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Benthic community status and mobilization of Ni, Cu and Co at abandoned sea deposits for mine tailings in SW Norway

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ABSTRACT

During 1960–94 tailings from an ilmenite mine in southwest Norway were placed in sea deposits in a sheltered fjord and a more exposed coastal basin. In 2015 both deposit sites were sampled to assess the state of metal contamination and macrobenthic communities 20–30 years after deposition was ended. The results showed that nickel and copper still exceeded environmental quality standards in sediment and pore water from the 0–1 cm layer, and fluxes of nickel, copper and cobalt to the overlying water was high compared to adjacent reference stations. Fauna communities were classified as *good*, but moderate disturbance was recorded along an environmental gradient defined by depth and tailings-induced parameters such as particle size and copper. The results were interpreted in terms of current discharges, biological sediment reworking and near-surface leaching of metal sulphides. No evidence was found for recycling of metals from tailings buried below the bioturbated surface layer.

1. Introduction

Mine tailings are wastes left over after the mineral product have been extracted from the crushed and grinded ore rock. In 2012, the global mineral production was 16 billion tons per year (Reichl et al., 2014), and the demand of metals and other mineral products tend to increase exponentially with time (Hudson-Edwards and Dold, 2015). The tailings consist of inert rock particles with trace amounts of potentially harmful substances such as bioavailable fractions of trace metals and remnants of production chemicals (Koski, 2012). The particles themselves may also have detrimental effects on living organisms due to hypersedimentation, and small size and sharp edges may disturb vital habitat and physiological functions (Ramirez-Llodra et al., 2015).

Under-water disposal of tailings in lakes and in the sea has been considered favorable due to the geochemical stability of sulphide minerals (Arnesen et al., 1997; Dold, 2014b) and eliminated risk of dam failure and catastrophic downstream consequences (Foster et al., 2000; ICOLD, 2001). In Norway and other coastal countries, the scarcity of suitable land areas and availability of sea areas near the locations of the mineral ores, may also favor sea deposition (Kvassnes and Iversen, 2013; Ramirez-Llodra et al., 2015; Berg et al., 2016).

Leaching of metals such as Cu, Ni, Co, As, Cd, Zn, Pb and Hg from sulphide minerals is a major issue in disposal of tailings (Schippers, 2004; Schaanning et al., 2011; Koski, 2012; Dold, 2014a). In the ore, metal sulphides are stable, but bioavailability and risk of toxic effects may increase in the environment due to oxidation and transformation into more soluble forms (Simpson and Spadaro, 2016). Leaching of trace metals to the environment has been reported to be a source of trace metal input for many decades after the closure of mining. In under-water deposits availability of oxygen is limited a few millimeters below the sediment-water interface, but exposure may be prolonged due to bioturbation driven mixing of tailings upwards into the oxidizing environment near the sediment surface (Simpson et al., 1998; Amato et al., 2016; Mil-Homens et al., 2016).

Titania AS exploits the Tellenes ore, which is one of the largest ilmenite deposits world-wide (Charlier et al., 2007; Duchesne and Schiellerup, 2001). The mining started in 1916 and has the potential to continue for another 100 years at the current production rates (Berg et al., 2016). The ilmenite mineral (norite) is a mixture of Fe- and Ti-oxides with small amounts of Fe-Ni-Co-Cu sulphides. Some of these sulphides are not recovered and pass through to the tailings together with remnants of production chemicals such as tall oil, xanthate, flocculants and sulphuric acid (Duchesne and Schiellerup, 2001; Anon, 2015).

Sea deposition of tailings from Titania has been applied during two periods. During 1960–84, Jøssingfjorden was filled up from the old maximum depth of 85 m to current maximum depth near the sill depth of 30 m. In 1984 the discharge pipe was relocated seawards to

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Dyngadjupet. This semi-enclosed basin was filled to reduce maximum depth from 172 m before 1984 to 130–140 m in 1994 when sea deposition was ended after a public debate on environmental consequences. Since 1994, the tailings have been disposed in a land-deposit with current dam height approaching 100 m and with significant leaching of nickel and copper to the downstream watershed area. Leaching of trace metals has been identified as a source of toxicity in fresh water samples from the area (Tobiesen, 2003) and the discharge of metals both from the processing plant and the land-deposit is regularly monitored in relation to discharge permits. Regarding the sea deposit, long sediment cores have revealed sediments with elevated concentrations of Fe, Cr, Ti, Ni, Cu and Co (Gravdal, 2013), but little information exists on the potential leakage and bioavailability of the huge amounts of metals stored in the sea deposits.

The soft bottom fauna in the sea deposits has been regularly monitored both during and after the periods of sea disposal. A study by Olsgard and Hasle (1993) on the effects of mine tailings on the soft bottom fauna represents one of the very few published studies based on monitoring of Norwegian sea deposits. Thus, the objectives of this investigation were primarily to assess the mobilization and bioavailability of trace metals in the old sea deposits, and secondly to update the current status of the macrobenthic communities.

2. Material and methods

2.1. Production and discharge information

The Tellnes ore is mined in an open pit. The ore rock (and tailings) is composed of 26–29% ilmenite ($FeTiO_3$), 40–43% silicates (SiO_2) and 27% aluminum, magnesium and calcium oxides (Charlier et al., 2006, Gravdal, 2013). In addition, the ore contains 2–3% Fe-Ni-Co-Cu-sulphides. Thus, the presence of minerals such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), covellite (CuS), bravoite (Fe, Ni, Co)S_2, millerite (NiS), pentlandite ($(FeNi)_9S_8$), violarite ($(FeNi)_3S_4$) and siegenite ($(NiCo)_3S_4$) have been identified (Krause et al., 1985; Diot et al., 2003). In the on-site process plant, the ore rock is crushed, grinded and refined by magnetic and gravimetric separation, acid leaching and flotation processes (Kingman et al., 1999; Charlier et al., 2007). The main product is a 46% titanium oxide (TiO_2) concentrate. Byproducts are a 64% magnetite (Fe_3O_4) concentrate and a 36% sulphide concentrate with 4% Ni, 2% Cu and 0.5% Co (Chernet, 1999).

80–99% of the ore rock is not utilized and deposited as tailings in land or sea deposits. During 2008–2015, annual discharge to the land-deposit was 2.0–2.7 mill. Tons including typically 800 tons of Ni and 400 tons of Cu. Rain water seeps through the deposit and in 2016 a leaching of 2700 kg Ni was recorded in the drain water flowing out at the base of the dam. Some of this water was recycled for use in the process plant and ultimately contributed to the total discharge of 1840 kg Ni and 496 tons of particles (d.wght.) from various mine related activities to the inner part of Jøssingfjorden (Fauske, 2017; Nilsen, 2018). Thus, the old deposit site in Jøssingfjorden still receives significant amounts of waste from the mining industry, although small compared to the deposition period (1984–94).

The location of the old sea deposits in Jøssingfjorden and Dyngadjupet are shown in Fig. 1. The Jøssingfjorden site is well protected by a narrow fjord entrance and shallow sill at about 30 m depth. Dyngadjupet is a more open basin exposed to ocean currents and storm surges (Ibrekk et al., 1989), and indications on dispersal of tailings across the deep sills at 80–97 m depth into the adjacent Knubedalsdjupet have been reported by Olsgard and Hasle (1993).

2.2. Field sampling and set-up in mesocosm

The macrofauna was investigated in situ by grab sampling whereas metal mobility and biogeochemical investigations were performed in box-cores transferred from the field locations and maintained in a sublittoral, benthic mesocosm at Solbergstrand by the Oslofjord (Berge et al., 1986).

Field samples were collected 17.-18.11.2015 (Fig. 1, Table S1). For the macrofaunal analyses, five stations with four replicates each were sampled with a 0.1 m^2 van Veen grab following the guidelines for quantitative sampling and sample processing of marine soft-bottom macrofauna (NS-EN ISO 16665:2014). The sediments were washed through a 1 mm sieve with circular holes for retrieval of macrofauna. The retrieved material was preserved with 10% buffered formalin.

For the mesocosm set-up, sediments were sampled using a KC-Denmark box corer modified with internal polycarbonate liners (Schaanning et al., 2008). Twelve cores with surface area 0.1 m^2 and depth of 30–40 cm were collected from the stations shown in Fig. 1. The overlying water in each liner was drained off to reduce erosion during handling and transport. In the mesocosm, the liners were submerged to the rim in a water bath flushed with seawater continuously supplied from 60 m depth in the Oslofjord outside the sill at Drøbak. This water provides stable conditions with respect to salinity (34–35 psu) and temperature (8–10 °C). Each liner was continuously flushed with the same source water by use of thin PVC and marprene tubes and two 6-channels Watson Marlow™ peristaltic pumps. Flow rates of 2 and 10 ml min^{-1} were used during the periods of metal and nutrient flux measurements, respectively. Stirring to ensure a well-mixed overlying water was performed using an airlift system (Josefsson et al., 2012). During measurements of O_2 and nutrient fluxes, the air-lift system was replaced by submersible pumps operating at low speed to avoid any suspension of sediments. Similar mesocosm set-ups and sampling techniques have been described previously (Trannum et al., 2010, 2011; Näslund et al., 2011).

2.3. Macrofauna analyses

In the laboratory, all specimens (> 1 mm) were identified to species or lowest taxon possible. Samples for sediment fine fraction (i.e. the pelite content measured as % particles < 0.063 mm) and Total Organic Carbon (TOC) were also collected. Sediment fine fraction was determined by wet sieving, while carbon was determined using a CHN (i.e. Carbon, Hydrogen, and Nitrogen) analyser after removal of inorganic carbons by acidification.

The ecological quality of the macrobenthic communities was determined using Shannon-Wiener diversity index (H'log_2) (Shannon and Weaver, 1963), Hurlbert's diversity (ES_{100}) (Hurlbert, 1971) and Norwegian Quality Index (NQI1) (Molvær et al., 2009), all of which are included in the WFD monitoring system for Norwegian coastal waters. NQI1 is calculated with the formulae:

$$NQI1 = \left[0,5 * \left(1 - \frac{AMBI}{7}\right) + 0,5 * \left(\frac{\left[\frac{ln(S)}{\ln(\ln(N))}\right]}{2,7}\right) * \left(\frac{N}{N+5}\right)\right]$$

where S = no. species/taxa, N = no. individuals and AMBI (the AZTI Marine Biotic Index) as presented in Borja et al. (2000).

To analyse for similarities in the soft bottom species data, cluster-analysis was performed, based on Bray-Curtis similarity measure. This was done on replicate-basis. Similarity-calculations were based on fourth-root transformed data. To determine which environmental parameters which show the highest correlation with the variation in the biological resemblance matrix, data were analysed by Distance-based Linear Model (DistLM, Anderson, 2001). Marginal tests were performed to quantify how much variation each variable explained individually, i.e. excluding other variables. To investigate the variables in combination (sequential tests), the forward selection procedure was run with 9999 permutations and with the adjusted R^2 selection criterion (i.e. R^2 adjusted for number of parameters). The environmental variables measured from the sediment cores, as well as fine fraction and TOC from the grab samples, were used in the analyses. As the environmental

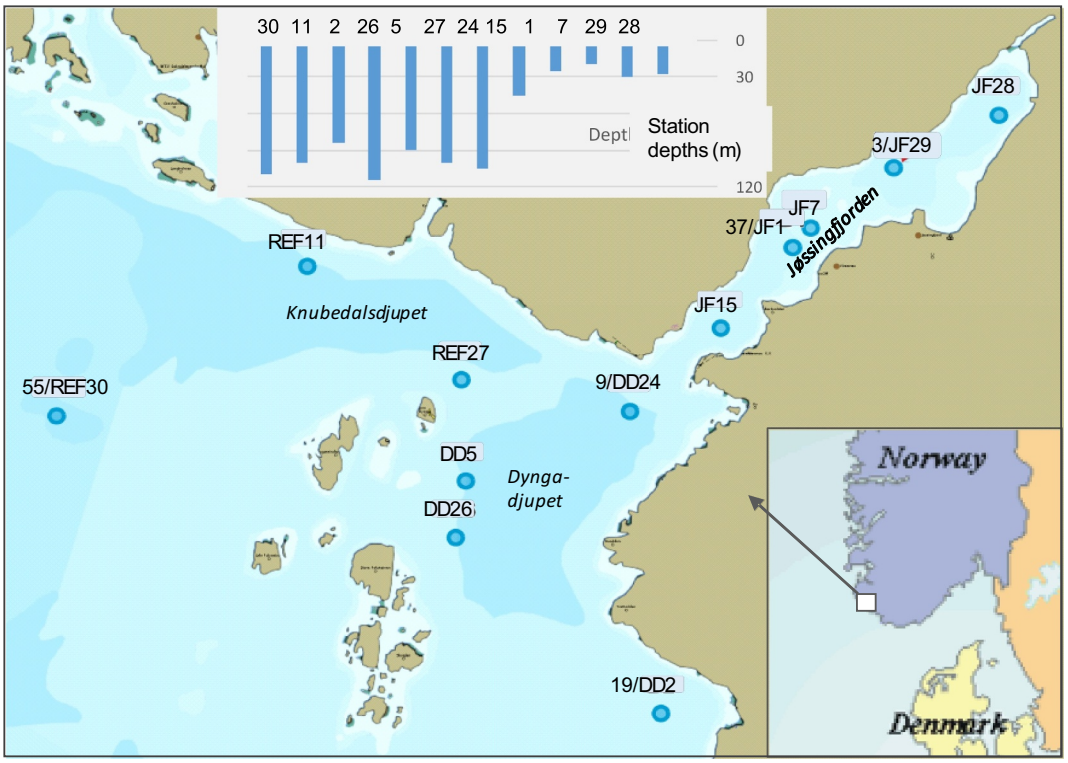

Fig. 1. Map of sampling area. The box core stations are denoted JF (Jøssingfjorden), DD (Dyngadjupet) and REF (reference). Lead numbers (3, 37, 9, 19 and 55) shows stations at which grab samples were collected for fauna investigation.

Table 1
Analyses of the sea water supplied for flux measurements (Oslofjord 60 m). C_{in} is the mean concentration (n = 6), LOQ is the limit of quantification given by the laboratory, S_c is the standard deviation and $S_{\Delta C}$ (see text) is the estimated uncertainty of the flux.

	C_{in} (µg L^{-1})	LOQ	S_c	$S_{\Delta C}$
O_2	8700	0	500	8%
NH_4	< 5	5	–	–
$NO_3 + NO_2$	140	1	2.3	2%
PO_4	31	1	1.4	6%
$Si(OH)_4$	716	25	40	8%
Pb	0.047	0.015	0.028	84%
Cd	0.017	0.007	0.001	8%
Cu	0.412	0.03	0.036	12%
Co	0.014	0.007	0.003	30%
Ni	0.330	0.08	0.009	4%
Zn	0.565	0.5	0.013	3%

variables were only available on station level and as the replicates showed low variation, the DistLM-analysis was performed on station-level. Distance-based redundancy analysis (db-RDA) was used to visualise the results, with vector overlays for displaying relationships between community patterns and environmental variables. The multivariate analyses were performed with PRIMER package version 6.1.13 (Clarke and Warwick, 2001).

2.4. Microelectrode measurements

Vertical profiles of pH and O_2 were measured using an assembly comprised of a single axis automated micromanipulator, potentiostat and 100 µm tip sensors for O_2 and pH (all from Unisense). The sensors were mounted on a single axis automated micromanipulator, and profiles were taken at a vertical resolution ranging from 0.1 to 1 mm. The oxygen microelectrode was calibrated using a two-point calibration consisting of fully aerated seawater for 100% O_2-saturation and N_2-purged seawater for zero O_2. The pH microelectrode was calibrated with appropriate pH 4, 7 and 10 buffers. The fragile sensors could not be applied in the liners sampled outside Jøssingfjorden due to frequent breakage on shell fragments. Therefore, supplementary measurements of pH were performed using a conventional pH glass combination electrode at 0–1 cm depth in all cores. The electrode was calibrated in standard IUPAC buffers 4 and 7 and inserted into the sediment, just enough to cover the bulb tip. The overlying water in each liner was drained off during the pH-measurements. Both calibration and measurements were done at the ambient temperature of 8–10 °C.

2.5. Sub-sampling and analyses of sediments and pore water

After the pH-measurements, sediments were sampled by pushing a 5 cm long section of a transparent acrylic tube (ID = 6 cm) into the sediment and transfer of the enclosed 0–1 cm layer of the sediment to a 50 ml polycarbonate centrifuge tubes. Within 30 min the pore water was extracted by centrifugation at 4000 rpm for 10 min at 10 °C. The supernatant was transferred to polyethylene test tubes, acidified, diluted 10× and stored at 4 °C until analyses of trace metals by ICP-MS. Detection limits (LOQ) are given in Table 1.

The sediments remaining in the centrifugation tubes were freeze dried, homogenized and analysed for metals using ICP-MS. Fine fractions (F) were determined using wet sifting at mesh size 0.063 mm and organic carbon (TOC) using high temperature (1100 °C) combustion and analysis of CO_2 after removal of inorganic carbon by acid treatment. TOC was normalized against fine fractions using the relationship nTOC = TOC + 18 × (1 − F) (Molvær et al., 1997). This normalized TOC (nTOC) is the basis for classification of organic carbon in standard environmental monitoring in Norway.

2.6. DGT-probes

A DGT probe was inserted vertically into the sediment in each box.

The DGT (Diffusive Gradients in Thin Films) technology uses a 1 mm layer of polyacrylamide diffusive gel and a backing layer impregnated with a Chelex resin for adsorption of trace metals (Zhang and Davison, 1995; Davison et al., 2000). The DGT-probes delivered from ExposMeter AB, Sweden, had a sampling window of 2 × 15 cm covered with a 0.14 mm thick 0.45 μm polyethersulphone filter paper.

The probes were inserted into the sediment so that 2 cm of the membrane was above the sediment surface. After 24 h exposure in the sediments the probes were retrieved. Sediment particles on the protective paper membrane were carefully washed off before placement in sealed plastic bags and storage at 4 °C until analysis. In the lab, the protective paper was carefully removed and the gel layers sectioned with a scalpel into 5 to 20 mm deep segments. Each segment was eluted in 10 ml acid, and metals determined by inductively coupled plasma mass spectrometry (ICP-MS). The 24 h metal uptake is here considered to be proportional to the concentration of bioavailable metals in the pore water (Zhang et al., 1995; Harper et al., 1998; Garmo et al., 2002).

2.7. Flux measurements

Fluxes (F) of dissolved metals, oxygen (O_2) and nutrient species ($NO_3 + NO_2$, NH_4, PO_4 and $Si(OH)_4$) were determined from the concentration difference between the inlet water (C_i) and the overlying water (C_o) in each core: $F = \Delta C * Q / A$, in which $\Delta C = C_o - C_i$, A is the sediment area and Q is the flow rate of seawater supplied to each core. The sampling for O_2 and nutrient fluxes was done three times during the period 18.–20.04.2016 at flow rates of 10 ml min^{-1}. Further details on sampling, sample preservation and chemical analyses are given in Schaanning et al. (2008).

After the final samples for nutrient fluxes were drawn, flow rates were reduced to 2 ml min^{-1} and aeration was installed to avoid O_2 depletion in the overlying water. Two weeks were allowed for the sediment-water system to reach the new steady state between release of metals from the sediment and exchange of overlying water. 250 ml samples were drawn for metal analyses in header tank and overlying water in each liner. Metals were extracted and rinsed to reduce interference on DigiSep blue SPE columns before analyses on ICP-MS. Limits of quantification (LOQ) given by the laboratory are shown in Table 1.

The uncertainty of the flow rate (Q) in each channel is small compared to the day to day variation in concentrations in the water. If the uncertainty of the concentration is the standard deviation (S), the uncertainty of the concentration difference should be $S_{\Delta C} = (2 * S^2)^{½}$. $S_{\Delta C}$ calculated from the concentrations determined in the source water during the period of flux measurements are shown in Table 1.

2.8. Statistical treatment of chemical data

The box core stations were grouped to represent either Jøssingfjorden (JF), Dyngadjupet (DD) or background reference (REF). Group means were calculated and compared using the Tukey-Kramer test for analyses of variance (ANOVA) between groups with different sample size in JMP®13.0.0 (Tukey, 1953; Kramer, 1956).

3. Results

3.1. Sediment 0–1 cm

All results of the chemical analyses are given in Tables S2 and S3.

The mean pH of 7.32 ± 0.04 measured in the sediment surface (0–1 cm) in the box core liners from Jøssingfjorden (JF) was lower than the range of 7.39–7.57 measured in the cores from Dyngadjupet (DD) and reference stations (REF) (Fig. 1, Table 2). Analyses of variance showed that the pH in Jøssingfjorden was significantly lower than the pH in the other two areas ($p < 0.05$).

Fine fractions (% < 63 μm) were significantly larger at both deposit sites (55 and 77% dw) compared to the reference stations (31% dw) (Table 2). After normalization to fine fractions, organic carbon (nTOC) was significantly less abundant in Jøssingfjorden than in the other two areas (Table 2).

The concentration of iron in sediments from Jøssingfjorden were significantly higher than the reference stations, whereas the concentrations of manganese were significantly lower (Table 2). This was consistent with ore composition and previous measurements of tailings and core samples from the sea deposit (Ibrekk et al., 1989; Gravdal, 2013).

The highest concentrations of Co, Cu and Ni were found in Jøssingfjorden and the lowest at the reference locations. The concentrations of Cu were significantly different between the three sites with JF > DD > REF (Table 2). The concentrations of Cu and Ni were well correlated (Fig. 2A), confirming that the tailings were a common source for both metals. The figure also includes data on tailings supplied from the current production and analysed after various dilution with non-contaminated sediments from the Oslofjord (Trannum and Schaanning, 2017) and concentrations measured in long sediment cores collected in Jøssingfjorden and Dyngadjupet in 2012 (Gravdal, 2013).

A principal component analyses (PCA) of all sediment parameters showed that the three groups of stations JF, DD and REF were reasonably well separated along the component 1 axis (Fig. 3, left). This axis explained 62.3% of the variability and the vector plot (Fig. 3, right) showed that the separation was primarily due to fine grained sediments with high concentrations of Fe, Cu, Ni and Co, low pH and low concentrations of Mn, Cd and Pb. The second component accounted for 24.3% of the variability and was dominated by high TOC and low water content. The separation along this axis appeared not related to the tailings disposal with high scores for the three most distant stations in each area, i.e. the most northern station in Jøssingfjorden (JF28), the most southern station in Dyngadjupet (DD2) and the most eastern of the reference stations (REF30).

3.2. Pore water

The microelectrode measurements performed directly in the liner from station JF29 on December 12th showed that O_2 was depleted below a sediment depth of 9 mm (Fig. 4). Contrasting the steady decrease of O_2, the pH was close to 7.30 down to 4 mm depth, after which it decreased to 7.18 at 10 mm depth and 7.13 at 18 mm which was the maximum depth reached by the electrodes.

The distribution pattern for trace metals resembled the distribution in the sediments with elevated concentrations of Ni, Cu and Co at the two deposit sites. As shown by the letter notations (A, B, C) in Table 2, the concentration of Ni and Co was significantly higher in JF than in DD and REF, and the concentration of Cu was significantly higher in JF than in REF.

The DGT profiles for Fe, Mn, Ni, Cu and Co showed similar distribution patterns in all three areas, but gradually more variable as the abundancy of tailings decreased from Jøssingfjorden towards the reference area (Fig. 5). In the deep end of the probes, the uptake of Fe was highest in Jøssingfjorden, as opposed to Mn which was highest at the reference stations. This was consistent with high concentration of Fe and low concentration of Mn in the tailings. However, the low uptake of Fe on probes exposed to sediments from the reference stations and Dyngadjupet may suggest additional differences between the three areas related to different redox conditions, speciation and transformation of iron minerals. In agreement with thermodynamic predictions, the uptake of Mn increased a few mm closer to the well oxygenated overlying water than Fe. At station JF29 comparison of the microelectrode measurements and the DGT-profile indicated co-occurrence of the major pH-transformation and sinks for upwards diffusing manganese ions and downwards diffusing O_2 within the 5–10 mm depth interval (Fig. 4). Cu and Ni peaked at about the same depth intervals (i.e. 5–15 mm) whereas Co peaked slightly deeper (20–30 mm) (Fig. 5). Different from Fe and Mn, significant uptake of Ni, Cu and Co was

Table 2
Results of box core study. Each frame gives substance measured, units and mean values for Jøssingfjorden (JF), Dyngadjupet (DD) and reference locations (REF), respectively. Letters (A, B, C) show the results of the statistical analyses of variance between station groups (Tukey's test). Thus, means connected with the same letter are not significantly different (α = 0.05).

Group	SEDIMENT			PORE WATER			FLUX		
JF	Ni	A	156	Ni	A	49	Ni	A	14.3
DD	μg g^{-1}	B	72	μg L^{-1}	B	23	μg m^{-2} h^{-1}	B	4.3
REF		B	23		B	11		B	1.7
JF	Co	A	31	Co	A	21.2	Co	A	2.23
DD	μg g^{-1}	B	19	μg L^{-1}	B	5.7	μg m^{-2} h^{-1}	B	0.55
REF		B	10		B	8.1		B	0.08
JF	Cu	A	128	Cu	A	17.0	Cu	A	2.00
DD	μg g^{-1}	B	77	μg L^{-1}	A B	10.0	μg m^{-2} h^{-1}	A	1.48
REF		C	29		B	7.0		A	0.51
JF	Zn	A	36	Zn	A	20.4	Zn	A	0.63
DD	μg g^{-1}	A	33	μg L^{-1}	A	10.6	μg m^{-2} h^{-1}	A	0.61
REF		A	27		A	8.7		A	0.46
JF	Pb	B	7	Pb	A	0.20	Pb	A	-0.035
DD	μg g^{-1}	A	14	μg L^{-1}	A	0.48	μg m^{-2} h^{-1}	A	0.092
REF		A	14		A	0.62		A	-0.003
JF	Cd	A	0.023	Cd	A	0.15	Cd	A	0.0074
DD	μg g^{-1}	A	0.048	μg L^{-1}	A	0.11	μg m^{-2} h^{-1}	A	0.0014
REF		A	0.066		A	0.10		A	0.0022
JF	Fe	A	21 400	pH	B	7.32	$-O_2$	A B	226
DD	μg g^{-1}	A B	11 050		A	7.50	μmol m^{-2} h^{-1}	B	235
REF		B	7 633		A	7.53		A	147
JF	Mn	B	83				NH_4	A	3.6
DD	μg g^{-1}	A B	148				μmol m^{-2} h^{-1}	A	4.0
REF		A	170					A	0.6
JF		A	76				PO_4	A	1.3
DD	$\%H_2O$	A	74				μmol m^{-2} h^{-1}	A	2.3
REF		A	73					A	0.7
JF		A	77				NO_3+NO_2	A	0.3
DD	%<63μm	A	57				μmol m^{-2} h^{-1}	A	3.5
REF		B	31					A	1.6
JF	nTOC	A	11.5				SiO_4	A	70
DD	(mg g^{-1})	B	18.7				μmol m^{-2} h^{-1}	A	131
REF		B	18.8					A	67

generally observed at the sediment surface (0–5 mm), indicating metal mobilization and release to the overlying water.

3.3. Flux measurements

Fluxes of O_2 were always directed from water to sediment, i.e. oxygen was consumed in the sediment. The fluxes of O_2 were, however, low in all three areas and lowest in the reference area (Table 2). All mean fluxes of nutrients were directed from sediments to water. Ammonia was not detectable ($< 5\,\mu g\,L^{-1}$) in the source water (Table 1). Ammonia and phosphate was released at higher rates from the two deposit areas than from the reference area, whereas the release of silicate and nitrate was highest in Dyngadjupet. The lowest release of nitrate occurred in Jøssingfjorden.

Except for occasional uptake of Pb and mean fluxes near zero, metals were consistently released from sediments to overlying water (Table 2). The release of Zn, Pb and Cd revealed no clear differences between the three areas. The fluxes of Ni, Co and Cu were, however, clearly ranked JF > DD > REF and significantly higher in Jøssingfjorden compared to DD and REF. Thus, the flux measurements confirmed the release indicated by the significant near-surface uptake on the DGT-probes.

3.4. In situ macrofauna communities

In total 259 taxa and 13,101 individuals were recorded in the field survey. Annelids, bivalves, phoronids and brittle stars dominated the fauna. Number of taxa and individuals and the indices H′, ES_{100} and NQI at each station are presented in Table 3, and the ten most abundant taxa are presented in Table 4. The complete species list can be found in Trannum (2016). The innermost station had the lowest number of taxa, and station 9 and 55 the highest. The number of individuals was by far highest at station 37. This high abundance was reflected in lowered diversity indices. Station 55, the reference station, showed considerably higher diversities than the other stations.

In the cluster-analysis (Fig. 6) there were two main groups; the two stations inside the fjord and the three stations outside. Further, there was a strong grouping according to station, and relatively minor differences between the replicates from each station. The difference between the stations was particularly large between station 3 and station 37. Notably, station 37 was different from the other stations also regarding environmental parameters like TOC and particle size (Table 3). Such heterogeneity may result from differences in local bathymetry and currents. This station was considered to be an outlier and hence excluded from the distLM-analysis. Removal of outliers is recommended to avoid severe interference in the grouping of the remaining stations

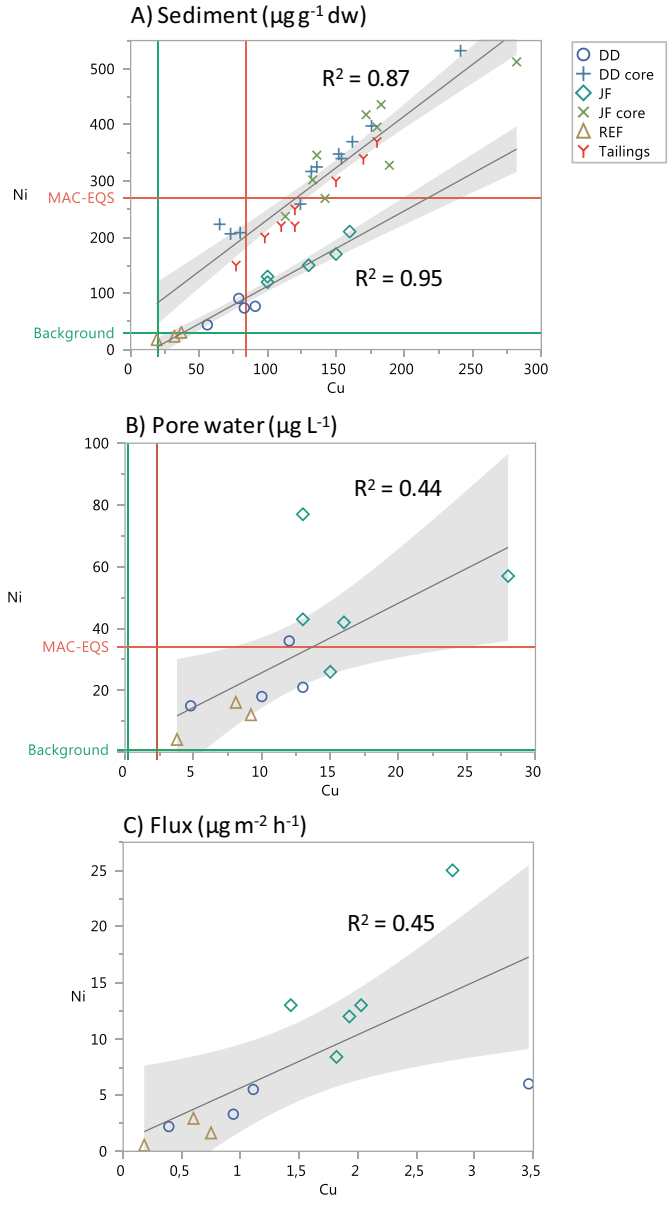

Fig. 2. Correlation between Ni and Cu in A) sediment, B) pore water and C) flux from sediment to water measured in core liners from Jøssingfjorden (JF), Dyngadjupet (DD) and reference stations (REF). Sediment concentrations measured in long cores from Jøssingfjoden (JF core) and Dyngadjupet (DD core) (data from Gravdal, 2013) and in fresh Titania tailings diluted in uncontaminated marine sediments (Tailings) (data from Trannum and Schaanning, 2017) are inserted in diagram A. Linear regression lines, confidence intervals and correlation coefficients (R^2) were calculated separately for 0–1 cm layer in core liners and the group containing long core and fresh tailings (see text). Background concentration limits (green lines) and MAC-EQS (red lines) for coastal sediments and water are given in Guideline M608.

(Jongman et al., 1987).

In the marginal test in distLM (Table 5), i.e. where the variables are tested individually, the parameters depth, sediment fine fraction and copper were identified as significant variables. In the sequential test, i.e. where the variables are tested in combination, Fe and TOC together gave the best fit with the species data, but they were not identified as significant. In the corresponding dbRDA-plot (Fig. 7), it is evident that the gradient in Fe also represents the gradients of the metals Ni, Co, Cu, and to a lesser extent Zn, sediment fine fraction and water-content. On the other hand, the metals Pb, Mn and Cd tended to increase outside the fjord. In the plot, as much as 77.6% of the variation was explained by the two first axes, and the plot is therefore assumed to adequately represent the main faunal patterns.

4. Discussion

4.1. Organic enrichment and nutrient fluxes

Organic carbon (nTOC) was generally low (< 20 mg g^{-1} dw), corresponding to class I in the classification system for eutrophication in coastal sediments in Norway (Molvær et al., 1997) and significantly lower in Jøssingfjorden than in the two other areas (Table 1). This was different from other fjords in the southern part of Norway, where TOC-levels are usually elevated compared to more seaward sediments (Fagerli et al., 2017), but reasonably explained by dilution of the natural sedimentation of organic matter by tailings discharged to the water column in the inner part of the fjord.

The highest nTOC (class II) was observed at the box core station DD2 and the nearby grab station 19 (Table 3). This station was different from the other stations in Dyngadjupet with regard to several of the chemical parameters as revealed by the PCA-analyses with a high score for component 2 (high TOC) and a near zero score on component 1, which can be assigned to relative high concentrations of Mn and Pb balancing out moderate contributions from low pH (7.39) and other tailings associated properties (Fig. 3). The higher TOC concentration at DD2 was confirmed by enhanced rates of mineralization as shown by maximum fluxes of oxygen (295 µmol $m^{-2} h^{-1}$), and ammonium (8.6 µmol $m^{-2} h^{-1}$) and generally high fluxes of nitrate (5.9 µmol $m^{-2} h^{-1}$), phosphate (2.6 µmol $m^{-2} h^{-1}$) and silicate (160 µmol $m^{-2} h^{-1}$) (Tables 2 and S3). The concentrations of tailings associated elements at DD2 were in line with the other stations in Dyngadjupet indicating the presence of both tailings and some other material enriched with labile organic matter.

TOC was not determined in the long cores sampled in 2012, but sulphate depletion, high alkalinities (20–40 mM) and high pore water concentrations of phosphate (100–400 µM) and ammonium (100–2500 µM) was attributed to anaerobic degradation of chemicals, primarily tall oil previously used in flotation processes (Gravdal, 2013). The 3–7× elevated release of ammonium and phosphate observed at both deposit sites compared to the reference locations (Table 2) was consistent with the elevated pore water concentrations observed by Gravdal, 2013.

Silicate is released from marine sediments partly from mineral dissolution and partly from degradation of skeletons of diatoms which are known to be abundant in northern seas (DiToro, 2001). Silicic acid may be used for mineral extractions in some mining industries. The mean release of silicate in Dyngadjupet (137 µmol $m^{-2} h^{-1}$), was 2× higher than the release from Jøssingfjorden (70 µmol $m^{-2} h^{-1}$) and Dyngadjupet (67 µmol $m^{-2} h^{-1}$), but differences were not significant at the $p < 0.05$ level (Table 2). Nitrate may be consumed in the sediments due to denitrification (reduction of nitrate to nitrogen gas) or released from the sediments due to nitrification (oxidation of ammonium to nitrate). In the present study the fluxes of nitrate varied between a consumption of 2.8 and release of 7.6 µmol $m^{-2} h^{-1}$ and no systematic trends were found in the area. Thus, no evidence was found for any impact of the mining activities on the processes controlling nitrogen or silicate nutrient fluxes across the sediment water interface.

Elevated rates of O_2 consumption and nutrient fluxes are primarily driven by degradation of recent sedimentation of labile TOC, e.g. from seasonal phytoplankton blooms (Kelly and Nixon, 1984, Cowan et al., 1996). In our samples, TOC was low in all areas. In addition, the samples were collected in November which represents a seasonal low for primary production and TOC input to the sediments. Accordingly, the observed range of oxygen consumption of 78–295 µmol $m^{-2} h^{-1}$ was within the lower range of fluxes reported from other coastal and oceanic environments (Devol and Christensen, 1993, Hall et al., 1996, Cowan et al., 1996, Olsgard et al., 2008, Trannum et al., 2010).

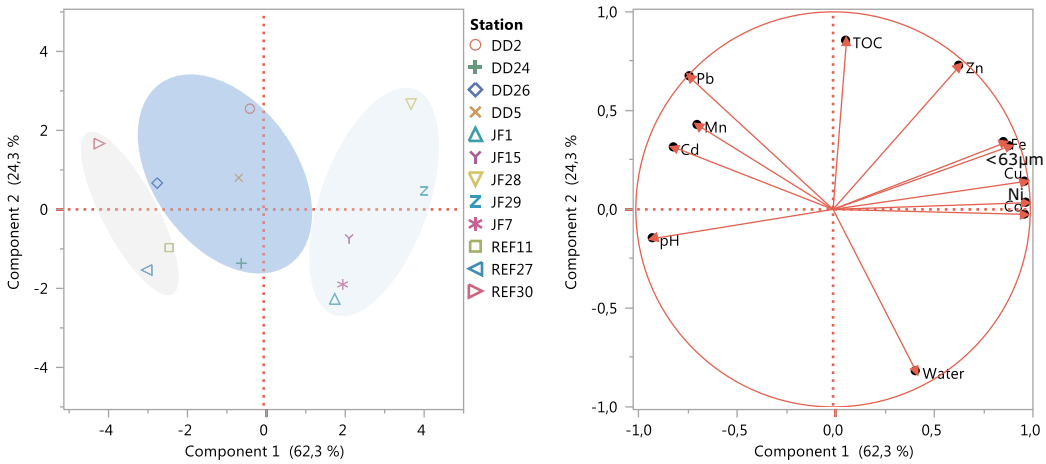

Fig. 3. PCA analyses of sediment properties in old sea deposit sites in Jøssingfjorden (JF), Dyngadjupet (DD) and reference locations (REF).

However, the mean rates were elevated at both deposit sites compared to the reference area and significantly elevated at one of the sites. Possibly these slightly elevated rates of O_2 consumption are sustained by chemotrophic or lithotrophic bacteria utilizing reduced compounds available at the deposits sites. This could be ammonium or sulphide diffusing upwards from deep deposit layers or metal-sulphide minerals and Fe^{2+} and Mn^{2+}-ions derived from the mine tailings (Schippers, 2004; Dold, 2014a). The co-occurrence of sinks for O_2, Fe^{2+} and Mn^{2+} revealed by the DGT- and microelectrode profiles (Figs. 4 and 5) indicates enhanced oxidation of dissolved metal ions, and the very consistent peaks of dissolved Ni and Cu within the same depth intervals suggests oxidative transformation of tailings minerals with potentially complex structures. These reactions frequently produce acid (Dold, 2014b) which would be consistent with the slight, but significantly lowered pH in Jøssingfjorden.

4.2. Metal mobility

4.2.1. Iron and manganese

The iron and manganese profiles shown in Fig. 5 are classical results of early diagenesis of organic matter causing oxygen deficiency and reducing conditions at some distance from the sediment surface (Berner, 1980; Zehnder and Stumm, 1988; Pakhomova et al., 2007). Reduction of iron and manganese oxides causes the more soluble divalent forms (Fe^{2+}, Mn^{2+}) to accumulate in the pore water until being removed by diffusion and precipitation when exceeding the solubility of some solid phase. For Fe this is frequently ferrous sulphide (FeS), which transforms further to pyrite (FeS_2), and for manganese frequently rhodochrosite ($MnCO_3$) (Davison, 1980; Schaanning et al., 1988; Konhauser et al., 2007; Swanner et al., 2014).

The dissolved divalent ions diffuse upwards until removal by re-precipitation in the oxidizing environment near the sediment surface or in the overlying water (Froelich et al., 1979; Burdige, 1993). The depletion of the divalent ions within the sediments and the absence of subsurface maxima frequently created by increasing concentrations of precipitation ligands (e.g. S^{2-}, CO_3^{2-}) below the redox transformation zone, was consistent with profiles typically found in sediments with low input of organic carbon (Burdige, 1993; Koschinsky, 2001; Koschinsky et al., 2001).

4.2.2. Nickel, copper and cobalt

The DGT-technique measures truly dissolved metal species (Zhang et al., 1995) and has been successfully used for assessment of bioavailability and toxicity of metals to sediment dwelling organisms (Simpson et al., 2012a; Amato et al., 2016). Furthermore, the high resolution of pore water profiles obtained with DGT-probes allows more accurate assessment of the vertical positioning of metal sinks and sources. Thus, the maxima of Ni and Cu observed at about 10 mm depth at the deposit sites (Fig. 5) indicated input to the pore water at this depth, whereas the Fe- and Mn-concentration gradients indicated

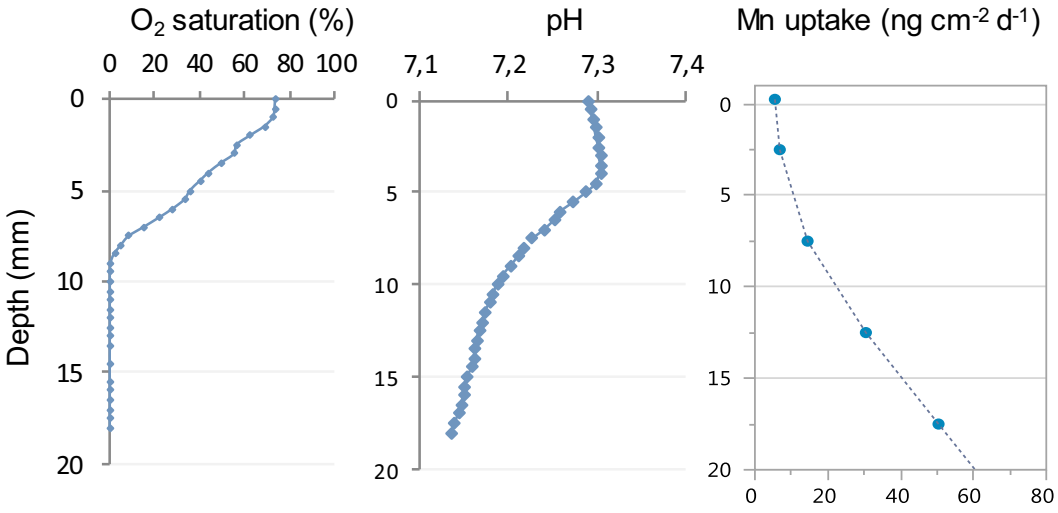

Fig. 4. Microelectrode profiles of O_2 saturation and pH and manganese uptake on DGT-probe within the top 20 mm of the sediments in Jøssingfjorden (JF29).

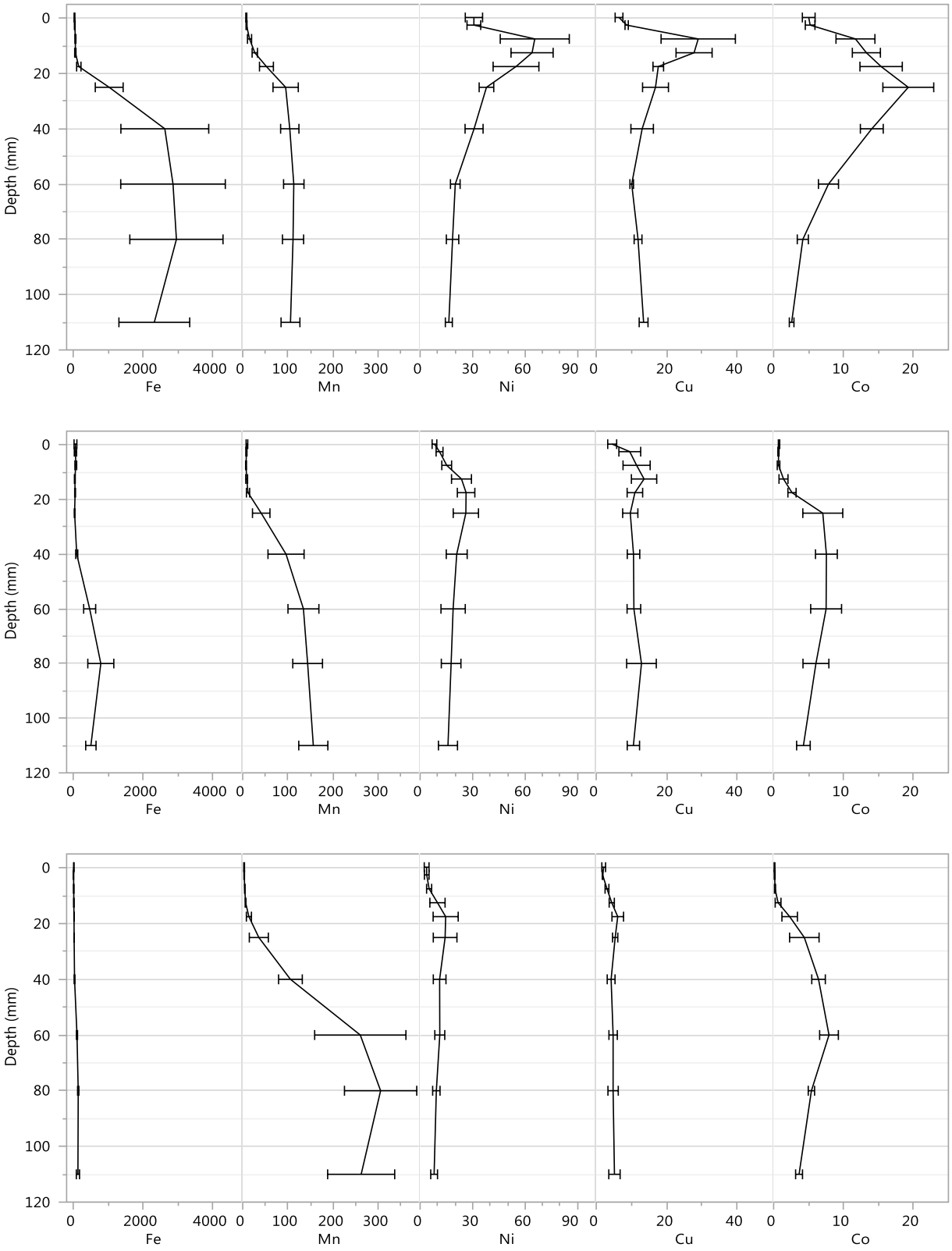

Fig. 5. Metal uptake on DGT probes (ng cm^{-2} day^{-1}) during 24 h exposure in sediments from Jøssingfjorden (top), Dyngadjupet (middle) and reference stations (bottom). Horizontal bars = 2 standard errors representing variation within each area.

dissolution of Fe- and Mn-oxides occurred at depths below 20 mm. This suggested that the Ni- and Cu-maxima were not coupled to reduction and dissolution of Fe- and Mn-oxides, but rather leached from tailings associated sulphide minerals which will be unstable in the oxic environment above 10 mm depth (Fig. 4) (Simpson et al., 2012b).

Leaching of metal sulphides is often mediated by microorganisms and may occur at a variety of transformation pathways depending on the mineral structure, available ligands and geochemical environment (Dold, 2014a). Leaching of millerite has been found to proceed at maximum rates at pH as low as 2.5 and greatly enhanced in the

Table 3
Comparison of observations in grab and core samples from nearby locations. S = mean number of taxa, N = number of individuals, H' = Shannon-Wiener diversity, ES_{100} = Hurlbert's diversity index, NQI1 = Norwegian Quality Index, nTOC = normalized organic carbon (see footnote).

Grab station	3	37	9	19	55
Nearby liner station	JF29	JF1	DD24	DD2	REF30
Depth (m)	30	25	100	83	102
Grab samples					
S	40.5	45.8	74.5	58.8	76.3
N	669	1183	488	488	351
H′	3.24	3.18	4.41	4.31	5.42
ES100	18.97	16.34	35.18	28.64	44.27
NQI1	0.68	0.71	0.78	0.73	0.84
< 63 µm (%)	89	14	59	72	35
nTOC[a] (mg g^{-1} dw)	7.9	16.0	12.9	23.3	17.4
Liner samples (0–1 cm)					
< 63 µm (%)	86	65	43	73	35
nTOC[a] (mg g^{-1} dw)	8.9	10.2	17.0	24.4	19.8
pH	7.27	7.37	7.56	7.39	7.53
Ni (µg g^{-1} dw)	210	120	91	74	17
Cu (µg g^{-1} dw)	160	100	79	83	19

[a] nTOC = TOC + 18(1 − f), f = fraction < 63 µm (Molvær et al., 1997).

presence of sulphate reducing micro-organisms such as *Thiobacillus ferroxidans* (Razzel and Trussel, 1963, Lors et al., 2004). At marine pH of 7–8 biological oxidation of metal sulphides will proceed more slowly, but bacteria has been identified to mediate leaching in oxic as well as in anoxic environments using O_2, nitrate or Mn(IV)-oxides as oxidants with elemental sulphur or thiosulphate as oxidation products (Schippers, 2004).

Chalcopyrite ($CuFeS_2$) is another potentially important sulphide present in the ilmenite tailings. Leaching of this mineral is a two-step process which involves intermediate reduction to chalcocite (Cu_2S) before oxidation to Cu^{2+} (Hiroyoshi et al., 2000, 2008; Sandström et al., 2005). Potentially important in the marine environment, the leaching rate has been found to be enhanced by the formation of chlorocuprate(I) ions in solutions with high concentrations of chloride ions (Yoo et al., 2010). Both Fe^{3+} and O_2 may be used as oxidants and elemental sulphur is likely to be formed (Hiroyoshi et al., 2000). Elemental sulphur and thiosulphate are unstable at the sediment surface and will eventually undergo oxidation to sulphuric acid ($2S^0 + O_2 = SO_4^{2-} + 2H^+$). Thus, metal leaching at the sediment surface is consistent not only with increased abundancies of metal ions, but also with the increased oxygen consumption observed in the deposit areas (Table 2) and the decline of pH observed at the depth of the Cu-maxima (Figs. 4 and 5).

Different from Ni and Cu, Co appeared to be mobilized primarily below the oxic layer, with frequent DGT-maxima at 25 mm depth (Fig. 5). Strong correlations between Co and Mn have previously been found both in surface sediments and anoxic water columns (Özturk, 1995; Tankere-Muller et al., 2007). E_h-pH diagrams show that, at the pH of marine environments, the boundary between Co(II)-ions and Co(III)hydroxide is close to the boundary between Mn(II)-ions and Mn(III-IV)-oxides (Swanner et al., 2014). Thus, the maxima at 25 mm depth result from Co^{2+} being fed into the pore water by reduction and dissolution of Co(III)hydroxides. The increasing abundancy of Mn^{2+} showed that also the Mn-oxides are unstable from about this depth and downwards, but maxima were not observed probably due to low concentration of manganese in the tailings and low TOC (Burdige, 1993). An additional interesting feature was that the Co- profile between the deep maxima and the sediment surface in Jøssingfjorden (Fig. 5) was not a typical, straight-line diffusion profile. Thus, the "hump" at about 10 mm depth indicated production of dissolved Co well correlated with the mobilization of Ni and Cu. If Co(II)-sulphides are oxidized and partially transformed to Co(III)-oxides at this depth the required input of Co(III)-hydroxides is explained. Thus, in accordance with the E_h-pH diagram proposed by Swanner et al. (2014), the Co-profile is interpreted as a cycle starting with oxidation of tailings associated Co(II)-sulphides and precipitation of Co(III)-oxides near the sediment surface. After burial, the oxides are dissolved by reduction to Co(II)-ions at the same depth at which Mn(IV)-oxides are reduced to Mn(II)-ions. The cycle is completed by upwards diffusion of Co(II)-and Mn(II)-ions which both are retained by oxidation and reprecipitation near the sediment surface.

Below the Fe-Mn transition zone, downwards diffusing metal ions may form new sulphides (Saito et al., 2003). Several trace metals (Cd, Pb and Zn) may precipitate as discrete metal sulphides, but Cu, Co and

Table 4
Overview of ten most dominant taxa pr. station (average pr. 0,1 m^2) in Jøssingfjorden, 2015. Faunal group in parenthesis; A = Annelida, M = Mollusca, E = Echinodermata, P = Phoronida, C = Cnidaria, N = Nemertea.

Taxon	St.3	Taxon	St.37	Taxon	St.9
Galathowenia oculata (A)	223	Phoronida indet (P)	325	*Galathowenia oculata* (A)	180
Kurtiella bidentate (M)	139	*Kurtiella bidentate* (M)	248	*Thyasira* sp.(M)	25
Amphiura filiformis (E)	105	*Amphiura filiformis* (E)	178	Phoronida indet (P)	19
Corbula gibba (M)	34	*Amphiura* sp. (E)	131	*Paramphinome jeffreysii* (A)	15
Ennucula tenuis (M)	25	*Galathowenia oculata* (A)	99	*Eclysippe vanelli* (A)	15
Pholoe baltica (A)	15	*Corbula gibba* (M)	38	*Spiophanes kroyeri* (A)	14
Pista lornensis (A)	12	*Edwardsia* sp. (C)	31	*Heteromastus filiformis* (A)	13
Thyasira sp. (M)	12	Nemertea indet (N)	30	*Trichobranchus roseus* (A)	12
Chaetozone setosa (M)	10	*Scoloplos armiger* (A)	23	Irregularia juv. (E)	11
Ophiuroidea juv. (E)	10	*Dosinia* sp. (M)	18	*Amythasides macroglossus* (A)	9

Taxon	St.19	Taxon	St.55
Heteromastus filiformis (A)	138	*Eclysippe vanelli* (A)	29
Thyasira sp. (M)	51	*Spiophanes kroyeri* (A)	22
Galathowenia oculata (A)	50	*Amythasides macroglossus* (A)	20
Diplocirrus glaucus (A)	47	*Thyasira* sp. (M)	20
Polycirrus sp. (A)	33	*Heteromastus filiformis* (A)	14
Pholoe baltica (A)	23	*Pholoe baltica* (A)	13
Eclysippe vanelli (A)	18	*Galathowenia oculata* (A)	13
Abyssoninoe hibernica (A)	18	*Notomastus latericeus* (A)	13
Notomastus latericeus (A)	15	*Yoldiella* sp. (M)	12
Spiophanes kroyeri (A)	11	*Polycirrus plumosus* (A)	9

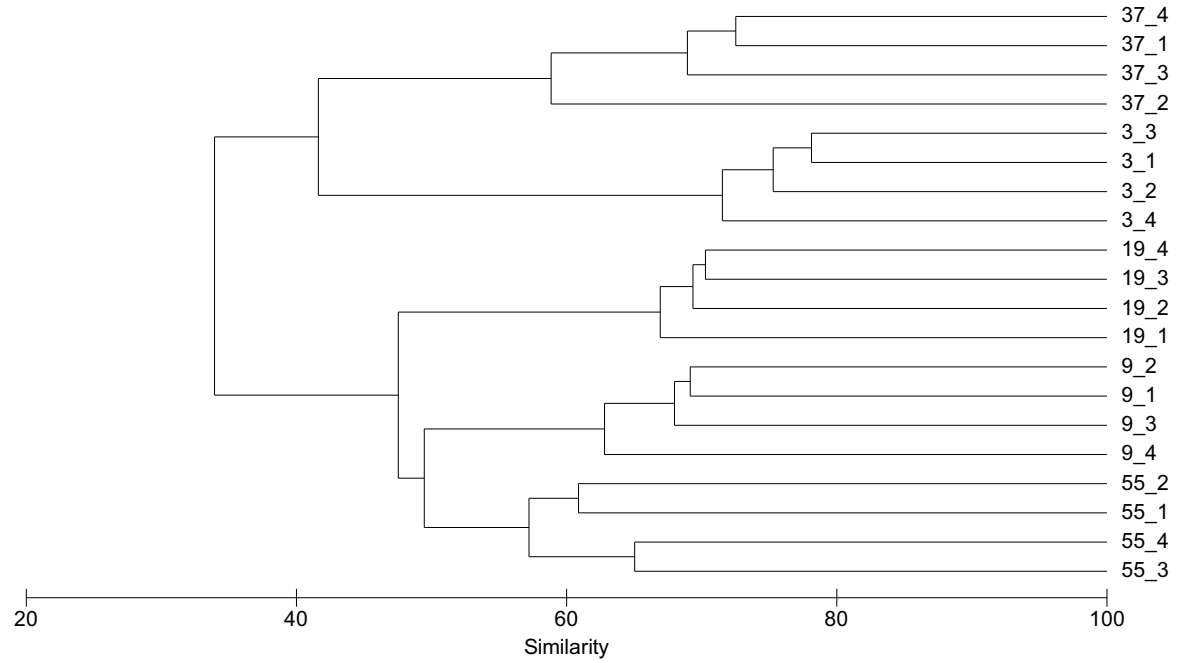

Fig. 6. Cluster-analysis of macrofauna in grab samples from Jøssingfjorden 2015 (fourth root transformed data, Bray Curtis similarity).

Table 5
DistLM marginal and sequential test results with sum of squares (SS_{trace}), pseudo F-statistic (*F*), p-value (*p < 0.05) and the proportional explained variance in the dataset (Prop.). Significant variables in bold.

Variable	SS_{trace}	*F*	p	Prop.
Marginal test				
Depth	**1935**	**1.923**	**0.040***	**0.490**
Water	1128	0.801	0.713	0.286
< 63 µm	**1752**	**1.596**	**0.045***	**0.444**
TOC	1134	0.806	0.538	0.287
Ni	1956	1.970	0.079	0.496
Co	1930	1.914	0.081	0.489
Cu	**1933**	**1.919**	**0.044***	**0.490**
Zn	1484	1.205	0.291	0.376
Cd	1403	1.103	0.380	0.355
Pb	1643	1.427	0.169	0.416
Fe	1967	1.987	0.086	0.498
Mn	1595	1.356	0.247	0.404
pH	1757	1.605	0.124	0.445
Sequential test				
Fe	1967	1,987	0,080	0,498
TOC	1097	1,242	0,501	0,776

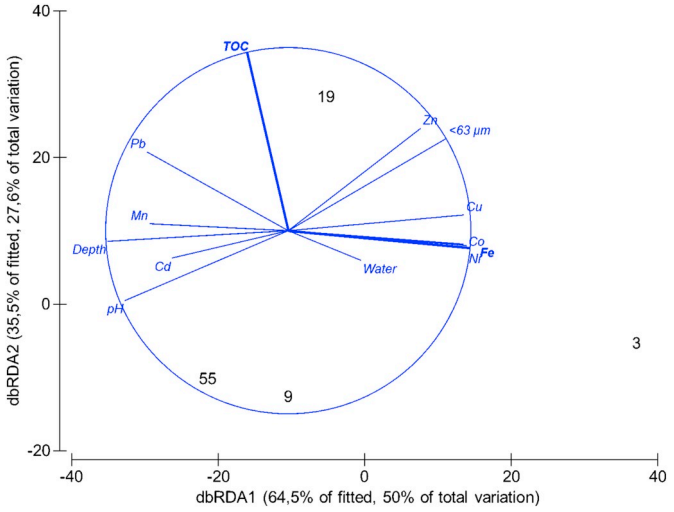

Fig. 7. dbRDA plot of Bray Curtis similarity between faunal samples, with environmental variables as vectors. The combination of variables which gave the best fit in DistLM, (forward selection) are typed with bold (TOC and Fe).

Ni are more likely to be trapped by substitution of Fe atoms in pyrite (FeS_2) (Morse and Luther III, 1999). Either way, the sea deposits act as permanent sinks for trace metals in tailings buried below the mobilization zone within the top 3–4 cm layer. However, bioturbation may recycle tailings from larger sediment depths by vertical sediment transport. Particularly bioturbation mediated by upward conveyors such as *Heteromastus filiformis* which is abundant in Dyngadjupet (Table 4), may have been involved. These are vertically oriented species that typically feed head-down at depth down to 10–20 cm in the sediment and transport particles from deep horizons to the sediment surface (Cadée, 1979; Kristensen et al., 2012).

4.2.3. Sea deposit as a source of bioavailable metals

Direct measurements of metal fluxes from marine sediments are not frequently reported. However, compared to fluxes determined in a contaminated sediment area off the Belgian coast (Gao et al., 2009), the fluxes of Cu in Jøssingfjorden were similar and fluxes of Ni were higher by a factor of 2. Also for Co, the fluxes measured in Dyngadjupet and at the reference stations compared well with fluxes reported in Swanner et al. (2014), whereas the fluxes measured in Jøssingfjorden were significantly higher.

The total flux from sediment to seawater in Jøssingfjorden (area = 0.61 km^{-2}) was estimated to be 76.3 kg Ni y^{-1}, 10.7 kg Cu y^{-1} and 11.9 kg Co y^{-1}. The total release from all investigated areas including Dyngadjupet and Knubedalsdjupet (an area of 1.4 km^{-2} between station REF11 and REF27) was estimated to be 143 kg Ni y^{-1}, 33 kg Cu y^{-1} and 18 kg Co y^{-1}. For scaling the magnitude, the flux of Ni corresponded to about 15% of the current leaching from the landdeposit (Fauske, 2017).

Leaching of metal sulphides at the sediment-water interface is a slow process which affects only a small fraction of the metal sulphides present in the tailings. Leaching will be restricted to the window of time between grinding of the ore rock and final burial below the oxygenated

sediment surface layer. In the mining processes and in the water-column before sedimentation, residence times are short, i.e. in the order of days to weeks as opposed to months to years and decades at the oxygenated sediment surface. Especially after deposition is finalized, slow sedimentation rates and bioturbation will increase the residence time of tailings at the sediment surface. Bioturbation will promote both downwards transport of O_2 and upwards transport of tailings. In locations such as Dyngadjupet in which natural sedimentation rates are low and bioturbation presumably high, this phase may last for several decades during which tailings metals will be made available for uptake in benthic fauna and dispersal into overlying water. This period may be shortened by placement of a few cm of fine-grained, inert mineral materials. In the longer time perspective, natural processes will act to seal off the remaining metal reservoir of the sea deposit from any interactions with the biosphere.

4.3. Chemical classification

Compared to environmental quality standards (EQS) (Guideline M-608), fresh tailings and deep deposit layers exceeded MAC-EQS ("maximum admissible concentration") for coastal sediments with regard to both Cu and Ni (Fig. 2A). These EQS values are harmonized with the European regulatory framework and per definition pose a "risk of acute toxic effects" in samples exceeding the MAC-EQS values.

In Jøssingfjorden and Dyngadjupet MAC-EQS was exceeded at several stations, but unlike the fresh tailings, only for Cu. The different slopes of the regression lines in Fig. 2A, suggest that this difference either result from preferential leaching of Ni, which is lost to the overlying water at flux rates 7× faster than Cu (Table 2), or a different composition of the particles discharged in Jøssingfjorden. 75% of these are particles suspended in drainage water pumped from the bottom of the mine.

Guidelines rarely define separate EQS values for pore water. Pore waters are, however, frequently extracted for risk assessment and presumably contribute to the empirical data on which the EQS values for coastal waters are based (Adams et al., 1992; Simpson and Spadaro, 2016). Compared to the EQS for Cu and Ni in coastal water (Guideline M608), background levels were exceeded for both metals at all stations (Fig. 2B). Also, MAC-EQS for Cu was exceeded at all stations and for Ni at the stations in Jøssingfjorden. The concentrations of Cu and Ni frequently exceeding EQS-values both in sediments and pore water at the pre-defined reference stations (REF11, REF27, REF30) confirmed dispersal of tailings across the deep sills surrounding the deposit site in Dyngadjupet, as noted by Olsgard and Hasle (1993).

The maximum concentrations of Cd, Pb and Zn (0.1 μg Cd g^{-1}, 17 μg Pb g^{-1} and 48 μg Zn g^{-1}) were all within background levels for coastal sediments (Guideline M608). For Pb and Cd the maximum concentrations were found at the most remote reference station (REF30). The maximum concentration of Zn was found in the inner part of Jøssingfjorden (JF28), but the statistical comparison showed no significant differences between Jøssingfjorden and the reference area for any of these metals (Table 2).

The surface sediments in Jøssingfjorden were clearly more contaminated than the surface sediments in the more recently abandoned deposit in Dyngadjupet. This is reasonably explained by the ongoing discharges, which will contribute to slow down the remediation process. The total discharge of 496 tons of particles corresponds to a sedimentation rate of about 2 mm y^{-1}. Compared to typical the typical background fluxes of 1 mm y^{-1} in such environments (Syvitski et al., 1986), the contribution of the ongoing discharges can be expected to have a significant impact on the current composition of the surface sediments in Jøssingfjorden. This was confirmed by the increasingly black appearance of the sediments when approaching the head of the fjord. Simultaneously, the light grey colour of the surface sediments in Dyngadjupet provided no evidence for any transport of these particles beyond the mouth of Jøssingfjorden.

4.4. Macrofaunal composition – past and present

All stations had a normal or high species richness, and the abundance was in general high (Table 3). According to the Norwegian classification system (Guideline 02:2013 - rev, 2015) and the Water-Framework Directive, the indices generally corresponded to "good" ecological status at stations 3, 37, 9 and 19, and "very good" at station 55. The only exception was ES_{100}, which corresponded to "moderate" status at station 37. In the multivariate analyses, the fauna was clustered in two main groups; the two stations 3 and 37 inside the fjord and the three stations 19, 9 and 55 outside (Fig. 6), which again shows that there is a clear gradient in faunal composition from the head of Jøssingfjorden towards the open sea.

Station 3, situated in the older deposit in Jøssingfjorden, has been monitored since 1983 when the fauna was highly impoverished with only three macrofaunal species recorded (Olsgard and Hasle, 1993). In 1985, just one year after relocation of the discharge to Dyngadjupet, the ecological status improved markedly. In 2015, the soft bottom fauna was classified as class II "good", but close to the limit value for class III "moderate" (Trannum, 2016). It is worth noting that in addition to the black appearance of the sediment surface, some of the specimen at this station were discolored and black particles were also present in the tube of the annelid *Galatowenia oculata*.

Station 37 had a very high number of individuals, which lead to lower diversity indices than station 3, although the species number was somewhat higher (Table 3). The faunal composition was markedly different from the other stations (Fig. 6). The reason for this is most likely the coarse sediment, low content of organic matter and presumably stronger bottom currents, which generally are important structuring variables for the faunal composition (Gray and Elliott, 2009). In 1988, the station was dominated by highly pollutant tolerant species (*Chaetozone setosa* and *Heteromastus filiformis*) (Olsgard and Hasle, 1993), but in 2015 the station was dominated by the filter feeding phoronids and the bivalve *Kurtiella bidentata* (Trannum, 2016). Notably, black sediments were observed on the surface at this station both in the grab samples and in the box-core sample from the nearby station JF1.

Station 9, situated in Dyngadjupet, where tailings were deposited during 1984–1994, has not been investigated previously. Although less visible on the sediment surface than the stations inside Jøssingfjorden, compact tailings were clearly present below the surface and pollution-tolerant species were recorded, like the annelids *Heteromastus filiformis* and *Paramphinome jefferysii*. Thus, also this station is considered to still show signs of disturbance due to the previous tailings deposition.

Station 19, south of the deposit sites, has previously been reported to be influenced by tailings (Det Norske Veritas, 2008), evidenced by high ilmenite levels and abundance of pollution-tolerant species. In 2015, the sediment was covered with a thin layer of grey sediment with some shell debris and anthropogenic waste (fishing line and cigarette butt), but black, compact tailings dominated below the sediment surface. The PCA-analyses of the chemical parameters on the nearby station DD2 showed that in spite of high TOC content, this station was most similar to the tailings-impacted Dyngadjupet cluster (Fig. 3). The tolerant annelid *Heteromastus filiformis* dominated the fauna, like in a previous monitoring (Det Norske Veritas, 2008), indicating some disturbance effect. The same species also dominated the fauna in the eighties, but the abundance was then considerable higher. In 2015, the diversity index H′ was on the same level as in 1983, prior to deposition in Dyngadjupet. Thus, this station has to a large extent improved, but still shows some disturbance effects.

Station 55 is the most remote from the deposition areas, but this location has previously shown some indications of elevated content of tailings in the sediment. In the late eighties the diversity index H′ was approximately 4.5 compared to 5.8 and "very good" conditions in 2015 (Olsgard and Hasle, 1993; Trannum, 2016). Further, in 2015 the faunal composition did not show any dominance of typically pollution-

indicator species. This was consistent with the observations at the nearby chemistry station (REF30) which had the lowest concentrations of tailings-enriched metals such as Ni, Cu and Co and the highest concentrations of the tailings-depleted metals Pb, Cd and Mn.

To conclude, there are clear signs of faunal restitution of the entire area. The general experience from restitution with regard to tailings deposition, is that the initial colonization of tailing-impacted sediments is rapid and occur within 1–2 years (Ellis and MacDonald, 1998; Burd, 2002), which also have been observed in Jøssingfjorden (Olsgard and Hasle, 1993). However, up to several decades may be required before the faunal composition has returned to its original state (Ellis and Hoover, 1990; Burd, 2002). This also seems to be the case in the present study, where there are still signs of prevailing disturbance effects. Further, as for the chemical status, the ongoing discharges of suspended particles is assumed to slow down the restitution process.

4.5. Relationship between fauna and environmental conditions

Only four stations could be tested for a relationship between the fauna and environmental variables, which restricted the variation in the biological data and the possibility for revealing correlative patterns. It is also important to be aware that three of the stations were placed outside the fjord, and one inside, and this difference dominated the ordination pattern. Such natural fjord gradient is considered highly important for the faunal structure, but not well reflected in the environmental data. This may explain why there were no significant environmental variables identified in the sequential test in DistLM.

On the other hand, in the marginal test in DistLM, depth and sediment fine fraction as well as Cu were identified as significant variables (Table 5). Depth and sediment characteristics are well-known descriptors for soft-bottom fauna (e.g. Ellingsen, 2002; Gray and Elliott, 2009). Depth is, however, less important as a factor per se, but rather represents several factors that determine the basic conditions for the fauna, for instance bottom currents, temperature, supply of food and quality of organic material (Oug, 1998; Goginaa et al., 2010; McCallumc et al., 2010). In the present study, sediment fine fraction can both reflect natural sediment variability as well as the presence of tailings. The tailings contain fine-grained fractions which also appears to be present in the current discharge at the head of Jøssingfjorden and which may disperse longer distances in the sea than the bulk of the tailings which will settle close to the discharge pipe. Thus, the ongoing discharge may explain the high concentration of fines at the innermost station, but at station 19 the high concentration of fines (Table 3) more likely result from lateral dispersal of fines from the old tailings discharge point near station 9.

Regarding Cu, which also came out as a significant variable in the marginal test, it is important to be aware that it co-varied with other tailings-associated parameters like sediment fine fraction, Fe, Co, Ni and to some extent Zn (Fig. 7). Such correlations make it more difficult to point out one single factor as responsible for the observed effects on the macrobenthic community. Thus, the tailings-induced gradient as such is considered a structuring factor, although the various parameters associated with it are ranged differently, with a likely most pronounced influence by Cu. Additional support for the impact of tailings distribution on faunal gradients is that the PCA-analyses based on chemical parameters in a higher number of samples (Fig. 3), and the DistLM-analysis including fauna communities (Fig. 7) gave highly similar patterns.

Ni and Cu are known to be toxic at high concentrations and, as mentioned above, both frequently exceeded EQS levels in pore water and sediments from both deposits (Fig. 2). Adverse effects of Cu on benthic macrofaunal structure have been documented in experimental approaches (Stark, 1998; Olsgard, 1999; Trannum et al., 2004) and from field data (Rygg, 1985). Community-level consequences of Cu-toxicity include macrobenthic changes in phylum, class and species representation, reduced diversity, altered lifestyles, biomass, density and body size (Neira et al., 2011). At Island Copper Mine (Canada), Cu-concentrations exceeding 300 mg/kg sediment initiated a distinct and consistent downward shift in species numbers (Burd, 2002). Furthermore, at the 40-year old sea deposit site in Repparfjorden, where Cu-mining took place in the 70ties, Cu-levels are still high and far exceeding EQS-values (Sternal et al., 2017). Like in the present study, Cu was found to be significantly correlated to the faunal structure (Trannum et al., in prep). Bioaccumulation of Cu from mining activities has been reported for blue mussels (*Mytilus edulis*) from Prince Williams Sound (Koski et al., 2008) and in year-rings of stone corals (Porites) after an accidental spill of sulphide tailings in the Philippines in 1996 (David, 2003). In the present study, the gastropods (*Hinia reticulate*) doubled their tissue concentrations of Cu, Ni and Co during the mesocosm exposure to sediments from Jøssingfjorden. In a recently conducted mesocosm experiment with fresh Titania-tailings, considerable faunal mortality was observed, which are in line with the field observations in the present study (Trannum and Schaanning, 2017).

A factor not measured, but which may have contributed to faunal impacts, is particle shape. Mechanical crushing of ore will most likely cause the tailings grains to have high angularity (Kvassnes and Iversen, 2013), and tailings from Titania have been observed to be rather sharp-edged compared to natural sediments (Skei, 1985). For Jøssingfjorden, Olsgard and Hasle (1993) stated that this may create additional difficulties for the deposit feeders and the interstitial fauna and reduce the number of species able to live in sediments dominated by tailings.

5. Conclusions and recommendations

Waste material from the mining operations was easily identified as black, fine-grained particles present on the sediment surface and beneath a thin layer of more greyish sediments in Dyngadjupet. Concentrations of Ni, Cu and Co in the top 0–1 cm sediment layer were high compared to natural back-ground levels and toxicity-based EQS values, but lower than the concentrations in currently produced tailings and deep deposit layers. DGT-profiles showed no release of metals from deep deposit layers. However, Ni, Cu and Co were mobilized in the oxidizing environment near the sediment surface, i.e. 10 mm depth in Jøssingfjorden and a few mm deeper in Dyngadjupet. The mobilized Co appeared to reprecipitate as Co(III)oxides which were stable until burial to the depth at which Mn(III-IV)oxides also became unstable, i.e. about 25 mm depth in both deposit sites. In addition to sedimentation of tailings from still active discharges to the water-column in Jøssingfjorden, tailings may be mixed upwards to the sediment surface from deeper deposit layers by the activity of bioturbators such as *Heteromastus filiformis* which were abundant at the old deposit sites. The total release of Ni from the investigated sea areas was estimated to be about 15% of the current leaching from the Tellenes land deposit. Below the bioturbated surface layer, the sea deposits appeared to act as permanent sinks for the tailings associated metals Ni, Cu and Co.

Organic carbon and fluxes of O_2 and nutrients were generally low throughout the investigated area. Increased release of phosphate and ammonia at the deposit sites were consistent with high abundancies of these compounds previously observed in deep deposit layers. The small, but significantly elevated consumption of O_2 may be explained by oxidation of metal sulphides or intermittently formed elemental sulphur. The classification of benthic communities varied from the lower range of “good” condition with clear signs of disturbance at the head of Jøssingfjorden to “very good” at the reference stations. A multivariate statistical analysis showed that in addition to depth and particle size, concentration of Cu was correlated to the gradients in the community structure. We conclude that the tailings-induced gradient is a main structuring factor for the faunal communities, although the various parameters associated with it are ranged differently, with the most pronounced influence by Cu. Although there are clear signs of faunal restitution of the entire area, the on-going discharge of particles in Jøssingfjorden is assumed a major factor contributing to slow down the

restitution process.

The improved understanding of metal cycling in the old sea deposits presented in this paper are potentially useful for development of best available technologies (BAT) for mine tailings disposal. Mobilization of Cu, Ni and Co from the sea deposit primarily depends on the surface area and time of exposure in the oxidizing environment near the sediment surface. Therefore, deep fjord basins with large deposit volume and small surface area provide suitable natural locations for deposition of sulphide tailings. If natural bathymetric structures with appropriate capacity are not available, subsea dam constructions may be implemented to increase the volume and reduce the areal extent of the sea deposit. After the discharge is closed, capping with marine clay or other suitable materials may be undertaken to reduce the time required for natural burial of the tailings beyond the depth of bioturbation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2019.02.047.

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