Progress in quantifying coastal N_2O emissions in order to close the (terrestrial) biogenic nitrogen budget

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Abstract
Aquatic nitrous oxide (N_2O) emissions are both a poorly constrained component of the global greenhouse gas budget and a rarely quantified loss pathway during transport of reactive nitrogen (N) from land to sea. Quantification of N_2O losses from coastal environments are particularly vital, as these regions are both biogeochemical hotspots and subject to dramatic increases in N loading from urbanisation and upstream agricultural intensification. This study aimed to link spatial intensive measurements of water-atmosphere N_2O fluxes with biogeochemical controls across a land-use intensity gradient. We used recently developed cavity enhanced laser absorption spectroscopy to obtain quasi continuous (1 sec^{-1}) measurements of dissolved N_2O across the salinity gradient in eight sub-tropical estuaries subjected to varying land-use intensities. Land use had a dramatic effect: N_2O fluxes from estuaries surrounded by >60% woody vegetation were an order of magnitude lower than from those surrounded by <30% woody vegetation, and the estuary mouth created a net N_2O sink only in the four least impacted systems. The fact that N_2O fluxes, but not nitrate concentrations, peaked at the freshwater-saltwater interface (1-5 psu) in seven of eight surveyed estuaries suggested that benthic processes, not point source pollution, controlled N_2O emissions. The fact that groundwater infiltration did not drive N_2O peaks supports the idea that benthic biology, rather than hydrology, regulates estuarine N_2O losses. As N_2O did not track the spatial patterns of the commonly measured N species (ammonium, nitrate), an accurate catchment N balance could only be achieved via directly measuring estuarine N_2O emissions.

Keywords
Aquatic greenhouse gasses, Continuous *in-situ* measurements, Surface water – groundwater interactions, Queensland, Estuaries, ^{222}Rn

Introduction
Despite increasing terrestrial nitrogen (N) inputs, the percentage that ends up in the food we eat has remained relatively constant, resulting in a 'cascade' of excess N moving from the land to the sea and atmosphere. The fact that ~15% of global N agriculture inputs remain unaccounted for (Schlesinger, 2009) currently limits both the effectiveness of N management strategies and the accuracy of environmental impact assessments. Nitrous oxide (N_2O) emitted from coastal environments, a hot spots of biological activity capable of regulating the movement of nutrients into the marine environment, represent a rarely measured pool that could prove instrumental in closing this gap (Gardner et al., 2016). The need to quantify how rapid urban development and agricultural intensification in regions such as sub-tropical Australia is altering N fluxes to the marine environment remains limited by the poorly understood relationship between N inputs and microbial N turnover during transport.

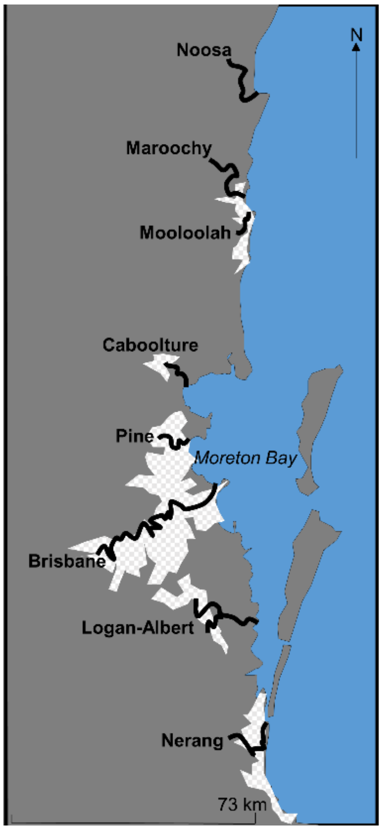
Current models assume a constant relationship between surface water labile N loading (nitrate (NO_3^-) concentrations) and aquatic N_2O emissions. However, evidence that N_2O producing microbes do not respond linearly to inputs means that this relationship falls apart under land-use change scenarios (Mulholland et al., 2008). The effect these changes will have on N export is further complicated by the knowledge that the expected alterations to benthic habitats due to, e.g., increased sediment loading, may have a direct impact on microbial N_2O production and reduction. A recent review found that coastal areas underlain by different benthic habitats can be significant N_2O sources, or even sinks (Murray et al., 2015). These factors indicate that the proportion of estuarine N inputs lost as N_2O will change as land use intensifies.

The purpose of this study is therefore to constrain the controls on estuarine N_2O concentrations over nutrient loading gradients. Continuous *in-situ* measurements of estuarine N_2O concentrations using cavity enhanced laser absorption spectroscopy made it possible to untangle the degree to which these fluxes are a product of, 1) N loading, 2) groundwater infiltration, or, 3) in-situ (benthic) production. This technology, recently developed to provide novel insights into coastal carbon (C) cycling (Call et al., 2015; Maher et al., 2013), was adapted here to assess changes in N_2O fluxes over the estuarine gradient in eight rivers under varying degrees of land-use development.

Methods

Surveys were carried out in eight estuaries that spanned an impact gradient from relatively pristine (Noosa) to highly impacted urban (Brisbane) systems (Table 1). Four catchments retained >50% of land area under woody vegetation (Noosa, Maroochy, Nerang, Pine), whereas agriculture was the dominant land-use in two catchments (Brisbane, Logan-Albert). Combining land-use information with 15 years data on N, phosphorous, and turbidity loads (EHMP, 03/2016), three systems were categorised as minimally impacted (Noosa, Nerang, Mooloolah), three as highly impacted (Brisbane, Logan-Albert, Caboolture), and two as moderately impacted (Pine, Maroochy).

Table 1: Dominant land-use in eight SE Queensland estuaries is categorised as either urban (%U: suburban + urban), agricultural (%A: pasture + cropping + feed lots), or woody (%W: scrublands + native forests + tree plantations). The number of sewage treatment plants (STPs) adjacent to the waterway are noted. Land-use %cover numbers are based on published values for 2012-2014 from the Queensland state government (www.qld.gov.au, accessed 18/04/2016). The map shows the sampled reaches of each estuary, with grey pattern indicating areas of urban-suburban land-use.



Catchment	Land-use			
Area	%U	%A	%W	STPs
Noosa *854 km²*	6	33	61	0
Maroochy *630 km²*	21	24	55	3
Mooloolah *223 km²*	45	26	29	0
Caboolture *468 km²*	32	46	22	2
Pine *825 km²*	14	26	60	1
Brisbane *9,612 km²*	11	67	22	3
Logan-Albert *5,863 km²*	6	73	21	3
Nerang *498 km²*	2	25	73	0

Longitudinal surveys were carried out by boat in each estuary in Mar-2016 (wet season). N_2O measurements were complemented by continuously on-line measurements of radon (^{222}Rn; which indicates groundwater infiltration) and basic water chemistry (salinity, pH, dissolved oxygen, and temperature). Concurrent measurements were made by continuously pumping water from ~20 cm below the surface through the gas equilibrator at a 3 l min^{-1}. On board, this water was split between the gas equilibrator, a water collection port, and a bucket holding two water chemistry Sondes (Hydrolab). Air from the gas equilibrator was then passed through a desiccator to remove residual moisture and passed through either a [$CH_4/N_2O/CO_2$] analyser (Picarro) or a RAD7 (Durridge), as described in (Erler et al., 2015). Surface water samples were collected every 2 psu (18 samples per estuary) to measure the concentration of non-gaseous dissolved N forms (NH_4^+,

NO_2^-, NO_3^-, and DON), as well as components known to influence N turnover including C (DOC and DIC) and phosphorous (P, as TP and PO_4^{2-}). This approach enabled the complete quantification of N_2O fluxes from the marine mouth to the freshwater source of each estuary. Fluxes were calculated by combining the continuously measured surface water N_2O concentrations with changes in salinity, water temperature, and wind-speed (Clough et al., 2007; Wanninkhof, 2014).

Results & Discussion

Overall there was an order of magnitude difference in both N_2O fluxes and concentrations in the estuaries under intensive land-use versus those from catchments with the majority of land-use under woody vegetation (Figure 1). As expected, within each estuary NO_3^- concentrations increased from the salt water mouth to the freshwater source (Table 2). In contrast, the highest N_2O fluxes tended to occur at intermediate salinities (Figure 1). These factors combined to create highly variable N_2O:NO_3^- (μg N_2O-N:μg NO_3^--N) ratios. N_2O:NO_3^- tended to be lowest near the mouth, but varied between estuaries. The highest ratio (0.2) occurred in the upstream portion of the Caboolture.

Table 2: NO_3^- concentrations in the freshwater (upstream) reaches v. in the most saline (mouth) reaches of eight SE Queensland estuaries.

Estuary	Upstream	Mouth
	NO_3^- *mg N l^{-1}*	**NO_3^-** *mg N l^{-1}*
Noosa	0.026 ± 0.04	0.0064 ± 0.02
Maroochy	0.094 ± 0.1	0.0097 ± 0.03
Mooloolah	0.042 ± 0.03	0.0045 ± 0.01
Caboolture	0.13 ± 0.1	0.0076 ± 0.02
Pine	0.030 ± 0.04	0.010 ± 0.04
Brisbane	0.16 ± 0.1	0.089 ± 0.1
Logan-Albert	0.28 ± 0.3	0.038 ± 0.1
Nerang	0.038 ± 0.07	0.014 ± 0.03

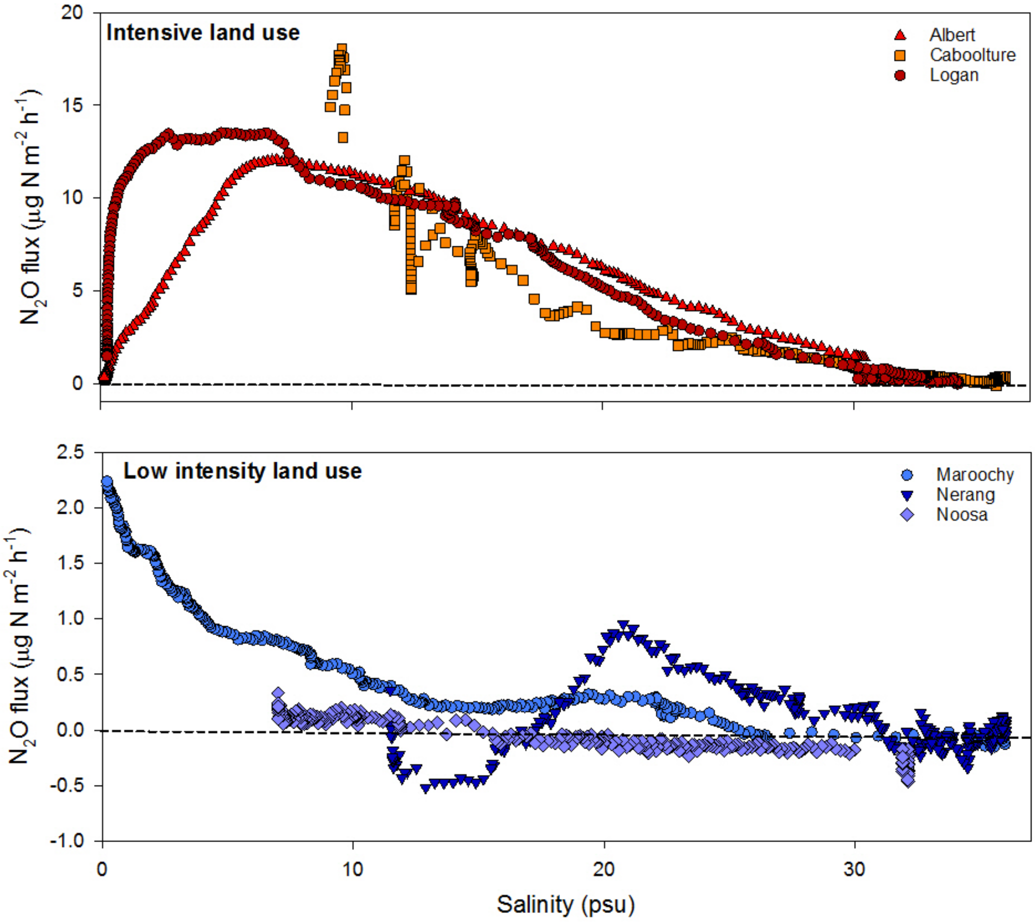


Figure 1: N_2O fluxes from selected estuaries under intensive land use (top) and lower intensity land use (bottom). The Albert branches from the Logan at ~21 psu.

Groundwater can provide a direct flux of terrestrial N to coastal systems, creating spikes in N gaseous emissions disproportionate to the surface water loads. We therefore measured ^{222}Rn in order to identify areas with large groundwater influxes. While there was an overall correlation between N_2O and ^{222}Rn concentrations (r = 0.2, p<0.05), N_2O concentrations did not relate to groundwater influx in the highest emitting estuaries (Caboolture, Albert-Logan). This indicates either that N_2O emissions in these systems are driven by the consumption of the sewage effluent that directly enters the groundwater (Table 1) or by the horizontal influx of agricultural DIN via drainage ditches, overland flow, and bank erosion. This lack of a clear relationship between N_2O and ^{222}Rn concentrations indicates that, even in highly impacted estuaries, N_2O concentrations are primarily the product of in-situ production, not of degassing terrestrial sources.

The finding that the most saline regions of 'pristine' estuaries served as N_2O sinks was surprising. While some chamber experiments found that mangroves can uptake N_2O (Murray et al., 2015), the scale of the current dataset provides the first evidence that these negative fluxes are relevant at the landscape scale. It is, however, unclear whether N_2O corresponds with higher N attenuation, as multiple microbial processes can control N_2O production and reduction. A combination of biogeochemical modelling and isotope work is underway to resolve this uncertainty.

Conclusions

A greater proportion of the surface water N is converted into N_2O in highly impacted estuaries than in minimally impacted estuaries. These intensive spatial surveys of dissolved N_2O show that intensifying land-use may be capable of changing these sub-tropical estuaries from net sinks to net sources of N_2O. This uniquely high resolution dataset revealed three unknowns that need to be resolved in order to accurately predict the role that coastal systems play in the terrestrial N budget:

- What conditions enable some estuaries to consume N_2O?
- How does N_2O production relate to estuarine N attenuation?

- Does the quality, or only the quantity, alter the relationship between NO_3^- concentrations and N_2O emissions?

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