Anthropogenic inputs from a coastal megacity are linked to greenhouse gas concentrations in the surrounding estuary

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Abstract

Coastal megacities deposit significant amounts of carbon (C), nitrogen (N), and pollutants into surrounding waters. In urbanized estuaries, these inputs, including wastewater discharge and surface runoff, can affect biogeochemical cycles, microbial production, and greenhouse gas (GHG) efflux. To better understand estuarine GHG production and its connection to anthropogenic drivers, we quantified carbon dioxide (CO₂) and methane (CH₄) surface-water concentrations and efflux in combination with a suite of biogeochemical parameters, including anthropogenic indicators, in the Hudson River Estuary (HRE) and adjacent waters surrounding New York, NY, over a 2-yr period. The HRE was a source of both CO₂ (33 ± 3 mmol CO₂ m⁻² d⁻¹) and CH₄ (177 ± 22 μmol CH₄ m⁻² d⁻¹) under all measured conditions. Surface-water salinity, oxygen saturation, fecal indicator bacteria, nitrate concentrations, and temperature best explained the variance in CO₂ and CH₄ concentrations in multiple regression analyses, producing robust predictive power for both GHGs. Our multifaceted data set demonstrated that CH₄ and CO₂ surface concentrations are explained in part by enterococci concentrations, a widely used wastewater biological indicator, explicitly linking wastewater inputs to GHG surface concentrations in the HRE. The greatest CO₂ and CH₄ surface-water concentrations were found in urban tributaries and embayments, primary wastewater delivery areas throughout the HRE. Estuarine tributaries and embayments have historically received less research attention than midchannel sites, but since these shallow sites may contribute to increased GHG efflux in anthropogenically impacted estuaries, further study is warranted.

Estuaries are among the most biologically productive ecosystems in the world, serving as critical intermediaries between terrestrial and aquatic ecosystems and are important zones of biogeochemical activity (Bianchi 2007). While estuaries cover 0.2% of the Earth's surface, they are estimated to have a disproportionately large impact on global greenhouse gas (GHG) production, including approximately 0.5% of methane (CH₄), 2–4% of nitrous oxide (N₂O), and 2–5% of carbon dioxide (CO₂) emissions (Borges and Abril 2011; Ciais et al. 2013; Murray et al. 2015). Despite its potential impact on climate, research on estuarine GHG efflux is sparse, resulting in poorly constrained emission estimates (Bange 2006). GHG fluxes are particularly unconstrained for estuaries that are urbanized, or otherwise anthropogenically impacted in ways that could enhance GHG production, such as through agricultural runoff,

wastewater discharges, or land-use changes (Frankignoulle et al. 1998; Doney 2010; Regnier et al. 2013).

Estuarine CO₂ surface concentrations and efflux into the atmosphere are generally greatest “upstream” in proximity to tributaries that serve as carbon (C) and nitrogen (N) sources (Chen et al. 2012). Substantial seasonal variability, linked to the strong correlation between temperature and net heterotrophy, has also been observed across estuaries worldwide (Frankignoulle et al. 1998). Surface concentrations have been shown to be positively correlated to temperature, dissolved organic carbon (DOC), and chlorophyll *a* (Chl *a*) concentrations, and negatively correlated with river flow and oxygen saturation (Borges and Abril 2011). In addition to typical upstream/downstream trends, natural or anthropogenic inputs of labile C and other nutrients (e.g., sources of N and phosphorus) can enhance microbial activity, stimulating CO₂ production via direct and indirect pathways (Turner and Rabalais 1994).

Like CO₂, CH₄ concentrations are often greater in the “upstream” portion of estuaries (Middelburg et al. 2002). CH₄ concentrations typically decrease with increasing estuarine

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salinity because sulfate carried with seawater increases competition between sulfate reducers and methanogens, limiting CH_4 production in more saline waters (Bartlett et al. 1987; Capone and Kiene 1988). However, rivers and estuaries with large urban and/or agricultural influences including the Scheldt, Pearl, Seine, and Hudson River estuaries/watersheds demonstrated supersaturated CO_2 and CH_4 concentrations in downstream regions (Kempe 1984; Raymond et al. 1997; Frankignoulle et al. 1998; Abril et al. 2000; Middelburg et al. 2002; Chen et al. 2013; Regnier et al. 2013; Marescaux et al. 2018), suggesting that anthropogenic inputs can alter upstream/downstream trends. Nevertheless, data explicitly linking anthropogenic inputs to enhanced estuarine GHG efflux are lacking (Burgos et al. 2015).

In this study, CO_2 and CH_4 surface concentrations and efflux were quantified for the Hudson River Estuary (HRE) at both midchannel and tributary sites. The HRE is a highly urbanized system that supports more than 12 million people and experiences among the highest external anthropogenic DOC and dissolved inorganic N (DIN) inputs in the world (Howarth et al. 2006). Including tributaries in this study is significant because tributary mixing zones typically receive the largest natural and anthropogenic (specifically wastewater) DOC and DIN inputs. Most prior studies have focused on mid-channel measurements, omitting potential hotspots of GHG production and associated anthropogenic inputs. In addition, the GHG measurements in this study were paired with a suite of anthropogenic wastewater indicators, providing one of the most comprehensive examinations of the relationship between GHG dynamics and wastewater inputs in urbanized estuaries.

Comparing urbanized regions in the brackish (New York City [NYC]) and fresh (Albany) sections of the estuary with less developed regions allowed us to separate anthropogenic impacts from salinity-dependent patterns of GHG surface concentrations and efflux. We hypothesized first that CO_2 and CH_4 surface concentrations would be greatest near urban centers (Albany and NYC) compared with less-developed areas, regardless of salinity (H1). Second, the greatest CO_2 and CH_4 surface concentrations would be found in urban and upriver tributaries (H2). Finally, CO_2 and CH_4 surface concentrations in the HRE would positively correlate with indicators of anthropogenic loading, such as DOC, nitrate (NO_3^-), and fecal indicator bacteria concentrations (H3).

Materials and methods

Site information

The HRE is a partially mixed estuary with a moderate salinity gradient and vertical stratification (Geyer and Chant 2006) (Fig. 1). It is tidal between the Battery (river kilometer [RK] 0 at the southern tip of Manhattan) and the Federal Dam at Troy, NY (RK 245). The salt front and an associated estuarine turbidity maximum are typically located between Haverstraw Bay (RK 60) and West Point, NY (RK 85), largely dependent on river flow (Geyer and Chant 2006). A stronger turbidity maximum is

Fig. 1. Map detailing the tidal HRE and the location of each midchannel ($n = 17$) tributary ($n = 7$), and nearshore sites ($n = 5$) in relation to New York City (NYC) and Albany. NYC is located at the ocean terminus and Albany is located at the upriver terminus of the tidal HRE. For this study, the lower estuary will refer to saline and brackish waters between the Battery (RK 0) and West Point, NY (RK 85) and the upper estuary will refer to tidal freshwaters between West Point, NY, and Troy, NY, as defined in previous HRE publications (Howarth et al. 2006; Levinton and Waldman 2006). Tributaries listed south to north are Gowanus Canal (GW), Newtown Creek (NC), East River (ER), Harlem River (HR), Rondout Creek (RC), Esopus Creek (EC), Catskill Creek (CC), Orangetown Outfall (OT), Peekskill (PK), Wappinger Creek (WC), and Inbocht Bay (IB). NY represents New York state, NJ represents New Jersey, CT represents Connecticut, and MA represents Massachusetts.

located closer to the mouth of the estuary in the zone of greatest salinity stratification (between 79th Street [RK 11] and the George Washington Bridge [RK 19], Bokuniewicz 2006).

The HRE has overlaying salinity and “urban” gradients with the most densely populated areas located at both the southern brackish (NYC) and northern fresh (Albany) termini. External inputs of DOC and DIN are split between upriver tributaries (42%) and wastewater effluent (58%) (Howarth et al. 2006). In NYC alone, recent measurements show an average of $4.9 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ of treated, and $1.9 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ of untreated

Table 1. Sampling dates and conditions.

No.	Year	Month	Day	Sites visited	River flow (m ³ d ⁻¹)*
1	2013	Jul	17–21	All	3.0E+07
2	2013	Aug	14–15	Half	3.3E+07
3	2013	Sep	18–21	All	1.3E+07
4	2013	Oct	16–17	Half	1.8E+07
5	2014	May	12–15	All	4.6E+07
6	2014	Jun	12–15	All	7.0E+07
7	2014	Jul	07–10	All	3.5E+07
8	2014	Aug	11–12	Half	1.4E+07
9	2014	Sep	07–10	All	1.3E+07
10	2014	Oct	12–16	All	1.5E+07

"All" indicates that we sampled each site.

"Half" indicates we sampled the brackish river (RK 0–69).

*River flow data procured from United States Geological Survey (USGS) Green Island station data.

wastewater discharge (City of New York Department of Environmental Protection [NYCDEP], accessed April 2018, <http://www.nyc.gov/html/dep/pdf/hwqs2012.pdf>) (Supporting Information Table S1). In the saline portion of the HRE near NYC, wastewater entering the estuary from submerged sewage outfalls accounts for large external DOC (ca. 94 g C m⁻² yr⁻¹) and DIN (ca. 374 g N m⁻² yr⁻¹) inputs. The N loading also enhances phytoplankton growth and turnover, ultimately leading to total DOC inputs estimated at ca. 944 g C m⁻² yr⁻¹ (Howarth et al. 2006). Sewage-derived DOC and DIN originating near NYC can likely be transported upriver by tidal action as far as the salt front (Brosnan et al. 2006) (Supporting Information Table S1).

In contrast, the majority of external DOC and DIN input to the upper fresh HRE is sourced from tributaries, not wastewater (Howarth et al. 1996). These tributaries include the upper Hudson and Mohawk Rivers (RK > 250), which account for 80% of freshwater input to the HRE (flow rate 2.9–4.8 L min⁻¹), with the balance coming from smaller tributaries (Cooper et al. 1988). Wastewater inputs from this region are dominated by Albany (6.3 × 10⁵ m³ d⁻¹) at the freshwater terminus of the HRE but are also sourced from the Kingston (1.8 × 10⁴ m³ d⁻¹), Poughkeepsie (2.3 × 10⁴ m³ d⁻¹), and Beacon/Newburgh (3.9 × 10⁴ m³ d⁻¹) metro areas (United States Environment Protection Agency [USEPA], accessed April 2018, <https://echo.epa.gov>). However, given that the cumulative discharge of these smaller metro areas is approximately 14% of the NYC discharge, the relative importance of sewage as a source of DOC and DIN is lower in the upper, freshwater portion of the HRE.

Sampling

In total, 17 midchannel sites were sampled between the Battery (RK 0) and the Troy Bridge in Albany (RK 244), an average of approximately 15 km between stations, in May–October of 2013 and 2014 (Table 1). In addition, nine tributary and nearshore sites in the freshwater region upstream and five sites in urban tributaries located near NYC were sampled

(Supporting Information Tables S2, S3). The majority of measurements were collected from the Riverkeeper patrol boat, R. Ian Fletcher, in coordination with their monthly water quality survey. Surface water was pumped from the side of the boat at ~ 2 L min⁻¹ to a Hydrolab DS5X sonde (Hach; Boulder, CO, U.S.A.) and Mini-pro CO₂ (Pro-Oceanus; Halifax, NS, Canada) probe. The Hydrolab sonde measured conductivity, turbidity, temperature, oxygen saturation, and chlorophyll fluorescence while on station (typically 8–10 min per site). The Mini-pro CO₂ probe directly measured the partial pressure of CO₂ or *p*CO₂ values every 2 s equating to > 240 measurements for each station. Exploratory bottom water samples were collected to ascertain potential sources of CH₄ and *p*CO₂ but were not used for statistical analyses because of a lack of replication (*n* = 1).

Additional surface samples were collected to quantify CH₄ (250 mL, *n* = 3–5 per site, per cruise), fecal indicator bacteria (enterococci, 100 mL, *n* = 1 per site, per cruise), as well as DOC and DIN (50 mL, *n* = 1 per site, per cruise) surface concentrations. Samples for CH₄ and enterococci were processed immediately on board, while samples for DOC and DIN analyses were placed immediately on ice and then kept at –20°C (within 24 h) until analyses were completed. Actual (not the partial pressure) CH₄ surface concentrations were determined using the extraction method detailed by McAuliffe (1971) that in brief, entails extracting CH₄ from water samples (30 mL) in syringes flushed and filled with N₂ gas (30 mL) followed by transfer and storage in 12 mL pre-evacuated exetainers (Labco; Lampeter, UK). Within 96 h, all gas samples were injected (via sample loop) onto a 3-m long molecular sieve column (Restek; Bellefonte, PA, U.S.A.) installed in a Hewlett-Packard 5890 Series plus II Gas Chromatograph (HP; Brielle, NJ, U.S.A.) equipped with a flame ionization detector for analyses. Fecal indicator bacteria, enterococci, were enumerated from surface samples within 6 h of collection following USEPA guidelines as described in Young et al. (2013). DIN concentrations defined as NO₃⁻ plus ammonium (NH₄⁺) of sample surface waters were determined using standard colorimetric assays (Weatherburn 1967; Doane and

Horwath 2003) performed with a Synergy H1 plate reader (Biotek, Winooski, VT, U.S.A.). Nonpurgeable organic C (referred to hereafter as DOC, a technical near equivalent and more common usage) was determined by the high-temperature combustion method (American Public Health Association 2005) with a TOC-V CSH analyzer (Shimadzu, Kyoto, Japan).

Efflux calculations

Efflux (F) was estimated using a simple model that assumes Fickian diffusion shown in Eq. 1:

$$F = k\Delta C \quad (1)$$

where k is the gas transfer velocity and ΔC is the gas concentration difference across the air–water interface (Liss and Slater 1974). CH_4 and $p\text{CO}_2$ were measured in surface waters to determine their difference across the water–air interface. Henry's law solubility was utilized to convert $p\text{CO}_2$ to the concentration at the water surface in equilibrium with the air (Weiss 1974). k is dependent upon the specific gas of interest and on wind speed, often as an exponential or squared function in most models. If the k was known for a particular gas, the k for other gases (in this case CH_4 and CO_2) can be calculated by the ratio of their respective Schmidt numbers (Sc). This number is the kinematic viscosity of water divided by the diffusion constant for the gas(es) of interest, obtained from Wanninkhof (1992) and adjusted according to each sample's salinity and temperature. The models used to calculate k were taken from two different publications allowing efflux estimates to be evaluated in the context of physical conditions specific to the HRE (Raymond and Cole 2001; Ho et al. 2011). Models representing open ocean conditions (Wanninkhof 1992; Nightingale et al. 2000; Ho et al. 2006) which may not reflect actual conditions in the HRE were included to allow comparisons to other estuarine studies, which commonly use these models. The models are listed in Eqs. 2–6, where u_{10} and Sc represent wind speed adjusted to 10 m height and the Schmidt number calculated from salinity and temperature from each sampling, respectively.

$$\text{Ho et al. (2006), } k_{sc} = 0.266u_{10}^2(Sc/600)^{-1/2} \quad (2)$$

$$\text{Ho et al. (2011), } k_{sc} = [0.06 + 0.266u_{10}^2](Sc/600)^{-1/2} \quad (3)$$

$$\text{Raymond and Cole (2001), } k_{sc} = 1.58e^{0.3u_{10}}(Sc/600)^{-1/2} \quad (4)$$

$$\text{Nightingale et al. (2000), } k_{sc} = [0.222u_{10}^2 + 0.333u_{10}](Sc/600)^{-1/2} \quad (5)$$

$$\text{Wanninkhof (1992), } k_{sc} = 0.31u_{10}^2(Sc/660)^{-1/2} \quad (6)$$

Efflux calculations were determined for midchannel sites only, which are located in the main shipping channel, and have average water depths of approximately 15 ± 5 m. At shallower depths, bottom shear, tides, fetch, and stratification,

not measured in this study, would be as important as wind speed for estimating efflux (Zappa et al. 2007). Therefore, tributaries and nearshore sites were excluded from efflux calculations. Wind speed data (scalar) were collected from a series of meteorological towers located in close proximity to Kingston, Beacon, and Scarborough, NY, provided by WeatherFlow (Scotts Valley, CA, U.S.A.).

Analyses

Potential connections between GHG efflux and urbanization were investigated in multiple regression analyses relating surface CO_2 and CH_4 concentrations from midchannel sites to parameters measured in situ at the time of sample collection (i.e., conductivity, turbidity, etc.) and to other available contextual data including rainfall, river flow (United States Geological Survey [USGS], accessed April 2018, https://waterdata.usgs.gov/nwis/uv?site_no=01358000), historic enterococci geometric means per station (Riverkeeper, accessed April 2018, <https://www.riverkeeper.org/water-quality/udson-river/>), and modeled wastewater input (NYCDEP, accessed April 2018, http://www.nyc.gov/html/dep/pdf/green_infrastructure/gi-performance-metrics-report-2016.pdf). All data were transformed (square root) to ensure assumptions necessary for ANOVA, regression analysis, and canonical correlation analysis (CCA) tests were met. For ANOVA analyses, data were binned into four regions: brackish urban (NYC; RK 0–19), brackish sub-urban rural (RK 30–69), fresh sub/urban (RK 84–182), and fresh urban (Albany; RK 197–244) determined by salinity and wastewater discharge (Fig. 2, Supporting Information Figure S1) to reflect a priori expectations in GHG surface concentrations. Subsequently, CH_4 and CO_2 concentrations from tributary sites were compared to midchannel sites (using Wilcoxon signed-rank tests) to assess whether tributaries were sources of elevated CH_4 and CO_2 values observed in urban areas. For regression analyses, data were binned only by salinity, with separate analyses for the brackish (Battery [RK 0] to Peekskill [RK 69]) and fresh (West Point [RK 84] to Troy [RK 244]) regions because exploratory analyses demonstrated that some underlying relationships were different in these two regions. All measured parameters and collected data were tested in multiple linear regression models (with CH_4 and CO_2 surface values separately) using both the Bayesian and Akaike information criteria to choose significant parameters for the final multiple linear regression models. All ANOVA, regression analyses, and Wilcoxon tests were conducted with SYSTAT (v.13.0, Systat Software, San Jose, CA, U.S.A.) while the CCA ordination was conducted with PC-ORD (v. 6.0).

Results

CH_4 and CO_2 surface values were elevated in urban areas

Surface CH_4 concentrations from midchannel sites in the HRE ranged $65\text{--}660 \text{ nmol L}^{-1}$ during the sampling period (Fig. 3a). These concentrations were greatest in both the lower

Fig. 2. Distribution of wastewater treatment plant flow (WWTP) normalized to river surface area of each region of the HRE individually including: brackish urban (NYC; RK 0–19), brackish suburban/rural (RK 30–69), fresh suburban/rural (RK 84–182), and fresh urban (Albany; RK 197–244). Daily WWTP flows are estimated from data available from <https://echo.epa.gov>. Distribution of WWTP flow normalized to river volume demonstrated in Supporting Information Figure S2.

and upper termini of the HRE, corresponding to urbanized areas that receive high anthropogenic C and N inputs. Lowest CH_4 concentrations were found in the midestuary (RK 20–197) suburban/rural regions, regardless of salinity. These data produced a U-shaped pattern of CH_4 surface concentrations along the length of the estuary. A blocked ANOVA with region and month as grouping variables demonstrated significant differences in CH_4 surface concentrations among regions ($F_{3,125} = 12$, $p < 0.001$), but not sampling months ($F_{9,125} = 2$, $p = 0.097$) (Supporting Information Tables S4a, S4b). Brackish urban tributaries had enhanced CH_4 surface concentrations ranging from 197 to 5672 nmol L^{-1} (Fig. 4a). Average CH_4 surface concentrations in brackish urban tributaries were significantly ($U_1 = 248$, $p < 0.001$) greater (3.1 $\times$) than in neighboring midchannel sites (Supporting Information Table S5). Similarly, enhanced (3.0 $\times$) CH_4 surface concentrations were also found in upriver fresh suburban/rural tributaries compared to nearby midchannel sites (Fig. 4b), although the magnitude of CH_4 concentrations in both these tributaries and bordering midchannel sites were lower (1.5 $\times$) than in the NYC region.

The pattern of surface $p\text{CO}_2$ from midchannel sites (spanning 460–1953 μatm) differed from those observed for CH_4 (Fig. 3b). Greatest $p\text{CO}_2$ values were observed in the lower and midestuary with the brackish urban, brackish suburban/rural, and fresh suburban/rural having significantly ($F_{3,83} = 9$, $p < 0.001$) higher concentrations than those in the fresh urban region (Supporting Information Tables S4a, S4b). Additionally, sampling month, a factor in the ANOVA analysis, was significant ($F_{5,83} = 9$, $p < 0.001$) with the greatest average $p\text{CO}_2$ surface values measured in August ($1694 \pm 28 \mu\text{atm}$) and the lowest in May

Fig. 3. Graphs illustrates average (a) methane (CH_4) and (b) carbon dioxide (CO_2) surface values measured at midchannel sites throughout the tidal HRE. CH_4 concentrations were significantly greater at both the fresh and brackish terminus of the estuary. Error bars are standard error of the mean. For analysis, the HRE was divided into four regions represented by the dash bar parallel to the x-axis including brackish urban (NYC; RK 0–19), brackish suburban/rural (RK 30–69), fresh suburban/rural (RK 84–182), and fresh urban (Albany; RK 197–244).

($749 \pm 31 \mu\text{atm}$). Surface $p\text{CO}_2$ values were significantly enhanced ($\sim 1.6\times$) in brackish urban tributaries compared to neighboring midchannel sites (Fig. 4b; Supporting Information Table S5), though the enhancement of $p\text{CO}_2$ in urban tributaries was lower than for CH_4 .

Overall, surface values of CH_4 and CO_2 in the HRE exceeded atmospheric saturation concentrations (2 μatm and 400 μatm , respectively) for almost all measurements (i.e., > 99% of sites and sampling dates). CH_4 and $p\text{CO}_2$ values from midchannel sites in the HRE were consistent with the range of values reported for macrotidal estuaries worldwide (Tables 2–3). Furthermore, CH_4 concentrations for tributary sites were within the top 25% percentile of these values. Measurements of CH_4 and $p\text{CO}_2$ from bottom waters were 10–30% greater than surface values, suggesting that bottom sediments were the likely source of both gases with little in situ loss in the water column. Last, DOC and NO_3^- concentrations (NH_4^+ concentrations were below the

Fig. 4. Graphs illustrate comparison of average midchannel to tributary methane (CH₄) and carbon dioxide (CO₂) surface values for the (a) brackish urban region surrounding NYC between RK 0 and RK 19 and (b) the fresh suburban/rural region located between RK 84 and RK 175. In both regions, at least three midchannel and tributaries sites were utilized to calculate average concentrations. Brackish suburban/rural (RK 30–69) and fresh urban (RK 197–244) regions lack a substantial number ($n \leq 1$) of tributaries to make similar comparisons. Error bars are standard error of the mean.

limit of detection of 0.3 mg L⁻¹) were not significantly different between midchannel and tributary sites. Average midchannel concentrations for DOC and NO₃⁻ were 3.1 ± 0.6 mg L⁻¹ and 0.4 ± 0.2 mg L⁻¹, respectively.

Biogeochemical parameters largely explain variance in pCO₂ and CH₄ surface values

Biogeochemical parameters quantified in this study were used to explain the variance in midchannel CH₄ and pCO₂ surface values in multiple regression models. Regional summaries of all measured midchannel and tributary parameters are shown in Tables 4–5, respectively. In the brackish region, midchannel surface CH₄ concentrations were significantly explained ($r^2 = 0.41$, $F_{5,63} = 9$, $p < 0.001$) by variation (listed in order of importance) in salinity ($t = 5.6$), Chl *a* fluorescence ($t = -3.3$), enterococci concentrations ($t = 2.6$), oxygen

saturation ($t = 2.5$), and temperature ($t = 2.5$). However, the trend was not significant ($r^2 = 0.061$) in the fresh region (Supporting Information Table S6). The variance in midchannel pCO₂ values was explained ($r^2 = 0.85$, $F_{4,37} = 52$, $p < 0.001$), in order of importance, by oxygen saturation ($t = -9.1$), temperature ($t = 4.5$), NO₃⁻ concentration ($t = 2.4$), and enterococci concentration ($t = 2.2$) in the brackish region of the HRE. In the fresh region, variances in pCO₂ values were significantly explained ($r^2 = 0.89$, $F_{5,39} = 63$, $p < 0.001$) by similar factors in addition to river discharge ($t = 2.7$). CCA tests using all midchannel parameters demonstrated that location (sampling sites) from each designated region grouped together in multivariate space whether they were analyzed in brackish or fresh regions for both CH₄ (Fig. 5a,b) and pCO₂ (Fig. 5c,d) values or over the entire estuary (data not shown).

CH₄ and CO₂ efflux

The range of average CH₄ efflux for sites in the HRE was 61–354 μmol CH₄ m⁻² d⁻¹. The brackish urban region (292 ± 85 μmol CH₄ m⁻² d⁻¹) had the greatest average efflux followed by fresh suburban/rural (179 ± 33 μmol CH₄ m⁻² d⁻¹), urban fresh (123 ± 24 μmol CH₄ m⁻² d⁻¹), and brackish suburban/rural (122 ± 15 μmol CH₄ m⁻² d⁻¹) regions (Table 6). This pattern differed from CH₄ surface concentrations due primarily to the different wind speeds characteristic of each region. Average CO₂ efflux ranged 9–69 mmol CO₂ m⁻² d⁻¹. Similar CO₂ efflux values were quantified in the brackish urban (29 ± 5 mmol CO₂ m⁻² d⁻¹), brackish suburban/urban (35 ± 6 mmol CO₂ m⁻² d⁻¹), and fresh suburban/rural (41 ± 6 mmol CO₂ m⁻² d⁻¹), with the lowest values observed in the fresh urban (13 ± 2 mmol CO₂ m⁻² d⁻¹) regions of the HRE (Table 6). All CH₄ and CO₂ efflux values are detailed in Supporting Information Tables S8, S9.

Discussion

CH₄ surface concentrations were highest in urban areas

Consistent with H1, significantly greater midchannel CH₄ concentrations were observed in close proximity to both NYC (brackish urban) and Albany (fresh urban) at opposite ends of the tidal HRE compared with the less developed midestuary (brackish and fresh suburban/rural), resulting in a U-shaped concentration pattern for CH₄. In contrast, midchannel pCO₂ surface values were similar throughout the HRE with no significant differences among average values across the brackish urban, brackish suburban/rural, and fresh suburban/rural regions. Elevated surface concentrations of CH₄ (3.1×) and CO₂ (1.6×) in urban tributaries, compared with adjacent midchannel sites, supported H2. The higher surface values of CH₄ and CO₂ quantified in urban tributaries and tidal straits, each containing up to 50 sewage delivery sites (NYCDEP 2009), are likely the result of direct inputs of GHGs transported along with sewage discharges, which have been quantified directly in streams and inland waters (Alshboul et al. 2016; Martinez-

Table 2. CH₄ surface concentrations and efflux ranges reported in estuaries.

Site	Concentration (nmol L ⁻¹)	Efflux (μmol m ⁻² d ⁻¹)	Reference
Guanabara Bay (BR)	19–11,803	242–4798	Cotovicz et al. (2016)
Pearl River (CN)	23–2984	NM	Chen et al. (2008a)
Rhine (NL)	4–1437	130*	Middelburg et al. (2002)
Oregon estuaries (US)	6–697	3–290	de Angelis and Scranton (1993)
Loire (FR)	16–671	130*	Middelburg et al. (2002)
Humber (GB)	13–667	NM	Upstill-Goddard et al. (2000)
Hudson River (US)	65–660	–6 to 1370	This study
Tributaries	105–5762	NM	
Tyne (GB)	13–654	NM	Upstill-Goddard et al. (2000)
Ivory Coast estuaries (CI)	56–602	54–877	Koné et al. (2010)
Gironde (FR)	4–559	130*	Middelburg et al. (2002)
Pulicat Lake (IN)	94–501	54–280	Shalini et al. (2006)
Scheldt (NL/BE)	20–485	130*	Middelburg et al. (2002)
Randers Fjord (DK)	28–420	70–410	Abril and Iversen (2002)
Thames (GB)	5–273	130*	Middelburg et al. (2002)
Douro (PT)	15–128	130*	Middelburg et al. (2002)
Lupar and Saribas (MY)	4–114	23–89	Müller et al. (2016a)
Elbe (DE)	4–111	130*	Middelburg et al. (2002)
Ems (DE)	51–91	130*	Middelburg et al. (2002)
North Creek (AU)	44–89	7–51	Maher et al. (2015)
Rio San Pedro (ES)	11–88	34–150	Ferrón et al. (2007)
Yangtze (CN)	6–49	41–225	Zhang et al. (2008)
Sado (PT)	37–40	130*	Middelburg et al. (2002)

List of reported values for methane (CH₄) surface concentrations and efflux ranges from predominantly macrotidal estuaries organized from highest to lowest maximum surface concentrations.

Efflux is reported as a range when data are available, otherwise as an average reported by the authors, or labeled as not measured (NM) if efflux was not determined.

*Average efflux determined with generalized global estuarine parameters (e.g., gas transfer velocity).

Cruz et al. 2017; Smith et al. 2017), but not in estuaries until recently (Garnier et al. 2013; Marescaux et al. 2018).

Increased microbial production of GHGs in response to DOC and DIN additions from wastewater inputs may be another possible mechanism, which was recently observed in a parallel study with NYC embayments (B. A. Brigham unpubl.). Similar conclusions about the importance of urban inputs in CH₄ concentrations have been previously posited for the lower HRE (de Angelis and Scranton 1993). The magnitude of midchannel CH₄ surface concentrations observed here were similar to those reported by de Angelis and Scranton (1993) but two times less than those reported by Hammond et al. (1977). Decreases in midchannel CH₄ concentrations since Hammond et al. (1977) likely reflect the decline in anthropogenic inputs that has occurred during the intervening years (Brosnan et al. 2006).

pCO₂ surface values were strongly linked to multiple biogeochemical parameters

Our combined CH₄, CO₂, and biogeochemical data enabled regression analyses relating GHG surface concentrations to anthropogenic indicators (e.g., enterococci) supporting H3

and allowing us to test the connection that has been speculated to exist in earlier publications. Here, we provide further data that support the link between urban wastewater input and enhanced CH₄ and CO₂ efflux. Multiple linear regression analyses demonstrated that enterococci concentrations (an indicator of anthropogenic inputs), as well as O₂ saturation (indicating the balance between net autotrophic and heterotrophic activity), NO₃⁻, and temperature (a driver of microbial rates) explained the majority CH₄ and pCO₂ surface value variance in brackish surface waters.

Anthropogenic indicators, however, did not explain variation in GHG surface concentrations in the fresh region of the HRE. Rather, surface pCO₂ values in freshwaters were positively correlated to oxygen saturation, river discharge, and temperature. In fact, the lowest pCO₂ surface values in the HRE were observed in Albany (for all sampling periods) at the fresh terminus of the HRE. Overall, the regression models indicate that physical and chemical factors such as salinity, temperature, and oxygen saturation, as well as the anthropogenic indicator enterococci, and NO₃⁻ concentrations were significant controlling factors of midchannel CH₄ and pCO₂ surface values. The regression models could be used to explore whether enterococci and

Table 3. CO₂ surface concentrations and efflux reported in estuaries.

Site	Concentration (μatm)	Efflux ($\text{mmol m}^{-2} \text{d}^{-1}$)	Reference
Recife (BR)	276–22,470	NM	Noriega et al. (2013)
Scheldt (NL/BE)	125–9425	19*	Frankignoulle et al. (1998)
Ivory Coast estuaries (CI)	0–9000	20–34	Koné et al. (2009)
Pearl River (CN)	560–8350	131	Guo et al. (2009)
Satilla River (US)	400–8200	116	Cai and Wang (1998)
Sado (PT)	575–5700	11*	Frankignoulle et al. (1998)
Lupar and Saribas (MY)	297–5504	63–95	Müller et al. (2016b)
Thames (GB)	505–5200	27*	Frankignoulle et al. (1998)
Yangtze (CN)	200–4600	0–266	Zhai et al. (2007)
Rio San Pedro (ES)	380–3760	14*	Ferrón et al. (2007)
Ems (DE/NE)	560–3755	24*	Frankignoulle et al. (1998)
Guanabara Bay (BR)	22–3715	–50 to 85	Cotovicz et al. (2015)
York River (US)	113–3467	–6 to 107	Raymond et al. (2000)
Randers Fjord (KD)	220–3440	–5 to 53	Gazeau et al. (2005)
Altamaha Sound (US)	493–3380	13 [†]	Jiang et al. (2008)
North Creek (AU)	600–3000	19–70	Maher et al. (2015)
Loire (FR)	630–2910	24*	Abril et al. (2003)
Gironde (FR)	465–2860	11*	Frankignoulle et al. (1998)
Duplin River (US)	500–2500	58*	Wang and Cai (2004)
Doboy Sound (US)	375–2400	33 [†]	Jiang et al. (2008)
Sapelo Sound (US)	375–2400	29 [†]	Jiang et al. (2008)
Douro (PT)	1330–2200	28*	Frankignoulle et al. (1998)
Tamer (GB)	380–2200	27*	Frankignoulle et al. (1998)
Oyster (US)	84–2003	12 [†]	Hunt et al. (2011)
Hudson River (US)	460–1930	1–196	This study
Tributaries	179–5530	NM	
Rhine (NE)	545–1990	15*	Frankignoulle et al. (1998)
Bellamy (US)	148–1515	13 [†]	Hunt et al. (2011)
Cocheco (US)	84–1187	10 [†]	Hunt et al. (2011)
Elbe (DE)	580–1100	19*	Frankignoulle et al. (1998)
Shark River (US)	1285 [‡]	44 [†]	Koné and Borges (2008)

List of reported values for carbon dioxide ($p\text{CO}_2$) surface concentrations and efflux ranges from predominantly macrotidal estuaries organized from highest to lowest maximum surface concentrations which have been summarized previously by a combination of Borges and Abril (2011) and Chen et al. (2013).

Efflux is reported as a range when data are available, otherwise as an average presented by the authors, or labeled as not measured (NM) if efflux was not determined.

*Average values procured from Borges and Abril (2011).

[†]Average values procured from Chen et al. (2013).

[‡]Average $p\text{CO}_2$ is reported as original data source is unavailable.

perhaps other anthropogenic indicators (e.g., micropollutants) explain patterns of GHG concentration and efflux data in other urbanized estuaries.

$p\text{CO}_2$, DOC, NO_3^- , and NH_4^+ spatial and temporal patterns in the HRE

Midchannel $p\text{CO}_2$ surface values were similar in the lower estuary and midestuary (Regions 1, 2, and 3) with significantly lower values observed in the fresh urban region. In tidal estuaries worldwide (Chen et al. 2012, 2013) including previous research in the HRE (Raymond et al. 1997), higher estuarine $p\text{CO}_2$ values are typically observed in the freshwater terminus

or the upper estuary, in contrast to the results reported here. In general, the highest $p\text{CO}_2$ concentrations in fresh estuarine waters have been explained by the large delivery of organic matter inputs from terrestrial surface runoff and subsequent heterotrophic consumption (McCallister et al. 2004; Cole and Caraco 2006). In addition, greater rates of biological productivity (CO_2 consumption) in brackish waters and the dilution of supersaturated $p\text{CO}_2$ riverine waters with less saturated coastal waters (Chen et al. 2008a,b; Guo et al. 2009) deplete $p\text{CO}_2$ in the brackish and saline waters. The reasons for the difference in $p\text{CO}_2$ patterns observed between Raymond et al. (1997) and our own data may be explained by the relatively

Table 4. Midchannel surface sample measurements.

Region*	CH ₄ conc. (nmol L ⁻¹)	pCO ₂ value (μatm)	Enterococci (most probable numbers)	DOC (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)
Surface measurements					
1	309 (20)	1203 (74)	12 (4)	2.6 (0.1)	0.4 (0.0)
2	182 (8)	1187 (75)	6 (2)	2.9 (0.1)	0.4 (0.0)
3	217 (15)	1327 (51)	52 (39)	3.3 (0.1)	0.5 (0.0)
4	284 (29)	868 (51)	337 (125)	3.5 (0.1)	0.5 (0.0)
Region*	Temp. (°C)	Salinity	O ₂ sat. (%)	Turbidity (nephelometric turbidity units)	Chl <i>a</i> (relative fluorescence units)
Probe measurements					
1	21.4 (0.7)	15.2 (1.1)	87.8 (2.1)	23.3 (4.3)	5.7 (1.3)
2	23.0 (0.6)	5.5 (0.5)	91.8 (1.4)	19.0 (1.4)	8.3 (1.1)
3	21.9 (0.6)	0.2 (0.0)	91.2 (1.1)	30.7 (2.9)	3.7 (0.5)
4	21.7 (0.8)	0.1 (0.0)	101.0 (1.5)	33.6 (6.4)	2.1 (0.4)

Parameters include methane (CH₄) concentrations, carbon dioxide (pCO₂) values, DOC, nitrate (NO₃⁻), oxygen (O₂) saturation, and Chl *a*.

Ammonium (NH₄⁺) concentrations were below the limit of detection (< 0.15 ppm).

Values in parenthesis are standard errors.

*The Hudson River was divided into four regions: region 1 (brackish urban, RK 0–19), region 2 (brackish suburban/rural, RK 30–69), region 3 (fresh suburban/rural, RK 84–182), and region 4 (fresh urban, RK 197–245) to bin data by both salinity and anthropogenic input.

lower river flow (50% compared to our study) during the Raymond et al. (1997) study (USGS, accessed April 2018, https://waterdata.usgs.gov/nwis/uv?site_no=01358000). Lower river flow would increase water residence time—increasing sedimentation of organic matter, enhancing heterotrophy (Crawford et al. 2016), and biogeochemical transformations, as well as facilitating the accumulation of GHGs (Raymond et al. 2012; Borges et al. 2018).

Month-to-month variations in pCO₂ surface values were similar to those in previous studies conducted in the brackish (Griffith and Raymond 2011) and fresh HRE (Raymond et al. 1997; Cole and Caraco 2001), and similarly the pCO₂ values varied by month. A similar enhancement was not observed

with CH₄ surface concentrations during warmer months. NO₃⁻, but not NH₄⁺, was detected throughout the HRE including tributaries and nearshore sites surrounding NYC. High oxygen saturation concentrations observed (>87%) for all cruises may account for detectable NO₃⁻ concentrations.

Efflux estimates vary with wind speed

GHG efflux calculations in estuarine systems are characterized by significant uncertainties, which have led to large ranges in reported worldwide values (Raymond and Cole 2001; Zappa et al. 2003; Borges and Abril 2011). Efflux is dependent on the concentration difference between the surface and atmosphere of each gas as well as the turbulence mediated transfer

Table 5. Tributary surface sample measurements.

Region*	CH ₄ conc. (nmol L ⁻¹)	pCO ₂ value (μatm)	Enterococci (MPNs)	DOC (mg L ⁻¹)	NO ₃ ⁻ (mg L ⁻¹)
Surface measurements					
1	957 (176)	1925 (109)	157 (56)	2.6 (0.1)	0.3 (0.0)
3	633 (93)	1022 (81)	197 (120)	3.3 (0.3)	0.3 (0.1)
Region*	Temp. (°C)	Salinity	O ₂ sat. (%)	Turbidity (NTUs)	Chl <i>a</i> (RFUs)
Probe measurements					
1	21.0 (0.6)	20.7 (0.7)	79 (2.1)	13.4 (1.7)	12.1 (1.3)
3	21.9 (0.9)	0.1 (0.0)	101 (1.1)	10.9 (2.3)	4.8 (0.5)

Parameters include methane (CH₄) concentrations, carbon dioxide (pCO₂) values, DOC, nitrate (NO₃⁻), oxygen (O₂) saturation, and Chl *a*.

Ammonium (NH₄⁺) concentrations were below the limit of detection (< 0.15 ppm).

Values in parenthesis are standard errors.

*The Hudson River was divided into four regions: region 1 (brackish urban, RK 0–19), region 2 (brackish suburban/rural, RK 30–69), region 3 (fresh suburban/rural, RK 84–182), and region 4 (fresh urban, RK 197–245) to bin data by both salinity and anthropogenic input. Regions 2 and 4 had no accessible tributaries—data from the nearshore sites were not used for analysis and can be found in Supporting Information Table S10.

Fig. 5. Canonical correlation analyses of CH₄ and CO₂ surface concentrations to biogeochemical parameters in the HRE. Analyses includes: **(a)** CH₄ surface concentrations in the brackish (RK 0–69) HRE, **(b)** CH₄ surface concentrations in the fresh (RK 84–244) HRE, **(c)** pCO₂ surface values in the brackish (RK 0–69) HRE, and **(d)** pCO₂ surface values in the fresh (RK 84–244) HRE. Data illustrate similarities in correlations between GHG concentrations and biogeochemical parameters for sampling sites (i.e., sites within each region group together in multivariate space). Error bars are standard error of the mean.

(or gas transfer velocity) as dictated by physical conditions (Wanninkhof et al. 1993). We used both daily and weekly wind speeds from a series of three towers with meteorological equipment above 10 m to calculate gas transfer velocity values. The accuracy of these values is critical as wind speed is typically utilized in a power or log function to ultimately determine efflux. Our methodology established *potential* ranges of CH₄ and CO₂ efflux rather than attempting to select a single model or gas transfer velocity value. In fact, the variability in efflux values

calculated using different models created enough uncertainty in spatial and temporal efflux patterns that we chose to focus instead on the analysis of surface concentration patterns described above. In our study, we did not attempt to select the “best” gas transfer velocity model, but instead attempted to highlight the importance of differing assumptions in the existing models, while constraining *potential* ranges of CH₄ and CO₂ efflux. Both comprehensive spatial coverage of wind speed (at each measurement site) and greater temporal coverage to

Table 6. CH₄ and CO₂ efflux from HRE.

Region*	River dist. (km)	Area (km ²)	CH ₄ efflux (μmol m ⁻² d ⁻¹)	CO ₂ efflux (mmol m ⁻² d ⁻¹)	CO ₂ e efflux (mmol m ⁻² d ⁻¹)	CO ₂ e total (MKT yr ⁻¹)
1	0–20	27	292 (84)	29 (5)	36 (6)	16 (2)
2	20–69	124	122 (15)	35 (6)	38 (6)	076 (12)
3	69–197	130	179 (33)	41 (6)	45 (5)	95 (13)
4	197–245	19	123 (23)	13 (2)	16 (2)	5 (1)
Total	0–245	300	—	—	—	177 (16)

Values in parenthesis are the standard error of mean.

MKT represents metric kilotons and CO₂e represents CO₂ equivalents.

*The Hudson River was divided into four regions: region 1 (brackish urban, RK 0–19), region 2 (brackish suburban/rural, RK 30–69), region 3 (fresh suburban/rural, RK 84–182), and region 4 (fresh urban, RK 197–245) to bin data by both salinity and anthropogenic input.

better quantify variation in GHG surface concentrations would improve the accuracy of our efflux values.

The entire HRE was a source of both CO₂ and CH₄

The vast majority (>99%) of CH₄ and CO₂ surface measurements, including all midchannel measurements, showed supersaturation. The HRE was thus a source of GHG to the atmosphere in all locations and times. Our comparison of CH₄ and *p*CO₂ surface values within the HRE to estuaries worldwide demonstrated that the range of CH₄ concentrations, as well as average efflux values, is among the top quartile of reported values (Middelburg et al. 2002; Borges and Abril 2011). High concentrations and efflux values were observed despite the short residence time of the HRE, especially in saline waters surrounding NYC, compared to other studied estuaries likely due in part to wastewater inputs (Howarth et al. 2006). Overall, the higher concentrations of CH₄ in sewage delivery areas in addition to the correlation between CH₄ and enterococci concentrations indicate that anthropogenic additions resulted in a higher baseline of CH₄ concentration (and likely flux) than would otherwise exist in an undisturbed HRE. The two estuaries with considerably higher CH₄ surface concentrations, Guanabara Bay and Pearl River estuaries, also have a history of extremely high anthropogenic inputs (Chen et al. 2008a; Cotovicz et al. 2016). CH₄ surface concentrations were greater, on average, in tributaries than in other sites, corroborating high values reported in small rivers and streams (Butman and Raymond 2011; McGinnis et al. 2016; Sawakuchi et al. 2017), especially those impacted directly by wastewater or agricultural inputs (Rajkumar et al. 2008; Garnier et al. 2013; Borges et al. 2018; Drake et al. 2018).

Conversely, *p*CO₂ surface and efflux values observed here are among the bottom quartile worldwide of reported estuarine values summarized by Chen et al. (2013). The range of CO₂ efflux (13–35 mmol CO₂ m⁻² d⁻¹) values observed was well below both the range (86–105 mmol CO₂ m⁻² d⁻¹) determined from the 2004 to 2005 data sets produced largely from polluted European estuaries (Borges 2005; Borges et al. 2005) as well as more recent averages (48–58 mmol CO₂ m⁻² d⁻¹) sourced from a larger diversity of estuaries (Laruelle et al.

2010). However, the values here are similar to the average values observed from the estuaries (*n* = 15) along the eastern seaboard of the United States (Chen et al. 2013). These worldwide differences are driven by two main factors: (1) European estuaries are consistently significantly windier (2–4×) than those found in North America, increasing average efflux values and (2) extremely high *p*CO₂ concentrations are largely reported in European, Chinese, and Brazilian estuaries.

Using average values for each region, we calculated that the tidal HRE annually releases a total of 191 metric kiloton CO₂ equivalents (Table 6). This represents 8% of NYC's reported wastewater treatment GHG footprint (City of New York, Accessed April 2018, https://www.dec.ny.gov/docs/administration_pdf/nycghg.pdf) and demonstrates the large impact of urban inputs. However, this estimate of total GHG efflux was based only on mid-channel data. Given higher surface GHG concentrations in tributaries, combined with greater frictional forces and higher gas transfer velocities, our total efflux value is likely an underestimate.

Hotspots and hot moments enhance production estimates and add measurement uncertainties

These results build upon those reported by Griffith and Raymond (2011) where net heterotrophy in the saline HRE was found to be dictated predominantly by available DOC from anthropogenic inputs. Our data illustrate that the higher baseline of GHG production in urban areas is due to enhanced DOC and DIN loading from terrestrial sources. The nature of anthropogenic inputs in the HRE, which are delivered by submerged outfalls that flow following both sewage treatment and precipitation events (NYCDEP 2004), likely lead to both “hot-spots” and “hot moments” of microbial heterotrophic activity (McClain et al. 2003). The majority of heterotrophy in anaerobic soils/sediments is often restricted to these “hot moments” (Guenet et al. 2010). Data focused on the impacts of anthropogenic (and natural) inputs in relevant scales are critically important areas for future study. In addition, we did not measure N₂O, a GHG with 298× warming potential compared with CO₂ over a 100-yr period (Ciais et al. 2013). Quantifying N₂O is of major import for estuaries as denitrification has been

demonstrated to be an important GHG source (Marescaux et al. 2018) in urban estuaries and surrounding wetlands due to high anthropogenic NO_3^- inputs (Schlesinger 2009; Doney 2010).

Conclusions

The HRE was a source of both CH_4 and CO_2 to the atmosphere throughout the sampling season, with the highest CH_4 concentrations observed in urbanized regions, notably the major sewage delivery areas of NYC. This comprehensive study was unique in that it linked GHG surface values to anthropogenic indicators supporting additional estuarine studies that demonstrated that urban influence enhances GHG production from estuaries. The urban influence on estuarine GHG production has rarely been explicitly linked from prior field measurements (Burgos et al. 2015).

Our study demonstrates that regression models can explain a very high percentage of the variability in $p\text{CO}_2$ and CH_4 surface values in this complex estuary with multiple natural and anthropogenic driven gradients. Moreover, the parameters used for these models are relatively simple to measure. More robust measurements including complete diel and seasonal cycle sampling as well as expanded testing in other estuaries (urban and otherwise) could assist with model validation. Using such models, the need for relatively expensive and time-consuming GHG measurements decreases, which would facilitate GHG flux estimates from estuaries, especially those located in the undeveloped world (Borges and Abril 2011). Our data demonstrate that inputs from a coastal megacity partially explain GHG concentrations in receiving estuarine waters. Multifactor data sets like this one provide additional insight into the processes that dictate urban estuarine GHG dynamics imparting scientists and management with more tools to better estimate estuarine urban climate impacts.

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Acknowledgments

We thank WeatherFlow and F.O. Nitsche for providing access and use of meteorological and volume data in the Hudson River Valley, respectively. We also thank Riverkeeper, especially John Lipscomb, Captain of the Riverkeeper patrol boat, R. Ian Fletcher, for logistical and sampling support. Carol Knudson of Lamont Doherty Earth Observatory also helped with logistics and sampling. In addition, we thank Lindsey Macpherson for editing of the manuscript. Last, we thank the efforts of the editors of *Limnology and Oceanography*, as well as our anonymous reviewers whose contributions greatly strengthened this manuscript. This research was supported by the Hudson River Foundation Mark B. Bain Graduate Fellowship, “Evaluating greenhouse gas efflux across a rural-urban estuarine gradient: assessing the impact of incomplete wastewater treatment on the Hudson River” awarded to BAB. Biogeochemical sampling was supported by the Sloan Foundation CUNY JFRASE, Riverkeeper, and PSC-CUNY awards to GDO and JAB.

Conflict of Interest

None declared.

Submitted 26 June 2018

Revised 27 October 2018

Accepted 25 April 2019

Associate editor: Bo Thamdrup