



Humic acids from an Arctic fjord, Krossfjorden, Spitsbergen

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Abstract: Humic substances are ubiquitous materials found in terrestrial and aquatic ecosystems. Humic acids, a diagenetic product can interact with various components present in aquatic sediments. The present research is on the evaluation of sedimentary humic acids from the Krossfjorden glacial fjord situated within the Svalbard archipelago. The results of this study are needed to understand the structural characteristics of humic acids isolated from the fjord. Surface sediment samples were collected from four stations throughout the fjord during a summer period in 2018. Various spectroscopic techniques such as UV-visible, Fourier-transform infrared spectroscopy (FTIR), and Nuclear magnetic resonance spectroscopy (NMR) were applied for studying the humic acids. The elemental composition as well as the presence of tannin and lignin were also analyzed. The results of this study revealed the variation in the structure of humic acids from aliphatic to aromatic from the outer to the inner region of the fjord. This change in humic acids was well supported by the FTIR and NMR results with differences in the spectrums.

Keywords: Arctic, Svalbard, sediment, organic matter, spectroscopy.



Introduction

The impacts of climatic variations are distinctively higher in the Polar environments when compared to the rest of the world. An appropriate site in connection with this distinctiveness is relevant to studying the effects of climatic changes in marine environments. One such site is an Arctic double fjord system located at the Svalbard Archipelago, a Norwegian Arctic Region. The specific characteristics of this fjord system include how the freshwater is supplied as meltwater from the surface and as icebergs at deeper levels of calving glaciers (Svendsen *et al.* 2002). The fraction of suspended particle accumulation in this fjord system was studied by various researchers (Koide *et al.* 1973; Meslard *et al.* 2018). This deposition process depends on the physical properties of suspending particles. The coarse grains deposit close to the glacier front whereas the fine particles accumulate near the glacial outflow and the rest of the particles were transported by surface waters and deposited in the middle and the outermost part of the fjord (Zaborska *et al.* 2006).

The transformation of organic particles in the Arctic region proceeds under specific conditions which are the characteristic features of this bioclimatic zone. The low temperature, humidity, and a short span of biological activity make the humification and mineralization processes unfavorable in these regions. Therefore, the polar sediment zone contains higher levels of organic matter, notwithstanding a limited input of organic matter remains determined by a low primary production (Dziadowiec *et al.* 1994). The humic acid formation in specific conditions can exhibit specific characteristics making it different from other environments.

The studies on the nature and characteristics of humic acids isolated from Arctic fjords, especially in the Krossfjorden are very scarce (Mathew *et al.* 2019). Most of the studies were performed in the Arctic tundra soils (Schnitzer and Vendette 1975; Dziadowiec *et al.* 1994; Abakumov *et al.* 2015; Chukov *et al.* 2017; Lodygin *et al.* 2017; Zhrebker *et al.* 2019). Other than tundra soils there are also works related to the molecular composition of humic acids isolated from lake sediments (Guzeva *et al.* 2021). Hence, this work is an attempt to find out the nature of humic acids isolated from the sediments of Krossfjorden and to understand the spatial variability in their structure.

Study area

The organic matter present in this north most regions on earth is suitable for studying the early stage of the humification process entirely different from those happening in the rest of the world. The climatic conditions prevailing in these regions are the major cause of the specificity of their organic matter components. The area under study is a glacial fjord system named Krossfjorden

located at 77°30'N and 13°06'E with the orientation in a north to south direction. The 30 km long fjord system has a width varying between 3 and 6 km. The Kong Haakons Peninsula divides the inner part of the fjord into two parts, Lilliehookfjorden and Mollerfjorden. The estimated volume of the Krossfjorden is about 25 km³ (Howe *et al.* 2016). The fjord system is influenced by the climatic changes from two directions, the inner part of the fjord with glacier inputs and the outer part of the fjord with an opening to the sea. Alterations in the glacier melting process will cause changes in the runoff pattern. The temperature and salinity changes in the adjacent Atlantic and Arctic water will cause changes in the fjord through exchange processes (Svendsen *et al.* 2002).

Methods

Sampling. — The sediment sampling from the fjord system was done once during summer in July 2018. Four samples were collected from upper 10cm sediments across the fjord. A Van Veen grab was deployed from the research boat *M.S. Teisten* for the purpose. Four stations from Krossfjorden, *i.e.*, K1, K2, K3, and K4 (Fig. 1) were located in the inner-outer region of the fjord. The sediment samples were transferred to –20°C at the earliest and were cold shipped to our laboratory for further analysis.

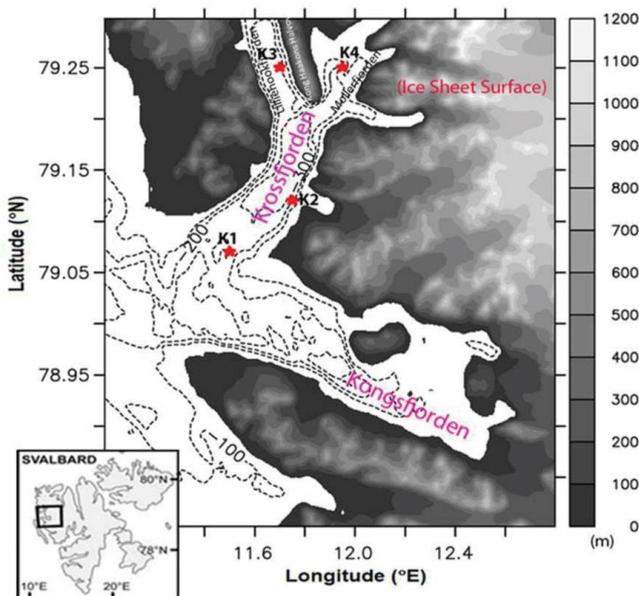


Fig. 1. Map of the Krossfjorden from the GEBCO 2020 data. The dashed contour lines represent the bathymetry. The red symbol represents the station locations. The shaded region represents the topography.

Isolation and characterization of humic acid. — About 1kg of air-dried sediment samples from each station were initially treated with 1N HCl for the elimination of weakly bound carbonates, sulfates, hydroxides, *etc.* (IHSS 2010a, 2010b). The removal of the HCl solution was done after a few minutes with the settlement of the sediment particles. It is then followed by the extraction process involving 1N NaOH. The samples were continuously shaken for 24 hours in a rotary shaker and allowed to rest overnight at room temperature. The soluble humic material was collected and acidified with 6M HCl for precipitation by adjusting the pH in the range 1–2. The solution was kept overnight for complete precipitation. The separation of precipitate was done with a centrifuge and then freeze-dried for further characterization with UV-visible (Thermofischer UV-visible spectrophotometer - Model no. 117), Fourier-transform infrared spectroscopy (FTIR) (IR prestige 21 model of Shimadzu), and Nuclear magnetic resonance spectroscopy (NMR) (400 MHz Bruker AVANCE III) spectroscopic techniques (IHSS 2010a, 2010b; Kachari *et al.* 2015; Mathew *et al.* 2019). The elemental composition of both humic acid and sediment was determined by a direct ash-free analysis using a Carbon, Hydrogen, Nitrogen, Sulphur (CHNS) elemental analyzer of Elementar Vario ELIII. Apart from these, the tannin and lignin component was extracted with NaOH and estimated by sodium tungstate phosphomolybdic acid method with a UV-visible spectrophotometer (Nair *et al.* 1989; APHA 1995). It was observed that there is no accurate and precise method for humic acid determination. But the best-recommended method for giving the highest reasonable results is the IHSS method (Shamia *et al.* 2017). For the rest of the components, an average value of multiple data set is provided in the results.

Results and interpretation

Elemental composition of humic acids. — Elemental composition is a useful tool for identifying the origin of humic acids. It gives an idea regarding the aliphatic nature and the degree of carboxylation of the humic acids (Rashid 1985; Davies and Gabor 1998; Giovanela *et al.* 2004). The elemental composition of humic acids isolated from the Krossfjorden sediments is given in Table 1 along with the tannin and lignin content present in the sediments.

The carbon content present in the humic acids under study ranged from 36–48% with N% not exceeding 2% (1.2–1.8). The percentage of hydrogen was found same for the first three stations K1, K2, and K3 with a value of 4%, and K4 had value slightly greater than the rest of the stations (6%). In the case of sulfur, it was undetectable in K1, K2, and K3, whereas K4 exhibited its presence with 0.22%. The presence of sulfur in the humic acids provides information regarding the type of sulfur-containing functional groups. An excessive amount of sulfur reflects a sulfate-reducing condition in the area under study (Christensen

Table 1.

Elemental composition and tannin and lignin components of sedimentary organic matter from Krossfjorden.

Station	C (%)	H (%)	N (%)	S (%)	O (%)	H/C	O/C	N/C	Tannin & Lignin (mg/g)
K1	40	4	1.2	ND	54.8	0.1	1.37	0.03	0.05
K2	48	4	1.2	ND	46.8	0.08	0.97	0.02	0.03
K3	46	4	1.8	ND	48.2	0.08	1.04	0.03	0.04
K4	36	6	1.4	0.22	56.38	0.16	1.56	0.03	0.06

1989; Solomon *et al.* 2003). Since the presence of sulfur in the humic acids was very low, groups such as sulfides, disulfides, thiols or thiophenes, sulfoxides or sulfonates, and sulfates might be absent in the molecule (Christensen 1989; Solomon *et al.* 2003).

The percentage of oxygen present in the humic acids ranged from 46.8 to 56.38%. The highest value was observed at K4 and the lowest at K2. The value for the H/C ratio ranged between 0.08–0.16 with the maximum observed in the K4 region of the fjord. This ratio is an indicator of aliphatic-rich humic acid moieties (Rashid 1985; Giovanela *et al.* 2004). Higher values of the H/C ratio reveal the presence of aliphatic moieties present in the humic acids (Rashid 1985; Rice and MacCarthy 1991; Giovanela *et al.* 2004). This statement is discussed furthermore with the FTIR spectrums of humic acids in this study.

The O/C ratio of station K4 has the highest value and hence the carboxylation process happening in this area is higher than in the other stations. There is not much difference in the values of the O/C ratio, even though the lowest value was observed at the K2 station. The degree of carboxylation that occurred during the humification process can be understood with the O/C ratio. The higher the value of the ratio, the higher will be the extent of carboxylation. The carboxylation degree varies significantly with spatial differences (Rice and MacCarthy 1991; Sierra *et al.* 2004; Klavins *et al.* 2013).

In terms of lignin contribution, the humic acids can be understood with the help of the N/C ratio. A lesser N/C ratio is due to rich lignin contents (Stuermer and Harvey 1978; Stuermer *et al.* 1978; Saito and Hayano 1981; Sierra *et al.* 2004). The values obtained for the N/C ratio of all Krossfjorden station is <1 and are comparable with each other. This value is attributed to a higher concentration of lignin present in the system. The result of lignin contribution is supported by the data of tannin and lignin components of the sedimentary organic matter from Krossfjorden. The results are in mg/g units and ranged from 0.03 to 0.06 mg/g.

UV-visible spectroscopic analysis of humic acids. — The UV-visible studies of humic acids are performed with the help of various ratios considering absorptions at 250, 270, 280, 365, 400, 465, 472, 600, 664, and 665 nm wavelength. E250/365 and E465/665 are the most commonly used ratios for

humic acids studied by researchers. Apart from these, there are a few other less common ratios that provide additional information about the humic acids. They are E270/400, E472/664, E280/472, and E280/664 ratios. Along with these ratios, there is also an additional term called $\Delta\log K = \log E400 - \log E600$ defined as the difference between the logarithms of the absorbance at 400nm ($\log E400$) and 600nm ($\log E600$) (Ghosh and Schnitzer 1979; Kumada 1987).

Humic acids are macromolecular compounds comprising numerous aromatic networks. The degree of condensation of these macromolecules and the process of humification are interrelated. The E4/E6 ratio relates the aromaticity and degree of condensation. Hence, the ratio can be used as a humification index. The E4/E6 ratio decreases as the degree of condensation increases, which is an inverse correlation (Stevenson and Schnitzer 1982; Kumada 1987). In our study, the values of the E4/E6 ratio range between 1.12–1.22. Initially, there was a gradual increase in the ratio from K1 to K3 stations and then decreased at K4. The values of the ratio obtained at K2 and K4 stations are in a closer range. Among the Krossfjorden stations, K3 showed the lowest degree of condensation and aromaticity. This variation of K3 may be due to the accumulation of suspended particles on the sediment surface (Koide *et al.* 1973; Meslard *et al.* 2018).

The E270/400 ratio (Fig. 2) is used to understand the degradation of phenolic/quinoid core to simple carboxylic aromatic compounds (Uyguner and Bekbolet 2004). Among the stations of Krossfjorden under study, the highest value is observed at K2. The values observed at K1 are very much closer to K2. The rest of the stations exhibited a lesser degree of degradation with the lowest value at K4. Thus, the humic acids isolated from stations closer to the ocean exhibit higher degradation of phenolic or quinoid core than that obtained from the region with glacier influence.

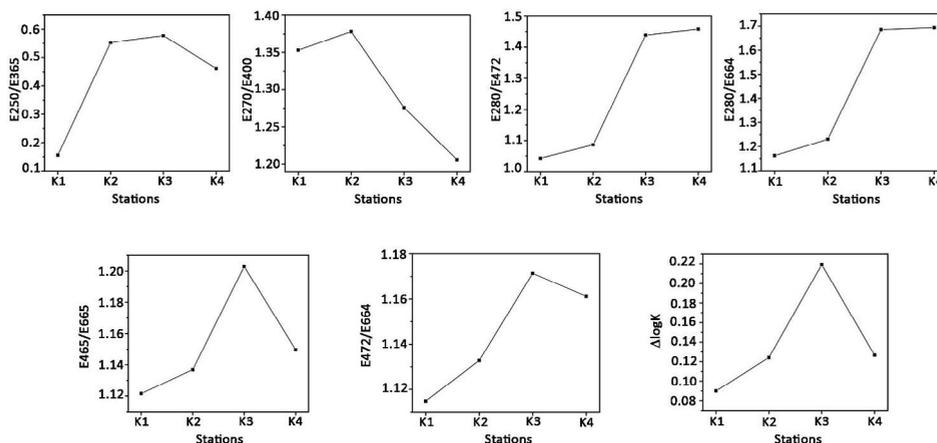


Fig. 2. UV-visible spectroscopic ratios of various humic acids isolated from Krossfjorden sediments.

The proportion between lignins and other materials during the initial stages of the humification process is obtained from E280/472 ratio. It also provides a similar proportion to the content of the material at the beginning of transformation (Albrecht *et al.* 2011). There is a gradual increase in the E280/472 values from K1 to K4. This indicates the presence of the highest lignin concentration at K4 which is supported by the sedimentary tannin and lignin values (0.06 mg/g).

A relation between non-humified and strongly humified material can be produced using absorbance for 280 and 664nm wavelength denoted by E280/664. The ratio E472/664 indicates the degree of condensation and polymerization of aromatic constituents and acts as a humification index. A higher degree of aromatic condensation and the level of organic material humification are reflected by a lower ratio and vice versa (Zbytniewski and Buszewski 2005; Albrecht *et al.* 2011). In this study, the E280/664 ratio has the same pattern as that of E280/472, providing the highest for K4 and the lowest for K1. Thus, the highest degree of aromatic condensation and organic material humification was observed at station K1.

A coefficient $\Delta\log K$ can be correlated with the degree of humification. According to the coefficient values, humic acids can be classified into three types. Type 1 includes humic acids with a high degree of humification with $\Delta\log K$ values up to 0.6. Type 2 has $\Delta\log K$ values corresponding between 0.6–0.8 and for type 3 the coefficient ranges from 0.8 to 1.1. Thus, the present work is provided with humic acids with a high humification degree having $\Delta\log K$ values <0.6. Among the stations under study, the lowest value is observed for K1 with the influence of oceanic inputs containing fresh organic matter (Fong *et al.* 2006).

FTIR spectroscopic analysis of humic acids. — Infrared spectroscopy is a frequently used tool for the identification of various fractions or sources of humic substances. Various researchers use this method to distinguish between marine and terrestrial humic acids. Also, it is a common tool used for understanding the variations in humic and fulvic acids. Even though there are differences in the spectrums of humic substances obtained from different sources, the overall similarity is more remarkable than the differences. This is due to the similarity in the net functional group content of various samples. The main difference occurs in the relative intensities of vibration bands than that of their positions (Fooker and Liebezeit 2003).

The four Krossfjorden stations under study can be understood in terms of their structure including the functional group with the FTIR spectroscopic method. In an overview, there are differences in the spectrums with some minor shifts of varying absorbance bands. The spectrums (Fig. 3) of K1 and K2 are more similar to K3 and K4 and vice versa.

In the region 3350–3450 cm^{-1} , a broad band is observed for all the humic acids under study. The presence of a band in this region is attributed to O-H stretching vibration. The absorbance of OH groups is around 3600 cm^{-1} even if it

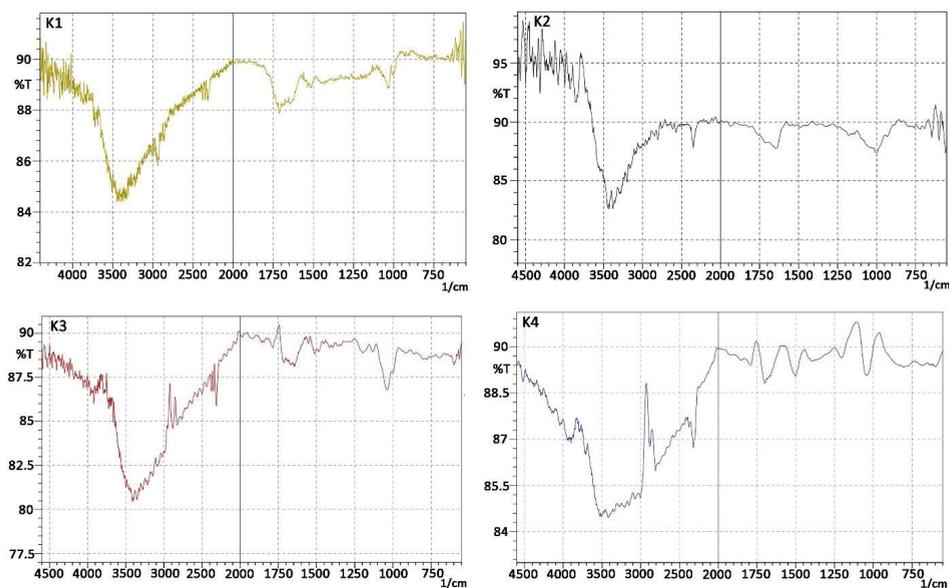


Fig. 3. Fourier-transform infrared spectrums of various humic acids isolated from Krossfjorden sediments.

is in the undissociated or free state. The frequency of O-H vibrations reduces if there is hydrogen bonding in the association of molecules. Hence, this broad band can be assigned to the O-H stretching vibration within the polymeric association of molecules (Silverstein *et al.* 1981; Kachari *et al.* 2015).

The characteristic absorption for C-H stretching vibration in the FTIR spectrum is observed as small but broad bands. The asymmetric and symmetrical stretching vibration of C-H of methylene groups occurs at 2926 and 2853 cm^{-1} , respectively. Also, the band occurring within the range of 2830–2695 cm^{-1} is attributed to the C-H stretching of aldehydes. The stretching vibrations for aromatic C-H appear within the region of 3100 and 3000 cm^{-1} (Silverstein *et al.* 1981). In the spectrums of humic acids isolated from Krossfjorden sediments, it is found that the C-H stretching vibrations of methylene groups are present in all the four spectrums whereas, the aromatic C-H stretching vibrations are not visible in the spectrums. This result indicates the extensive substitution of aromatic rings causing masking of the band due to O-H stretching (Kachari *et al.* 2015).

The stretching vibrations of C=O of carboxylic acids, aldehydes, and ketones are identified in the spectrum with bands that appear slightly above 1700 cm^{-1} , most commonly at 1720 cm^{-1} . This band is weak and is observed in all the humic acid samples under study. The weakening of the band is due to hydrogen bonding and resonance. The frequency of C=O stretching is reduced to a great extent by internal hydrogen bonding. According to the substituents, the band can shift to a slightly higher or lower wavelength than normal (Silverstein *et al.* 1981).

Bands appearing in the region of 1650–2000 cm^{-1} specify the C-H bending of the aromatic compounds. Around 1650 cm^{-1} C=C stretching mode of unconjugated olefins produces moderate to weak bands. The aromatic C-C ring stretching can be observed within the region of 1300–1500 cm^{-1} with bands appearing near 1497 cm^{-1} and 1460 cm^{-1} . The asymmetrical bending vibrations of C-H bonds of methyl and methylene groups are seen near 1430 cm^{-1} . Also, the symmetrical C-H bending vibrations of methyl groups appear near 1380 cm^{-1} . In the spectrums under study, the bands corresponding to the C-C stretching of aromatic nature are found absent in the K1 and K2 spectrums, whereas it is slightly visible in the K3 and K4 spectrums. This can be due to the presence of a higher aromatic nature of humic acids isolated from the K3 and K4 stations located at the glacier-influence regions of the fjord (Kachari *et al.* 2015).

The bands appearing in the region 1000–1100 cm^{-1} are due to the stretching vibrations of C-O present in polysaccharides (Stevenson and Goh 1971; Hatcher *et al.* 1980a). This characteristic band is present in all four spectrums under study indicating the absence of polysaccharides. The rest of the region 500–700 cm^{-1} exhibits characteristic bands of mono-substituted benzene. Mostly, two strong bands appear between 690–780 cm^{-1} (Kachari *et al.* 2015). These types of bands are not found in the spectrums and thus provide information regarding the absence of mono-substitution in the compounds.

NMR spectroscopic analysis of humic acids. —The NMR spectrums of humic acids isolated from the sedimentary organic matter of Krossfjorden are provided in Fig. 4. There was no considerable variation in the spectrums obtained, but a slight change is noticed in the spectrums of glacier-influenced fjord stations. An additional resonance at 8.3 is observed in stations K3 and K4 and is found absent in K1 and K2. The resonance at $>8.1\delta$ is due to the presence of polycyclic aromatics having sterically hindered peri protons also termed bay protons. Thus, the major fraction of the aromatic carbon in the case of inner fjord regions could be comprised of polycyclic aromatics. The signals produced in the range of 6–8.4 ppm arise from the aromatic hydrogen. The presence of phenols can be suggested by the presence of signals that extends as low as 6 ppm (Wilson *et al.* 1983). All spectrums produce resonance at $\sim 1.2\delta$ and are due to a variety of aliphatic carbons (Hatcher *et al.* 1980b; Wilson *et al.* 1983).

Comparison with previous studies. — A comparative study of present data with the previous ones was performed. The elemental composition of humic acids isolated from the study area and the nearby areas are provided in Table 2. The data are limited and hence for comparison, a similar polar environment (Antarctica) was also included in the table. The FTIR spectrums of humic acids isolated from the Krossfjorden have properties similar to those reported earlier. But there are shifts in the spectral peaks which might be due to the differences in the mass of the molecule isolated from diverse environments (Schnitzer and Vendette 1975; Campanella *et al.* 1994; Dziadowiec *et al.* 1994; Braguglia *et al.* 1995; Guzeva *et al.* 2021).

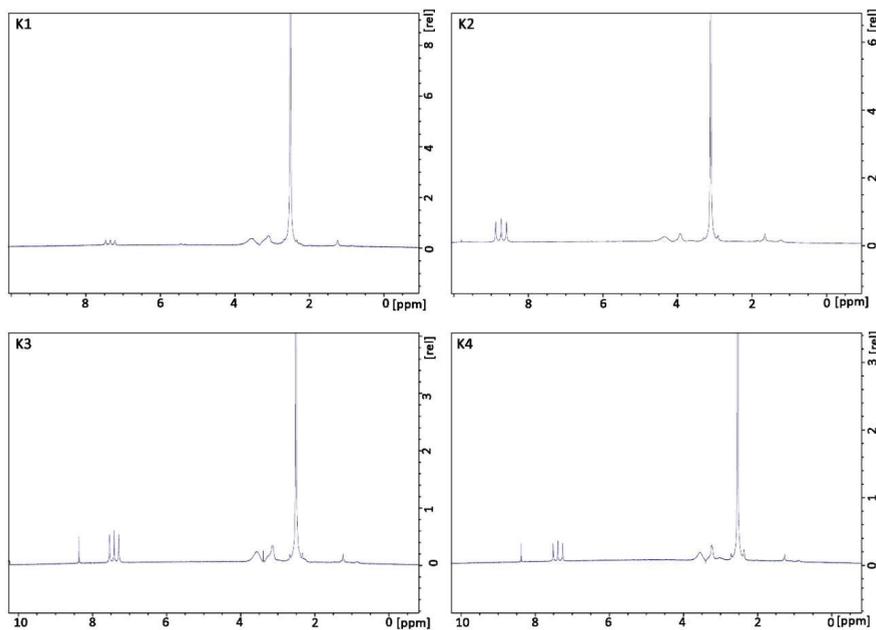


Fig. 4. ^1H Nuclear magnetic resonance spectrums of various humic acids isolated from Krossfjorden sediments.

Table 2.

Comparison of elemental composition of humic acid with previous data.

Study Area	C (%)	H (%)	N (%)	S (%)	O (%)	H/C	O/C	Reference
Krossfjorden, Arctic	42.5	4.5	1.4	0.22	51.54	0.105	1.235	This study
Arctic tundra	56.2	6.2	4.3	0.5	32.8	0.110	0.583	Schnitzer and Vendette (1975)
Arctic tundra, Spitsbergen	46.76	5.52	4.46	43.24 (O+S)		1.42	0.695	Dziadowiec <i>et al.</i> (1994)
Arctic lake	37.37	4.3	1.83	–	51.83	1.36	1.1	Guzeva <i>et al.</i> (2021)
Antarctica	54.91	7.34	6.21	–	–	1.62	–	Campagnella <i>et al.</i> (1993)
Ross Sea (Antarctica)	66.26	7.21	6.57	–	19.94	1.32	–	Braguglia <i>et al.</i> (1995)

Conclusions

The humic acids isolated from the sedimentary organic matter of Krossfjorden glacial fjord were studied with various spectroscopic techniques which included UV-visible, FTIR, and NMR. UV-visible spectroscopy has used different ratios to understand the nature of these humic acids. It is clearly understood that the humic acids isolated from the fjord stations influencing glacial melt water are more aromatic than those present in the fjord region having oceanic influence. This fact is well supported by the FTIR spectrums showing the absence of vibrations corresponding to aromatic C-C bands in the K1 and K2 fjord stations. The NMR spectrums of these humic acids also provide evidence for this variation in the structural nature with additional resonance peaks corresponding to polycyclic aromatics, which are observed in the spectrums of K3 and K4 fjord stations. Thus, it can be concluded that the humic acids from the K1 and K2 regions of the fjord are more aliphatic than the humic acids obtained from K3 and K4.

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