The Gas Transfer at Water Surfaces (GTWS) symposium normally occurs every 5 years and has brought together scientists from countries all over the world. This topic is globally-important. Gas transfer is of great import for quantifying carbon dioxide (CO$_2$) uptake by the ocean as well as the emission of climate-relevant gases such as dimethylsulfide (DMS) and other volatile organic compounds. The focus is the physicochemical and biogeochemical processes that govern atmosphere-water gas exchange and fluxes. These include turbulence, shear, breaking waves, bubbles, and surfactants as well as the biology and chemistry of the microlayer. The conference covered all domains where air and water meet, including freshwater, estuarine, marine (coastal and open ocean) and polar regions, as well as laboratory and numerical studies.

GTWS was due to be held in Plymouth, UK in May 2020. At the last moment, we had to take the difficult decision to postpone the meeting due to the Covid outbreak. This put the local organising committee into a holding pattern, organising for an event ‘at some point’! A year down the line, we hosted a short ‘bitesize’ online event. This was attended by nearly 200 people online, was a great success and gave us confidence that we could run

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the main event in hybrid mode. A hybrid event would have the dual benefit of facilitating the participation of those unable to travel whilst also enabling those from further afield to reduce their (and the community’s) carbon emissions.

In May 2022, the main event finally took place, which was a great relief to the organising committee! The event was well-attended with nearly 100 participants (approx. 75% in-person, 25% online). Using Plymouth Marine Laboratory’s new technology for hybrid events, and with the help of an external company (Mindfully Wired; https://www.mindfullywired.org/), we hosted the hybrid event and switched effortlessly between the room and online participants during the Q&As. Those in the room and online clearly enjoyed the opportunity to have an open debate again.

We are pleased with how the GTWS symposium went, and particularly pleased that it clearly showed that you no longer have to travel to actively participate at a conference and present to the international community.

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Katherine Adler received a Bachelor’s degree in Environmental Engineering at Massachusetts Institute of Technology, USA, in 2016. She received a Master’s degree at Cornell University, USA, and is finishing her PhD at Cornell, investigating passive hydrodynamic mechanisms, such as capillary-gravity bow waves, impacting air-water gas transport enhancement in environmental and industrial applications. Katherine won the ‘Best Student Presentation’ at the 8th International Symposium on GTWS.

Laboratory investigation of significant gas transfer enhancement via capillary-gravity bow waves

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The rate at which gases, like carbon dioxide (CO₂) and oxygen, are absorbed into or released from water bodies depends on the aqueous bulk concentration and on the physical properties of the water surface and water-side near-surface motions. As wind speed increases, the gas transfer velocity increases. Gas transfer increases more rapidly with wind speed after waves begin to form on the water surface (e.g., Kanwisher, 1963; Broecker et al., 1978). When waves are present, the gas transfer velocity scales with the mean square slope of the waves (e.g., Jähne et al., 1987; Saylor and Handler, 1997). Capillary-gravity waves (~1 cm in length) are of particular interest because they are more common and steeper than gravity waves. Saylor and Handler (1997) isolated non-breaking capillary waves and achieved almost two orders-of-magnitude enhancement in gas transfer velocity, $k$, compared to the static case, over a 0.016-m²-area interface. However, analytical models have yet to explain such a dramatic increase, predicting up to 3- or 3.5-fold enhancement due to the steepest capillary waves, which are likely unstable over a large area (Szeri, 1997; Maclntyre, 1971; Hasse and Liss, 1980). Additionally, isolating the effect of these waves from the effect of wind-driven shear is difficult in the field or over a large area in general.

To further investigate the interfacial scalar flux enhancement due to capillary-gravity waves over a large area, we conducted several reaeration experiments with bow waves in a straight, open, recirculating flume (Figure 2). Bow waves form upstream of objects disturbing the water surface at sufficient relative flow speed (23 cm/s at standard conditions on an air-water interface). Based on analytical models relating capillary-gravity bow wave amplitude to peak external pressure at the object and velocity (assuming the object imposes a pressure field in the form of a Dirac delta function or imposes a fixed surface draw-down depth (Raphaël & de Gennes, 1996; Chevy & Raphaël, 2001), and estimating a peak pressure that scales with the stagnation pressure ($\frac{1}{2} \rho v^2$), it is hypothesised that the mean squared slope of these waves and the drag force on the object due to the waves scale approximately with velocity to the fourth power or greater. Such a dependence would suggest that gas transfer rate in the presence of these waves has a similarly strong dependence on flow velocity.
Capillary-gravity bow waves were generated over a 2-m² area using an array of vertical, 3.2-mm-diameter cylinders (dowels) suspended above the interface to penetrate the water surface by up to 1 cm. The total area of the air-water interface was 5.95 m², meaning 34% was populated with bow waves. In some cases, dowels were suspended from a conveyor belt apparatus to isolate the influence of relative dowel speed from that of flow speed, which contributes to other sources of mixing. Gas transfer velocity was measured by chemically removing dissolved oxygen from the water using cobalt chloride and sodium sulphite and fitting the curve of dissolved oxygen concentration over time, during reaeration, to a conservation of mass equation.

Cases with no dowels, stationary dowels, and moving dowels were compared at several relative velocities between 5 and 60 cm/s. The presence of the capillary-gravity bow waves increased gas transfer velocity by at least 20-68% compared to cases with similar background flow speeds and no dowels (Figure 3). When the base flow was reduced to about 5 cm/s and the dowels were conveyed against the flow at 60 cm/s, gas transfer was enhanced 607% over the 5 cm/s control case without dowels. It is clear that the enhancement in gas transfer due to these waves increases with velocity but it is not yet clear if that dependence is to the fourth power as hypothesized based on the analytical slope models mentioned previously.

It is also interesting to note that, while surfactants are associated with suppressed capillary wave amplitudes in the ocean, reducing surface tension while maintaining a constant relative velocity may actually increase the steepness of capillary-gravity bow waves (Broecker et al., 1978; Raphaël and de Gennes, 1996; Yeung and Ananthakrishnan, 1997). Therefore, the impact of these waves may be greater in salty water or in the presence of surfactants than that observed in our experiments, which were thus far conducted in clean, fresh water. Future experiments will test this hypothesis.

These results further support the significant role that capillary-gravity waves play in the transport of carbon dioxide and other low solubility gases.
across the air-water interface, even in the presence of other mixing-enhancing mechanisms, such as boundary layer shear.

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Charel Wohl did his PhD at Plymouth Marine laboratory in the UK, where he focused on the development and deployment of an air-sea equilibrator to measure dissolved volatile organic chemicals (VOCs) in seawater. In 2021, Charel moved to Barcelona, Spain, where he studies the broad range of VOCs emitted by the oceans.

Sea ice concentration impacts dissolved organic gases in the Canadian Arctic

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The marginal sea ice zone has been identified as a source of different climate-active gases to the atmosphere due to its unique biogeochemistry (Collins et al., 2017; Mungall et al., 2017). However, it remains highly undersampled, and the impact of summertime changes in sea ice concentration on the distributions of these gases is poorly understood. To address this, we present underway and depth profile measurements of dissolved methanol, acetone, acetaldehyde, DMS, and isoprene in the marginal sea ice zone of the Canadian Arctic during summer from the surface down to 60 m. The measurements were made using a segmented flow coil equilibrator coupled to a proton-transfer-reaction mass spectrometer.

These gases varied in concentrations with depth, with the highest concentrations generally observed near the surface. Underway (3-4 m) measurements showed higher concentrations in partial sea ice cover compared to ice-free waters for most compounds. The large number of depth profiles at different sea ice concentrations enables the proposition of the likely dominant production processes of these compounds in this area. Methanol concentrations appear to be controlled by specific biological consumption processes. Acetone and acetaldehyde concentrations are influenced by the penetration depth of light and stratification, implying dominant photochemical sources in this area. DMS and isoprene both display higher surface concentrations in partial sea ice cover compared to ice-free waters due to ice edge blooms. Differences in underway concentrations based on sampling region suggest that water masses moving away from the ice edge influences dissolved gas concentrations. DMS concentrations sometimes display a subsurface maximum in ice-free conditions, while isoprene more reliably displays a subsurface maximum. In the Arctic sea ice zone, subsurface maximum VOC concentrations are typical for biogenic gases due
to the high levels of productivity at the deep chlorophyll a maximum (Burgers et al., 2020).

Surface gas concentrations were used to estimate their air-sea fluxes. Despite obvious in situ production, we estimate that the sea ice zone is absorbing methanol and acetone from the atmosphere. In contrast, DMS and isoprene are consistently emitted from the ocean, with marked episodes of high emissions during ice-free conditions, suggesting that these gases are produced in ice-covered areas and emitted once the ice has melted. Largest air-sea fluxes were generally observed in ice-free areas as we linearly scale our computed flux to the open water fraction (Prytherch et al., 2017).

Our measurements show that the seawater concentrations and air-sea fluxes of these gases are clearly impacted by sea ice concentration (Figure 4). These novel measurements and insights will allow us to better constrain the cycling of these gases in the polar regions and their effect on the oxidative capacity and aerosol budget in the Arctic atmosphere (Abbatt et al., 2019).

![Figure 4: Schematic summarising the impact of seasonal sea ice melt on dissolved gas concentrations. Methanol, acetone and acetaldehyde are shown as “oxygenated volatile organic chemicals (VOCs)”, and dimethylsulfide (DMS) and isoprene are shown as “biogenic VOCs”. The shorter light beam represents ultraviolet rays, while the longer one represents photosynthetically active radiation.](image)

### References


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Raquel Renó de Oliveira is a PhD candidate at the Faculdade de Oceanografia da Universidade do Estado do Rio de Janeiro (FAOC/UERJ), Brazil. She is investigating the carbon dioxide fluxes at the interface between the ocean and atmosphere at the Brazilian continental shelf. Also, she is part of the Brazilian Research Network on Ocean Acidification (BrOA).

The CO₂ fluxes at the ocean-atmosphere interface on the Brazilian continental shelf: A review of its behaviour as a source or sink of atmospheric CO₂

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Most studies on the global carbon cycle have neglected the Southern Hemisphere oceans, especially in continental shelves and coastal zones, due to limitations of spatiotemporal sampling and the complexity of this region (Roobaert et al., 2019). The Brazilian coast, for example, although with continental size, it remains poorly studied in terms of the carbonate system and the carbon dioxide (CO₂) fluxes between ocean and atmosphere (Horta et al., 2020).

We prepared an overview from published papers about the ocean-atmosphere CO₂ fluxes along the Brazilian continental shelf, including nearshore areas, to characterise the current knowledge about the carbonate system, and to assess the Brazilian coastal zones behaviour as a source or sink of CO₂. For methodological purposes, the Brazilian shelf was divided into the regions South-South-east (S-SE, around -34°S to -18°S), North-North-east (N-NE, around -18°S to 5°N), and we further considered the whole Brazilian continental shelf in the global context.

In the literature we found about 50 regional papers (19 for S-SE, 31 for N-NE) and 53 papers about the Brazilian shore in the global context, between 2000 and early 2022. The main list was built by combining the search results from Web of Science and Scopus repositories. Studies in the N-NE region are concentrated in the Amazon River plume influence area, and the S-SE region presents studies on different coastal ecosystems, especially in the SE part of Brazil. In general, studies indicate that locally the CO₂ fluxes are widely influenced by seasonality, mesoscale, and synoptic oceanographic and meteorological processes, also by the large plumes from Da Plata (at the south) and Amazonas (at the north) rivers. Hence the same area can be a source or sink of CO₂, depending on the combination of different conditions.

The large-scale studies show that the continental shelf presents latitudinal range of CO₂ fluxes, where the Northeast region acts as a source of CO₂ to the atmosphere, the Southeast shows the neutral condition, and the South region acts as a sink of CO₂. This pattern is well summed up by Padin et al. (2010), showing that the mean CO₂ fluxes in these large areas during the boreal autumn between 2000 and 2008 were, respectively:
1.6 ± 0.6 mol CO\textsubscript{2} m\textsuperscript{2} year\textsuperscript{-1} (between 1\degree N to 15\degree S), 0.5 ± 0.7 mol CO\textsubscript{2} m\textsuperscript{2} year\textsuperscript{-1} (between 15\degree S to 31\degree S) and −3.2 ± 2.7 mol CO\textsubscript{2} m\textsuperscript{2} year\textsuperscript{-1} (between 31\degree S to 40\degree S). Due to the Amazon River plume, the North region acts mainly as a sink of CO\textsubscript{2}. We identified regional knowledge gaps, thus highlighting the need for long-term observations and monitoring initiatives alongshore to better understand the Brazilian continental shelf role in the global carbon budget.

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Greenhouse gases (CO₂, CH₄ and N₂O) emissions from a tropical microtidal estuary (Cochin, India)

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Greenhouse gases (GHGs) emissions from human activities are an important trigger of observed climate change since the mid-20th century. Carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) are the three primary GHGs and their emissions from the inland aquatic systems significantly contribute to global GHGs emissions. The tropical inland ecosystems are di-verse and have many region-specific characteristics and are currently not well integrated in global GHG budgets. The present study was conducted in a tropical region from Cochin estuary, south-west coast of India (Ramsar site: 1204, Figure 5). Rapid industrialisation and urbanisation in the last 4 to 5 decades in the regions adjoining the Cochin estuary and its upstream rivers have resulted in six-fold increase in nitrate and phosphate concentrations and four-fold increase in sediment organic carbon in this estuary (Martin et al., 2011). Consequent to this eutrophication, this estuary which was highly autotrophic about five decades ago (Qasim et al., 1969) has now been trans-formed to highly heterotrophic system (Gupta et al., 2009). Such changes can significantly impact the GHGs cycling in the Cochin estuary.

Surveys during early monsoon (April), monsoon (September), and post-monsoon (December) of 2012 showed highest supersaturation of CO₂ in the upstream but gradually decreased towards the sea. The strong negative correlations with pH (p = 0.005) and salinity (p = 0.05) pointed out riverine inputs as the main source of CO₂ in the estuary.
(Figure 6). The significant seasonal variation in $p$CO$_2$ ($p=0.005$) is attributed to the significant seasonality in substantial heterotrophic activities and the riverine inputs. On the other hand, the weak negative correlations for CH$_4$ with salinity and pH seemed to suggest that the riverine inputs are only a mild source (Figure 6). High concentrations of dissolved CH$_4$ in bottom waters as compared to that in surface waters and its significant positive correlation ($r^2=0.65$, $n=32$) with ammonia indicates that sediment methanogenesis is the major contributor of CH$_4$ in the estuary. High concentrations of N$_2$O during the monsoon and its positive correlation with NO$_3^-$ + NO$_2^-$ indicates that nitrification is the major pathway for N$_2$O production. The annual efflux of 1.01, 0.62, and 0.03 Gg yr$^{-1}$ respectively for CO$_2$, CH$_4$ and N$_2$O from the Cochin estuary to the atmosphere is largely resulted by the eutrophication, fuelled by the input of large amount of allochthonous organic matter.

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