Indian Journal of Geo Marine Sciences
Vol. 49 (12), December 2020, pp. 1801-1809

Sedimentary organic matter composition of Arctic Kongsfjorden sediments – A study emphasizing the biochemical composition and indices

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Received 02 December 2019; revised 04 February 2020

Kongsfjorden is a glacial fjord system influenced by the Atlantic and Arctic water masses. The spatial variability in the biochemical composition of the fjord sediments was studied during July 2016 and July 2017. The presence of the sedimentary Proteins, Carbohydrates and Lipid components was analyzed and studied with the support of biochemical indices and elemental ratios. The Kongsfjorden sedimentary system was dominated by the carbohydrate concentration in comparison with proteins and lipids. The labile fraction was maximum towards open ocean influenced by Atlantic water masses and minimum near to the glaciers. The fjord sediments were found to be enriched with an aged or degraded organic matter with a low quality labile organic matter.

[**Keywords**: Arctic, Biochemical composition, Biochemical indices, Kongsfjorden, Sediments]

Introduction

Kongsfjorden is a glacial fjord system located in the Svalbard Archipelago of the Arctic region. It is an open fjord with the absence of sill at the entrance. Hence, the exchange process occurring in the shelf-boundary impacts largely on the variations happening in the fjord system involving both physical and biological conditions[1]. The influence of both Atlantic and Arctic water masses plays a major role in the formation of Kongsfjorden waters. The Atlantic waters make this fjord Sub-Arctic rather than the Arctic[2]. The exchange of this water mass varies with days, weeks or longer and is controlled by the geostrophic coastal flow regimes[3]. The source of sedimentation occurring in this fjord system is from the sub-glacial melt-water discharge from the tide-water glaciers[1]. This glacial input creates steep environmental gradients in sedimentation and salinity throughout the fjord system[2].

The organic matter deposited on the surface sediments in a marine environment has their own characteristic feature and are used for understanding various oceanic processes. It includes, surface productivity, presence of land-derived materials, water mass dynamics, redox potential and rate of sedimentation[4]. Varied factors like origin, composition, biochemical transformations and so on, determine the nature of organic content in sediments. Sedimentary organic matter includes labile and also refractory organic constituents[5]. Degradation and transformation alters the levels of these substances in nature[6,7]. Humic acids, fulvic acids and structural carbohydrates that undergo low degradation and consequently get preserved in sediments, eventually form refractory organic compounds[8,9]. Sedimentary organic matter includes labile components that are organic biopolymers like carbohydrates, proteins and lipids. These are degraded by benthic organisms and undergo mineralization[7]. The Biopolymeric Carbon BPC fraction is determined by the sum of carbohydrate, protein and lipid carbon which makes the total carbon content accessible to benthic consumers[10].

Organic material is augmented by inputs of rapidly sinking particles. These accumulate and continue to undergo degradation, mixing and transformation[11-13]. The origin and transformation of organic matter is determined by various methodologies. Their origins and diagenesis can be studied by analyzing their biochemical constituents. This also helps to assess the quality of organic material as it serves as food for benthic life forms[14-16]. The understanding of these biochemical parameters characterizes the biogeochemistry of the sedimentary environments[17-19].

Studies regarding the nature of sedimentary organic matter within the fjord regions of Arctic are lacking in perspective of biochemical composition of sediments;

hence, this study is an attempt to find out the nature and quality of sediments in terms of biochemical composition and indices. A lower quantity of sedimentary organic matter is expected to be prevailing in these unique environmental conditions.

Materials and Methods

Study area

The study area is the Kongsfjorden fjord system situated on the west coast of Spitsbergen in the Arctic Ocean. The length of the fjord is 26 km and its breadth is 6-14 km. The inner section of the fjord system is relatively shallow in comparison with that of the outer section having a depth of around 350 m. The location map of the fjord system is given in Figure 1.

The North Atlantic Current impacts the western Svalbard marine waters that transfer warm, salt water to the West Spitsbergen Current[1,2]. Climatic variations impact the current intensity as indicated by the North Atlantic Oscillation. The outer fjord of Kongsfjorden is influenced by oceanographic conditions and the inner fjord is mostly affected by large tidal glaciers[1,2].

Sediment sampling from Kongsfjorden was done during July 2016 and 2017 (Arctic Summer) as part of the Indian expedition to the Arctic. The collection of samples from the sedimentary surface was performed with Van Veen grab. The samples were then packed in high-quality polythene zip lock bags and were preserved in a deep freezer (-80 °C) for transportation to lab in Kochi, India.

Chemical analysis

The samples kept in the deep freezer were taken out and freeze-dried for further analysis. The freeze-dried samples were homogenized with an agate

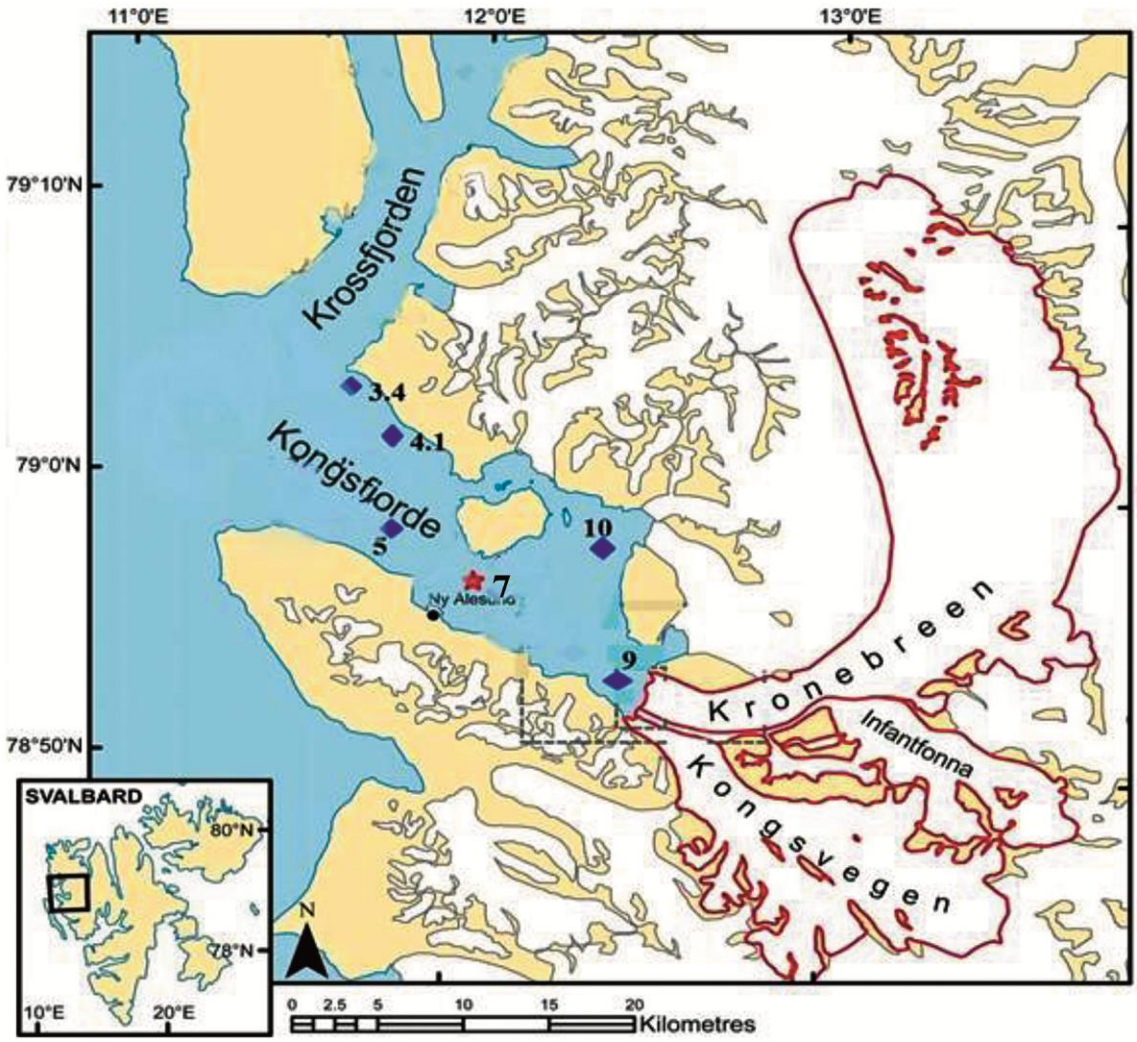

Fig. 1 — Locations of sampling sites within the fjord system under study (Kongsfjorden)

Table 1 — Biochemical composition of the sedimentary organic matter from Kongsfjorden fjord system during 2016 & 2017

Stations	Proteins (mg/g)		Carbohydrates (mg/g)		Lipids (mg/g)		Tannin & Lignin (mg/g)	
Year	2016	2017	2016	2017	2016	2017	2016	2017
KN3.4	0.09	0.318	0.09	1.458	0.283	0.321	0.091	0.171
KN4.1	0.18	0.306	1.18	2.249	0.153	0.156	0.194	0.202
KN5	0.19	0.265	1.14	2.232	0.191	0.262	0.174	0.193
KN7	0.08	0.121	1.12	1.018	0.117	0.197	0.059	0.058
KN9	0.06	0.294	0.86	1.018	0.172	0.212	0.088	0.088
KN10	0.01	0.136	0.28	1.222	0.105	0.235	0.019	0.020

mortar and were kept in a desiccator. The analysis of biochemical composition is based on the UV - Visible spectrophotometric methods (Thermo fisher Model No.117). Proteins (PRT), Carbohydrates (CHO) and Lipids (LPD) were the major components analyzed. The protein analysis was performed accordingly with the modified (by Rice in 1982) Lowry procedure[20] after the extraction with 1M NaOH for 2 h with Albumin as standard. The carbohydrates in sediments were analyzed using the procedure described by Gerchacov & Hachter[21] using glucose as the standardization equivalents. The extracted lipids were estimated by the sulphophosphoanilin method[22] using Cholesterol as the standard. The estimation of Tannin & Lignin was done spectrophotometrically following sodium tungstate phosphomolybdic acid method[23,24].

The Biopolymeric Carbon (BPC) fraction was also calculated by summing up the values of proteins, carbohydrates, and lipids[14]. The carbon equivalents were obtained by multiplying each fraction with 0.49, 0.4 and 0.75 µg of C μg^{-1} respectively[25]. The sum of all PRT, CHO, and LPD was referred to as the labile or easily assimilated organic fraction (LOM)[16,26]. The concentrations of Total Organic Carbon (TOC) in sediments were determined by using Skalar Primacs MCS total organic carbon analyzer.

Results and Discussion

Biochemical composition

Proteins

Proteins constitute approximately 50 % of organic matter and 85 % of the organic nitrogen in marine organisms. The prominent constituents of the Particulate Organic Carbon (POC 13-37 %) are proteins and peptides. These also contribute to nitrogen content (PON 30-81 %) as well as Dissolved Organic Carbon (DOC 3-4 %) and Dissolved Organic Nitrogen (DON 5-20 %) in the marine ecosystem. Around 7-25 % of organic carbon and 30-90 % of total nitrogen[27,28] in sediments are due to the protein content. The concentration of proteins in the sediments of Kongsfjorden does not exhibit a significant spatial variation throughout the fjord, but a considerable change in the concentration on a yearly basis was observed with an average increase in the concentration from 0.1 to 0.24 mg/g. The outer part of the fjord exhibited a higher protein concentration compared to the inner and the middle part of the fjord even though the variation was very little. The higher concentration is attributed to the mixing happening in the outer regions with the Atlantic water masses. The lower concentrations observed close to the glaciers are may be due to the limited exchange as well as the low productivity.

The station wise concentration of proteins for the two consecutive years (2016-2017) is represented in Figure 2a and detailed in Table 1 along with the rest of the components. It showed an increase in the spatial variability of protein in 2017 than in 2016. The trend was the same in all the stations with a yearly increase in concentration. There have been differences in the maximum and minimum values observed in both the years. The productivity of a marine ecosystem can be reflected in terms of sedimentary protein concentrations. Hence, an increase in the protein concentration can be an indication for the increasing nature of benthic systems at different spatial scales[9,29].

Carbohydrates

The most abundant class of biopolymers present on earth is carbohydrates. It includes polyhydroxylated compounds having size range of 5-6 carbon sugars to large biopolymers. Carbohydrates are the main form of organic matter in soil and sediments. It also serves as the predecessors for the creation of humic material[30,31].

The spatial and yearly (2016-2017) variability of carbohydrate concentration is shown in Figure 2b. The carbohydrates present in the Kongsfjorden sediments has an average value of 0.77 mg/g during July 2016, whereas, the concentration in July 2017 sediment samples showed a hike with an average value of

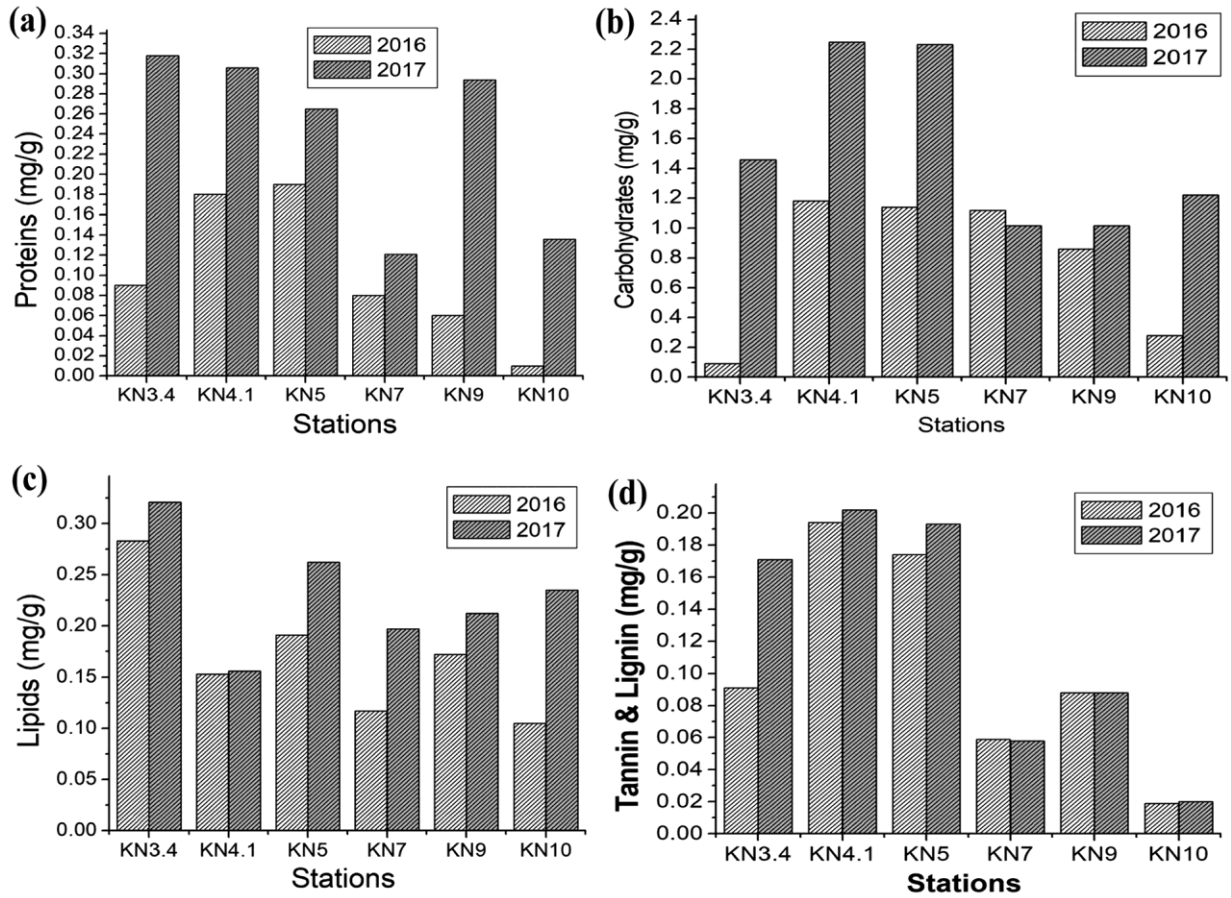

Fig. 2 — Biochemical composition of sedimentary organic matter from the Kongsfjorden fjord system during 2016 & 2017: a) Proteins; b) Carbohydrates; c) lipids; and d) Tannins and lignins

1.53 mg/g. While discussing the spatial variability of carbohydrate concentration in fjord sediments, the concentration of carbohydrate at station 7 was exhibiting a different pattern in comparison with the rest of the stations with a decrease in the carbohydrate concentration in July 2017. The outer part of the fjord was having the highest concentration of carbohydrates *i.e.* in the range of 1.4-2.2 mg/g in 2017 and 0.09-1.18 mg/g in the year 2016. The lower concentration of carbohydrates was observed in the stations close to the glacier having a range of 1-1.2 mg/g in 2017 and 0.28-0.86 mg/g in 2016. The elevated amount of carbohydrates in sediments has been attributed to the accretion of aged organic debris. This is due to the faster consumption of proteins than carbohydrates by bacteria[7,31].

Lipids

Lipids in sediments are formed jointly from aquatic biota and higher plant wax. The plentiful lipid contents in sediments are showed in eutrophic systems than in oligotrophic systems. Like proteins, lipids also act as an indicator of the productivity of the system[15].

The spatial, as well as year wise variations in the lipid concentration, are represented in Figure 2c. The amount of lipids present in the sedimentary organic matter of the Kongsfjorden system has showed a slight increase in the year 2017 when compared with that of 2016 with an average variation from 0.17 to 0.23 mg/g. The concentration of lipid in station 4.1 was almost the same in both the years, whereas, the rest of the stations have a considerable change in values for both the sampling years. As observed in the case of other biochemical parameters, the fjord part opening to the ocean is showing the highest value for lipid concentration and the lowest corresponds to the stations in the inner part of the fjord i.e. close to the glaciers.

In our attempt to assess the sedimentary organic matter composition of 2016 and 2017 (Fig. 3) in the Kongsfjorden system it was found that carbohydrate is the dominant fraction, whereas, protein

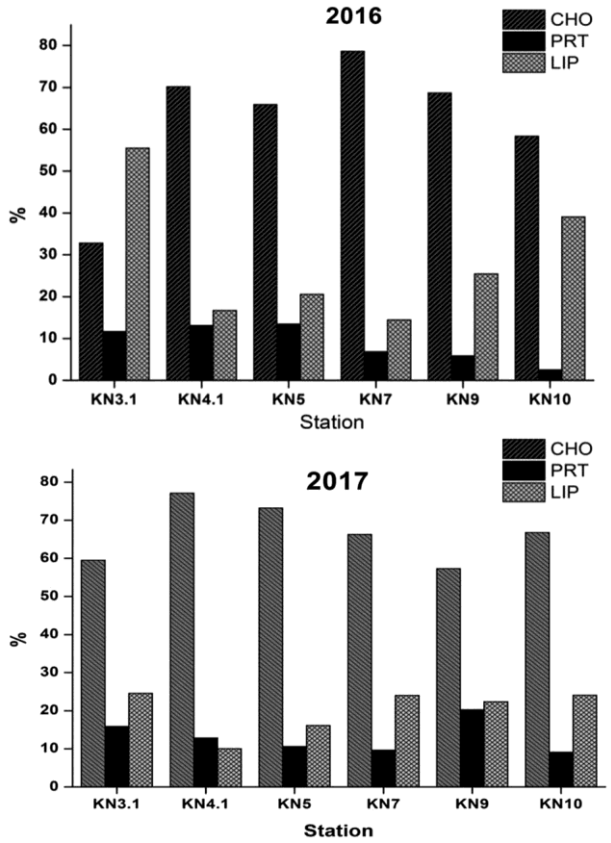

Fig. 3 — Biochemical composition of sedimentary organic matter from Kongsfjorden system: a) 2016; and b) 2017

concentration was found to be least in both the years. The dominance of lipids and proteins over carbohydrates would have indicated the nutritive value as we all as the freshness of the labile organic matter in the sediments of the study region, but the results are the opposite having the dominance of carbohydrates indicating aged organic matter. Another important observation was the increase in the concentration of sedimentary biochemical components towards the open ocean stations which are influenced by Atlantic water masses, whereas, the inner parts particularly stations towards the glaciers showed slightly lower concentrations of labile sedimentary organic compounds.

Tannin & Lignin

Tannin and Lignin are polycyclic aromatic compounds of high molecular weight[32]. Vascular plants particularly contain lignin, a phenyl propenyl alcohol polymer (nitrogen free). This makes it a unique tracer of terrestrial plant remains. Tannin has a biomarker potential along with the contributions to the properties of bulk organic matter.

The average concentration of Tannin & Lignin components during July 2016 was 0.1 mg/g. But, the amount of Tannin & Lignin showed a higher value of 0.12 mg/g in July 2017. In station 10, the concentration of the Tannin & Lignin was very low when compared with the other stations. This station exhibited a value of 0.01 mg/g in 2016 and 0.02 mg/g in 2017. In station 7 and 9, the change in the concentration was not much in the consecutive year. But, the rest of the stations exhibited an appreciable change in the amount of Tannin and Lignin in the surface sediments of the Kongsfjord. The comparison between the inner and outer fjord system showed almost double the value for the concentration of Tannin and Lignin in the outer part of the fjord than the inner portion. Figure 2(d) represents the Tannin & Lignin variation from 2016 to 2017. Tannin & lignin is mainly distributed to the aquatic surroundings through terrestrial runoff. These form a main division of refractory organic matter and its measurable determination delivers evidence on the input of terrestrially derived organic detritus into the sediments. The enriched levels of tannin and lignin detected in the sediments, appeared to be originated from vascular plant debris accumulated in sediments which can be due to the deposition of foreign materials transported via the Atlantic currents.

Biochemical indices

PRT/CHO ratio

The PRT/CHO ratio in sediments is used as an index for defining the origin of materials existent and to discriminate the presence of fresh materials of currentdeposition[16,26]. PRT/CHO > 1 has been ascribed to fresh material of new formation, whereas PRT/CHO < 1 has been documented to more degraded organic matter[26] which suggests that carbohydrates are governing in the organic pool which is a salient feature of detrital heterotrophic environment[33]. Table 2 provides biochemical indices of the sedimentary organic matter from Krossfjorden fjord system during the years 2016 and 2017.

In both these years (2016 & 2017) the PRT/CHO ratio of the Kongsfjorden sediments was having a value less than 1 which indicates the presence of aged or degraded organic matter. In 2016 the PRT/CHO ratio for station 3.4 exhibited a higher value which equals to 1 and is found to be the highest in both the years which may be due to the influence of ocean currents with fresh organic matter, the station being more close to the open ocean with Atlantic water

Table 2 — Biochemical indices of the sedimentary organic matter from Kongfjorden fjord system during 2016 & 2017

Stations	PRT/CHO		LPD/CHO		BPC (µg/Cg)	
Year	2016	2017	2016	2017	2016	2017
KN3.4	1	0.2181	3.1444	0.2201	292.35	979.77
KN4.1	0.1525	0.1360	0.1296	0.0693	674.95	1166.54
KN5	0.1666	0.1187	0.1675	0.1173	692.35	1219.15
KN7	0.0714	0.1188	0.1044	0.1935	574.95	614.24
KN9	0.0697	0.2888	0.2	0.2082	502.4	710.26
KN10	0.0357	0.1112	0.375	0.1923	195.65	731.69

inputs. The ratio within the sediments of the stations having glacier inputs shows lowest values and the trend is similar in both the sampling years.

The low hydrodynamic condition prevailing in the fjord favors the accumulation of sedimentary organic matter. All the stations in the Kongsfjorden are classified as meso-oligotrophic according to the protein (< 5 mg/g) and Carbohydrate (< 1.5 mg/g) threshold levels in sediments[29]. The PRT/CHO ratio of the Kongsfjorden sediments for the years 2016 and 2017 are depicted in Figure 4a.

LPD/CHO ratio

Lipid content and LPD/CHO ratio is used as an index to define the energetic quality of the organic content in the sediment[15,34]. Moreover, lipids in the sediments may be related with the labile fraction of sedimentary organics and were measured as the best descriptor for biomass over enzymatically hydrolyzable amino acids or proteins[15,34]. The lower values of LIP/CHO ratio (< 1) estimated for the sediments in all stations for both the years (2016 & 2017) indicates low quality of labile organic matter to support benthic fauna. But, an exception in the ratio is observed in station 3.4 similar to that of PRT/CHO. A higher value (3.1) of LPD/CHO in the outermost part of the fjord region (station 3.4) influenced by ocean currents depicts the prevalence of higher quality of organic matter in comparison with the rest of the fjord stations which can be probably of external input. Figure 4b indicates the LPD/CHO ratio during the year 2016-2017 of the Kongsfjorden sediments.

Biopolymeric Carbon (BPC)

The summation of PRT, CHO and LPD carbon is mentioned to as Biopolymeric Carbon (BPC)[14,35]. The conversion factors such as 0.49, 0.40, and 0.75 g of Cg could be used to convert the carbon equivalence of PRT, CHO and LPD concentrations respectively[13]. The values of BPC > 5000 µg/Cg suggest a hypertrophic environment. An algal contribution of BPC > 3000 µg/Cg suggests a eutrophic condition, 1000 to 3000 µg/Cg

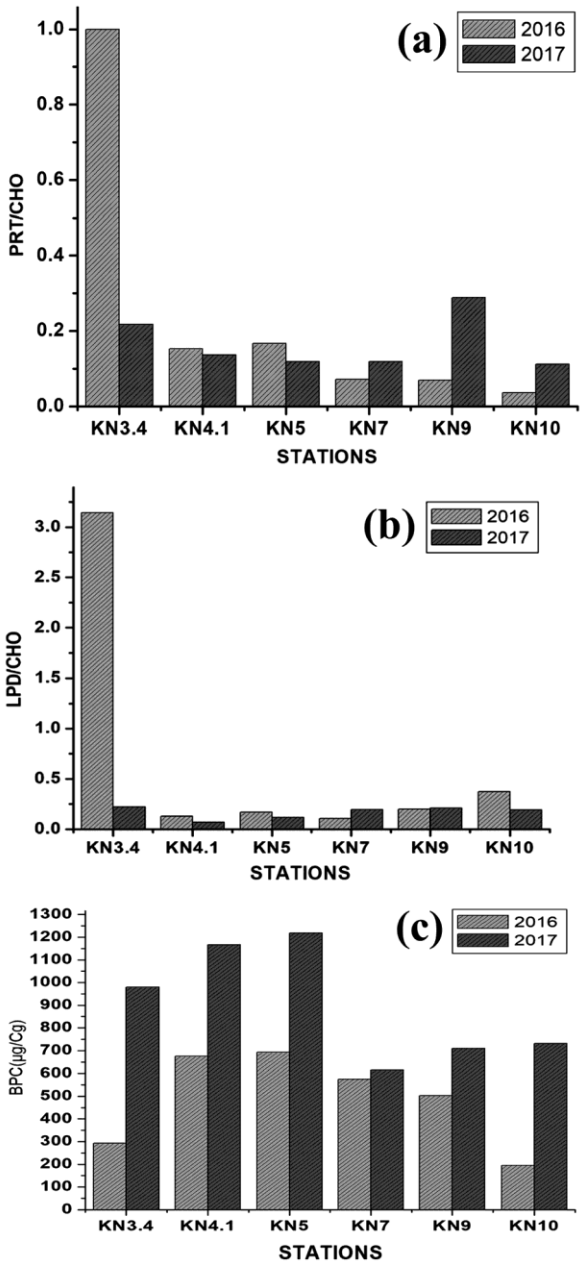

Fig. 4 — Biochemical Indices of the sedimentary organic matter from Kongsfjorden fjord system during 2016 & 2017: a) PRT/CHO ratio; b) LPD/CHO ratio; and c) Biopolymeric Carbon (BPC) concentration

Table 3 — Elemental composition (total carbon & total nitrogen) of the sedimentary organic matter from Kongsfjorden fjord system during 2016 & 2017

Stations	Total Organic Carbon (TOC %)		Total Nitrogen (TN %)		TOC:TN	
Year	2016	2017	2016	2017	2016	2017
KN3.4	3.18	2.5	0.27	0.06	11.78	41.67
KN4.1	2.99	3.2	0.13	0.13	23.00	24.62
KN5	1.18	3.32	0.11	0.16	10.73	20.75
KN7	3.08	1.39	0.1	0.1	30.80	13.90
KN9	2.08	2.66	0.05	0.04	41.60	66.50
KN10	2.21	2.6	0.06	0.05	36.83	52.00

suggests mesotrophic condition and BPC < 1000 μg/Cg suggests oligotrophic conditions.

The average concentration of the Biopolymeric Carbon in the Kongsfjorden sediments during the year 2016 was found to be 1050.16 μg/Cg and that of 2017 was 2003.33 μg/Cg. The BPC value of all the stations except 3.4 and 10 during 2016 ranges between 1000 to 3000 μg/Cg suggesting a mesotrophic condition of the fjord. Later in 2017, the oligotrophic nature of these two exempted stations has shown a shift to mesotrophic condition. There has been an increase in BPC concentration on moving towards 2017 (Fig. 4c).

Elemental ratio

The application of the bulk parameters such as stoichiometric elemental ratios can be used in the calculation of the origin and transformation of organic matter[36]. Organic carbon to nitrogen ratios has been used to trace the organic matter sources based on the detail that marine and terrestrially resultant organic matters have a TOC/TN ratio of 5 – 8 and > 15 respectively. Naturally lower TOC/TN ratio (between 4 and 10) is owed for bacteria and algae; however greater values > 20 have been showed by vascular land plants[37,38]. Intermediate values for TOC/TN ratios noted in the present study indicated a combined input of mutually autochthonous and terrestrial organic matter to the estuarine sediments[39,40].

The elemental ratios of Kongsfjorden sediments for both 2016 and 2017 are detailed in Table 3. In 2016, all the stations in the Kongsfjord system have a TOC/TN ratio > 10 indicating the presence of marine and terrestrial derived organic matter. Except for stations 3.1 and 5, the rest of the stations has a value > 20 for the TOC/TN ratio revealing the possibility of the presence of vascular plant debris that could have transported and deposited via the ocean circulatory currents. In 2017, all stations except KN 7 were having a TOC/TN ratio > 20 indicating the presence of the terrestrial vascular debris distribution throughout the fjord system. This distribution can be attributed to a mixing phenomenon occurring in the fjord system with that of the open ocean water mass causing the introduction of organic matters of different origin to this isolated water body.

Conclusion

The biochemical constituents of Kongsfjorden sediments were dominated with carbohydrates in the labile fraction and exhibited lower protein content. The concentration of these labile components was maximum towards the open ocean part of the Fjord which is influenced by the Atlantic currents. The stations exhibiting lower organic matter were found to be the ones close to the glaciers and hence can be related to limited primary production which is most likely due to limited transparency of water caused by suspended matter. The presence of aged or degraded organic matter in the fjord systems was understood with the help of PRT/CHO ratios and also the low quality of the labile organic matter to support benthic fauna was confirmed with LPD/CHO ratio which exhibited a lower value throughout the fjord system in both the years. According to the PRT and CHO threshold levels, the Kongsfjorden system is exhibiting a meso-oligotrophic nature. The elemental ratio (TOC:TN) of the sedimentary organic matter revealed the involvement of the terrestrially derived vascular plant debris in the fjord system. An increase in the concentration of biochemical composition of sediments was observed in the successive samplings done from 2016 to 2017 with an expectation of the trend to be continued in the coming years.

Acknowledgments

The authors wish to express their sincere gratitude to the Indian Arctic Expedition Team 2016 and 2017, National Centre for Polar and Ocean Research and the Ministry of Earth Sciences, Government of India. Also, we like to convey our thanks to the whole team of Kings Bay AS for providing all the needs during the sampling days.

Conflict of Interest

The authors declare that they do not have any conflict of interest.

Author Contributions

AS: Preparation of the manuscript; JM: Lab analysis, preparation of data tables and graphs; and AG: Sampling (from Arctic), and manuscript preparation.

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