



Pb isotopes as tracers of mining-related Pb in lichens, seaweed and mussels near a former Pb-Zn mine in West Greenland

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Lead isotopes can be used to monitor uptake of mining-related lead in lichens, seaweed and mussels.

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ABSTRACT

Identification of mining-related contaminants is important in order to assess the spreading of contaminants from mining as well as for site remediation purposes. This study focuses on lead (Pb) contamination in biota near the abandoned 'Black Angel Mine' in West Greenland in the period 1988–2008. Stable Pb isotope ratios and total Pb concentrations were determined in lichens, seaweed and mussels as well as in marine sediments. The results show that natural background Pb ($^{207}\text{Pb}/^{206}\text{Pb}$: 0.704–0.767) and Pb originating from the mine ore ($^{207}\text{Pb}/^{206}\text{Pb}$: 0.955) have distinct isotopic fingerprints. Total Pb in lichens, seaweed, and mussels was measured at values up to 633, 19 and 1536 mg kg⁻¹ dry weight, respectively, and is shown to be a mixture of natural Pb and ore-Pb. This enables quantification of mining-related Pb and shows that application of Pb isotope data is a valuable tool for monitoring mining pollution.

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1. Introduction

Mining for lead (Pb) and zinc (Zn) poses a well-known environmental problem due to the potential release, spread and uptake of Pb, Zn and other associated heavy metals in biota. Identification of mining-related heavy metals and their contribution to the surrounding environment is therefore important in order to assess the impact from mining, for subsequent site remediation as well as to assess various legal issues, particularly where the polluter-pays-principle is applied. Traditionally, total concentrations of heavy metals have been used to evaluate the contribution from mining (Riget et al., 1997; Sanchez et al., 1998; Johansen et al., 2008), but often there is a need to further identify the metals relating to the mining activity as natural background concentrations are often unknown, may vary considerably and may be higher near the mine area due to weathering of natural exposed ore material (Graham and Kelley, 2009). Use of Pb isotopes provides such an identification tool as the isotopic composition of Pb exhibits a large natural variability and often provides a fingerprint that can be used to determine its source (e.g. Komárek et al., 2008).

In the natural environment Pb is mainly present as four isotopes: ^{208}Pb (~52%), ^{206}Pb (~24%), ^{207}Pb (~23%), and ^{204}Pb (~1%). Of these, ^{208}Pb , ^{207}Pb , and ^{206}Pb are radiogenic and products of the radioactive decay of ^{238}U , ^{235}U , and ^{232}Th , respectively.

Consequently, the Pb isotopic composition of a given sample depends on the age and content of ^{238}U , ^{235}U , ^{232}Th , ^{208}Pb , ^{206}Pb , ^{207}Pb and ^{204}Pb in the parent material from which the Pb was derived (Köppel and Grünfelder, 1979). Pb ores most often consist of galena (PbS), which contains negligible amounts of U and Th (Willan and Swainbank, 1995). Therefore, the Pb isotopic composition of galena is preserved from the moment of formation. The lack of U and Th in galena in contrast to most other rock types often allows for a Pb isotopic distinction between ore/galena Pb and natural background Pb (Hansmann and Köppel, 2000; Zhang et al., 2009). In contrast to many of the lighter isotopes, Pb isotopes are not measurably fractionated in industrial and biological processes, allowing them to serve as long-term tracers of anthropogenic and natural Pb sources (Ault et al., 1970; Graney et al., 1995).

Traditionally, highly precise and accurate isotope ratio measurements of Pb have been taken using Thermal Ionisation Mass Spectrometry (TIMS) (e.g. Weiss et al., 1999), at the expense of time-consuming sample preparation and analysis. For simpler and faster analysis, studies using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with a quadrupole-type mass spectrometer have demonstrated that, although not as precise as TIMS, this

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technique provides sufficient precision for most environmental applications (Quétel et al., 1997; Monna et al., 1998; Munksgaard et al., 1998).

Lichens, seaweed and mussels have been used in numerous studies as biological indicators of metal contamination from mining (Riget et al., 1997; Komárek et al., 2008; Turner et al., 2009). These species are well-suited as they are easy to analyse, widely distributed, able to concentrate metals, and reflect contamination both in the terrestrial and marine environment. A number of studies have applied Pb isotopes measured in lichens to identify anthropogenic Pb sources of air pollution (Spiro et al., 2004; Dolgoplova et al., 2006; Monna et al., 2006). However, few studies have used isotopic Pb data in marine biota to identify anthropogenic Pb sources in the marine environment, including mining (Spencer et al., 2000; Labonne et al., 2001; Ip et al., 2005).

In this study, Pb isotope ratios have been determined by ICP-MS in lichens, seaweed and mussels as well as in marine sediment sampled near the abandoned 'Black Angel Mine' in Maarmorilik, West Greenland (Fig. 1). The mine was in operation in the period 1973–1990, during which exploitation of a Pb–Zn (galena-sphalerite) deposit took place. Prior to mining some environmental studies were performed, but these were insufficient to quantify baseline conditions with regards to Pb concentration in biota. Later, due to high Pb and Zn concentrations observed in sediment and biota, a programme of detailed environmental monitoring was implemented in Maarmorilik (Loring and Asmund, 1989; Asmund et al., 1991; Asmund, 1992; Elberling et al., 2002) and still continues (2010).

This study aims to: 1) investigate the use of stable Pb isotopes to identify mining-related Pb in lichens, seaweed and mussels collected within the Maarmorilik area over the last 20 years; 2) quantify the temporal and spatial trends of mining-related Pb contamination in lichens, seaweed and mussels in Maarmorilik; 3) based on the above discuss the use of lichens, seaweed and mussels as bio-indicators; and 4) discuss the more general application of Pb isotopes as tracers of mining pollution.

2. Site description

Maarmorilik is located adjacent to the two small fiords, Affarlíkassaa and Qaamarujuk, in the inner part of the Uummannaq fiord system in West Greenland (71°07' N; 51°15' W) (Fig. 1). Qaamarujuk is part of a fiord complex that is connected directly to Baffin Bay (the open sea). The closest community is Ukkussissat, 25 km to the west, and the main settlement, Uummannaq, is situated 80 km south of Maarmorilik. The climate in Maarmorilik is arctic with maximum summer temperatures of 10 °C and winter temperatures below –30 °C. Water temperatures in the fiords range from –2 to +5 °C and ice usually covers the fiords from October to May, with a maximum ice thickness of 0.5–1 m. The tidal range in the fiords is approx. 1 m. The wind regime in Maarmorilik is dominated by strong easterly winds coming from the inland ice cap in the bottom of the Qaamarujuk fiord, resulting in sparse precipitation in the area.

Geologically, the name 'Maarmorilik' refers to a formation of calcitic and dolomitic marble, and in the 1930s a small marble quarry was located in Maarmorilik (Thomassen, 2003). The Maarmorilik Formation is part of the Palaeoproterozoic Karrat Group, which belongs to the Archean Foxe-Rinkian mobile belt complex of North-East Canada and Central West Greenland (Escher and Pulvartaft, 1976). Carbonate-hosted lead-zinc ores are common in the Maarmorilik Formation, primarily in the 'Black Angel' mountain. The name 'Black Angel' refers to a pelite outcrop that forms a dark angel-like figure high on a 1100 m cliff face of marble above the Affarlíkassaa fiord. The massive ores consist of galena (PbS), sphalerite (ZnS) and pyrite (FeS₂), with accessory ore minerals such as pyrrhotite, chalcopyrite, tennantite and arsenopyrite. Originally, the Black Angel deposit comprised ten ore bodies with a total of 13.6 million tonnes, grading 4.0% Pb, 12.3% Zn, and 29 ppm Ag. Out of these, 11.2 million tonnes were extracted in the period 1973–90 by the mining company Greenex A/S (Thomassen, 2003).

In the mining process, ore material was transported from 600 m altitude by means of cable cars across Affarlíkassaa to

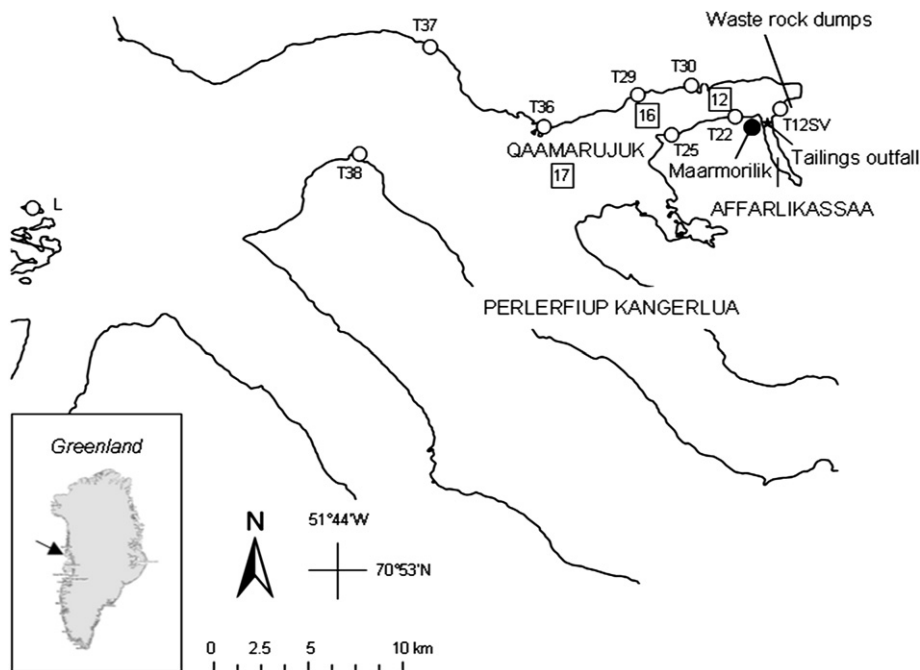


Fig. 1. Map of Maarmorilik and the surrounding area in West Greenland. The location of the tailings disposal area, waste rock dumps, sediment sampling sites (12, 16, and 17), and biota sampling sites (T12SV to L) are illustrated. The dot marks the location of the ore treatment plant (now removed).

a flotation plant in Maarmorilik. Here, concentrates were produced, loaded onto ships and transported to smelters in Europe. The ore treatment included conventional rod milling/ball milling to liberate Pb and Zn, followed by froth flotation to produce separate Pb and Zn concentrates, with production of a waste product, tailings (Poling and Ellis, 1995). Permission for submarine disposal of tailings was given to the mining company and the tailings were discharged directly into the inner fiord, Affarlikassaa, at around 30 m depth. In the 1970s, the annual tailings input from the flotation mill to the Affarlikassaa fiord was 4.5×10^5 t, which increased to 6×10^5 t in the 1980s. During the mining period it is estimated that more than 8×10^6 t of mine tailings containing more than 2.2×10^4 t Pb and 5×10^4 t Zn were discharged into Affarlikassaa (Elberling et al., 2002).

Affarlikassaa, which covers an area of 2 km² and has an average water depth of 30 m is partly separated from the outer fiord, Qaamarujuk, by a sill at 23 m depth. During summer a distinct, well-defined, stagnant water mass develops below the sill. However, in winter, a complete mixing of the stratified water body takes place due to the cooling of the surface water (Møller, 1984). Exchange of metal-saturated bottom water in Affarlikassaa in the years after mine closure resulted in increased oxidation and dissolution of the tailings and subsequently a significant dispersal of contaminants to the outer fiord, Qaamarujuk. Other important sources of pollution were dust caused by ore crushing and handling of concentrates during the mining period and outwash from waste rock dumps left on the steep mountain sides. As part of the mine closure plan, 1990–91, one of the most polluting waste rock dumps was moved to the extent that was possible and dumped on the tailings deposit in Affarlikassaa. After mine closure, the concentration of Pb in the bottom water in Affarlikassaa decreased by a factor of 1000 from $255 \mu\text{g Pb L}^{-1}$ in 1988 to $11 \mu\text{g Pb L}^{-1}$ in 2005 (Johansen et al., 2006). The latter is near the concentration measured in unpolluted reference sites. Continued dispersal of Pb-containing dust, however, has been monitored in Maarmorilik using transplanted lichens. This indicates that the most important source of pollution to the marine environment in Maarmorilik has changed in the years after mine closure from being tailings deposits to, in recent years, being the dispersal and outwash of contaminated dust as well as metal release from waste rock dumps left on the slopes of mountains that were mined (Johansen et al., 2006).

3. Methods and instrumentation

3.1. Sampling of sediment and biota

Sampling was carried out as part of the environmental monitoring programme in Maarmorilik. Lichens, seaweed and mussels included in this paper were sampled in the period 1988–2008 at the nine sites (T12SV to L) shown in Fig. 1. Only lichens (*Cetraria nivalis*) growing on dead organic matter were collected. The lichens collected thereby represent a measure of atmospheric dust deposition as they almost entirely accumulate metals from atmospheric dust and not from the underlying rock (it cannot, however, be ruled out that a minimal amount of Pb may accumulate from the dead organic matter). Lichens were kept in paper bags until analysis. Seaweed (*Fucus vesiculosus* or *Fucus distichus*) was sampled in the tidal zone directly from the shore, rinsed three times in demineralised water in the mine camp and frozen in polyethylene bags. Only the growing tips were sampled in order to represent recent metal uptake. Likewise, blue mussels (*Mytilus edulis*) were also collected from the shore. A sample consisted of 20 individual mussels and only mussels having a 5–7 cm shell length were included in the present study. Following collection, the adductors of the mussels were cut and the mussels were allowed to drain. The soft tissue was then cut out of the shells using a stainless steel scalpel, weighed and frozen in polyethylene bags.

Sediment sampling was conducted in August 2005 onboard R/V Adolf Jensen at Site 12, 16, and 17 as well as at the location of the tailings disposal area (Fig. 1). Cores from each site were collected using a sediment box corer (HAPS) made of stainless steel with an inner diameter of 13.5 cm. Penetration depths of the cores were between 15 and 20 cm, and only cores containing both bottom water and an intact water/sediment interface were considered intact and sampled. Bioturbation could not be observed. The cores were cut into slices at 1 cm intervals and sediment that

had been in contact with the HAPS was carefully removed prior to sampling. Samples were then kept in polyethylene bags at temperatures near 2 °C until analysis took place in Denmark.

3.2. Chemical analysis

Biological samples were freeze-dried, homogenised in an agate mortar and microwave-digested in suprapure nitric acid using Teflon bombs at the National Environmental Research Institute (NERI) in Denmark. Sediment samples were digested in hydrofluoric acid. Thereafter, Pb and Zn concentrations were determined either using flame AAS (Perkin-Elmer 3030) or graphite furnace AAS (Perkin-Elmer Zeeman 3030). A few Pb and Zn measurements were also determined using an Agilent 7500ce ICP-MS. The analytical methods have earlier been described in Asmund et al. (2004) and quality was continuously checked by analysing blanks and duplicates as well as the certified reference materials Tort-2, Dorm-2 and Dolt-3 among others.

Selected sediment samples and biological samples were subsequently analysed for Pb isotopes. The sediment samples selected include five deep samples (below 7 cm's depth) from Site 12, 16, and 17 (Fig. 2), representing layers older than 10 years prior to the opening of the mine in 1973. The site-specific age of the sediment is based on previously established chronologies using the ²¹⁰Pb isotope (Elberling et al., 2002). These deep sediment samples were used to determine the natural (pre-mining) background isotopic fingerprint at the three locations. Pb concentrations measured in deep sediment at the three sites were consistent with depth and varied only slightly between sites (Site 12: $25 \pm 0.4 \text{ mg kg}^{-1}$; Site 16: $21 \pm 3 \text{ mg kg}^{-1}$; Site 17: $18 \pm 1 \text{ mg kg}^{-1}$), indicating that the sediment samples have not been influenced by the 1973–1990 mining activity. Note, however, that elevated Pb concentrations were observed below the 1973 line at Site 16 (Fig. 2), which is likely either to be due to bioturbation or to inaccuracy in the chronology. Five sediment samples (2–6 cm's depth) from the tailings disposal area were taken to determine the Pb isotopic composition of the tailings. These samples contained very high Pb concentrations (3000–4400 mg kg⁻¹), similar to concentrations reported in the tailings production record (Dahl, 1994). Biological samples selected for Pb isotope analysis included lichens, seaweed and mussels sampled in the years 1988, 1992, 1995, 1998, 2002, 2005, 2007 and 2008.

Lead isotope ratios in samples were analysed using an Agilent 7500ce ICP-MS (with a quadrupole mass spectrometer) and the masses 202, 204, 206, 207 and 208 were measured. The instrument was set in 'Isotope Ratio Analysis' mode with 1000 scan/s, and integration times were set to: 20 s for 202 and 204; 10 s for 206 and 207; and 5 s for 208. Each data point is the average of 3 repetitions. Corrections for Hg interference on mass 204 were made by using the counts detected on mass 202 and the IUPAC isotopic abundance of ²⁰²Hg and ²⁰⁴Hg. A 20 ppb solution of NIST SRM 981 isotope ratio standard was measured after every five samples and the samples corrected for instrument mass bias. The ratio correction factors obtained were typically in the range 0.99–1.01 for corrections to ²⁰⁸Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁴Pb/²⁰⁶Pb ratios. Samples were diluted to a concentration of < ~50 ppb Pb to ensure that detection always remained within the range of the 'pulse' mode. Analytical precision of the measured ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios (RSD on 3 replicate measurements) ranged from 0 to 1% but was typically <0.5% for both the ratios. Precision of the ²⁰⁴Pb/²⁰⁶Pb was slightly poorer due to the low content of ²⁰⁴Pb in the samples (~1% of total Pb) and ranged from 0 to 2% but was generally <1%. The precisions obtained show that for this study the applied ICP-MS provided a fast, cost-effective and adequately precise analytical technique.

4. Results and discussion

4.1. Pb isotopes in tailings and sediment

The characteristics of tailings from Maarmorilik and of natural sediment (from before the mine started) measured at Site 12, 16, and 17 are listed in Table 1.

The observed ²⁰⁴Pb/²⁰⁶Pb, ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb ratios reveal that the isotopic composition of Pb found in tailings (²⁰⁴Pb/²⁰⁶Pb: 0.0621; ²⁰⁷Pb/²⁰⁶Pb: 0.955; and ²⁰⁸Pb/²⁰⁶Pb: 2.253) is very different from Pb found in natural sediment in Maarmorilik (²⁰⁴Pb/²⁰⁶Pb: 0.0438–0.0488; ²⁰⁷Pb/²⁰⁶Pb: 0.704–0.767; and ²⁰⁸Pb/²⁰⁶Pb: 1.842–1.934). This enables a differentiation to be made between mining-related Pb and natural background Pb. The term 'mining-related Pb' used here covers Pb found in tailings, waste rock and concentrates associated with the mine ore, as Pb isotopes are not measurably fractionated during the mining process. Natural background Pb originates presumably mainly from natural weathering of Pb-bearing rocks within the catchment area of the fiord. Similar Pb isotope compositions have previously been

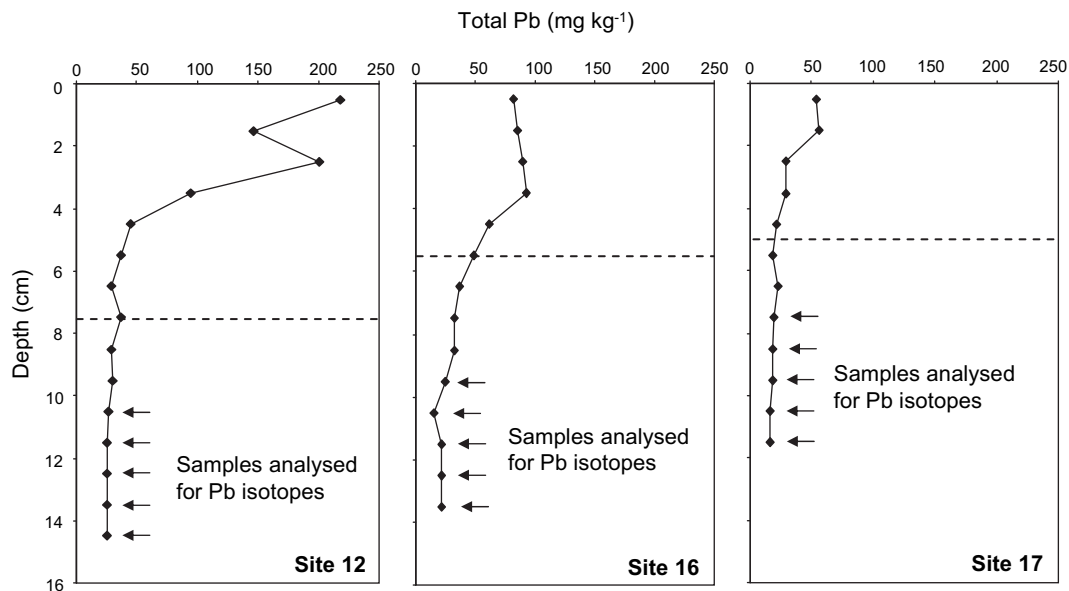


Fig. 2. Profiles at Site 12, 16, and 17 showing total Pb concentration in the sediments. The dashed line corresponds to 1973, when mining commenced (based on chronologies established by Elberling et al. (2002) using ^{210}Pb). The sediment samples analysed for Pb isotopes and used as natural background Pb isotopic fingerprints for the three sites are indicated with arrows.

reported for Pb ores and Pb contained in Precambrian rocks, comprising most of the geologic setting in Maarmorilik (Munkegaard et al., 1998; Frei et al., 2009).

The background fingerprint of Site 12, which is situated nearest to the mine, is closer to the tailings fingerprint than that of Site 16 and 17. Similarly, Pb concentrations in sediment from Site 12 are slightly higher ($25 \pm 0.4 \text{ mg kg}^{-1}$) compared to Site 16 ($21 \pm 3 \text{ mg kg}^{-1}$) and Site 17 ($18 \pm 1 \text{ mg kg}^{-1}$). The concentrations measured at Site 12 correspond to those reported in Elberling et al. (2002) for similar layers as well as for deeper layers dating back to before 1880 at Site 12. These slightly elevated Pb concentrations and $^{204}\text{Pb}/^{206}\text{Pb}$, $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios observed in background sediment nearest to the mine site are likely to be due to weathering of natural exposed ore material. Natural, elevated Pb concentrations in biota near Pb-Zn ores in other parts of the Uumannaq fiord system have previously been observed (Johansen et al., 1996).

4.2. Pb isotopes in biota and quantification of mining-related Pb

The isotopic compositions of Pb found in all lichens, seaweed and mussels are listed under 'Supporting Information', Tables S1–S3. The data expressed as $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ ratios measured in lichens, seaweed and mussels is shown in Fig. 3a,b and c, respectively. Data points for all the three species are well-described using a linear regression fit ($r^2 = 0.99$; $p < 0.001$) between a concentrated and well-defined tailings Pb fingerprint and a natural background Pb fingerprint. The latter is less well-defined and varies slightly between sites. The linearity of the data

points with natural background Pb and mining-related Pb as end-members shows that Pb contained in the biota in Maarmorilik can be described as a two-phase mixture between natural background Pb and mining-related Pb. The same conclusion can be applied also if ^{204}Pb is included (a $^{204}\text{Pb}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ plot gives a linear trend with $r^2 = 0.98$; $p < 0.001$). Consequently, the fraction of mining-related Pb taken up in lichens, seaweed and mussels in the affected area can be quantified. The mining-related Pb fraction is here estimated based on a simple binary mixing equation (Shotyk et al., 1997):

$$\frac{(^{207}\text{Pb}/^{206}\text{Pb})_{\text{sample}} - (^{207}\text{Pb}/^{206}\text{Pb})_{\text{background}}}{(^{207}\text{Pb}/^{206}\text{Pb})_{\text{ore}} - (^{207}\text{Pb}/^{206}\text{Pb})_{\text{background}}} \cdot 100(\%) \quad (1)$$

where $(^{207}\text{Pb}/^{206}\text{Pb})_{\text{sample}}$, $(^{207}\text{Pb}/^{206}\text{Pb})_{\text{ore}}$, and $(^{207}\text{Pb}/^{206}\text{Pb})_{\text{background}}$ are the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios measured in the biota sample, in the mine tailings ($^{207}\text{Pb}/^{206}\text{Pb}$: 0.955) and in the background sediments, respectively. As the isotopic background fingerprint varies slightly between sites, the quantification of mining-related Pb in biota at Site T12SV and T22 is based on the background fingerprint found in natural sediments at Site 12 ($^{207}\text{Pb}/^{206}\text{Pb}$: 0.767); T25, T29, and T30 at Site 16 ($^{207}\text{Pb}/^{206}\text{Pb}$: 0.704); and T36, T37, T38, and L at Site 17 ($^{207}\text{Pb}/^{206}\text{Pb}$: 0.709). Note that when using this method and a background isotopic fingerprint specific for the area close to the mine (Site 12), it is possible to account for the pre-mining level of natural ore-Pb weathering near the mine when assessing the mining-related Pb contribution. As average $(^{207}\text{Pb}/^{206}\text{Pb})_{\text{background}}$ values were used for Site 12, 16, and 17 and since this ratio showed some variation (Fig. 3, Table 1) the quantification of mining-related Pb in samples with an isotopic

Table 1
Total Pb and Zn and measured Pb isotope ratios (mean \pm one std. dev.) contained in tailings dumped in the Affarlikassaa fiord near Maarmorilik and in natural sediments at Site 12, 16, and 17 (n = number of samples).

	Pb (mg kg^{-1})	Zn (mg kg^{-1})	$^{204}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	n
Tailings A. Fiord	3500 ± 500	4500 ± 900	0.0621 ± 0.0002	0.955 ± 0.002	2.253 ± 0.006	5
Natural sediment Site 12	25 ± 0.4	146 ± 2	0.0488 ± 0.0004	0.767 ± 0.004	1.934 ± 0.011	5
Natural sediment Site 16	21 ± 3	109 ± 16	0.0438 ± 0.0009	0.704 ± 0.011	1.842 ± 0.029	5
Natural sediment Site 17	18 ± 1	90 ± 4	0.0444 ± 0.0009	0.709 ± 0.012	1.862 ± 0.019	5

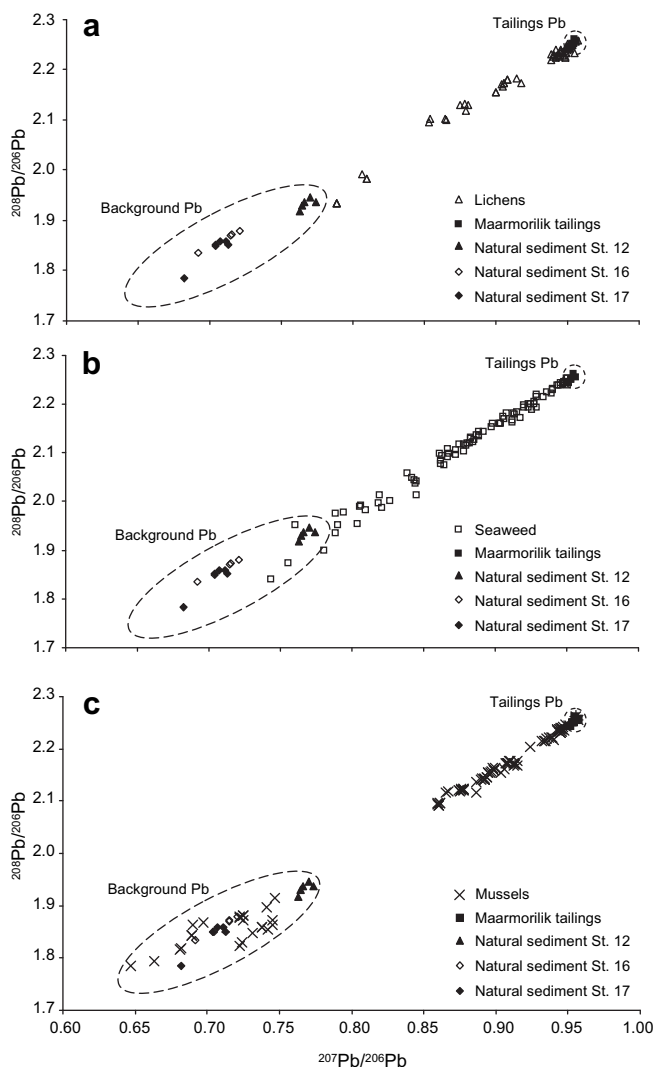


Fig. 3. Relationship between $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in tailings from the Affarlikassaa Fiord near Maarmorilik; in sediment from before the mine opened taken at Site 12, 16 and 17; and in sampled lichens (a), seaweed (b), and mussels (c). The isotopic fingerprint areas of natural background Pb measured in sediments and Pb contained in tailings are indicated.

composition close to that of background Pb will only be a very rough estimate.

4.3. Temporal and spatial variation in Pb contamination

Temporal variation in total Pb measured in lichens, seaweed and mussels in the period 1988–2008 for a typical high-, medium- and low-impact site is shown in Fig. 4. In addition, based on the isotopic fingerprint of Pb contained in the samples, the fraction of mining-related Pb and background Pb (100% – mining-related fraction) is quantified using Equation (1) and the concentrations of background Pb are plotted. The mining-related Pb amount corresponds to the difference between total Pb and background Pb in Fig. 4.

Lichens, seaweed and mussels from the high-impact site (T12SV) contained the highest Pb concentrations; 633, 19, and 1536 mg kg^{-1} dry weight, respectively. This site is situated closest to the waste rock dump, the tailings deposit in Affarlikassaa and the ore treatment plant in Maarmorilik; these being the main sources of pollution in the area. The concentrations measured at T12SV for lichens and mussels were up to ~ 1000 times higher than for

corresponding samples collected at the site furthest away from the mine (Site L) located 35 km from Maarmorilik. Concentrations of Pb in seaweed were up to ~ 100 times higher. The isotopic fingerprints show that almost all the Pb in biota at Site T12SV can be attributed to the mining activity that commenced in 1973 (Fig. 4). Generally, as the distance from Maarmorilik increases, concentrations of total Pb in lichens, seaweed and mussels decreases (Fig. 4), but local site-specific conditions such as wind patterns, currents, sea-bed conditions, streams, etc also affect the uptake of mining-related Pb.

Total Pb concentrations in lichens, seaweed and mussels at all the sites included in this study show a decreasing trend from 1988, when the mine was still in operation, up until 2008 (Fig. 4). There is no clear explanation for the peak in total Pb observed in biota at several sites in 1998, but this could be due to a particularly effective dispersion of wind-borne particles and/or mixing and transport of metal-laden water from Affarlikassaa that year. The typical trend observed for biota in the Maarmorilik area including all sites (a total of 22–27 stations) is a log-linear decreasing trend in total Pb concentration in the period 1980–2007 (Johansen et al., 2008).

Despite the observed decrease in total Pb, in 2007–08, almost 20 years after mine closure, lichens, seaweed and mussels in Maarmorilik were still significantly contaminated by the past mining activity (Fig. 5). Closest to the mine, mining-related Pb accounts for almost 100% of the Pb found in all three species. At increasing distances from the mine the fraction of mining-related Pb in lichens, seaweed and mussels generally decreases. However, great variation in the fraction of mining-related Pb between the species analysed is evident. At the most distant site (Site L), approximately half of the total Pb in lichens and seaweed could be attributed to the 1973–90 mining activity, whereas significant amounts of mining-related Pb could not be traced in mussels further away than Site T36.

4.4. Lichens, seaweed and mussels as bio-indicators of mining contamination

The uptake of mining-related Pb is significant in lichens, seaweed and mussels in Maarmorilik and therefore provides information on mining contamination both in the terrestrial and marine environment. However, uptake and exclusion of metals by biota in response to increasing/decreasing environmental contamination is complex and depends on many factors such as species, biota-specific living conditions, feeding mechanisms, growth rates, age etc (Riget et al., 1997; Komárek et al., 2008; Turner et al., 2009).

The Pb contamination in lichens in Maarmorilik can be attributed to the spreading of Pb as dust (dry deposition) and most dust generation in Maarmorilik was associated with the milling process, which ceased when the mine was closed in 1990. However, although the amount of dust dispersed decreased after 1990, monitoring studies using lichens transplanted from unpolluted reference sites to Maarmorilik and collected the year after show that there is still significant dispersal of Pb-contaminated dust in the area (Johansen et al., 2006). In recent years, dust dispersal has possibly become the main source of contamination in Maarmorilik together with metal-release from waste rock dumps left on the mountain slopes (Johansen et al., 2006). The continuously high percentage of mining-related Pb observed in stationary lichens in Maarmorilik (Fig. 5) can be explained by the relatively low influence of other sources of dry deposited Pb in the area, the longevity of lichens (Hestmark et al., 2005) as well as an effective spreading of dust by the predominantly strong easterly winds.

In 2007–08, seaweed and mussels appeared to be less contaminated than lichens (except at Site L, where seaweed contained more mine-related Pb than lichens), indicating that the natural sources of Pb, presumably mainly the weathering of Pb-containing rocks in the area, contribute more to these marine

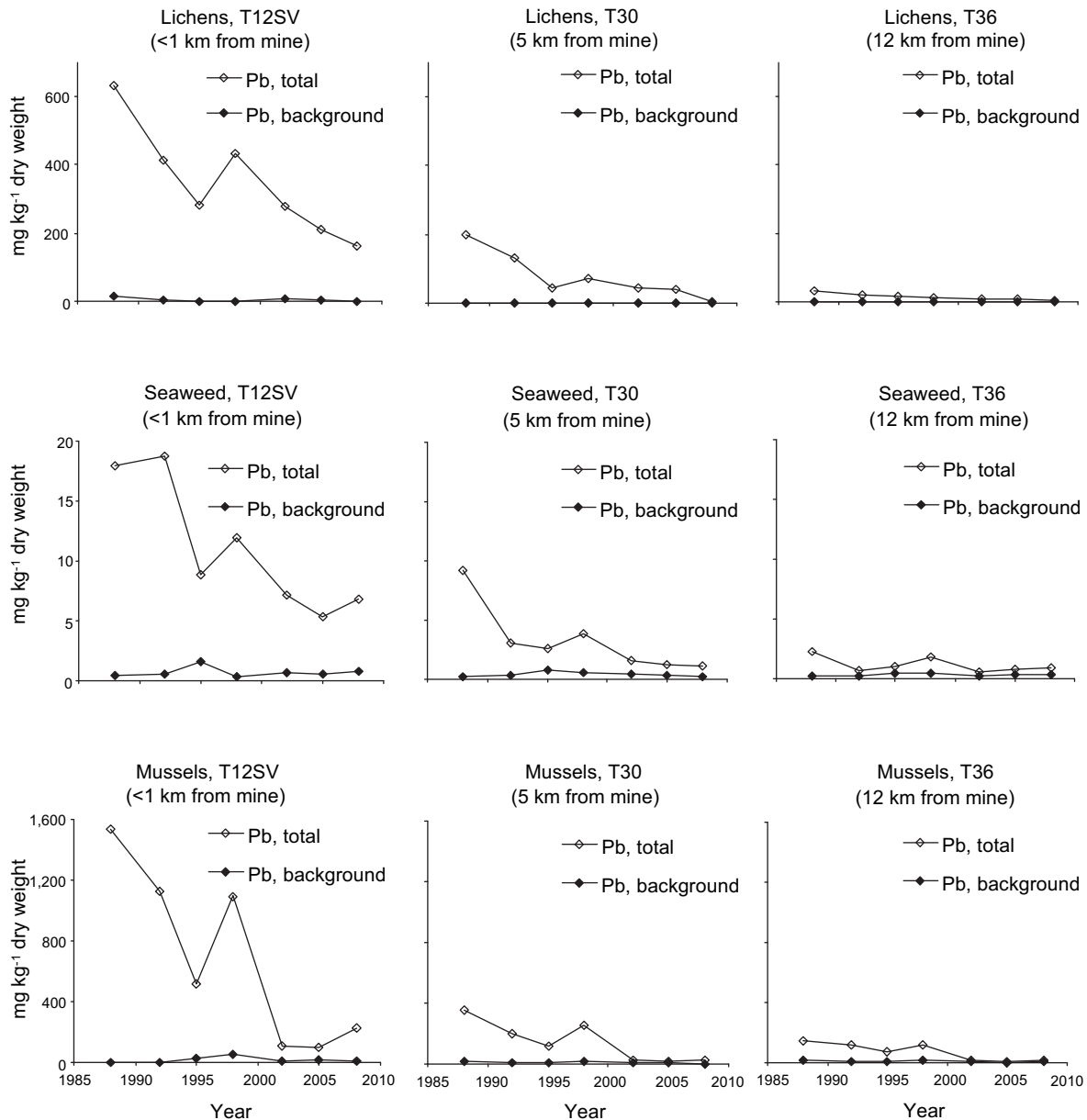


Fig. 4. Lead concentrations in lichens, seaweed and mussels from a typical high-impact site (T12SV), medium-impact site (T30), and low-impact site (T36) in the period 1988–2008 ($n = 1-2$). Both measured total Pb and quantified background Pb are shown. The mining-related Pb can be calculated as the difference between the two. Background Pb and mining-related Pb are quantified based on the isotopic fingerprints using Equation (1).

species than to lichens (Fig. 5). Mussels at the sites most distant to the mine (T37, T38, L) contained negligible amounts of mining-related Pb, whereas seaweed still contained 40–60%. These three sites are influenced by water from the side fiord to Qaamarujuk, Perlerfiup Kangerlua (Fig. 1). In seaweed the main source of metals is metals dissolved in the water, whereas metals accumulated in mussels reflect both dissolved metals as well as metals bound to food particles and sediment (Rainbow, 1995; Larsen et al., 2001). The observed differences in the percentage of mining-related Pb contained in seaweed and mussels situated at Site T37, T38, and L are therefore likely to be due to differences in the Pb fraction taken up as well as in the modes of dispersal and uptake, accumulation time, ability to excrete Pb, etc. Further studies are needed to address the differences observed in seaweed and mussels due to site-specific environmental conditions.

4.5. Pb isotope fingerprints as tracers of mine pollution

Baseline studies made prior to mining operations in Maarmorilik in 1972 and 1973 were not up to the standard of today. Consequently, it was unknown if concentrations of Pb and other elements in biota were naturally elevated in the area or exhibited a natural variation that differed from the sites used as reference sites. In this study, the Pb isotope data gave new insight in this regard and provided a way of tracing mining contamination in biota. The accuracy of using Pb isotopes as tracers of mining contamination in Maarmorilik was limited mainly by finding an adequate isotopic background fingerprint using natural (pre-mining settled) sediment. Natural sediment could not be sampled at the specific location where the biota was sampled and some site-specific isotopic variation was observed in the Qaamarujuk fiord (Fig. 3a–c; Table 1). However, for all sites (Site 12, 16 and

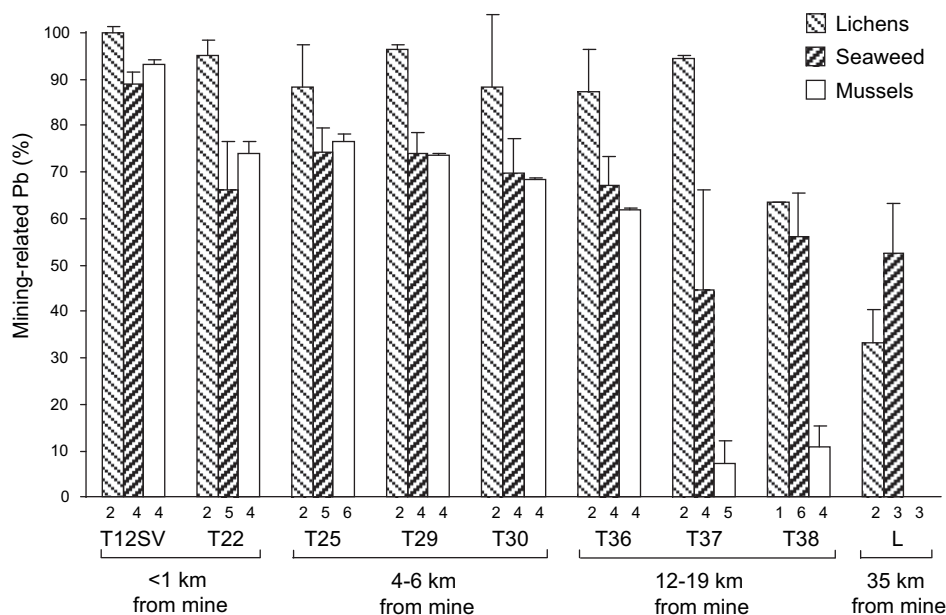


Fig. 5. Fractions of mining-related Pb relative to the total Pb amount in lichens, seaweed and mussels at the sites T12SV to L in 2007–08 estimated using Equation (1). The number of replicates is listed below each bar. The fraction of mine-related Pb in mussels at Site L was calculated to be slightly negative and was set to zero.

17) the isotopic background fingerprints differed widely from the tailings fingerprint. This situation is not uncommon in mining areas as Pb ores (galena) typically has an isotopic composition that differs from Pb contained in other rock types (Hansmann and Köppel, 2000; Miller et al., 2007; Zhang et al., 2009). Consequently, the use of Pb isotopes provides a valuable tool when adequate baseline studies prior to mining, revealing natural concentration levels and variability, do not exist or when an adequate reference site cannot be found. In addition, the Pb isotopic fingerprint may be effective in identifying a contamination source where Pb itself is not the critical element if the contaminant of interest has a mobility comparable to that of Pb.

5. Conclusion

This study shows that Pb isotope data can be used to trace mining-related Pb contamination in biota near a former Pb–Zn mine in Maarmorilik, West Greenland. Since no sufficient baseline studies exist, the isotopic Pb fingerprint offers a unique way of attributing the Pb subsequently measured in lichens, seaweed and mussels directly to the mining activity. In addition to determining the spatial and temporal variation in contamination in biota in the impacted area, the fingerprint provided information on the use of the species used as bio-indicators of mining contamination. Specifically, it is shown that at the same location and distance from the source, mining-related Pb in mussels was significantly less than in seaweed. Pb ores often have a distinct isotopic Pb fingerprint that differs from natural background fingerprints and in this study these could easily be separated using a standard quadrupole ICP-MS, and at relatively low cost. Consequently, isotopic Pb data could be applied more often as a routine monitoring tool for environmental dispersal of mining-related Pb and perhaps also other contaminants associated with mining.

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Appendix. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.envpol.2010.01.006.

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