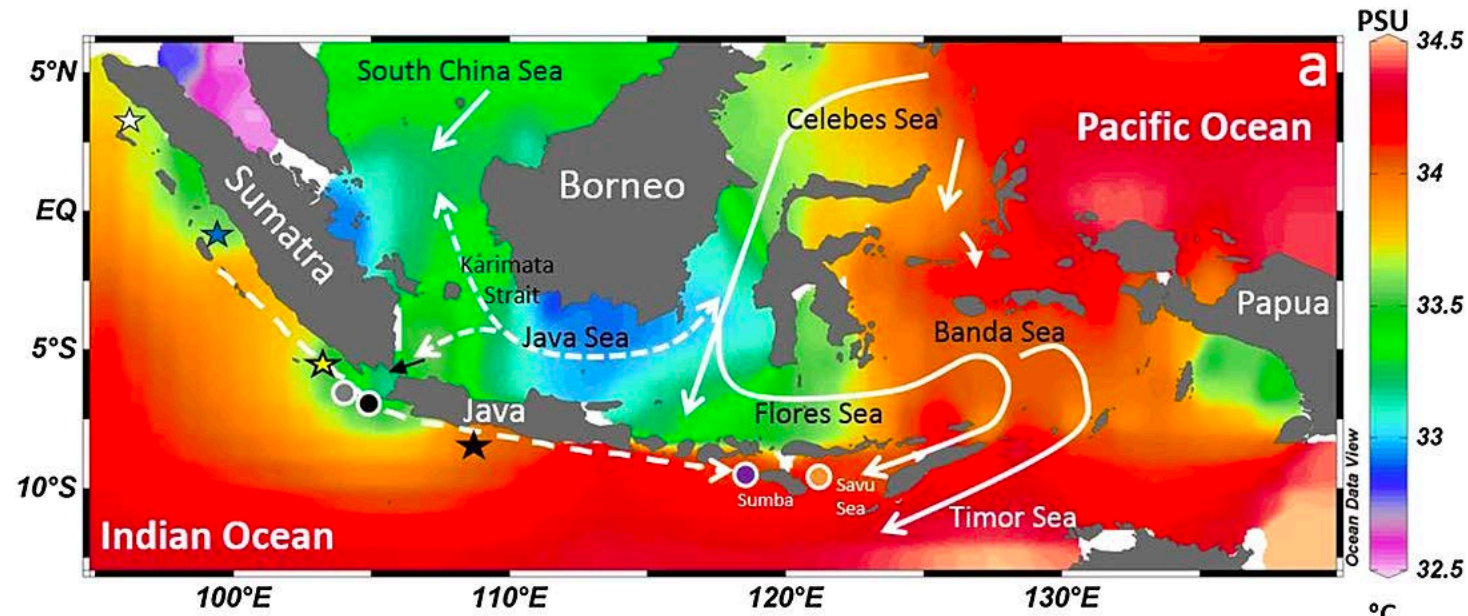


# Novel Insights into the origin of dissolved organic carbon in the Sunda Shelf Sea using stable isotope ratios of hydrogen ( $\delta^2\text{H}$ ) and carbon ( $\delta^{13}\text{C}$ )



- [Link](#) to session
- [Link](#) to presentation abstract
- **Session date and time:** 27<sup>th</sup> April 2021, Tuesday, 13:30 – 15:00 CEST
- **PICO Presentation date and time:** 27<sup>th</sup> April 2021, Tuesday, 14:15 – 14:17 CEST
- Find *your* time-zone specific date and time [here](#)
- **Contact:** Nikita Kaushal (nkaushal@ntu.edu.sg)

Image: [Setiawan et al, 2015](#)

# Outline

- Abstract
- Author information
- Dissolved organic carbon (DOC) significance
- DOC sources
- DOC source discrimination: challenges
- DOC source discrimination: using hydrogen isotopes
- Study site and time-series sampling
- Methods
- Results 1: end-member data and degradation effects
- Results 2: time-series data
- Results 2: mass balance calculations
- Further ongoing work
- Thank you

# Abstract

Rivers deliver  $\sim 0.25 \text{ Pg C year}^{-1}$  of terrigenous dissolved organic carbon (tDOC) from land to shelf seas. As tDOC moves along the river, coastal ocean and deep ocean continuum, it undergoes complex biogeochemical processing that results in both chemical alteration and remineralisation. Remineralisation of tDOC to  $\text{CO}_2$  can contribute significantly to coastal ocean acidification and  $\text{CO}_2$  emissions to the atmosphere. Our understanding of tDOC processing in coastal seas is still limited, in part because it is challenging to distinguish between marine and terrigenous DOC. The stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) of the dissolved inorganic and organic carbon pools are commonly used to quantify tDOC, because terrestrial vegetation is typically more isotopically depleted ( $-32$  to  $-25 \text{ ‰}$ ) compared to marine organic carbon ( $-24$  to  $-20 \text{ ‰}$ ). However, this relatively small difference between the marine and terrigenous end-members can introduce large uncertainties in  $\delta^{13}\text{C}$ -based estimates, particularly if tDOC originates from both  $\text{C}_3$  and  $\text{C}_4$  vegetation. End-member isotope ratio values with larger separation could potentially help to better quantify tDOC. Recent studies in freshwater ecosystems have shown that the stable isotope ratios ( $\delta^2\text{H}$ ) of the carbon bound non-exchangeable hydrogen fraction of dissolved organic matter (DOM) typically differs by more than  $50 \text{ ‰}$  between terrestrially derived and aquatically derived dissolved organic matter. However,  $\delta^2\text{H}$  has not yet been used as a tracer for tDOC in marine environments.

Here, we present results from a one year-long monthly time series of  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  at a coastal location in Southeast Asia's Sunda Shelf Sea, where the southwest monsoon delivers a seasonal input of tDOC from tropical peatlands on Sumatra. We found that  $\delta^2\text{H}$  of solid-phase extracted DOM, as measured after dual water steam equilibration, ranged between  $-150$  to  $-130 \text{ ‰}$  during the southwest monsoon, but between  $-167$  to  $-160 \text{ ‰}$  during other months. Fresh tDOC from peatland-draining rivers had values close to  $-100 \text{ ‰}$ , and decreased somewhat upon partial photodegradation, while DOM produced in plankton enrichment cultures had values around  $-174 \text{ ‰}$ . Values of  $\delta^{13}\text{C}$  of DOC ranged from  $-25.5$  to  $-23.0 \text{ ‰}$  during the southwest monsoon, and between  $-23.0$  to  $-21.0 \text{ ‰}$  at other times. We will present preliminary mass balance calculations to estimate tDOC concentrations based on  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$ . Our results suggest that  $\delta^2\text{H}$  can be a sensitive tracer of tDOC in the marine environment.

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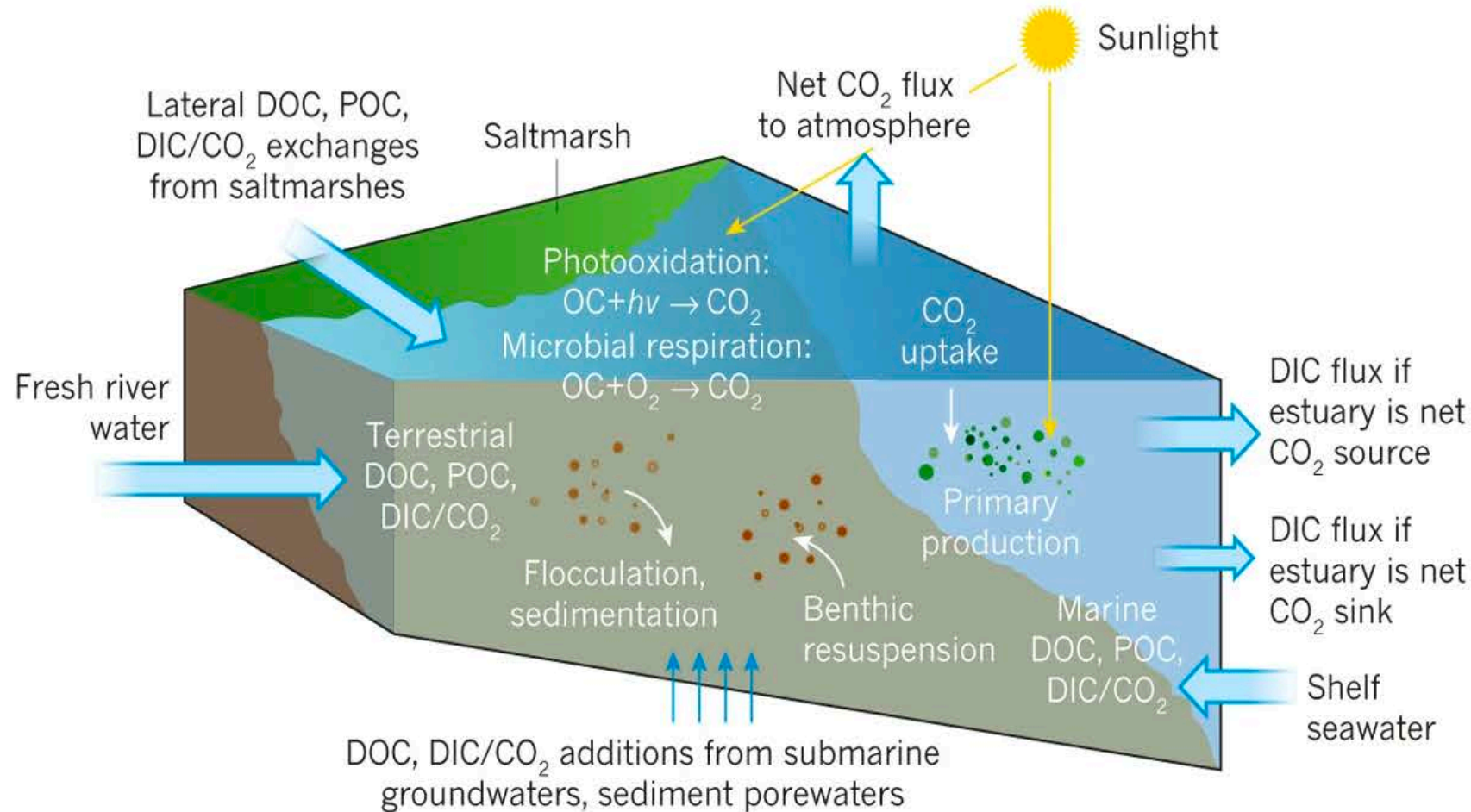


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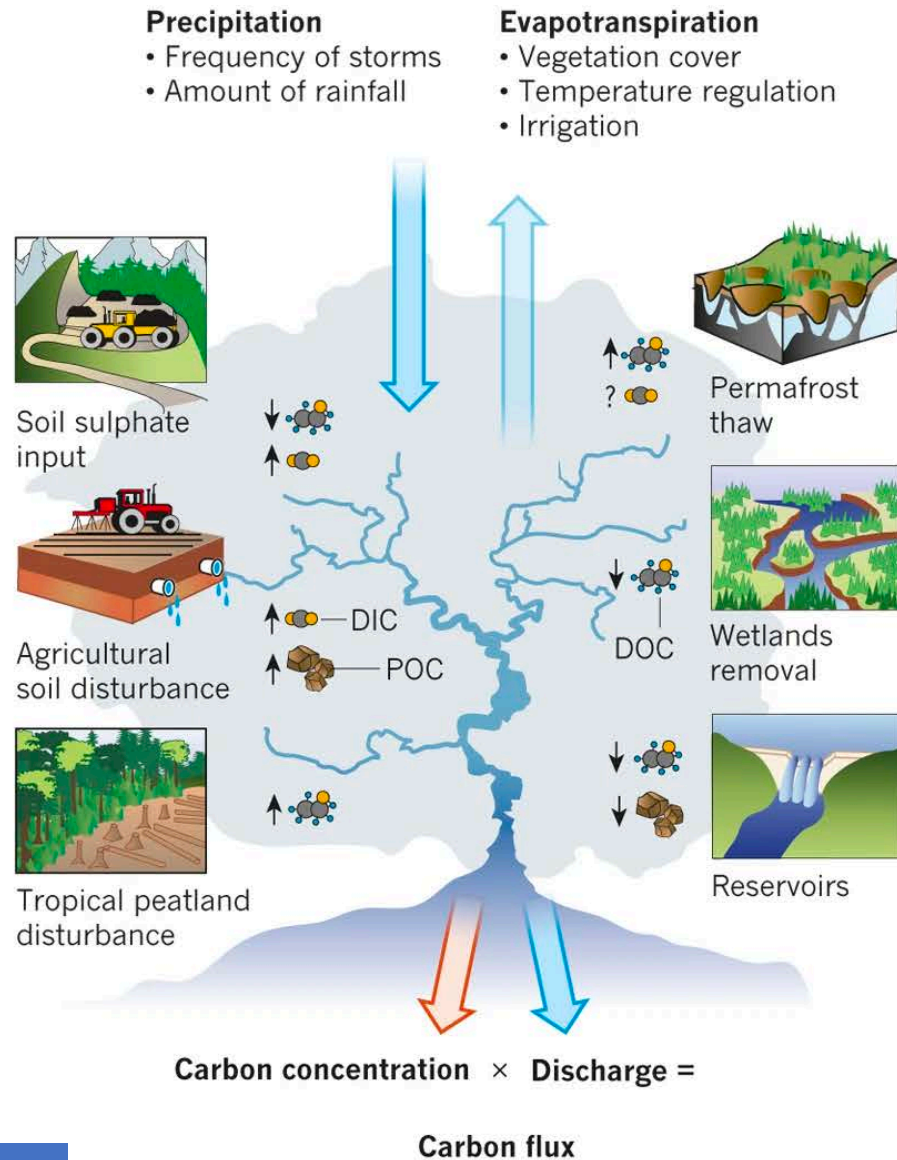


# DOC significance

- Dissolved Organic Carbon (DOC) mineralization in the Shelf Sea can cause coastal acidification and CO<sub>2</sub> emissions to the atmosphere.
- But DOC sources and source variability over time are not well constrained.



# DOC sources



**Shelf Sea DOC concentration**

=

carbon produced in the Shelf Sea by organisms like plankton

+

carbon produced on land by vegetation and carried to the Shelf sea by rivers

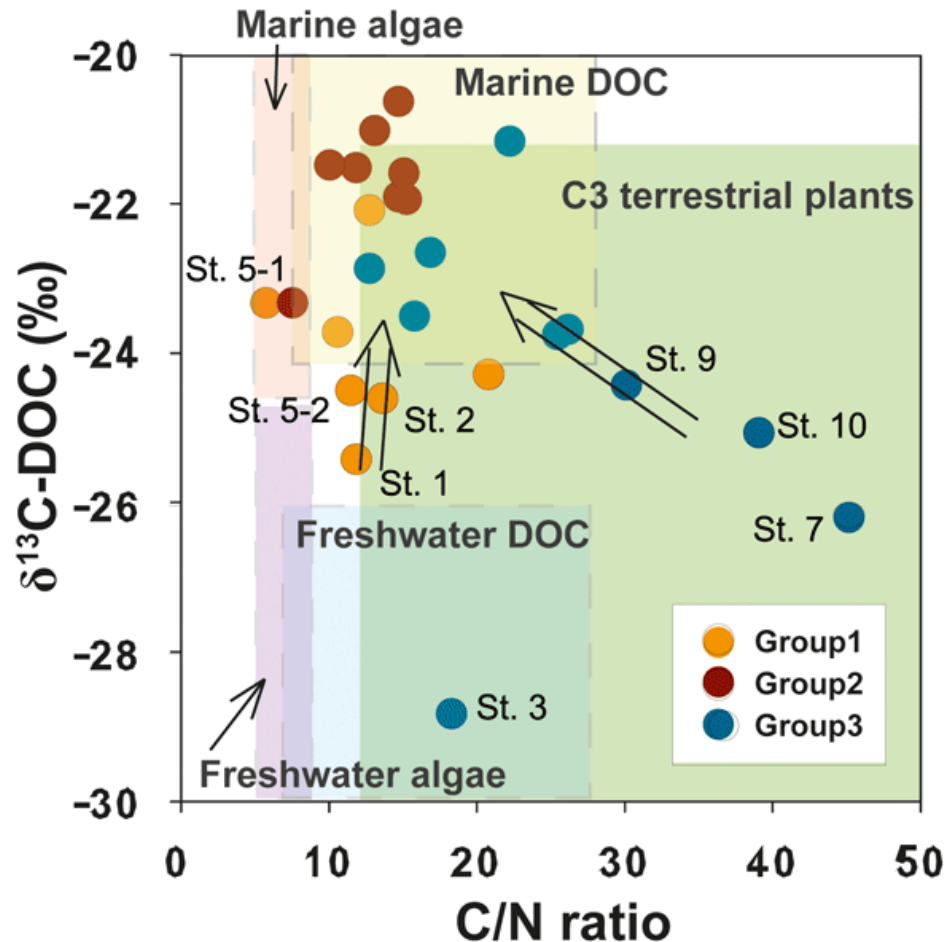
**DOC concentration of the Shelf Sea can vary over time due to processes like:**

- Land management practices e.g. agricultural soil and peatland disturbance
- Changing rainfall and evaporation patterns
- Photo-oxidation and microbial respiration in the rivers and/or the Shelf Seas
- Seasonal mixing and dilution by currents in the Shelf Seas

**Image: [Bauer et al, 2013](#)**

# DOC source discrimination: challenges

- Carbon isotopes are typically used for source discrimination.
- But there is little separation in the isotopic composition between marine and terrestrial sources.
- A system with higher end-member isotopic separation will allow better source discrimination.



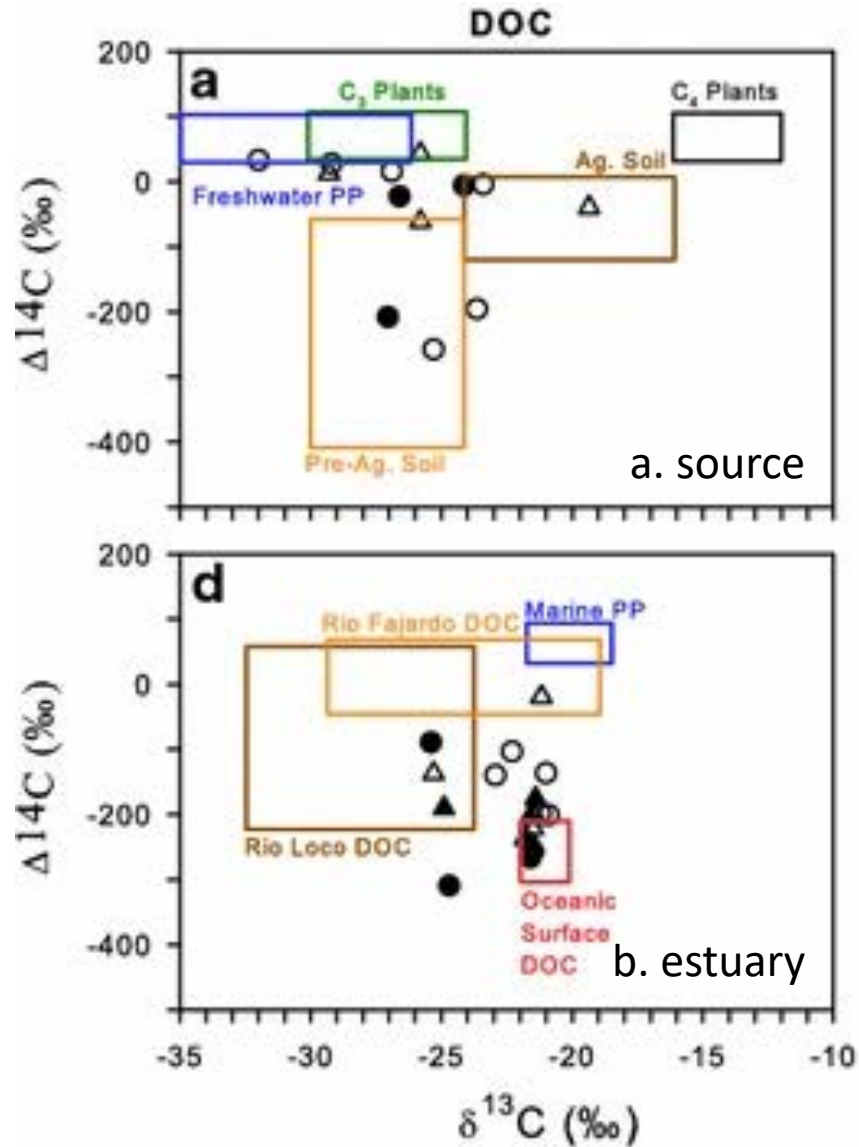
## Example 1

- $\delta^{13}\text{C}$  DOC of terrestrial vegetation is typically more isotopically depleted than marine organic carbon.
- However, the difference is small and is further modified by mixing and other processes.
- Figure shows  $\delta^{13}\text{C}$  of DOC measurements made along Masan Bay, Republic of Korea.
- Group 1 -> 3, low -> high salinity, 10 -> 32 psu.
- It is challenging to discriminate DOC source despite using  $\delta^{13}\text{C}$  DOC and coupled  $\delta^{13}\text{C}$  DOC and C/N ratio measurements.

Lee et al, 2020

# DOC source discrimination: challenges

- The variability in  $\delta^{13}\text{C}$  of DOC decreases from the source to the estuary through dilution, mixing and degradation processes.



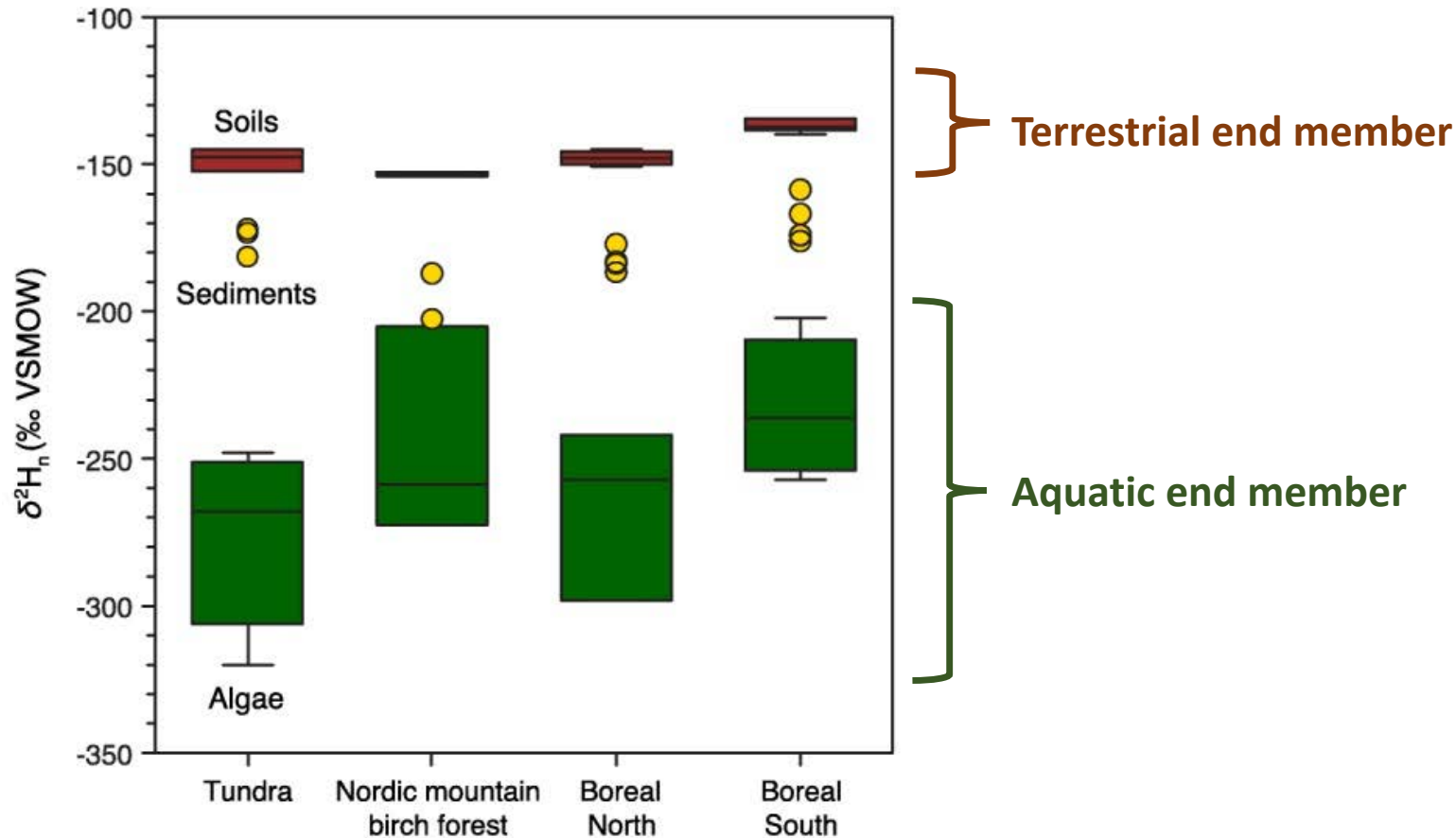
## Example 2

- $\delta^{13}\text{C}$  of DOC measurements made along tropical small mountain rivers and estuary of Puerto Rico.
- The variability in  $\delta^{13}\text{C}$  of DOC decreases from 12 to 4 ‰ from the source to the estuary as a result of different processes.

[Moyer et al, 2013.](#)

# DOC source discrimination: using hydrogen isotopes

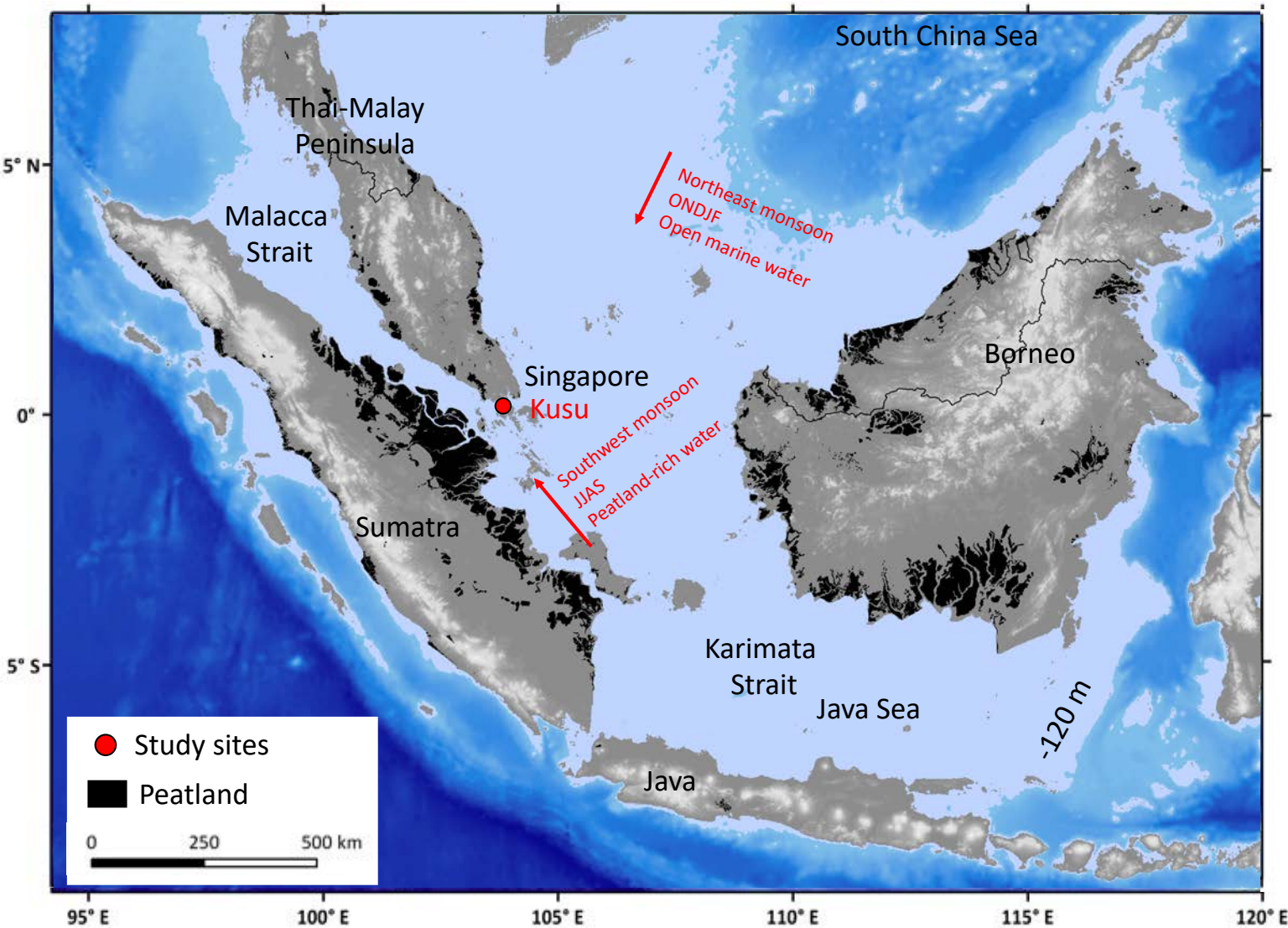
- $\delta^2\text{H}$  of DOM has > 50 % end-member separation between terrestrial and aquatic DOC.
- Method shows promising results for source discrimination in fresh water systems.



Hydrogen isotopes of the non-exchangeable fraction of Dissolved Organic Matter (DOM) have been used in fresh water systems for DOC source discrimination.



# Study site and time-series sampling



- Sunda Sea Shelf receives more than 10% of the land-to-sea terrigenous DOC (tDOC) flux from the abundant peatlands in the region.
- During the months of JJAS, southwest monsoon wind driven currents carry the peatland-rich waters from Sumatra to the Singapore coastal region.
- During the months of ONDJF, northeast monsoon wind-driven currents carry open marine waters from the South China Sea to the Singapore coastal region.
- This generates a sharp seasonal contrast in the Singapore coastal region between a dominantly terrestrial peatland end-member and a dominantly marine end-member, giving an ideal study site.
- Monthly time-series seawater samples were collected from the Singapore coastal region (Kusu) from August 2019 to July 2020 (n=14).
- Terrestrial end-member samples were collected from peatland-rich rivers ( $> 1000 \mu\text{mol l}^{-1}$  DOC) in Borneo (n=2). One sample was subjected to photodegradation for a period of 3 months.
- A marine end-member sample was derived from a laboratory grown plankton culture (n=1). Plankton was collected from Kusu.

# Methods



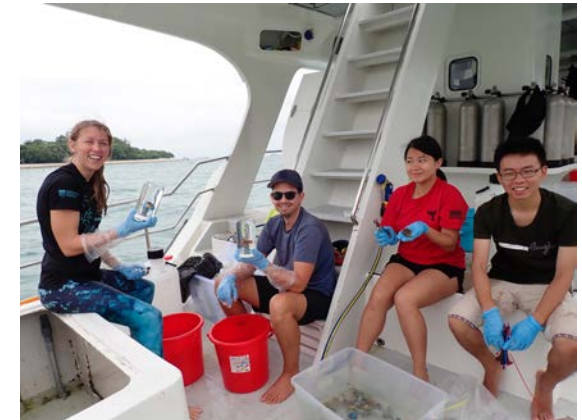
## Marine end-member

- Enrichment cultures were grown from natural phytoplankton collected from Kusu (Singapore) in November 2019.
- Natural plankton was added to artificial sea water amended with f/2 growth media (after [Osburn et al, 2019](#)).
- The culture flasks were placed on a shaker table for 20 days on 12:12 light dark cycle at 24°C and then permanent dark conditions for 25 days to allow bacterial reprocessing by heterotrophic microbes.



## Terrestrial end-members

- Peatland draining river waters were collected from Maludam and Simunjan rivers of Borneo.
- Photodegradation experiments were further conducted with Maludam water. It was exposed to natural sunlight in Singapore for a period of 3 months in 250 ml quartz bottles.
- See [Kaushal et al, 2020](#) for further information on marine and terrestrial end members.

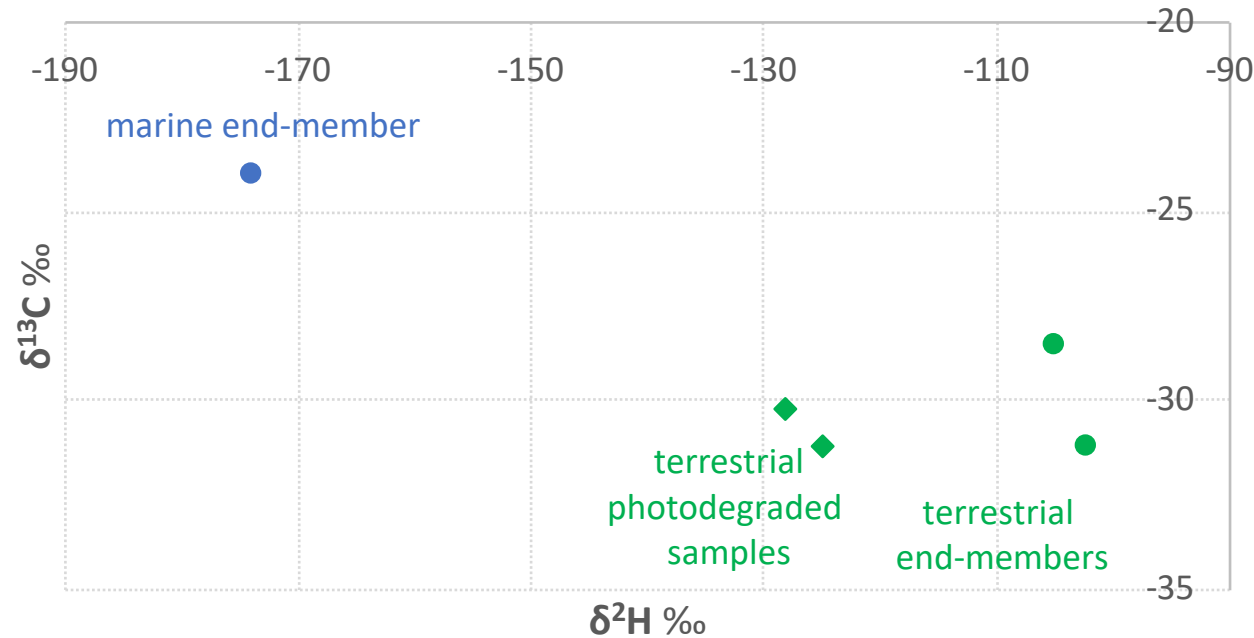


## Measurements

- $\delta^{13}\text{C}$  of DOC was measured directly in water samples.
- $\delta^2\text{H}$  of DOM was measured after Solid Phase Extraction.

# Results 1: end-member data and degradation effects

- There is more than 50 ‰ difference in  $\delta^2\text{H}$  composition between marine and terrestrial end-members.
- The  $\delta^2\text{H}$  composition of terrestrial end-members decreased when partially photodegraded.



# Results 2: time-series data

- Time-series samples show higher DOC concentrations during the southwest monsoon period.
- $\delta^2\text{H}$  isotopic measurements show that the high DOC southwest monsoon samples are likely to be due to increased terrestrial DOC input to the Shelf Sea waters.

## DOC times-series plot:

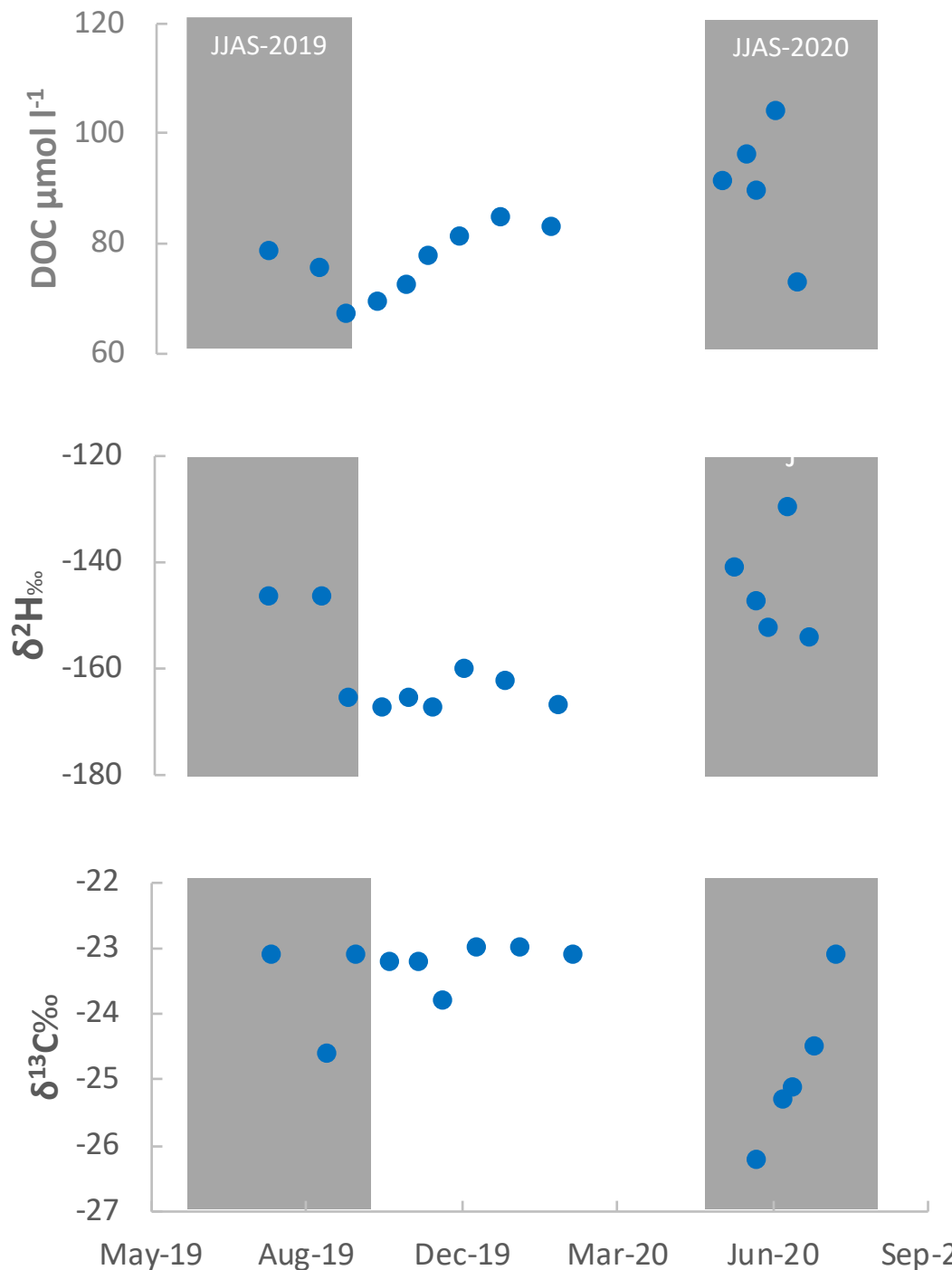
The JJAS samples generally have higher DOC concentrations likely resulting from the additional terrestrial peatland DOC contribution.

## $\delta^2\text{H}$ time-series plot:

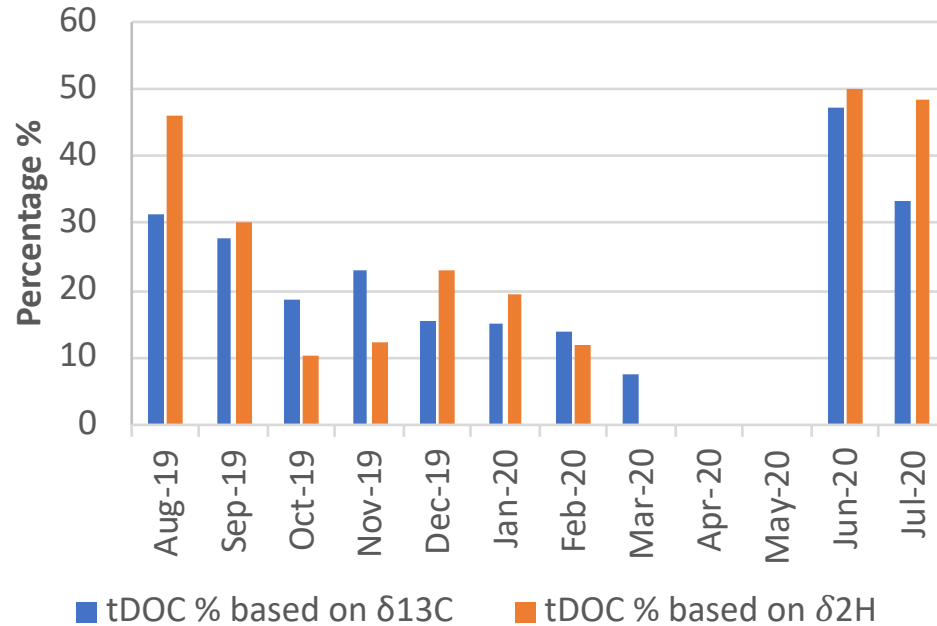
The JJAS samples range between -154 to -130 ‰ during the southwest monsoon (JJAS). The samples from remaining months are lighter than -160 ‰.

## $\delta^{13}\text{C}$ time-series plot:

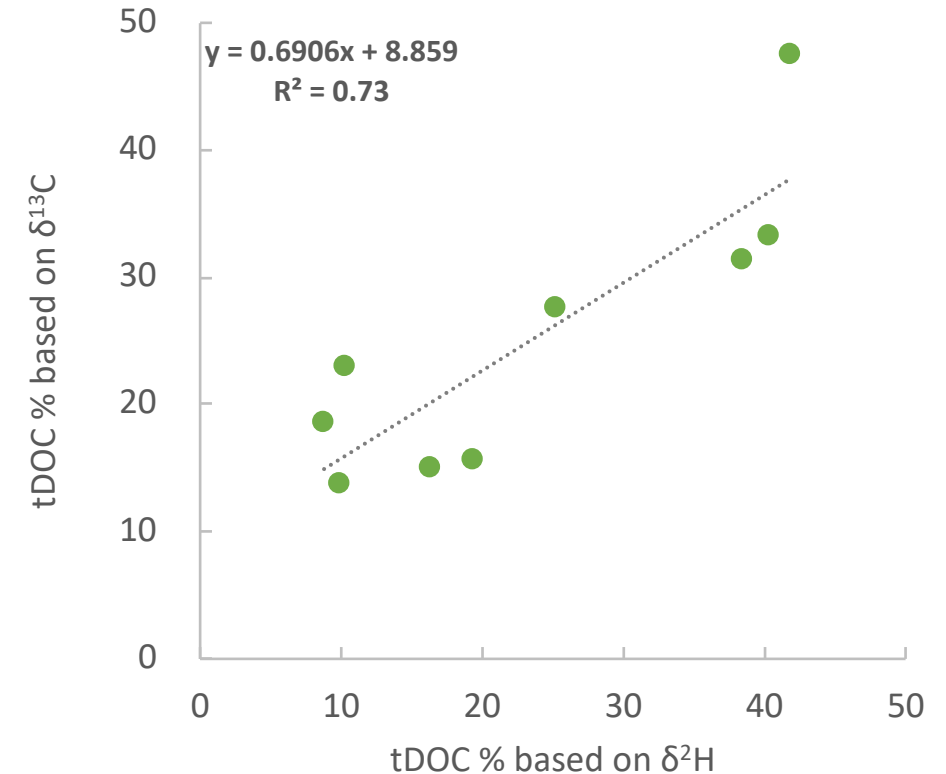
Values of  $\delta^{13}\text{C}$  of DOC ranged from -26.2 to -23.0 ‰ during the southwest monsoon (JJAS), and between -23.8 to -23.2 ‰ at other times.



# Results 3: mass balance calculations



$\delta^2\text{H}$  can be a sensitive tracer of tDOC in the marine environment.



Time-series of percentage terrigenous Dissolved Organic Matter (tDOM) in Kusu waters calculated using  $\delta^{13}\text{C}$  and  $\delta^2\text{H}$  mass balance approaches.

Note: The calculation of tDOC% is based on Kusu time series  $\delta^{13}\text{C}$  of DIC measurements sampled in the same campaign as the  $\delta^2\text{H}$  sample. It is an isotope mass balance where the terrestrial end-member (-29 ‰) is the typical  $\delta^{13}\text{C}$  DOC of peatland draining rivers and the marine end-member (-22 ‰) is an average of the late February to early April time-series samples of the inter-monsoon period of 2019.

- Zhou et al, submitted to JGR-Oceans
- PREPRINT available [here](#).

The strong correlation in the cross plot shows that, similar to the more commonly used carbon isotopes,  $\delta^2\text{H}$  of shelf sea waters successfully reflect source composition of DOC.



## Further ongoing work

## Better end-member characterization

## Movement of tDOC from the Sunda Sea Shelf to the open ocean



Field Notebook and Sample Inventory

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|    | A          | B                         | C           | D      | E      | F  | G  | H    | I  | J       | K     | L    | M   | N       | O    | P      | Q         | R         | S        | T     | U          | V   |          |
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| 1  | Date       | Location                  | Nan         | d13C D | d13C D | DO | DI | CDOM | Ti | Nutrien | Enzym | DMSO | ATP | Sterive | Ross | Mengli | CTD       | Niskin    | Radiomet | CRISP | Inorg Prec | D/H | Other M  |
| 2  | 25/02/2019 | Kusu Main (N 01° 13.552'  | Nikita, I Y |        | Y      | Y  | Y  | Y    | Y  | Y       | Y     | Y    | Y   | Y       | Y    | N      | Y (11:18' | 5 Surface | N        |       |            |     | NA       |
| 4  | 25/02/2019 | Hantu Main (N 01° 13.600' | Nikita, I Y |        | Y      | Y  | Y  | Y    | Y  | Y       | Y     | Y    | Y   | Y       | Y    | N      | Y (14:00  | 5 Surface | N        |       |            |     | NA       |
| 6  | 07/03/2019 | Hantu Main                | Molly, K Y  |        | Y      | Y  | Y  | Y    | Y  | Y       | Y     | Y    | Y   | Y       | Y    | N      | Y (11:00' | 5 N       | N        |       |            |     | Osmo p   |
| 7  | 11/03/2019 | Kusu Main                 | Molly, K Y  |        | Y      | Y  | Y  | Y    | Y  | Y       | Y     | Y    | Y   | Y       | Y    | N      | Y (11:27' | 5 N       | N        |       |            |     | pCO2 se  |
| 8  | 14/03/2019 | Hantu Main - Incubations  | Molly, K Y  |        | Y      | Y  | Y  | Y    | Y  | Y       | Y     | N    | Y   | Y       | N    | Y      | Y (13:00  | 5 N       | N        |       |            |     | Molly in |
| 10 | 21/03/2019 | Kusu Main - Incubations   | Molly, K Y  |        | Y      | Y  | Y  | Y    | Y  | Y       | Y     | N    | Y   | Y       | N    | Y      | Y (15:00  | 5 Surface | N        |       |            |     | Molly in |



- Thank you for reading our presentation!
- Do leave comments and questions and we will respond quickly.
- If the subject of coastal tDOC is of interest, information of an allied study using coral luminescence measurements as a proxy to reconstruct tDOC over time can be found [here](#).