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Source, bioavailability, and toxicity of metals in modern fjord sediments, west Spitsbergen, and their influence on sediment-associated biota

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Metal contamination in the Arctic region has increased over the years despite its remote and isolated location. Thus, to evaluate the bioavailable fractions of various metals and their effects on sediment-associated biota, the surface sediments from the fjords were analyzed for bulk concentration of metals and their speciation in different fractions. Metals concentrations were higher in the inner fjord region and decreased towards the outer fjord, supported by the terrigenous influence (TI%) calculated. Cr and Pb showed higher excess values attributed to their additional source other than the catchment rocks. So, to assess the metal-related ecological risk, the bulk concentration of metals was compared with Arctic sediment quality guidelines (ASQGs). Cr, Cd, and Pb concentrations were high, indicating potential adverse biological effects in the study. To avoid the risk of overestimation, metal speciation was conducted, showing that overall metal concentrations were higher in the residual fraction; however, higher concentrations of Mn in labile phases pose a moderate risk to the sediment-associated biota. Additionally, the population density of foraminifera in the sediments was calculated to assess the influence of bioavailable metal on benthic foraminifera. It was found that the presence of metals in bioavailable fractions affected the abundance of the foraminifera. However, no morphological abnormalities were observed in the species.

KEYWORDS

fjord, metals, terrigenous influence, excess values, foraminifera, ecological risk, sediment-associated biota

1 Introduction

The rise in atmospheric temperature in response to increasing greenhouse gas concentrations has led to the "Arctic amplification" phenomenon. Consequently, a significant reduction of sea ice extent and a large volume of fresh water is exported into the Arctic fjords. These fjords are located at the junction of the ocean, atmosphere, terrestrial, and cryospheric domains and are very sensitive to changes in climate (Bianchi et al., 2020). The source of freshwater in these Arctic fjords is primarily the marine-terminating/tidewater glaciers. The glacial meltwater runoff dominates these glaciers and regulates the primary productivity and terrestrial material flux influencing the delivery of metals accumulated in glacier ice to these fjords over the last century. Moreover, the West Spitsbergen Current (WSC) is gaining strength, transporting warm water to the fjords, responsible for the long-range transportation of significant soluble metals such as Cd and Pb (Maccali et al., 2013).

Along with the interplay of glacial fresh water and seawater, physicochemical variables such as pH, Eh, salinity, and dissolved oxygen determine the fate/form of metals in the sediments. The metals derived from different sources are adsorbed onto sorbent phases and preserved in the sediment. Due to changing chemical and hydrological conditions, metals undergo geochemical modifications and are recycled via sediment resuspension into the water column (Gibson et al., 2015; Zhang et al., 2014; Burton et al., 2006). Thus, sediments act as the sink and source of metals in the marine environment, and they play an essential role in transporting and accumulating metals.

Environmental pollution in the northern polar region has been studied for several decades (Poland et al., 2003; Barrie, 1986; Ottar, 1989); however, increasing varieties of toxic contaminants (such as pesticides and industrial chemicals) have been reported in the Arctic in recent years (Dietz et al., 2022). This indicates that pollutants from around the globe are being transported to the Arctic region by wind, sea ice, and long-range oceanic and atmospheric transport (Li et al., 2018). Due to the extreme environmental conditions in the Arctic, such as frigid temperatures, the contaminants accumulate and degrade slowly compared to tropical environments (Chen et al., 2018). Metal accumulation and their extended existence in this area may affect marine organisms, fish, birds, and mammals (Jakimska et al., 2011; Kock et al., 1996; Akeredolu et al., 1996) and sediment-associated benthic communities. Benthic foraminifera is less mobile and affected by natural and anthropogenic processes (Martins et al., 2019; Schintu et al., 2015) and variations in metal concentrations. Numerous researches have been carried out to assess the effect of metal pollution on benthic foraminifera (Alve, 1995; Yanko et al., 1994, 1998; Samir and El-Din, 2001; Geslin et al., 2002; Bergin et al., 2006; Ferraro et al., 2006; Jayaraju et al., 2008; Frontalini et al., 2009; Mendes et al., 2013; El Kateb et al., 2020; Gildeeva et al., 2021). Samir and El-Din (2001) reported that high concentrations of metals like Pb, Cu, Cr, Cd, and Zn deformed the foraminifera tests. Lintner et al. (2021) suggested that higher content of Mn and Zn ceased the growth of foraminifera. The population density and diversity of foraminifera are affected by increased metal pollution (Bergin et al., 2006; Debenay and Fernandez, 2009; Saalim et al., 2017; Barik et al., 2022) and developed morphological abnormalities (Frontalini and Coccioni, 2008). However, the studies on the impacts of metal concentrations on foraminiferal population and density in different geochemical phases are limited. Numerous studies have used bulk concentration to evaluate toxicity; however, the leachability of metals changes with varying environmental parameters, leading to an overestimation of the ecological risk associated. Therefore, the speciation of metals in different geochemical phases has been carried out to avoid the risk of overestimation and to assess the mobility, bioavailability, and toxicity of metals and their influence on benthic fauna. With this background, the objectives are i) to study the source and spatial variations of the metals in different fjords, ii) to assess the mobility, bioavailability, and toxicity of metals in different geochemical fractions, and iii) their influence on benthic fauna in the surface sediments of Arctic fjords.

2 Materials and methodology

2.1 Study area, sample collection, and storage

Sixteen surface sediment samples have been collected from the high Arctic fjords such as northernmost Raudfjord, Magdalenefjord, and St. Jonsfjord, situated on the west coast of Spitsbergen, Svalbard, Arctic (74 and 81°N and 10 to 28°E) (Figure 1). The sediment samples have been collected from various water depths between 20 and 115 m from the inner fjord to the outer fjord (Figure 1). Sediment samples were collected onboard RV Clione in July 2019 using a Van Veen grab sampler. The sediment samples were packed in clean and labeled plastic bags and stored at 4°C.

2.2 Foraminiferal analysis

The surface sediment samples have been used to study the modern distribution of (living and dead) benthic foraminifera. The samples were divided into two halves, one half was stained onboard using rose-Bengal ethanol solution (2 g rose-Bengal in 1 l of ethanol) to identify living foraminifera, and the other half unstained was used for dead foraminifera. The rose-Bengal stained samples were stored for a minimum of two weeks and then processed following the standard sediment processing procedure (Saalim et al., 2022b). The samples were freeze-dried, weighed, and washed using a 63 µm sieve. The >63 µm sieved material (coarse fraction) was dried and stored in plastic vials. A small aliquot of the dried coarse fraction was weighed and used to pick living and dead benthic foraminifera. A minimum of 300 stained specimens were picked from each sample using a stereo-zoom microscope (Nikon SMZ 1500) and mounted on the micropaleontological slides. The relative abundance of each species was counted in all the surface samples. Foraminiferal density (FD) is the total number of foraminifera (live + dead) per gram of dry sediments (Barik et al., 2019).

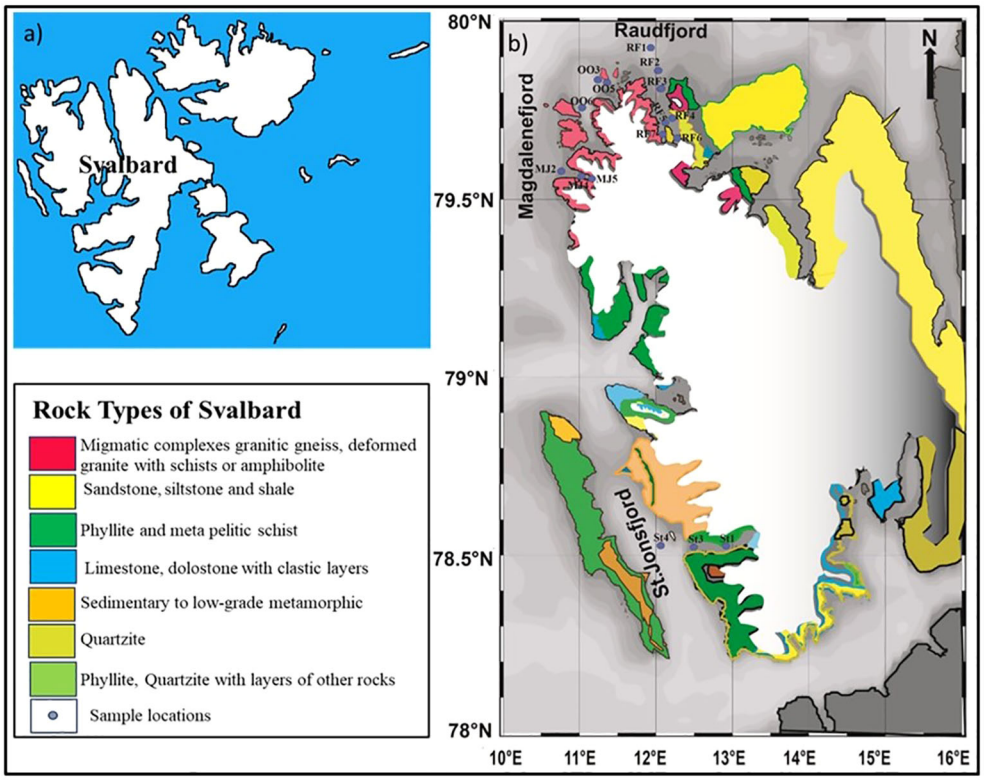

FIGURE 1
(A) Map showing the location of Svalbard **(B)** sampling locations in Raudfjord, Magdalenefjord, St. Jonsfjord and the open ocean in Svalbard.

2.3 Elemental analysis

A minimum of 1 g dry sediment was powdered and homogenized in a mortar pestle for the total carbon (TC), nitrogen (TN), and inorganic carbon (TIC) analysis. TC and TN were analyzed by using an elemental analyzer (Isoprime, Vario Isotope Cube). The precision for TC ± 0.3% and ± 0.63% (1σ standard deviation) for TN% was obtained by repeatedly running sulphanilamide as the standard. The inorganic carbon was measured by using a UIC CM 5017 coulometer. The organic carbon (Corg) was estimated by subtracting TIC from TC. The total phosphorus was determined following the procedure given by Murphy and Riley (1962). The accuracy of phosphorus analysis was determined using a digested sample of JLK-1 and relative error was noted to be less than 4%. The biogenic silica (BSi) was extracted following the wet alkaline extraction method, modified by Mortlock and Froelich (1989) and Muller and Schneider (1993). Each sample was measured in duplicate, with the relative error less than 3%.

2.4 Geochemical analysis

Further, the samples were transported to the laboratory and freeze-dried for further analysis.

For estimating bulk element concentration, sediment samples were finely ground and digested (Jarvis and Jarvis, 1985). 0.2 g of homogenized sediment sample was taken in acid-washed Teflon beakers. To this, a mixture of 10 ml HF–$HClO_4$–HNO_3 in the ratio of 7:3:1 was added, and the solution was completely digested on a hot plate at 150°C. If any particle persisted in the solution, the digestion steps were repeated to obtain a clear solution. The solution was then diluted up to 50 ml and preserved in a cool and dark place. The concentrations of trace elements were determined using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (Thermo scientific iCAP 7000 series). Further, the salt-free and decarbonated sediments were analyzed for major elemental oxides using an X-ray fluorescence (XRF).

Sequential extraction of metals such as Fe, Mn, Co, Cr, Cu, Ni, Pb, Cd, and Zn was performed using the European Community Bureau of Reference (BCR) procedure (Supplementary Figure S1) (Lu and Kang, 2018). In this procedure metals have been extracted into four geochemical fractions viz. i) acid exchangeable phase (F1), ii) Fe-Mn oxide (F2, reducible phase), iii) organic matter/sulfide (F3, oxidizable) bound, and iv) residual phase (F4). The modified BCR method efficiently extracts trace metals like Cr, Cu, Pb, and Zn validated by certified reference material BCR-701, freshwater sediment, from the European Commission. In this study, metals like Fe, Mn, Co, Cr, Cu, Ni, Pb, Cd, and Zn have been considered for fractionation as these metals can pose a considerable ecological risk to the sediment-associated biota. All the extracted fractions were measured using ICP-OES (Thermo scientific iCAP 7000 series).

2.5 Quality assurance and quality control

All the glassware and labware used during the digestion and speciation were soaked in nitric acid and rinsed with Mili Q water thoroughly. During the extraction procedure, the blank was analyzed, and after every ten samples analysis was repeated to ensure the precision of the results, which was within ± 6%. The samples were spiked with known multielement standard solutions to validate the analysis. All the reagents used during the analysis were suprapure. With the samples, a certified reference standard (NIST-1646A, National Institute of Standards and Technology), US, was digested and run, to test the analytical accuracy of the bulk metal analysis method, which varied from 94.5% to 98.7%. Further, recovery (%) of the extracted metals is calculated by [(F1+F2+F3+F4)/total concentration]∗100 (Lu and Kang, 2018), and recovery is between 95 and 103% for all the extracted metals.

2.6 Data analysis using statistical methods

Principal component analysis was performed to assess the impact of metals in different fractions on the benthic foraminifera. The PCA was performed on different metal fractions as primary variables and foraminifera genus as secondary variables using the Statistical software (version 5.5), Statsoft. The three axes, axis 1 (Eigen value 3.26), axis 2 (Eigen value 2.52), and axis 3 (Eigen value 0.90) account for 50.68%, 15.53%, 12.25% of the total variation in the data, respectively making a total of 78.46%. On the biplot, the length of the arrow indicates the intensity of the metal fractions. Foraminifera genus are projected orthogonally on the arrows to understand the relationship between the metals and the foraminifera. The angle between the arrows suggests the correlation. Some figures have been plotted in the Ocean data view (Schlitzer, 2023).

2.7 Pollution load index

Pollution Load Index (PLI) is the aggregate of all contamination factors and the overall level of metal contamination in sediments. PLI >1 suggests metal contamination, whereas <1 indicates no metal pollution (Tomlinson et al., 1980; Choudhary et al., 2023; Salazar–Rojas et al., 2023).

$$PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \times CFn}$$

CF = contamination factor (Element 'X' in *sample*/ Element 'X' in the *crust*) and n is no. of metals (nine in the present study)

3 Results

3.1 Elemental composition (Corg, TN, TP, and BSi)

The concentration of organic elements (Corg, TN, TP, and BSi) is provided in Figure 2. Among the organic elements, Corg ranges from 0.71 ± 0.43% to 1.13 ± 0.69% (avg. 0.96 ± 0.40%) (Figure 2). Corg concentration varied from 1.09% to 2.83% (Winkelmann and Knies, 2005; Koziorowska et al., 2016; Kumar et al., 2016; Choudhary et al., 2018a; Limoges et al., 2018; Saalim et al., 2022a) in the west Spitsbergen fjords which are higher than the Corg content in the study area. Organic carbon content generally increased in almost all fjords from the inner to the outer fjord. TN varied from 0.12 ± 0.02% to 0.19 ± 0.10% (avg. 0.15 ± 0.06) and showed a trend like Corg (Figure 2). Total Nitrogen (TN) concentration ranged from 0.12% to 0.28% (Winkelmann and Knies, 2005; Koziorowska et al., 2016; Choudhary et al., 2018a), in the west Spitsbergen fjords which is higher than the TN content reported in the study area. TP is almost constant at 0.02 ± 0.00% for all the samples (Figure 2). BSi ranges from 3.26 ± 0.40% to 5.61 ± 1.36% (avg. 5.06 ± 1.33%) (Figure 2). These values agree with concentrations from other high-Arctic fjords, such as the Young Sound-Tyrolefjord, Krossfjord and Kongsfjord, where the average value is almost similar (Ribeiro et al., 2017; Choudhary et al., 2018b; 2020).

3.2 Major Oxides and trace elements in fjord sediments

The major oxide concentrations of the sediments from the northernmost Raudfjord, Magdalenefjord, and St. Jonsfjord have been analyzed. The bulk sediment composition indicates primarily a felsic source based on SiO_2 (66.41 wt.%) and Al_2O_3 (16.23 wt.%) abundances. The SiO_2 and Al_2O_3 abundances are lower than the upper continental crust (UCC) (Taylor and McLennan, 1995; McLennan, 2001). The rest of the major oxides in descending order of concentration are Fe_2O_3> MgO> K_2O>CaO> Na_2O>P_2O_5 and MnO with abundances of 5.39, 3.74, 2.98, 2.89, 1.44, 0.17 and 0.06 wt.% respectively. Among these oxides, most of them (SiO_2, TiO_2, MnO, K_2O) have concentrations like average UCC values except for Na_2O (1.76 wt.%), which is approximately half of the UCC value (3.25 wt.%). In contrast, MgO shows a higher abundance (3.63 wt.%) in the sediments of fjords, approximately double as compared to the UCC value (1.33 wt.%).

The Fe concentration of the fjord sediments ranges from 1.38 ± 0.52 to 2.39 ± 0.82%, with an average concentration of 2.14 ± 0.71% (Table 1; Figure 3A). The Mn concentration varies from 0.02 ± 0.01 to 0.04 ± 0.01% with an average concentration of 0.04 ± 0.01%. Cr concentration ranges from 25.98 ± 13.98 to 74.36 ± 13.07 ppm with an average concentration of 51.14 ± 21.96 ppm lower than the UCC value (Table 1). Co concentration ranges from 6.02 ± 3.28 ppm to 13.69 ± 4.99 ppm with an average concentration of 11.56 ± 4.65 ppm (Figure 3B). The Cu concentration varies from 2.53 ± 0.92 to 7.40 ± 2.74 with an average concentration of 5.12 ± 2.24 ppm, which is very low compared to the UCC values. The Zn concentration varied from 45.79 ± 13.30 ppm to 89.63 ± 31.30 ppm with an average concentration of 71.24 ± 23.92 ppm. Pb concentration ranges from 10.06 ± 2.08 to 24.66 ± 12.87 ppm with an average concentration of 15.29 ± 9.65 ppm. Their concentrations are

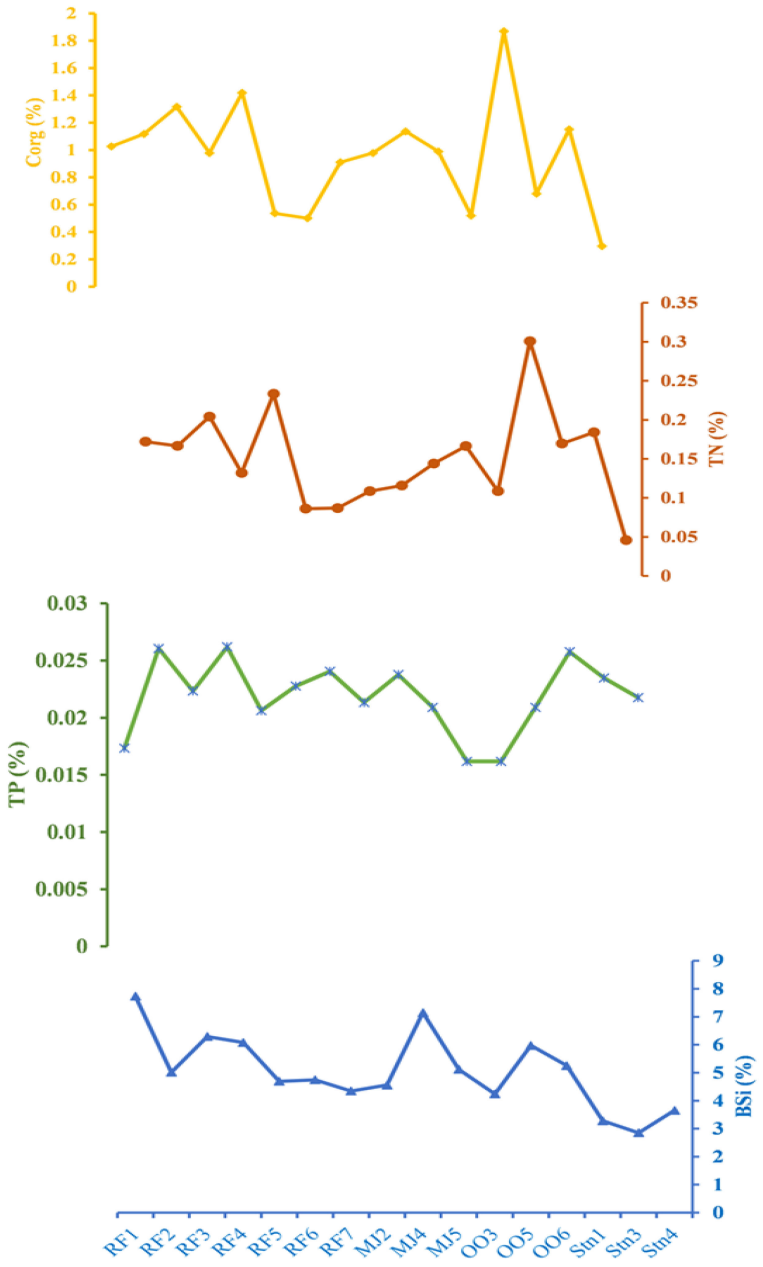

FIGURE 2
Spatial variations of organic components Corg (%), TN (%), TP (%), BSi (%) in the sediment of Raudfjord, Magdalenefjord and St. Jonsfjord and open ocean.

comparable to the UCC values (Table 1). Cd concentration ranges from 1.77 ± 0.85 to 4.11 ± 1.53 ppm with an average concentration of 3.30 ± 1.35 ppm, two to three times lower than UCC values. Sr and Ba concentration varies from 178.55 ± 67.07 and 316.20 ± 43.87 to 286.39 ± 209.03 and 389 ± 50.63 ppm with an average concentration of 245.51 ± 149.53 and 354.78 ± 83.81 ppm, respectively, which is compared lower than average crustal abundance (350 and 550 ppm respectively, Taylor and McLennan, 1995; McLennan, 2001).

3.3 Terrigenous (TI%) and non-terrigenous (Excess) influence in sediments

To determine the terrigenous matter percentage available in the sediments, titanium (Ti) concentration can be used (Schroeder et al., 1997; Sensarma et al., 2017). Ti is mostly considered detrital with a composition similar to Post-Archean Australian Shale (PAAS; Taylor and McLennan, 1985) and is the most conservative element under changing physicochemical conditions.

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TABLE 1 Elemental concentrations, pollution load Index and terrigenous influence (%) in Raudfjord, Magdalenefjord and St. Jonsfjord and the open ocean.

Samples	Al	Ti	Fe	Mn	Cr	Co	Cu	Zn	Ni	Pb	Cd	Sr	Ba	Sr/Ba	$\frac{Al2O3}{TiO2}$	PLI	TI (%)
	(%)				(ppm)												
RF1	1.64	0.10	1.20	0.02	26.72	6.27	4.31	44.15	8.73	8.91	1.72	393.33	211.29	1.86	38.77	0.61	16.52
RF2	1.67	0.11	1.33	0.02	30.05	7.24	3.03	43.67	9.57	7.75	1.89	522.44	237.19	2.20	36.39	0.64	18.99
RF3	1.74	0.26	2.81	0.04	68.69	16.06	4.68	77.71	19.03	11.15	4.11	151.96	411.38	0.37	27.31	1.21	43.60
RF4	1.70	0.20	2.30	0.04	53.97	13.34	4.86	72.20	15.57	9.96	3.44	584.58	315.52	1.85	32.33	1.06	33.47
RF5	1.81	0.30	3.12	0.05	74.46	17.57	6.66	95.44	20.53	13.43	4.75	149.49	491.98	0.30	24.50	1.40	50.17
RF6	1.71	0.29	3.08	0.04	73.53	17.93	5.27	89.43	20.10	11.90	4.45	80.47	439.02	0.18	26.86	1.30	47.58
RF7	1.75	0.29	2.92	0.05	65.59	17.40	8.20	79.16	17.26	16.29	4.79	122.43	472.64	0.26	23.35	1.36	48.48
Avg.	**1.72 ± 0.06**	**0.22 ± 0.09**	**2.39 ± 0.82**	**0.04 ± 0.01**	**56.15 ± 20.15**	**13.69 ± 4.99**	**5.29 ± 1.68**	**71.68 ± 20.47**	**15.83 ± 4.87**	**11.34 ± 2.89**	**3.59 ± 1.30**	**286.39 ± 209.03**	**368.43 ± 113.77**	**1.15 ± 0.88**	**29.93 ± 5.98**	**1.08 ± 0.33**	**36.97 ± 14.24**
MJ2	1.79	0.41	1.62	0.03	35.12	8.14	3.27	54.09	9.02	10.02	2.35	210.90	347.61	0.61	41.60	0.84	69.09
MJ4	1.67	0.22	2.55	0.05	48.33	12.89	5.08	101.72	12.86	29.77	4.04	150.03	374.90	0.40	31.19	1.20	36.19
MJ5	1.61	0.22	2.27	0.05	40.79	12.37	6.68	113.08	11.06	34.19	3.59	178.68	445.70	0.40	37.72	1.19	36.00
Avg.	**1.69 ± 0.09**	**0.22 ± 0.09**	**2.15 ± 0.48**	**0.04 ± 0.01**	**41.41 ± 6.62**	**11.13 ± 2.61**	**5.01 ± 1.71**	**89.63 ± 31.30**	**10.98 ± 1.92**	**24.66 ± 12.87**	**3.32 ± 0.87**	**179.87 ± 30.45**	**389.40 ± 50.63**	**0.47 ± 0.12**	**36.84 ± 5.26**	**1.08 ± 0.20**	**47.09 ± 19.05**
OO3	1.62	0.07	0.89	0.02	21.01	4.10	2.41	34.88	5.98	8.17	1.35	397.02	262.42	1.51	22.06	0.46	32.94
OO5	1.56	0.08	1.32	0.02	15.16	4.15	1.67	41.89	3.90	9.74	1.20	242.09	339.32	0.71	34.73	0.46	35.06
OO6	1.70	0.17	1.93	0.03	41.77	9.80	3.50	60.61	11.17	12.29	2.75	209.08	378.96	0.55	35.46	0.88	23.56
Avg.	**1.63 ± 0.07**	**0.11 ± 0.06**	**1.38 ± 0.52**	**0.02 ± 0.01**	**25.98 ± 13.98**	**6.02 ± 3.28**	**2.53 ± 0.92**	**45.79 ± 13.30**	**7.01 ± 3.75**	**10.06 ± 2.08**	**1.77 ± 0.85**	**282.73 ± 100.35**	**326.90 ± 59.25**	**0.57 ± 0.20**	**30.75 ± 7.53**	**0.62 ± 0.27**	**30.52 ± 6.12**
STN1	1.64	0.20	2.46	0.04	83.39	13.50	7.76	90.57	29.09	37.88	5.80	109.21	322.18	0.34	59.96	1.44	11.13
STN3	1.60	0.21	2.52	0.05	80.31	14.44	9.94	85.13	24.76	14.20	3.71	243.09	356.77	0.68	58.08	1.33	13.33
STN4	1.57	0.14	2.00	0.04	59.37	9.76	4.50	56.18	16.71	8.93	2.81	183.34	269.65	0.68	37.61	0.94	28.68
Avg.	**1.61 ± 0.03**	**0.18 ± 0.04**	**2.32 ± 0.28**	**0.04 ± 0.01**	**74.36 ± 13.07**	**12.57 ± 2.48**	**7.40 ± 2.74**	**77.29 ± 18.49**	**23.52 ± 6.28**	**20.34 ± 15.42**	**4.11 ± 1.53**	**178.55 ± 67.07**	**316.20 ± 43.87**	**0.93 ± 0.51**	**51.88 ± 12.40**	**0.60 ± 0.24**	**17.71 ± 9.56**
Avg. of all sediments	**1.67 ± 0.08**	**0.20 ± 0.09**	**2.14 ± 0.71**	**0.04 ± 0.01**	**51.14 ± 21.96**	**11.56 ± 4.65**	**5.12 ± 2.24**	**71.24 ± 23.92**	**14.71 ± 6.92**	**15.29 ± 9.65**	**3.30 ± 1.35**	**245.51 ± 149.53**	**354.78 ± 83.81**	**0.87 ± 0.66**	**35.50 ± 10.91**	**1.02 ± 0.34**	**34.05 ± 15.51**
UCC	8.04	0.41	3.50	0.06	85	17	25	71	44	17	0.098	350	550				–

The average upper continental crustal composition (UCC) of these elements was obtained from Taylor and McLennan (1995).
TI%, Terrigenous influence.
PLI, Pollution load Index.
*L abundance, Living Abundance; D abundance, Dead abundance.
Uncertainties estimated for the average data presented in Table 1 are in 1σ.
Average values are marked in Bold.

To determine the terrigenous influence percentage (TI%) of sediments, the following equation has been used:

$$\text{Terrigenous\%} = \frac{(\text{Ti total} - \text{Ti PAAS}) * 100}{\text{Ti total}}$$ (Schroeder et al., 1997)

where the concentration of Ti in PAAS is 0.6 (wt.%).

Thus, a higher percentage of the terrigenous influx in a given area is attributed to more terrigenous influence. The highest values of terrigenous percentage were reported from the inner fjords, and the lowest values were reported from the outer fjords (Table 1; Figure 4) suggesting higher terrigenous supply in the inner fjord region or it is diluted in the outer fjord region.

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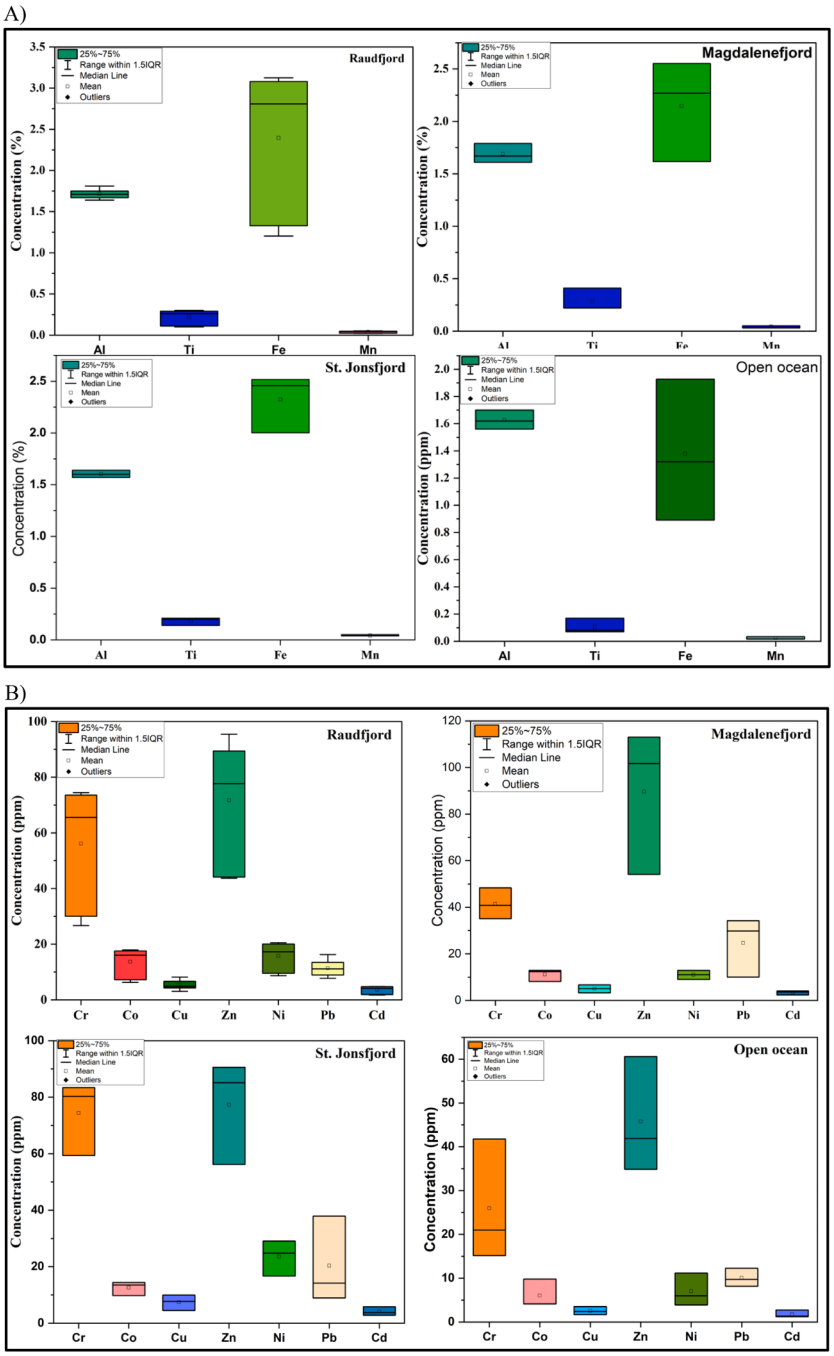

FIGURE 3
(A) Major such as Al, Ti, Fe and Mn and **(B)** Trace elements such as Cr, Co, Cu ,Ni, Zn, Pb and Cd in the sediment of Raudfjord, Magdalenefjord and St. Jonsfjord and open ocean.

The amount of an element not supported by the structurally bound detrital terrigenous fraction or derived from sources other than terrestrial influx is called "excess," i.e., non-terrigenous fraction, and evaluated using the equation proposed by Murray and Leinen (1996).

$$Elexcess = Mtotal - [Tisample\star(\frac{M}{(Ti}))shale]$$

———————— Schroeder et al. (1997)

In the present study, Cu and Ni showed negative excess values in all the fjords at all the stations suggesting their detrital source. Fe,

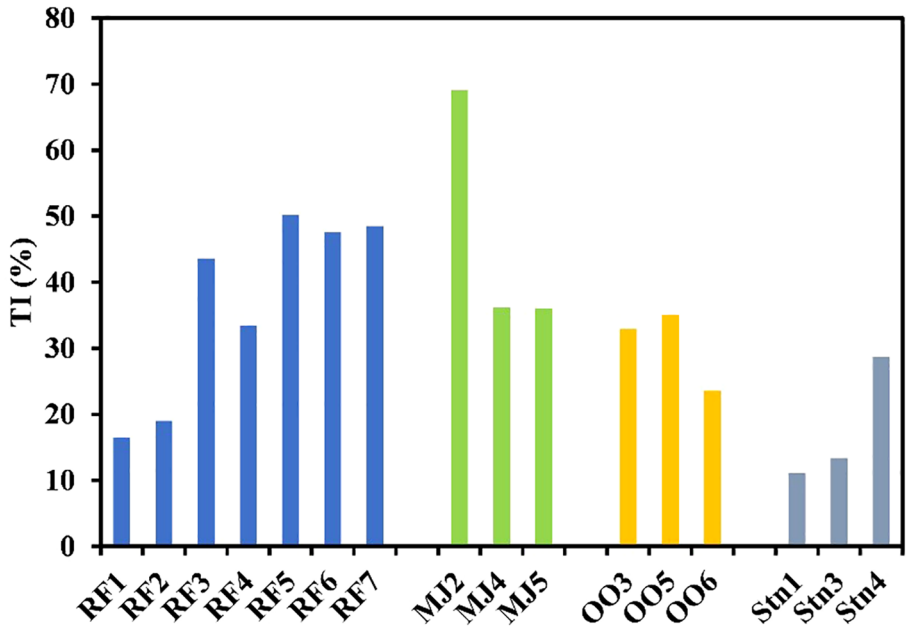

FIGURE 4
Terrigenous influence (TI%) in sediment in Raudfjord, Magdalenefjord and St. Jonsfjord and open ocean.

Mn, and Co showed very low excess values indicating a minor contribution from another source besides terrigenous (Figure 5).

3.4 Speciation of metals

The fractionation of metals Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb, and Cd varied spatially in different fractions (F1 to F4). The overall concentration of the analyzed elements like Fe, Ni, Cr, and Co was high in the residual fraction (F4), Mn, Cd, and Zn were high in the organic-sulfide fraction (F3), while Cu and Pb were found to be high in Fe-Mn hydroxide fraction (F2).

In Raudfjord, metals like Fe, Ni, Pb, and Co showed the highest concentration in the residual phase (F4). However, in other fractions, Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb, and Cd had an average concentration of 1.84%, 20.75%, 4.27%, 5.99%, 14.49%,7.11%, 7.79%, 5.06%, and 2.89% respectively in F1 fraction. In the F2 fraction, Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb, and Cd had an average concentration of 21.14%, 20.92%, 17.54%, 15.58%, 37.10%, 24.35%, 9.57, 47.70 and 21.26% respectively. F3 fraction has an average concentration of 37.51%, 29.40%, 39.41%, 19.93%, 22.09%, 42.87%, 31.43%, 8.17%, and 50.99% of Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb and Cd respectively (Figure 6)

In Magdalenefjord, Fe, Cr, and Co were higher in the residual phase (F4). The average concentration of Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb, and Cd in the F1 fraction was 1.16%, 13.71%, 10.32%, 5.19%, 2.72%, 9.25%, 14.02%, 5.56%, 3.23% respectively. In the F2 fraction, Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb, and Cd had an average concentration of 23.54%,19.45%, 28.55%, 14.54%, 53.98%, 22.31%, 18.49%, 48.98%, 22.63% respectively. The F3 fraction had Fe (37.09%), Mn (54.93%), Cr (25.25%), Co (24.96%), Cu (13.15%), Zn (39.23%), Ni (43.81%), Pb (15.23) and Cd (54.19%) (Figure 6)

In St. Jonsfjord, Fe, Ni, Cr and Co were high in the residual phase (F4). The average concentration of Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb, and Cd in the F1 fraction was 0.85%, 13.59%, 7.67%, 7.18%, 8.32%, 9.25%, 6.08%, 2.93%, 1.80%. In the F2 fraction Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb, and Cd have an average concentration of 16.66%, 18.73%, 17.15%, 16.7546.43%, 22.47%, 12.52%, 67.16%, 16.15%. F3 fraction had Fe (40.71%), Mn (35.48%), Cr (32.97%), Co (20.28%), Cu (28.82%), Zn (42.66%), Ni (39.46%), Pb (15.91%) and Cd (59.57%) (Figure 6).

Thus, the overall order of availability of the analyzed element in different fractions is:

Fe- F4>F3>F2>F1
Mn-F3>F4>F2>F1
Cr- F4>F3>F2>F1
Co-F4>F3>F2>F1
Cu-F2>F4>F3>F1
Zn-F3>F4>F2>F1
Ni-F4>F3>F2>F1
Pb-F2>F4>F3>F1
Cd-F3>F4>F2>F1

3.5 Foraminiferal abundance and density

Total foraminiferal (dead and living) number per gram dry sediment i.e. Foraminiferal density decreases from the outer to inner regions of Raudfjord, Magdalenefjord, and St. Johnsfjord (Figure 7) The distribution of *N.labradorica* showed high abundance in the outer fjords and the open ocean stations with a decrease towards the inner fjord. *Elphidium* was more abundant in the inner fjords and decreased towards the outer fjord. The abundance of *Cassidulina reniforme* decreased from the outer

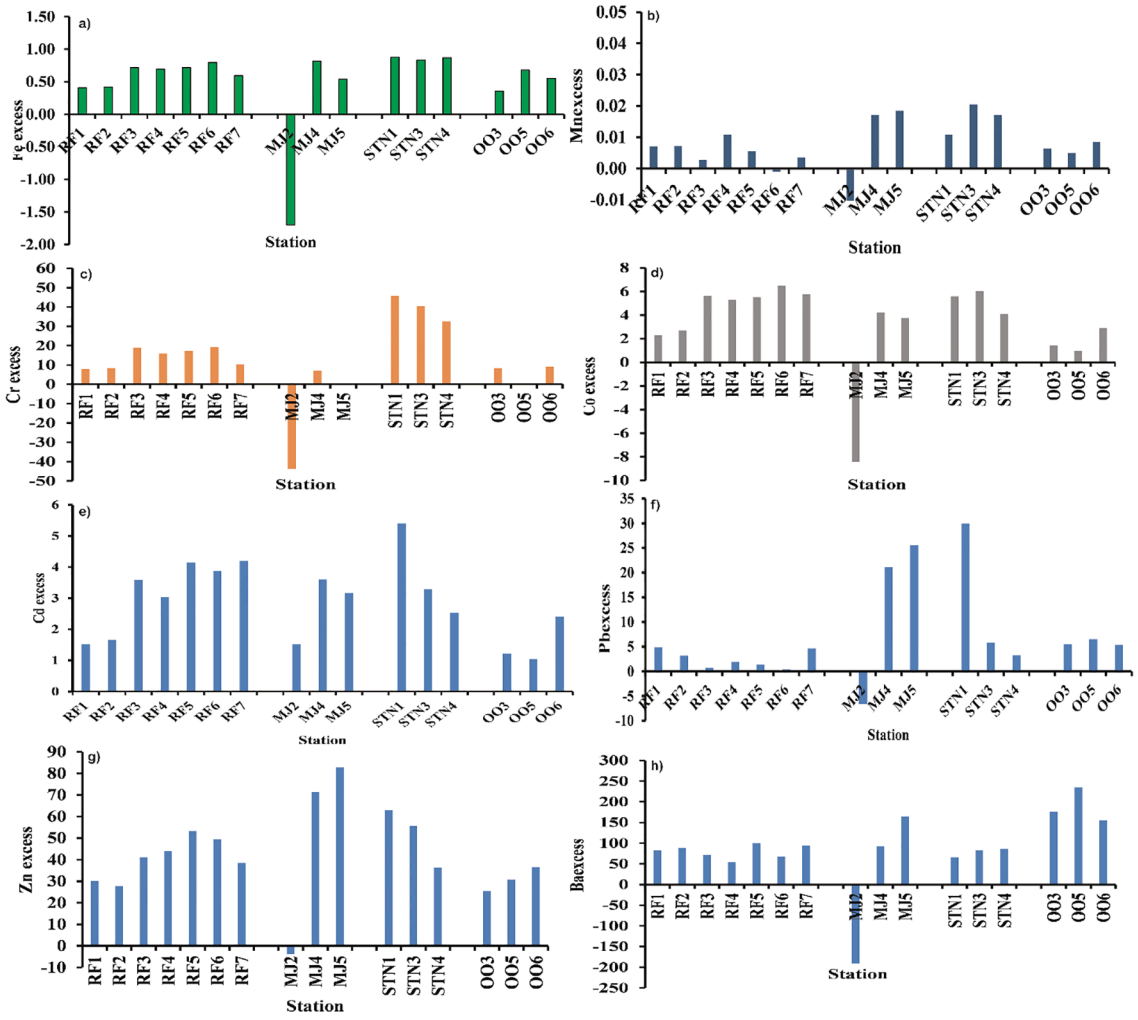

FIGURE 5
(A) Fe excess, **(B)** Mn excess, **(C)** Cr excess, **(D)** Co excess, **(E)** Cd excess **(F)** Pb excess **(G)** Zn excess and **(H)** Ba excess in sediments of Raudfjord, Magdalenefjord, St. Jonsfjord and open ocean.

fjords to the inner fjord. *Cibicides* showed higher abundance in the outer fjords and low abundance in the inner fjords.

4 Discussion

4.1 Distribution and source of trace elements in fjords

Increased concentrations of terrigenous elements such as Al, Ti, Si, and K suggest high concentrations of siliciclastic materials in marine sediment having fluvial or aeolian origin (Chen et al., 2013). Major elements (Al, Ti, Fe, Mn, Mg, Ca, Na, and K) decreased from the inner fjord to the outer fjord in Raudfjord and St. Jonsfjord, suggesting that they have been derived from rock weathering. The significant positive correlation between the major elements is attributed to their common lithogenic origin and similar modes of transportation (Ganugapenta et al., 2018). The Al_2O_3/TiO_2 ratio has been used to assess the source rock type of the sediments. Al_2O_3/TiO_2 ratio <10 indicates mafic source rocks, ratios between 10 and 20 suggest intermediate, and >20 are indicators of felsic source rocks (Hayashi et al., 1997). The Al_2O_3/TiO_2 ratio for all the samples is greater than 20 (22.06–59.96, avg. 35.50), suggesting that felsic rocks are the primary source rock types. The Al_2O_3/TiO_2 ratio of samples from different fjords does not vary much, except for the samples from the open ocean, which have the highest Al_2O_3/TiO_2 ratio. TiO_2 showed a strong positive correlation with Fe_2O_3 (r=0.99), MnO (r=0.87), and MgO (r=0.79), suggesting that ilmenite is one of the minerals forming the source rock. Al and Ti are conservative elements and remain constant or become enriched in the weathered products compared to the parent sediments (Wei et al., 2006; Choudhary et al., 2018b). Al concentration ranged from 1.56% to 1.81%, indicating its uniform terrestrial source suggesting limited Al accumulation changes along the fjords. The average elemental concentrations were lower than the PAAS values and were in the range of other geochemical studies in the fjords of West Spitsbergen (Lu et al., 2013; Grotti et al., 2013; 2017; Singh et al., 2018; Choudhary et al., 2020). This implied that

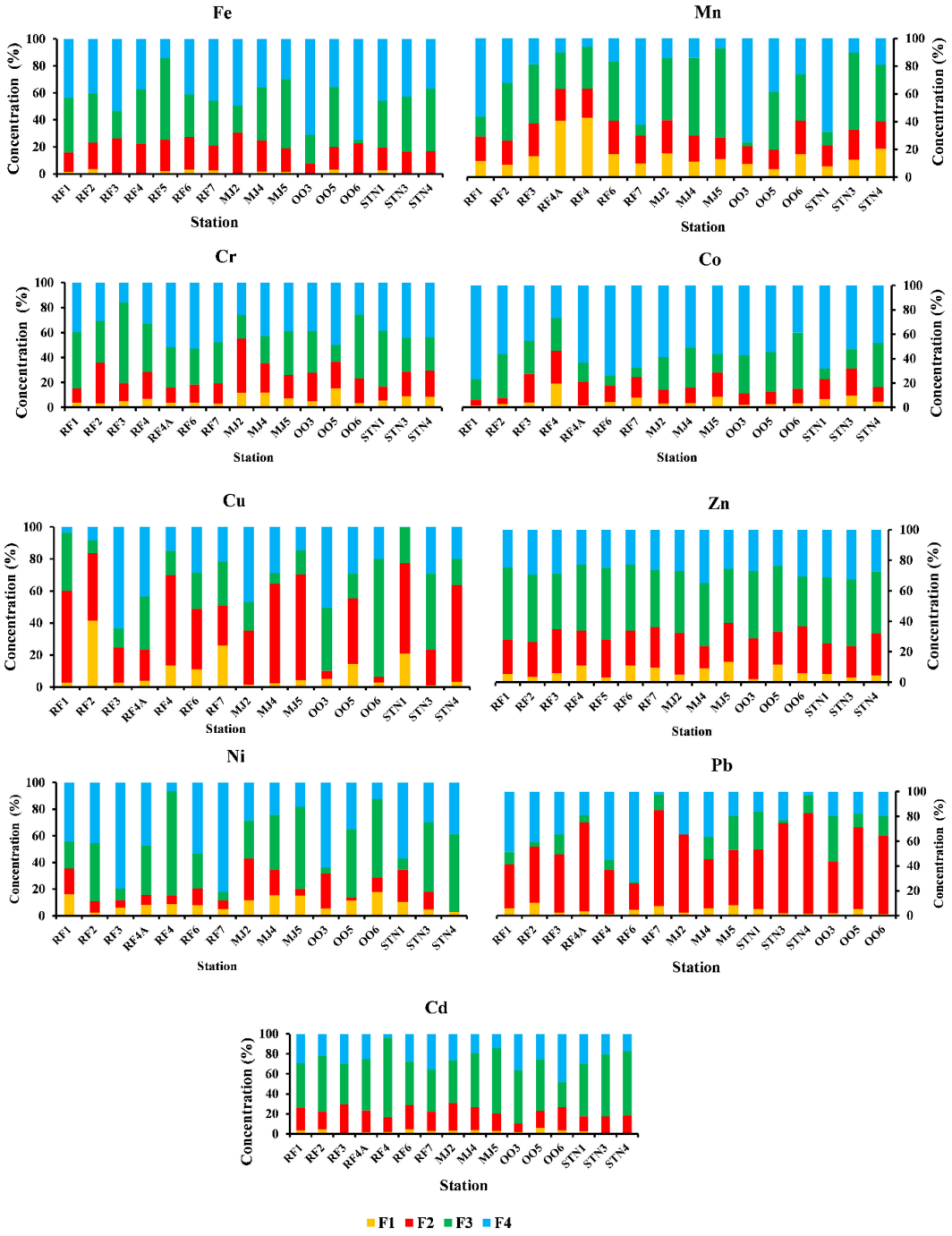

FIGURE 6
Fractionation of metals like Fe, Mn, Cr, Co, Cu, Zn, Ni, Pb, and Cd in different fractions (F1-Exchangeable and Carbonate, F2- Reducible, F3-Oxidisable and F4- Residual).

most of the elements have been derived from the weathering of catchment rocks. Potassium (K) is generally derived from K-feldspar or clay mineral illite and is least weathered by chemical weathering (Govin et al., 2012). In contrast, Na and Ca get easily removed from the parent sediment and depleted in the weathered product (residue) due to their higher mobility. Na content is low in the inner fjord and increases towards the outer fjords due to the seawater influx.

Trace elements such as Fe, Mn, Cr, Co, Cu, Zn, Cd, and Ba showed high concentrations in the inner fjords as Al and Ti, respectively (Table 1), suggesting their similar terrigenous source derived from the bedrock. Pb showed a significant positive correlation ($r = 0.61$, $p = <0.05$, $n = 16$) with Cd, indicating their common source and post-depositional processes. Sr does not significantly correlate with other elements except Ca, indicative of calcareous rocks in the catchment. Sr/Ba ratio is often used as a

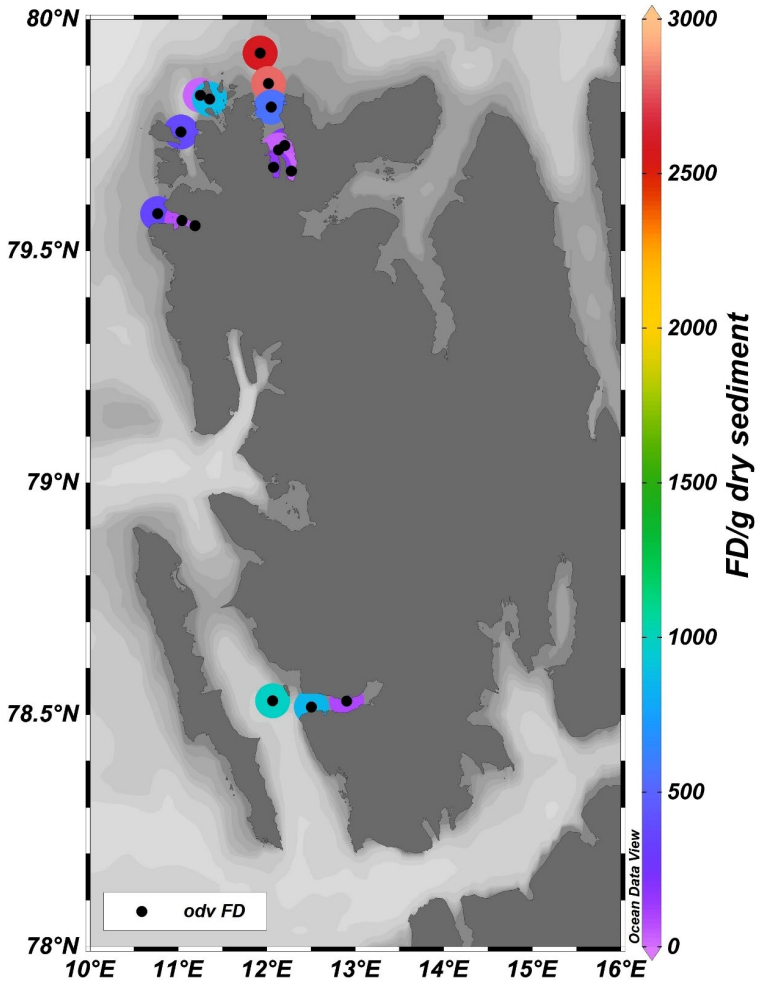

FIGURE 7
Spatial variations of Foraminiferal density/g dry sediment in Raudfjord, Magdalenefjord, St. Jonsfjord, and open ocean.

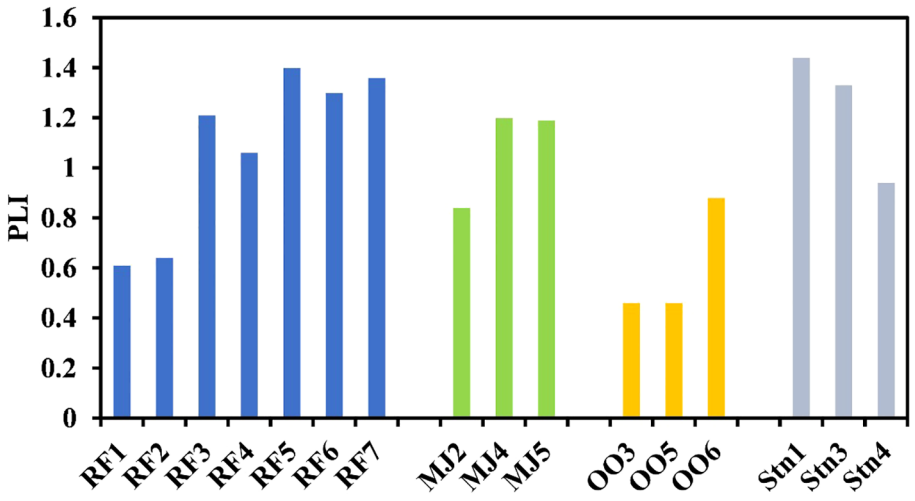

FIGURE 8
Pollution load index (PLI) in the sediment of Raudfjord, Magdalenefjord, St. Jonsfjord open ocean.

geochemical indicator distinguishing between the sedimentary environments i.e. terrestrial and marine environments (Wang et al., 2021). Gradual increase in Sr/Ba ratio from the inner fjord to the outer fjord indicates the influence of seawater influx towards the outer fjord (Table 1). Sediment components like grain size and organic matter do not play any role in the distribution of metals in these fjords. Metals are regulated mainly by Fe-Mn oxyhydroxides and aluminosilicates. Other sources of these metals include atmospheric deposition, long-range transportation by currents, and discharge by glacial meltwater, sea ice, and terrestrial runoff (Rudnicka-Kępa and Zaborska, 2021).

4.2 Terrigenous (TI%) and non-terrigenous (excess) influence in the sediments

TI% (Terrigenous influence) and excess values are calculated to evaluate the terrigenous and non-terrigenous contributions of the elements. TI% decreases from the inner to the outer fjord in all three fjords as the sea water influx increases (Table 1; Figure 4).

Fe_{excess}, Mn_{excess}, Co_{excess}, and Cd_{excess} values obtained (Figure 5) in most of the surface samples exhibited positive values, and the excess percentage was low, indicating less input of Fe and Mn from other sources in addition to terrigenous. Zn excess showed positive values with a high excess percentage varied from 40 to 80%, suggesting high input of Zn other than terrigenous. Cu_{excess} and Ni_{excess} showed negative values indicating their detrital nature. Cr_{excess} and Pb_{excess} showed higher excess values attributed to their additional source other than the catchment rocks. Ba showed high excess values for all the samples except MJ2, wherein almost all the metals showed negative excess values other than Cd. Thus, to assess the metal accumulation and metal-related ecological risks in the fjord, the bulk concentration of elements has been compared with Arctic sediment quality guidelines (ASQGs).

4.3 Assessment of sediment quality

The bulk concentration of elements was compared with Sediment Quality Guidelines available for the Arctic region (ASQGs) proposed by Lu and Kang (2018) to assess the contamination in marine and estuarine sediments (Hubner et al., 2009) and understand the impacts on the sediment-associated biota. It has been observed that Cu, Ni, and Zn contents are below ASQG-low in all three fjords suggesting that these elements can rarely cause adverse biological effects in the study area. Cr, Cd, and Pb were higher than ASQG-low but were lower than ASQG-high, indicating adverse biological effects in the study area. High metal accumulation and retention rates in the freshwater environment cause more adverse effects on the biota (Barik et al., 2022).

Further, the element contamination indices, such as the Pollution Load Index (PLI), have been used to assess the sediment quality of the fjords. This index helps evaluate the changes in sediment quality at different environmental conditions as they use the background elemental concentrations of the particular region (Sarkar, 2018). The pollution load index showed lower values (<1) at station RF1 and RF2 towards the mouth in Raudfjord. In Magdalenefjord, PLI was <1 at station MJ2, at station STN4 in St. Jonsfjord, and in the open ocean at all the stations indicating no pollution at these stations (Table 1). PLI was found above 1 in the inner fjord, indicating high elemental contamination compared to the outer fjord. The contamination levels are frequently assessed using bulk concentrations of metals. However, sometimes it may lead to an overestimation of the ecological risks associated. Thus, to avoid the overestimation of risk, the metal speciation has been carried out using the Bureau of Certified Reference (BCR) extraction method into four different fractions: 1. Exchangeable + Carbonate (F1-labile phases) 2. Fe-Mn (F2-Reducible) 3. Organic sulfide (F3-oxidisable), and 4. Residual phase. The F1, F2, and F3 fractions are known as bioavailable phases.

4.4 Risk assessment of metals in different fractions

Martins et al. (2013) suggested that the metals in the F1 fraction are loosely bound and are susceptible to release with changes in pH and redox potential. Exchangeable and carbonate fractions are highly mobile and readily available for biota uptake and enter the food chain, risking the lives of the organisms. Mn is available in significant concentration in F1 fraction along with Cu and Ni in considerable concentration leading to the toxicity in sediment-associated biota in these fjords (Figure 6).

Fe-Mn oxides and hydroxides (F2 fraction) are considered carriers of metals due to their large surface area-to-volume ratio and significantly impact the mobility of elements (Turner, 2000). Cu and Pb have significant concentrations in the Fe-Mn oxide phase (F2 fraction). Pb can form stable bonds with Fe–Mn hydroxides. These hydrous oxides act as scavengers of Pb in the marine environment (Ramos et al., 1994). A considerable amount of Fe, Mn, and Zn is also available in this phase (Figure 6). Metals in this fraction are bound to Fe-Mn oxides and hydroxides. Under the reduced conditions, they can be released in the aqueous environment (Okbah et al., 2020).

Significant Mn, Zn, and Cd concentrations are available in the organic/sulfide phase (F3) (Figure 6). An appreciable quantity of Fe is available in the organic/sulfide phase. Metals from F3 fractions can only be released by oxidizing agents causing bioaccumulation (Okbah et al., 2020). Due to their less mobile nature, organic matter and sulfides are associated with humic substances having high molecular weight. Generally, elements associated with the organic/sulfide phase are the least bioavailable due to the strong bonding between metal and organic matter.

Metals like Fe, Cr, Ni, and Co are available in the maximum concentration in the residual phase (F4 fraction, Figure 6), suggesting that these metals have been released by the weathering of rocks in the catchment region of a fjord. The metals in this fraction are immobile as they are bound to detrital minerals and a matrix of silicates, which are difficult for ingestion and accumulation in the sediment-associated biota. Almost 40 to 50% of metal concentrations are available in the F4 fraction, except for Mn (28.81%), Cu (26.14%), and Cd (25.22%), bound to primary and

secondary minerals, which are immobile. Therefore, it is not available for the uptake of the organisms. The remaining 50 to 60% is distributed among the bioavailable phases and is potentially available for biota uptake. During the spring and early summer, oxygen deficiency in the fjords makes these fractions leachable into the water, posing a significant risk to the sediment-associated biota.

The metal bonding strength with the sediment fractions determines the bioavailability and risk associated with metals in aquatic systems (Lu and Kang, 2018). The metal association in the labile fraction (exchangeable and carbonate) suggests that these can be easily released into the water column posing a risk to the aquatic organisms due to slight changes in the pH and redox potential (Saleem et al., 2018). A risk assessment code (RAC) was used to evaluate the risk posed by releasing metals from the F1 fraction into the aquatic environment (Perin et al., 1985). <1% of any metal poses negligible risk to the environment, while >30% poses a high risk to the sediment-associated biota. It has been observed that Fe is under the safe range with RAC<1%. However, significant concentrations of Fe in the F2 fraction can adversely affect the biological community in a reducing environment. Ni, Cu, Pb, Cd, Cr, Zn, and Co pose a low risk to the sediment-associated biota. However, Cu and Ni have significant concentrations in the F1 fraction compared to other metals. Higher concentrations of Mn in labile phases pose a medium risk to the sediment-associated biota. Similar concentrations of Mn were found in the sediments of the Krossfjord-Kongsfjord system (Choudhary et al., 2020).

4.5 Effect of metals on benthic foraminifera in sediment

The density and abundance of foraminiferal assemblages can be affected by the trace metals (Bergamin et al., 2005; Debenay and Fernandez, 2009; Vilela et al., 2011). The variation in Foraminiferal density (FD) is an important tool for assessing pollution (Nigam et al., 2006). The inner fjord is drained by glacial meltwater and surface runoff, which does not support the benthic foraminifera population. Thus, the foraminiferal density (FD) showed an increasing trend towards the outer fjord in all three fjords (Figure 7). Inner fjords have high metal concentrations and, thus, high PLI (Figure 8), posing

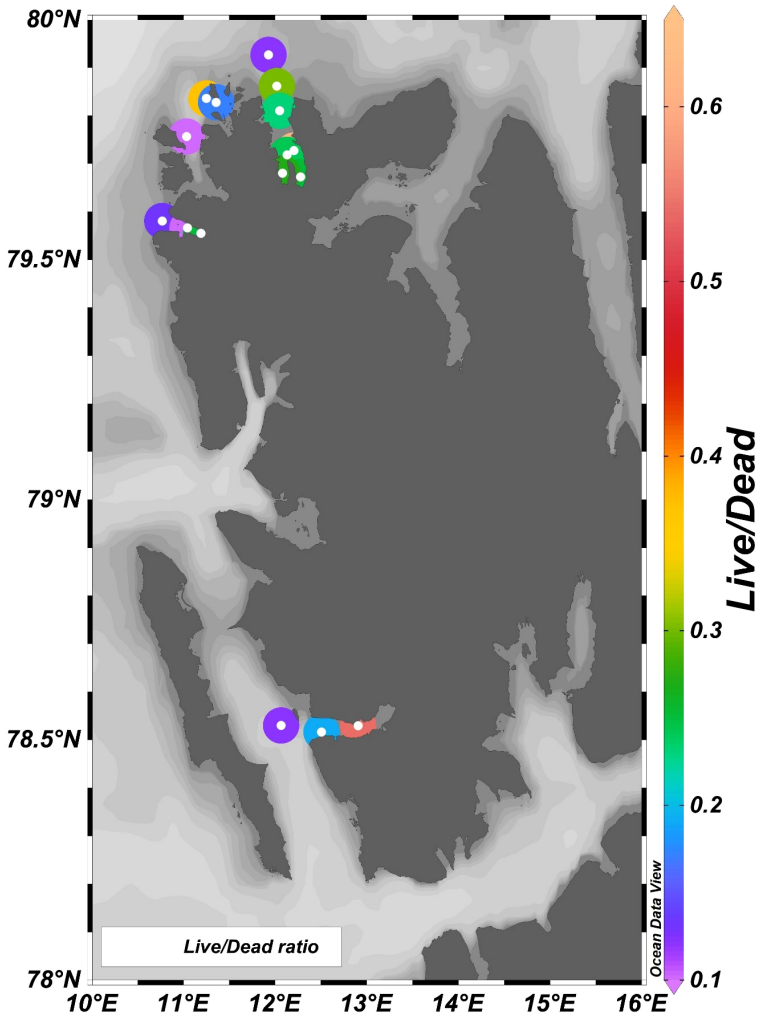

FIGURE 9
Spatial variations of Live/dead ratio of benthic foraminifera in sediments of Raudfjord, Magdalenefjord, St. Jonsfjord, and open ocean.

an ecological threat to the sediment-associated biota. The inner fjord region is dominated by the genus *Elphidium*. *Elphidium* tolerates most contaminants and effluents in polluted coastal environments (Pregnolato et al., 2018; Buckley et al., 1974; Schafer et al., 1991). Due to their high mobility, *Elphidium* flourishes in contaminated areas (Murray, 1991; Schafer and Young, 1977). Agglutinated foraminifera were also highly abundant in the inner fjord. The influence of tidewater glaciers and colder environments caused the dissolution of $CaCO_3$ at inner fjords. Also, the higher sediment flux from the glacier mouth dilutes the calcitic microfossils in the inner fjords leading to increased foraminiferal density towards the outer fjord. The live/dead test ratio in these fjords is low (Figure 9) due to the high sedimentation rate increasing the turbidity affecting the living benthic foraminifera, resulting in a reduced benthic foraminifera population (Saraswat et al., 2018). Principal component analysis (Figure 10) showed that Ni and Cu in the bioavailable fraction are associated with *Elphidium* and agglutinated foraminifera. Cu contamination has a deleterious effect on foraminifera; particularly, high concentrations of Cu (>120 µg/l) lead to a lowering of foraminiferal density (Frontalini and Coccioni, 2011). Bioavailable fractions (F1 and F3) of Cd and Pb correlated well with *Cibicides*. Cadmium is detrimental to benthic foraminifera. Gradual increase in Cd concentration mainly affects normal growth and causes morphological abnormalities (Linshy et al., 2013). Pb is toxic, but due to its large ionic size, it is least absorbed by the foraminifera (Samir and El-Din, 2001; Barik et al., 2022). Metals like Mn, Fe, Cd, Ni, and Zn in F2 and F3 fractions are associated with *N. Labradorica*. Fe in F2 fraction and seasonal hypoxia causes a low benthic foraminiferal population (Gustafsson and Nordberg, 2000) and increases pyritization in the tests of foraminiferal species (Yanko et al., 1999). Mn can be easily incorporated into the calcite in reducing environments (Barras et al., 2018) but causes low toxicity. Mn, Co, Zn, Cr, Co, Cd, and Cr in bioavailable fractions are associated with *Cassidulina*. High concentrations of metals like Cu (73.86%), Ni (58.32%), Pb (71%), Cd (63.18%), and Cr (61.76%) are available in bioavailable fraction, suggesting their availability for uptake and accumulation in benthic fauna. Cr, Zn, and Cu are more readily absorbed in the shells of foraminifera (Banerji, 1991), affecting the growth and reproduction of benthic foraminifera in marginal zones (Coccioni et al., 2009). Therefore, it can be deciphered that higher concentration of metals and their accumulation in different bioavailable phases have affected the foraminiferal density in the Arctic fjords.

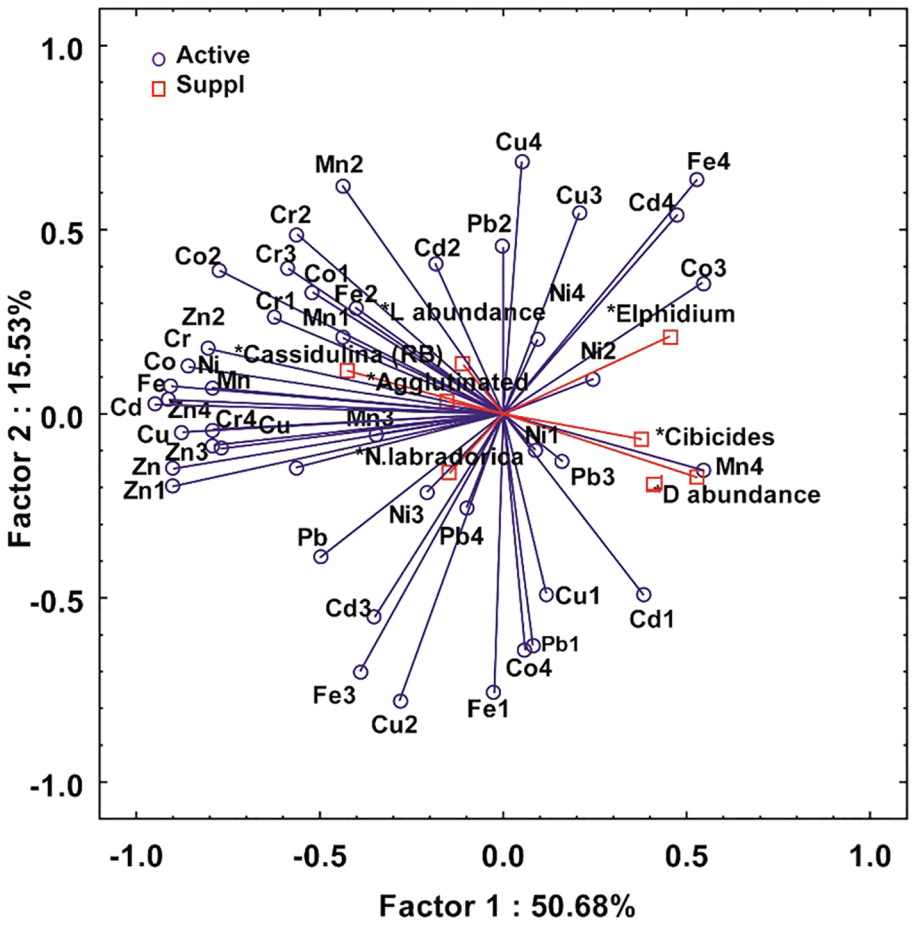

FIGURE 10
Principal component analysis (PCA) of bulk metals, metal concentration in different fractions (F1, F2, F3, and F4) along with foraminiferal genera and their living and dead abundance in sediments of Raudfjord, Magdalenefjord, St. Jonsfjord, and open ocean.

5 Conclusions

The study conducted on the surface sediments of Raudfjord, Magdalenefjord, and St. Jonsfjord showed considerable variations in metal accumulation within the fjords and are regulated mainly by Fe-Mn oxyhydroxides and aluminosilicates. The Al_2O_3/TiO_2 ratio shows that felsic rocks are the primary source rock of the fjord sediments. Terrigenous influence (TI%) decreases from the inner to the outer fjord. Higher excess values for Cr and Pb are attributed to their additional source other than the catchment rocks. Further, the Speciation showed that Mn concentration poses a medium ecological risk to the sediment-associated biota. Although the overall concentration of metals in the bioavailable fractions (F1, F2, and F3) is low, they have affected the abundance of foraminifera. Besides the bioavailable fraction of metals, glacial meltwater, and terrigenous influx have affected the foraminiferal density in the fjords. Detailed studies on the bioavailability of contaminants are needed to comprehend their effects on fjord ecosystems, particularly on sediment-associated biota. Additionally, continuous and comprehensive monitoring is required to track the sources and levels of metal contamination over time, facilitating the implementation of targeted mitigation strategies.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author/s.

Author contributions

SC: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. SS: Writing – review & editing, Resources, Methodology, Data curation, Conceptualization. RM: Writing – review & editing, Supervision, Resources, Project administration, Investigation. MT: Writing – review & editing, Resources, Methodology.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2024.1429998/full#supplementary-material

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