



Figure 1: A, The SOLAS session on “Surface Ocean and Lower Atmosphere Study - Air-Sea interactions and their climatic and environmental impacts” at XMAS-IV. B, Invited speaker, Yinon Rudich, Weizmann Institute of Science, Israel. C, Invited speaker, Yuzo Miyazaki, Hokkaido University, Japan. © Li Li

science community and, in particular, promoted interdisciplinary studies.

SOLAS themes were covered by a couple of sessions but we would like to focus here on session C4 entitled “Surface Ocean and Lower Atmosphere Study - Air-Sea interactions and their climatic and environmental impacts” (Figure 1), co-chaired by Guiling Zhang and Huiwang Gao (both Ocean University of China, China), Mohd Talib Latif (Universiti Kebangsaan, Malaysia), Jun Nishioka (Hokkaido University, Japan), Senchao Lai (South China University of Technology, China) and Bingbing Wang (Xiamen University,

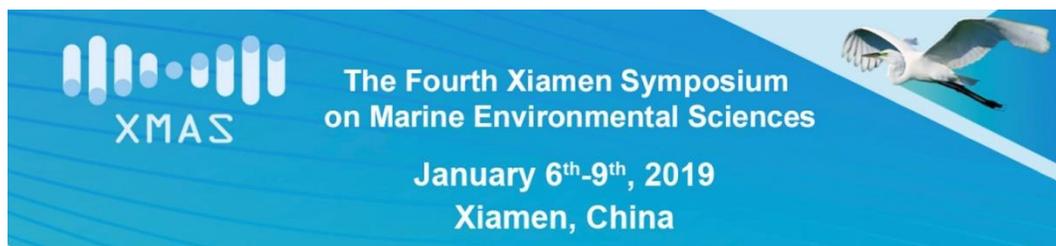
China). In this session, the SOLAS scientific community exchanged new ideas and discussed the latest achievements in our understanding of the key biogeochemical-physical interactions and feedbacks between the ocean and the atmosphere, and of how this coupled system affects and is affected by climate and environmental change.

Two invited presentations were given to overview recent research activities on biogeochemical linkage in the ocean-atmosphere interface via microbial activity and particulate organic matter. Prof. Yinon Rudich (Figure 1B) from Weizmann

Institute of Science presented coupling between oceanic microbial interactions and atmospheric biological aerosol composition. Assoc. Prof. Yuzo Miyazaki (Figure 1C) from Hokkaido University presented biogeochemical linkage between marine organic aerosols and surface seawater in the North Pacific, especially the sea-to-air transfer of dissolved organic carbon and nitrogen. Studies focusing on atmosphere-ocean exchange of climate active gases, atmospheric

deposition, chemical transformations of gases and particles, interactions between anthropogenic pollution with marine emissions, feedbacks from ocean ecosystems and impacts to environments and climate were also presented in particular.

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Surface Ocean - Lower
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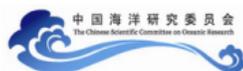
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Jing Dou holds a Master of Science in atmospheric chemistry from Hong Kong University of Science and Technology since 2015. She started her PhD in 2016 at the Institute for Atmospheric and Climate Science, ETH Zürich, in Switzerland. She focuses on the feedbacks between microphysics and photochemical aging in viscous aerosols.

Photochemical aging processes in iron containing aerosols

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Iron (Fe) is not only abundant in the marine and terrestrial environments, but also quite important in the atmosphere. By wind erosion of soil or mineral dust, as well as anthropogenic emissions (e.g., traffic and combustion processes), Fe enters the troposphere in particulate form, and can be transported over long distances (Deguillaume *et al.*, 2005). In the atmospheric aqueous phase, Fe concentration can vary from 10^{-9} to 10^{-6} mol/L in raindrops and from 10^{-6} to 10^{-3} mol/L in cloud droplets, which are generally much higher than other transition metals (Hoigné *et al.*, 1994). Depending on chemical parameters such as pH, ionic strength and concentration of involved substances, Fe can combine with organic (e.g., carboxylate ions) and inorganic ligands (e.g., sulfate (SO_4^{2-}) and nitrate (NO_3^-)) to form stable complex species. Fe-carboxylate complexes (e.g., Fe^{III} -oxalate and Fe^{III} -citrate) are photosensitive, potentially representing an important sink of organic acids in the troposphere (Weller *et al.*, 2013).

In my PhD project, we choose Fe^{III} -citrate as a model complex, since it plays an important role in aerosol aging processes, especially in the lower

troposphere, with low intensities of ultraviolet light. The photochemistry of Fe^{III} -citrate has been widely recognised in both solution (Abida *et al.*, 2012; Faust and Zapp, 1993; Pozdnyakov *et al.*, 2012) and solid (Abrahamson *et al.*, 1994) states. It can absorb light up to around 500 na-

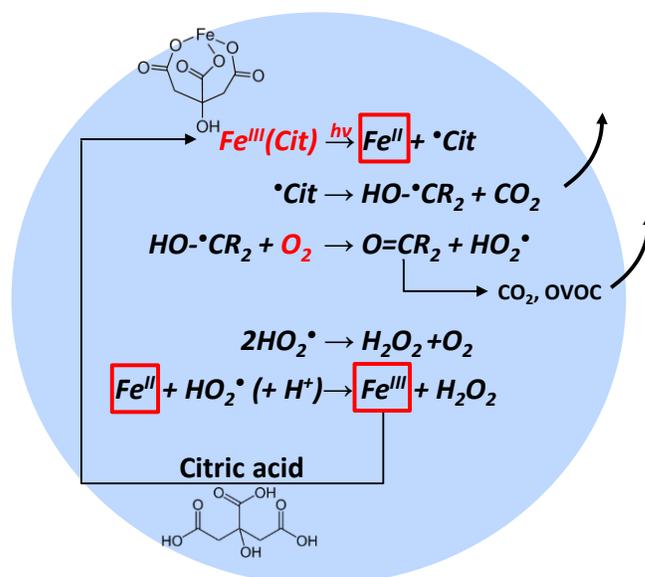


Figure 2: Photocatalytic cycle of Fe^{III} -citrate/citric acid system.

nometre (nm), inducing the reduction of Fe^{III} and the oxidation of carboxylate ligands. In the presence of oxygen (O₂) ensuing radical chemistry will likely lead to more decarboxylation and production of peroxides (e.g., hydroxyl radical (OH•), hydroperoxyl radical (HO₂•) and hydrogen peroxide (H₂O₂)) and oxygenated volatile organic compounds (OVOC). The peroxides in turn allow the re-oxidation of Fe^{II} to Fe^{III}, closing this photocatalytic cycle, in which Fe acts as a catalyst (Weller *et al.*, 2013) (Figure 2).

Little is known about how the viscosity of an aerosol might slow these catalytic cycles. To investi-

gate this question, the basic instrument we are using in the lab is an electrodynamic balance (Zobrist *et al.*, 2011) (Figure 3). A single mixed Fe^{III}-citrate/citric acid aerosol droplet (radius ~10 micrometre (µm)) is levitated in this balance with controlled temperature and relative humidity. During photochemical processing under irradiation in the visible (473 nm) light, the mass and size changes of the particle are tracked. We measure a substantial mass loss of the droplet during photochemical processing due to the evaporation of volatile (e.g., carbon dioxide) and semi-volatile (e.g., ketones) products. We focus the experiments on the high viscosity case (i.e., reduced molecular mobility and low water content), which slows the transport of products and thus affects chemical reaction rates. For a coherent description, we developed a numerical model, which includes main equilibria, chemical reactions, and transportations of major species. It allows to simulate the concentration gradients of each species inside of the particle, and to derive the size and mass changes. Comparing model output with experimental data enables us to determine some crucial parameters, such as equilibrium constants, chemical reaction rates, and

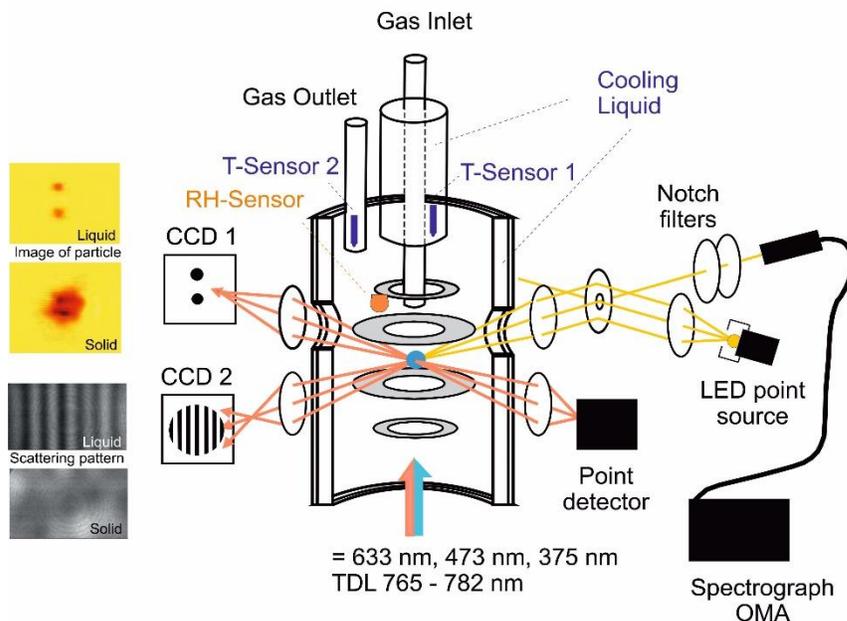


Figure 3: Schematic of the electrodynamic balance.

Abbreviations: Charge-coupled device (CCD), relative humidity (RH), Temperature (T), light-emitting diode (LED), optical multichannel analyser (OMA), tunable diode laser (TDL), and nanometre (nm).

liquid phase diffusion coefficients. With such well-defined and physically constrained parameters, we will predict the evolution of products as well as organic acid degradation in the condensed phase under atmospheric conditions.

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Yu Wang completed her Master's degree in Atmospheric Science at Peking University, Beijing, China, in 2017. Afterwards, she continues her research as a PhD student at The University of Manchester, Manchester, United Kingdom. She uses chamber experiments to investigate the behaviour of particles as seeds for secondary organic aerosol formation.

Aerosol Liquid Water and its influences on gas-particle conversion in North China Plain

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Water is ubiquitous in the atmosphere and it is one of the most important components of the atmospheric particles (Nguyen *et al.*, 2016). Hygroscopic particles take up water as ambient relative humidity increases, in which this ability of water uptake depends on the chemical composition of the particles (Twomey, 1954). For example, water contributes ~67% of aerosol volume for a ammonium sulphate particle under relative humidity of ~80%; water dominates mass loading of most types of aerosols when relative humidity is over 90% (Kreidenweis and Asa-Awuku, 2014). Higher water content leads to larger light scattering, and hence greater visibility degradation. Thus, particle hygroscopicity plays a profound role in visibility degradation, cloud formation thereafter climate change (Figure 4) (Dusek *et al.*, 2006; Kreidenweis and Asa-Awuku, 2014).

In addition, aerosol liquid water can act as a plasticiser and change the phase state of the particles, in which the molecular diffusion coeffi-

cient increase by several orders of magnitude as the particles transit from solid to liquid phase (Koop *et al.*, 2011). Besides, aerosol liquid water provides a medium for multi-phase reactions throughout the atmospheric particles (Wu *et al.*, 2018). These diffused gaseous precursors and the ongoing multi-phase reactions contribute to the formation of secondary inorganic and organic aerosols, accelerating the development and evolution of the haze events over North China Plain, especially during winter.

In my master's research, I focused on the influences of aerosol liquid water on the gas-particle conversion of gaseous precursors (e.g. sulfur dioxide (SO₂), nitric acid (HNO₃), glyoxal), and its further impact on particulate inorganic and organic formation in the atmosphere. In this study, a long-term measurement during 2014.05-2015.01 at PKUERS (PeKing University Environment monitoring Station), Beijing, China and two intensive campaigns in Huairou (sub-urban site near Beijing), IAP (Institute of Atmospheric Phys-

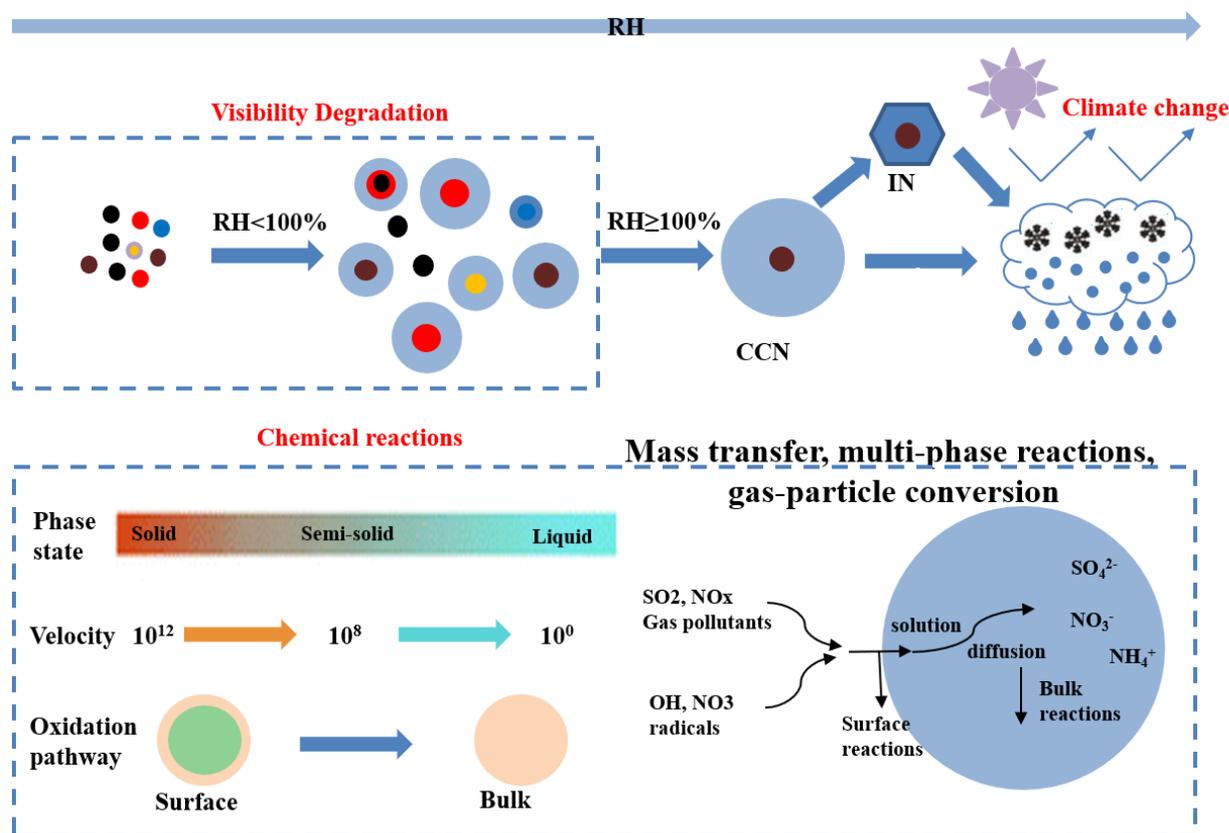


Figure 4: Environmental effects of interaction between aerosol and water.

ics, Beijing, China) in 2016 were conducted. A detailed dataset was obtained by a series of the state-of-art instruments, including the measurements of chemical composition in both gas and particle phase, size-resolved particle hygroscopicity, particle number size distribution and meteorological parameters. By that, we have found a clear clue of the influences of aerosol liquid water on gas-particle conversion and quantified it. The calculated aerosol liquid water ranged from $\sim 4 \mu\text{g}/\text{m}^3$ to $\sim 180 \mu\text{g}/\text{m}^3$ in the long-term measurement, constituting up to $\sim 50\%$ of the total aerosol mass loading (PM_{2.5} + aerosol liquid water). The ambient relative humidity, as well as the mass fraction of aerosol liquid water showed a co-increasing trend with the elevated pollution levels. The molar fraction of particulate sulphate/nitrate in the sum of the particulate sulphate/nitrate and the gas precursors such as sulfur dioxide (SO₂) and nitric acid (HNO₃) and the formation rate of estimated aqueous secondary organic aerosol from glyoxal increased with the elevated aerosol liquid water

via gas-particle conversion process. This indicates higher aerosol liquid water substantially accelerates the formation of particulate matter during the polluted episodes.

For future work, the potential influences of aerosol water uptake on visibility degradation will be evaluated and quantified. Advices on mitigation measures for government will be proposed based on our results. For my PhD study, I will investigate the interaction of aerosol liquid water influences and secondary organic aerosol formation from biogenic and anthropogenic volatile organic compounds, which are widely observed in the atmosphere.

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Short-term dynamics of sea surface $p\text{CO}_2$ in a large subtropical estuary system: The Pearl River estuary

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Estuarine systems feature highly dynamic short-term variability of sea surface partial pressure of carbon dioxide ($p\text{CO}_2$) (e.g., Yates *et al.*, 2007; Dai *et al.*, 2009). Lacking of high-resolution samplings of sea surface $p\text{CO}_2$ could thus result in large uncertainties in estimation of air-sea CO_2 fluxes (Jiang *et al.*, 2008; Bozec *et al.*, 2011; Lanso *et al.*, 2017). However, mechanistic understanding towards the diurnal to weekly dynamics of $p\text{CO}_2$ in estuarine systems remains challenging due to the complex interactions between biogeochemistry and physics therein. Here we examined the controlling factors on the short-term variability of sea surface $p\text{CO}_2$ recorded by a Battelle Seatology $p\text{CO}_2$ Monitor amounted on a buoy located in the outer Pearl River Estuary (PRE), a large subtropical estuary system in the

northern South China Sea, from July 2 to August 11, 2015 (Figure 5).

Surface seawater $p\text{CO}_2$ in the PRE was highly

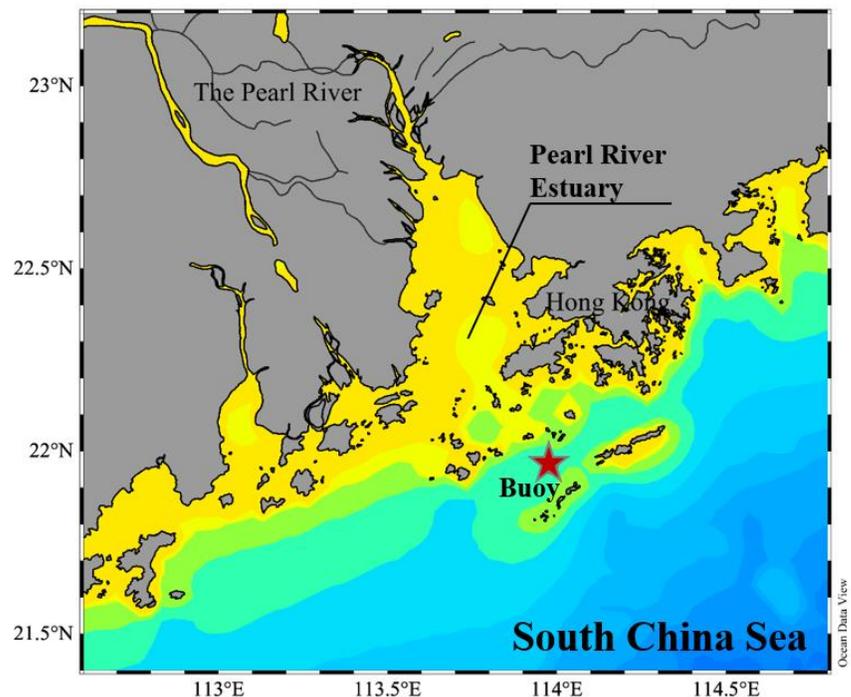


Figure 5: Location of the buoy in the outer Pearl River Estuary

variable, ranging from 78 to 640 micro atmosphere (μatm) with an average of 279 μatm , ~ 100 μatm lower than the atmospheric $p\text{CO}_2$ (Figure

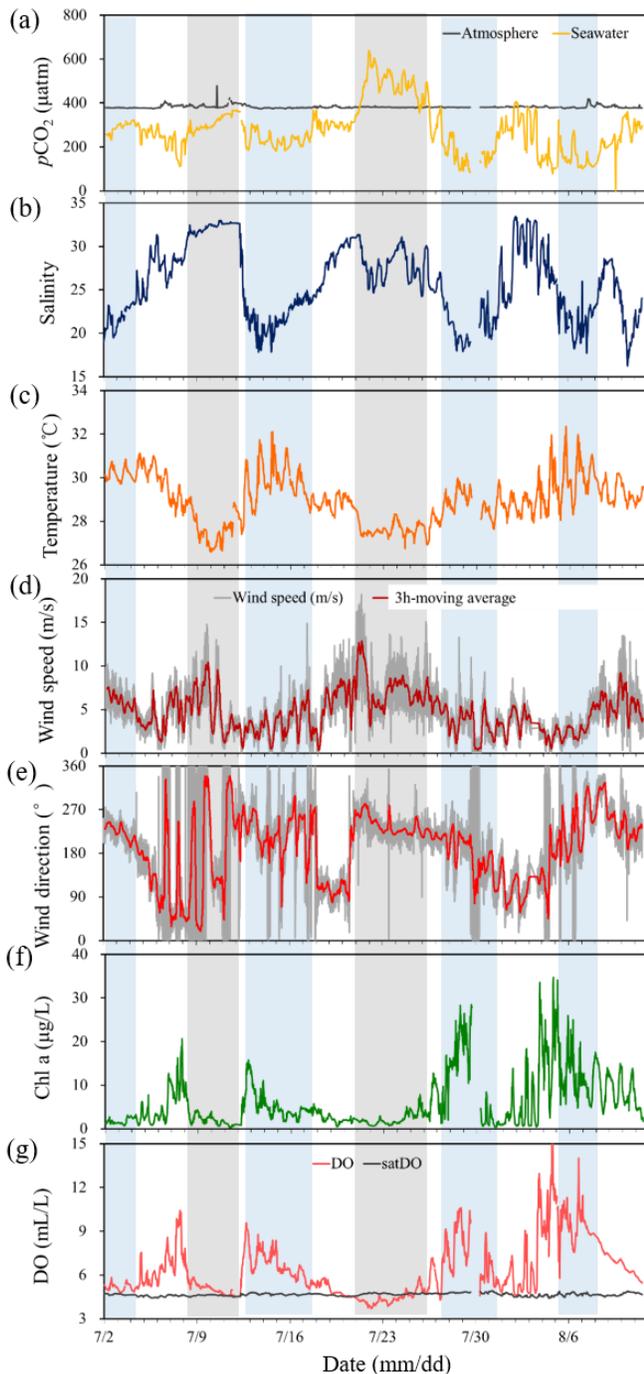


Figure 6: Time-series variability of (a) partial pressure of CO_2 ($p\text{CO}_2$, μatm), (b) salinity, (c) temperature ($^{\circ}\text{C}$), (d) wind speed (m/s), (e) wind direction, (f) chlorophyll a concentration (Chl a, $\mu\text{g/L}$), and (g) dissolved oxygen (DO, mL/L) in the outer Pearl River Estuary from July 2 to August 13, 2015. The blue and grey shadows denote the events of eastward expanding of brackish water and large winds, respectively.

6a). On diel timescales, $p\text{CO}_2$ changes of 50-90 μatm occurred in response to diurnal primary production and respiration; temperature and tidal effects played a minor role. Over weekly timescales, the low $p\text{CO}_2$ (~ 100 -200 μatm) was strongly correlated with the eastward expanding of brackish water (salinity < 25) under the favourable southwest winds (Figure 6), which had allowed for rapid phytoplankton production due to attenuated turbidity to the west of the estuary mouth. The low $p\text{CO}_2$ also corresponded well to the high river discharge despite of a time lag of nearly 7-10 days between the Wuzhou hydrological station and the estuary mouth (data not shown). In addition, large wind events were probably responsible for the $p\text{CO}_2$ increase, resulting from enhanced upward mixing of high-salinity, CO_2 -enriched subsurface water as reflected in relatively low temperature, Chlorophyll a concentration and dissolved oxygen level (Figure 6).

Net fluxes of CO_2 for the observation period (-4.8 $\text{mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$) were directed from atmosphere to ocean, but with a wide range from ~ -30 to $+20$ $\text{mmol CO}_2 \text{ m}^{-2} \text{ d}^{-1}$ depending largely on wind speeds. Therefore, careful consideration of the short-term variability of surface seawater $p\text{CO}_2$ and wind regimes was needed to accurately estimate air-sea CO_2 fluxes in the subtropical estuary system.

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