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Dissolved Organic Carbon cycle in the Yellow Sea and the East China Sea : Insights from radiocarbon analysis

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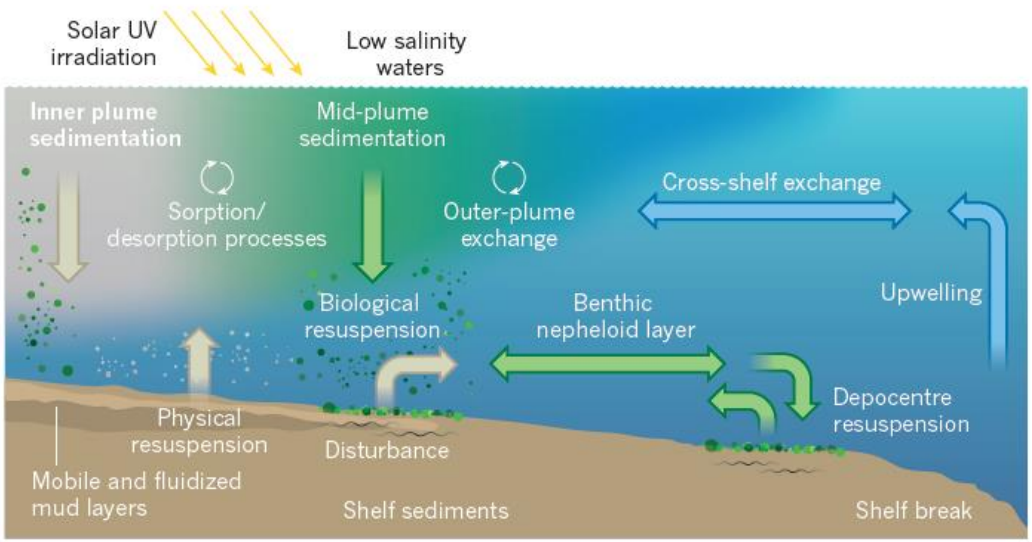
DOC cycle in the continental shelves

DOC: operationally defined by filtration (0.2 or 0.7 μm)

Global DOC flux

Source	Flux (Pg C yr^{-1} = 10^{15} g C yr^{-1})	References
Marine Primary production	15–25	Biddanda & Benner (1997); Ducklow et al. (1995)
River	0.2–0.4	Bauer et al. (2013)
Precipitation	0.1–0.4	Willey et al. (2000)
Benthic diffusion	0.35	Burdige & Komada (2014)
Groundwater	< 0.01	McDonough et al. (2022)

Complex OC cycle in coastal ocean

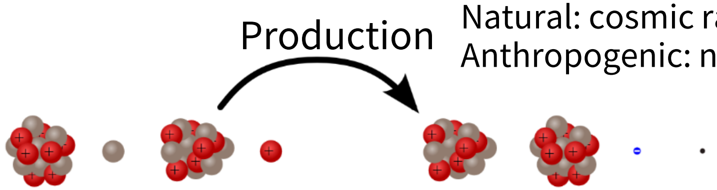


Bauer et al. (2013)

- Terrestrial input & dynamic physical processes
  -> complex DOC cycle in the coast

- Most of organic carbon exported from coastal ocean to open ocean in the form of DOC

Radiocarbon (^{14}C) as a (DOC) tracer

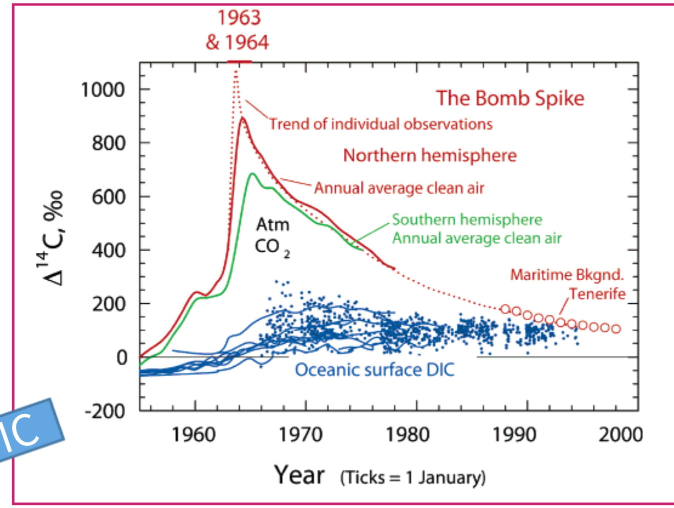


Natural: cosmic ray
Anthropogenic: nuclear test

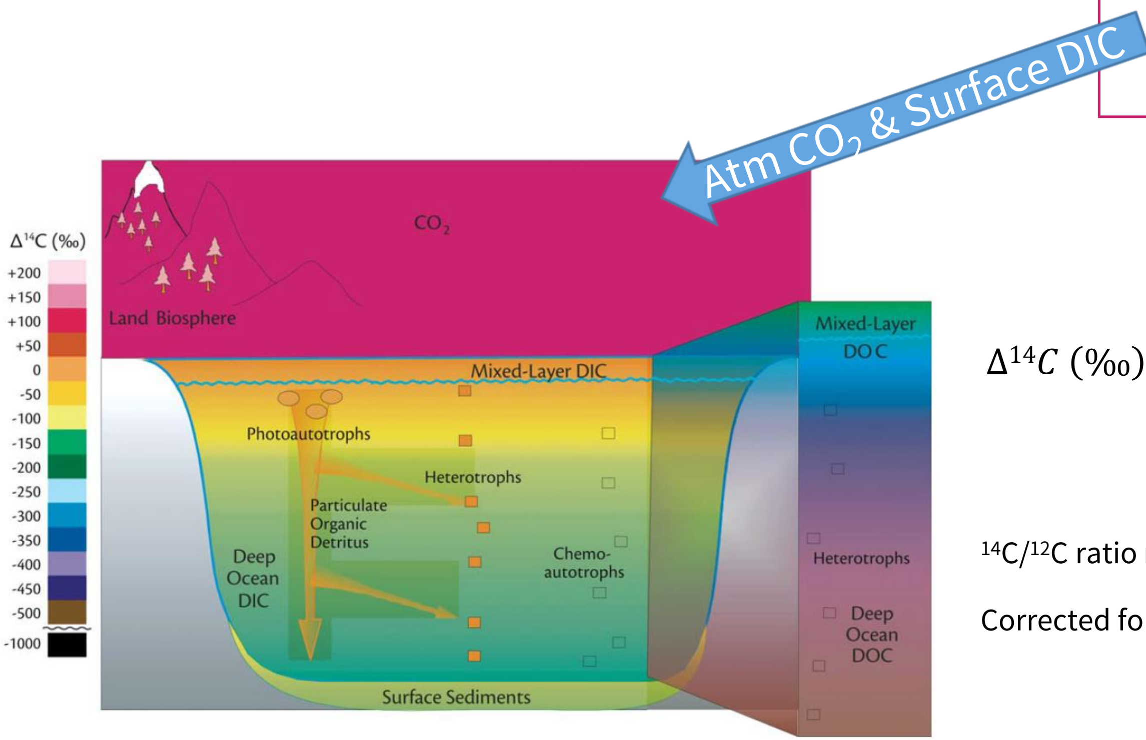
$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{14}_{6}C + ^{1}_{1}p$

$^{14}_{6}C \rightarrow ^{14}_{7}N + ^{0}_{-1}e + \overline{\nu}$

Radioactive decay
(Half-life = 5,730 years)



McNichol & Aluwihare (2007)



Pearson (2000)

$\Delta^{14}C = -1000$‰ => ^{14}C age ~50,000 yr
$\Delta^{14}C = -10$‰ => ^{14}C age ~0 yr

$$\Delta^{14}C\ (‰) = \left[\left(\frac{\left(\frac{^{14}C}{^{12}C}\right)_{s,-25}}{\left(\frac{^{14}C}{^{12}C}\right)_{OX-I,-19}}\right) e^{-\lambda(y-1950)} - 1\right] \times 1000$$

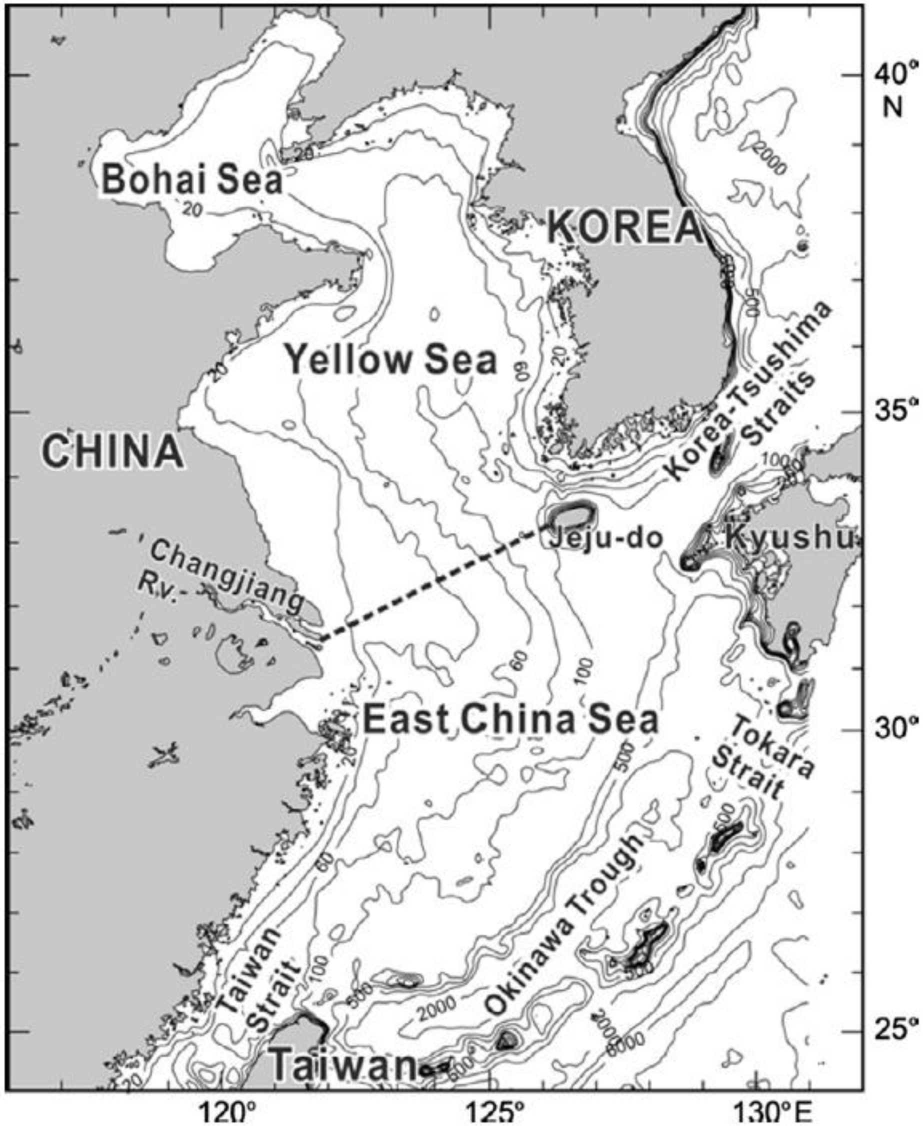
$\lambda = 1/8267$; y = the year of sample analyzed

$^{14}C/^{12}C$ ratio relative to standard material(OX–I)

Corrected for mass-dependent fractionation

^{14}C can be used as a Source identification & chronometer

Previous studies using ^{14}C in the YS and ECS

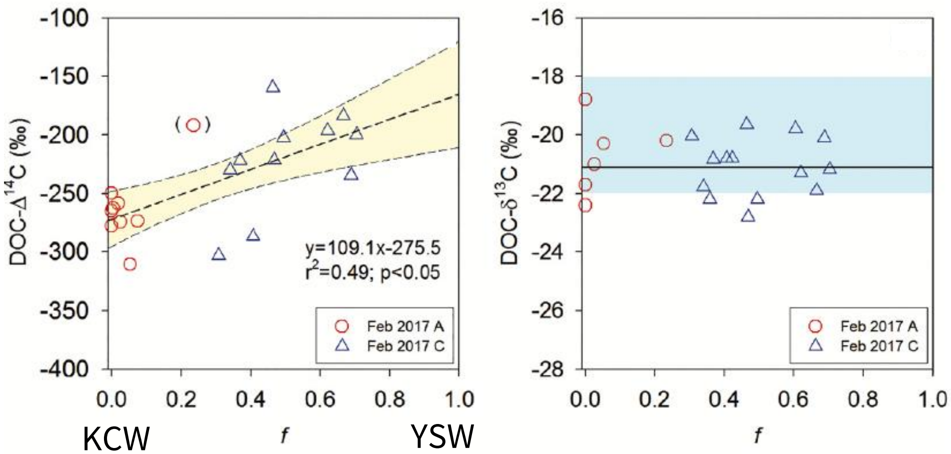


Lie & Cho (2016)

Studies using ^{14}C

Source	Region	References
Riverine OC	Yellow River Yangtze River Korea rivers	Wang et al. (2012, 2016) Lee et al. (2021)
Suspended POC	YS & ECS	Seo et al. (2022)
Aerosol POC	Bohai Sea Chinese coast	Ren et al. (2022) Yu et al. (2018)
Precipitation (DOC)	Seoul (Korea)	Yan & Kim (2018)
Sedimentary POC	YS & ECS	Bao et al. (2016)
Pore-water DOC	YS & ECS	Fu et al. (2022)
Marine DOC	YS & ECS	Han et al. (2022)

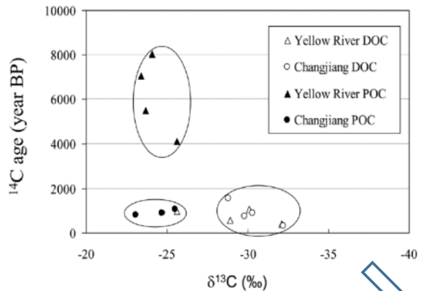
DOC $\Delta^{14}C$ in the ECS (Han et al., 2022)



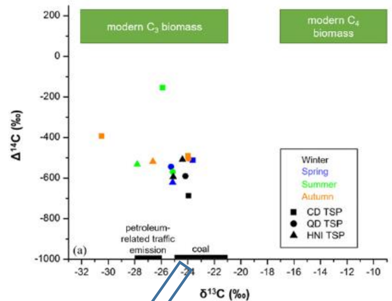
Various types of OC in the East China Shelf can contribute to **DOC pool**

Previous studies using ^{14}C in the YS and ECS

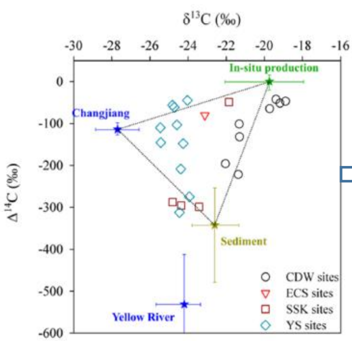
Riverine DOC & POC

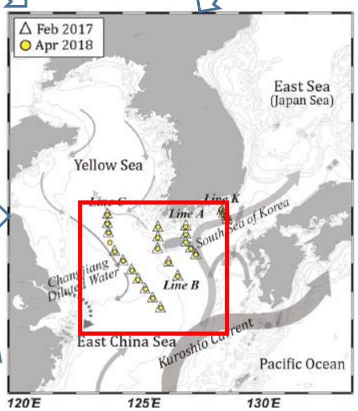


Aerosol POC

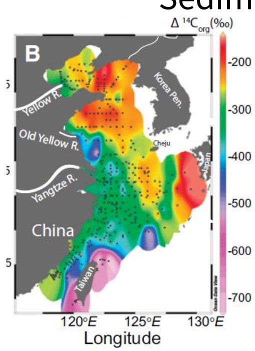


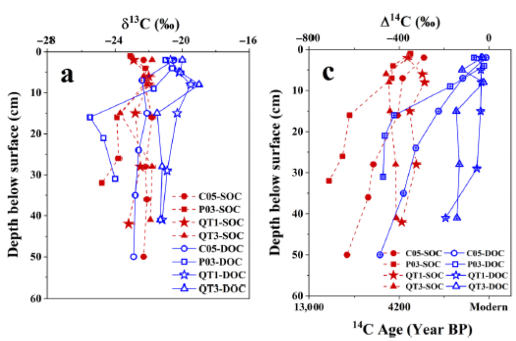
Suspended POC





Sedimentary OC & pore-water DOC





Studies using ^{14}C

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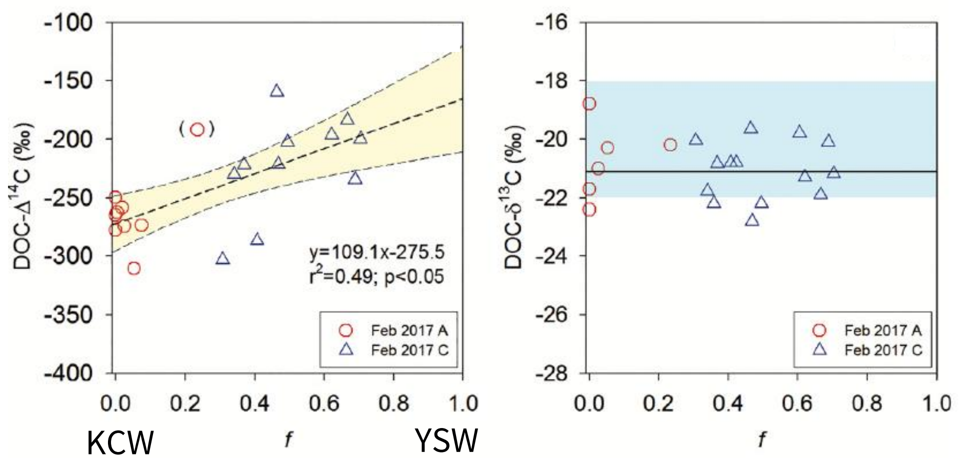
Marine DOC	Ys & ECS	Han et al. (2022)

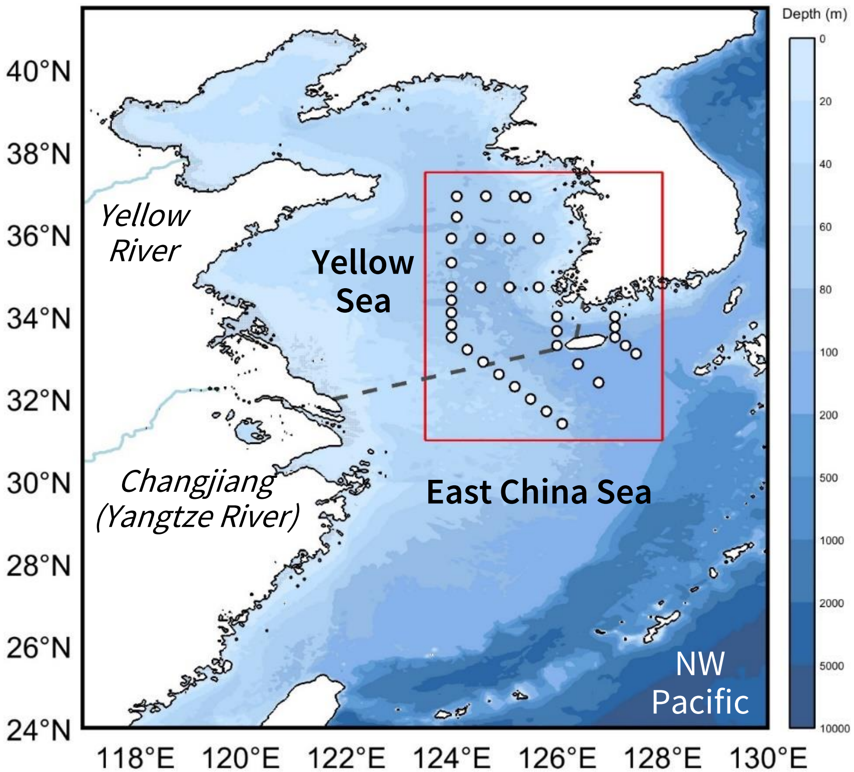
DOC $\Delta^{14}C$ in the ECS (Han et al., 2022)

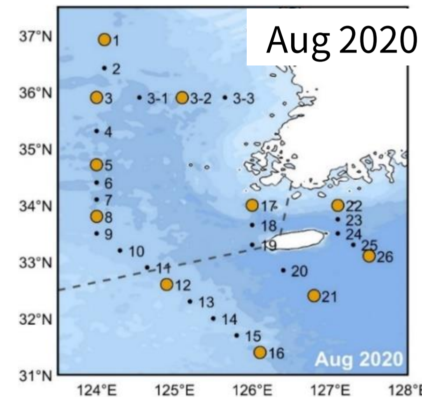


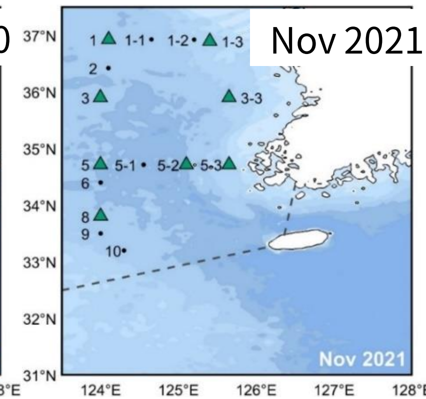
Various types of OC in the East China Shelf can contribute to **DOC pool**

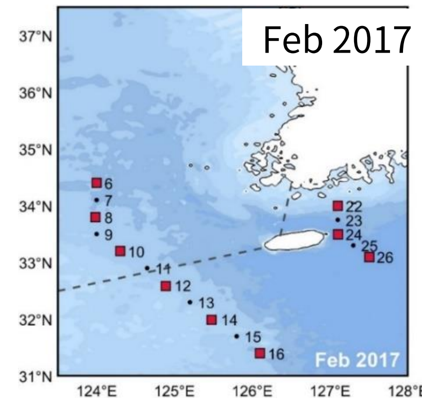
Sample collection

CTD casting & sampling site









* Colored: DOC sampling station
  Black: only CTD casting station
* Depth: surface, middle, bottom
* Feb 2017 data: Han et al. (2022)

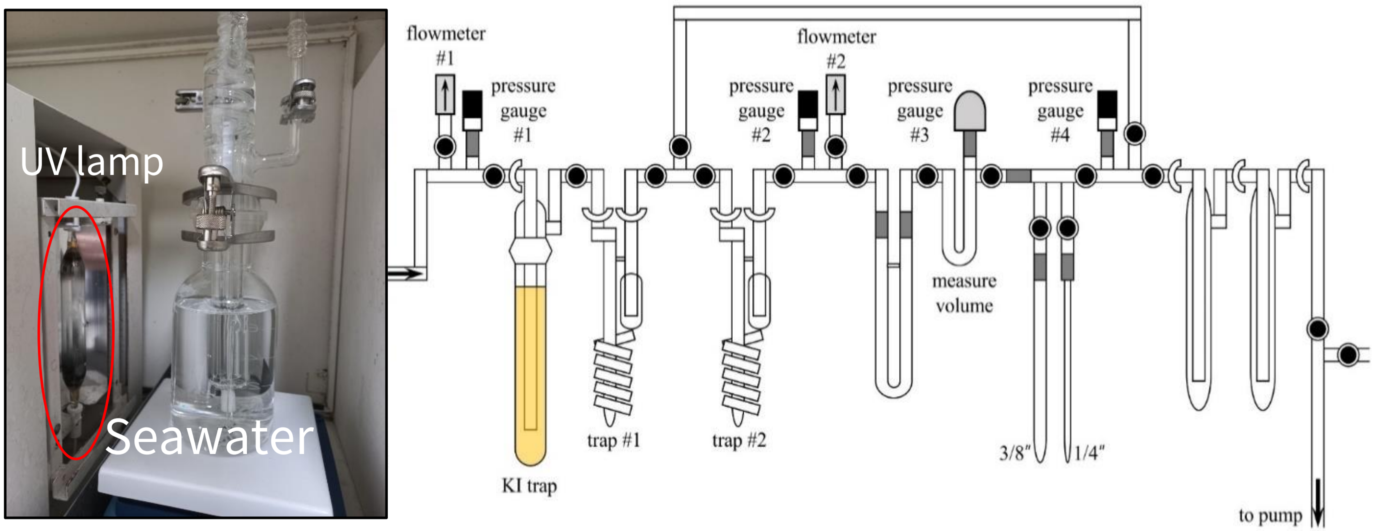
Sampling

Filtration (GF/F filter, 0.7 μm) ~800 mL of seawater → Sample storage (frozen at –20°C)

Sample analysis

Radiocarbon

UV oxidation method (Beaupre et al., 2007): UV for 6 hours to **oxidize DOC to CO_2**



DOC concentration ([DOC])

High temperature catalytic oxidation method

$\sigma = \pm 2\%$

TOC analyzer

^{14}C analysis at:

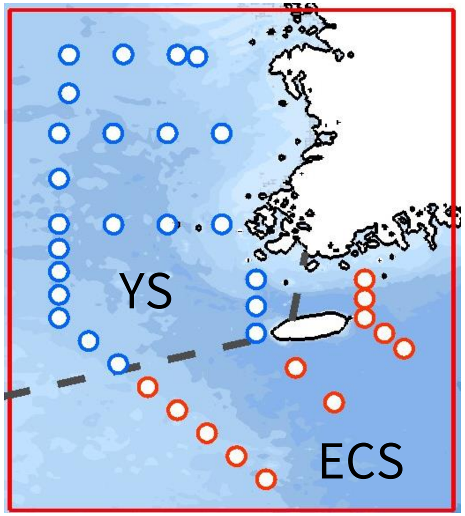
National Ocean Sciences AMS at WHOI

Keck Carbon Cycle AMS in UC Irvine

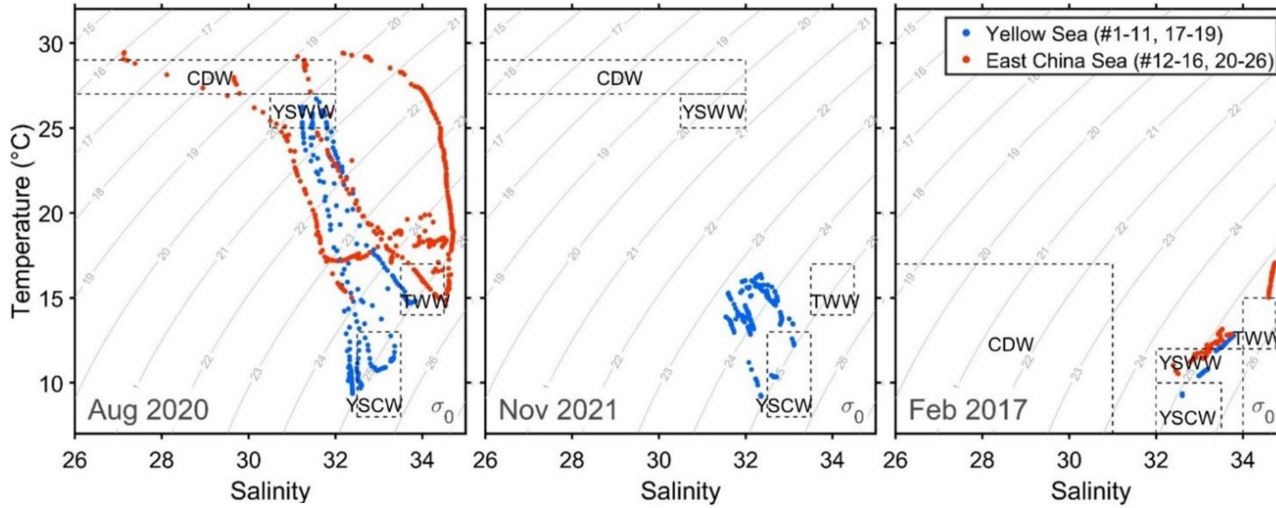
Analytical uncertainty

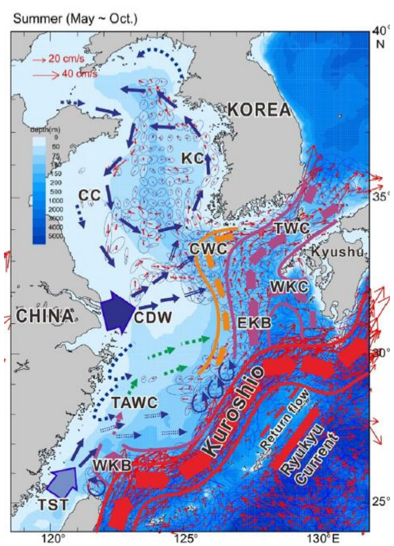
DOC $\Delta^{14}C$ (‰): ±8‰

Hydrography

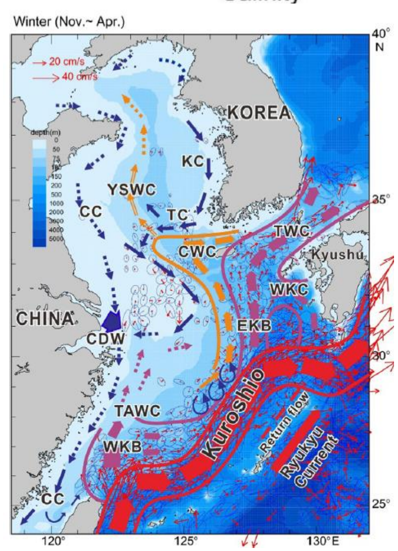


Summer (Aug 2020) Autumn (Nov 2021) Winter (Feb 2017)





Summer (May – Oct)



Winter (Nov – Apr)

*** Water mass categorization (Chen, 2009):**

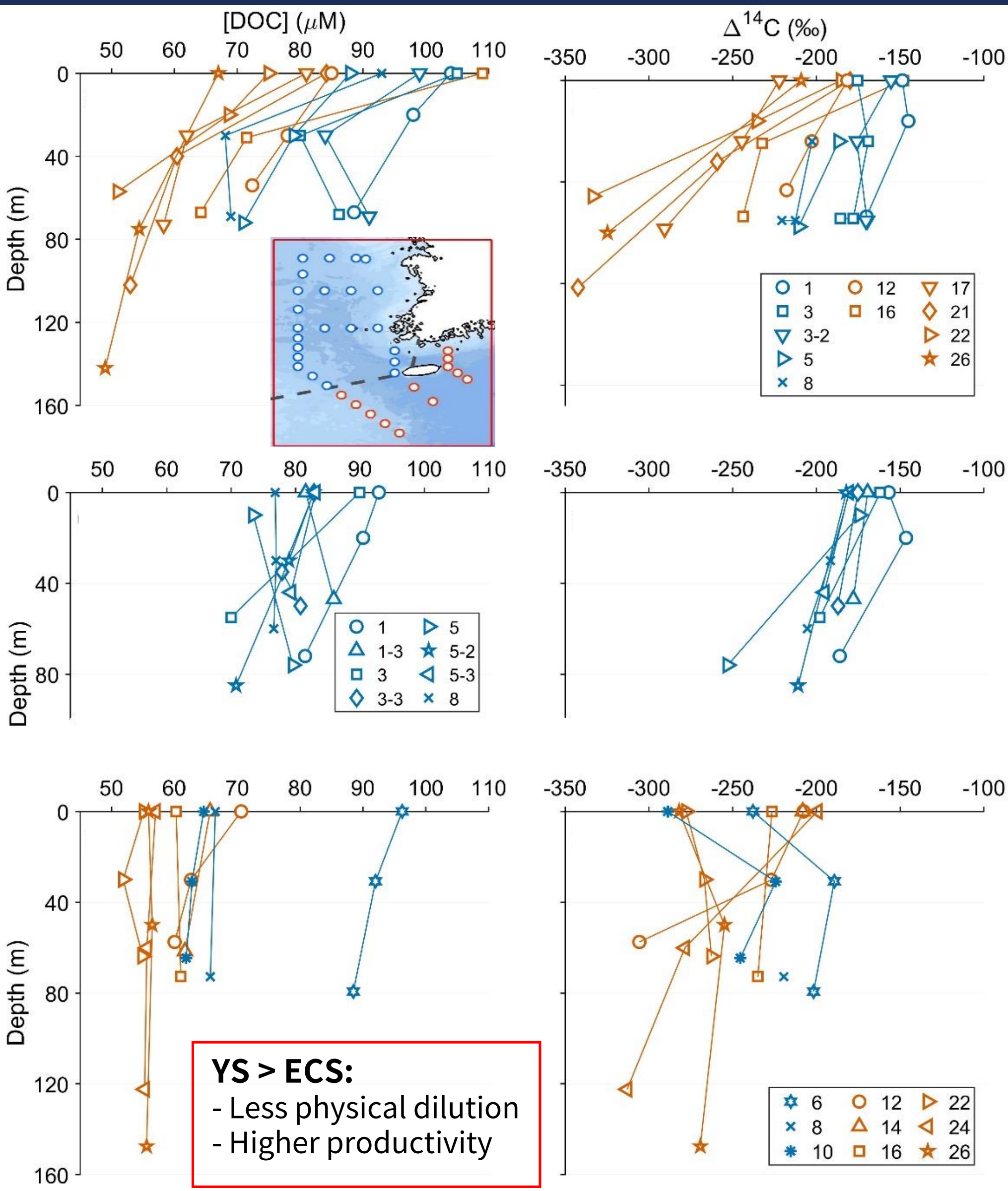
Changjiang Diluted Water (CDW)

Yellow Sea Water (YSCW & YSWW)

Tsushima Warm Water (TWW): Kuroshio-originated

Lie & Cho (2016)

Distribution of [DOC] and $\Delta^{14}C$



Summer (Aug 2020)

Surface > Bottom
- Stratification
-> accumulation at the surface
  & degradation with depth

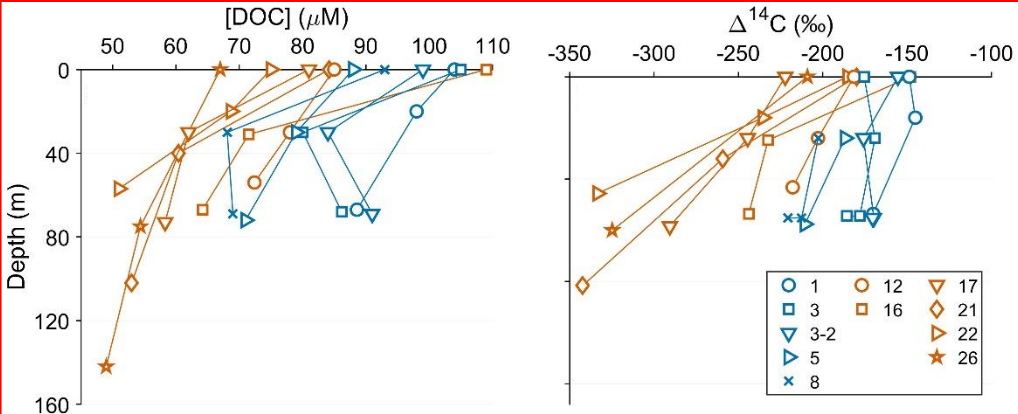
Autumn (Nov 2021)

Similar trend with summer, but with narrow ranged
- Lower productivity in late autumn than summer

Winter (Feb 2022)

Small variation of [DOC] with depth
- Vertical mixing due to strong monsoon

Distribution of [DOC] and Δ¹⁴C



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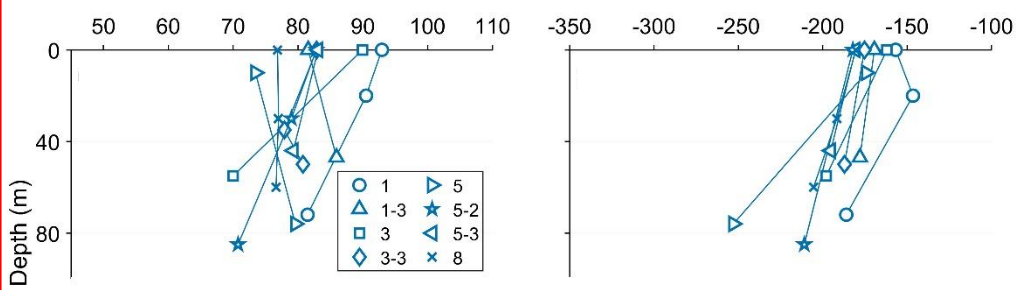

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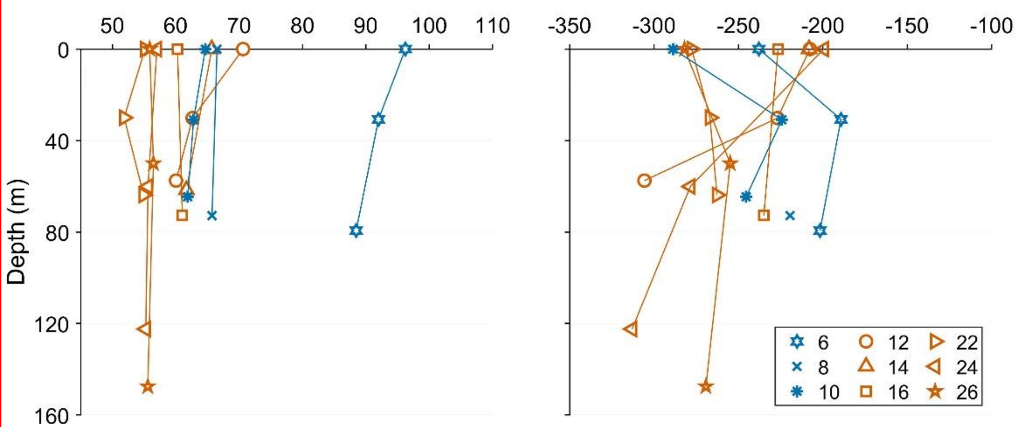

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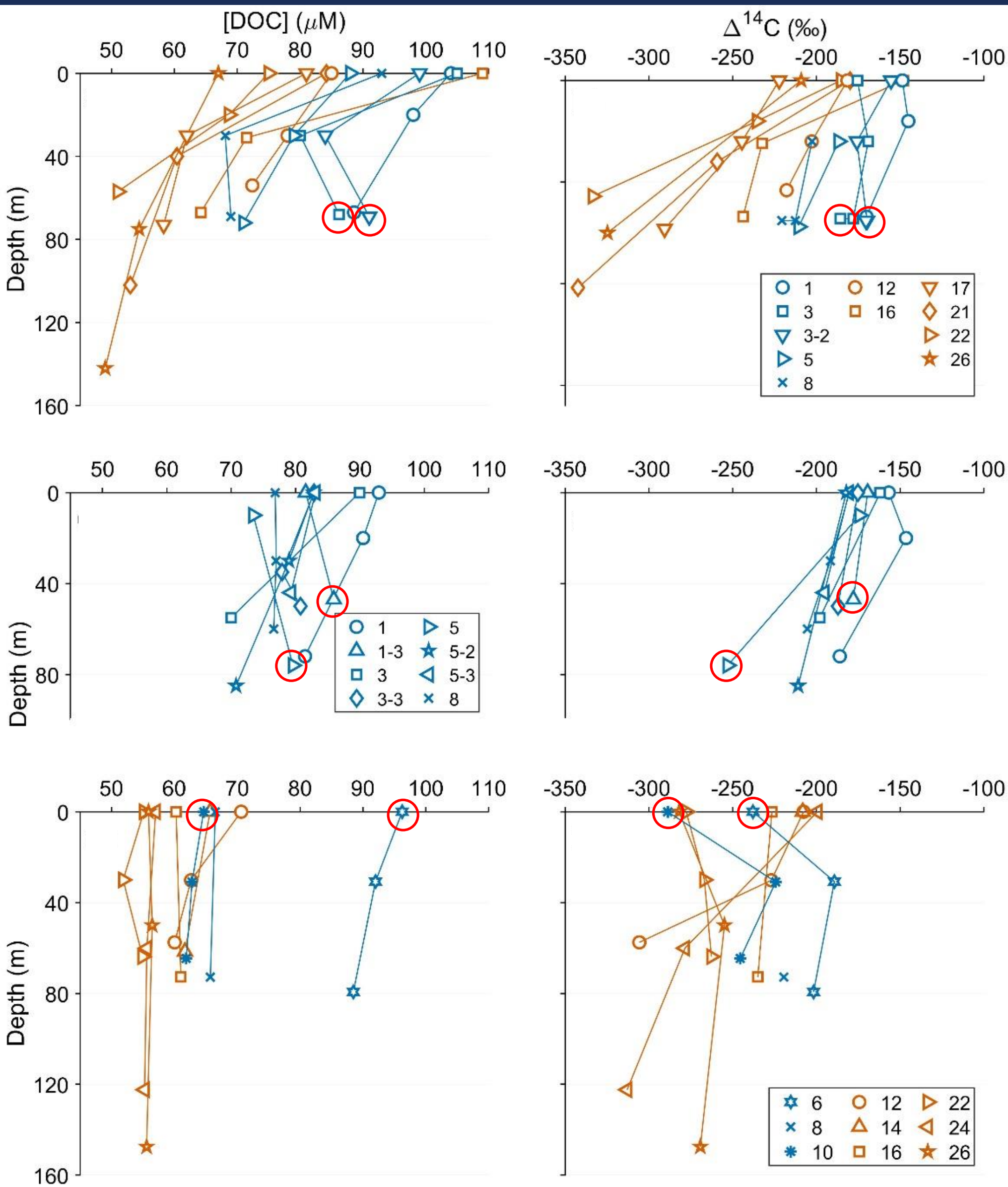
Distribution of [DOC] and $\Delta^{14}C$



* High [DOC], but low $\Delta^{14}C$ (red circles)

- Addition of ^{14}C-depleted DOC

* mobilization of aged POC to DOC

(sedimentary or atmospheric aged OC)

Sedimentary POC $\Delta^{14}C$ = –305 ± 102‰

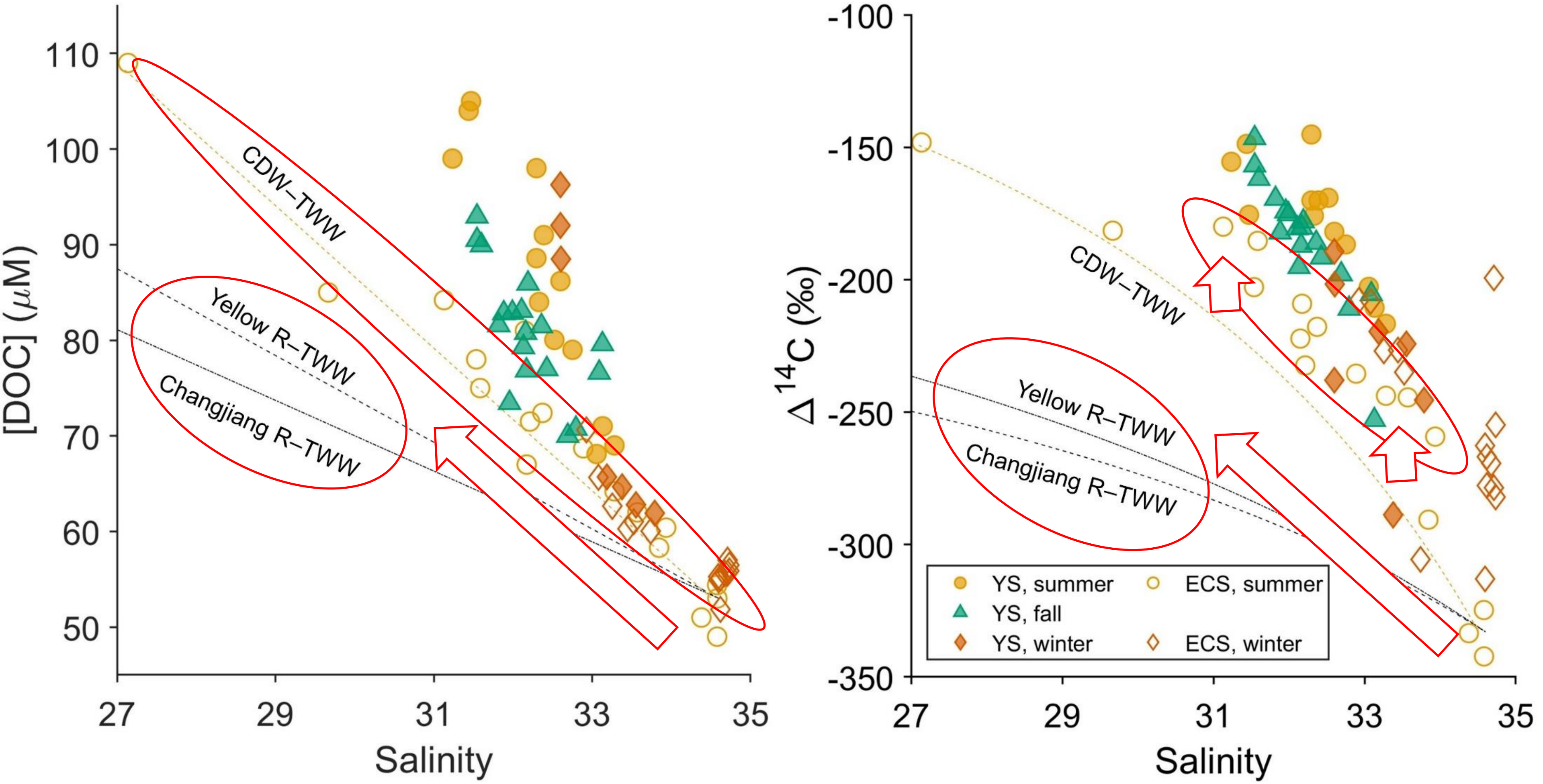
(Bao et al., 2016)

Aerosol POC $\Delta^{14}C$ = –304 to –640 ‰

in winter

(Ren et al., 2022)

DOC distribution with salinity

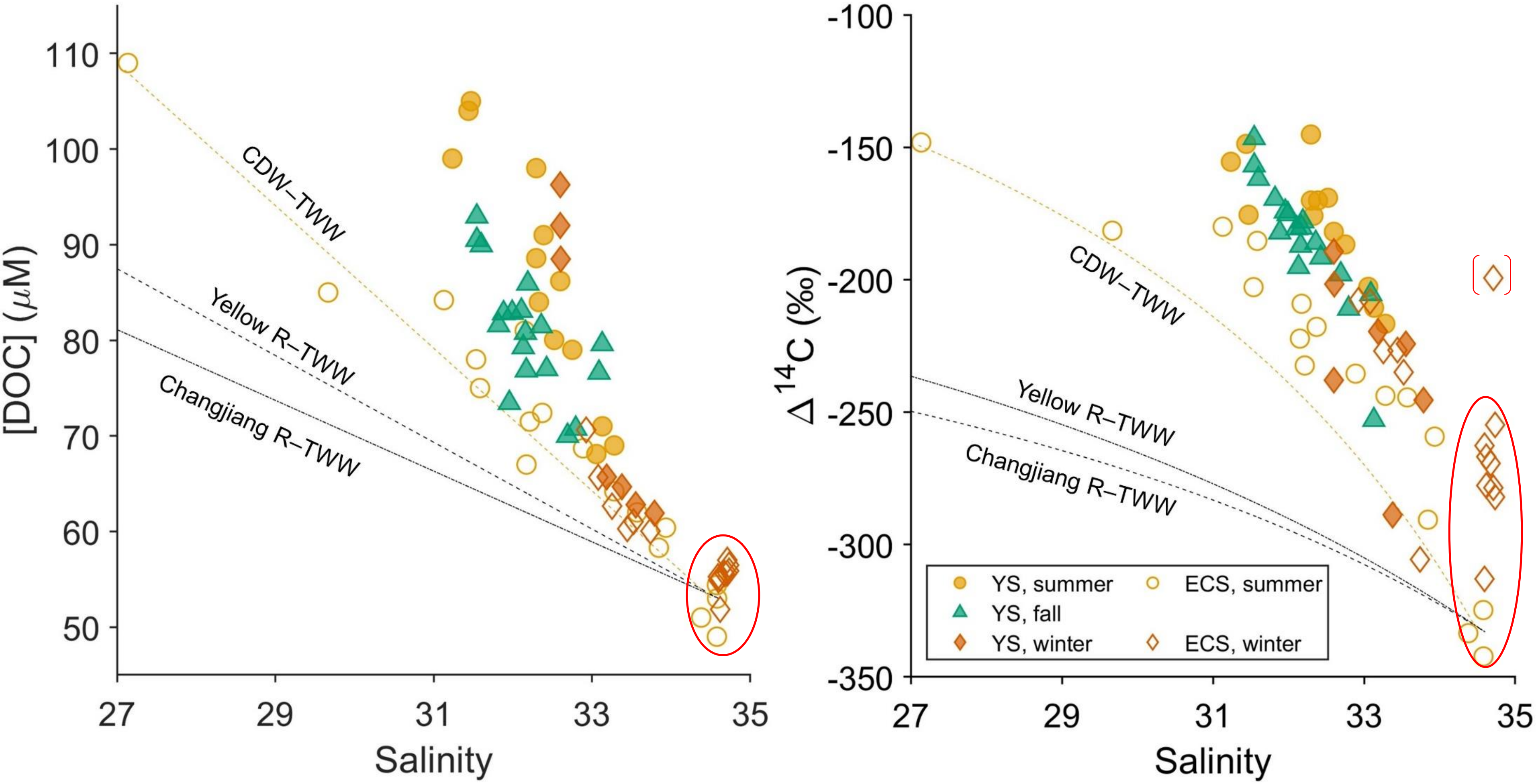


(3) Conservative behavior of [DOC] along CDW–TWW in the ECS, but higher $\Delta^{14}C$

- Removal of aged DOC & addition of fresh DOC during mixing

Addition of in-situ produced fresh DOC in the coastal water

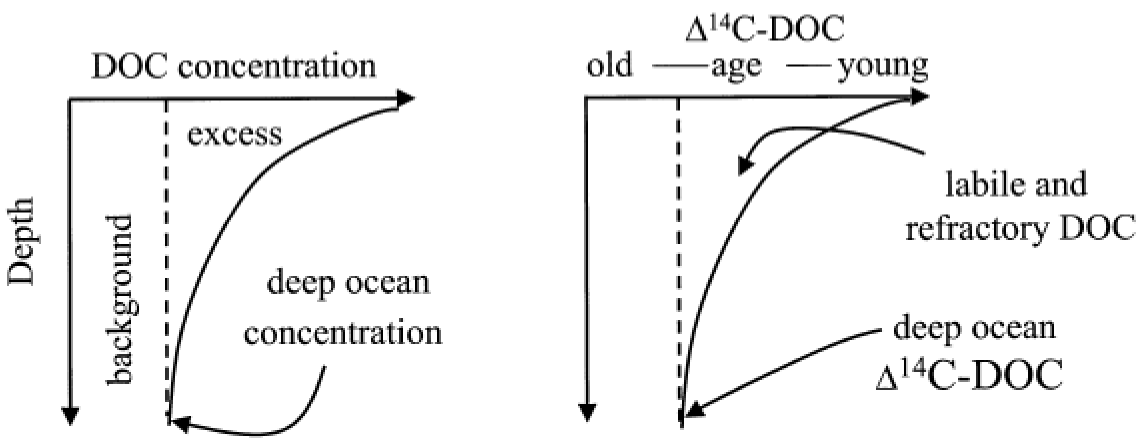
DOC distribution with salinity



(4) Significant seasonal variation of $\Delta^{14}C$ (~80‰) in TWW-DOC

- Degradation (production) of fresh DOC (aged DOC) in summer, or vice versa in winter

Major source of DOC in the YS & ECS: Keeling plot approach



Mortazavi & Chanton (2004)

Two-component mixing model

$$[DOC]_{total} = [DOC]_{bg} + [DOC]_{xs} \qquad \text{Eq. (1)}$$

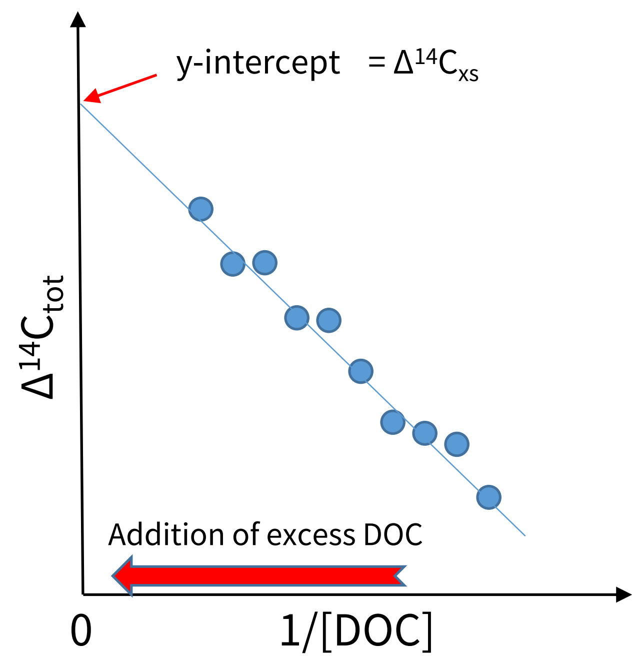
$$[DOC]_{total}\Delta^{14}C_{total} = [DOC]_{bg}\Delta^{14}C_{bg} + [DOC]_{xs}\Delta^{14}C_{xs} \qquad \text{Eq. (2)}$$

Combining Eq. (1), and (2)

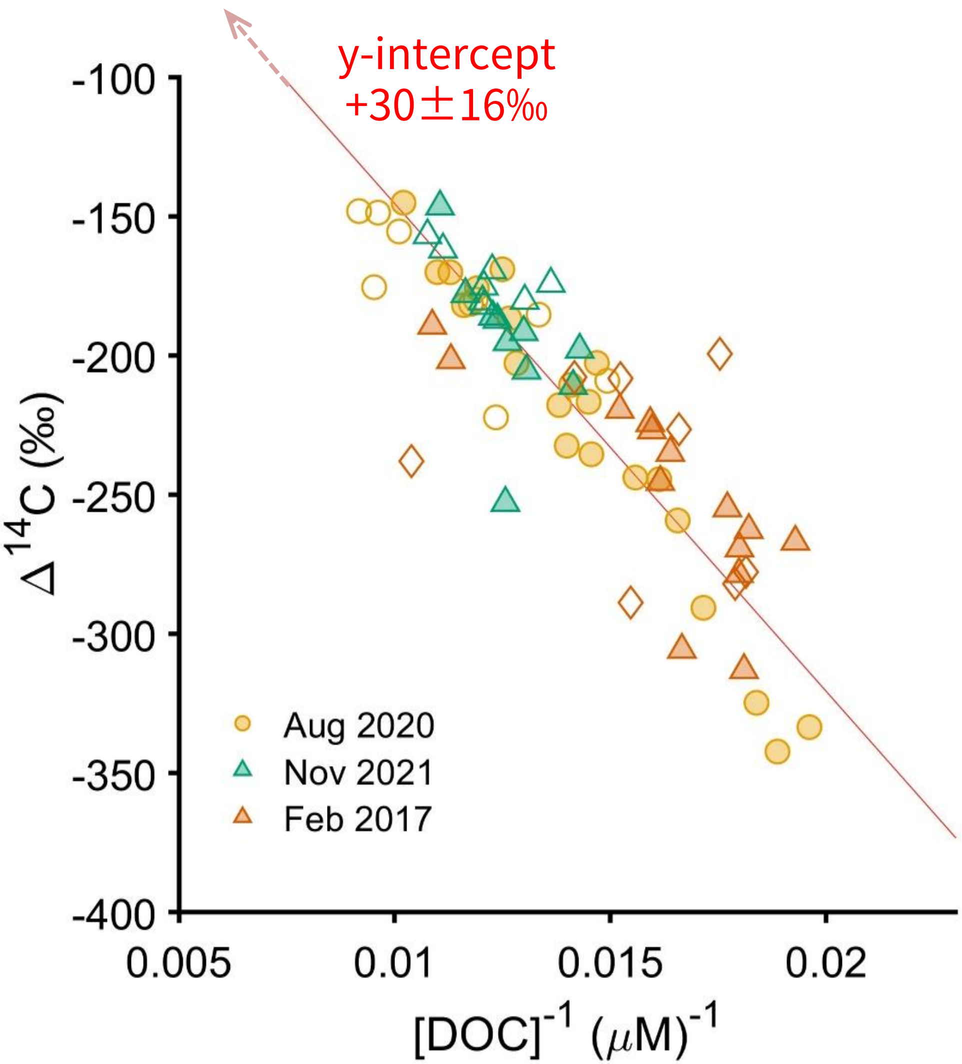
y = slope*x + y-intercept

$$\Delta^{14}C_{tot} = ([DOC]_{bg}\Delta^{14}C_{bg} - [DOC]_{bg}\Delta^{14}C_{xs})\left(\frac{1}{[DOC]_{tot}}\right) + \Delta^{14}C_{xs}$$

(tot: total, bg: background, xs: excess)



Major source of DOC in the YS & ECS: Keeling plot approach



Two-component mixing model

y = slope*x + y-intercept

$$\Delta^{14}C_{tot} = \left([DOC]_{bg}\Delta^{14}C_{bg} - [DOC]_{bg}\Delta^{14}C_{xs}\right)\left(\frac{1}{[DOC]_{tot}}\right) + \Delta^{14}C_{xs}$$

(tot: total, bg: background, xs: excess)

Date	R^2	y-intercept (‰)	DIC $\Delta^{14}C$ (‰)
Aug 2020	0.89	+49±18	
Nov 2021	0.46	+27±49	-8 to +12 (n = 3)
Feb 2017	0.36	-13±42	
All	0.74	30±16	

* Marine PP: same $\Delta^{14}C$ to DIC (-8 to 12‰)
pore-water DOC $\Delta^{14}C$: -66 to -12‰ (Fu et al., 2022)

Fresh ($\Delta^{14}C$ > 0‰) DOC (PP & pore-water DOC) dominate the DOC input in the YS & ECS

Summary

- Mixing among water masses is an important control of DOC cycle in the YS and ECS.
- Marine primary production is the dominant source of DOC.
- DOC supplied from sediment is another source of DOC in bottom layer.
- Using [DOC] and $\Delta^{14}C$ together provides information on various sources of DOC.

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