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Published in:
Water, Air, and Soil Pollution

Link to article, DOI:
[10.1007/s11270-015-2416-4](https://doi.org/10.1007/s11270-015-2416-4)

Publication date:
2015

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Pedersen, K. B., Lejon, T., Jensen, P. E., & Ottosen, L. M. (2015). Chemometric Analysis for Pollution Source Assessment of Harbour Sediments in Arctic Locations. *Water, Air, and Soil Pollution*, 226(5), 1-15. DOI: 10.1007/s11270-015-2416-4

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Chemometric analysis for pollution source assessment of harbour sediments in Arctic locations

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Abstract

Pollution levels, pollutant distribution and potential source assessments based on multivariate analysis (chemometrics) were made for harbour sediments from two Arctic locations; Hammerfest in Norway and Sisimiut in Greenland. High levels of heavy metals were detected in addition to organic pollutants. Preliminary assessments based on Principal Component Analysis (PCA) revealed different sources and pollutant distribution in the sediments of the two harbours. Tributyltin (TBT) was, however, found to originate from point source(s) and the highest concentrations of TBT in both harbours were found adjacent to the former shipyards. Polyaromatic hydrocarbons (PAH) ratios and PCA plots revealed that the predominant source in both harbours was pyrogenic related to coal/biomass combustion. Comparison of commercial polychlorinated biphenyls (PCB) mixtures with PCB compositions in the sediments indicated relation primarily to German, Russian and American mixtures in Hammerfest; and American, Russian and Japanese mixtures in Sisimiut. PCA was shown to be an important tool for identifying pollutant sources and differences in pollutant composition in relation to sediment characteristics.

Keywords: Harbour sediments, heavy metals, PAH, PCB, TBT, Principal Component Analysis

1 Introduction

International focus on the Arctic environment has increased during the past decade due to the environmental and geopolitical changes in the region. The effects of climate change in the Arctic have become apparent, accumulation of persistent pollutants in the environment as well as bioaccumulation in the food chain of Arctic mammals has been reported (Hung et al., 2010; OSPAR, 2008; Rigét et al., 2010) and the northern areas are continuously becoming more accessible for transport and economic exploitation of mineral resources. There is an international acknowledgement that countries outside the Arctic regions have an impact on the environment via air- and waterborne transport (LRTAP, 2010). The European Union (EU) is for instance developing an Arctic policy based on the environmental and geopolitical changes in the Arctic with the aim of supporting the industrial development opportunities in an environmentally sound way for the benefit of the European Arctic population and citizens of the EU (Commission, 2012) /. In addition, the EU has qualified the impacts/effects of human activities of the EU countries on the Arctic environment in the Arctic

Footprint and Assessment project (Institute, 2010). With respect to global sources of pollution via long-range transport of pollutants and effect on human health and the environment in the Arctic, the Arctic Monitoring and Assessment Programme (AMAP) of the Arctic Council focuses on persistent organic pollutants (POPs), among these polychlorinated biphenyls (PCB) and the heavy metals Cd, Hg and Pb. Bioaccumulation of these priority pollutants have been registered in mammals and humans in the Arctic due to both local/regional and global sources (AMAP, 2002; Hung et al., 2010). In addition to these pollutants countries represented in the Arctic Council include polyaromatic hydrocarbons (PAH), tributyltin (TBT) and the heavy metals As, Cr, Cu, Ni and Zn as priority pollutants (CCME; DanishEPA, 2005; SFT, 2007; USEPA). Research on the long-range transport of these pollutants has not been extensive.

The increasing human activities in Arctic regions such due to the economic exploitation increase the potential local and regional environmental loads. The ongoing and expected increasing industrial development especially within the mining, and oil and gas industries in for instance Greenland, Northern Norway and NW Russia accentuate the need for continuously improving environmental management systems and technologies for minimising the environmental impact of the increasing local/regional human activities. One area of concern is the removal of pollutants that pose risk to human health and the environment.

Harbours acts as sinks for a wide variety of pollutants caused by anthropogenic activities in the harbour as well as on land. Examples of harbours located in Arctic regions that have been exposed to several local sources of pollution over the past 50-60 years are Hammerfest in Northern Norway and Sisimiut in Greenland. In Hammerfest, environmental investigations have revealed complex composition of pollutants such as heavy metals, PAH, PCB and TBT in the harbour sediments at levels posing risk for human health and the environment (NorwegianEnvironmentAgency, 2014). In Sisimiut high levels of Cd and Cu have been registered (Ottosen and Villumsen, 2006), investigations of organic pollutants have however not been conducted. Hammerfest harbour has been identified as one of 17 harbours of highest priority for remedial actions by the Norwegian national action plan for polluted seabed (MinistryofEnvironment, 2007). In 2008 remedial actions to remove and stabilise 1,200m³ of polluted sediments from part of the harbour was implemented (NorwegianEnvironmentAgency, 2014). There however still remain large areas of the harbour in need of remedial actions in order to meet the environmental goals of Hammerfest municipality. There are currently no remedial action plans for the harbour in Sisimiut, however, due to the increased national/international focus on the Arctic environment; similar remediation plans from the authorities may be expected in the future.

Prior to implementing remedial action plans, it appears to be instrumental to identify the potential pollution sources to better understand and control/prevent further pollution of the sediments. Statistical analyses of the distribution of pollutants in relation to sediment properties, e.g. grain size, content of organic matter and buffer capacity, can extract trends linked to the pollution sources. Principal Component Analysis (PCA) is a chemometric statistical tool for visualising the differences and similarities in large data sets by calculating principal components. These are mutually orthogonal vectors that represent independent and uncorrelated variation of the initial descriptors (pollutants/sediment properties), so correlated descriptors are then described by the same principal component. The systematic variation in the data set can hence be simplified by using fewer new descriptors than the original number of variables and this simplification is done without loss of systematic information (Carlson and Carlson, 2005).

Score plots are obtained by projecting the original data onto the calculated orthogonal principal component vectors. The influence of each original descriptor to the principal component is reflected in a loading plot. Descriptors which have a strong contribution to the variation depicted in the score plot are found far from the origin in the loading plot. Positively correlated descriptors are projected close to each other, while negatively correlated descriptors are projected opposite each other with respect to the origin (Carlson and Carlson, 2005).

PCA has previously been used to obtain information on pollutant distribution in sediment/soil/water and to assess sources of pollution (Cheng et al., 2009; De Luca et al., 2004; Feng et al., 2014; Gao et al., 2013; Jan et al., 2010). In some studies PCA plots were used to assess the distribution of PCB congeners and PAH components in sediments and coupled with ratio calculations of selected components, possible sources of pollution were identified (Countway et al., 2003; Feng et al., 2014; Gao et al., 2013; Hartmann et al., 2004).

The main focus of this study was to compare distribution of pollutants related to sediment properties for two harbours, Hammerfest and Sisimiut, located in the Arctic for the assessment of possible differences in pollution sources. This involved a preliminary chemometric (PCA) assessment of the pollutant distribution patterns in relation to sediment properties and in depth evaluation of PCA plots of PAH components and PCB congeners to evaluate possible pollution sources.

2 Methods and materials

2.1 Statement of Human and Animal Rights

The procedures and experiments undertaken in this study were in accordance with the Helsinki Declaration of 1975, as revised in 2000 and 2008.

2.2 Sample collection

Sediments from Sisimiut, Greenland and Hammerfest, Norway were sampled from the top 10 cm of the seabed using a Van Veen grab and were kept frozen during transport and stored in a freezer until analysed. Sediments were sampled at different locations in the harbours based on potential land-based pollution sources resulting in 5 sediments from Hammerfest and 4 sediments from Sisimiut. Sample points and adjacent potential sources of pollution are listed in Table 1.

Table 1: Sample points and potential sources of pollution

Harbour	Sampling point	Point sources of pollution
Hammerfest	H_1	Former shipyard
	H_2	Petrol station
	H_3	Outlet from Storvatn (freshwater lake)
	H_4	Sewage discharge
	H_5	
Sisimiut	S_1	Former shipyard
	S_2	Petrol station
	S_3	Shrimp factory
	S_4	Marina

Potential sources of pollution in Sisimiut include;

- Petrol station adjacent to the harbour (local oil spills, leakage from pipes/tanks etc.)

- Fish factory adjacent to the harbour (discharge of processed shrimp/crab with possible biomagnifications of pollutants in shells)
- Former shipyard
- Discharge of untreated wastewater
- Discharge from boats
- Diffuse sources include boat traffic, urban run-off, incineration of waste, district heating (limited use of fossil fuels for energy production), and household heating (stoves/oil boilers)

Potential sources of pollution in Hammerfest include;

- Petrol station adjacent to the harbour
- Former shipyard
- Discharge of untreated wastewater and sewage
- Outlet from freshwater lake, Storvatn, in which elevated concentrations of PAH and PCB in the lake sediments has been measured (Akvaplan-Niva, 2008)
- Fire of Hammerfest 1944 (in connection with the withdrawal of the German occupation)
- Diffuse sources include boat traffic, district heating (mostly sustainable energy sources and limited incineration of waste), household heating (stoves/oil boilers), Melkøya (liquefied natural gas processing station).

Based on the pollution sources in the two towns, harbour sediments may be polluted by the following pollutants; heavy metals, PAH, PCB and TBT. Dispersion pathways from land based sources include subsurface water, rainwater, cable routes, freshwater outlets and snow melting (annually approximately 6 months of snow cover in both towns). Dispersion pathways in the harbour sediments include resuspension of sediments and marine species.

2.3 Analytical

Major elements and heavy metal concentrations (P, Al, Ca, Fe, K, Mg, Mn, Na, V, Cr, Cu, Ni, Pb, Zn) were measured based on digestion (Danish standard DS259). Sediment dried at 105°C (1.0g) and HNO₃ (9M, 20mL) were autoclaved (200kPa, 120°C, 30 minutes). Solid particles were subsequently removed by vacuum filtration through a 0.45 µm filter and the liquid was diluted to 100mL. Metal concentrations in the liquid were measured by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) and are given as mg metal per kg dry matter.

Mercury, TBT and organic components (PAH16, PCB, total hydrocarbons (THC)) were measured at a licensed laboratory, Eurofins in Moss, Norway. Mercury was measured by Norwegian Standard NS 4768. PAH, PCB and THC were measured by ISO/DIS 16703. The measurements included 16 PAH components and 7 PCB congeners, selected based on sediment quality criteria for Denmark, Norway and OSPAR (Protection of the Marine Environment of the North-East Atlantic). The PAH components were acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorine, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene. The 7 measured PCB congeners were PCB28, PCB52, PCB101, PCB118, PCB138, PCB153 and PCB180.

Chloride content was measured by agitating sediment (10 g) dried at 40 °C with micropore water (40 mL) for 20 hours. Solid particles were removed by 0.45 µm vacuum filtration and the chloride concentration was measured by ion chromatography. Measurement deviation was 10%.

Carbonate content was measured by treating dried sediment (5.0 g) with HCl (3 M; 20 mL) and the developed CO₂ was measured volumetrically in a Scheibler apparatus, calibrated with CaCO₃. Measurement deviation was 15%.

Organic matter was based on loss of ignition of dried sediment (2.5 g) being heated at 550 °C for an hour. Measurement deviation was 10%.

Total Carbon (TC) and Sulphur (S) were measured by high temperature combustion. Dried sediment (0.5 g) was combusted (1,350 °C) converting all carbon and sulphide into carbon dioxide and sulphur dioxide, respectively. The gasses were passed through scrubber tubes to remove interferences and the carbon dioxide and sulphur dioxide were measured by infrared detector. Measurement deviation was 5-10%.

Nitrogen (N) was measured by the Kjeldahl method. Dried sediment (1.0 g) was heated to 370 °C with H₂SO₄ (conc., 15 mL) and K₂SO₄ (7 g) until white fumes were observed (approx. 90 minutes) and subsequent to cooling 250 mL distilled water was added to the mixture. pH of the mixture was raised by adding NaOH (45 %) and subsequently the mixture was distilled and the vapours were trapped in HCl (15 %, 85 mL). The trapped vapour solution was subsequently titrated with NaOH (5 M). Measurement deviation was 10%.

Cation exchange capacity (CEC) was measured by extraction with NH₄OOCCH₃ and subsequent cation exchange with NaCl. Dried sediment (10 g) was agitated with NH₄OOCCH₃ (1 M, pH 7, 30 mL) for 5 minutes and subsequently centrifuged (2500 rpm, 10 min). The liquid was discarded and the step was repeated 2 additional times. Subsequently the step was repeated two times using NH₄OOCCH₃ (0.1 M, 30 mL). The sediment was then agitated with NaCl (10 %, 20 mL) for 5 minutes and subsequently centrifuged (2500 rpm, 10 min) and the step repeated three additional times. The liquids from all four NaCl treatments were combined, diluted to 200 mL and ammonium content was measured by flow injection analysis. Measurement deviation was 10%.

pH (KCl). Dried sediment (5.0 g) was agitated with KCl (1 M, 12.5 mL) for an hour and pH was measured using a radiometric analytical electrode. Measurement deviation was 1%.

Conductivity. Dried sediment (5.0 g) was agitated with distilled water (25 mL) for an hour and the conductivity was measured using a radiometric analytical electrode. Measurement deviation was 10%.

Grain size was measured by wet sieving and dry sieving. Wet sediment (75 g), distilled water (350 mL) and Na₄P₂O₇·10H₂O (0.1 M, 10 mL) were agitated for 24 hours. The slurry was then sieved through a 63µm sieve and the fraction above 63µm was subsequently dried and sieved for 15 minutes in a mechanical shaker using sieves with screen openings of 0.063, 0.080, 0.125, 0.25, 1.0 and 2.0 mm. The slurry fraction below 63 µm was transferred to Andreasen pipette for gravitational sedimentation. Stoke's law was used for estimating the time required for particles to settle 20 cm and samples representing the sizes 40, 32, 16, 8, 4, 2 and 1 µm were measured.

Sequential extraction was made in four steps based on the improvement of the three-step method (Rauret et al., 1999) described by Standards, Measurements and Testing Program of the European Union. Air-dried sediment (0.5 g) was first extracted with acetic acid (0.11 M, 20 mL, pH 3) for 16 hours; secondly extracted with hydroxylammonium chloride (0.1 M, 20 mL; pH 2) for 16 hours; thirdly extracted with hydrogen peroxide (8.8 M, 5 mL) for 1 hour, followed by extraction at 85 °C for 1 hour, followed by evaporation of liquid at 85 °C, subsequently the cooled solid fraction was extracted with ammonium acetate (1 M, 25 mL, pH 2) for 16 h; and fourthly digestion according to DS259 on the remaining solid particles was made, following the description above. Measurement deviation was 5-20%.

2.3 PCA modelling

In this study SimcaP11 Software was used for PCA of the sediment properties and pollutant levels. Since values of the descriptors of the sediments varied in magnitude, the data was logarithmically transformed and subsequently centred and scaled to unit variance in the calculated PCA models. The number of significant components was determined by cross-validation.

3 Results and discussion

3.1 Pollutant levels in harbour sediments

The concentrations of heavy metals, organic pollutants and TBT in the studied sediments are given in Table 2 and 3, and are compared to the background assessment concentrations (BAC) of OSPAR. Concentrations of all PAH components and PCB congeners are provided in supplementary material (Table 7). BACs are based on statistical calculations in which there is a 90 % probability that the observed mean concentration will be below the BAC when the true mean concentration is equivalent to the background concentration (BC) (OSPAR, 2009). OSPAR recommends using hydrofluoric acid in metal analysis (digestion) in order to dissolve all metal in the sediment matrix. Nitric acid, though not as effective as hydrofluoric acid, was used in this study due to health, safety and environmental considerations, and the true concentrations may thus be higher than registered. BAC values are none the less used for assessing pollutant levels in the sediments.

The concentrations of As, Cr and Ni are well below BAC levels in all of the sediments; and are assumed to be equivalent to igneous levels. Concentrations of the other heavy metals (Cd, Cu, Hg, Pb and Zn) exceed the BAC levels in some or all of the sediments with up to 17 times the BAC (Figure 2). Concentrations of the organic pollutants (PAH, Benzo(a)pyrene (B(a)P), PCB exceed the BAC levels with up to 500 times for the organics (Figure 2) and 1,800 times for TBT (Table 4).

Table 2: Heavy metal concentrations in the sediments

Sample	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	mg/kg							
H_1	6.3±0.8	0.13±0.03	15.2±0.1	116±39	0.31±0.01	9.5±0.4	48.6±3.6	82.8±6.0
H_2	4.0±0.5	0.25±0.14	8.4±0.3	33.1±2.5	0.92±0.02	5.1±0.3	220±10	64.4±5.9
H_3	5.0±0.3	0.27±0.04	22.7±0.5	54.3±9.9	0.54±0.01	14.8±0.4	46.3±1.1	140±7.5
H_4	21.0±0.7	1.10±0.14	46.5±11	167±29	1.19±0.03	23.0±0.8	152±44	537±72
H_5	5.9±0.4	0.14±0.03	24.3±0.7	46.8±1.3	0.32±0.01	15.3±0.7	41.7±2.4	94.0±6.5
S_1	18.7±0.2	0.54±0.05	37.1±1.2	216±8.9	0.30±0.01	18.3±0.5	72.8±3.7	343±21
S_2	8.5±0.3	0.70±0.09	24.0±1.6	125±3.8	0.10±0.02	13.0±1.4	38.6±4.1	239±12.4
S_3	9.2±0.1	0.38±0.06	25.2±3.7	184±39	0.09±0.01	18.0±6.2	57.1±6.0	957±173
S_4	3.3±0.1	0.09±0.02	10.0±1.3	42.2±4.2	0.01±0.00	6.0±0.5	7.8±3.3	81.8±10.1
OSPAR BAC	25.0	0.31	81	27.0	0.07	36.0	38.0	122

Table 3: Concentrations of organic pollutants and TBT in the sediments

Sample	PAH	B(a)P	PCB	THC	TBT
	mg/kg				µg/kg
H_1	6.2±1.9	0.50±0.13	0.08±0.02	410±123	1,800±720
H_2	4.6±1.4	0.34±0.09	0.03±0.01	240±72	290±116
H_3	8.9±2.7	0.66±0.17	0.28±0.07	380±114	71±28
H_4	70.0±21	4.30±1.1	0.55±0.14	1,000±300	110±44
H_5	9.1±2.7	0.71±0.18	0.08±0.02	340±102	32±13
S_1	38.0±11	2.00±0.50	0.18±0.04	2,300±690	590±236
S_2	7.6±2.3	0.52±0.13	0.22±0.05	1,800±540	220±88
S_3	13.0±3.9	0.74±0.19	0.14±0.04	1,600±480	160±64
S_4	10.0±3.0	0.55±0.14	0.02±0.003	330±99	14±5.6
OSPAR BAC	0.36	0.03	0.001		1.0

B(a)P – benzo(a)pyrene

The sediment quality criteria of OSPAR do not include THC, which nonetheless has been included in Table 3 since it is related to the organic pollutants and/or the organic matter in the sediments. The THC content in all of the sediments is mainly related to the fraction C₁₆-C₃₅ and may be phytogetic rather than petrogenic hydrocarbons. The highest level of THC in Hammerfest was found in sample H4, which was sampled adjacent to the former sewage discharge point in the harbour (Table 1). Generally, higher levels of THC were found in Sisimiut with the highest concentrations found in the sediments sampled adjacent to the shoreline (points S1, S2 and S3 in Table 1).

Elevated concentrations of PAH and PCB were observed in all sample points in the two harbours (Table 3, Figure 2). In Hammerfest the highest concentrations were found in H4 adjacent to the former sewage outlet. The highest concentrations of organic pollutants in Sisimiut harbour were found adjacent to the former shipyard (S1), the shrimp factory (S3) and the petrol station (S2).

The concentration of Hg is generally high in Hammerfest harbour, especially at H2 (petrol station), H3 (freshwater lake outlet) and H4 (sewage discharge). The concentrations of Cd, Cu, Pb and Zn are high at the sewage discharge, which could indicate either urban origin or that heavy metals have higher affinity for organic matter. The concentration of Pb is in addition high in the vicinity of the petrol station (H2), which might be due to earlier use of leaded gasoline. In Sisimiut, the concentrations of heavy metals are generally low at the marina (S4), while high levels of Cu was registered in the remaining sampling points of the harbour and a high concentration of Zn was registered at the petrol station. The concentrations of Cd and Pb in Sisimiut around or slightly elevated compared to the BACs.

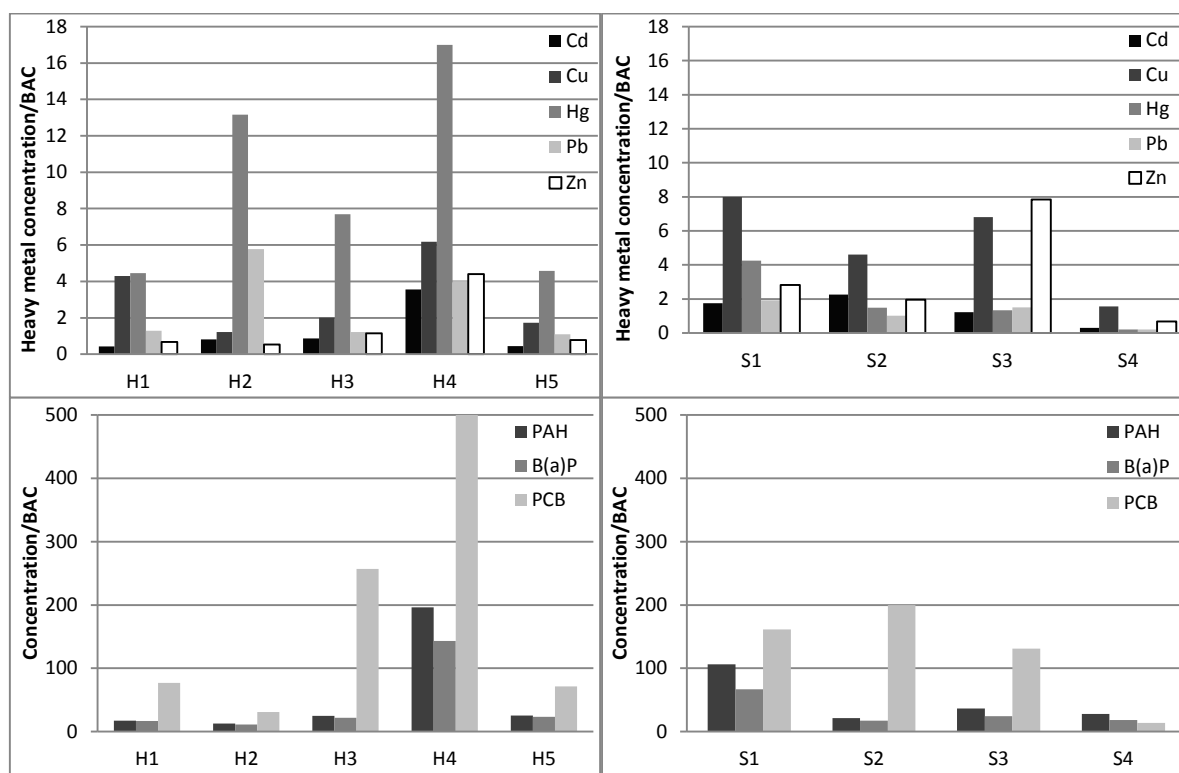


Fig 1 Pollutant concentrations compared to BAC in sediments from Hammerfest (H) and Sisimiut (S)

In both harbours PAH, PCB, TBT, Cu and Zn exceeded the sediment quality criteria and in Hammerfest Cd, Hg and Pb also exceeded the criteria. These pollutants were hence the focus of this study.

It is worth noting that although POPs and TBT have been observed in sediments of pristine areas in the Arctic, the concentrations are much lower than those registered in this study (Evenset et al., 2007; Evenset et al., 2004; Harris et al., 2011; Jiao et al., 2009; Strand et al., 2006; Viglino et al., 2004). The concentrations of As, Cd, Cr and Ni in the sediments from the two harbours are equivalent to those found in remote areas (Evenset et al., 2007; Lu et al., 2013). Previous studies found that parts of the metal content originate from global dispersion, however, levels are not significantly higher than background levels (Evenset et al., 2007; Evenset et al., 2004). The concentrations of Cu, Hg, Pb and Zn observed in remote Arctic areas, although affected by global sources, are lower than concentrations of Cu, Hg, Pb and Zn observed in parts of the harbours. Even though long-range transport of pollutants has occurred to pristine areas in the Arctic, local sources appear to have had larger impact on pollutant levels in Hammerfest and Sisimiut harbours.

3.2 Sediment characteristics

Ranges of the sediment characteristic in the two harbours of Hammerfest and Sisimiut are summarised in Table 4. In general, the ranges in the sediment characteristics are larger in Hammerfest than in Sisimiut, which is accentuated by the PCA scores plot (Figure 2) with a larger dispersion of the Hammerfest sediments. The two first components in the plot explain 70 % of the variation in the sediment characteristics. In addition, the scores plot illustrates that sediments from the same harbour do not necessarily exhibit the same variation in sediment characteristics.

Table 4: Sediment characteristic ranges in the sediments from Hammerfest and Sisimiut.

Characteristic	Units	Hammerfest	Sisimiut
<i>Carbonate</i>	%	0.7-59	0.7-9
<i>Organic matter</i>	%	4.8-15	2.4-8.5
<i>TC</i>	%	3.1-10	1.1-5.3
<i>S</i>	%	0.2-1.2	0.3-0.8
<i>N</i>	%	0.01-0.5	0.1-0.5
<i>CEC</i>	meq/100g	2.4-13	0.7-4.3
<i>pH</i>		7.0-8.4	7.0-8.0
<i>Conductivity</i>	mS/cm	7.8-20	5.6-10
<i>Grain size</i>			
<i>Clay (<2µm)</i>	%	4.3-8.9	0.8-8.8
<i>Silt (2-63µm)</i>		12.2-38	5.0-52
<i>Sand (63-200µm)</i>		54-77	38-90
<i>Gravel (>200µm)</i>		0.3-22	0.6-4.0
<i>Chloride</i>	mg/kg	6400-14100	5700-7900
<i>P</i>		645-3100	790-2900
<i>Al</i>		1900-8700	2500-6600
<i>Ba</i>		59-1340	42-160
<i>Ca</i>		4500-171000	6000-14200
<i>Fe</i>		4300-18600	5000-14500
<i>K</i>		950-4400	740-2300
<i>Mg</i>		4600-9000	1900-6000
<i>Mn</i>		40-130	40-110
<i>Na</i>		3800-15500	2500-7200
<i>V</i>		15-80	15-70

The accompanying loadings plot (Figure 1) illustrates which sediment characteristics have strong contributions to the variations in the scores plot. All parameters apart from Ba have an influence in the dispersion of the first component (p1) while the strongest contributions to the second component (p2) is related to grain size, Ca, carbonate, Mg and C, as they are found far from the origin in either dimension. The clustering of Al, Fe, K, Mn, Na and chloride close to organic matter and silt indicates a relation between these variables. The clustering of Ca and carbonate close to gravel may be related to shells and corals larger than 2mm.

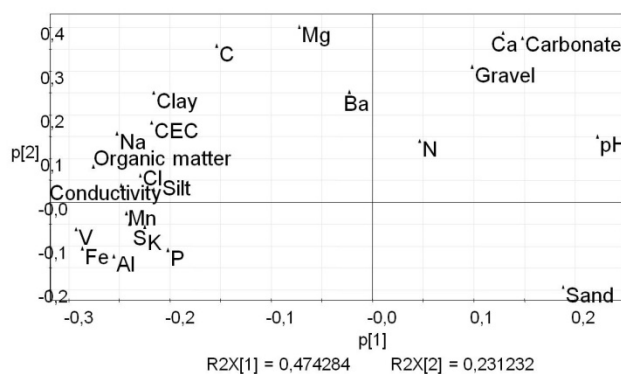
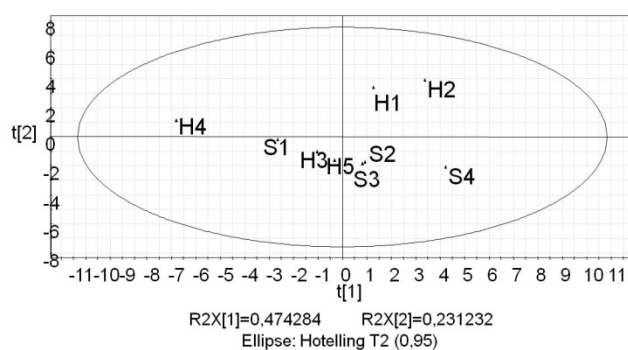


Fig 2 PCA score and loading plot of sediment characteristics.

3.3 Distribution of pollutants related to sediment characteristics

For both harbours loading plots (Figure 3) show that the major part of the target pollutants is clustered around organic matter and/or finer grain sizes (silt/clay). In Sisimiut, Zn may differ slightly from this trend, which would be in line with the much higher level registered adjacent to the petrol station (S3 in Table 2). In Hammerfest TBT, Hg and Pb deviate from the general trend which may be related to pollutant sources and/or different binding patterns to the sediment. TBT is known to have higher affinity for organic matter, accordingly the deviation from this trend in Hammerfest may be related to specific pollutant sources rather than sediment properties, which is in line with the highest concentration of TBT being found adjacent to the former shipyard (H1); the elevated concentrations of TBT in other parts of the harbour (Table 3) may be due to general boat traffic. Even though the use of TBT as a biocide in anti-fouling was completely banned in 2008, TBT can remain in eco-systems for many years; hence remaining an environmental issue for the aquatic environment of harbours for many years to come.

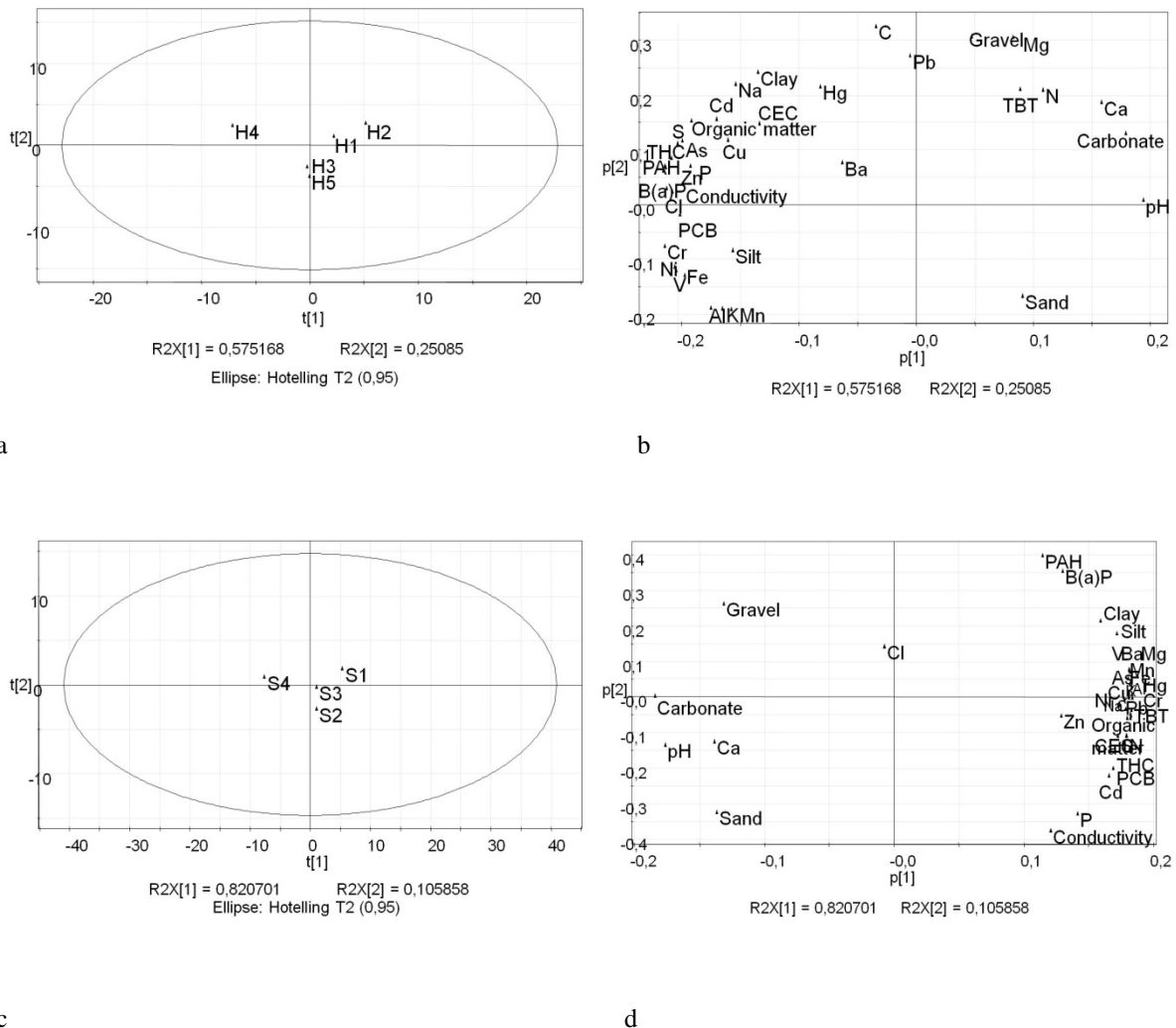


Fig 3 PCA score and accompanying loading plots of sediment characteristics and pollutant levels in Hammerfest (a and b) and Sisimiut (c and d).

The loading plot for Hammerfest implies that PAH is related to the organic matter in the sediments and the pollutant levels (Figure 2) further support a point source of PAH which may be related to sewage discharge (H4). In Sisimiut the same trend is not apparent, which may indicate that the PAH pollution originates from several diffuse sources such as harbour activities, urban run-off, and to a lesser extent from long-range atmospheric transportation. In both harbours PCB is not closely related to the content of organic matter indicating that the PCB pollution in the sediments may be due to several point sources as well as diffuse sources such as urban run-off and to a lesser degree long-range atmospheric transportation. A point source in Hammerfest may be Storvatn, in which high levels of PCB has previously been found in the sediments (Akvaplan-Niva, 2008); high PCB levels were found adjacent to the freshwater outlet in the harbour (H3 in Table 3).

In this study, the binding of heavy metals in the sediments was assessed by determining the metal partitioning by sequential extraction of the exchangeable (including carbonates), reducible, oxidisable and residual fractions. In order to investigate the possible correlations between the heavy metals in each sediment fraction, PCAs were conducted applying the metal/heavy metal concentrations in each fraction and relevant sediment characteristics. Carbonate and CEC were included in the exchangeable fraction and the organic matter, TC, S and N were included in the oxidisable fractions. The loading

plots of metal concentrations in each fraction (not shown) did not reveal any correlations between sediment characteristics and metal concentrations, apart from carbonate and Ca and to a lesser extent Mg.

Plotting of the different metal concentrations against each other for each sediment fraction showed correlations between some of the metals. Metals which were correlated were different in the two harbours as well as in the different fractions and were related to the mineral composition. It is interesting to note that for both harbours correlations between Al, Fe, K, Mg, Mn, Cr and Ni were found as exemplified by Al-Ni correlation in the Hammerfest sediments (Figure 4). In addition, no correlations between major elements and Cd, Cu, Hg, Pb and Zn were found indicating different binding patterns in the sediment implying that besides igneous content, these heavy metals may also stem from anthropogenic sources. This is also in line with the high concentrations found in the sediments (Figure 2). Based on PCA alone it is however not possible to evaluate potential pollutant sources. The environmental investigations however indicated that heavy metal pollution in both harbours is related to diffuse sources from both land- and sea-based activities.

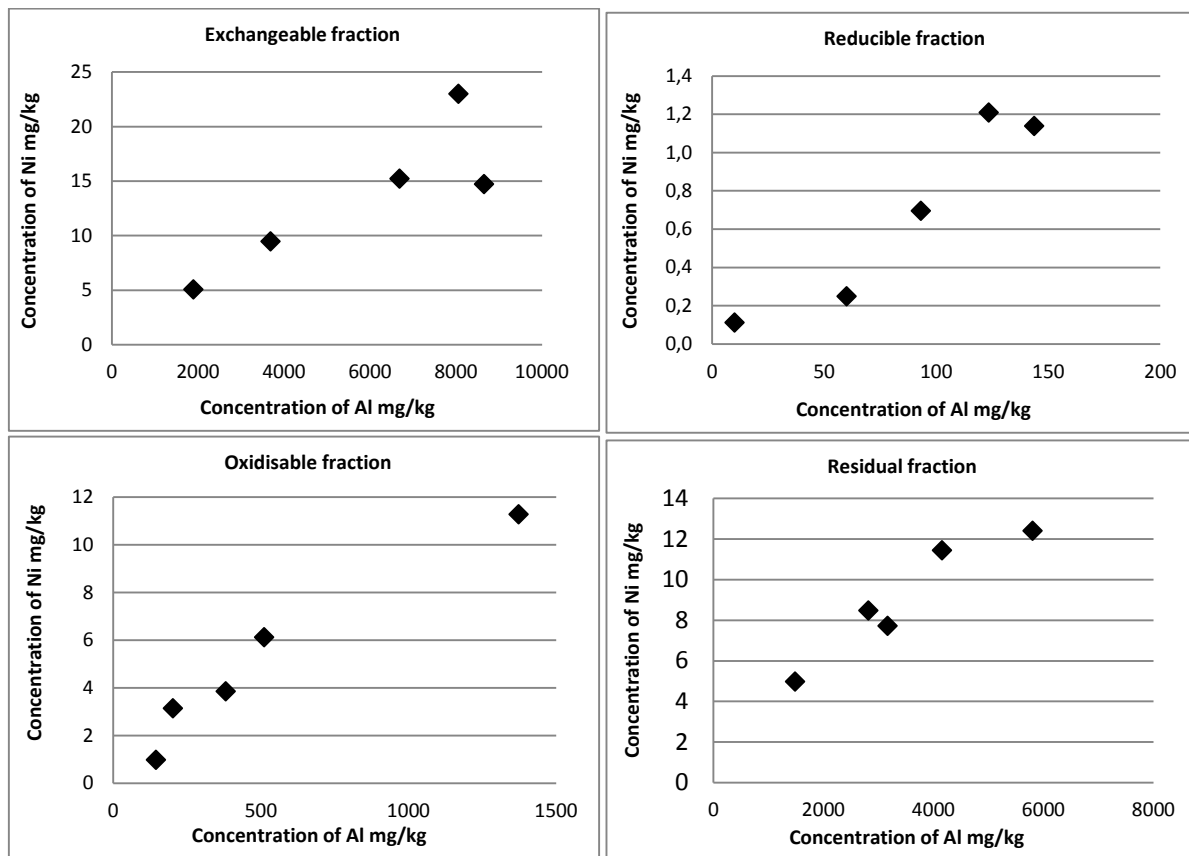


Fig 4 Correlation between the Al and Ni concentrations in the following fractions of the sediment: a). exchangeable; b). reducible; c). oxidisable and d). residual.

3.4 Distribution of PAH

The preliminary assessment of the PAH pollution in the sediment indicated a point source in Hammerfest and several, diffuse sources in Sisimiut. Ratios of selected PAH components have been widely used to identify pollution sources in sediments (Countway et al., 2003; Feng et al., 2014; Soclo et al., 2000; Yunker et al., 2002). In cases of mixed PAH pollution derived from diffuse sources, the PAH ratios can be used for evaluating predominant sources, if such exist. The PAH ratio

anthracene/(anthracene/phenanthrene) has previously been used as an indication for petrogenic (<0.1) and pyrogenic (>0.1) sources (Socolo et al., 2000); the sediments from Hammerfest and Sisimiut all have values above 0.1 indicating pyrogenic source(s) of PAH pollution (Table 5). The PAH ratios *fluoranthene/(fluoranthene+pyrene)* and *indeno(123-cd)pyrene/(indeno(1,2,3-cd)pyrene+benzo(ghi)perylene)* can in addition indicate whether pyrogenic sources originate from liquid fossil fuel combustion (0.4-0.5/0.2-0.5) or coal/biomass combustion (>0.5/>0.5) (Feng et al., 2014). Calculations of these ratios (Table 5) give ambiguous results with no clear indication of combustion sources, which could be due to mixed pollution sources, for instance combustion from incineration plants and fuel combustion from vehicles/vessels. It appears that the PAH pollution in Sisimiut stems from mixed combustion sources to a larger extent than in Hammerfest.

Table 5: PAH ratios of Hammerfest and Sisimiut sediments

	An/(An+Phe)		(Fl/Fl+Py)		Ip/(Ip+BghiP)	
	<i>Ratio</i>	<i>Source</i>	<i>Ratio</i>	<i>Combustion</i>	<i>Ratio</i>	<i>Combustion</i>
H1	0.23	Pyrogenic	0.55	Coal/biomass	0.46	Fuel
H2	0.21	Pyrogenic	0.56	Coal/biomass	0.47	Fuel
H3	0.30	Pyrogenic	0.52	Coal/biomass	0.45	Fuel
H4	0.29	Pyrogenic	0.57	Coal/biomass	0.45	Fuel
H5	0.24	Pyrogenic	0.56	Coal/biomass	0.43	Fuel
S1	0.23	Pyrogenic	0.59	Coal/biomass	0.50	Coal/biomass
S2	0.21	Pyrogenic	0.58	Coal/biomass	0.49	Fuel
S3	0.24	Pyrogenic	0.61	Coal/biomass	0.52	Coal/biomass
S4	0.26	Pyrogenic	0.61	Coal/biomass	0.52	Coal/biomass

An – anthracene

Phe – Phenanthrene

Fl – fluoranthene

Py – pyrene

Ip – ideno(1,2,3-cd)pyrene

BghiP – Benzo(ghi)perylene

To further assess the possible PAH sources, PAH ratios of petrogenic and combustion sources based on data from (Yunker et al., 2002) were compared to the PAH ratios of the sediments (Figure 5). The plot of the *fluoranthene/(fluoranthene+pyrene)* ratio versus the *indeno(123-cd)pyrene/(indeno(1,2,3-cd)pyrene+benzo(ghi)perylene)* ratio indicates that sources of the PAH pollution in the sediments of both Hammerfest and Sisimiut are combustion of coal/biomass rather than liquid fossil fuels.

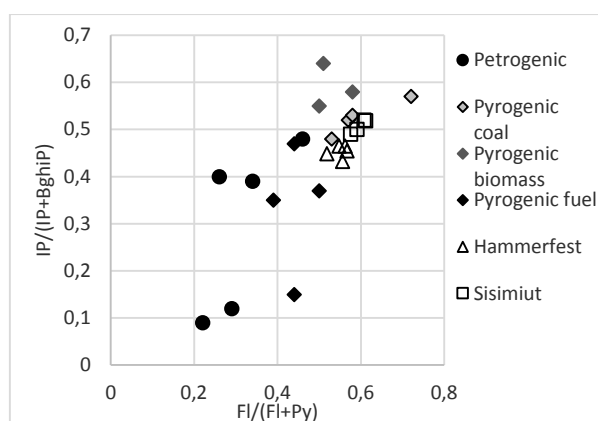


Fig 5 Comparison of PAH ratios of petrogenic and pyrogenic sources; and the studied sediments. Petrogenic and pyrogenic PAH ratio data from Yunker et al., 2002.

According to Statistics Norway, the main sources of PAH air emissions in 2012 were aluminium industry (50%), fuelwood (23%) and traffic (15%) (SSB, 2014), and since production of aluminium

does not take place in Hammerfest, it is not unlikely that the biggest source of PAH pollution is from the combustion of wood, and may partly include components from the burning of Hammerfest town in 1944. In Sisimiut, the pyrogenic sources may stem from present and past incineration of waste and combustion of fuel from vehicles or household heating by oil boilers.

3.5 Distribution of PCB

The preliminary assessment of the PCB pollution in both harbours indicated diffuse sources such as urban run-off and/or long range atmospheric transport. PCB is expected to constitute part of the waste cycle for years to come since PCB is still present in products and materials; e.g. cable insulation, thermal insulation materials, paint, plastics, transformers, hydraulic oil; produced before the production and use of PCB was prohibited on a global scale more than 10 years ago. In addition, several studies have revealed inadvertent production of PCB congeners in the manufacturing of paint pigments (Anezaki and Nakano, 2014; Guo et al., 2014; Hu and Hornbuckle, 2009; Shang et al., 2014).

In this study, seven of the 209 PCB congeners were analysed. Since the seven analysed PCB congeners in this study represent tri- (28), tetra- (52), penta- (101, 118), hexa- (138,153) and hepta- (180) chlorobiphenyls the composition of these congeners may reveal difference in the diffusive sources of PCB pollution in the sediments. The PCA score plot of the variation in the seven congeners of the sediments in Hammerfest and Sisimiut (Figure 6) reveal that H4 and S4 stand out compared to the clustering of the sediments with respect to the specific harbour. S4 has PCB pollution level a magnitude lower than registered in the other Sisimiut sediments. The ratio of PCB180/PCB28 is approximately 1 for S4 and 24-30 for the other sediments in Sisimiut indicating lower relative content of the more highly chlorinated biphenyls.

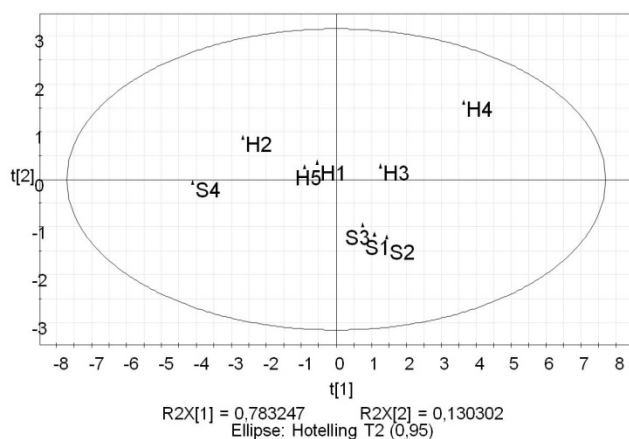


Fig 6: PCA score plot of seven PCB congeners in the Hammerfest and Sisimiut sediments.

As was the case with PAH, H4 displays different variation in the composition of PCB indicating different sources or sediment binding/degradation than for the other sediments in Hammerfest. The preliminary assessment revealed that there was not a clear relation between organic matter and PCB, which could indicate that PCB is dispersed differently than PAH, and there may be additional sources to sewage discharge at H4. Dispersion from Storvatn could be a source, which would explain that H3 (Storvatn outlet) is situated closer to H4 in the PCA plot than the other sediments.

The commercially produced PCB mixtures contained different compositions of PCB congeners according to their use. PCA has been used in several studies for comparing specific PCB mixture compositions with observed PCB pollution in sediments to assess which commercial mixture(s) the PCB pollution may originate from (Hartmann et al., 2004; Zhang et al., 2007). In this study, the seven analysed PCB congeners in the 9 sediments were compared to the composition of the following PCB mixtures: Kanechlor (manufactured in Japan), Aroclor (US, UK), Clophen (Germany) and Sovol (Russia).

Table 6: Composition of seven PCB congeners in the harbour sediments as well as in Aroclor, Clophen, Sovol and Kanechlor PCB mixtures calculated as percentage of the total PCB7, based on data from (Hop et al., 2001; Takasuga et al., 2005; USDepartmentofHealthandHumanServices, 2000).

PCB mixture	PCB28	PCB52	PCB101	PCB118	PCB138	PCB153	PCB180
H1	1	12	11	9	30	24	13
H2	1	12	10	6	29	26	16
H3	0	3	9	5	31	29	22
H4	1	5	9	5	32	29	18
H5	1	13	8	7	31	26	14
S1	0	16	19	15	27	18	6
S2	0	10	21	20	25	18	5
S3	0	17	20	15	21	17	10
S4	3	27	19	19	15	13	4
AC1016	65	35	0	0	0	0	0
AC1242	58	30	6	6	1	1	0
AC1248A	23	44	14	15	2	2	0
AC1248B	34	34	12	14	3	2	1
AC1254A	0	3	19	48	21	6	1
AC1254A	1	19	25	23	18	12	2
AC1260	0	1	10	2	21	29	37
Clophen A50	0	19	22	29	15	14	1
Clophen A60	0	3	13	8	28	29	19
Sovol	0	2	23	27	27	16	5
KC200	17	56	11	8	5	3	0
KC300	85	2	5	4	2	2	0
KC400	22	42	16	12	4	3	0
KC500	1	13	26	19	23	17	1
KC1000	1	13	27	18	22	17	1
KC600	1	2	10	2	20	39	26

AC – Aroclor

KC – Kanechlor

The PCA score plot of the commercial PCB mixtures and the harbour sediments indicate that the PCB pollution in Hammerfest is mainly related to Clophen A60 and Sovol (Figure 7). This is in line with a study of 64 PCB congeners in Storvatn, in which the major part of the PCB pollution (approximately 82%) was found to be related to Clophen A60, Aroclor 1254, Aroclor 1260 and Sovol (Akvaplan-Niva, 2008). This further implies that applying the seven PCB congeners in this study can be used in PCA for qualitative indications of PCB mixture sources. The PCB pollution in Sisimiut is clustered in a different part of the PCA score plot (Figure 7) and appears to be related to Kanechlor 500, Kanechlor 1000, Sovol and Aroclor 1254. Whether the relation to the Kanechlor and Sovol mixtures is due to long-range atmospheric or local emissions of products manufactured with the Russian/Japanese mixtures is not clear and further analysis to confirm/rule out such indications entails analysis of more PCB congeners.

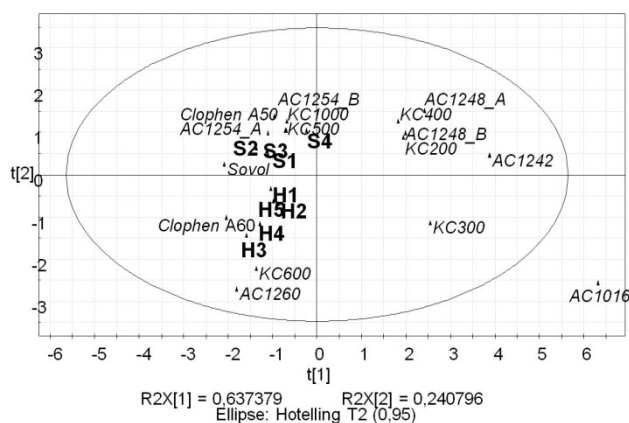


Fig 7 PCA score plot of the seven PCB congeners of the Hammerfest and Sisimiut sediments compared to commercial PCB mixtures.

4 Conclusion

The preliminary PCA assessment based on concentrations of heavy metals, PAH, PCB and TBT and respectively the sediment characteristics indicated different sources and pollutant distribution in the two harbours. One exception was TBT which was not found to be related to sediment characteristics, indicating point sources resulting in locally high TBT concentrations. In both harbours TBT concentrations were highest; up to 1,800 times the non-polluted level; in sediments adjacent to the former shipyards.

The in depth PAH source analyses was based on both a PAH ratio assessment and PCA and indicated that the predominant source of PAH pollution in both harbours was pyrogenic coal/biomass. This was in line with the second largest PAH air emissions in Norway being related to wood combustion. PCA of PAH composition indicated that the PAH pollution in the two harbours may origin from diffuse as well as point sources such as sewage discharge.

The PCB composition (7 congeners) in the sediments was compared to commercial PCB mixtures in a PCA plot. The PCB pollution in Hammerfest was found to mainly be correlated to European, Russian and American manufacturers, while the PCB pollution in Sisimiut was related to other PCB mixtures manufactured in the US, Russia and Japan. PCA of the PCB congeners in the sediments indicated several diffuse sources of pollution.

Although long-range transport of POPs, TBT and metals has previously been established, the concentration levels of pollutants in this study were higher than those reported in pristine areas of the Arctic, indicating that local sources were more significant than global sources.

The study showed that PCA can be used as an important tool, along with pollutant levels and mapping of potential sources, for identifying pollutant sources and differences in pollutant composition in relation to sediment characteristics.

Acknowledgements

The Northern Environmental Waste Management (EWMA) project, which is funded by the Research Council of Norway through NORDSATSNING (grant number 195160) and Eni Norge AS, is acknowledged for funding. Hammerfest municipality is acknowledged for providing boat and assistance in sampling of sediments in Hammerfest. Tore Lejon and Kristine B. Pedersen acknowledge

The Arctic Technology Centre at DTU for funding the trip to Greenland and in addition the technical staff is acknowledged for assistance with sampling and sediment analyses.

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