Table 4. Average (±SE) percentage contribution of C (DOC, POC) and N (DON, DIN, PON) forms to the total C and N concentrations in the Wailuku River, Hawai'i Island, Hawai'i, during base- and stormflow conditions. Data from the two sites along the river were combined in this table because C and N forms were similar between sites ($p > 0.200$), but differed between flow conditions ($p < 0.001$), except for DON ($p = 0.772$).

Flow type	Date collected	% DOC	% POC	% DON	% DIN	% PON
Base	15 Feb 2005	76.60±2.90	23.40±2.90	33.03±1.04	46.16±1.94	20.82±1.03
	19 Jul 2005	86.18±1.42	13.82±1.42	42.57±3.65	40.97±5.85	16.46±2.44
	14 Nov 2005	83.81±1.20	16.19±1.20	31.24±4.13	50.72±3.22	18.04±1.05
	11 Sep 2006	89.91±3.31	10.09±3.31	24.36±2.16	56.18±4.66	19.46±4.62
	13 Nov 2006	60.05±7.66	39.95±7.66	0.00±0.00	73.35±4.12	26.65±4.12
	Average	79.29±3.05	20.71±3.05	25.93±3.60	53.71±3.18	20.36±1.52
Storm	23 Jun 2005	74.80±1.51	25.20±1.51	41.80±0.73	11.54±0.46	46.66±0.84
	01 Oct 2005	19.55±1.37	80.45±1.37	13.57±0.32	10.85±1.64	75.57±1.85
	21 Jan 2006	51.82±3.19	48.18±3.19	33.02±1.05	13.50±0.80	53.47±1.51
	03 Dec 2006	58.42±4.52	41.58±4.52	21.03±1.91	25.95±3.45	53.03±5.27
	Average	51.15±5.35	48.85±5.35	27.36±2.85	15.46±1.81	57.18±3.12

* DOC, dissolved organic carbon; POC, particulate organic carbon; DON, dissolved organic nitrogen; DIN, dissolved inorganic nitrogen; PON, particulate organic nitrogen.

constant at the upper site (S1) during both flow conditions (average ± SE, baseflow 3.52 ± 0.11 μmol L^{-1} vs. storms 3.31 ± 0.57 μmol L^{-1}) and decreased by half during storms ($p < 0.001$) at the lower site (S2) (baseflow 5.11 ± 0.54 μmol L^{-1} vs. storms 2.73 ± 0.46 μmol L^{-1}).

Forms of C and N were similar between sites ($p \geq 0.200$), but significantly differed between flow conditions ($p < 0.001$) in the Wailuku River (Table 4). The C pool was dominated by DOC during baseflow conditions (79% ± 3%), whereas DOC and POC contributed equally during storms (Table 4). The N pool was dominated by NO_3^- under baseflow conditions (54% ± 3%) and by PON during storms (57% ± 3%) (Table 4). DON comprised a similar percentage of the N pool under base- (26% ± 4%) and stormflow (27% ± 3%) conditions ($p = 0.772$) (Table 4).

DOC and DON bioavailability were generally similar between sites ($p \geq 0.154$). In contrast, significantly higher percentages of DOC and DON were bioavailable during baseflow conditions than during storms (Fig. 3). This pattern was observed for both sites; however, DOC bioavailability was slightly higher at the lower site (S2, 9% ± 1%) compared to the upper site (S1, 3% ± 1%) during storms ($p = 0.023$). Average percentage DOC bioavailability during baseflow conditions (15% ± 2%) was more than double that during storms (6% ± 1%; Fig. 3A). Similarly, average percentage DON bioavailability during baseflow conditions (31% ± 4%) was two times higher than during storms (14% ± 2%; Fig. 3B).

During both 2005 and 2006, stormflow contributed 83% and 85%, respectively, to the annual discharge from the Wailuku River. The average discharge measured in 2005 (4361 L s^{-1}) was almost half of the 74-yr average (7759 L s^{-1}) for the river, as compared to 2006 (8099 L s^{-1}), which was comparable to the 74-yr average. There were 109 d of storm conditions each year. The annual DOC and POC yields from the Wailuku River during 2005 and 2006 were comparable, and stormflow comprised >90% of the annual yields for both constituents (Table 5). The majority of the annual N yield was comprised of PON, followed by DON and NO_3^- (Table 5). Stormflow comprised >90% of the annual PON and DON yields and 72% of the NO_3^- yield (Table 5).

Discussion

Concentrations—Across biomes, DOC concentrations in streams and rivers generally increase with discharge (Mulholland 2003). In the Wailuku River, DOC concentrations tripled during storms, which is comparable to patterns reported for streams and rivers in temperate and tropical regions (Newbold et al. 1995; Buffam et al. 2001). DOC concentrations measured in the Wailuku River during baseflow conditions (80 ± 6 μmol L^{-1}) were similar to values previously measured in semiarid regions and lower than those measured in other biomes, particularly those in the humid tropics (Meybeck 1982). DOC concentrations in the Wailuku River during storms (257 ± 5 μmol L^{-1}) fall within the range of DOC concentra-

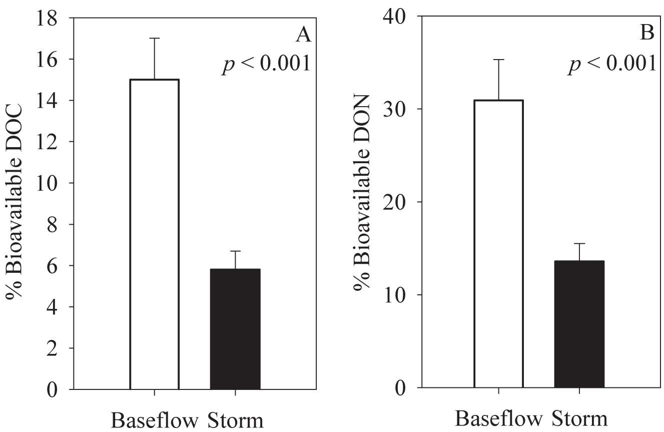

Fig. 3. Average (±SE) percentage (A) DOC and (B) DON bioavailability in the Wailuku River, Hawai'i Island, Hawai'i, during base- and stormflow conditions. Data from the two sites were combined because there were no significant differences in DOM bioavailability between sites. p values indicate results from two-way ANOVAs for flow conditions.

Table 5. Yields of dissolved and particulate forms of C and N from Site 1 (S1) in the Wailuku River, Hawai‘i Island, Hawai‘i. All yields are reported in kg km^{-2} yr^{-1}. Regressions were used to estimate concentrations for yield calculations (see text for details). Estimates for the yields of bioavailable DOC (BDOC) and DON (BDON) were calculated as the product of the yield and average percentage bioavailability. The percentage contributions of baseflow and stormflow to annual yields from the Wailuku River are shown in parentheses.*

	2005			2006		
Yield	Annual total	Baseflow	Stormflow	Annual total	Baseflow	Stormflow
DOC	829	78 (9)	751 (91)	1282	105 (8)	1177 (92)
BDOC	57	12 (21)	45 (79)	87	16 (18)	71 (82)
POC	819	22 (3)	797 (97)	1778	30 (2)	1748 (98)
DON	24	2 (9)	22 (91)	38	3 (8)	34 (92)
BDON	3.8	0.7 (18)	3.1 (82)	5.7	0.9 (16)	4.8 (84)
PON	63	2 (4)	61 (96)	127	3 (3)	124 (97)
NO_3^-	9	3 (28)	6 (72)	11	3 (28)	8 (72)

* DOC, dissolved organic carbon; POC, particulate organic carbon; DON, dissolved organic nitrogen; PON, particulate organic nitrogen.

tions reported for streams and rivers from different biomes during storms (148–550 μmol L^{-1}; Buffam et al. 2001).

Both flowpaths of water across the Wailuku River watershed and soil mineral chemistry may explain the DOC concentration changes observed during baseflow and storm conditions. During baseflow conditions in the Wailuku River watershed, water flowpaths are probably deep (Lohse and Dietrich 2005) and through noncrystalline minerals (allophane, imogolite, ferrihydrite) with high DOC sorption capacity (Torn et al. 1997; Chorover et al. 2004), as the substrate in this watershed is highly porous and relatively young (14×10^3–65×10^3 yr; Wolfe and Morris 2001). During storms, when the soils are saturated and the water table is high, the flowpath of water to the Wailuku River probably shifts from deep flowpaths to shallow flowpaths through upper organic-rich soil horizons. Previous studies have attributed increased DOC concentrations in streams and rivers during storms from the flushing of litter and upper soil horizons in the riparian zone (Hornberger et al. 1994; Frank et al. 2000).

In contrast to DOC, less is known about how DON concentrations change with flow conditions in lotic systems. The increase in DON concentrations observed in the Wailuku River from baseflow to storm conditions is comparable to increases documented in temperate streams and tropical rivers (Lewis and Saunders 1989; Buffam et al. 2001). Baseflow DON concentrations in the Wailuku River (2.2 $\pm$ 0.2 μmol L^{-1}) were approximately a fourth of measured concentrations for the Orinoco River (Lewis and Saunders 1989) and an eighth of those reported for temperate streams and rivers (Wiegner et al. 2006). Although DON concentrations differ among these lotic systems, they all experienced a doubling of their DON concentrations during storms. DON concentrations were significantly correlated with DOC concentrations in the Wailuku River across flow conditions ($r = 0.717$, $p < 0.001$), suggesting that factors controlling DOC concentrations are controlling DON concentrations and/or that C and N components of the DOM pool are the same molecules. This correlation has been observed in several lotic systems and is attributed to DON losses resulting from the leaching of organic acids from soils (Hedin et al. 1995).

Similar to DOM concentrations, both POC and PON concentrations generally increase with riverine discharge (Meybeck 1982). The reported worldwide range for riverine POC concentrations is 83–2500 μmol L^{-1} (1–30 mg L^{-1}) (Meybeck 1982). Measured POC concentrations in the Wailuku River during base- and stormflow generally fall within this range, averaging 17 ($\pm$1.5) μmol L^{-1} during baseflow conditions and 410 ($\pm$111) μmol L^{-1} during storms (Table 3). Variability in POC concentrations in the Wailuku River was low during baseflow conditions (range, 14–23 μmol L^{-1}) and increased dramatically (range, 85–1136 μmol L^{-1}) during storms (Table 3). This large variability in POC concentrations during storms is most likely a function of the river's discharge, because the river's discharge varies over the storm's hydrograph, as well as a function of differences in the duration and intensity of precipitation among storms. Changes in PON concentrations with riverine discharge are less widely reported than changes in POC; however, their patterns are consistent with those of POC, because they are often part of the same molecules and particles.

In contrast to DOM and POM, NO_3^- concentrations respond differentially to storms depending on a watershed's dominant land cover and hydrology (Cronan et al. 1999; Lehrter 2006). In the Wailuku River, NO_3^- concentrations decreased at the lower site (S2) in the watershed during storms, while remaining fairly constant at the upper site (S1). The differential response of NO_3^- during storms at the two sites may be attributed to the small portion of urban area in the lower section of the watershed (Table 1). Groundwater entering the Wailuku River during baseflow conditions in the lower section of the watershed is probably enriched in NO_3^- leaching from cesspools and septic tanks, because most of the homes in this area are not connected to the sewer line (K. Silvius unpubl.). During storms, the NO_3^--enriched groundwater is probably diluted by surface runoff from the upstream forested areas, resulting in lower concentrations; this pattern has been previously observed in other watersheds (Lehrter 2006). Use of stable N and oxygen isotopes for NO_3^- and those for boron, in conjunction with other chemical and biological tracers of human sewage, are needed to confirm this source of N to the river at this location.

DOM bioavailability—Although DOM concentrations in lotic systems generally increase with discharge, the effects of these conditions on DOM bioavailability are neither consistent nor well understood, and the primary focus has been on DOC (Leff and Meyer 1991; Buffam et al. 2001). In the Wailuku River, both DOC and DON bioavailability decreased during storms. A similar pattern for DOC bioavailability was observed for a blackwater river in Georgia (Leff and Meyer 1991), but a contrasting pattern of increased DOC and DON bioavailability during snowmelt in boreal rivers has been documented (Wikner et al. 1999; Stepanauskas et al. 2000). In comparison, other stream studies have observed no effect of storms on DOC bioavailability (Volk et al. 1997; Buffam et al. 2001).

Differences in DOM flowpaths and sources are most likely responsible for the discrepancies in reported effects of high discharge on DOM bioavailability among lotic systems. In the Wailuku River during baseflow conditions, water flowpaths are deep through minerals with high DOC sorption capacity (Torn et al. 1997; Chorover et al. 2004; Lohse and Dietrich 2005), resulting in groundwater with low DOC concentrations and likely low bioavailability (Grøn et al. 1992). Yet DOM bioavailability was higher during baseflow conditions than during storms, which suggests the presence of an autochthonous source of bioavailable DOM. The most likely autochthonous source of bioavailable DOM is exudates from benthic algae (T. Wiegner pers. comm.), which are known to be highly bioavailable because of their high monomeric and combined carbohydrate content and low C : N ratios (Bertilsson and Jones 2003). During storms, the water flowpaths to the Wailuku River were probably through upper organic-rich soil horizons. Soil-derived DOM is generally less bioavailable than algal-derived DOM because it is comprised of high-molecular-weight organic molecules that are more chemically complex with high C : N ratios (Sun et al. 1997). Therefore, increased inputs of soil-derived DOM during storms may dilute the more bioavailable autochthonous DOM. Low DOM bioavailability during storms may also result from inactive bacteria, less capable of DOM uptake, being washed into the river from the soils (Leff and Meyer 1991). However, this latter scenario is an unlikely explanation, because the bioavailability experiments were conducted over 4 d, which is sufficiently long for several generations of bacteria to create an adequate inoculum.

Yields—Yields of DOC and DON from the Wailuku River were substantially lower than yields measured in other streams and rivers in the humid tropics, but were comparable to those measured in taiga and temperate regions (Table 6; Meybeck 1982). Factors behind the low yields measured in the Wailuku River relative to other streams and rivers in similar climates may be substrate age and soil organic matter development. The Wailuku River watershed is on geologically young substrate, which is extremely porous and comprised of minerals with high DOC sorption capacity (Torn et al. 1997; Chorover et al. 2004), covered by weakly developed soils (Vitousek 2004). The porous substrate allows for the formation of only a few very small wetlands within the watershed (Table 1), a factor often cited as greatly influencing DOC export (Mulholland 2003). The high DOC sorption capacity of the substrate results in groundwater with low DOC concentrations discharging into the river during baseflow conditions. Additionally, the weakly developed soils with low organic matter content probably result in lower DOM exports during storms as compared with similar watersheds with well-developed soils and high organic matter content, because soil organic matter content greatly influences DOM yields (Hornberger et al. 1994). It is likely because of these above reasons that the DOM yield from the Wailuku River is lower than yields from geologically older islands of Oceania (Harrison et al. 2005) and from other watersheds in the humid tropics.

POC and PON yields for the Wailuku River were generally lower than those measured in other tropical rivers, but higher than those measured in temperate rivers (Table 6). The most commonly used factors used to predict POM yields in rivers are precipitation, watershed slope, and lithology (Beusen et al. 2005). Of these factors, precipitation and lithology most likely affected the Wailuku River's POM yield. The Wailuku River watershed receives a tremendous amount of precipitation annually (3400–7700 mm), which weathers the young, easily eroded basalt and erodes the weakly developed soils with low organic matter content (Vitousek 2004). The low organic matter content of the soils is most likely responsible for the low POM yield in the Wailuku River as compared with other rivers in the humid tropics.

Nitrate yields for the Wailuku River were one to two orders of magnitude lower than those reported for other rivers in the humid tropics, as well as those in more developed temperate areas (Table 6). A recent global model suggests that biological N fixation from crops and fertilizers are the two dominant sources of NO_3^- to world rivers (Dumont et al. 2005). These two sources are probably small in the Wailuku River watershed, because agriculture accounts for only 0.2% of the land cover (Table 1). Additionally, the relatively low NO_3^- yield for the Wailuku River may result from the geology of the basin, which is comprised of young volcanic rock lacking N and weakly developed soils with low amounts of organic N (Vitousek 2004).

Implications—Coastal water quality models have long ignored inputs of DOM from rivers because it was assumed that the C and N components from this pool were biologically unavailable. Our study, in conjunction with several others, demonstrates that DOM is an important energy and nutrient source for heterotrophic bacteria (Seitzinger and Sanders 1997; Wiegner and Seitzinger 2001; Wiegner et al. 2006) and that storms are responsible for delivering the majority of DOM to coastal waters. Total C and N yields are commonly used in coastal water quality models; however, they do not accurately predict the portion of the DOM yield that is bioavailable, may support primary and secondary production, and can possibly contribute to hypoxia and eutrophication. We calculated the annual bioavailable DOM yield from the Wailuku River as the product of the calculated yields (Table 5) and

Table 6. Yields of C and N from selected streams and rivers. All yields are in units of kg km^{-2} yr^{-1}.

Streams and rivers	Continent	DOC	POC	DON	NO_3^-	PON
Niger River	Africa	400[a], 672[b]	500[a], 600[c]	37.1[b]	—	100[c,d]
Orange River	Africa	54[b]	600[c]	3.7[b]	—	100[c,d]
Zaire (Congo) River	Africa	3300[a], 1646[b]	400[a], 1400[c]	91.5[b]	—	200[c,d]
Chang Jiang	Asia	4200[a]	1600[c]	—	327.5[e,f]	200[c,d]
Ganges	Asia	2000[a], 2664[b]	6400[c]	163.9[b]	—	800[c,d]
Huang He	Asia	600[a]	300[c]	—	120.5[e,f]	0[c,d]
Lena	Asia	987[b]	300[c]	58.7[b]	21.1[e,f]	0[c,d]
Quebrada Sonadora[g]	Caribbean	6900–7910	640–910	357–384	130–144	41–55
Quebrada Toronja[g]	Caribbean	2610–4280	413–900	232–350	75–108	32–67
Rio Icacos[g]	Caribbean	8330–10,900	2000–5200	450–523	238–278	120–220
Quebrada El Jobo[h]	Central America	2600	—	200	430	—
Quebrada Kathia[h]	Central America	1900	—	150	560	—
Quebrada Marilin[h]	Central America	2400	—	190	400	—
Quebrada Zompopa[h]	Central America	4300	—	340	600	—
Rio Tempisquito[h]	Central America	3700	—	300	610	—
Rio Tempisquito Sur[h]	Central America	2700	—	210	490	—
Danube	Europe	1152[b]	1000[c]	89.7[b]	—	100[c,d]
Erlenbach[i]	Europe	8400–18,500	—	550–620	270–380	—
Po	Europe	3046[b]	4600[c]	262.5[b]	—	600[c,d]
Rhine	Europe	1700[a], 1388[b]	1000[a], 900[c]	—	2200.4[e,f]	100[c,d]
Seine	Europe	917[b]	500[c]	113.0[b]	1364.9[e,f]	100[c,d]
Columbia	North America	700[a], 1646[b]	200[a], 500[c]	—	74.1[e,f]	100[c,d]
Mackenzie	North America	800[a], 1127[b]	300[c]	47.0[b]	—	0[c,d]
Mississippi	North America	1100[a], 898[b]	300[a], 400[c]	54.4[b]	255.6[e,f]	100[c,d]
Paine Run[j]	North America	516	—	13	73.2	—
St. Lawrence	North America	1100[a], 1734[b]	100[a], 700[c]	103.0[b]	—	100[c,d]
Yukon	North America	2800[a], 2201[b]	400[a], 400[c]	103.1[b]	30.6[e,f]	100[c,d]
Amazon River	South America	5235[b]	2900[c]	327.3[b]	—	500[c,d]
Orinoco River[k]	South America	5241	1492	192	95	190[d]
Tributaries of the Amazon River[l]	South America	1900–12,000	600–2900	—	—	—
Wailuku River	Oceania	829[m], 1282[n]	819[m], 1778[n]	24[m], 38[n]	9[m], 11[n]	63[m], 127[n]

[a] Esser and Kohlmaier 1991.
[b] Harrison et al. 2005.
[c] Beusen et al. 2005.
[d] Beusen et al. 2005 and Lewis and Saunders 1989 report as PN. Most PN in rivers is PON (Meybeck 1982).
[e] Dumont et al. 2005.
[f] Dumont et al. 2005 report as DIN. Most DIN in rivers is NO_3^-; 15% is NH_4^+ and 1% is NO_2^- (Meybeck 1982).
[g] McDowell and Asbury 1994.
[h] Newbold et al. 1995.
[i] Frank et al. 2000.
[j] Buffam et al. 2001.
[k] Lewis and Saunders 1989.
[l] Tributaries include: Rio Japurá, Rio Juruá, Rio Jutaí, Rio Içá, Rio Madeira, Rio Negro, and Rio Purús; Richey et al. 1990.
[m] This study (2005).
[n] This study (2006).

measured percentage DOM bioavailability (Fig. 3). These are the first bioavailable DOM yields reported for any river or stream, because previous studies provided only estimates from hypothetical watersheds of different land covers (Seitzinger et al. 2002). On average, storms accounted for 81% and 83% of the bioavailable DOC and DON yields, respectively, from the Wailuku River (Table 5), even though DOC and DON bioavailability were lower under these conditions (Fig. 3). Additionally, the bioavailable DON yield is about half as large as the NO_3^- yield and thus may be a significant available N source for coastal algae and bacteria. Overall, our results suggest that storms are responsible for delivering not only the majority of the DOM to coastal waters, but the majority of the bioavailable DOM as well. Once in coastal waters, this watershed-derived DOM may further stimulate primary and secondary production, and possibly contribute to hypoxia and eutrophication, because riverine DOM has been shown to be more bioavailable in coastal waters than in freshwaters (Stepanaukas et al. 1999; Wikner et al. 1999).

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