



# Source, mobility, and bioavailability of metals in fjord sediments of Krossfjord-Kongsfjord system, Arctic, Svalbard

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## Abstract

Krossfjord-Kongsfjord system situated on the west coast of Svalbard archipelago is an ideal location to investigate the impacts of climate change on the environment. As a consequence of global warming, metal concentrations in the Arctic region are increasing due to permafrost melting and changes in biological processes. Therefore, the fjord sediments were studied for identification of provenance, mobility, bioavailability, and potential toxicity of metals in the fjord environment. Finer sediments and organic matter were found to be higher away from the glacier outlets, while coarser sediments were found to be higher near the glacier head. Illite, kaolinite, and chlorite constituted the clay mineral assemblage which had slightly influenced the metal distributions. The variations in metal abundance were attributed largely to the glacial activity along with the influence of Atlantic water mass in western Spitsbergen. Fjord system received sediment from the weathering of rocks indicating an input of terrigenous material. Comparison of metals in bulk sediment with Arctic sediment quality guidelines (ASQGs) showed that Zn and Cu were enriched in the sediment. However, to avoid the overestimation of the risk associated, fractionation of the metals was carried out which revealed higher Mn and Co in labile phases that pose a considerable risk to the biota.

**Keywords** Krossfjord-Kongsfjord · Svalbard · Clay minerals · Metals · Speciation · Ecological risk

## Introduction

Fjords act as a nexus between the oceanic and the terrestrial domain, providing a potential for continuous exchange between the fjord and the coastal waters on the adjacent shelf (Cottier et al. 2005). The Krossfjord-Kongsfjord system is a glacial fjord, situated on the west coast of the Svalbard archipelago, equilibrates Atlantic, Arctic, brine, and freshwater input, which are potential indicators of environmental changes (Nilsen et al. 2008). This glacial fjord system has been regarded as a natural laboratory for the study of climate change in the Arctic region (Fendeng et al. 2018). The fjord system is mainly affected by the Western Spitsbergen Current (WSC) which brings in warm and saline Atlantic water at one

side and from the other side, it is affected by extensive glacial runoff from different tidewater glaciers. Warm saline Atlantic water and glacier runoff are composed of terrestrial and marine particulates which on mixing of these waters, facilitate suspended material to deposit on the sediment surface (Howe et al. 2010). The influx of particulate metals into the fjord and their transport through the marine circulation and sedimentation processes determine their distribution along the water column and the sediments (Grotti et al. 2017). Metals occur in different forms such as dissolved species, free ions, or forming organic complexes (Noronha-D'Mello and Nayak 2015). The carbonates, oxyhydroxides, sulfides, and clay minerals can adsorb or coprecipitate particulate metals (Spencer and MacLeod 2002). Metals cannot be degraded, either they may accumulate locally (Marchand et al. 2006) or remobilized in an aqueous environment. The contamination levels are often evaluated using bulk metal concentrations; however, it can overestimate the risk associated as it does not take the factors such as bioavailability, mobility, and toxicity which depends on the chemical form (Cuong and Obbard 2006; Nemati et al. 2011) into consideration. Thus, the assessment of different chemical forms of metals in the sediment is essential.

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High latitude and polar regions are promising areas of capturing even the minute changes to the environment. The pristine environment of these regions is devoid of much anthropogenic input. However, in recent past, there are reports of increasing concern of toxicity in the Arctic region due to input from various sources including long-range atmospheric transport. Several studies have been carried out on sediment characteristics, source, distribution, and bioavailability of metals in sediments of Kongsfjord (Zaborska et al. 2006; Grotti et al. 2013; Lu et al. 2013; Bazzano et al. 2014; Ardini et al. 2016; Zaborska et al. 2017; Grotti et al. 2017). Grotti et al. (2013) assessed the bioavailability of trace elements in marine sediments from Kongsfjord and stated that the impact of trace elements from anthropogenic sources in the area is negligible. Further, Grotti et al. (2017) studied bulk concentration of metals, their enrichment factors, and speciation which suggested low anthropogenic influence of trace elements in the fjord. This implied that metal concentration in the Arctic region is increasing may be due to changes in biological processes and permafrost melting (Lu and Kang 2018) as a consequence of global warming. In the present study, the spatial distribution of metals in sediments of Krossfjord-Kongsfjord system was investigated for identification of

provenance and factors regulating their accumulation in the fjord sediments. In addition, mobility, bioavailability, and potential toxicity of metals have also been assessed in the fjord environment.

### Study area

Krossfjord-Kongsfjord, a typical fjord system, is located between 78° 40' and 77° 30' N and 11° 3' and 13° 6' E on the northwest coast of Svalbard archipelago (Fig. 1). The Svalbard archipelago is covered by the ice caps and glaciers. The ice cap front of the Svalbard-Barents Sea gradually receded to the west shore of the archipelago (Landvik et al. 1998; Lehman and Forman 1992) and formed a series of extremely deep fjords at the entrance of the sea, thus, leading to the formation of Kongsfjord during this period (Fendeng et al. 2018). Kongsfjord, the southern arm of the fjord, is oriented spatially from southeast to northwest and Krossfjord, the northern arm of the fjord, is from north to south (Svendsen et al. 2002). The fjord consists of two submarine channels, which converge to a deep glacial basin, the Kongsfjorddrenna. Kongsfjord is 20 km long and 4–10 km wide, while the Krossfjord is

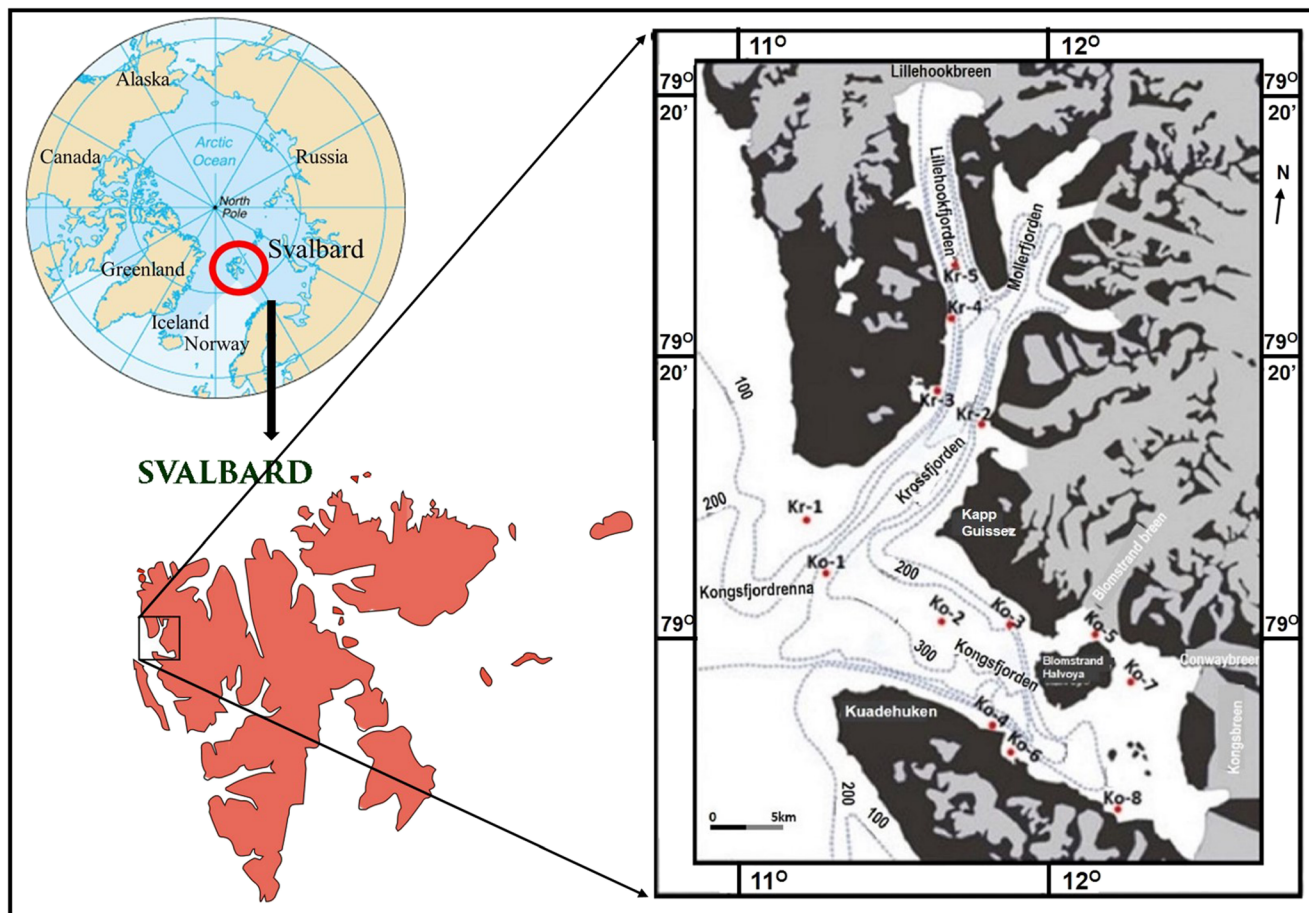


Fig. 1 Map showing the study area (modified after Svendsen et al. (2002))

relatively longer (~30 km) but narrower (3–6 km) as compared with Kongsfjord (Svendsen et al. 2002).

A northern extension of the North Atlantic Current known as the West Spitsbergen Current (WSC) is responsible for modifying the climate of Svalbard as it supplies heat and saline water to the region (Svendsen et al. 2002; Saraswat et al. 2018). Kongsfjord is influenced by Atlantic water, which has affected the winter situation in Kongsfjorden, strongly reducing the sea-ice formation in the fjord in recent years (Cottier et al. 2005). The seawater temperature, wind direction, and freshwater supply in Kongsfjorden and Krossfjorden system vary seasonally (Farmer and Freeland 1983; Saraswat et al. 2018).

The bedrock north of Kongsfjorden and on the islands in the fjord medium-grade metamorphic rocks of middle-Proterozoic age, mainly marbles, mica schists, and a minor amount of Quartzites occur (Svendsen et al. 2002). While on the south of Kongsfjord, structurally above the basal tertiary thrust, sedimentary rocks of late Paleozoic and tertiary age occur; although some Proterozoic, low and medium-grade metamorphic rocks (mica-schists, marbles, phyllites, Quartzites) occur in the southeastern part (Svendsen et al. 2002). The coastal part of the fjord system constitutes unconsolidated deposits of quaternary age which includes moraines, marine shore, and fluvial deposits (Kumar et al. 2014; Choudhary et al. 2018a, 2018b).

## Materials and methods

### Sample collection and storage

A total of thirteen surface sediment samples have been collected from Krossfjord and Kongsfjord at different water depths as part of the Indian Arctic program (summer phase) during the month of August 2016 (Table 1). Surface

**Table 1** Sampling depth and location

Sample name	Water depth (m)	Latitude (°N)	Longitude (°E)
Kr-1	285.00	79.0675	11.2193
Kr-2	130.00	79.1346	11.7843
Kr-3	180.00	79.1535	11.6501
Kr-4	189.00	79.1995	11.6928
Kr-5	265.00	79.2337	11.6894
Ko-1	332.00	79.0365	11.2955
Ko-2	180.00	79.0081	11.6083
Ko-3	283.00	79.0087	11.7887
Ko-4	235.00	78.9510	11.8278
Ko-5	41.70	79.0073	12.1797
Ko-6	302.00	78.9403	11.9622
Ko-7	90.00	78.9725	12.3309
Ko-8	70.10	78.9045	12.2300

sediment samples have been collected onboard workboat “MS Teisten” using stainless steel Van Veen Grab sampler for geochemical characterization of the fjord. The samples were chosen to represent the glacial input as well as depth from the head to the mouth of the Fjord. Samples were labeled and transported to the laboratory in a frozen condition. In the laboratory, each sample was dried at 60 °C in the oven and utilized for further analysis.

### Analytical procedure

The samples have been analyzed for grain size following the pipette method (Folk 1968). Clay minerals in sediments have been analyzed by the procedure detailed by Rao and Rao (1995); further, they were identified and quantified using the method detailed by Biscaye (1965). Total carbon (TC) was analyzed with Elementar, Vario isotope cube elemental analyzer. The analytical precision is  $\pm 0.30\%$  ( $1\sigma$  standard deviation) which was attained using sulfanilamide as the standard and repeated after every ten samples. Total inorganic carbon (TIC) was analyzed using UIC carbon coulometer. TIC was subtracted from TC to obtain total organic carbon ( $C_{org}$ ). Further, 0.2 g ground sediment samples were digested in teflon beakers using HF, HNO<sub>3</sub>, and HClO<sub>4</sub> acid mixture (Jarvis and Jarvis 1985) with a ratio of 7:3:1 for total metal analyses. The metals Fe, Mn, Al, Co, Zn, Ba, and Ti were analyzed using flame atomic absorption with an air/acetylene flame for all the metals except Al for which nitrous oxide/acetylene flame was employed at specific wavelengths and Cd, Pb, and Cr using graphite furnace atomic absorption spectrophotometer (Thermo Scientific-SOLAAR M6 AAS model). Together with the samples, certified reference standards JLK-1 from the Geological Survey of Japan were digested and run to test the analytical accuracy of the method. The average recoveries were 94.2% for Ba and Ti, 95.3% for Mn and Co, 96.2% for Fe, Cu, Ni, Cr, and Al, and 97.1% for Zn, Cd, and Pb. The coefficient of variation (C.V.) for different elements was Al (4.81%), Ti (5.02%), Fe (2.8%), Mn (5.00%), Mg (4.89%), Ca (4.85%), Cr (3.97%), Co (5.89%), Cu (9.50%), Pb (4.91%), Cd (7.54), Ni (5.49), Zn (3.11), and Ba (7.95%). A modified sequential extraction procedure proposed by Tessier et al. (1979) was applied to samples to determine metal speciation. The procedure involves extraction of five geochemical fractions viz. exchangeable phase, carbonate phase, Fe-Mn oxide (reducible phase), organic matter/sulfide (oxidisable) bound, and residual phase. The fractions were analyzed on AAS. Internal chemical standards obtained from Merck were used to calibrate the instrument, and recalibration checks were performed at regular intervals in all analysis. Pearson’s correlation ( $p < 0.05$ ) and factor analysis were employed to verify the possible correlation between the different parameters by using the computer software STATISTICA-6 (Statsoft 1999).

Enrichment factor was computed to evaluate metal enrichment in sediments using the equation:

$$EF = (M_{sed}/R_{sed}) / (M_{bk}/R_{bk})$$

where ( $M_{sed}/R_{sed}$ ) is the ratio of trace metal concentration ( $M_{sed}$ ) to that of the reference element ( $R_{sed}$ ) in sediment and ( $M_{bk}/R_{bk}$ ) is the same ratio in the natural background. Aluminum was used as the reference element to counterbalance the lithogenic influences of granulometric and mineralogical variations of sediments (Qi et al. 2010).

Pollution load index (PLI) has been evaluated to estimate metal contamination in sediments following the method proposed by Tomlinson et al. (1980). This parameter is expressed as:

$$PLI = (CF_1 \times CF_2 \times CF_3 \dots \dots \dots CF_n)^{1/n}$$

where  $n$  is the number of metals (thirteen in the present study) and  $CF$  is the contamination factor. The concentration of metals in the bulk sediments and labile phases was compared with the Arctic sediment quality guidelines (ASQGs) proposed by Lu and Kang (2018) and risk assessment code (RAC) (Perin et al. 1985) respectively to explain the toxicity level of the metals.

## Results

### Distribution of sediment components and organic carbon ( $C_{org}$ )

Among the sediment components, fine fraction (silt and clay) dominates the fjord system (> 80%) (Fig. 2a and b). The coarse fraction is higher in Kongsfjord (average 18.21%) as compared with Krossfjord (average 10.46%) as it is mainly affected by many tidewater glaciers viz. Kronebreen and Kongsvegen towards the head and on the northern coast, it is influenced by Conwaybreen and Blomstrandbreen debouching in the Kongsfjord (Svendsen et al. 2002), while in the Krossfjord, glacial outlets are relatively far from the main channel (Saraswat et al. 2018). Further, the organic carbon ( $C_{org}$ ) concentration ranged from 0.04 to 1.70% along the Krossfjord and from 0.20 to 1.74% along the Kongsfjord (Fig. 2a and b).  $C_{org}$  content in the surface sediment of both the fjords showed high concentration away from the glacier outlets due to high turbidity resulting in the shallow photic zone near the glacial outlets (Choudhary et al. 2018a, 2018b).

### Spatial variation and possible source of clay minerals in surface sediments

The clay mineral assemblage of the Krossfjord-Kongsfjord system comprised kaolinite, chlorite, and illite (Fig. 3a and b). Illite is the predominant clay mineral in the study area followed by

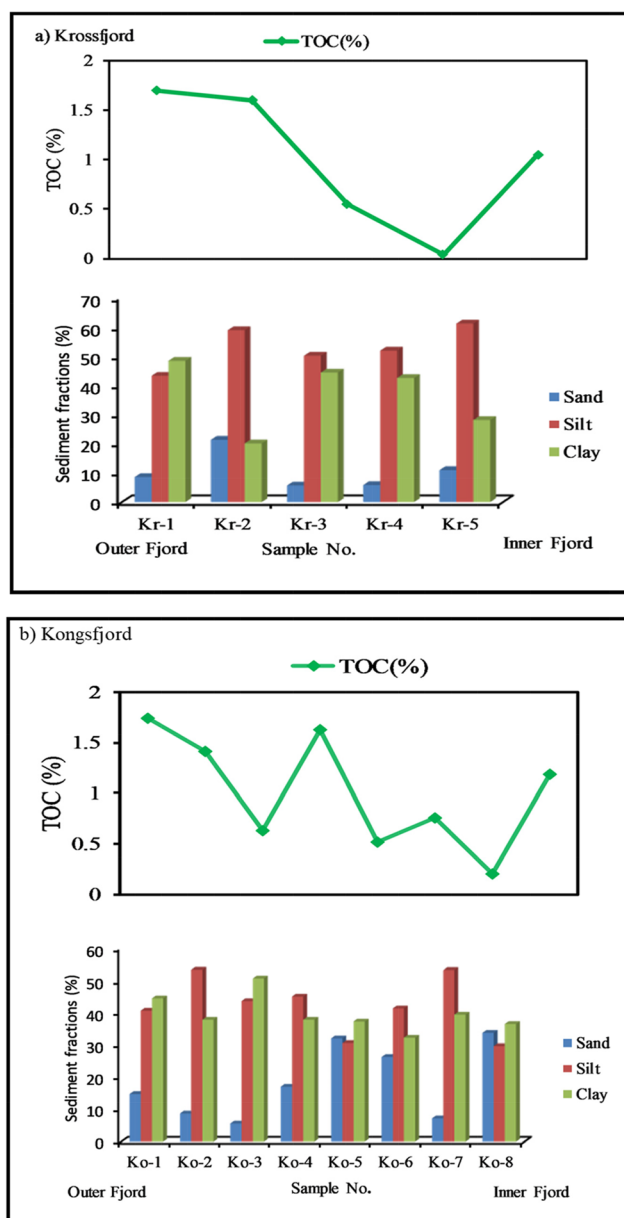
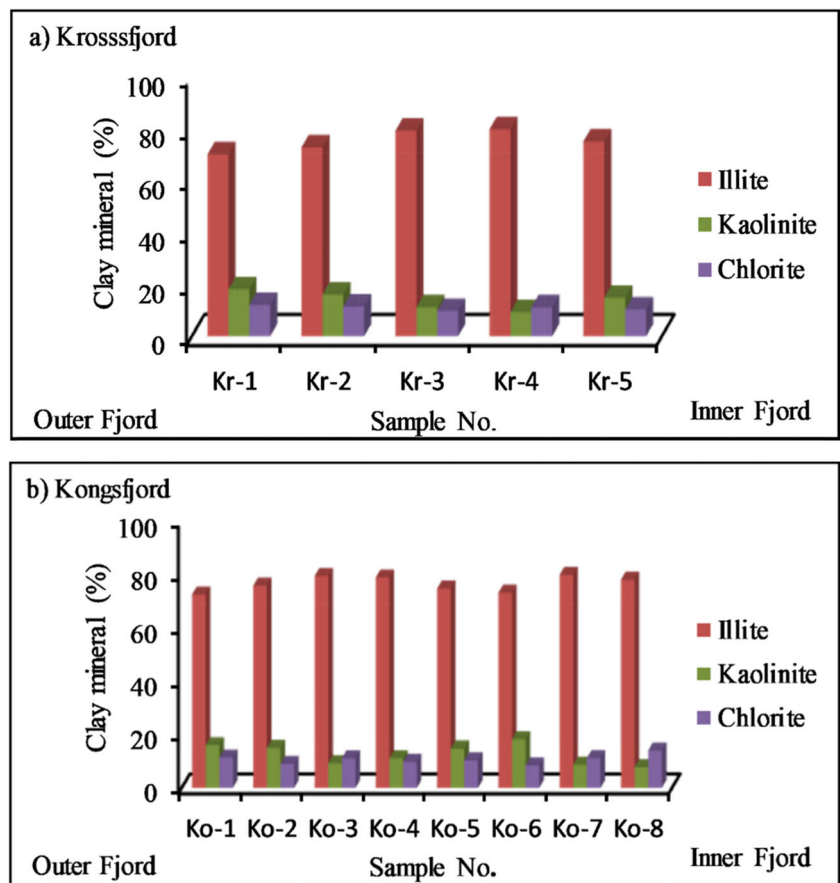


Fig. 2 Distribution of sediment components and organic carbon in the surface sediments along the a) Krossfjord and b) Kongsfjord

kaolinite and chlorite. Along the Krossfjord (Fig. 3a), illite varied within a range of 69.90% at station Kr-1 to 79.53% at station Kr-4. Illite showed a decreasing trend on moving away from the glacial outlets in both the fjords similar to that of sand suggesting its source to be terrigenous originated from glacial weathering of the source rocks. The bedrock north of Kongsfjorden consists of mid-Proterozoic metamorphic rocks, mainly mica-schists and phyllites which act as the major source for illite in the study area. Abundant illite concentration in the study area supports its major supply from Northern Greenland and from Svalbard into the Arctic Ocean (Stein et al. 1994). Illite formation in high latitude region from muscovite is quite common. Generally, illite is considered a detrital clay derived from acidic crystalline rock

**Fig. 3** Distribution clay minerals in the surface sediments along the a) Krossfjord and b) Kongsfjord



(Biscaye 1965; Griffin et al. 1968; Windom 1976). Illite may have also been formed by alteration of potassium feldspars supplied by pre-Devonian igneous rocks (gneisses) transporting through streams draining this region. The decreasing illite concentration towards the outer fjord indicates dilution by the clays brought by Arctic and Atlantic water mass. Kaolinite content fluctuated from 9.30% at station Kr-4 to 18.06% at station Kr-1. An appreciable amount of kaolinite in this region might have been formed either in an interval of warmer and colder conditions resulting in chemical weathering of quartzites or possibly it is of detrital nature, transported from a distant source, probably located underneath the ice (Srivastava et al. 2011). Hjelle (1993) suggested that the kaolinite present in the study area originated from the fluvial facies dominated by reddish sandstone and conglomerate in the middle Carboniferous. Smectite concentrations are particularly absent in Svalbard areas. Among the clay minerals, chlorite content was low (average 10.96% Krossfjord and 10.69% Kongsfjord) which may be due to the highly unstable nature of chlorite. The minimum concentration (8.45%) of chlorite is at station Ko-6 and the maximum (14.04%) is at station Ko-8. The chlorite in the study area mainly comes from low-grade Proterozoic metamorphic phyllite and mica schists that surround Kongsfjord (Fendeng et al. 2018).

Illite crystallinity and illite chemistry were estimated to understand the degree of weathering and source for clay

minerals. Crystallinity defines the degree of “opening” of the clay structure and is considered an index of hydrolyzing power of the source area (Chamley 1989; Bejugam and Nayak 2017). A larger opening (poor crystallinity) suggests strong hydrolyzation of clay minerals during enhanced rainfall and temperature conditions (Thamban et al. 2002). The illite crystallinity in all the sediment samples studied was noted  $< 0.4 \Delta 2\theta$  suggesting the availability of very well crystalline illite (Ehrmann et al. 2005) in the region derived from physical weathering. Illite chemistry showed values  $< 0.5$  indicating Fe, Mg-rich illites supplied through strong physical weathering (Gingele 1996) of mica schists present in the north of Kongsfjorden. This is also supported by lower chemical index of alteration (CIA) ranging between 39 and 47% reported by Kumar et al. (2014) suggesting least degree of chemical alteration of the sediments in the study area.

### Distribution of major elements in surface sediments

Along the Krossfjord (Table 2, Fig. 4a), Al content fluctuated in a range between 3.49% at station Kr-1 and 5.01% at station Kr-5. Ti varied within a small range of 0.20% in sample Kr-1 and 0.29% in sample Kr-5. Fe and Mn content were largely consistent from shallow to deeper water regions and varied from 4.22% and 0.04% respectively at

**Table 2** Major and trace metal concentration along Krossfjord (Kr) and Kongsfjord (Ko)

Sample name	Depth (m)	Al (%)	Ti (%)	Fe (%)	Mn (%)	Mg (%)	Ca (%)	Cr (ppm)	Co (ppm)	Cu (ppm)	Pb (ppm)	Cd (ppm)	Ni (ppm)	Zn (ppm)	Ba (ppm)
Kr-1	285.00	3.49	0.20	5.44	0.08	1.56	0.37	20.18	14.67	19.56	13.19	0.65	17.50	63.36	448.49
Kr-2	130.00	4.12	0.21	5.22	0.06	1.61	0.89	19.53	17.28	18.50	9.25	0.45	17.94	61.43	366.72
Kr-3	180.00	4.14	0.24	4.95	0.05	1.66	1.19	12.47	15.69	22.95	12.01	0.25	17.99	70.49	435.61
Kr-4	189.00	4.27	0.28	4.22	0.04	2.20	0.81	19.53	16.68	24.36	13.31	0.23	26.22	50.28	505.03
Kr-5	265.00	5.01	0.29	5.34	0.05	2.32	1.13	12.44	12.44	24.36	14.61	0.22	26.83	82.91	567.52
Ko-1	332.00	5.11	0.36	3.89	0.05	1.14	1.70	16.71	14.67	29.46	7.26	0.20	27.50	66.69	324.30
Ko-2	180.00	5.15	0.37	5.62	0.07	1.63	0.45	20.01	20.18	20.81	13.74	0.19	27.78	63.93	539.84
Ko-3	283.00	5.25	0.37	4.51	0.06	1.77	0.96	16.71	14.43	22.35	16.11	0.18	27.78	67.43	585.45
Ko-4	235.00	5.37	0.40	5.75	0.05	1.86	0.69	20.56	20.18	22.16	17.26	0.16	28.83	58.24	655.03
Ko-5	41.70	5.59	0.41	4.43	0.06	2.29	1.19	15.69	14.43	24.13	13.26	0.14	29.53	75.42	497.97
Ko-6	302.00	5.83	0.47	5.37	0.08	4.04	1.70	19.18	19.53	26.83	18.96	0.13	29.88	80.87	683.26
Ko-7	90.00	5.86	0.55	5.84	0.05	4.21	3.11	16.68	20.01	19.38	15.39	0.12	31.90	98.05	580.12
Ko-8	70.10	7.96	0.58	5.10	0.06	4.50	0.87	19.98	19.78	24.13	10.88	0.13	32.55	107.01	408.67

station Kr-4 to 5.44% and 0.08% at station Kr-1. Mg ranged between 1.56% at station Kr-1 and 2.32% at station Kr-5. Ca decreased from inner fjord to the outer fjord and ranged between 0.37% at station Kr-1 and 1.19% at station Kr-3. Along the Kongsfjord (Table 2, Fig. 4b), Al content varied from 5.11 to 7.96% from the outer fjord to the inner fjord. Ti showed relatively higher values along the Kongsfjord and varied from 0.36 to 0.58%. Fe and Mn fluctuated without any particular trend, while Mg and Ca showed an increasing trend from the mouth of the fjord towards the head similar to the other metals like Al and Ti.

### Distribution of trace elements in surface sediments

Along the Krossfjord (Table 2, Fig. 5a), trace metals like Cr varied from 12.44 ppm at station Kr-5 to 20.18 ppm at station Kr-1. Co varied from 12.44 ppm in the inner fjord at station Kr-5 to a maximum of 17.28 ppm at station Kr-2. Cu content varied from 18.50 ppm at station Kr-2 to 24.36 ppm at station Kr-4 and Kr-5. Pb and Ba showed similar variations with their minimum concentrations at station Kr-2 (9.25 ppm and 366.72 ppm respectively) and maximum (14.61 ppm and 567.52 ppm respectively) in the inner fjord at station Kr-5. Cd showed decreasing trend with a minimum of 0.20 ppm and a maximum of 0.65 ppm, while Ni showed an increasing trend with a minimum of 17.50 ppm and a maximum of 26.83 ppm from the outer fjord towards the inner fjord. Zn content varied from 50.28 ppm at station Kr-4 to a maximum of 82.91 ppm at station Kr-5. Along the Kongsfjord (Fig. 5b), trace metals fluctuated from one station to the other without showing any particular variation. Metal

concentrations are relatively higher in Kongsfjord as compared with the Krossfjord.

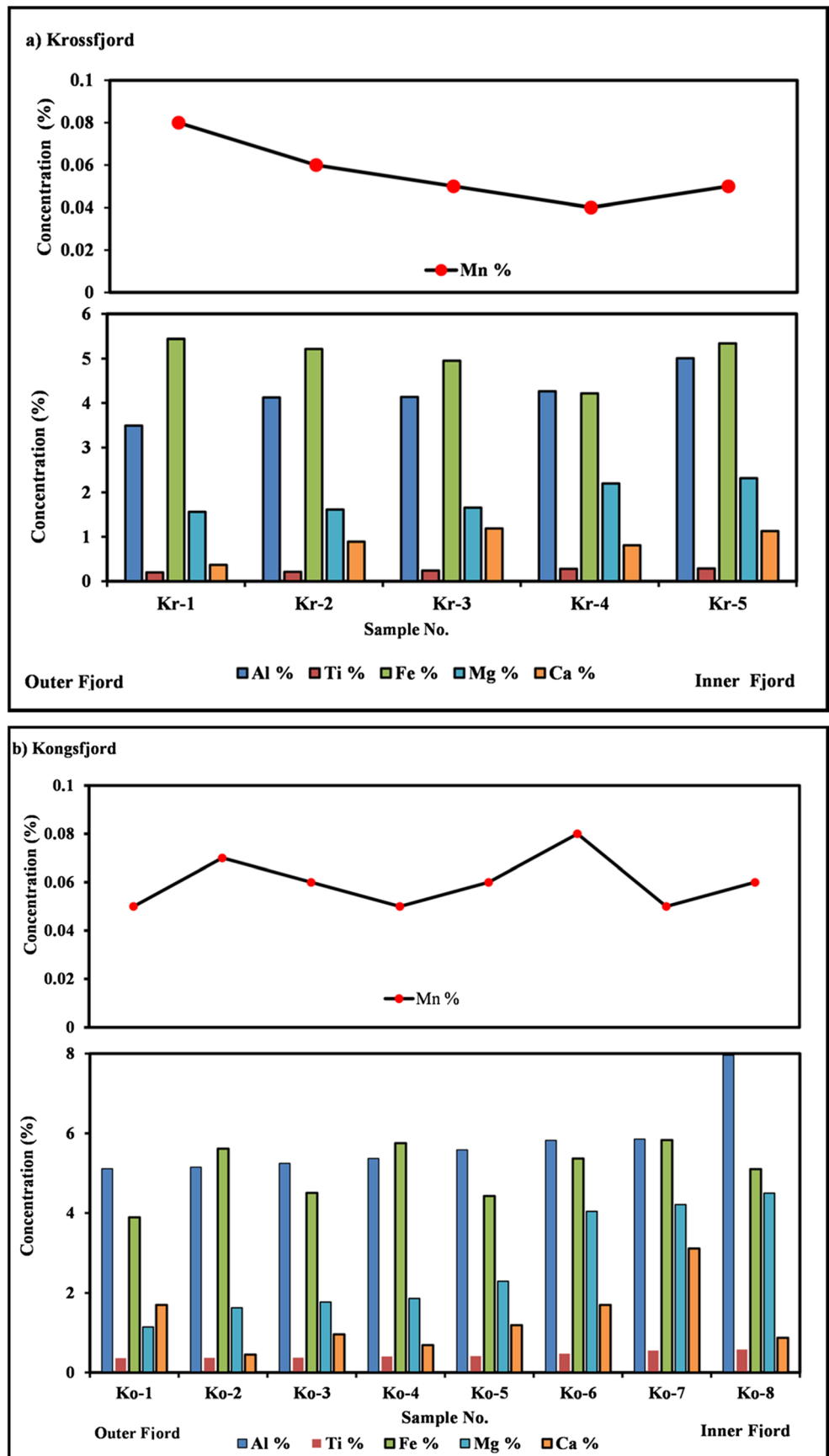
## Discussion

### Source of major and trace elements in surface sediments

Metal distribution exhibited considerable spatial variations in both the fjords on moving away from the glacier outlets. Major metals like Al and Ti showed an overall decreasing trend from the inner fjord towards the outer region in both the fjords (Fig. 4a and b) indicating their lithogenic nature. However, average concentration (0.31% and 0.40%) in Krossfjord and Kongsfjord respectively of Ti is low indicating felsic source rocks. Al and Ti are dominant components derived from the catchment rocks (Taylor and McLennan 1985) and are good indicators of the degree of deposition of lithogenic material (Murray and Leinen 1996). Elements like Mg and Ca showed a similar distribution to that of Al and Ti suggesting their source to be lithogenic in nature.

Trace elements like Ni, Ba, and Pb showed higher concentration in the glacier-dominated inner fjord (Fig. 5a and b) similar to that of major elements indicating their similar source and post-depositional processes. High Ba and Pb content in surface samples along the Krossfjord and Kongsfjord supports that sediment was mainly derived from felsic rocks. Ba and Pb are usually accommodated in rocks rich in feldspars (Prinz 1967; Sensarma et al. 2016) such as gneisses and granites. Pb is higher in most of the samples along the Krossfjord and Kongsfjord where illite is also high. The higher Pb concentration in the sediments is attributed to the tendency of illite to adsorb Pb more easily into its structure (Serrano et al. 2005).

**Fig. 4** Distribution of major metals in the surface sediments along the a) Krossfjord and b) Kongsfjord



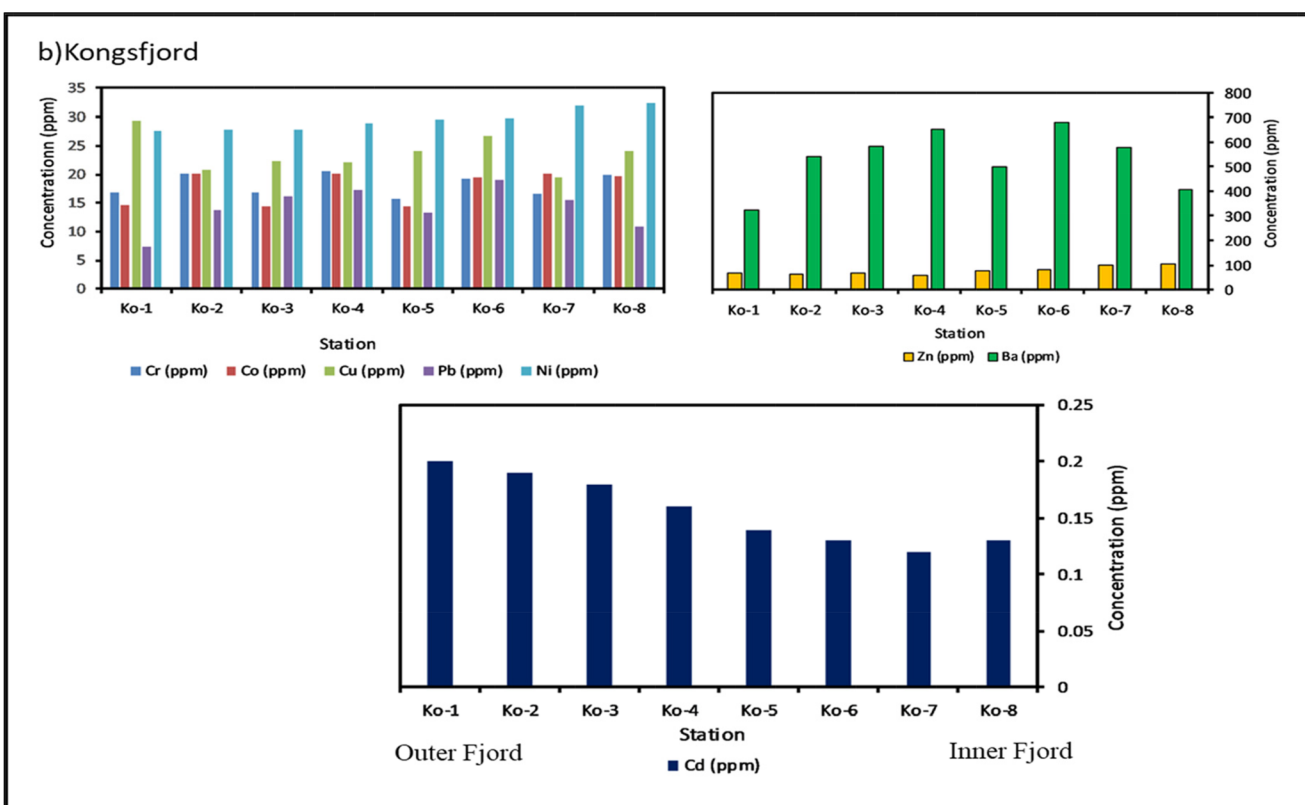
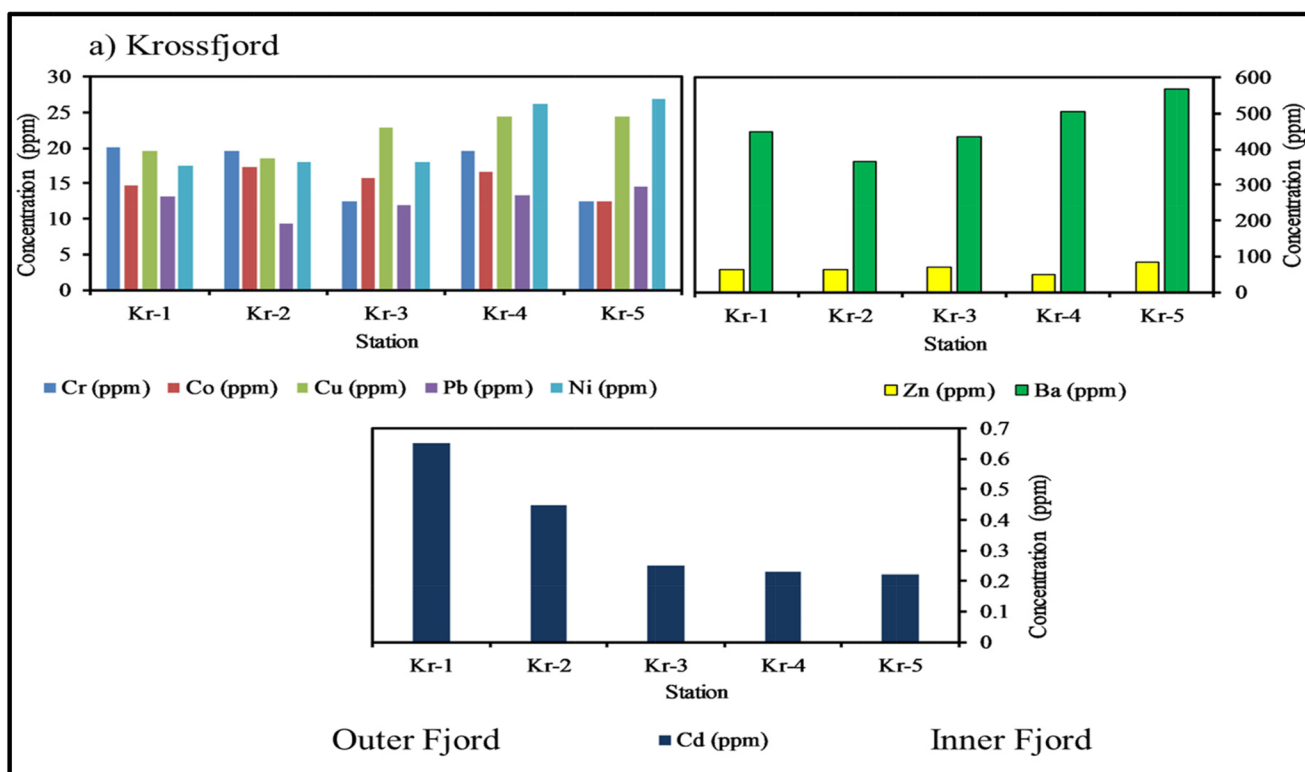


Fig. 5 Distribution of trace metals in the surface sediments along the a) Krossfjord and b) Kongsfjord

Due to the similarity in ionic radii (Wedepohl 1995), Ba replaces K in the lattice structure (Pais and Jones 1997) and

perhaps gets enhanced in micas and K-feldspars. Illite is formed by weathering of rocks having higher content of micas



**Table 3** Comparison of trace metal concentration in sediment with world wide dataset

Location	Metals (ppm)										References
	Cr	Co	Cu	Pb	Cd	Ni	Zn	Ba			
Krossfjord-Kongsfjord, Arctic	17.67	16.92	23.00	13.48	0.23	26.33	72.78	507.54	Present study		
Kongsfjorden, Arctic	64.71	15.08	26.38	22.59	0.19	29.98	85.47	Lu et al. (2013)			
Kongsfjorden, Arctic	74.23	12.45	20.15	17.08	0.30	31.4	74.23	Grotti et al. (2013)			
Kongsfjorden, Arctic	58.21	12.41	14.92	23.99	Singh et al. (2018)						
Kongsfjorden, Arctic	29.27–234.18		14.091–77.24	41.27–401.75	12.33–98.98	0.15–1.05	31.1–178.82	(190.62)			
Prydz Bay, Antarctica	16.57	166.56		1.56	6.82	110.29	22.91	Choudhary et al. (2018a, 2018b)			
Amery Ice Shelf, Prydz Bay	1.14		3.05		Sun et al. (2013)						
Continental shelf, Prydz Bay	2.63		3.18		Dessai and Nayak (2009)						
Deep ocean, Prydz Bay	26.25–172.25		8.93–8.91		Ramesh et al. (1999)						
Tropical estuary (Zuari), west coast of India	22.75–02.00	27–67	10.5–169.50								
Tropical estuary (Godavari), east coast of India	16.08–140.03	2.44–14.39	8.08–13.05								

**Table 4** Factor loadings of the surface sediments of Krossfjord

	Factor1	Factor2	Factor3	Factor4
% of total Variance	52.64	22.71	15.23	9.42
Cumulative % of total Variance	52.64	75.35	90.58	100.00
Depth	0.67	<b>-0.72</b>	-0.18	0.02
Sand	0.38	<b>0.79</b>	0.45	-0.18
Silt	-0.54	<b>0.77</b>	0.30	-0.16
Clay	0.12	<b>-0.88</b>	-0.42	0.19
Illite	<b>-0.79</b>	-0.45	0.35	0.21
Kaolinite	<b>0.73</b>	0.55	-0.40	-0.08
Chlorite	<b>0.76</b>	-0.09	-0.01	-0.65
TOC	<b>0.77</b>	0.60	-0.23	0.00
TN	<b>0.99</b>	0.09	-0.08	-0.04
TP	0.37	<b>-0.84</b>	-0.26	0.29
BSi	<b>0.99</b>	0.12	-0.04	-0.12
Al	<b>-0.86</b>	0.50	-0.05	-0.10
Ti	<b>-0.96</b>	-0.03	-0.08	-0.26
Fe	0.50	0.66	-0.50	0.26
Mn	<b>0.90</b>	0.13	-0.41	0.04
Mg	<b>-0.84</b>	0.07	-0.20	-0.49
Ca	<b>-0.77</b>	0.34	0.25	0.49
Cr	0.66	-0.28	0.30	-0.63
Co	0.31	-0.33	<b>0.89</b>	-0.03
Cu	<b>-0.93</b>	-0.28	-0.24	-0.04
Pb	-0.49	-0.25	<b>-0.80</b>	-0.23
Cd	<b>0.97</b>	0.01	-0.20	-0.12
Ni	<b>-0.81</b>	0.02	-0.18	-0.56
Zn	-0.30	0.63	-0.57	0.43
Ba	<b>-0.71</b>	-0.04	-0.62	-0.33
Explored Variance	13.16	5.68	3.81	2.36
Proportion Total	0.53	0.23	0.15	0.09

Extraction: Principal components (marked loadings are significant > 0.7)

and potash feldspars resulted in the formation of illite supporting the higher concentration of Ba in the surface samples of Krossfjord and Kongsfjord. Ba is found to be higher at deeper water depths at station Kr-1 and Kr-5 along the Krossfjord and at station Ko-3, Ko-4, and Ko-6 in Kongsfjord as in the water column, the formation of barytes takes place below the photic zone and requires adequate water depth for its preservation (Schoepfer et al. 2015). Cd exhibited an increasing trend towards the outer fjord similar to that of finer sediments and organic carbon suggesting that Cd is biologically active and behaves as nutrients; therefore, its distribution is regulated by the organic matter. In addition, Cd is a redox sensitive element and may have been enriched in anoxic sediments by cadmium sulfide precipitation (Grotti et al. 2017). The concentrations of the trace element in sediments of Krossfjord and Kongsfjord are comparable with the sediments of the coastal and estuarine sediments of the world (Table 3).

**Table 5** Factor loadings of the surface sediments of Kongsfjord

	Factor1	Factor2	Factor3	Factor4
% of total Variance	36.43	20.04	15.56	12.00
Cumulative % of total Variance	36.43	56.47	72.03	84.03
Depth	<b>-0.72</b>	0.23	0.10	-0.12
Sand	0.42	-0.52	0.69	0.04
Silt	-0.22	<b>0.79</b>	-0.39	-0.07
Clay	-0.48	-0.21	<b>-0.76</b>	0.03
Illite	0.47	0.34	-0.68	-0.17
Kaolinite	-0.54	0.05	0.69	0.32
Chlorite	0.41	-0.68	-0.41	-0.44
TOC	-0.57	-0.06	0.29	-0.74
TN	<b>-0.75</b>	0.14	0.30	-0.55
TP	0.09	-0.38	0.30	0.57
BSi	<b>-0.84</b>	-0.03	-0.18	-0.03
Al	<b>0.80</b>	-0.37	0.18	-0.40
Ti	<b>0.94</b>	-0.09	0.00	-0.17
Fe	0.51	<b>0.80</b>	0.05	-0.21
Mn	0.08	0.29	<b>0.70</b>	0.24
Mg	<b>0.93</b>	0.02	0.16	-0.01
Ca	0.33	-0.01	-0.35	0.33
Cr	0.14	0.49	0.46	-0.69
Co	0.51	0.63	0.24	-0.48
Cu	-0.42	-0.58	0.50	-0.03
Pb	0.26	<b>0.78</b>	0.13	0.39
Cd	<b>-0.91</b>	-0.03	-0.16	-0.26
Ni	<b>0.96</b>	-0.14	0.01	-0.11
Zn	<b>0.88</b>	-0.31	-0.05	-0.10
Ba	0.19	<b>0.84</b>	0.12	0.36
Explored Variance	9.11	5.01	3.89	3.00
Proportional Total	0.36	0.20	0.16	0.12

Extraction: principal components (marked loadings are significant > 0.7)

Further, interpretations made on the source of elements in sediments of the Krossfjord and Kongsfjord are supported by R-mode factor analysis. The factor loadings are presented in Tables 4 and 5. For the surface samples collected from Krossfjord, four factors could be extracted contributing to about 52.64, 22.71, 15.23, and 9.42% of the variance respectively which account for a cumulative percentage of 100.00 with eigenvalue > 1. For the first factor, kaolinite, chlorite, TOC, TN, BSi, Mn, and Cd are observed to be positively loaded, thus indicating their association with organic matter. Illite, Al, Ti, Mg, Ca, Cu, Ni, and Ba are found to be negatively loaded indicating their common lithogenic nature. For the second factor, sand and silt are observed to be positively loaded and depth, clay, and TP are observed to be negatively loaded. Factor 3 and 4 are less significant and does not represent any major association of elements. Along the Kongsfjord, four factors could be extracted contributing to about 36.43,

20.04, 15.56, and 12.00% of the variance respectively which account for a cumulative percentage of 84.03 with eigenvalue > 1 (Table 5). For the first factor, depth, TN, BSi, and Cd are observed to be negatively loaded, thus indicating that Cd is regulated by organic matter along with the depth. Elements like Al, Ti, Mg, Ni, and Zn are found to be positively loaded indicating their common lithogenic nature. For the second factor in Krossfjord, sand and silt are observed to be positively loaded and depth, clay, and TP are observed to be positively loaded. For the second factor, silt, Fe, and Ba are observed to be positively loaded indicating their similar source.

Pearson’s correlation was also carried out. It showed significant correlations although a number of samples were very less. Along the Krossfjord, TP showed good correlation with depth suggesting high productivity towards fjord mouth. Clay displayed good correlation with TP and TOC showed good correlation with Fe indicating the association of Fe with organic matter in Krossfjord. Kaolinite showed strong positive correlation with TOC, Fe, and Mn suggesting its association with organic matter and Fe-Mn oxyhydroxides. Chlorite showed good correlation with Cr indicating their similar source. TN showed significant correlation with BSi, Mn, and Cd. Ti showed good correlation with Mg, Cu, and Ni. Mn showed good correlation with Cd. Mg showed good correlation with Ni and Ba and Pb with Ba. Along the Kongsfjord, TOC showed good correlation with TN indicating their similar source. TN showed good correlation with Cd. Al showed good correlation with Ti, Mg, Ni, and Zn. Fe showed good correlation with Co. Mg showed good correlation with Ni and Zn. Cr showed good correlation with Co and Pb showed good correlation with Ba. Elements like Cr and Cu does not show similarity with any of the trace elements indicating their different sources (Tables 6 and 7) or post-depositional remobilization.

**Pollution indices**

The enrichment factor (EF) values were calculated to evaluate the enrichment of metals in sediments and it was observed that in Krossfjord, almost all the metals at all the stations showed lower values (< 3) indicating no to minor enrichment in the Krossfjord; however, metals like Fe, Cd, and Ba showed a decreasing trend of enrichment factor from station Kr-1 to Kr-5 (Fig.6). Cd showed severe enrichment at station Kr-1, and decreased to moderate enrichment at station Kr-5 may be due to high productivity indicating its biogenic nature having 83.33% biogenic input and 16.67% lithogenic input (0.30 biogenic input and 0.06 lithogenic input) associated with finer sediments in Krossfjord. In the Kongsfjord, almost all the metals from station Ko-1 to Ko-8 showed no to minor enrichment; however, Mg showed moderate enrichment from station Ko-6 to Ko-8 and Zn at station Ko-1 (Fig.6).

**Table 6** Pearson's correlation between sediment components including major and trace elements of Krossford

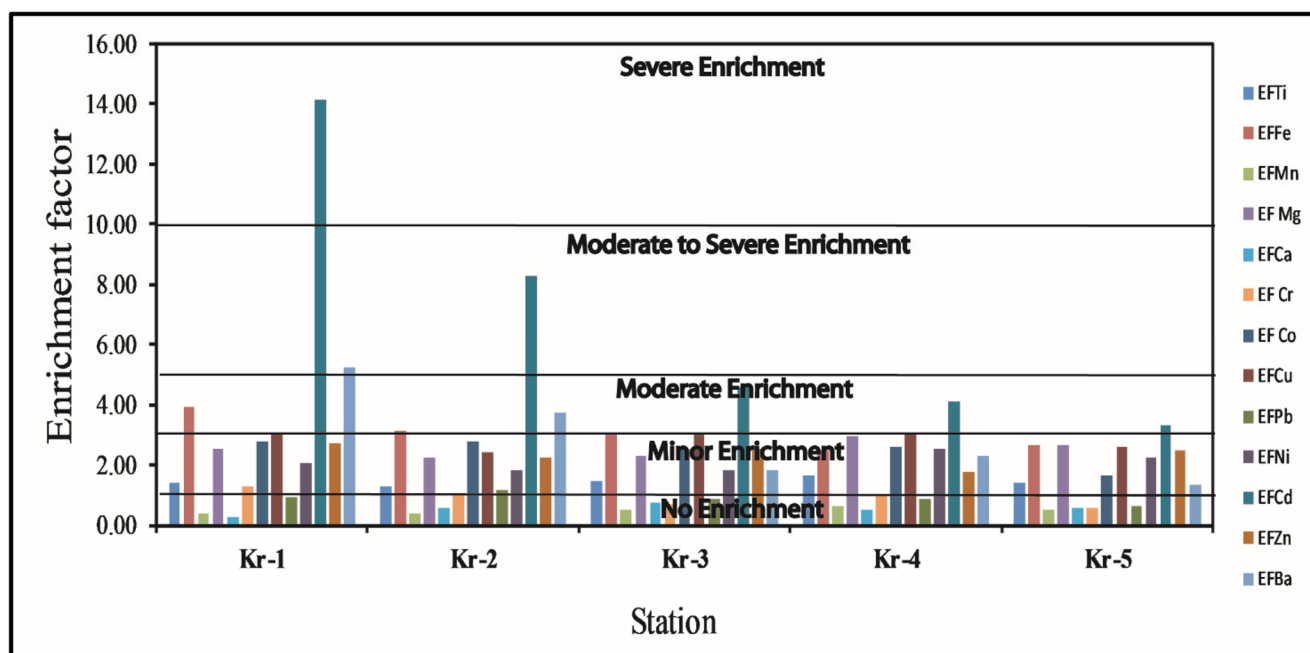
	Depth	Sand	Silt	Clay	Illite	Kaolinite	Chlorite	TOC	TN	TP	BSi	Al	Ti	Fe	Mn	Mg	Ca	Cr	Co	Cu	Pb	Cd	Ni	Zn	Ba
Depth	1.00																								
Sand	-0.40	1.00																							
Silt	<b>-0.97</b>	0.57	1.00																						
Clay	0.79	-0.87	<b>-0.90</b>	1.00																					
Illite	-0.26	-0.54	0.15	0.20	1.00																				
Kaolinite	0.16	0.54	-0.08	-0.24	<b>-0.98</b>	1.00																			
Chlorite	0.56	0.33	-0.37	0.05	-0.70	<b>0.98</b>	1.00																		
TOC	0.12	0.65	-0.02	-0.34	<b>-0.96</b>	<b>0.98</b>	0.53	1.00																	
TN	0.61	0.42	-0.48	0.06	-0.86	0.81	0.77	0.84	1.00																
TP	<b>0.91</b>	-0.69	<b>-0.97</b>	<b>0.95</b>	0.06	-0.11	0.17	-0.16	0.30	1.00															
BSi	0.58	0.47	-0.43	0.01	-0.87	0.81	0.81	0.84	<b>1.00</b>	0.25	1.00														
Al	<b>-0.93</b>	0.06	0.85	-0.54	0.42	-0.33	-0.63	-0.35	-0.80	-0.76	-0.77	1.00													
Ti	-0.61	-0.38	0.51	-0.10	0.70	-0.67	-0.56	-0.74	<b>-0.94</b>	-0.38	<b>-0.92</b>	0.84	1.00												
Fe	-0.06	0.44	0.06	-0.27	-0.81	<b>0.90</b>	0.15	<b>0.89</b>	0.58	-0.17	0.55	-0.09	-0.52	1.00											
Mn	0.58	0.25	-0.52	0.17	<b>-0.91</b>	<b>0.89</b>	0.65	0.87	<b>0.94</b>	0.35	<b>0.92</b>	-0.70	-0.85	0.74	1.00										
Mg	-0.59	-0.27	0.53	-0.17	0.47	-0.46	-0.32	-0.56	-0.80	-0.46	-0.76	0.82	<b>0.95</b>	-0.40	-0.69	1.00									
Ca	-0.79	0.00	0.67	-0.40	0.64	-0.51	<b>-0.93</b>	-0.45	-0.77	-0.50	-0.78	0.77	0.58	-0.15	-0.73	0.38	1.00								
Cr	0.57	0.28	-0.38	0.07	-0.43	0.26	<b>0.93</b>	0.27	0.63	0.22	0.68	-0.66	-0.49	-0.17	0.41	-0.33	-0.83	1.00							
Co	0.29	0.26	-0.15	-0.05	0.21	-0.31	0.27	-0.17	0.20	0.16	0.23	-0.47	-0.36	-0.52	-0.13	-0.45	-0.14	0.58	1.00						
Cu	-0.37	-0.67	0.22	0.23	0.77	-0.73	-0.65	-0.82	<b>-0.93</b>	-0.06	<b>-0.93</b>	0.67	<b>0.93</b>	-0.54	-0.78	0.83	0.54	-0.59	-0.41	1.00					
Pb	0.00	-0.71	-0.14	0.46	0.17	-0.16	-0.19	-0.34	0.43	0.17	-0.45	0.35	0.60	-0.07	-0.16	0.67	-0.02	-0.35	-0.78	0.72	1.00				
Cd	0.67	0.31	-0.55	0.17	-0.87	0.81	0.81	0.80	<b>0.99</b>	0.37	<b>0.98</b>	-0.81	<b>-0.89</b>	0.56	<b>0.96</b>	-0.72	-0.85	0.65	0.12	-0.86	-0.29	1.00			
Ni	-0.53	-0.27	0.48	-0.14	0.45	-0.46	-0.25	-0.57	-0.76	-0.43	-0.72	0.77	<b>0.94</b>	-0.45	-0.68	<b>1.00</b>	0.31	-0.24	-0.40	0.81	0.66	-0.68	1.00		
Zn	-0.55	0.05	0.41	-0.27	-0.15	0.32	-0.55	0.28	-0.21	-0.38	-0.25	0.56	0.21	0.67	0.06	0.20	0.51	-0.82	-0.82	0.22	0.35	-0.22	0.12	1.00	
Ba	-0.34	-0.53	0.21	0.15	0.30	-0.27	-0.31	-0.42	-0.64	-0.16	-0.64	0.65	0.82	-0.16	-0.41	<b>0.88</b>	0.21	-0.44	-0.75	0.83	<b>0.93</b>	-0.53	0.87	0.40	1.00

Bold values represent correlation significant at  $p < 0.05$ ,  $N = 5$

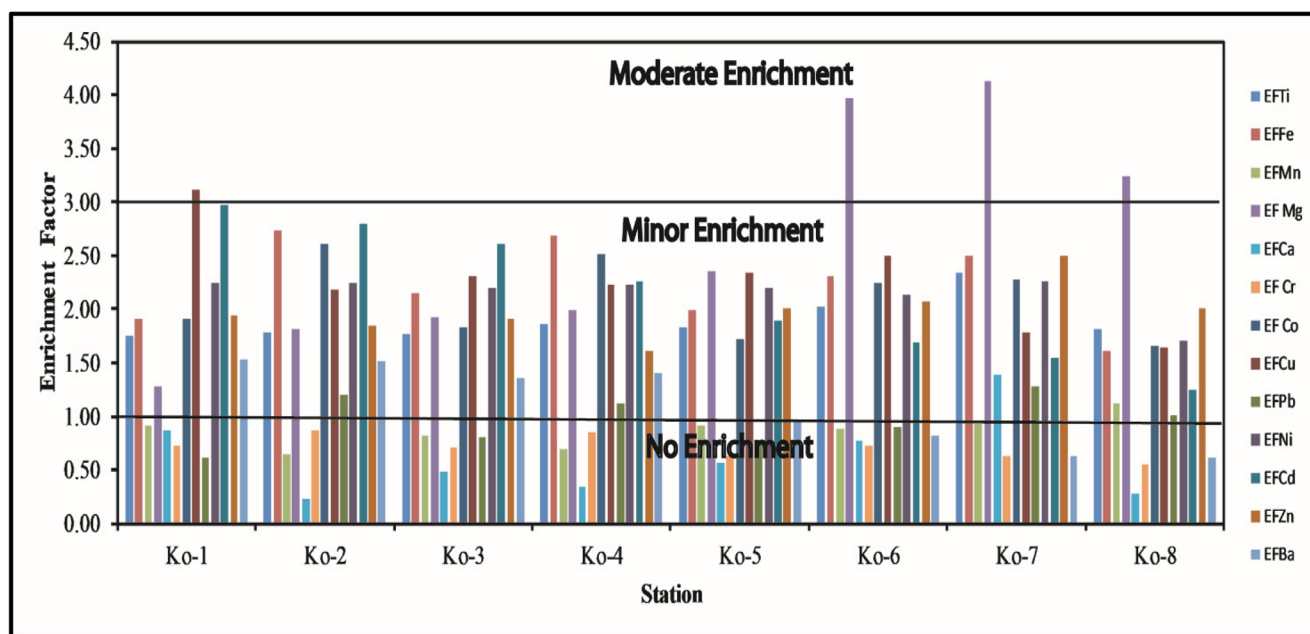
**Table 7** Pearson's correlation between sediment components including major and trace elements of Kongsfjord

	Depth	Sand	Silt	Clay	Illite	Kaolinite	Chlorite	TOC	TN	TP	BSi	Al	Ti	Fe	Mn	Mg	Ca	Cr	Co	Cu	Pb	Cd	Ni	Zn	Ba
Depth	1.00																								
Sand	-0.40	1.00																							
Silt	0.28	<b>-0.87</b>	1.00																						
Clay	0.35	-0.62	0.15	1.00																					
Illite	-0.36	-0.37	0.28	0.29	1.00																				
Kaolinite	0.44	0.17	0.00	-0.35	<b>-0.91</b>	1.00																			
Chlorite	-0.39	0.23	-0.48	0.30	0.35	<b>-0.71</b>	1.00																		
TOC	0.44	0.01	-0.02	0.01	-0.31	0.23	0.00	<b>0.92</b>	1.00																
TN	0.70	-0.20	0.22	0.06	-0.46	0.48	-0.30	<b>0.92</b>	1.00																
TP	-0.52	0.61	-0.61	-0.25	-0.21	0.20	-0.09	-0.24	-0.37	1.00															
BSi	0.63	-0.47	0.34	0.41	-0.40	0.43	-0.29	0.48	0.67	-0.22	1.00														
Al	-0.53	0.63	-0.56	-0.38	0.23	-0.49	0.70	-0.10	-0.40	0.00	<b>-0.75</b>	1.00													
Ti	-0.57	0.40	-0.20	-0.47	0.35	-0.49	0.51	-0.43	-0.59	-0.13	-0.69	<b>0.84</b>	1.00												
Fe	-0.26	-0.16	0.55	-0.54	0.49	-0.24	-0.30	-0.13	-0.13	-0.28	-0.40	0.16	0.44	1.00											
Mn	0.15	0.27	-0.04	-0.46	-0.42	0.54	-0.51	-0.15	0.00	0.05	-0.41	0.07	0.00	0.16	1.00										
Mg	-0.46	0.42	-0.19	-0.55	0.24	-0.31	0.30	-0.52	-0.61	-0.10	<b>0.74</b>	<b>0.77</b>	<b>0.96</b>	0.46	0.25	1.00									
Ca	-0.09	-0.20	0.27	-0.03	0.05	-0.07	0.08	-0.57	-0.42	-0.25	0.13	-0.01	0.46	0.09	-0.26	0.46	1.00								
Cr	0.10	0.14	0.14	-0.50	0.12	-0.03	-0.14	0.56	0.45	-0.32	-0.28	0.32	0.16	0.62	0.31	0.17	-0.52	1.00							
Co	-0.20	0.01	0.40	-0.65	0.31	-0.17	-0.14	0.11	0.06	-0.40	-0.39	0.36	0.53	<b>0.92</b>	0.21	0.53	0.04	<b>0.79</b>	1.00						
Cu	0.51	0.44	-0.53	-0.03	<b>-0.81</b>	0.59	0.04	0.40	0.45	0.06	0.40	0.00	-0.22	-0.69	0.14	-0.17	-0.03	-0.14	-0.45	1.00					
Pb	0.10	-0.13	0.34	-0.28	0.34	0.01	-0.60	-0.43	-0.28	0.00	-0.34	-0.17	0.09	0.63	0.42	0.27	0.03	0.26	0.39	-0.45	1.00				
Cd	0.60	-0.51	0.26	0.60	-0.27	0.27	-0.16	0.65	<b>0.74</b>	-0.24	0.70	-0.61	<b>-0.86</b>	-0.46	-0.13	<b>-0.90</b>	-0.47	-0.02	-0.41	0.25	-0.41	1.00			
Ni	-0.68	0.47	-0.28	-0.50	0.36	-0.50	0.51	-0.45	-0.65	0.03	<b>-0.71</b>	<b>0.84</b>	<b>0.99</b>	0.41	-0.05	<b>0.93</b>	0.43	0.11	0.49	-0.25	0.08	<b>-0.89</b>	1.00		
Zn	-0.59	0.40	-0.30	-0.33	0.24	-0.46	0.62	-0.48	-0.65	-0.08	-0.67	<b>0.85</b>	<b>0.95</b>	0.20	0.02	<b>0.90</b>	0.48	-0.04	0.31	-0.12	-0.12	<b>-0.76</b>	<b>0.93</b>	1.00	
Ba	0.13	-0.20	0.42	-0.28	0.33	0.05	-0.66	-0.37	-0.20	-0.03	-0.25	-0.25	0.03	0.67	0.38	0.20	0.03	0.29	0.43	-0.46	<b>0.99</b>	-0.35	0.01	-0.19	1.00

Bold values represent correlation significant at  $p < 0.05$ ,  $N = 8$



a)



b)

**Fig. 6** Enrichment factor (EF) of the surface sediments along the Krossfjord (a) and Kongsfjord (b)

Pollution load index showed lower values (< 1) at all the stations in Krossfjord, indicating no pollution at these stations except at station Kr-5 having values (1.07) which is attributed to slight pollution at station Kr-5 (Table 8). In Kongsfjord, almost all the stations showed values > 1 suggesting slight pollution in the Kongsfjord except station Ko-1 indicating no pollution at this station. Overall, low values (<2) throughout the Krossfjord and Kongsfjord implied no appreciable

inputs of metals from the anthropogenic sources in the fjord system (Table 8).

**Fractionation of metals (Fe, Mn, Cr, Co, and Cu): potential bioavailability**

The potential bioavailability of the metals for the investigated environment has been assessed by the metal fractionation

**Table 8** Values of contamination factor (CF) and pollution load index (PLI) in (a) Krossfjord and (b) Kongsfjord

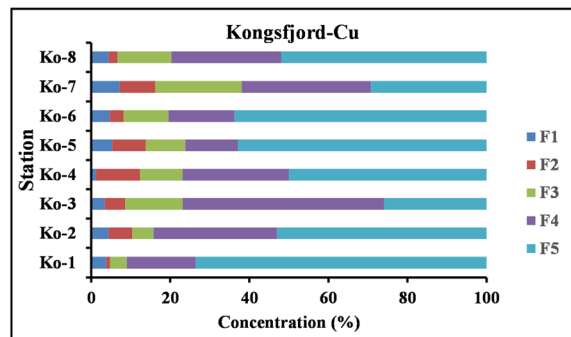
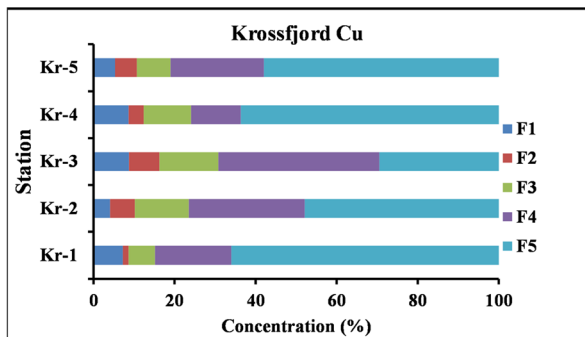
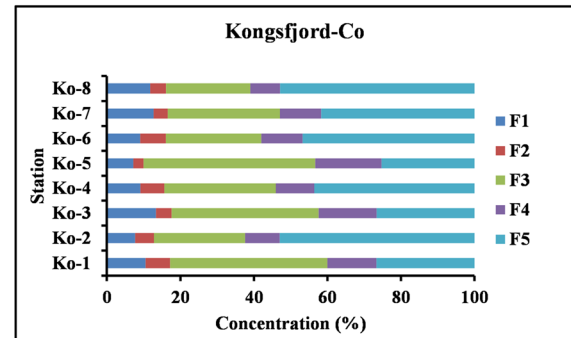
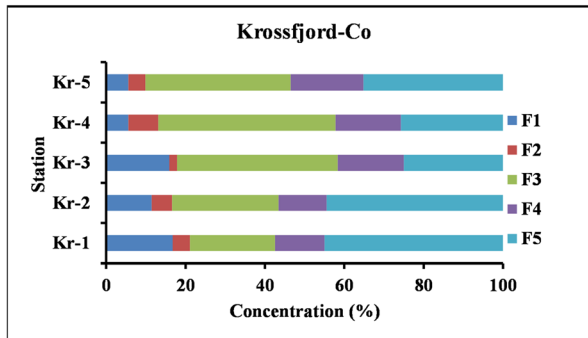
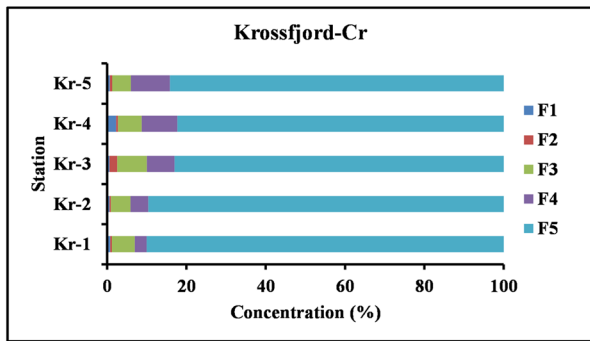
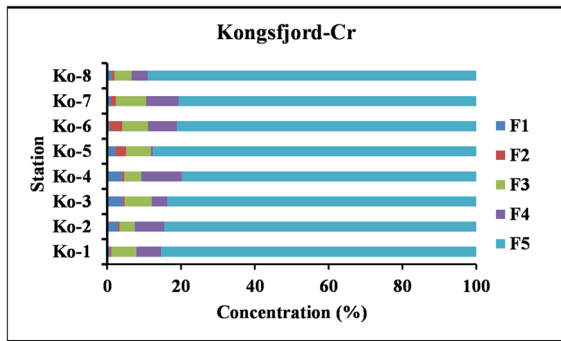
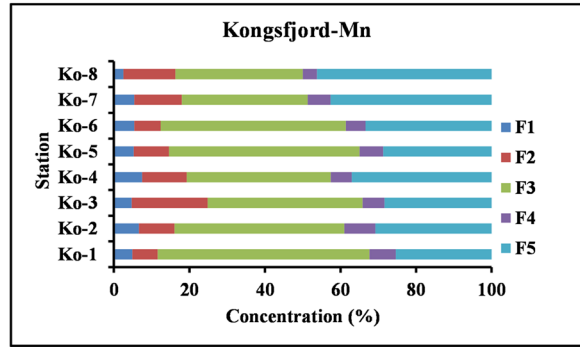
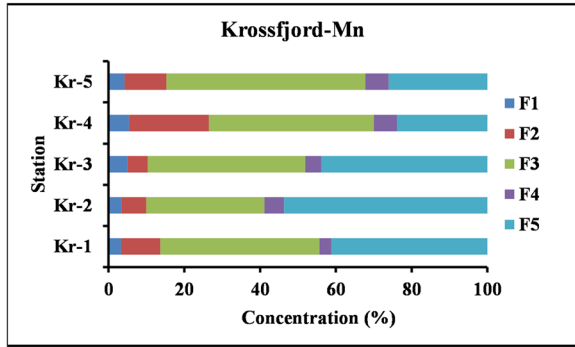
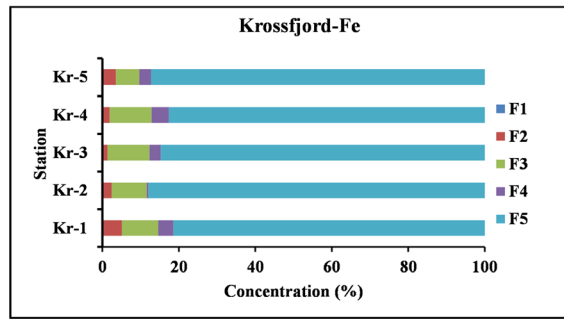
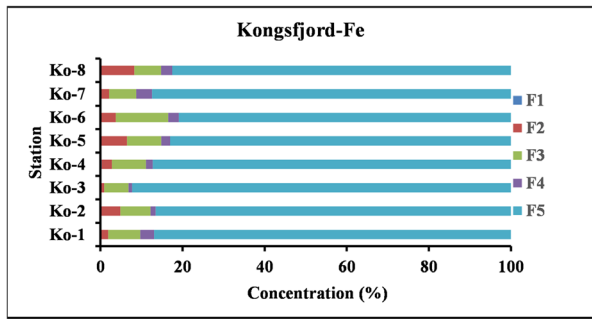
(a) Sample	CF-Ti	CF-Fe	CF-Mn	CF-Mg	CF-Ca	CF-Cr	CF-Co	CF-Cu	CF-Pb	CF-Ni	CF-Cd	CF-Zn	CF-Ba	PLI
Kr-1	0.64	1.76	1.52	1.15	0.13	0.58	1.26	1.37	0.78	0.94	6.37	1.22	0.67	<b>1.00</b>
Kr-2	0.68	1.69	1.14	1.19	0.30	0.56	1.49	1.29	0.54	0.96	4.41	1.18	0.55	<b>0.98</b>
Kr-3	0.77	1.60	0.95	1.23	0.40	0.36	1.35	1.60	0.71	0.97	2.45	1.36	0.65	<b>0.97</b>
Kr-4	0.90	1.37	0.76	1.63	0.28	0.56	1.44	1.70	0.78	1.41	2.25	0.97	0.76	<b>1.00</b>
Kr-5	0.92	1.73	0.95	1.72	0.38	0.36	1.07	1.70	0.86	1.44	2.16	1.59	0.85	<b>1.07</b>
b)														
Ko-1	1.16	1.26	0.95	0.85	0.58	0.48	1.26	2.06	0.43	1.48	1.96	1.28	0.49	<b>0.97</b>
Ko-2	1.19	1.82	1.33	1.20	0.15	0.57	1.74	1.46	0.81	1.49	1.86	1.23	0.81	<b>1.04</b>
Ko-3	1.19	1.46	1.14	1.31	0.33	0.48	1.24	1.56	0.95	1.49	1.76	1.30	0.88	<b>1.06</b>
Ko-4	1.29	1.86	0.95	1.38	0.23	0.59	1.74	1.55	1.02	1.55	1.57	1.12	0.98	<b>1.09</b>
Ko-5	1.32	1.43	1.14	1.70	0.40	0.45	1.24	1.69	0.78	1.59	1.37	1.45	0.75	<b>1.07</b>
Ko-6	1.52	1.74	1.52	2.99	0.58	0.55	1.68	1.88	1.12	1.61	1.27	1.56	1.02	<b>1.34</b>
Ko-7	1.77	1.89	0.95	3.12	1.06	0.48	1.73	1.36	0.91	1.72	1.18	1.89	0.87	<b>1.31</b>
Ko-8	1.86	1.65	1.14	3.33	0.30	0.57	1.71	1.69	0.64	1.75	1.27	2.06	0.61	<b>1.20</b>

approach. The fractionation of the metals has been carried out in the five geochemical phases: exchangeable (F1), carbonate (F2), Fe-Mn oxide (reducible-F3), organic matter/sulfide bound (oxidizable-F4), and residual (F5) for the surface samples of Krossfjord and Kongsfjord. The most extractable fractions among these five fractions significantly affect the aquatic ecosystems. A sum of the first four fractions (F1 + F2 + F3 + F4) is considered the potential bioavailability, and residual fraction (F5) is of detrital or primary mineral origin which is an indicator of the natural source (Salomons and Forstner 1980).

In the surface sediments of Krossfjord and Kongsfjord, Fe concentrations varied in the order of F5 > F3 > F2 > F4 > F1. Iron was concentrated in substantial amount in the residual fraction at all the stations along the Krossfjord and Kongsfjord (Fig. 7). High concentration of Fe (> 80%) in the residual phase indicated an input of terrigenous material from weathering of rocks available in the catchment area. In the residual fraction, Fe is immobile due to its bonding with primary and secondary minerals and therefore, it is unavailable for uptake of organisms (Tessier et al. 1979). Among the bioavailable phases, Fe was concentrated in the Fe-Mn oxide phase at all the stations in both the fjords. The concentration of Fe in the organic/sulfide bound phase is attributed to the formation of iron sulfides. It is known that Fe prefers oxide phase in oxic conditions and sulfides in anoxic environments.

Chester and Jickells (2012) suggested that Mn is a redox-sensitive element similar to that of Fe which exhibits active biogeochemical behavior in the aqueous environment and transforms easily from dissolved phase to the particulate phase and vice versa due to the physicochemical changes. Further, various parameters like redox conditions, pH, and presence of carbonate ions regulate the geochemical association of Mn in the form of oxides, carbonates, organometallic complexes, or sulfides (Farias et al. 2007). Residual phase consists of relatively lower concentration of Mn in the sediments of the Krossfjord (average 37.73%) and Kongsfjord (average 34.05%) and was found concentrated in the Fe-Mn oxide bound phase in both the fjords (average 42.16% in Krossfjord and 43.33% in Kongsfjord) due to the formation of oxides (Fig. 7). Carbonate fraction is a loosely bound phase. Considerable quantity of Mn (average 10.90% in Krossfjord and 11.34% Kongsfjord) is concentrated in carbonate fraction. Similar ionic radii of Mn as that of Ca enable Mn to replace Ca in the carbonate fraction (Noronha-D'Mello and Nayak 2015; Grotti et al. 2017). Loosely bound exchangeable and carbonate Mn can be released from surface sediments to water and preferentially bioavailable to the biota

**Fig. 7** Speciation of metals Fe, Mn, Cr, Co, and Cu in Krossfjord and Kongsfjord where F1 is the exchangeable, F2 is the carbonate bound, F3 is the Fe-Mn oxide, F4 is the organic/sulfide bound, and F5 is the residual fraction



living in sediments and water. Manganese is relatively low (4.96% in Krossfjord and 5.98% in Kongsfjord) in the organic/sulfide phase due to low organic affinity of Mn (Bendell-Young and Harvey 1992).

Chromium was largely associated with the residual phase in the sediments of Krossfjord (average 85.80%) and Kongsfjord (average 83.92%) as it mainly gets transported to the sediment within the residual phase (Noronha-D'Mello and Nayak 2015). Among bioavailable phases, a considerable quantity of Cr was found associated with organic/sulfide bound fraction. Tribovillard et al. (2008) stated that because of structural and electronic incompatibilities with pyrite, Cr(III) uptake by authigenic Fe sulfides is very limited. Therefore, Cr is preferably associated with organic matter as compared with sulfides. Additionally, Cr does not form an insoluble sulfide (Huerta-Diaz and Morse 1992; Tribovillard et al. 2008). The concentration of Cr in the exchangeable and carbonate bound fraction was very less compared with the other two bioavailable fractions (Fig.7).

Cobalt was predominantly bound to the residual fraction both in Kongsfjord (average 39.55%) and Krossfjord (average 35.05%) indicating its preferential association with silicates and aluminosilicates (Grotti et al. 2017). Higher Co concentration in Fe-Mn oxide (average 34.00%) fraction in the Krossfjord explains the adsorption of Co on the surface of Fe-Mn colloids as observed by Nasnodkar and Nayak (2017) in the sediments of the tropical estuaries. Fe-Mn colloids have played an important role in controlling the mobility of Co in the fjord environment due to their ability of scavenging Co in sediments (Kaasalainen and Yli-Halla 2003). Considerable percentage of Co was available in reducible fraction (average 33.01%) in Kongsfjord. Lower amount of Co was found in the oxidizable (12.20%) and exchangeable (10.18%) fraction in both the fjords.

Average 50% of Cu was found associated with the residual fraction and the remaining 50% was found distributed in the bioavailable fractions in both the fjords indicating their availability to the sediment-associated biota. Among bioavailable phases, Cu in oxidizable (organic/sulfide) fraction was appreciable (average 27.11% in Krossfjord and 24.49% in Kongsfjord) suggesting its partial association with the refractory organic matter as humic substances or sulfides (Grotti et al. 2017). Thus, grain size, Fe-Mn oxyhydroxides and organic matter along with pH and Eh have affected the fractionation of metals in different geochemical phases within the sediments of Krossfjord and Kongsfjord. Thus, grain size, Fe-Mn oxyhydroxides and organic matter along with pH and Eh have affected the fractionation of metals in different geochemical phases within the sediments of Krossfjord and Kongsfjord.

The metal fractionation approach showed > 50% concentration of metals viz. Fe, Cr and Cu in the residual phase

indicating their source to be lithogenic derived from the weathering of source rock while bio-available phases consist of the remaining 50%. However, Mn and Co showed <40% concentration in the residual phase and >60% concentration of these metals were distributed in the bioavailable phases suggesting their availability for uptake and accumulation in aquatic biota (Gambrell 1994; Ladigbolu 2014).

Bioavailability of metals like Mn, Co and Cu showed considerable spatial variations from inner fjord to the outer fjord. Mn showed an increasing trend from station Kr-1 to station Kr-5 while in the Kongsfjord Mn decreased from station Ko-1 to Ko-8 with an overall decreasing trend towards the inner fjord. In the Kongsfjord, bioavailability of Co increased station Kr-1 to station Kr-5 with highest concentration at station Kr-3 and Kr-4 whereas in the Kongsfjord, Co fluctuated from one station to the other with an overall decreasing trend from station Ko-1 to station Ko-8. Higher bioavailability was noted at station Ko-1, Ko-3, Ko-5, and Ko-7, while lower bioavailability was at station Ko-2, Ko-4, Ko-6, and Ko-8. Further, Cu showed an increasing trend from station Kr-1 to station Kr-5 with the highest bioavailability percentage at station Kr-3 in Krossfjord. In the Kongsfjord, bioavailability of Cu showed an increasing trend from station Ko-1 to Ko-8 with high percentage of bioavailability at station Ko-2 and Ko-7.

In labile fractions (F1 + F2), due to weak electrostatic interaction, metals are sorbed weakly and retained on the surface of sediment and can precipitate with carbonates present in the sediments after releasing by ion exchange processes (Filgueiras et al. 2004; Nasnodkar and Nayak 2017). In the labile fraction (F1 + F2), Mn showed 15.15% average in Krossfjord and 16.64% average in Kongsfjord, Co showed 11.06% average in Krossfjord and 10.18% average in Kongsfjord posing a medium risk to the sediment-associated biota. Cu showed 6.83% in Krossfjord and 4.33% average in Kongsfjord posing low risk to the sediment-associated biota. The metals available in labile fractions can migrate easily in neutral or slightly acidic waters (Alvarez-Valero et al. 2009) causing a potential ecological risk to the sediment-associated biota.

### Risk assessment

As the Arctic region is pristine, the aquatic organisms in the polar regions are highly sensitive to the contaminants as compared with the organisms from the lower latitudes; hence, potential risks of metal contaminants to the Arctic ecosystem are intensified (Lu and Kang 2018). When the concentration

**Table 9** The Arctic sediment quality guidelines (ASQGs) (mg/kg)

Category		Cd	Cu	Pb	Zn	Cr	Ni
Arctic	ASQG-low	0.6	16	30.2	120	26	16
	ASQG-high	4.2	108	112	271	110	75



**Table 10** Risk assessment code (RAC)

Category	Risk	Metal in carbonate and exchangeable fractions (%)
1	No risk	< 1
2	Low risk	1–10
3	Medium risk	11–30
4	High risk	31–50
5	Very high risk	> 50

of metals in the bulk sediments was compared with the Arctic sediment quality guidelines (ASQGs, Table 9), it was observed that Cd, Pb, Zn, and Cr contents are below ASQG-low in both the Fjords suggesting that these elements can rarely cause adverse biological effects (Lu and Kang 2018) in the fjords. Zn and Cu contents exceeded ASQG-low but lower than the ASQG-high indicating occurrence of adverse biological effects (Lu and Kang 2018) in the study area.

Risk assessment code (Table 10) was also used to evaluate the toxicity of the labile phases (exchangeable + carbonate bound) of Fe, Mn, Cr, Co, and Cu based on classification scheme described by Perin et al. (1985). Fe, Cr, and Cu concentrations (Table 11) in the labile phases posed a low risk to the organisms (RAC between 1 and 10%). Mn and Co, however, posed a medium risk to the biota (RAC 11–30%). Thus, the source and concentration of Mn and Co need to be monitored on regular basis to understand the risk to the biota available in the fjord.

### Conclusion

The study carried out on the surface sediments of Krossfjord-Kongsfjord system revealed that metal accumulation within the fjords varied largely due to the glaciomarine contrast. Low Ti and high concentration of Ba and Pb indicated the source of sediment of Krossfjord-Kongsfjord system to be felsic rocks. Metals in sediment were mainly derived from the weathering of rocks available in the catchment area. Speciation study showed high concentration of Mn and Co in the labile phases of sediments, which can detrimentally affect sediment-

**Table 11** Average concentration of labile fraction (F1+ F2) in Krossfjord and Kongsfjord

	F1 + F2 (labile fraction %)	
	Krossfjord	Kongsfjord
Fe	2.86	3.89
Mn	15.15	16.64
Cr	1.00	2.12
Co	11.06	10.18
Cu	6.83	4.33

associated biota. Therefore, there is a need to monitor the changes in the concentration of metals and protect the pristine environment.

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