^{1}H NMR spectroscopy of dissolved organic matter in the Changjiang Estuary

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Introduction

Submarine groundwater discharge (SGD), which includes Submarine Fresh Groundwater Discharge (SFGD) and Recirculated Saline Groundwater Discharge (RSGD), is recognized as an important pathway between sea and land. More and more works showed that SGD is the source of dissolved compounds (e.g., nutrients, metals, carbon) to the ocean, and dissolved organic carbon (DOC) is one of the most important matters. The labile DOC (LDOC) has high biological reactivity and can be directly used by organisms (such as carbohydrates, etc.). The Refractory DOC (RDOC) can be regarded as an effective burial of carbon and has a special contribution to climate change (such as carboxyl-rich alicyclic molecules (CRAM), etc.). The structures of SGD-dissolved organic matter (SGD-DOM) are different from rivers and oceans due to its special water environment. Considering the behavior differences between DOM components in biogeochemical cycles, to distinguish the structure of DOC in SGD-DOM may help us to understand the biogeochemical cycle and carbon budgets of coastal waters.

In this study our objectives were to (1) identify, quantify and compare the different structural components (LDOC; RDOC) in SGD (statistically analysis and quantify by 0.1 ppm chemical shifts in 1D NMR spectra) and (2) estimate the contribution of different SGD-DOM type to the offshore organic carbon pool. This work would help deepen the understanding of their biochemical behaviors in the coastal areas.

Methods

Study sites and Sampling

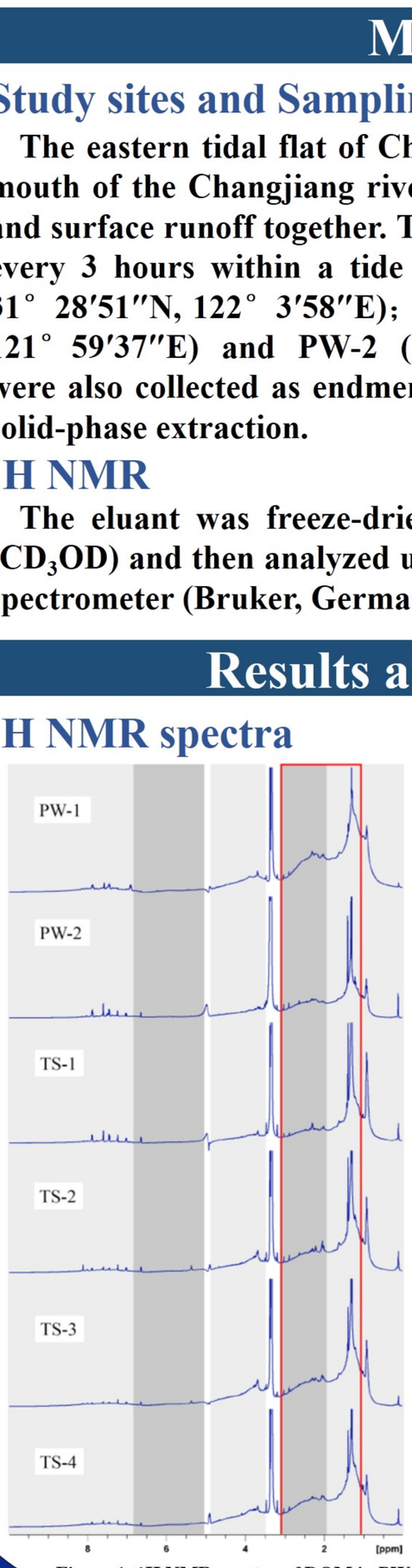
The eastern tidal flat of Chongming Island, which located at the mouth of the Changjiang river, is Influenced by semi-diurnal tides and surface runoff together. The coastal surface DOM was collected every 3 hours within a tide cycle at a time series station (TS, 31° 28′51″N, 122° 3′58″E); PW-1 (RSGD + FSGD, 31° 31′17″N, 121° 59′37″E) and PW-2 (FSGD, 31° 43′13″N, 121° 13′54″E) were also collected as endmembers and the DOM were isolated by solid-phase extraction.

^{1}H NMR

The eluant was freeze-dried, dissolved in deuterated methanol (CD_3OD) and then analyzed using a Bruker Avance DRX 500 NMR spectrometer (Bruker, Germany).

Results and Discussion

◆^{1}H NMR spectra



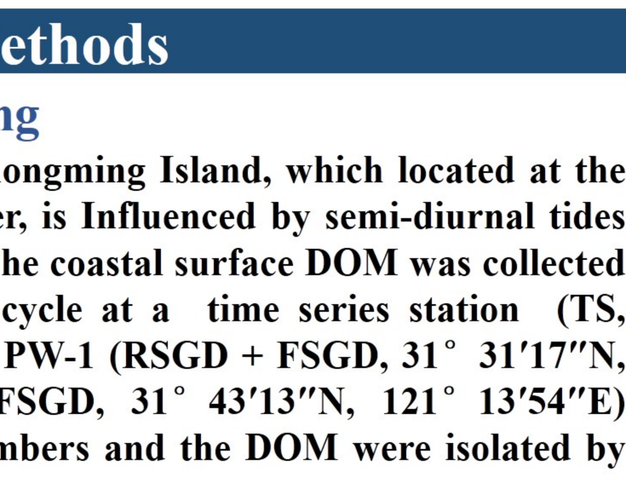


Figure 2. Magnified spectrum of the aromatic regions of all samples

Figure 1. 1H NMR spectra of DOM in PW and TS(1-4).

- The constituents of DOM in endmembers and coastal surface waters are similar
- The DOM molecular diversity of PW is more complex

◆ Quantify the different structural components

Table 1. Percentages of different constituents of DOM in 1H NMR spectra

^{1}H ppm	10-6.8	6.8-5.05	4.85-3.48	3.17-1.9	1.9-0
Key substructures	$\underline{H}_{ar}$	$\underline{H}C=C$ $\underline{H}CO2$	$\underline{H}CO$	$\underline{H}C$-N $\underline{H}C$-C-X	$\underline{H}$-C-C-C
PW-1	4.89	1.69	11.74	28.67	53.01
PW-2	5.34	3.84	13.01	28.40	49.40
TS-1	4.54	2.23	10.28	19.34	63.61
TS-2	4.49	3.16	14.05	24.43	53.86
TS-3	5.28	4.40	16.69	25.75	47.88
TS-4	5.11	3.79	15.22	28.00	47.87

- Aliphatic constituted a major part of the majority components (47.87-63.61%) of the total DOM .
- the content of carbohydrates (10.28-16.69%) is lower than ocean water.
- CRAM comprised 62.29-66.38% of the DOM in all SGD-DOM samples.

◆ Cluster analysis

Table 2. The physical and chemical parameters of the samples

	DO(mg/L)	pH	Salinity	Tide/m
PW-1	0.7	7.38	12.8	
PW-2	6.83	7.45	0.5	
TS-1	11.17	8.28	10.7	1.71
TS-2	11.34	8.3	5.3	2.47
TS-3	11.12	8.21	6.9	3.15
TS-4	10.99	8.23	6.1	2

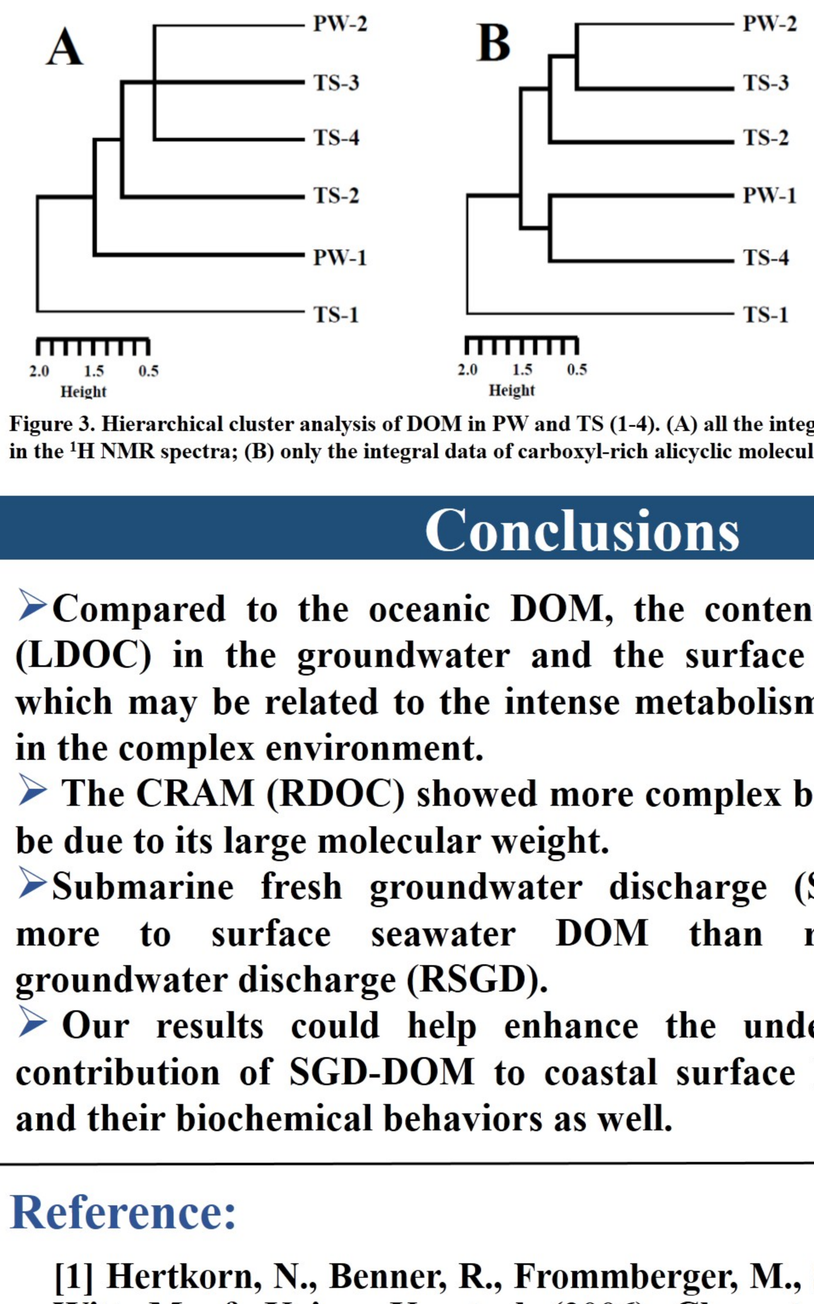


Figure 3. Hierarchical cluster analysis of DOM in PW and TS (1-4). (A) all the integral data in the ^{1}H NMR spectra; (B) only the integral data of carboxyl-rich alicyclic molecules.

- ✓ PW-2 was correlated better with TS with low salinity
- ✓ The CRAM showed more complex behavior

Conclusions

➢Compared to the oceanic DOM, the content of carbohydrates (LDOC) in the groundwater and the surface seawater is lower, which may be related to the intense metabolism of microorganism in the complex environment.

➢ The CRAM (RDOC) showed more complex behavior, which may be due to its large molecular weight.

➢Submarine fresh groundwater discharge (SFGD) contributes more to surface seawater DOM than recirculated saline groundwater discharge (RSGD).

➢ Our results could help enhance the understanding for the contribution of SGD-DOM to coastal surface DOM composition, and their biochemical behaviors as well.

Reference:

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[3] Dittmar, T., Koch, B., Hertkorn, N., & Kattner, G. (2008). A simple and efficient method for the solid‐phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnology & Oceanography Methods, 6(6), 230-235.