Molecular and isotopic characterization of DOM on the Siberian Shelf, Arctic Ocean.

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Scatter plots

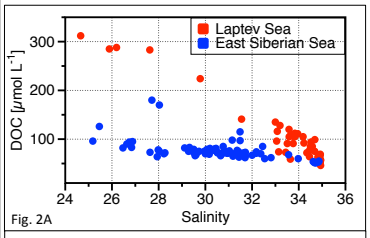


Fig. 2A

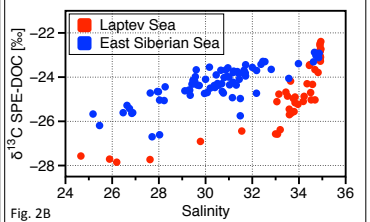


Fig. 2B

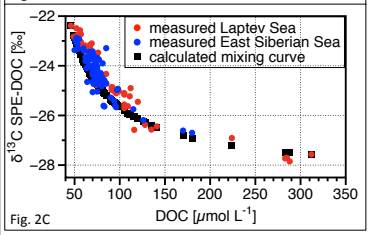


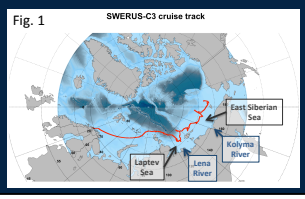
Fig. 2C

For both areas DOC concentrations and $\delta^{13}C$ values of the SPE-DOC are correlated to salinity, but show a different slope (Fig. 2A, B).
A comparison between a calculated mixing curve and the measured values indicates, that mixing is mainly determining the DOM distribution (Fig. 2C).

Background

- The composition and fate of terrestrial DOM reaching the Arctic Ocean via the large Siberian rivers is still largely unknown [1].
- During July/August 2014 the outer Siberian shelf of the Laptev Sea and East Siberian Sea was sampled with the Swedish research I/B ODEN (51 stations, Fig. 1, 5).
- Stable carbon isotope analyses of SPE-DOC were performed to distinguish between marine ($\delta^{13}C$: > -23 ‰) and terrestrial ($\delta^{13}C$: < -27 ‰) DOM.
- Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) was used to gain more information about the molecular DOM composition.

Fig. 1



DOM sources and calculation of terrestrial DOC

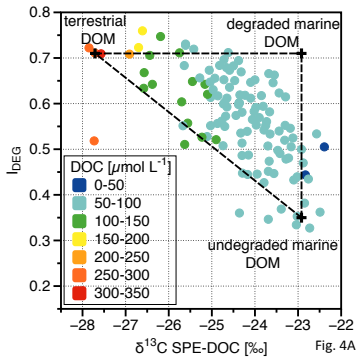


Fig. 4A

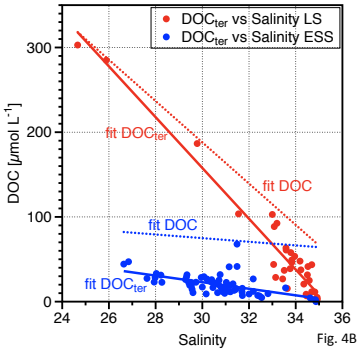
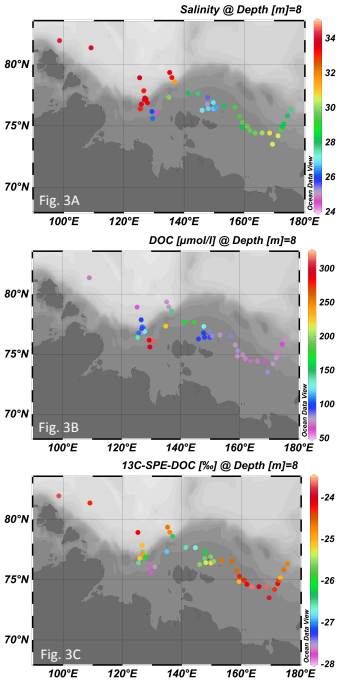


Fig. 4B

The PCA results of the FT-ICR MS data showed, that it is possible to distinguish degraded from un-degraded marine DOM, as well as terrestrial from marine DOM, by plotting I_{DEG} versus $\delta^{13}C$ SPE-DOC (Fig. 4A). The calculated terrestrial end-member $\delta^{13}C$ value of -27.1‰ from our data agrees with the $\delta^{13}C$ values of DOC measured in the the Lena River (load weighted average: -27.1‰, [3])
Based on calculations with a linear mixing model it was possible to calculate the concentrations of terrestrial DOC (DOC_{ter}) for both areas and plot them versus salinity (Fig. 4B).

Surface distribution



In the inner parts of the Laptev Sea, the influence of the Lena river is clearly visible in the surface salinities (Fig. 3A), high DOC concentrations (Fig. 3B) and low $\delta^{13}C$ SPE-DOC (< -27‰, Fig. 3C)). At the outer parts marine conditions dominate (salinity >30, DOC ≅ 50 µmol L^{-1}, $\delta^{13}C$ SPE-DOC > -23‰).
The East Siberian Sea shows generally lower DOC concentrations (around 50 µmol L^{-1}) and higher $\delta^{13}C$ values (< -25‰) which indicates a higher contribution of marine DOM and not a high influence of the Kolyma River.

Fig. 5: The Swedish research-icebreaker ODEN

Conclusions

- **Mixing is the dominant process that determines the DOM distribution on the Siberian shelf (Fig. 2C).**
- **Terrestrial DOM can be distinguished from marine DOM by means of the $\delta^{13}C$ SPE-DOC values, degraded from un-degraded marine DOM by means of the degradation index (I_{DEG})(Fig. 4A).**
- **Our results suggest, that terrestrial DOC behaves rather conservative on the Siberian Shelf (Fig. 4B).**

Results from the Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS)

The number of identified compounds ranged from 3807 to 5053, and the DOM composition is dominated by highly unsaturated compounds (rel. contribution 73 – 90%). The compounds that highly correlate to $\delta^{13}C$-SPE-DOC (Spearman correlation) are shown in a Van Krevelen plot (Fig. 6). Clearly visible is the shift from compounds dominating marine DOM (H/C <1) to terrestrial DOM compounds (H/C >1) with increasing $\delta^{13}C$ values. A degradation Index (I_{DEG}) was calculated from 10 formulas, that can be used to describe the degradation state of DOM [4].

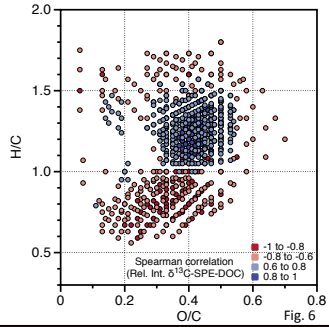


Fig. 6

A Principal Component Analysis (PCA) was performed with all molecular data. It showed that 84% of the variance in the molecular composition can be explained by two PCs (PC1: 60%, PC2: 24%). A correlation of the PC-scores with the environmental data showed that PC1 is highly correlated to I_{DEG} – describing the degradation state of the material, whereas PC2 shows a good correlation to all parameters that distinguish between marine and terrestrial sources, like $\delta^{13}C$-SPE-DOC, salinity, and δ^2H-H_2O (Fig. 7).

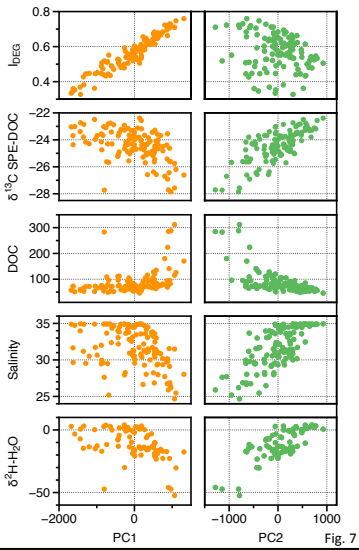


Fig. 7

Methods

- Sampling of surface samples (8m depth) was done from the vessels' seawater-intake. All other samples were taken from Niskin-bottles attached to a Seabird 911plus CTD system.
- DOC was analyzed on a Shimadzu TOC Analyzer, after GFF-filtration.
- SPE was performed following the procedure described in [2] with Bond Elut-PPL cartridges (1gm / 6mL).
- $\delta^{13}C$ values of the SPE-DOC were analyzed with a Thermo Finnigan DeltaV advantage IRMS after combustion in a CarloErba NC2500.
- δ^2H-H_2O values were analyzed on a Picarro LWIA analyzer.
- The molecular characterization of the samples was done via FT-ICR-MS (Bruker Solarix, 15 Tesla) using electrospray ionization in negative mode. Scanning range was 150-2000 Da; peak intensities were normalized.

Acknowledgements

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Cited Literature

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