



Heterogeneity of natural organic matter from the Chena River, Alaska

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Abstract

Water samples were collected in July 2001 from the Chena River in central Alaska. The natural organic matter (NOM) was size fractionated into particulate (POM, > 0.45 μm), colloidal (COM, 1 kDa–0.45 μm) and dissolved (DOM, < 1 kDa) organic matter fractions, using filtration and ultrafiltration. The size-fractionated organic matter was then analyzed for organic carbon (OC) and nitrogen (N), isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) and molecular composition, using continuous flow isotope ratio mass spectrometry and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Results of phase partitioning showed that, on average, about 6% of OC and 16% of N occurred in the form of POM while 66% of OC and 57% of N occurred in the form of COM, and 28% of the OC and 27% of the N were in the DOM form. Organic matter in the river water was found to be highly heterogeneous in terms of chemical composition and isotopic signatures. The C/N ratio was as low as 16 ± 1 in the POM ($n = 2$) to as high as 48 ± 1 in the COM ($n = 3$) and 38 ± 4 in the DOM ($n = 3$), suggesting a diagenetically younger POM. Values of $\delta^{13}\text{C}$ increased with decreasing size, varying from $-29.59 \pm 0.45\%$ in the POM to $-27.47 \pm 0.06\%$ in the COM to $-16.93 \pm 0.08\%$ in the DOM. In contrast, values of $\delta^{15}\text{N}$ decreased with decreasing size, from 2.64% in POM to 1.64% in COM to 1.33% in DOM. These results, together with radiocarbon measurements, suggest a preferential decomposition of lighter C isotope (^{12}C) and heavier N isotopic (^{15}N) from POM to COM to DOM. Results of py-GC/MS showed that the percentage of polysaccharides decreased with decreasing size, further supporting a degradation pathway of NOM from POM to COM and DOM in Chena River waters. More studies are needed to examine the seasonal and spatial variations of size-fractionated organic matter.

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1. Introduction

Natural organic matter (NOM) plays an important role in the biogeochemical cycles of many trace elements and the quality of aquatic environments [1,2]. Therefore, chemical composition, origin, and transport of NOM in riverine systems have received increasing attention (e.g., [3,4]). It is likely that the partitioning of NOM between

dissolved, colloidal and particulate phases governs the mobility and bioavailability of NOM in aquatic systems [5,6]. In addition, the chemical composition of NOM may play a critical role in controlling the fate and transport of NOM in riverine waters. However, NOM partitioning between dissolved, colloidal and particulate phases in natural waters is not well understood. Furthermore, organic matter of different size fractions remains poorly characterized, but knowledge of chemical characterization is essential for better understanding organic carbon cycling and other biogeochemical processes [3,7].

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Available evidence projects a significant polar amplification of the global warming signal for the Circum-Arctic region. It is estimated that northern ecosystems have accumulated 25–33% of the world's soil carbon [8]. Carbon currently sequestered in permafrost is likely to be exposed to physicochemical and biological degradation in a warming climate. For example, the upper 100 m layer of permafrost contains approximately 10,000 Gt of organic carbon that could be involved in biogeochemical cycling as CH₄ and CO₂ forms [9]. Therefore, knowledge of the composition of NOM and its fate and transport in the Northern aquatic environment is needed to gain a better understanding of the carbon cycle and climate change in the time scale of human concern [10].

Recently, cross-flow ultrafiltration and other size-fractionation techniques have been used in both freshwater and marine systems to examine the size distribution of NOM [11–13]. These separation techniques have also been used to isolate organic matter for physical and chemical characterization [14–16]. However, these previous studies are mostly on colloidal organic matter (COM). Characterization of all three NOM phases is needed to better understand NOM transportation and transformation processes.

In the present study, filtration and ultrafiltration were used to size-fractionate NOM from the Chena River, Alaska, into particulate organic matter (POM) (> 0.45 μm), COM (1 kDa–0.45 μm) and DOM (< 1 kDa) for elemental, isotopic, and molecular characterization. It was found that NOM is highly heterogeneous in both chemical composition and isotopic signatures, suggesting different environmental fate for different size fractions of NOM.

2. Materials and methods

2.1. Sampling and size-fractionation procedures

Water samples were collected from the Chena River in central Alaska (Table 1). The Chena River has a drainage area of ~5190 km² and the monthly mean stream flow ranges from < 10 to ~100 m³ s⁻¹, with the highest flow in May and lowest in March (see <http://waterdata.usgs.gov/ak/nwis/monthly>). Water conductivity was about 290 μS cm⁻¹ and the total suspended particulate matter (SPM) concentration was 4.98 mg l⁻¹ (Table 1). The NOM in water samples was size fractionated into three operationally defined size fractions using filtration and ultrafiltration (Fig. 1). Water was pumped peristaltically and filtered through a pre-rinsed 0.45 μm Nuclepore cartridge to separate organic matter into particulate (> 0.45 μm) and filter-passing (< 0.45 μm) phases. The 0.45 μm filtrate was then further size fractionated into COM (1 kDa–0.45 μm)

Table 1

Concentrations of organic carbon and nitrogen and other ancillary data of Chena River waters collected during July 2001 from Fairbanks, Alaska (147°42'W; 64°50'N)

Parameter	Value	Description
COC (mg-C l ⁻¹)	4.01	1 kDa–0.45 μm
DOC (mg-C l ⁻¹)	1.77	< 1 kDa
POC (mg-C l ⁻¹)	0.345	GF/F filter retained
PON (mg-N l ⁻¹)	0.026	GF/F filter retained
Conductivity (μS cm ⁻¹)	290	Whole water
SPM (mg l ⁻¹)	4.98	> 0.45 μm

COC denotes colloidal organic carbon (1 kDa–0.45 μm), and DOC denotes the < 1 kDa low molecular weight DOC. POC (or PON) is particulate organic carbon (or particulate organic nitrogen) retained by glass fiber filter (GF/F). SPM is suspended particulate matter (> 0.45 μm).

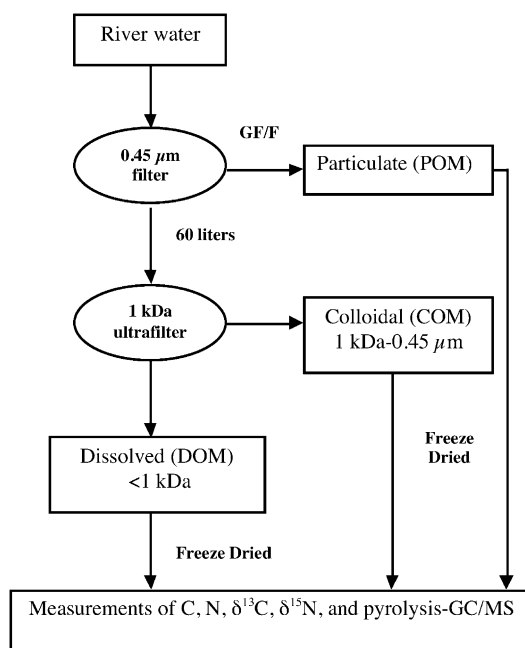


Fig. 1. Schematic of organic matter size fractionation using filtration and ultrafiltration [17,26].

and DOM (< 1 kDa) fractions, using cross-flow ultrafiltration (Fig. 1).

The COM was isolated from prefiltered river water using an ultrafiltration system equipped with an Amicon 1 kDa (S10Y1) ultrafiltration cartridge. Therefore, the COM is operationally defined here as the fraction with size or molecular weight ranges between 1 kDa and 0.45 μm. The ultrafiltration cartridge was checked for integrity using standard macromolecules with known molecular weights (such as vitamin B₁₂) and thoroughly cleaned before sampling using Microdetergent, NaOH, HCl, and Milli-Q water (with a DOC concentration of

$\sim 2 \mu\text{mol C l}^{-1}$) using procedures described in [17]. Before ultrafiltration, 2 l of pre-filtered water was used to condition the ultrafiltration cartridge. Mass balance was checked for OC recovered from both retentate and the $< 1 \text{ kDa}$ fractions. A concentration factor of ~ 30 was used for ultrafiltration.

The isolated COM was then freeze dried to yield a powder sample for further characterization. A fraction of DOM was also freeze dried to result in powder samples.

Duplicate POM samples were collected on pre-combusted glass fiber filters (GF/F, Whatman 47 mm). An aliquot of whole water was also filtered on a pre-weighed Nuclepore filter ($0.45 \mu\text{m}$) to determine the concentration of SPM. Filter samples were dried at 60°C and reweighed to yield an SPM concentration in terms of mg of particulate matter per liter of river water.

2.2. Measurements of organic C, N, $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$

Aliquots of DOM and COM fractions were measured for the concentrations of organic carbon [11], to examine ultrafiltration mass balance and the size distribution of OC in the Chena River water. In addition to the analysis of OC in liquid samples, elemental (C and N) and isotopic ($\Delta^{14}\text{C}$, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) composition were analyzed on the freeze-dried samples of POM, COM, and DOM.

Both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ as well as C and N contents were measured by a continuous flow isotopic ratio mass spectrometer [18]. Stable carbon and nitrogen isotope ratios were calculated in terms of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, $(R_{\text{sample}}/R_{\text{standard}} - 1) \times 1000$, where R is the ratio of $^{13}\text{C}/^{12}\text{C}$, or $^{15}\text{N}/^{14}\text{N}$, in NOM samples or standard (PDB for carbon and atmospheric N_2 for nitrogen). The precision and accuracy of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis were $\pm 0.1\%$, and $\pm 0.2\%$, respectively, as determined by replicate analysis of standards and samples. $\Delta^{14}\text{C}$ was measured by accelerator mass spectrometer. All samples were treated with HCl before organic carbon determination and characterization [15].

2.3. Molecular characterization

Size-fractionated organic matter samples, including filter samples and freeze-dried powder samples, were fingerprinted using pyrolysis-gas chromatography/mass spectrometry (py-GC/MS) techniques [19,20]. Briefly, pyrolysis was conducted with a CDS Analytical Pyroprobe 2000 pyrolyzer and AS 2500 auto-sampler in tandem with a GC/MS. The pyrolysis reactor was mounted on an HP 6890 GC, with a Restek Rtx35-MS column, $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$. Before pyrolysis, the sample was held in the 280°C interface chamber for 15 s while the chamber was purged with He carrier gas. During pyrolysis the sample was heated from a starting

temperature of 280°C to 700°C at 10°C ms^{-1} and held at a constant 700°C for 10 s. Pulsed splitless injection was used, with pulse pressure 25 psi. After 1 min, the pyrolyzer was switched offline and column head pressure was reduced to provide constant flow of He at 2.0 ml min^{-1} . The GC temperature program was 40°C for 10 min, then ramp at 1°C min^{-1} to 110°C . A final ramp at $20^\circ\text{C min}^{-1}$ to 280°C and hold for 10 min was used to clean out the column in preparation for the next sample. The GC was plumbed directly to an HP 5973 mass selective detector on electron impact mode. The MS scanned mass units 45–650. All mass spectra were compared to the Wiley275 spectral library.

Approximately 100 of the most abundant compounds in each pyrogram were identified using a mass spectral library. An index set of 21 compounds, divided into seven categories, was selected to show key differences between the three different size fractions. The ion chromatograph of the most abundant ion in each of the 21 index compounds was extracted from the total ion chromatograph. The area assigned to each index compound was equal to the area under the trace of the major ion only. This facilitated separation of overlapping peaks in the total ion chromatograph. A “fraction of index” for each category was calculated by summing the areas of all compounds in that category and dividing by the sum of areas of all 21 index compounds in that sample. The use of an index to display relative concentrations of various components in pyrolyzates of different samples has been used previously [19,21].

3. Results and discussion

3.1. Concentrations of organic carbon and its size distribution

Measurements of OC in three size-fractionated phases are summarized in Table 1. Particulate organic carbon (POC), which refers to the carbon equivalent of POM, in the Chena River water was $0.345 \text{ mg-C l}^{-1}$. Likewise, colloidal organic carbon (COC) and dissolved organic carbon (DOC) refer to the carbon equivalent of COM and DOM, respectively. The concentration of COC was 4.01 mg-C l^{-1} and the DOC concentration was 1.77 mg-C l^{-1} .

Using the sum of POC, COC and DOC as total organic carbon (TOC) concentration, the size distribution of the TOC among particulate, colloidal and dissolved phases can be calculated. On average, $\sim 6\%$ of the TOC occurred in the form of POM and 66% of the TOC was the form of COM, and 28% of the TOC was in the DOM phase (Fig. 2). The low percentage of POC ($\sim 6\%$) may be related to the relatively low stream flow in July ($< 60 \text{ m}^3 \text{ s}^{-1}$) and low biological

productions during the sampling time (see Section 3.2). However, as shown in Fig. 2, a considerable portion (66%) of the TOC was associated with a colloidal phase, defined as the size fraction between 1 kDa–0.45 μm . The high COM percentage was consistent with those previously reported for other rivers (e.g. [3,13,22]). Since environmental behavior, such as mobility, bioavailability and degradability of COM and its associated trace elements could be significantly different from those of POM and DOM phases [5,6], the high concentration of COM in the river waters may have significant impacts on pollutant transport, carbon cycling, and the ecosystem as a whole.

For the size partitioning of nitrogen, about 16% of total nitrogen (TN) was in the POM, 57% of the TN was in COM, leaving 27% of TN in the DOM phases (Fig. 2). As shown in Fig. 2, both organic carbon and nitrogen had a similar size distribution pattern, with the COM having the largest share for both OC and N.

3.2. Elemental composition of size-fractionated NOM

Elemental (C and N) composition of the three freeze-dried organic matter size fractions is shown in Table 2. Organic carbon content in the particulate sample was relatively low, with an average of $69 \pm 2 \text{ mg-C g}^{-1}$, indicating that the suspended particles of the Chena River water during the sampling time period were mostly composed of inorganic materials. However, higher OC content ($259 \pm 17 \text{ mg-C g}^{-1}$) was found in the powder COM samples. Using an average ratio of organic matter to organic carbon of 2.5 [1,22], a concentration of $259 \pm 17 \text{ mg-C g}^{-1}$ -COM implies that over 64% of the colloidal materials were organic in nature. Higher concentrations of OC in the colloidal phase indicate that riverine organic matter is transported largely in the colloidal phase, consistent with previous observations [3,22,13]. Moreover, the OC

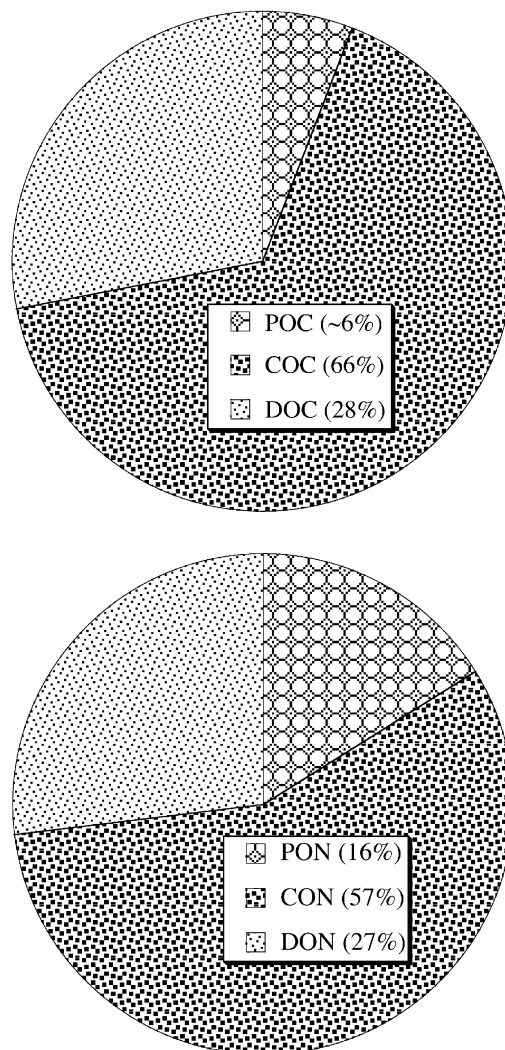


Fig. 2. Size distributions of organic carbon and nitrogen in the Chena River water.

Table 2

Organic carbon and nitrogen contents and their isotopic composition of size-fractionated organic matter from Chena River water

	Particulate (POM)	Colloidal (COM)	Dissolved (DOM)
Size fraction ^a	> 0.45 μm	1 kDa–0.45 μm	< 1 kDa
Organic C (mg-C g^{-1})	69.2 ± 1.5	259 ± 17	49.5 ± 2.3
N (mg-N g^{-1})	5.2 ± 1.3	6.3 ± 0.5	1.5 ± 0.1
C/N (molar ratio)	16 ± 1	48 ± 0.9	39 ± 4
$\delta^{13}\text{C}(\text{‰})$	-29.58 ± 0.45	-27.47 ± 0.06	-16.93 ± 0.08
$\delta^{15}\text{N}(\text{‰})$	2.64 ± 0.54	1.64 ± 0.50	1.33 ± 0.23
Fraction of modern	—	1.022 ± 0.004	0.928 ± 0.005
^{14}C age (y BP)	—	>modern	600 ± 45

^aThe 1 kDa cutoff defined here corresponds to approximately a 1 nm pore size. Standard deviations are those from replicate analysis ($n = 2$ for POM and $n = 3$ for COM and DOM samples). Date reported here are from freeze-dried powder samples.

content in the powder DOM sample was low ($49 \pm 2 \text{ mg-C g}^{-1}$ matter), corresponding to a mass concentration of only 12% of organic matter in the freeze-dried DOM material. Low percentage of OC in the DOM observed here is contradictory to those measured for salt waters in marine environments [11]. However, it is consistent with the fact that riverine organic matter contains mostly macromolecular or colloidal organic matter [4,15,16].

Calculated C/N atomic ratios were found to increase from 16 ± 1 in the particulate phase to 48 ± 1 in the colloidal phase and 39 ± 4 in the $<1 \text{ kDa}$ dissolved fraction (Table 2). Due to the preferential decomposition of N-containing organic compounds, organic C/N ratios can be used as an index of diagenetic status of organic matter in natural waters. Lower C/N ratio in the particulate phase indicates that the POM was relatively fresh and contained less altered organic material while the higher C/N ratio in both DOM and COM pointed to a more degraded allochthonous or refractory organic material. The higher C/N ratios in both colloidal and dissolved phases seemed to suggest a direction for the degradation, decomposition, and transformation of riverine organic matter from particulate to dissolved phases. This is consistent with other observations for estuarine and marine organic matter, which showed similar degradation or diagenetic pathways from particulate to colloidal and to dissolved phases [15]. However, more studies are needed to examine whether this is a representative processes in the river system.

3.3. Isotopic composition of size-fractionated NOM

Stable C and N isotopic composition is listed in Table 2. The $\delta^{13}\text{C}$ signature of POM was relatively low, with a value of $-29.59 \pm 0.45\text{‰}$, showing a typical ratio for terrestrial organic matter. However, it was relatively high in both DOM and COM, with a value of $-16.39 \pm 0.08\text{‰}$ and $-27.47 \pm 0.06\text{‰}$, respectively. More interestingly, values of $\delta^{13}\text{C}$ increased consistently with decreasing size of organic matter, varying from $-29.59 \pm 0.45\text{‰}$ in the particulate to $-27.47 \pm 0.06\text{‰}$ in the colloidal and $-16.93 \pm 0.08\text{‰}$ in the dissolved phase. Significant differences in the $\delta^{13}\text{C}$ values between organic matter phases support the fact that NOM is highly heterogeneous in aquatic environments [1]. If the degradation pathway of organic matter is from POM to DOM, as supported by the diagenetic index of C/N ratio among size-fractionated organic components, then the increasing $\delta^{13}\text{C}$ with decreasing size would point to a preferential decomposition of lighter isotope (^{12}C) from POM to COM to DOM.

Values of $\delta^{15}\text{N}$ varied from 1.33‰ to 2.64‰ between the three OM phases. These values are similar to those reported for fresh-water and marine organic matter samples. It is generally believed that biogeochemical

cycling of nitrogen is more dynamic compared with carbon in aquatic environments, with trophic transfer, microbial processes and isotopic fractionation being important factors in affecting N isotope distribution [18]. In contrast to $\delta^{13}\text{C}$ signatures, nitrogen isotopic composition showed a different variation trend, with decreasing $\delta^{15}\text{N}$ values with decreasing size (Fig. 3). For example, the value of $\delta^{15}\text{N}$ was $2.64 \pm 0.54\text{‰}$ in the POM, decreasing to $1.64 \pm 0.50\text{‰}$ in the COM and $1.33 \pm 0.23\text{‰}$ in the DOM fraction. Contrasting

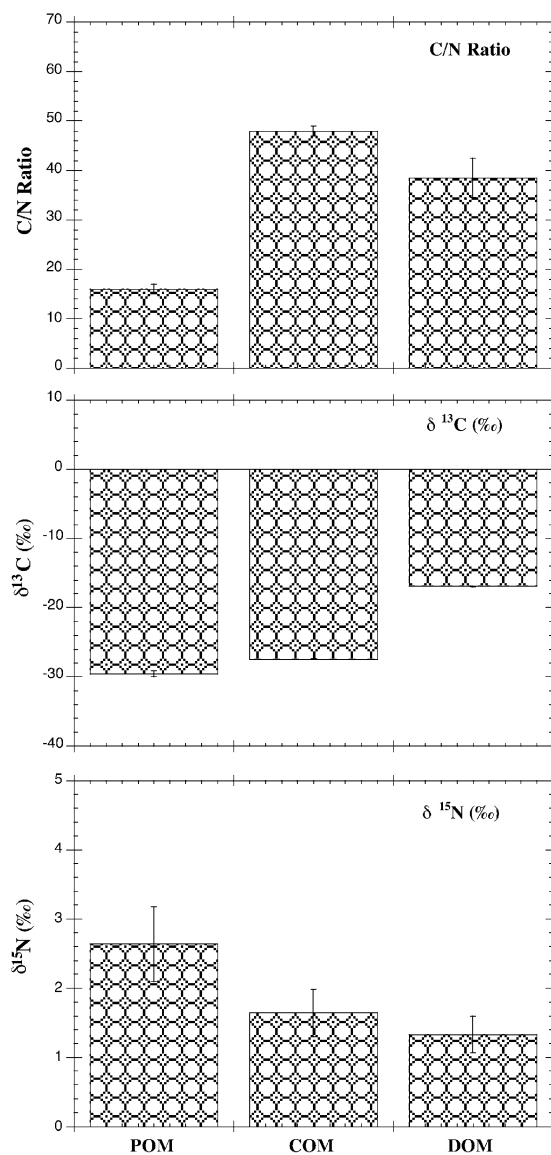


Fig. 3. Variations of C/N ratio, stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopic composition among different size fractions of NOM, including particulate (POM), colloidal (COM) and dissolved organic matter (DOM) phases.

distribution patterns between stable C and N isotopes also suggest a preferential decomposition of heavier $\delta^{15}\text{N}$ components in Chena River waters. Alternatively, it may point to a different source function for different size fraction of organic matter in the riverine water system, with higher $\delta^{13}\text{C}$ and lower $\delta^{15}\text{N}$ in the DOM fraction and lighter $\delta^{13}\text{C}$ and heavier $\delta^{15}\text{N}$ in the POM and COM fractions (Fig. 3). Overall, stable isotopic composition seems distinct between different organic matter size fractions. This heterogeneous nature suggests that different size fractions of organic matter could have varying biogeochemical pathways or environmental behaviors in the aquatic environment, consistent with their different apparent ^{14}C ages (Table 2).

3.4. Molecular characterization of size-fractionated NOM

Results of molecular characterization using py-GC/MS for the size-fractionated organic matter samples are summarized in Table 3 and compared with COM samples collected from other regions. The py-GC/MS fingerprints provided information about the molecular composition of NOM. A typical pyrogram with the compounds considered is showed in Fig. 4. Approximately 100 of the most abundant compounds in each pyrogram were identified using a mass spectral library. The major compounds were the same in all three pyrograms, but occurred in different proportions. An

Table 3
Comparison of % of index distributions in seven major organic groups of pyrograms

Major organic group	% of index				
	POM	COM	DOM	Mississippi COM	Oceanic COM
Furfurals	22.7	3.8	1.8	8.5	41.1
Pyridines	4.5	2.5	3.0	4.8	3.8
Cyclopentenones	11.5	17.6	27.7	18.6	15.8
Benzenes	19.0	39.3	27.0	21.3	16.8
Phenols	30.2	19.3	23.0	34.4	12.3
Indenes	7.4	12.0	14.1	9.5	7.2
Naphthalenes	4.7	5.4	3.5	3.0	3.0

POM, COM, and DOM denotes particulate ($>0.45\ \mu\text{m}$), colloidal ($1\ \text{kDa}$ – $0.45\ \mu\text{m}$) and dissolved ($<1\ \text{kDa}$) organic matter, respectively. Data of COM from Mississippi River and oceanic (Middle Atlantic Bight) waters are from Guo et al. (unpublished results).

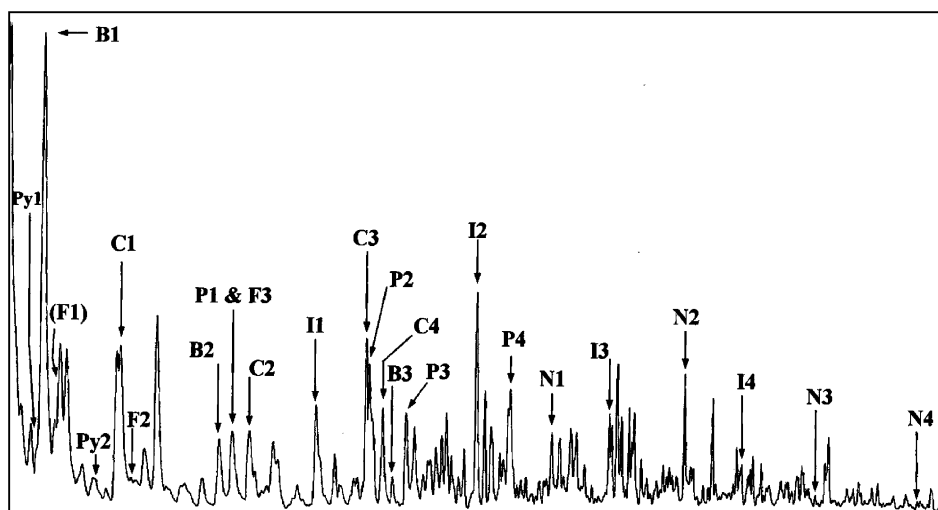


Fig. 4. Typical chromatogram with peaks identified. Label compound: F1 for furfural, F2 and F3 for methyl furfural, C1 and C2 for methyl cyclopentenone, C3 for dimethyl cyclopentenone, C4 for trimethyl cyclopentenone, P1 for phenol, P2 and P3 for methyl phenol, P4 for dimethyl phenol, B1 for dimethyl benzene, B2 for trimethyl benzene, B3 for tetramethyl benzene, I1 for indene, I2 for methyl indene, and I3 for dimethyl indene.

index set of 21 compounds, divided into seven categories, was selected to show key differences between the samples. The relative proportions of compounds in the seven categories are shown in Table 3.

Furfurals, a pyrolysis product of polysaccharides [23], comprised nearly 23% of the total index in the POM sample but less than 5% in the COM and DOM samples.

Cyclopentenones are common in the pyrolyzates of aquatic organic matter. Bracewell et al. [23] identified 2-cyclopenten-1-one as a product of polycarboxylic acids. Coban-Yildiz et al. [21] lump cyclopentenones with furans as carbohydrate indicators; similarly, van Heemst et al. [24] refer to cyclopentenones and furans as polysaccharide products. In the Chena river water samples, the relative abundance of cyclopentenones increased with decreasing molecular size, whereas furfurals exhibited the opposite trend, implying that cyclopentenones and furfurals have distinct sources (Table 3).

Alkylbenzenes comprised 39% of the index in the COM fraction, 19% in the POM, and 27% in the DOM. The organic compounds which produce alkylbenzenes when pyrolyzed have not been identified, but are believed to be refractory [16]. The relative abundance of alkylbenzenes in the Chena river size fractions follows the same pattern as the C/N ratio, providing further evidence that the COM fraction contains the greatest proportion of highly, refractory OM, the POM fraction contains the least, and the DOM fraction is intermediate.

Phenols, including alkylphenols, are pyrolysis products of diverse sources including lignin, protein, algal-derived polyphenols, and hydrolyzed polysaccharide/protein mixtures [24]. Pyrolysis of lignin produces methoxyphenols in addition to alkylphenols [23,24]. No methoxyphenols were found in any of the pyrograms, ruling out fresh lignin as a possible source of the phenols produced by pyrolysis of the Chena River water samples. This is consistent with the findings of van Heemst et al. [16], in which phenol and alkylphenols but no methoxyphenols were found in pyrograms of OM from the Ems River and Ems–Dollart estuary. The relative proportion of phenols in the Chena River pyrolyzates did not consistently increase or decrease with respect to NOM size, being lowest in the middle size fraction (COM) and highest in the largest size fraction (POM). The diverse origin of the phenols may obscure a size-related pattern. Within the phenols category, the relative proportion of the index compounds varied between the samples. The ratio of phenol to alkylphenols (two methylphenol compounds and one dimethylphenol) in the Chena river pyrolyzates decreased from 1.22 for POM, to 0.63 for COM, to 0.47 for DOM, suggesting that the sources of the phenols varied with NOM size fraction.

The greater relative abundance of polysaccharides observed in the POM sample was consistent with its freshness and its relatively lower C/N ratio (Table 2). Interestingly, the percent of index for polysaccharides (furfurals) decreased with decreasing NOM size, from ~23% in POM to 3.8% in COM and 1.8% in DOM phases. Changes of polysaccharide content between size fractions indicated a decrease in organic matter “freshness” from particulate to colloidal to dissolved phases. Compared with other COM samples, the percent of furfurals of the Chena River COM was similar to that of the Mississippi River COM. However, the polysaccharide proportion of these riverine COM samples was considerably lower than their counterparts in oceanic waters (Table 3). Lower polysaccharide proportions in riverine COM samples was consistent with its terrestrial origins and refractory nature [16] while the greater proportion of furfurals in oceanic COM samples was related to its marine source and high abundance of polysaccharides [25].

4. Summary and conclusions

Laboratory size fractionation protocols were established to study the heterogeneity of riverine organic matter collected from the Chena River, Alaska. Characterization of size-fractionated NOM included measurements of organic C and N, stable isotopic ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) composition and molecular fingerprinting using py-GC/MS. It was found that the riverine organic matter was highly heterogeneous in terms of elemental (C and N) and molecular composition as well as isotopic signatures. Values of $\delta^{13}\text{C}$ increased with decreasing size whereas values of $\delta^{15}\text{N}$ increased with decreasing size of NOM, implying different source functions and distinctive environmental behaviors, such as degradation pathway and bioavailability, for different size fractions of organic matter in aquatic systems. Therefore, it is important to examine also different size fractions of organic matter in river waters when concerning its biogeochemical cycling and environmental chemistry. Py-GC/MS techniques provide information about molecular composition that was complementary to elemental composition and isotopic signatures providing a better understanding of the heterogeneous nature of NOM. Further studies are in progress to compare different river systems and different sampling seasons.

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