Analyses of polyaromatic compounds (PACs) and metals in sediment and mussels near Kubal aluminium smelter

Photo: Per Holmlund, WSP

Norwegian Institute for Water Research

REPORT

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Summary

In 2019 analyses of polyaromatic compounds (PACs) and metals was conducted in coastal waters around the Kubal smelter and surrounding waterbodies. Levels in both sediments (19 stations) and mussels (*Limecola balthica*, 5 stations) were investigated. More than 50 different PACs (including alkylated PACs) and 8 metals were analysed. The concentrations of most PACs correlated negatively with distance from Kubal, but this pattern was not observed for metals. PACs that did not correlate negatively with distance from Kubal probably had other sources in addition or instead of Kubal. The PAC pattern in sediments and mussels correlated well, indicating an uptake of PAC from sediment. Concentrations of PACs and metals in sediment were compared with data from 2002 and showed an overall reduction in concentrations for PACs. A mean of 62% reduction of PAC was observed, and a reduction was observed for 75% of the stations investigated both years (n=12). For metals, increasing concentrations were found for As, Mn and Hg, while Cu, Cr and Vn concentrations were decreased. The stations associated with the greatest increase in concentrations were not close to the discharge points of Kubal.

Four keywords	Fire emneord
1. Aluminium smelter	1. Aluminiumsverk
2. Polyaromatic compounds (PAC)/ metals	2. Polyaromatiske forbindelser (PAC)/metaller
3. Sediment	3. Sediment
4. Mussels	4. Muslinger

This report is quality assured in accordance with NIVA's quality system and approved by:

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ESPIAL

Analyses of polyaromatic compounds (PACs) and metals in sediment and mussels near Kubal aluminium smelter

Preface

The monitoring and analysis of sediment and mussels from Sundsvall was conducted by WSP and the Norwegian Institute of Water Research (NIVA) on behalf of the Aluminiumindustriens Miljøsekretariat (AMS) under the auspices of the ESPIAL project. Fieldwork was conducted by WSP, Sweden. Chemical analysis was conducted by Eurofins (metals) and NIVA in Oslo (PAH). The main report authors were Per Holmlund and Merete Grung. Ailbhe Macken was the project manager for the work. The contact person for the AMS was Leif Ongstad. Thanks to the following colleagues at NIVA and WSP who contributed to the project:

- Fieldwork and preparation of mussel samples: Per Holmlund and Linea Johannesson (WSP)
- Chemical analysis: Alfhild Kringstad (PAHs)
- Statistical analysis: Merete Grung and Sondre Meland
- Map production: Per Holmlund
- Professional quality assurance was performed by Anders Ruus

Oslo, 04.11.2020

Ailbhe Macken

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Summary

In 2008, Söderberg furnaces were faced out at Kubal aluminum smelter, and production of aluminium continued with prebaked anodes. Analyses of polyaromatic compounds (PACs) and metals was conducted in 2019 and levels in both sediments (19 stations) and mussels (*Limecola balthica*, 5 stations) were investigated. More than 50 different PACs (including alkylated PACs) and 8 metals were analysed. Many PACs exceeded the environmental quality standards (EQS) near the outlet of Kubal, while exceedances of metals were more seldom.

The concentrations of most PACs correlated negatively with distance from Kubal, but this pattern was not observed for metals. PACs that did not correlate negatively with distance from Kubal probably had other sources in addition or instead of Kubal. The PAC pattern in sediments correlated well with the pattern observed in mussels, indicating an uptake of PAC from sediment. Concentrations of PACs and metals in sediment compared with historical data from 2002 revealed an overall reduction in concentrations for PACs. A mean of 62% reduction of PAC was observed, and a reduction was observed for 75% of the stations investigated both years (n=12). For metals, increasing concentrations were found for As, Mn and Hg, while Cu, Cr and Vn concentrations were decreased. The stations associated with the greatest increase in concentrations were not close to the discharge points of Kubal.

Sammendrag

I 2008 ble Søderbergelektrodene faset ut ved Kubal aluminiumsverk, og produksjon av aluminium etter det har blitt gjort ved hjelp av prebake-teknologi. Analyser av polyaromatisk forbindelser (PAC) Og metaller ble gjort I 2019 og konsentrasjoner i både sediment (19 stasjoner) og muslinger (*Limecola balthica*, 5 stasjoner) ble undersøkt. Mer enn 50 ulike PAC (inkludert alkylerte PAC) og 8 metaller ble analysert. Mange PAC overskred miljøkvalitetsstandardene (EQS) nær utløpet av Kubal, mens overskridelser av miljøkvalitetsstandardene for metaller var mer sjeldent.

Konsentrasjonene av de fleste PAC korrelerte negativt med avstanden til utløpet fra Kubal, men dette mønsteret ble ikke observert for metaller. PAC som ikke korrelerte negativt med avstand fra Kubal hadde sannsynligvis en annen opprinnelse i tillegg til, eller i stedet for Kubal. PAC-mønsteret i sedimenter samstemte godt med det som ble funnet i muslinger, som indikerer et opptak av PAC fra sediment. Konsentrasjoner av PAC og metaller i sediment ble sammenlignet med historiske data fra 2002. Resultatene viste at det var en nedgang i konsentrasjonene av PAC. Gjennomsnittlig ble konsentrasjonene redusert med 62%, og 75% (n=12) av stasjonene hadde en nedgang in PAC-konsentrasjon. For metallene ble det funnet en økende konsentrasjon for AS, Mn og Hg, mens Cu, Cr og Vn hadde en synkende konsentrasjon sammenlignet med 2002. Stasjonene som var assosiert med de største økningene av metaller var ikke nær utløpet fra Kubal.

1   Introduction

At the end of November 2008, the last Söderberg furnace was discontinued at the Kubal Aluminum Smelter as production of aluminium continued with the prebake production method. Since then the Kubal Smelter has had no recorded emissions of PACs. There are very few comprehensive emission data with regard to PACs from the Söderberg production era but based on Kubals own calculations the smelter gave rise to approximately 3000-5000 tons of PAH emissions during 66 years. That is between 45-75 tons per year on average. This emission estimate is for both air and water. The distribution between air and water is assumed to be 2/3 of emissions to air and 1/3 discharged to the coastal waters. Monitoring results from local waterbodies in 2002 showed elevated levels of both PAH and metals in sediment and mussels (Byrne Ó Cléirigh, 2003). A chemical characterization and biological effect study of Kubal's discharge effluent from today's prebake production technique (Gardfors. L., et al. 2016) showed that with an approximately 25 x dilution rate of the discharged effluent, concentration falls below the PNEC-value (predicted no effect concentration). Evaluation of dispersion and dilution of Kubals discharge to coastal waters has shown a predominantly southbound discharge effluent plume in the surface layer of the water column (Holmlund, P. et al., 2016). Results indicate that only a limited part of the concerned waterbody could be affected by elevated concentrations of environmentally disturbing content from the smelters discharged effluent today.

The PAH monitoring results from Byrne O Cleirigh, 2003 included data collected from four local waterbodies. Results showed that locations close to Kubal had a higher concentrations while locations further away had lower concentrations, indicating that there is a contribution from Kubal to the PAH levels in the bay but also that this effect is largely limited to the immediate vicinity of the smelter and diminishes rapidly at greater distances from the plant.

Objective 1.
Clarify environmental status in the concerned waterbody. What is the environmental status of collected samples of sediment and mussels according to: the water framework directive, the Swedish environmental quality standard SFÄ (särskilda förorenade ämnen) and the Norwegian River Basin Specific Pollutants (RBSP).

Objective 2.
Follow up of the results from Byrne O´Cleirigh, 2003.
  A.   Is there a source allocation of PAH in sediment and mussels, and are levels in sediment and mussels correlated in the local bay area as indicated in previous monitoring results (Byrne O´Cleirigh 2003)? (*Clarification of spatial resolution by including additional sampling locations and a wider screening of PAC compounds).*
  B.   Is there evidence of change over time of previously noted levels of PAH and metals in surface sediment and mussel tissue?

The Work described in this report is part of the ESPIAL project. ESPIAL (=Ensuring the Environmental Sustainability of production of PrImary ALuminium) is a multidisciplinary study on the local environmental effects around aluminium smelters in the Nordic countries. The study is initiated and sponsored by "Aluminiumsindustriens Miljøsekretariat" (AMS), and is building on a similar, but more extensive study of the Norwegian smelters from 1991-94, called the "Effect Study". ESPIAL involves new field studies conducted in 2018 and 2019 on the marine environment, air quality, effects on vegetation and on wildlife, in addition to a review of studies conducted through the period after the Effect Study on these subjects. The report at hand is a contribution to ESPIAL.

2   Methods

1.1. Description of sampling sites

Sampling stations from previous monitoring was selected based on distance from smelter and budget. In addition to stations from Byrne O´Cleirigh 2003 stations K1- K6 were added to ensure data collection in the most prevalent path of the discharge plume from the smelter (Figure 1). Five stations where selected for collection of mussels. The distance from the smelter was calculated as the minimum distance to either the northern outlet (outletN) or southern outlet (outletS) (Table 1). Station 91 is to be regarded as a reference location based on distance from the smelter and exposure from other sources.

Table 1. Details of sampling stations. The colours of the cells of the various stations are used for visual reference for the figures in the report. Matrices analysed: S= sediment, B= biota (mussels).

Station	Latitude	Longitude	Distance smelter (km)	Depth (m)	Matrices analysed	Previously investigated (year, name)
Outlet N	62 22 36	17 22 02	0.00	0		
Outlet S	62 22 18	17 22 28	0.00	0		
K2	62 22 18	17 22 31	0.049	15	S	New 2019
K1	62 22 35	17 22 11	0.12	7	S	New 2019
62	62 22 21	17 22 50	0.35	26	S, B	New 2019
K3	62 22 00	17 22 32	0.53	18	S, B	New 2019
58	62 22 58	17 22 13	0.72	18	S, B	58
K4	62 21 46	17 22 35	0.97	13	S, B	New 2019
56	62 23 15	17 21 39	1.28	21	S	56
K5	62 21 33	17 22 47	1.42	16	S	New 2019
68	62 21 30	17 23 07	1.58	22	S	68
K6	62 21 03	17 23 14	2.40	51	S	New 2019
50	62 23 40	17 23 56	2.57	27	S	50
78	62 20 35	17 23 22	3.27	46	S	Draget
74	62 21 06	17 25 31	3.43	44	S	74
89	62 19 25	17 23 22	5.37	17	S	89
91	62 21 13	17 30 02	6.81	23	S, B	91 (Reference station)
46	62 26 27	17 23 43	7.29	31	S	46
42	62 28 13	17 21 57	10.4	30	S	42
16	62 29 06	17 20 33	12.1	21	S	16
29	62 28 57	17 25 59	12.3	20	S	29
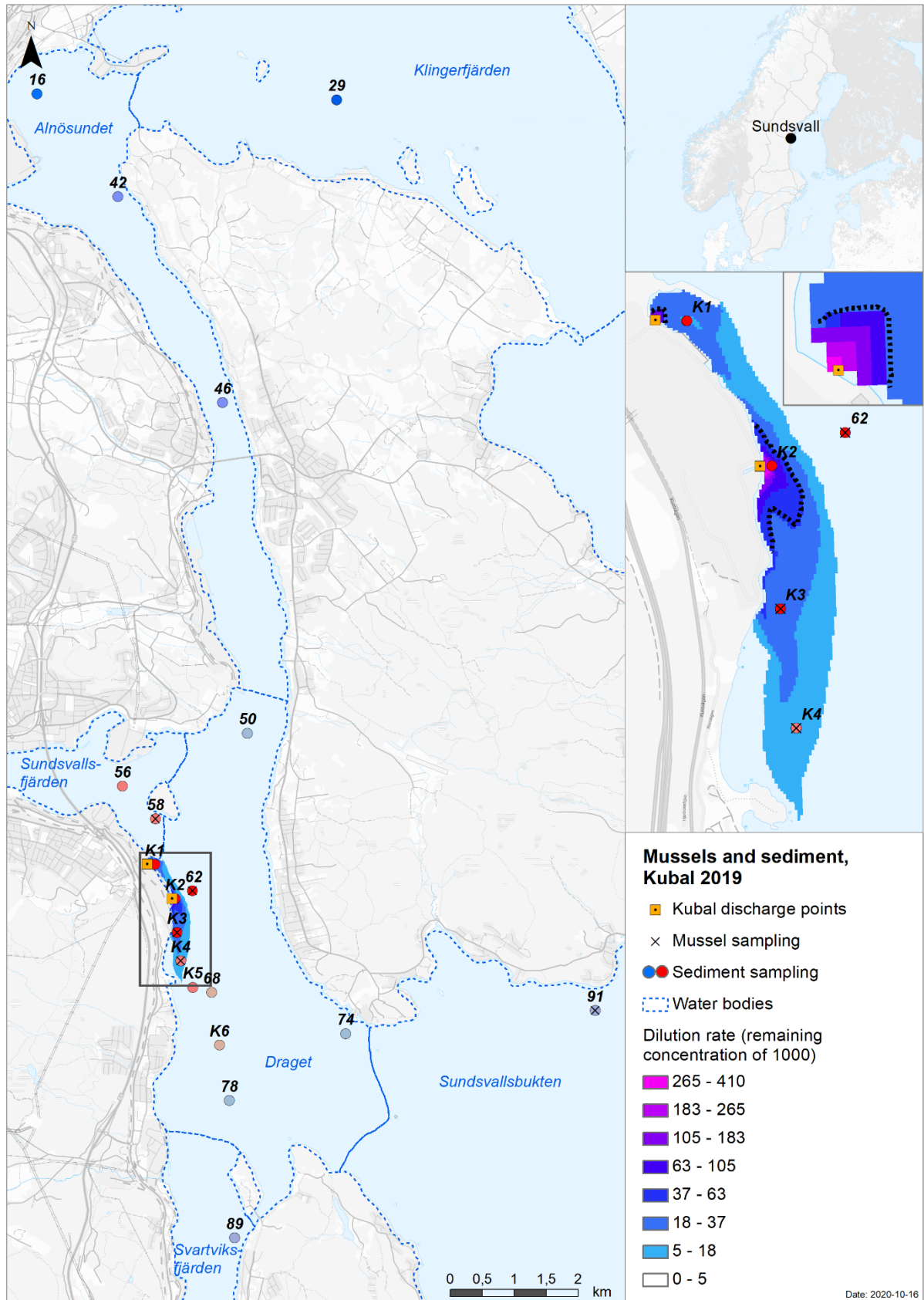
Figure 1. Map of sampling locations located on the east coast in central Sweden. The stations are coloured according to the distance from the smelter (Table 1). The map includes a gradient of dilution of Kubal's wastewater from the two different discharge locations in the waterbody Draget (Holmlund and et al., 2020). The dotted line in the discharge plumes shows where calculated dilution rate (25 x) exceeds value of "no effect concentration" of the current discharge from Kubal smelter.

1.2. Local hydrodynamics

In coastal waters around the Kubal smelter and surrounding waterbodies, the movement of water is mainly driven by wind-induced currents and currents generated by three river outlets. These consist of Indalsälven to the north, Ljungan to the south, and Selångersån which runs through the city of Sundsvall. Together these three freshwater outlets create an estuarine circulation, often with a stratified water column and southbound current in the surface water that is balanced by a north bound bottom current in the project area (Figure 2) (Göransson, 1990; Holmlund et al., 2016). Regional larger scale ocean currents have a small impact on water movements at Kubal's location of discharge to the water (Holmlund et al., 2016). Kubal's wastewater is discharged in the surface and follows the southbound current as visualized as the outer boundary of light blue colour representing a dilution rate of 200 (value of 5) (Figure1).

Figure 2. General flow pattern (velocity and direction) in bottom water (left) and in the surface water (right) in Sundsvall's coastal waters where the Kubal smelter is located.

1.3. Collection of sediment and mussel samples

Sediment samples from the project area were collected in August 2019. The sediments were collected by means of a van Veen grab, sampling approximately the upper 25 cm of sediment layer over a surface of 0,1 m^2. Each sample consisted of 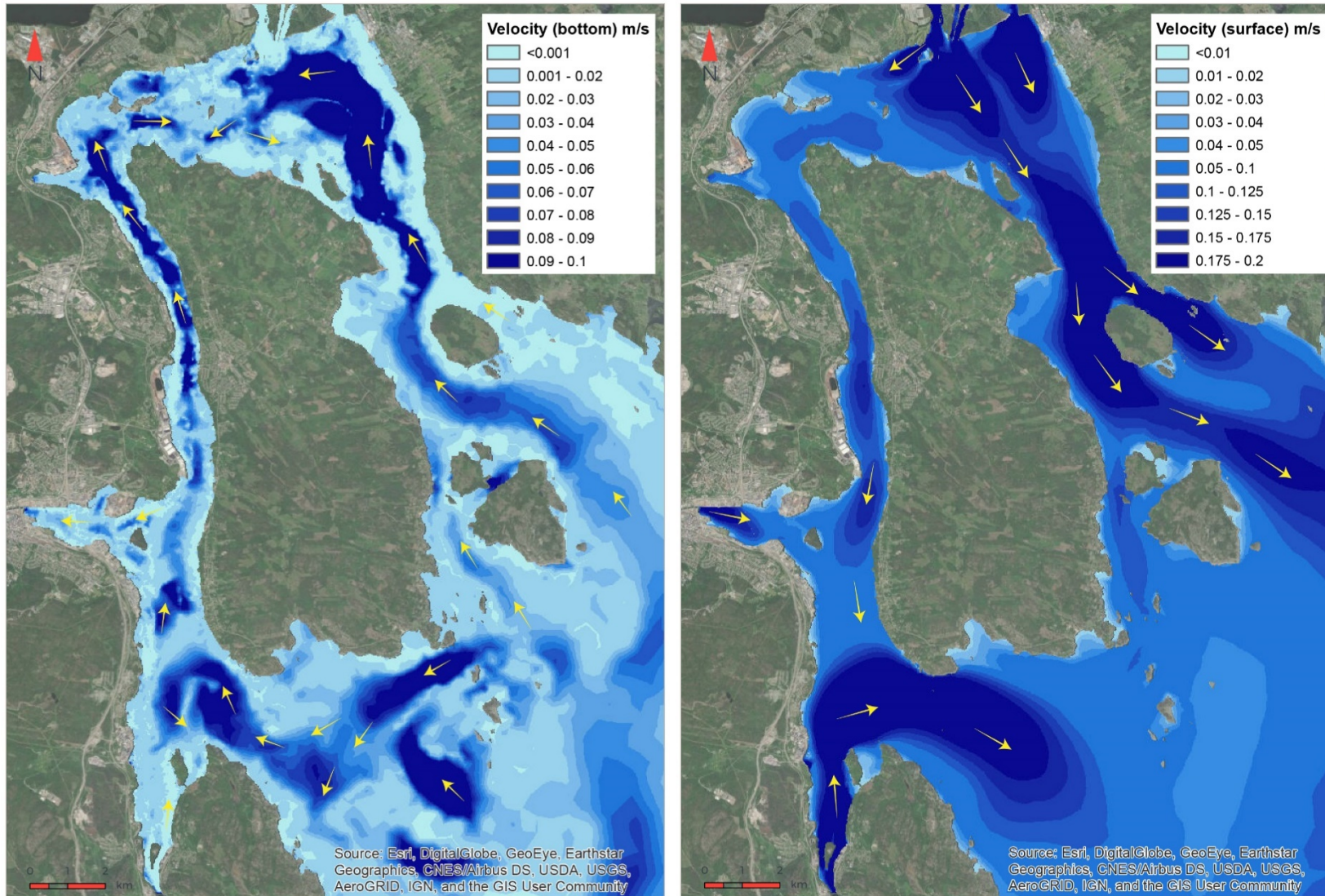a mixture of three to five subsamples from the upper 1-2 cm of sediment of each grab collected. The sediment was sampled in 100 mL glass jars that had been incinerated at 600°C and was stored at -20°C prior to analysis. The mussels (*Limecola balthica*) were also collected with the van Veen grab by sifting the sediment samples with water through a 0,4-mm steel mesh. Sediment free mussels where sampled in diffusion tight bioplastic bags. Samples were placed in coolers and transported to the laboratory where biometric measurement (length and weight) was taken before tissue extraction to 100 mL glass jars that had been incinerated at 600°C and were stored at -20°C prior to analysis. Approximately 800-1000 mussels where collected at each sampling station. Both sediment and mussel samples were then transported via express delivery to NIVA's research laboratory in Oslo, Norway for analysis.
The analyses of PACs were performed at NIVA's research laboratory. Samples were sent to Eurofins Norway (www.eurofins.no) for analyses of metals.

Figure 3 Images of the sediment and mussel collection from August 2019. The mussels, Limecola balthica (right and bottom left (the mussel size (white) can be compared to the hand size) and sediment were collected with the van Veen grab (top left). By sifting the sediment samples with water through a 0,4-mm steel mesh the mussels (middle) approximately 800-1000 mussels where collected at each sampling station.

1.4. Analyses of PACs and metals

The method utilised for analyses of PACs are described in detail in Meland et al. (2019), and the analytical details are therefore not described here, but a brief summary is provided. The number of analytes for this work has been extended somewhat with an increased number of heavier (5-6 ring) PACs than previously described in Meland et al. (2019).

Freeze dried sediment samples (2-5 g) were extracted with dichloromethane (20 ml) in an ultrasonic bath for 120 min. Internal standards were added during the first extraction step. This step was repeated with fresh dichloromethane (20 ml) for 60 min and the extracts combined. Biota samples were homogenised, and sodium sulphate added prior to extraction with cyclohexane: ethyl acetate (1:1). The extract was further cleaned by means of gel permeation chromatography before analysis

by GC/MS in single ion monitoring mode. A total of 7 internal standards were used for quantification, and several PACs were analysed including the PAH16 compounds (Table 2). Alkylated PACs of naphthalene (C1-4), fluorene (C1-3), dibenzothiophene (C1-3), phenanthrene/anthracene (C1-4), pyrene/fluoranthene (C1-2) and chrysenes (C1-2) were also analysed. In addition, some alkylated PAC of heavier PACs were also included in the analysis.

The following metals were analysed at Eurofins: As, Cd, Cr, Cu, Hg, Ni, Pb and Zn.

Table 2. PACs analysed with abbreviations used in text and figures. The colouring scheme of the cells are used in figures of fingerprinting of PACs. The m/z ratio used for GC/MS quantification are also shown. PACs with an asterisk included in the PAH16. The PACs and metals that are included in the WFD are marked as either EU priority substances (PS), Norwegian river basin specific pollutants (N-RBSP) or as Swedish prioritised substances (SFÄ), both for sediment and biota concentrations. The colour in the cell with PAC abbreviation are used in some figures of PAC pattern to ease identification of isomers.

Compound	Abbreviation	PAC-group	*m/z*	*WFD* sediment	WFD biota
Naphthalene-*d8***			136		
Acenaphthylen-*d8***			160		
Biphenyl-*d10***			164		
Dibenzothiophene-*d10***			192		
Pyrene-*d10***			212		
Benzo(a)anthracene-*d12***			240		
Perylene-*d12***			264		
Naphthalene *	N	1	128	PS	PS
C1-Naphthalenes	N_C1	1	142		
C2-Naphthalenes	N_C2	1	156		
C3-Naphthalene	N_C3	1	170		
C4-Naphthalenes	N_C4	1	184		
Acenaphthylene *	ACY	2	152	N-RBSP	
Acenaphthene *	ACN	2	154	N-RBSP	
Fluoren *	F	3	166	N-RBSP	
C1-Fluorenes	F_C1	3	180		
C2-Fluorenes	F_C2	3	194		
C3-Fluorenes	F_C3	3	208		
Anthracene *	A	4	178	PS	PS
Phenanthrene *	P	5	178	N-RBSP	
C1-Phenanthrenes	PA_C1	5	192		
C2-Phenanthrenes	PA_C2	5	206		
C3-Phenanthrenes	PA_C3	5	220		
C4-Phenanthrenes	PA_C4	5	234		
Retene	R	15	234		
Dibenzothiophene	D	6	184		
C1-Dibenzothiophenes	D_C1	6	198		
C2-Dibenzothiophenes	D_C2	6	212		
C3-Dibenzothiophenes	D_C3	6	226		
Fluoranthene *	FLA	7	202	PS	PS
Pyren *	PY	8	202	N-RBSP	
C1-Pyrene/Fluoranthene	PY_C1	8	216		
C2-Pyrene/Fluoranthene	PY_C2	8	230		
Benzo(a)anthracene *	BaA	9	228	N-RBSP	N-RBSP
7,12-dimethylbenz(a)anthracene	BaA_C2	9	256.3		
Chrysen *	C	10	228	N-RBSP	
C1-Chrysenes	C_C1	10	242		
C2-Chrysenes	C_C2	10	256		
Benzo(b,j)fluoranthene *	BbjF	11	252	PS (b not j)	
Benzo(k)fluoranthene *	BkF	11	252	PS	
Benzo(a)pyrene *	BaP	11	252	PS	PS
Indeno(1,2,3-cd)pyrene *	IP	11	276	PS	
Benzo(ghi)perylene *	BgP	11	276	PS	

Compound	Abbreviation	PAC-group	*m/z*	*WFD* sediment	WFD biota
Dibenz(ac/ah)anthracene *	DahA	11	278	N-RBSP	
7H-benzo(c)fluorene	BcF	11	216		
cyclopenta(cd)pyrene	CcP	12	226		
benzo(ghi)fluoranthene	BgF	12	226		
benz(c)phenanthrene	BcP	12	228		
benzo(e)pyrene	BeP	12	252		
benzo(j)fluoranthene	BjF	12	252		
Perylene	PER	12	252		
benzo[j]aceanthrylene	BjeAA	12	252.3		
Anthanthrene	ANE	12	276.3		
dibenzo(a,e)fluoranthene	DaeF	12	302.4		
dibenzo(a,l)pyrene	DalP	12	302.4		
dibenzo(a,e)pyrene	DaeP	12	302.4		
dibenzo(a,i)pyrene	DaiP	12	302.4		
dibenzo(a,h)pyrene	DahP	12	302.4		
6-methylbenz(a)anthracene	BaA_C1	13	242.3		
6-methylbenzo(a)pyrene	BaP_C1	13	266.3		
3-methylcholanthrene	CA_C1	13	268.4		
PAH16	PAH16			N-RBSP	
Arsenic	As			N-RBSP	
Cadmium	Cd			PS	
Chromium	Cr			N-RBSP	
Cupper	Cu			N-RBSP, SFÄ	
Mercury	Hg			PS	PS
Lead	Pb			PS	
Nickel	Ni			PS	
Zinc	Zn			N-RBSP	

** Internal standards

1.5. Comparison with WFD guidelines

The water framework directive (WFD) has environmental quality standards (EQS) values for priority substances. In Norway, both the priority substances and the river basin specific pollutants (RBSP) are classified according to five classes based on ecotoxicity. The five classes can be described as: background, good, moderate, bad and very bad. The first two (background and good) pose no hazard to the environment, while the latter three (moderate, bad and very bad) pose an increasing risk to sediment dwelling organisms. The PAHs and metals that are assigned with EQS limits and classification schemes according to Norwegian regulation (Direktoratsgruppen vanndirektivet, 2018) are presented in Table 2. The five classes are derived on ecotoxicity effects where the chronic effect is the lower level of the "moderate" class (class 3), and the acute toxicity is the lower level of the "bad" class (class 4). This means that the lower level of class 3 corresponds to the EQS AA (environmental quality standard, annual average) in the WFD directive (EU European Union, 2013) and concentrations in class 1 and 2 are not exceeding the EQS AA. Concentrations above five times the chronic toxicity is the lower level of the "very bad" class. The five classes are shown in relevant figures with the following colours: blue, green, yellow, orange and red.

ĬRŇŇÒŒo PŇØÖŒ ÍØØřRŇŅÒMŌ PŇØÖŒ

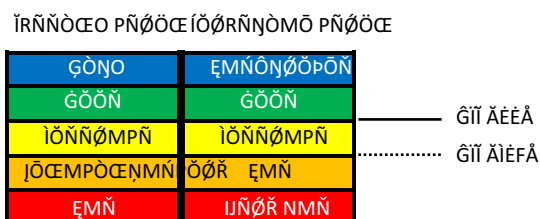| ĢÒŅO	ĘMŇÔŅØÖPÕŇ	
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Figure 4. Explanation of the relationship between Norwegian/Swedish environmental classes and the EQSs in the WFD. For classification in biota, only above and below EQS are used.

In cases where the concentration has been normalised to the environmental class, concentration ≤ lower level for Class 5 (very bad) has been normalised by interpolation between the upper and lower for each class. For boxplots, the concentrations above Class 5, the resulting environmental class was normalised so that each increment in concentration of Class 5 gave an increase of +1 Class.

$$Environmental\ class\ for\ conc. > conc.\ Class\ 5 = \frac{[conc.] - [conc.\ Class\ 5]}{[conc.\ Class\ 5]} + 5$$

Eq 1

This means that an environmental class of 6 is 10 times the EQS MAC, while class 7 are 15 times the EQS MAC. This normalisation is only used in the presentation of environmental class in boxplots, otherwise a class 5 is used for classification. The purpose of the normalisation was to prioritize which contaminants that represented the largest environmental risk.

1.6. Statistical treatment

Data treatment, statistical analyses and graphical outputs were performed with JMP version 15.0.0 (SAS Institute Inc.). Whenever assumptions of normality and equal variance on data or log-transformed data were met, ANOVA followed by a t-test or Tukey post hoc test was performed. The level of statistical significance was set to p<0.5. Regression analyses was performed by the least squares' method.

3 Results

3.1 Objective 1: Environmental levels in sediments

3.1.1 Treemaps of environmental classes

The concentrations of PACs in sediments were classified according to EU and Norwegian guidelines (see Table 1 for details of which guideline that was used). Norway has a classification system for all the members of the EPA PAH16, and in addition for the PAH16 (sum of 16 individual PAHs). The environmental classes for all sediment stations according to individual PAHs are shown in Figure 5. Many of the sediment stations exceed the limits of the chronic and acutely toxic levels for individual PAC (yellow (class 3) and orange colour (class 4), respectively). For station K1, all PACs except ACY were exceeding the chronic toxicity limit (all PACs were in class3, 4 or 5). Conversely, for station 91 only one PAC (A) exceeded the limit for the chronic toxicity (yellow). There is an improvement of environmental class with distance following the currents. For station 91, most of the PACs were in class 1 or 2.

Discharge water from the smelter is at the surface and the main currents southwards. The stations to the north (stations 16, 42, 16 in Alnösundet and 29 in Klingerfjärden), can likely therefore be attributed to another source of PACs. Since the end of the nineteenth century, several factories have operated in the local bay area. Each factory has its own history, but common to them all has been the long-term discharge of wastewater. Sediment sampling by (Apler et al., 2014) included sediment samples from the concerned waterbodies. Analyses and related classification showed elevated levels of contaminants in the sediments in several locations. Many of the metals and organic pollutants present were attributed to several different sources.

Figure 5. Treemap showing the environmental class for all PACs (n=16) with assignment according to EU/Norwegian guidelines for classifications for each station. Stations are ordered by the distance to the nearest outlet of Kubal (Table 1).

The sediment stations were also classified for metal concentrations according to EU/Norwegian guidelines (Table 2). Six of the sediment stations had concentrations exceeding acutely toxic levels, and only station 16 had mercury levels in the "red" (5 times the acute toxicity level). In contrast to

the PACs, the metals in stations near the outlets of the aluminium smelter were not especially contaminated, and some were comparable to the cleanest station (91).
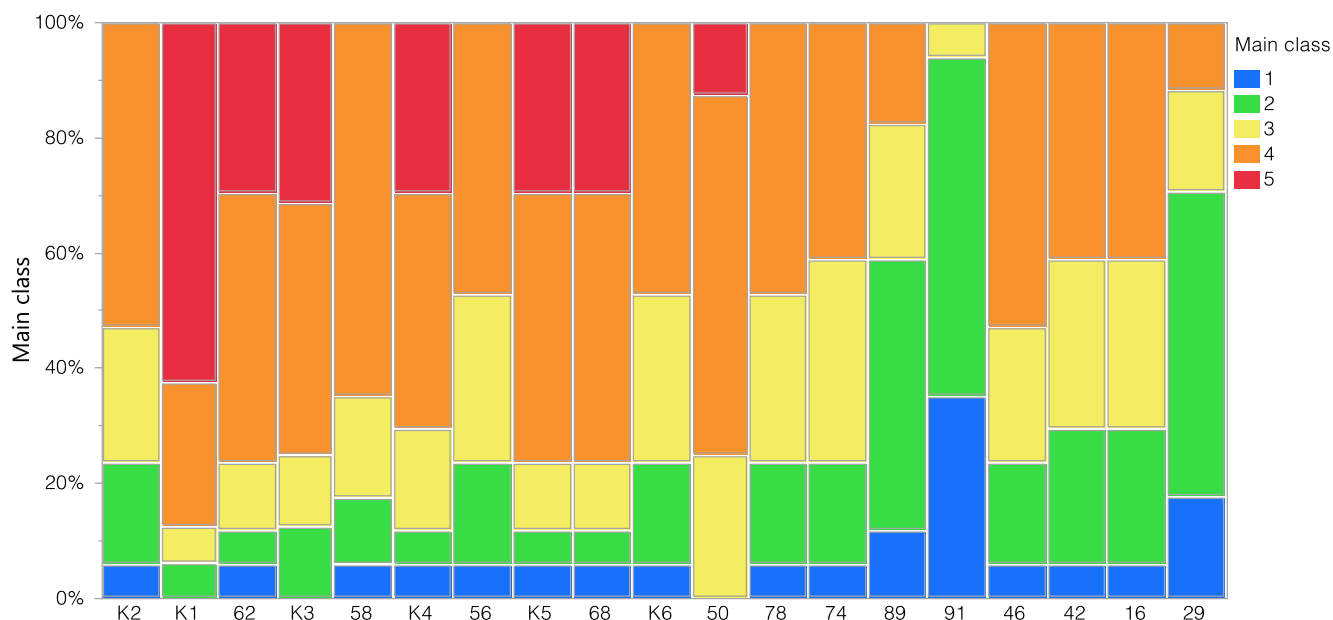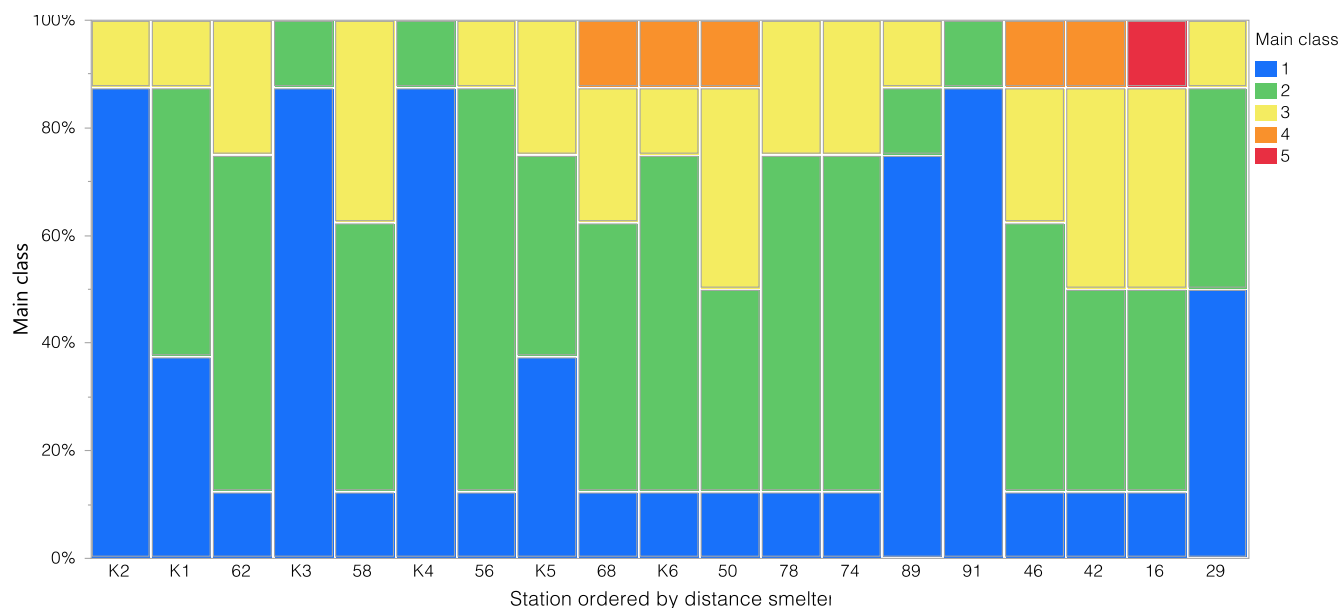

Figure 6. Treemap showing the environmental class for all metals (n=8) with assignment according to EU/Norwegian guidelines for class for each station.

3.1.2 Boxplots of estimated environmental classes

A boxplot of the sum PAH16 are shown in Figure 6. It shows that the spread of concentrations was large, from 440 µg/kg dw (station 91) to >302,000 µg/kg dw (station K1). Three of the stations are closer to the outlet than 500 m and can be considered being part of the discharge mixing zone EC (European Commission), 2010; Ranneklev et al., 2013) where exceeding of EQS can be permitted depending on the national regulations. However, the concentrations in sediments are caused by a historic release and not an ongoing release. Considering the historic discharge load from the smelter results of exceeding EQS in the vicinity of the smelter are to be expected.

Many of the closest stations to one of the two outlets from the aluminium smelter exceeded the highest classification of 5 times the acute toxicity level, indicating that sediment dwelling organisms are probably affected by the concentrations. In order to distinguish between the individual PACs, a boxplot of the PACs normalised to environmental class is therefore presented in Figure 8. The normalisation enables a presentation in a common figure for all PACs since the scaling is common.

The boxplot of individual PACs normalised to environmental classes are shown in Figure 8, including also the PAH16. Since the figure shows the PACs ordered by the median environmental class, fluoranthene is the PAC exceeding the environmental class the most. It is also obvious that the environmental class in station K1 are exceeding the acute toxicity for most PACs that have an environmental class assignment. In general, the higher ring PACs exceed the environmental classes most frequently, the exception being A (anthracene). The other small ring PACs such as ACY, N, P, ACE and F have low environmental class, and for the latter three the medians are in class 2 (good status).
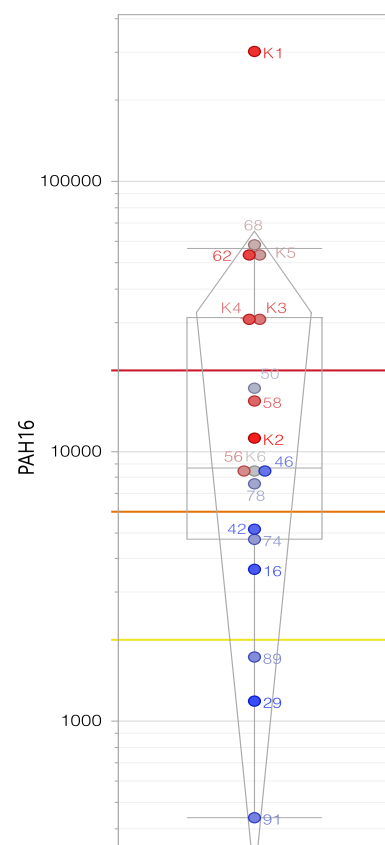
Figure 7 Boxplot of PAH16 (ng/g dw) in sediment stations (logarithmic scale). The lower limits of environmental classes are shown wit coloured lines. The points are coloured by distance to outlet.

For metals, the boxplot of individual metals normalised to environmental class are shown in Figure 9. Mercury was the metal that had the highest mean of assigned environmental class. However, all means of all metals were in class 2 with the exception Cr which had a mean in class 1.
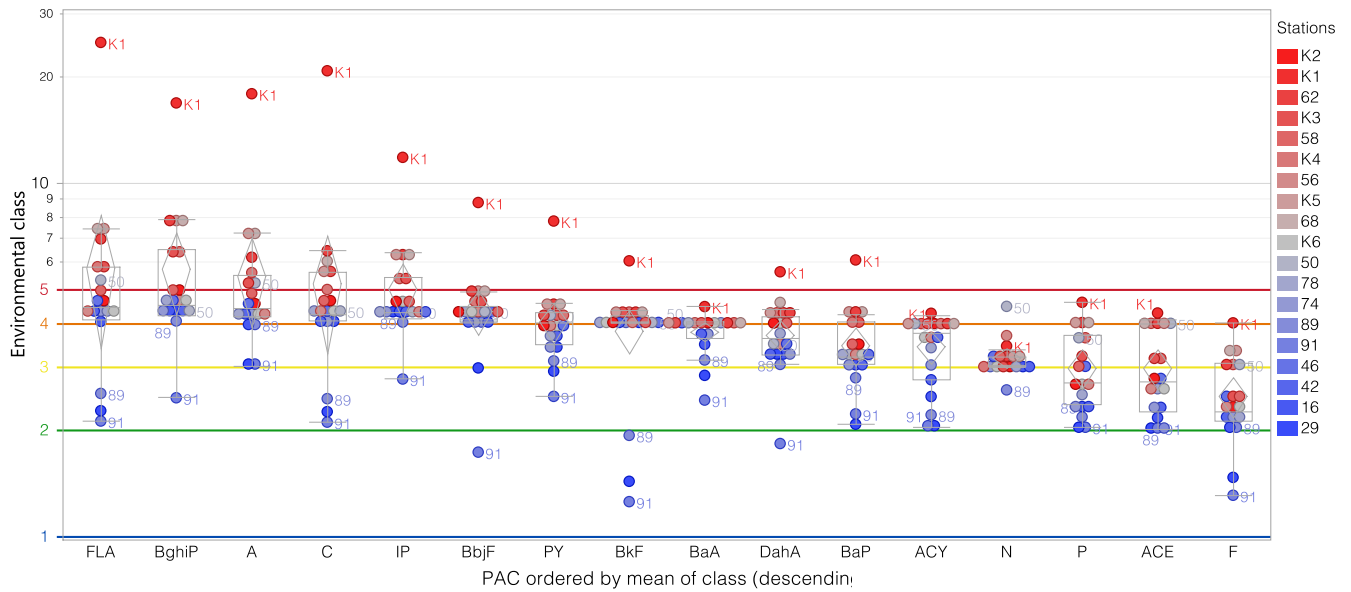
Figure 8. Boxplot of environmental class of individual PAH16 in sediments for all station (left) vs environmental class assignment by descending means. The coloured lines indicate the lower level of the environmental classes according to Norwegian guidelines (Direktoratsgruppen vanndirektivet, 2018). Each PAC has been normalised to environmental class as described in Materials and Methods section. Stations K1, 50 89 and 91 are labelled. The colours of the points are according to distance from nearest outlet.
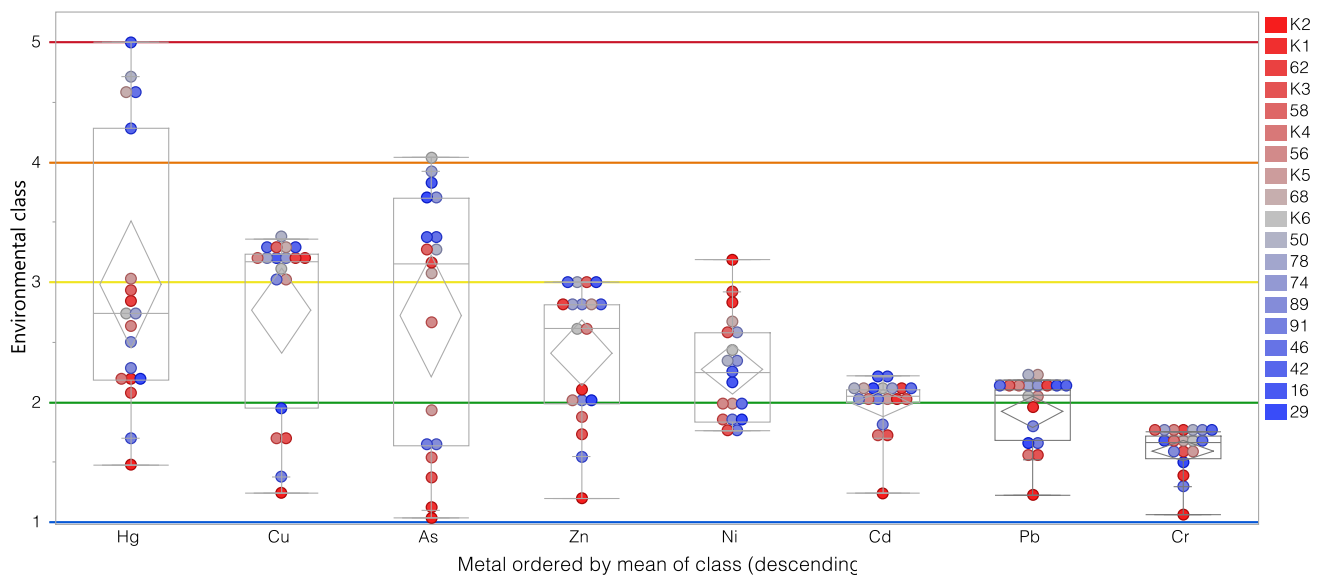
Figure 9. Boxplot of environmental class assignment for metals in sediment for all stations. The coloured lines indicate the lower level of the corresponding environmental class according to Norwegian guidelines (Direktoratsgruppen vanndirektivet, 2018).

3.2   Objective 1: Environmental levels in mussel tissue

For mussel tissue there are fewer PACs and metals that have been assigned an EQS, and only 5 PACs and mercury (Table 2) can therefore be classified in mussel tissue. For biota, there are only two classes: below EQS (blue) and above EQS (red). The environmental classes are shown in Figure 10 and Figure 11 respectively. From these, the conclusions are that PACs in mussel tissue from stations near the aluminium smelter were exceeding the EQS for two of the PACs, while two were below. At the reference station (91), all five PACs were below EQS. Mercury did not exceed the EQS at any stations.
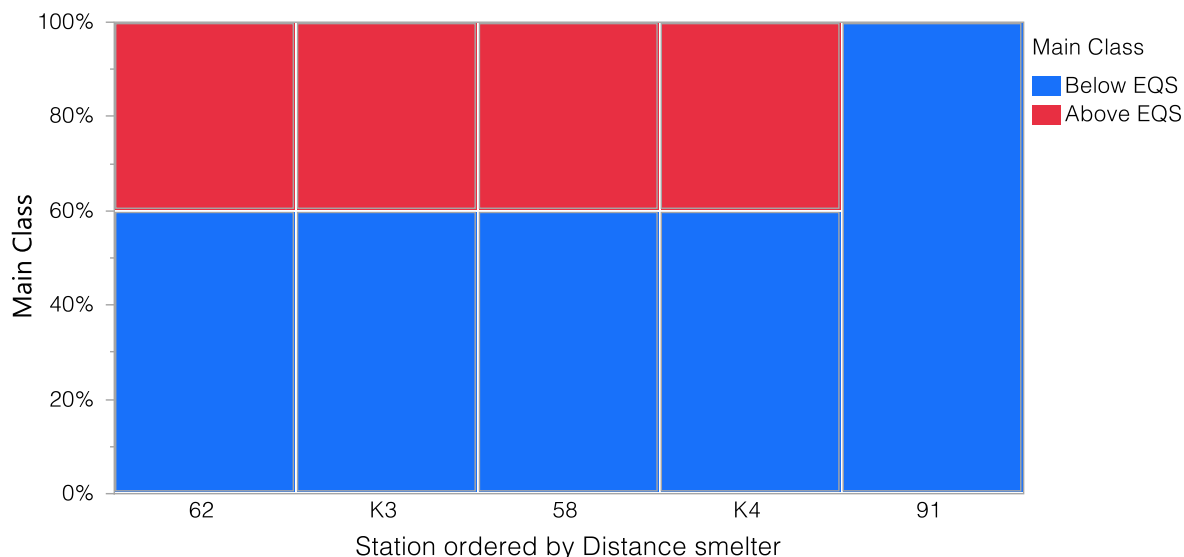
Figure 10. Classification of PAC concentrations in mussels. Only four PACs have environmental classification in biota (see Table 2).
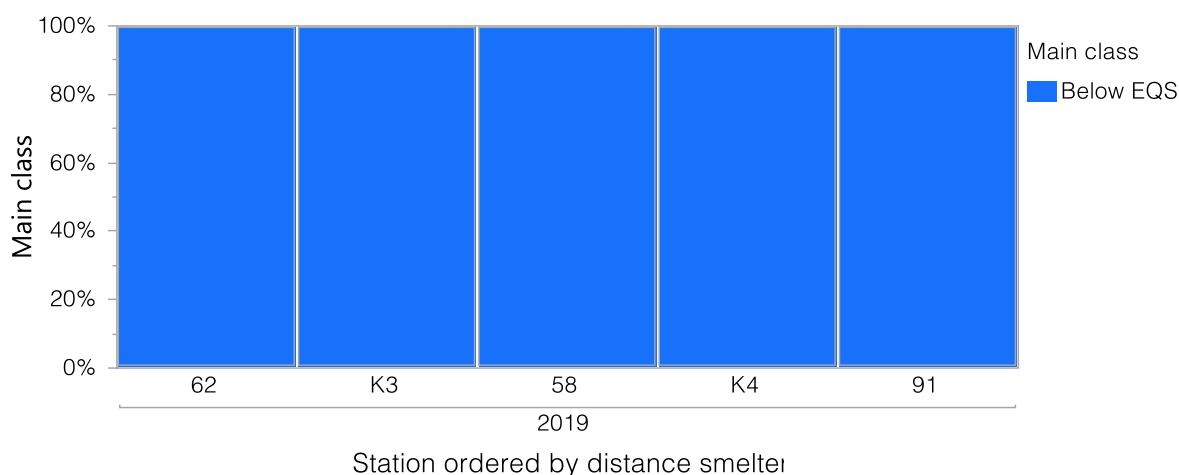
Figure 11. Classification of mercury concentration in mussels.

3.3   Objective 2A: Is there a correlation with distance from smelter in sediment samples

Most PACs correlated negatively with the minimum distance from one of the outlets of the smelter, suggesting that the smelter was the source of most of the PACs measured. Examples of the correlation are shown in Figure 12 for selected PACs; PAH16, R and N. The R^2 for the negative correlation of PAH16 with distance from the smelter was 0.48.

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There were a few exceptions to the negative correlation to distance of the PACs, and the most noteworthy are shown. R (retene - 1-methyl-7-isopropyl phenanthrene) is a C4-alkylated phenantrene. According to the review by (Stogiannidis and Laane, 2015), three-ringed alkyl PAHs such as 1-methylphenanthrene, 1,7-dimethylphenanthrene and retene are produced from abietic and pimaric acid, both present in pine wood resin. They are frequently used as markers for softwood combustion. Since R is positively correlated with distance from the smelter, we believe that R has another or additional source than the smelter. The concentrations of R in the sediments were very much higher at Sundsvall than at Sunndalsøra near the smelter there (results from Sunndalsøra are not published yet but were also investigated in 2019 by NIVA. The median of R at Sunndalsøra and Sundsvall were 1.4 and 120 µg/kg dw respectively, while the highest concentrations were 9.4 (Sunndalsøra) vs 730 (Sundsvall) µg/kg dw.

Also, N (naphthalene) and a few of the small ring PACs such as ACY and alkylated N were not correlated with distance to the smelter. These PACs are typically petrogenic PACs (i.e. from oil/gasoline). The likely source of some of these PACs in sediments near Sundsvall are therefore probably mixed, but gasoline or related products are probably partly the source. Some of the D (dibenzothiophenes) may also partly originate from gasoline/diesel.
All correlations with distance can be found in the appendix, (Figure 29) ordered by the goodness of the fit (best to worst).
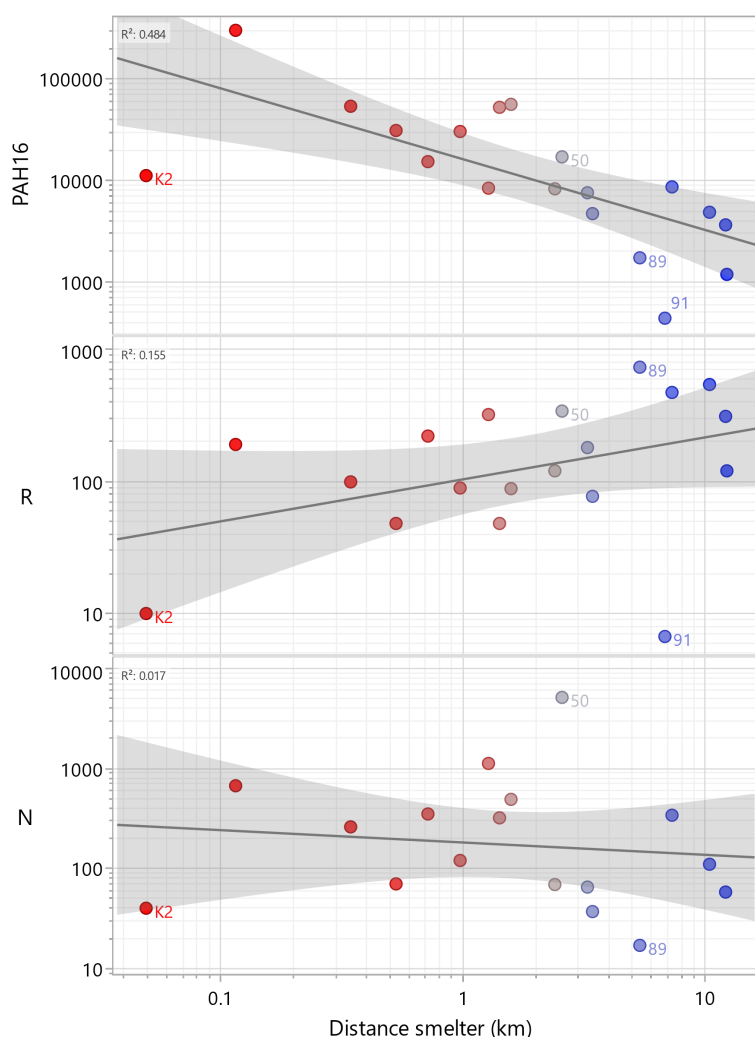

Figure 12. Selected examples of correlation of PACs with distance from the aluminium smelter. All correlations can be found in the appendix. The colour of the station is according to Table 1.

The origin of PACs can be determined by determining the ratios of different PAC in relation to each other. PACs are classified according to the temperature at which they form and can be classified as 1) pyrogenic - originating from different pyrolysis substrates 2) petrogenic – originating from petroleum-related sources and 3) natural PACs of biogenic or natural. One ratio that can be used to characterise the source if PACs is the pyrogenic index (Stogiannidis and Laane, 2015). The ratio ranges from 0.8 to 2.0 for pyrogenic sources and is much lower for petrogenic PACs (<0.01 for crudes and <0.05 for heavy oils/fuels). Combustion processes significantly alter the value of PI, whereas weathering has little effect on PI, and therefore the ratio is very reliable. The PI for PACs in sediment stations has been plotted vs the distance to the smelter in Figure 13. The PI shows a negative correlation with distance from the smelter, indicating that further away from the smelter, the origin of the PACs is less influenced by PACs formed by high temperatures (pyrogenic origin). Most of the stations north of the smelter have PIs in the lower confidence interval, typically stations 50, 56, 58, 46, 42 and 16. However, station 29 which is also north of the smelter, had a PI above the upper confidence interval. Some of the stations closest to the smelter had PI above the confidence interval, such as stations 62, K4, K5 and 68. Also the reference station 91 had a PI above the confidence interval.
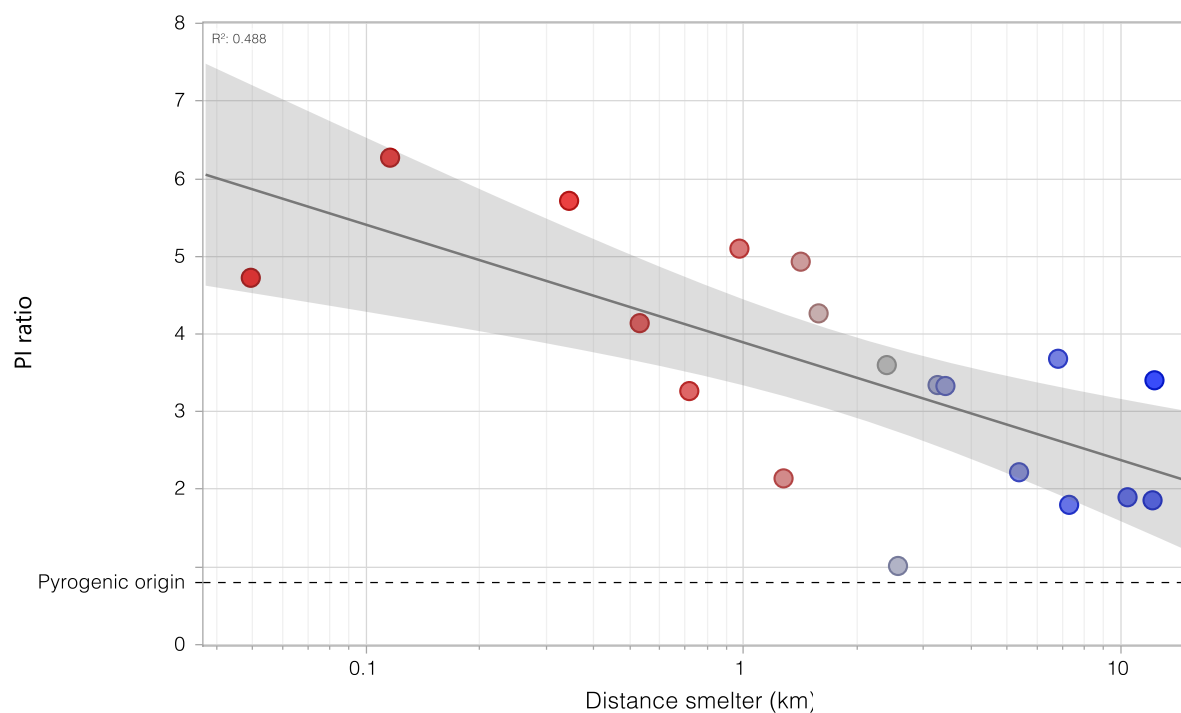
Figure 13. Pyrogenic Index (PI) (Stogiannidis and Laane, 2015) plotted vs. the distance to the outlet from the smelter (logarithmic scale). The lower limit of pyrogenic origin (0.8) is shown as a dashed line.

For metals, there was an opposite trend, most metals were either positively correlated or not correlated with distance to the smelter. The exception was Ni, which was negatively correlated with the distance to the smelter, indicating that the smelter could be a source. However, the R^2 for Ni was only 0.18, so a less clear picture than with the PACs.
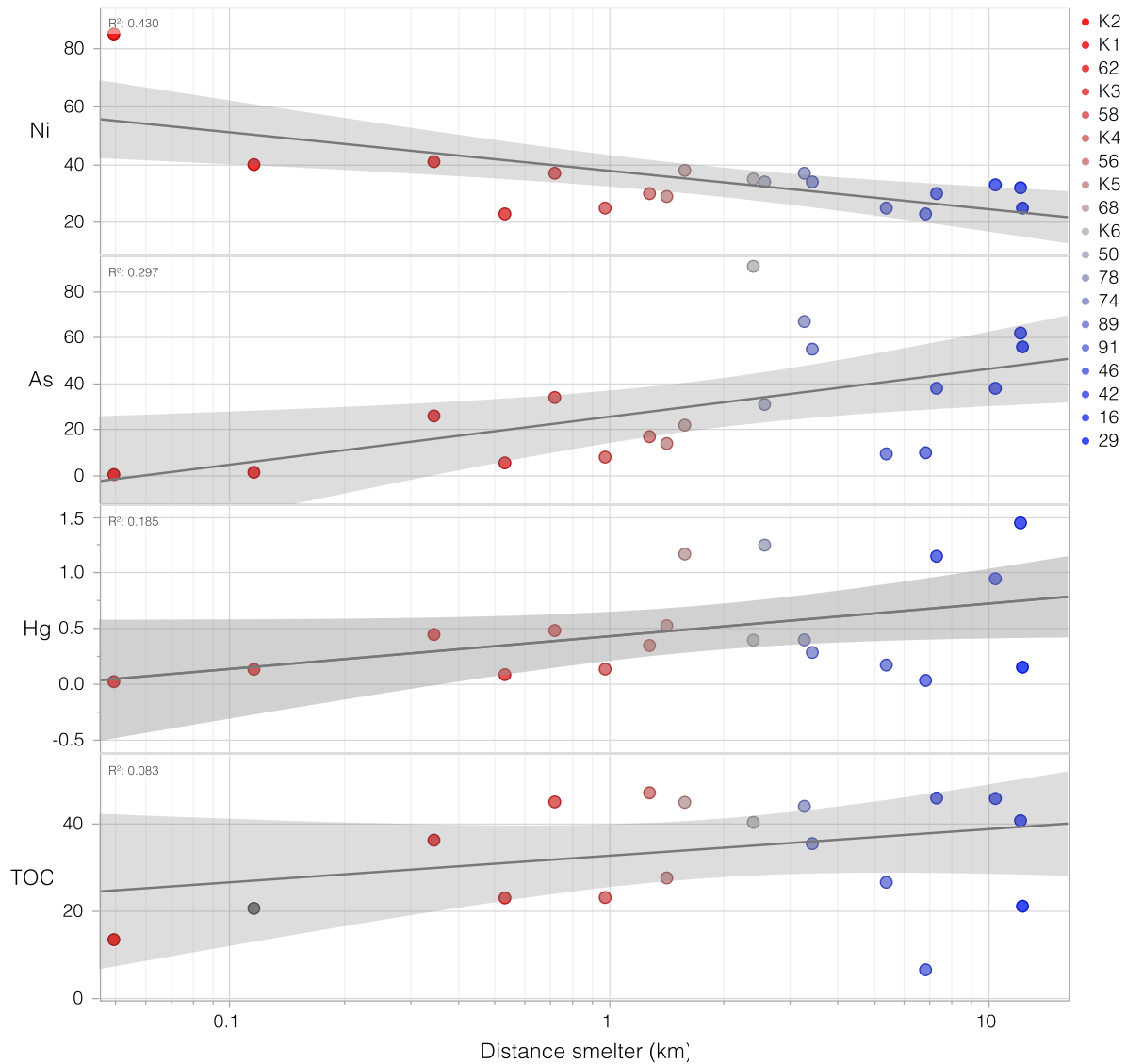
Figure 14. Selected examples of correlation of metals and grain size with distance from aluminium smelter (logarithmic scale). All correlations can be found in the Appendix.

3.4 Objective 2A: Is there a correlation with distance from smelter in mussel tissue?

For PACs in mussel tissue many PACs correlated negatively with distance from the smelter, indicating that mussels bioaccumulate PACs from the smelter. The correlations for all PACs are shown in Figure 31 in the appendix. Even though many PACs correlate well with distance from the smelter, like fluoranthene (FLA) and PAH16, there were also some PACs in mussel tissue that did not correlate well with distance from the smelter (Figure 15). Naphthalene (N) is one example, and R (retene) another. Also, some of the alkylated smaller ring PACs did not correlated well, probably because these PACs have other sources (fuel and wood burning) mentioned in the previous chapter. Mussels were analysed in triplicate from each station, and therefore fewer (n=5) stations were investigated. The variations in PACs between mussel tissues from the same station were small, indicating that for future investigation, analysing more stations rather than several subsamples can be prioritised.
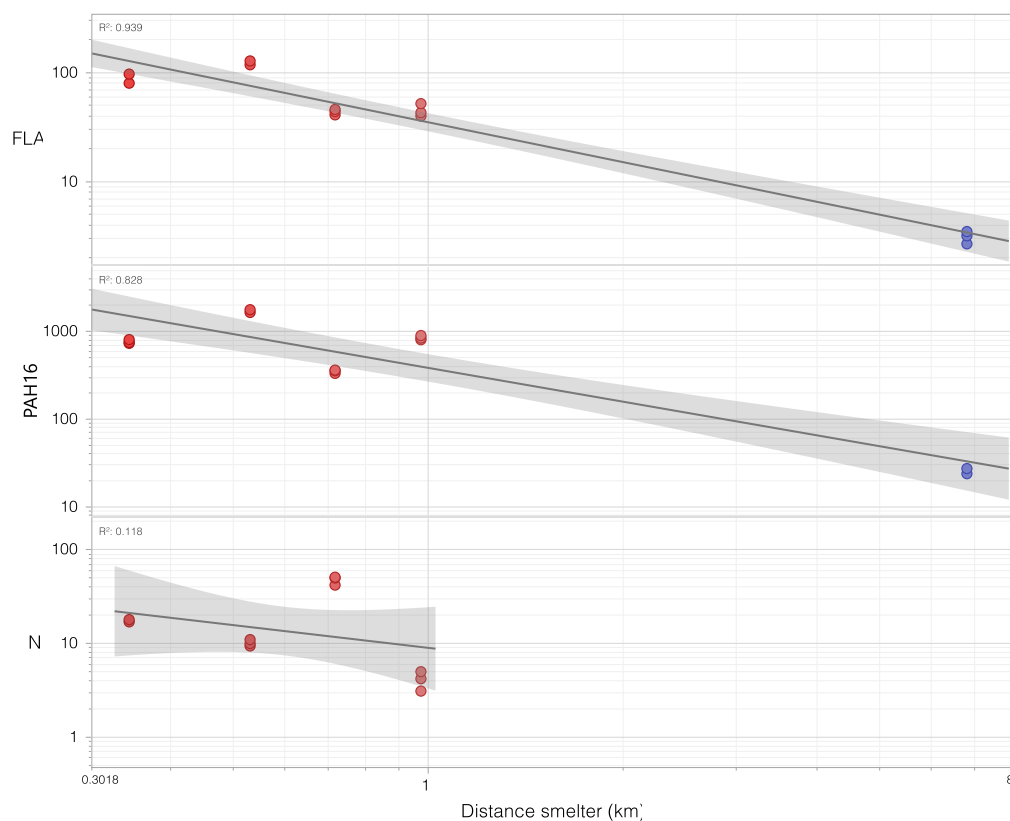
Figure 15. Selected PACs in mussel tissue vs distance to smelter. For N the concentrations in station 91 were below detection limits.

3.5 Objective 2A: Is there a correlation between results from sediment and mussel, including PAC pattern

3.5.1 PAC patterns in sediment indicate several sources of PACs

As mentioned for the PI, the PAC pattern can be used to discern sources of PACs, and also to pinpoint differences. In the sediments there was some noticeable differences between some stations, and these points have been illustrated in Figure 16. The majority of the stations resembled the pattern shown for K1 (upper part of the figure). At the same time as sediments near Kubal were sampled, sediments near the aluminium smelter at Sunndalsøra were also sampled. The sediments sampled at Sunndalsøra was very similar to the pattern shown for K1, so is probably reflecting the aluminium smelter profile. To our knowledge, this is the first time that an extended analysis of PACs, including many heavy PACs (up to 6 rings as well as many alkylated isomers) have been performed in Sweden and Norway.

The notable differences in some of the stations are illustrated below the pattern of K1, with stations 50, 16 and 89 as examples. For station 50, the differences were the relatively higher concentration of the red bars, which represent the concentration of naphthalene (N), and alkylated isomers (C1-C4). They are also present in K1, but the relative concentration was much higher at station 50. The source of N and alkylated N is mainly oil/gasoline as mentioned in chapter 3.3 (Stogiannidis and Laane, 2015). Also, the relative concentration of C3 alkylated F (fluorene) was higher at station 50 than at most other stations investigated. We are not sure of the source of F-C3, and this PAC was noticeably higher in sediments from Sundsvall than from Sunndalsøra. Another difference was noted for station 16, where the concentration of the F-C3 was much higher than at station 50. As

mentioned, we are not sure of the source to this isomer. Since fluorene is a small ring PAC, and the fluorene is C3-alkylated the source is probably fuel of some sort.

For station 89, the most striking difference to the PAC pattern at station K1 is the relatively high concentration of R (retene). As discussed in chapter 3.3, the origin of this PAC is most probably wood burning. Also, in stations 16 and 50 the concentration of R is relatively higher than in the stations most affected by the aluminium smelter such as K1.
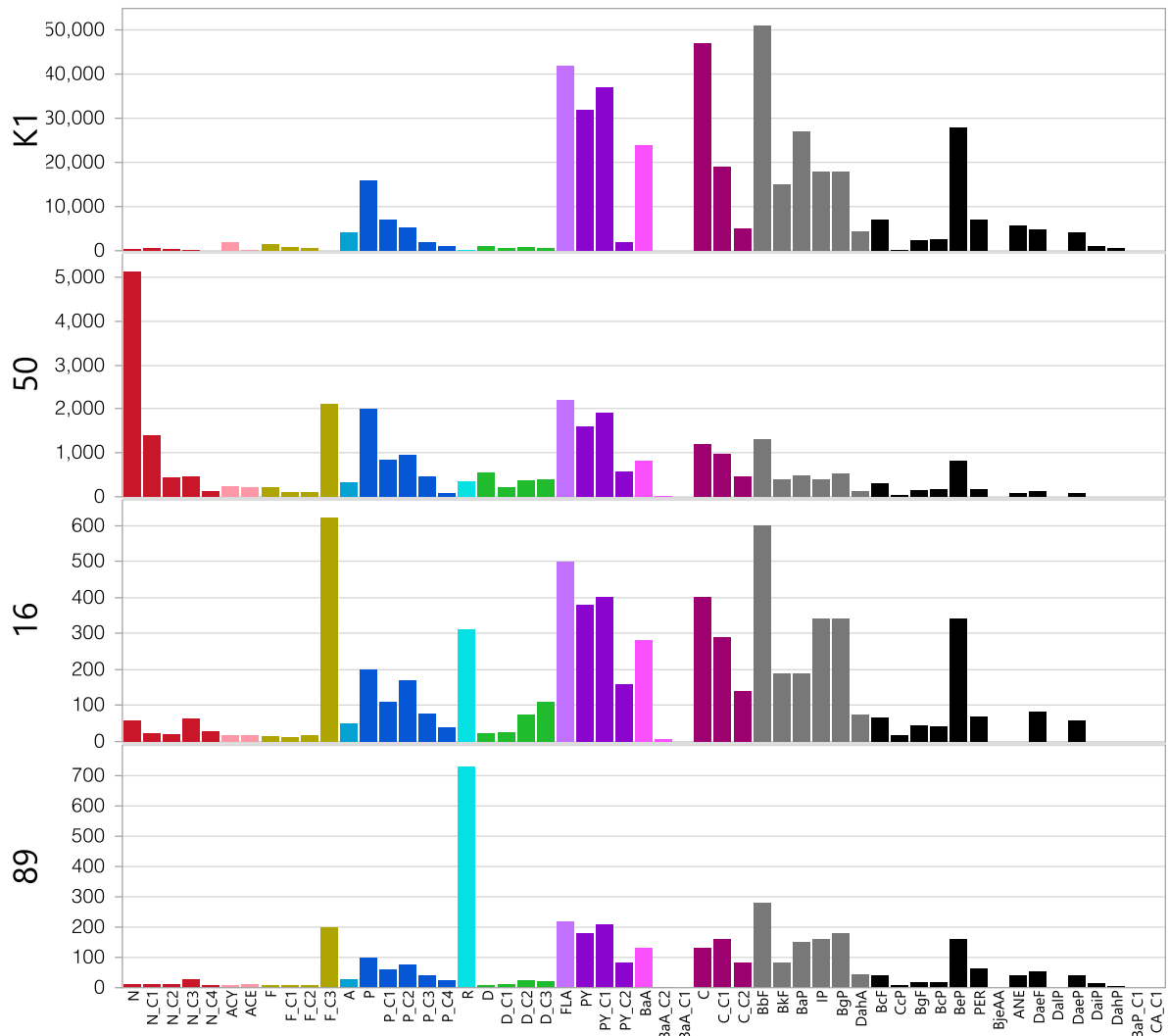
Figure 16. Isomeric patterns of PACs in selected sediment stations. The colours of individual PACs are according to the scheme presented in Table 2. The data are presented as µg/kg dw sediment.

To tease out and clarify the results of the indication of several sources, a hierarchical clustering of PAC result combined with stations were performed. Hierarchical clustering, also known as hierarchical cluster analysis, is an algorithm that groups similar objects into groups called clusters. The endpoint is a set of clusters, where each cluster is distinguished from one another and objects within each cluster are broadly similar. The results are shown in Figure 17. In the figure, each station is portrayed horizontally, while each PAC is portrayed vertically. The heatmap is coloured in a scale from blue (lowest concentration among stations) to grey to red (highest concentrations among stations investigated). Therefore, it is easy to see from the figure that station K1 has the highest concentrations for many PAC, while station 91 has many of the lowest concentrations. The clustering of the stations is shown to the right, while the clustering of the PACs is shown below the heatmap. The clustering of the stations is also shown in the dendrogram to the bottom right, and the colours

here correspond to the colours of the station names in the heatmap. We have divided the stations in 6 groups: cluster 1 (red: K2, K6, 78, 74, 42, 16), cluster 2 (green: 58, 56. 46, 50), cluster 3: (blue, 89, 29) cluster 4 (orange: 91), cluster 5 (bluegreen: K1) and cluster 6 (lilac: 62, K5, 68, K4, K3).

The hierarchy of clustering shows that the greatest difference is between clusters 5 and 6 and the other clusters (in the dendrogram – the circle in the middle represents the starting point). The main difference is that PAC concentrations are higher (more red cells) in the cluster 5 and 6. The next level of difference is between cluster 1+2 on one side and cluster 3+4 on the other. Cluster 3 and 4 contains virtually no red and are mostly blue (low concentrations). The reference station and stations far from outlets are in clusters 3 and 4, so this makes sense. The next level of hierarchy is two: it separates cluster 1 from cluster 2, and cluster 5 from cluster 6. For the latter, cluster 5 is only one station (K1), where the concentrations contain more red (higher concentrations) than the stations in cluster 6. The difference between cluster 1 and cluster 2 are that cluster 2 contains higher concentration of PACs to the left, which is typically the PACs associated with fuel (small ring PACs with alkyl groups). The next hierarchy of clusters was separating cluster 3 (stations far away from outlets) and 4 (91, the reference station). Reference 91 had lower concentrations than the other stations and was therefore cleaner than the stations in cluster 3.

The PACs were also subject to hierarchical clustering, but only a few points will be mentioned. The largest difference was between the small ring PACs to the left, and the larger, more heavy PACs to the right. The next level of difference separated retene from the other small ring PACs, indicating that this PAC behave different than the other two groups of PACs, and therefore likely has a different source.

3.5.2 Correlation between PAC pattern in sediment and mussel tissue

A comparison between PAC patterns in sediment and mussel tissue was conducted, and selected examples are shown in Figure 18, while the other mussel stations are shown in the Appendix (Figure 32). The overall impression is that the PAC pattern in sediments were reflected by the PACs accumulated in mussel tissue. The same PACs are detected in sediments and in mussels. However, some small differences can be found, the smaller ring PACs (2-4 rings – to the left in Figure 18) seem to be more bioaccumulated than larger ring PACs (5-6 rings, to the right in grey and black colour). Also, there are some indication that alkylated PACs are more easily bioaccumulated in mussels (e.g. alkylated P, dark blue colour). This is line with expectations based on the physicochemical properties of individual PACs.
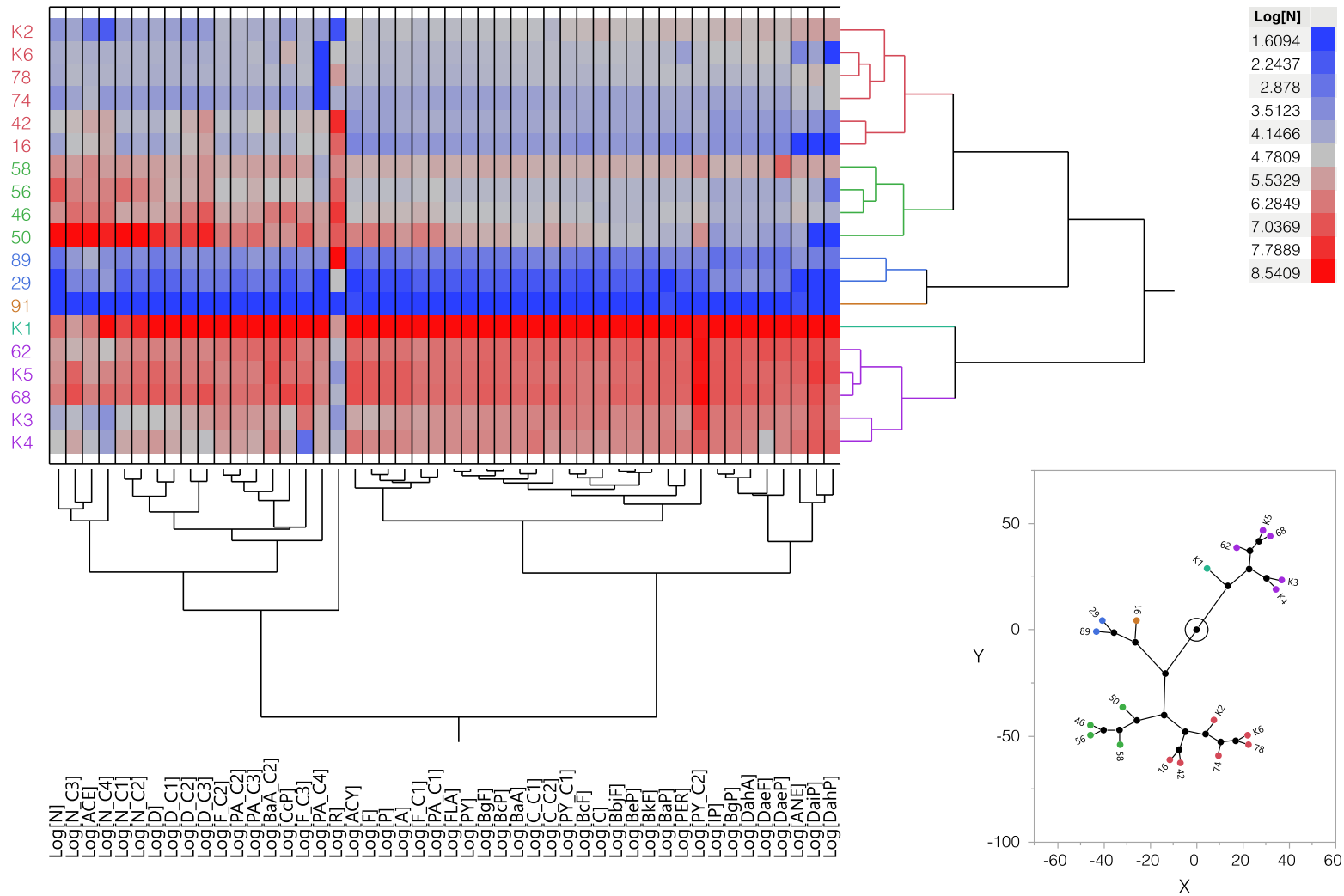
Figure 17. Two-way hierarchical cluster analysis of PAC concentrations in sediment and stations. Concentrations below LOD were replaced by half LOD, and were log transformed prior to analysis. The constellation plot has been inserted in the bottom right to ease identification of similar stations. The colours of the cells are from red to grey to blue according to the relative concentration of the compound measured for all station. The range of concentrations for logN are shown, but the scale differs for each PAC.
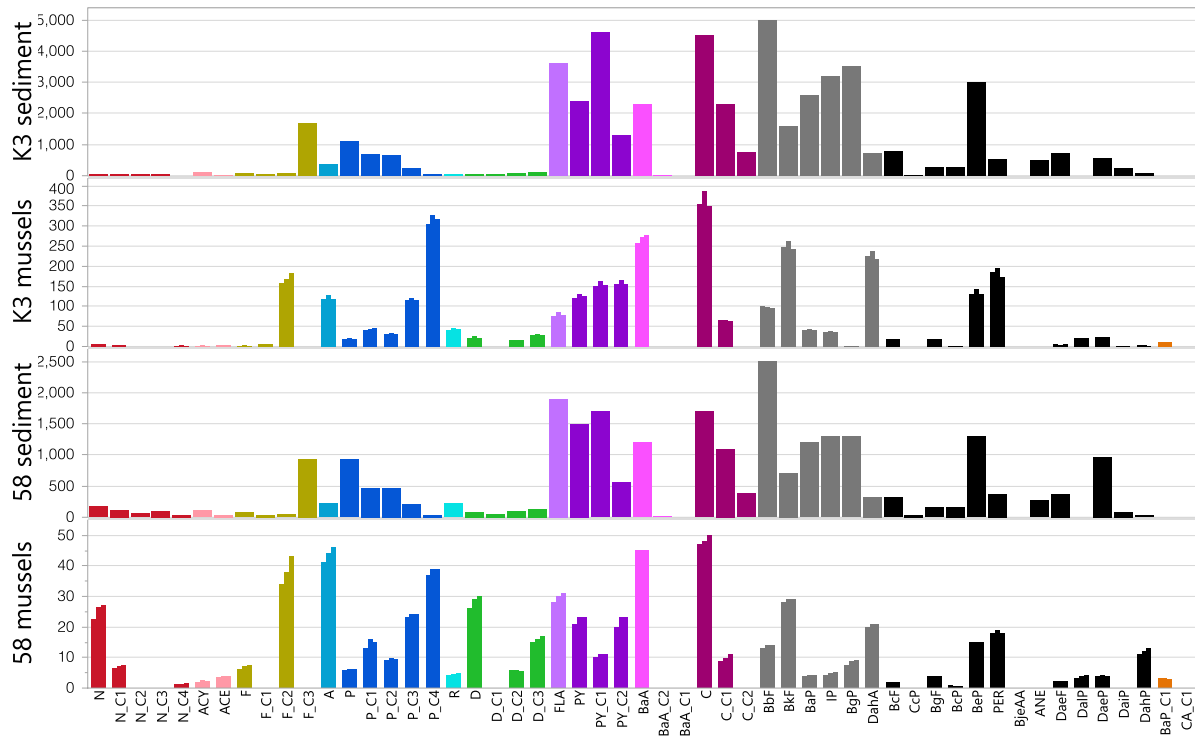
Figure 18. Comparison of isomeric pattern of PACs for stations K3 and 58 in sediment (upper panel) and biota (lower panel, 3 replicates shown as individual bars). The data are presented as µg/kg dw for sediment and µg/kg ww for mussels.

3.6 Objective 2B: Is there any sign of change over time over previously noted levels of PACs and metals in surface sediment and mussel tissue?

3.6.1 Summary of reductions of PACs in sediment

Sediments and mussels have been investigated previously, in 1988 and 2002, while the Søderberg process was still in use at Kubal. A drawback for comparison is that the stations investigated are not the same for all the surveys.

The historical data for PAH16 are shown in Figure 19. The stations from 2002 with PACs below LODs were (station followed by number of PACs below LOD): 91:16, 78:15, 89:12, 29:5, 68:1 and 74:1. For these stations there is therefore uncertainty about the data from 2002.
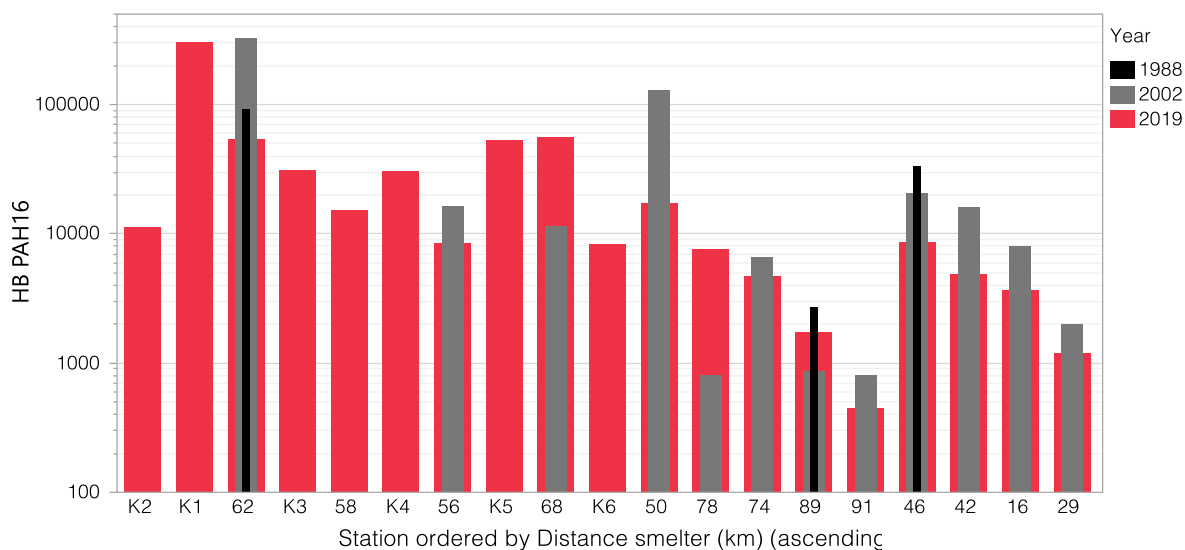
Figure 19. Bar plot for sum PAH16 in sediments investigated in 2019 and for stations also investigated previously. The presented data are the upper bound of data (i.e. that concentrations below LOD are included in the sum of PAH16).

Figure 19 shows the difference in concentration between stations investigated over time for 12 sediment stations that were investigated both in 2002 and 2019. The results for stations also investigated in 1988 are shown, but not included in the comparisons. Nine of the stations had reduced PAC concentration between 275,000 and 350 µg/kg dw, and a percent reduction between 87% and 29%. Three stations had an increase from 870 to 45,000 µg/kg, with amounts from twice to >9 times the concentration in 2002. In total, the sum of reduction for all stations was 69%, showing an overall improvement of environmental concentrations of PAH16. No comparisons can be made with the other PACs measured in 2019, as these were not routinely monitored in previous years.

Table 3. Upper bound of PAH16 for stations investigated in 1988, 2002 and 2019 are shown. The difference between 2002 and 2019 (decreasing order) and percent reduction from 2002-2019 are also presented.

Station	Min. distance to outlet (km)	1988	2002	2019	Difference 2002-2019	percent reduction 2002-2019
62	0.34	92,200	328,820	54,007	274,813	84%
50	2.6		128,300	17,130	111,170	87%
46	7.3	33,500	20,650	8,658	11,992	58%
42	10		16,180	4,871	11,309	70%
56	1.3		16,270	8,413	7,857	48%
16	12		8,030	3,655	4,375	54%
74	3.4		6,640	4,719	1,921	29%
29	12		2,000	1,198	802	40%
91	6.8		800	450	350	44%
89	5.4	2,700	860	1,731	-871	-101%
78	3.3		810	7,580	-6,770	-836%
68	1.6		11,530	56,412	-44,882	-389%
All		**128,400**	**540,890**	**168,823**	**372,067**	**69%**

3.6.2 Comparison of environmental class

All stations investigated were classified and the levels compared directly when the same station was investigated as in 2019 (Figure 20) (for classifications of all stations investigated historically this can be found in Figure 33 in the appendix). For the classification the lower bound concentrations were used (concentrations below LOD is set to 0).

The stations that had an improvement in environmental class from 2002 to 2019 were: 62, 56, 50, 74, 91, 46, 42, 16 and 29. The stations with a reduced environmental class were stations 68, 78 and 89. Therefore, the reduction of PAC concentration in sediment (Table 3) is reflected in the assigned environmental class.
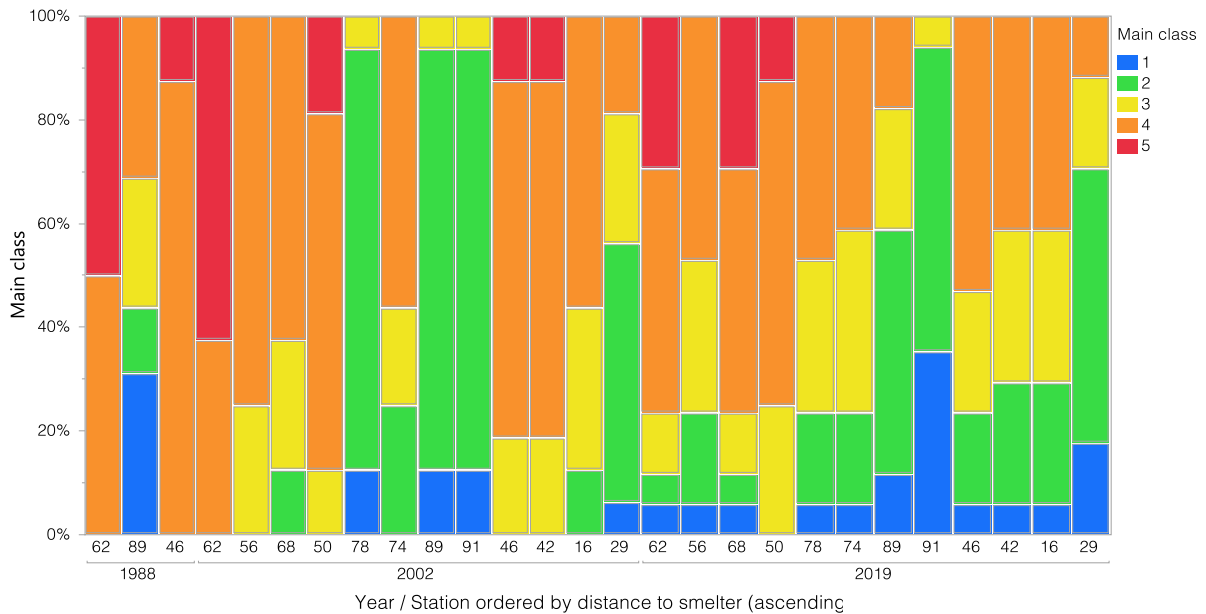
Figure 20. Assigned class for sediment stations investigated for PAH16 historical and in 2019. The data are based on lower bound data (limits below LOD are set to 0).
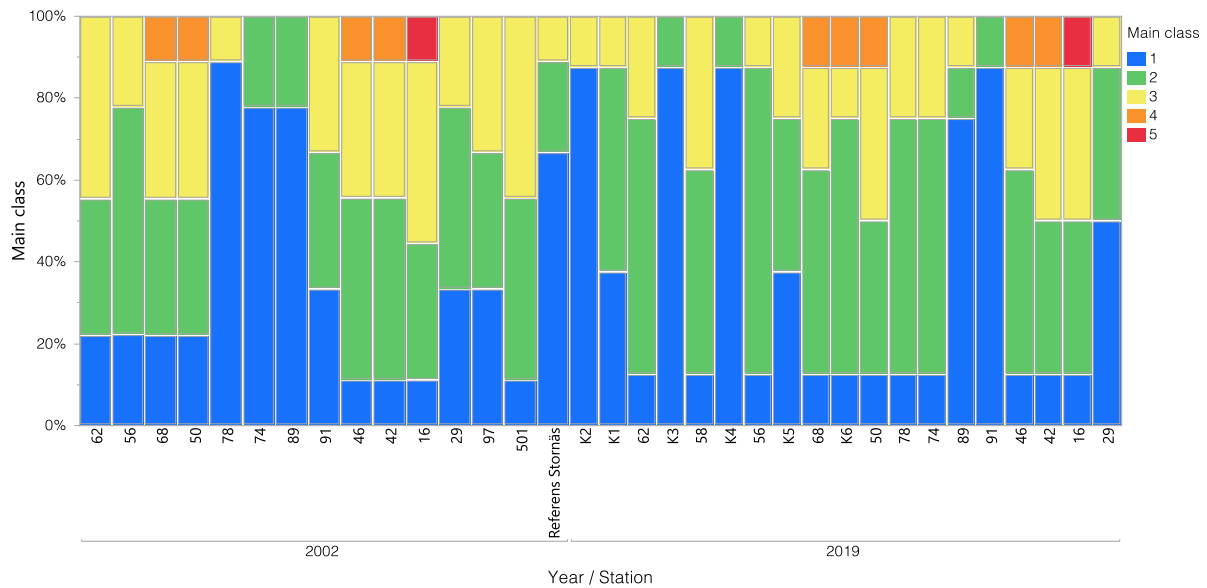
Figure 21. Classification of sediment concentration of metals for stations analysed in both 2002 and 2019 according to Norwegian/EU guidelines.

Metals were not investigated in 1988, and therefore only data from 2002 were available for comparison (Figure 21). The main difference between PACs and metals are that the environmental classes were lower for metals than PACs, both in 2002 and 2019 with fewer orange and red classifications. For metals the overall picture of the environmental class shows that there is no significant change.

3.6.3 Historical correlations with distance from smelter

PAH16 correlated with distance from smelter in 2019. The correlation of the upper bound of sumPAH16 was calculated for the stations for which distance to the smelter was available. For all the years the PAH16 correlated negatively with distance from smelter (Figure 22). Since very few stations investigated in 2019 were investigated in 1988, the confidence interval for this curve is very wide. For 2019, the curve is lower than in 2002, but the confidence limit is within the limits for 2002.
For sum PAH16 in mussel tissue, the trend was similar in both years, but the concentrations of PACs in mussel tissue was lower in 2019 than in 2002 with little overlap of the confidence intervals. However, fewer stations were investigated in 2019 than in 2002. The difference between the years was roughly 10-fold (i.e that the concentrations in mussels in 2002 were 10 times higher than in 2019).

Ni was the only metal that had higher concentrations near the smelter than further away. The historical Ni concentrations for the stations investigated in 2019 are shown in Figure 24. In 2002 there was no clear trend of Ni concentration with distance from the smelter (at least for the stations investigated both in 2019 and 2002). In 2019 there was a decreasing trend with distance from the smelter. However, the confidence interval for the curve in 2019 is within the confidence interval for the curve in 2002, so it is difficult to conclude if there have been any significant changes.
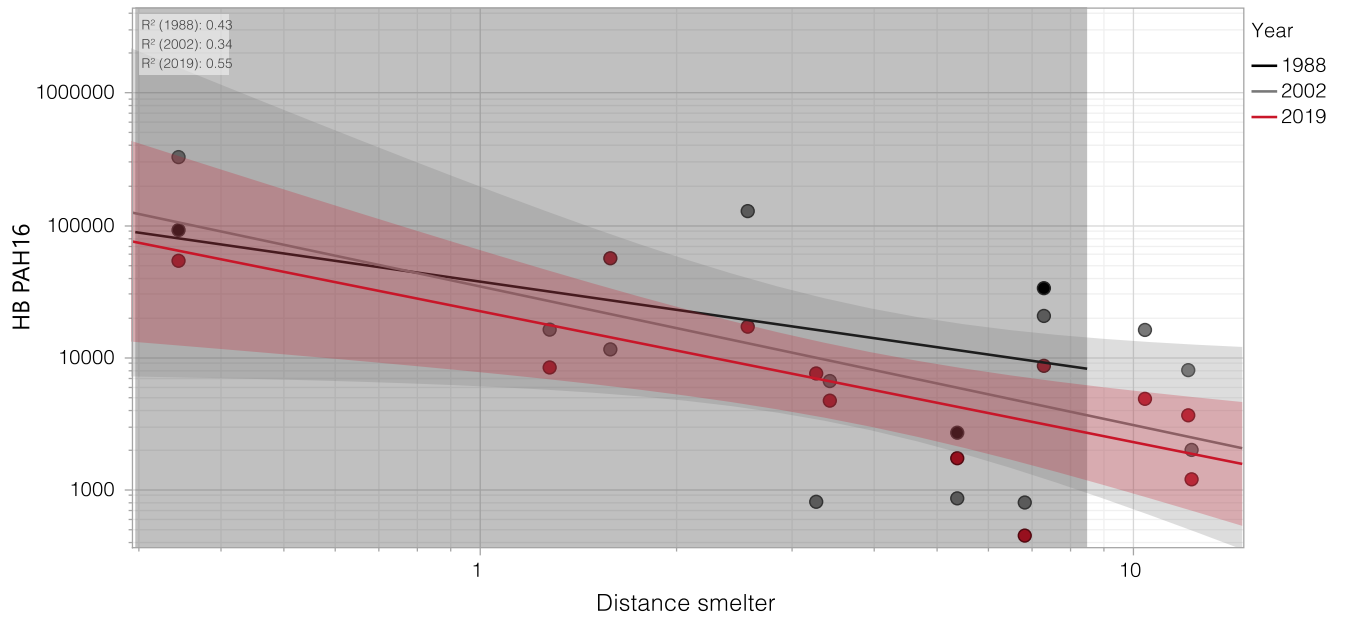
Figure 22. Upper bound of PAH16 for stations investigated in 1988, 2002 and 2019[1]. Only stations that was investigated in 2019 were included.
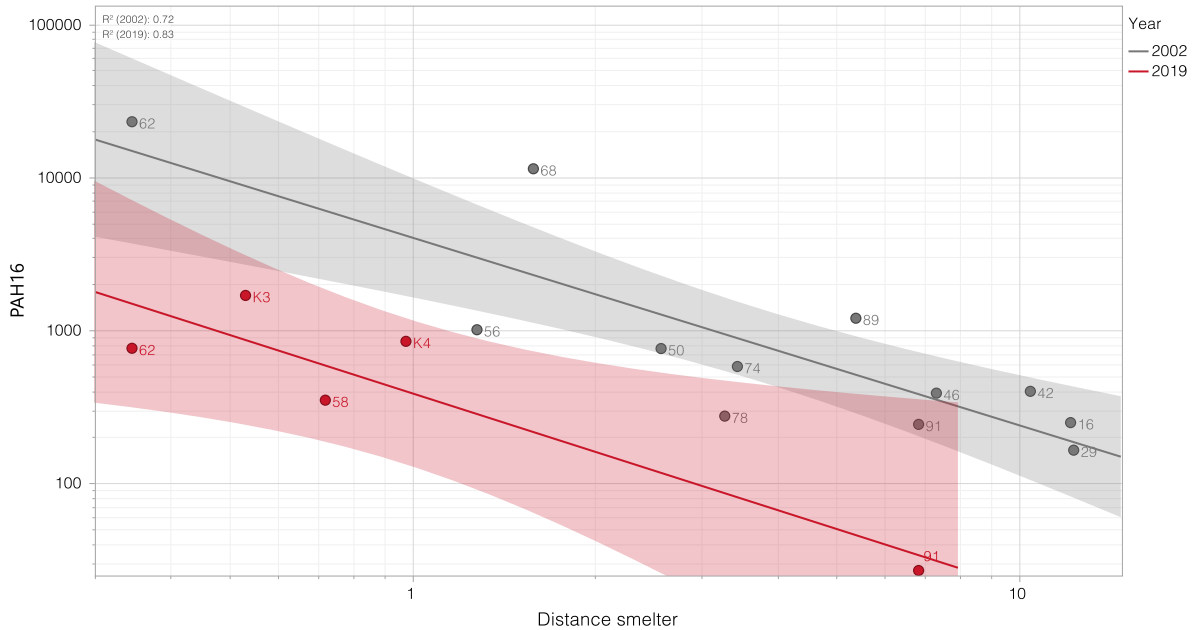
Figure 23. Correlation with distance of PAH16 in mussel tissue in 2002 and 2019. For 2019 concentrations the mean of three individual samples are shown. Only stations that have been designated with a distance are included.

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[1] The upper bound means that for PACs not detected above the LOQ, the LOQ replaces the concentration for the PAC in question in the sum (of PAH16)
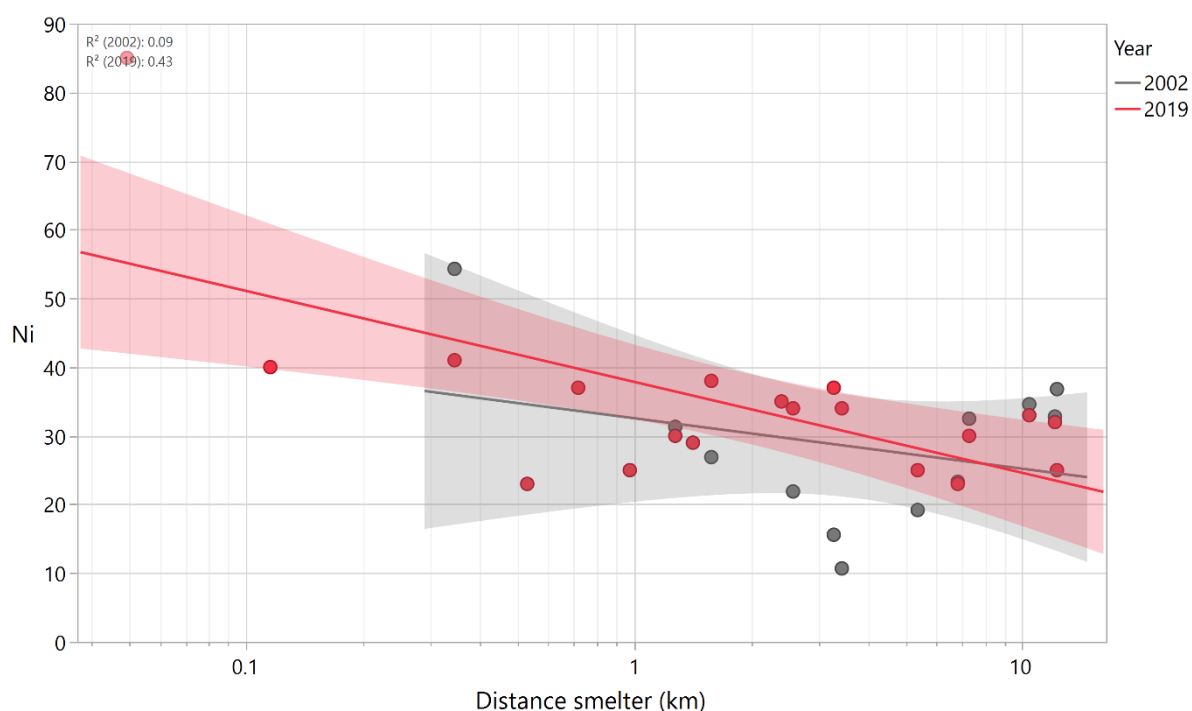
Figure 24. Nickel in sediments measured in 2002 and 2019 in correlation with distance from smelter. Only stations investigated both years are included.

3.6.4 Further comparison of concentrations in 2019 vs. 2002

In Figure 25 the concentrations for individual PACs at stations investigated in 2002 and 2019 are compared. The concentrations measured in 2019 has been divided by the concentrations measured in 2002 (normalised). If the concentrations are equal, the result is 1, which means that the concentration both years were equal. If the concentrations in 2019 are lower, the resulting number will be lower than 1. The line plot shows each PAC as a line for an individual station. The stations are ordered by the mean of the PACs, so stations to the left (e.g. station 68 and 89) have higher concentrations of PACs on average in 2019 than 2002. The main result is that most stations have reduced concentration over time. The station to the far left is station 68, where on average most PACs increased from 2002 to 2019. This could be a result of several things; a) local conditions may vary, for example due to extreme weather situations such as storms, resuspension of sediments can occur, b) it is difficult to sample exactly the same location twice. Also, station 89 has increased individual PACs, but as discussed above, the increase can be explained by lower LODs employed in 2019.

Since the overall picture is that most stations had lower concentrations in 2019, this indicates that replacing the Søderberg process has had a positive influence on the environment with reduced PAC levels in sediments as a result.

The same data as in Figure 25 are presented as boxplots for individual PACs with the stations as points in Figure 26. They are ordered by the means of all PACs at each station, which means that PACs to the left are less reduced than PACs to the left. To the left are the higher ring PACs, which are less biodegradable and more prone to adhere to particles. Three of the high ring PACs are on average increased from 2002 to 2019 (BgP, BbF, and IP). The rest of the PACs are on average lower. The lower

ring PACs (2-3 rings) such as N, ACE, ACY, A, are less prone to bind to particles and are more easily degraded. As a result, they are on average reduced more than the 5-ring PACs.
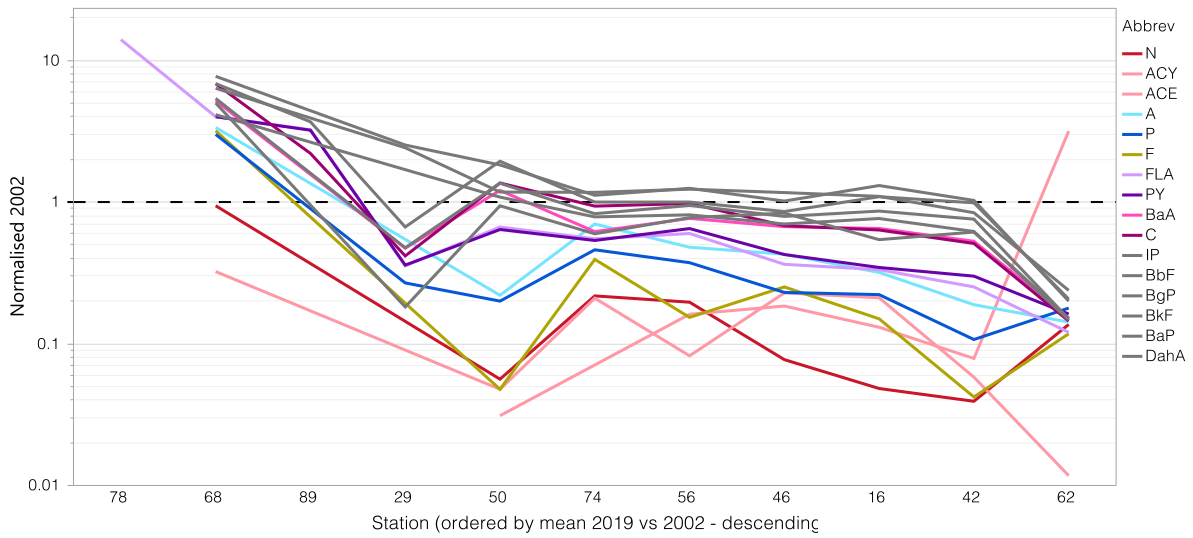
Figure 25. Line plot of PAH concentrations (logarithmic scale) in sediment 2019 normalised to concentrations measured in 2002.
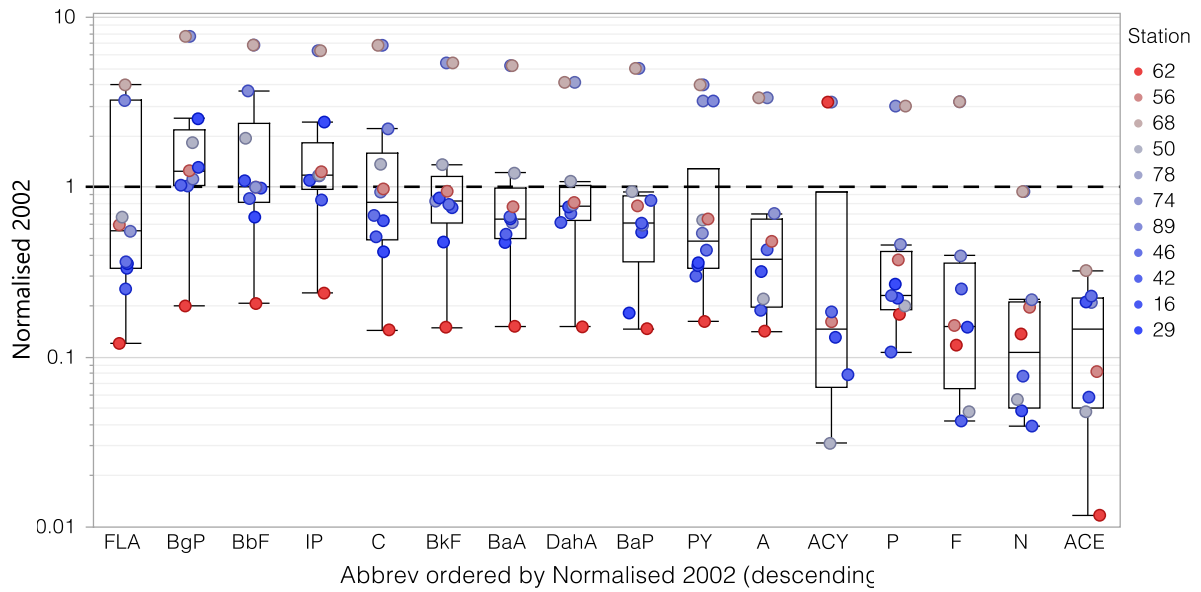
Figure 26. Boxplot of individual PACs (logarithmic scale) where concentrations in 2019 have been normalised to 2002.
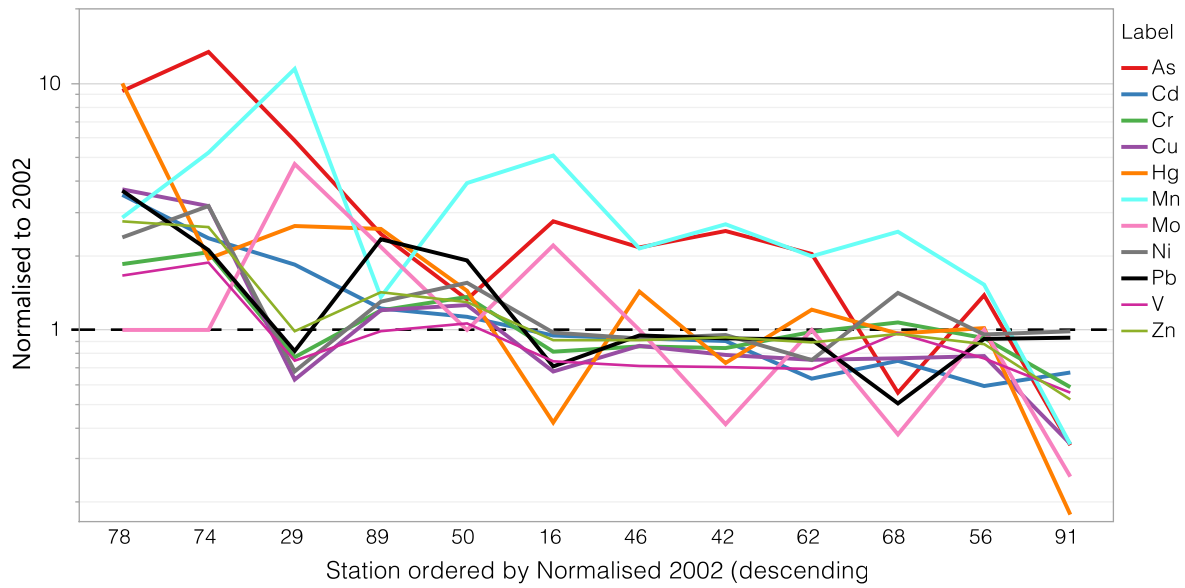
Figure 27. Line plot of metals (logarithmic scale) investigated in 2019 and 2002. The 2019 data has been normalised to 2002.
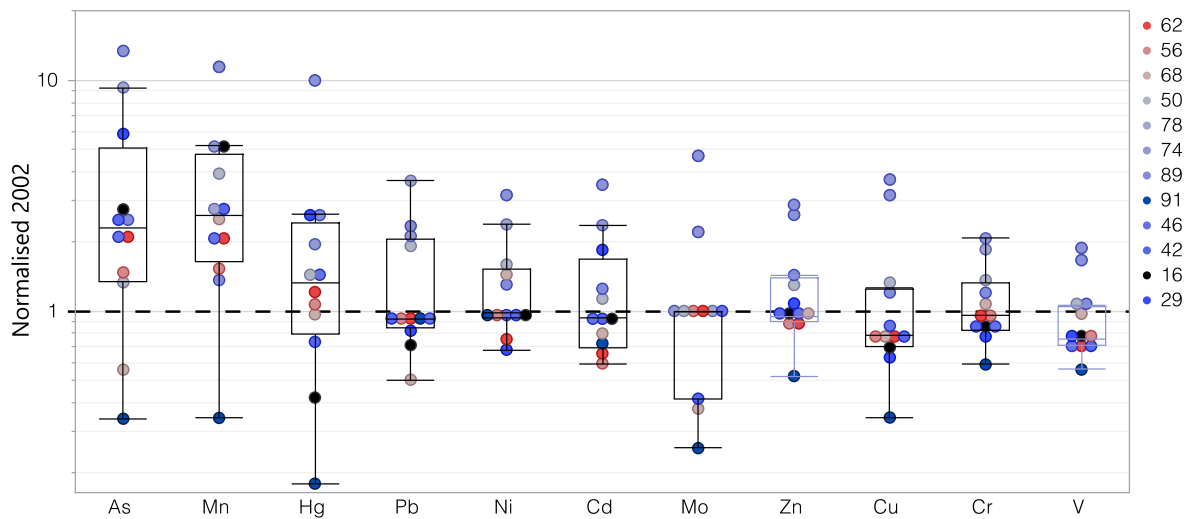
Figure 28. Boxplot of metals (logarithmic scale) vs station. The concentration of each metal measured in sediment in 2019 have been normalised to the concentration measured in 2002. The boxplots are arranged in descending order based on the mean of concentrations in 2019 vs 2002.

4 Conclusions

4.1 Environmental levels in sediments (Objective 1)

- Environmental level of PACs in sediments closer than 500 m to outlet of Kubal exceed the EQS to a large extent. The station most affected was K1, with very large exceedances of the acutely toxic levels for many PACs. However, this station is very close to one of the discharge points, and are normally not analysed in environmental investigations. Sediment stations further away from the outlet were less affected, with station 91 being the least affected. The PACs for which mean of stations were exceeding class 5 (5 times acutely toxic levels) were fluoranthene, benzo(ghi)perylene, anthracene chrysene and indeno(1,2,3,cd)pyrene.
- The water bodies Alnösundet and Klingerfjärden north of Sundsvall were also affected by PACs, but as discussed in Chapter 3.1.1, other sources to PACs were probably present here.
- For metals, there were less frequent exceedances of EQS, and less stations were classified in class 3, 4 or 5. Stations near the outlet of Kubal did not have more frequent exceedances of the EQS compared to other stations e.g. reference station. The only metals with exceedances of the acutely toxic levels (class 4 and 5) in sediments were mercury and arsenic at stations not close to the outlet of Kubal.

4.2 Environmental levels in mussels (Objective 1)

- Only five PACs have assigned EQS in biota, of these two PACs (fluoranthene and benzo(a)pyrene) exceeded EQS in 3 of the four stations analysed. The closest stations to the outlet of Kubal were exceeding EQS. Only station 91 had no exceedances of EQS of PAC in mussels.
- Of the metals, only mercury has an assigned EQS level in biota, and no mussels at any station investigated had exceedances of the EQS.

4.3 Is there a correlation with distance from smelter in sediment samples? (Objective 2 A)

- Most PACs correlated negatively with the distance to the outlets of Kubal, suggesting that the smelter was the source of most of the PACs measured. There were however a few exceptions to this pattern:
  - Retene is a C4-alkylated phenantrene which is a PAC marker of wood burning. This PAC did not correlate negatively with distance from Kubal
  - Naphthalene, alkylated naphthalenes and acenaphtylene and potentially other small-ring PAC did not correlate negatively with distance from Kubal, and therefore have other sources in addition to the smelter. The sources are probably originating from e.g. gasoline or kerosene (jet fuel).
- For metals there were no clear trends for with decreasing trends with distance from Kubal. Most metal concentrations increased with increasing distance from Kubal
  - Nickel was the only metal with a weak negative correlation as seen for PACs, but the correlation was less certain than some of the PACs since the R^2 was only 0.19
  - EQS for Ni concentrations in sediments were not exceeding EQS except at station K2 (class 3 – chronic toxicity)

4.4 Is there a correlation with distance from smelter in mussel tissue? (Objective 2 A)

- For PACs in mussel tissue many PACs correlated negatively with distance from the smelter, indicating that mussels bioaccumulate PACs from the smelter.
    - o Roughly the same exceptions as observed in sediments were also observed in sediment.
- For metals in mussels we have not analysed the data because 1) fewer stations were investigated for mussels than sediments and 2) there seemed to be only nickel in sediments that correlated negatively with distance from Kubal and 3) there were fewer exceedances of metals in sediments than biota

4.5 Is there a correlation between results from sediment and mussel, PAC isomeric patterns (objective 2 A)

- PAC pattern in sediments were roughly repeated in mussel tissue, so the correlation seems to be good. However, some minor differences between the pattern in sediments and biota were observed, probably due to different bioaccumulation rates.

4.6 Is there any sign of change over time of previously noted levels of PAH and metals in surface sediment and mussel tissue? (Objective 2 B)

- For sediments, we compared concentrations at stations investigated both in 2002 and 2019. The sum of PAH16 (including LOQs) were reduced at 9 stations and increased at 3 stations. By summing the concentrations at all stations, a mean of 62% overall reduction in sediments of sum PAH16 was observed. The small ring PACs showed the most reduction in concentrations, while the heavier PACs (4-6 rings) showed the least reduction. Stations 62 and 50 showed the largest reduction in concentration, with more than 84 and 87% reduction respectively observed.
- For metals, there were increased median concentrations of arsenic, manganese and mercury, while copper, chromium and vanadium were decreased. These metals were in all likelihood not the result of releases from Kubal, and therefore the reason for the increase is not known. The stations associated with the greatest increase in concentrations were not the nearest stations to the outlet of Kubal (e.g. 78, 74, 29 and 89)

For PACs in mussel tissue, only two stations were investigated both years. However, the lines for correlation with distance from outlet of Kubal and sum PAC16 indicate that concentrations in mussel tissue in 2002 were 10 times higher than in 2019.

5 References

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Appendix A.

Table 4. PAH concentrations (ng/kg dw) in sediment where cells are coloured by class. Levels below LODs have been replaced by half LOD when LOD is known, otherwise denoted as «0».

Year	Station	N	ACY	ACE	F	P	A	FLA	PY	C	BaA	BbF	BkF	BaP	IP	BgP	DahA
1988	62	4600	600	900	800	3900	2100	5900	4800	7600	12500	12200	11300	14000	3900	4600	2500
1988	89	100	0	0	0	200	0	300	300	300	400	300	200	400	100	100	0
1988	46	6900	900	1100	800	2500	1200	2900	2500	2200	3700	2500	2500	2600	400	500	300
1988	21	600	100	0	100	800	100	800	700	400	800	500	400	300	100	100	0
1988	27	1300	100	100	100	1200	300	1400	1200	900	1500	1100	800	700	100	100	0
1988	33	3500	700	600	700	2800	1100	3400	3000	2400	3900	2200	2100	2300	300	400	200
1988	41	5300	1400	1600	1300	3100	1400	3800	3200	2200	3500	1700	1500	1500	100	100	100
1988	52	7400	1100	1600	1100	3000	1200	2500	2900	2400	3900	2600	2400	2600	400	500	300
1988	54	7800	1000	500	600	4100	1200	4000	3300	4200	7700	6000	5200	3600	400	500	200
1988	61	7600	1100	800	800	4000	1700	4100	3600	4400	7500	5200	4700	5300	800	1000	500
1988	69	1800	300	300	300	1900	600	2300	2000	2100	3500	2300	2100	2400	500	600	300
1988	76	1200	200	200	200	1200	400	1600	1400	1600	2600	1800	1700	1900	400	600	200
2002	62	1900	120	2300	1700	14000	4500	49000	29000	47000	27000	45000	18000	34000	21000	27000	7300
2002	56	5700	390	450	280	1500	250	1600	1200	860	730	1200	370	670	430	480	160
2002	68	520	25	130	110	1200	280	1700	1300	790	790	1400	520	900	850	700	290
2002	50	91000	7400	4400	4400	10000	1500	3300	2500	880	670	670	280	510	340	290	120
2002	78	25	25	25	25	25	25	60	25	25	25	25	25	25	25	25	25
2002	74	170	25	62	66	630	110	1000	840	470	550	750	290	670	410	430	140
2002	89	25	25	25	25	25	25	68	56	59	25	76	25	25	25	25	25
2002	91	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
2002	46	4400	390	210	270	3300	420	3300	2300	1100	940	1400	480	790	540	610	200
2002	42	2800	330	430	570	2800	440	2700	1800	960	700	790	330	570	440	370	150
2002	16	1200	130	90	100	900	160	1500	1100	630	430	550	220	350	310	260	98
2002	29	150	25	25	25	160	25	310	220	180	110	210	82	110	120	95	25
2002	501	1900	93	130	93	740	140	1200	960	480	368	480	230	420	320	270	110
2002	97	150	25	25	25	63	25	100	71	25	25	60	25	25	25	25	25
2002	Referens	160	25	25	25	93	25	140	95	74	53	91	25	25	56	25	25
2019	K2	40	76	3.6	40	530	140	1100	920	1500	770	1800	540	980	1200	1300	250
2019	K1	670	2000	47	1500	16000	4100	42000	32000	47000	24000	51000	15000	27000	18000	18000	4400
2019	62	260	380	27	200	2500	640	5900	4700	6800	4100	9300	2700	5000	5000	5400	1100
2019	K3	70	120	9.2	71	1100	360	3600	2400	4500	2300	5000	1600	2600	3200	3500	730
2019	58	350	110	38	74	930	220	1900	1500	1700	1200	2500	710	1200	1300	1300	330
2019	K4	120	310	15	150	1800	440	3600	3000	2800	2200	4700	1500	2900	3100	3200	640
2019	56	1120	63	37	43	560	120	960	780	840	560	1200	350	520	530	600	130
2019	K5	320	570	28	340	3500	950	6310	5000	4600	3700	8400	2800	4600	5300	5300	1000
2019	68	490	590	42	350	3600	940	6800	5200	5400	4100	9600	2800	4500	5400	5400	1200
2019	K6	69	63	11	41	460	110	900	730	890	600	1400	410	540	920	910	240
2019	50	5120	230	210	210	2000	330	2200	1600	1200	810	1300	380	480	400	530	130

Year	Station	N	ACY	ACE	F	P	A	FLA	PY	C	BaA	BbF	BkF	BaP	IP	BgP	DahA
2019	78	65	55	12	38	410	110	840	680	780	570	1300	410	640	740	750	180
2019	74	37	36	13	26	290	77	550	450	440	340	750	240	400	480	480	110
2019	89	17	8.2	11	9.4	100	27	220	180	130	130	280	84	150	160	180	44
2019	91	5	4	0.9	2.1	30	5.5	56	44	34	28	66	23	33	54	49	10
2019	46	340	72	48	68	760	180	1200	980	750	630	1200	380	660	630	620	140
2019	42	110	26	25	24	300	83	680	540	490	370	780	250	350	370	380	93
2019	16	58	17	19	15	200	51	500	380	400	280	600	190	190	340	340	75
2019	29	5	2.9	4.5	3.2	43	7.6	110	79	75	52	140	39	20	290	240	82

Table 5. Metal concentrations (µg/kg dw) in sediment where cells are coloured by environmental class. Levels below LODs have been replaced by half LOD when LOD is known, otherwise denoted as «0».

Year	Station	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Al	Ba	Be	Co	Fe	Li	Mn	Mo	Sn	Sr	V	Vn
2002	16	22.5	0.748	49	45.7	3.44	32.8	52		19300	112	0.834	11.6	38200	34	1100	1	2.5	61.9	53.6	
2002	29	9.57	0.212	38.7	30.2	0.0584	36.8	20.7		18000	289	0.673	15.5	33000	27.6	832	1	2.5	35.5	45.3	
2002	42	15.1	0.754	53.3	44.2	1.29	34.6	42.2		22300	131	0.928	12.3	37300	35.6	821	2.41	2.5	54.1	59.4	
2002	46	17.6	0.541	47.8	40.6	0.804	32.5	42.1		21400	132	0.9	10.5	35200	33.1	748	1	2.5	56.2	57.4	
2002	50	23.3	0.469	31.6	34.1	0.868	21.9	25.1		14000	94.2	0.559	8.11	26200	22.1	381	1	2.5	65	41.4	
2002	56	12.3	0.422	46.4	42.1	0.343	31.3	34.8		22700	103	0.889	11.4	34400	37	459	1	2.5	49.7	57.4	
2002	62	12.8	0.646	42.8	43.6	0.37	54.3	38.3		54000	99.7	1.51	12.5	33300	32.9	704	1	2.5	55	69.1	
2002	68	39.5	0.587	37.3	45.6	1.21	26.9	93.3		18200	88.7	0.775	13.5	28200	28.2	388	2.65	2.5	39.2	47.3	
2002	74	4.11	0.136	21.8	9.76	0.147	10.7	15.2		8740	47.8	0.34	4.29	12600	16.1	153	1	2.5	19	25.6	
2002	89	3.88	0.131	27.5	18.3	0.0674	19.2	8.58		12100	36.1	0.418	8.44	23400	24.6	338	1	2.5	19.1	34.4	
2002	91	29.3	0.357	30.7	22	0.196	23.3	17.2		13800	92	0.486	9.87	34000	27.7	4360	3.93	2.5	39.6	35.9	
2002	97	35.6	0.318	40.3	27.1	0.0504	28.8	20.9		17800	141	0.718	12.1	38300	30.5	1160	1	2.5	46.1	49.5	
2002	501	16.9	0.67	43.9	54.7	0.683	34.2	95.5		20500	112	0.996	11.5	33700	32.7	527	2.28	2.5	69.7	54.5	
2002	Draget	7.21	0.122	23.8	8.62	0.04	15.6	8.73		9710	470	0.32	7.08	20500	20.2	596	1	2.5	31.7	28.3	
2002	Ref Stornäs	17.7	0.256	26.3	17.6	0.04	19.5	11.1		11900	80.1	0.446	8.96	25700	23.4	3990	3.11	2.5	125	30.9	
2019	16	62	0.71	40	31	1.45	32	37	140							5600	2.2				40
2019	29	56	0.39	30	19	0.154	25	17	92							9500	4.7				34
2019	42	38	0.68	45	35	0.948	33	39	140							2200	1				42
2019	46	38	0.5	41	35	1.15	30	40	130							1600	1				41
2019	50	31	0.53	43	43	1.25	34	48	140							1500	1				44
2019	56	17	0.25	43	33	0.349	30	32	120							700	1				44
2019	58	34	0.3	45	35	0.483	37	38	140							1700	1				44
2019	62	26	0.41	42	33	0.447	41	35	130							1400	1				48
2019	68	22	0.44	40	35	1.17	38	47	130							970	1				46
2019	74	55	0.32	45	31	0.286	34	32	130							800	1				48
2019	78	67	0.43	44	32	0.399	37	32	130							1700	1				47
2019	89	9.5	0.16	33	22	0.173	25	20	89							460	1				34
2019	91	10	0.24	18	7.6	0.035	23	16	49							1500	1				20
2019	K1	1.5	0.26	21	32	0.135	40	24	95							250	1				20
2019	K2	0.53	0.048	3.8	4.9	0.024	85	5.7	18							330	1				4.2
2019	K3	5.6	0.14	32	14	0.087	23	13	66							250	1				34
2019	K4	8.1	0.15	40	14	0.137	25	15	79							440	1				41
2019	K5	14	0.2	34	21	0.527	29	26	91							810	1				38
2019	K6	91	0.34	40	27	0.397	35	28	120							13000	6.2				48

Table 6. PAH concentrations (ng/kg ww) in mussels where cells are coloured by environmental class. Levels below LODs have been replaced by half LOD when LOD is known, otherwise denoted as «0

| Year	Station	Sub-sample	N	A	FLA	BaP	ACE	ACY	F	P	PY	C	BaA	BbF	BgP	BkF	DahA	IP
2002	16	1	7.1	9	28	26	6.7	0.5	1.3	4.6	36	34	18	42	13	13	3.8	8.4
2002	29	1	0.5	0.75	25	7.6	7.1	0.5	1.1	4	18	29	15	22	11	15	2.5	7
2002	42	1	7.3	1.7	28	73	7.5	0.5	1.8	5.4	27	59	35	65	31	27	8.3	25
2002	46	1	4.5	1.6	38	35	4.7	0.5	1.6	6.7	38	67	45	69	25	26	6.9	22
2002	56	1	7.2	3.5	140	54	9.5	0.5	1.5	8.8	130	180	150	170	51	72	11	28
2002	56X	1	10	4.5	210	60	9.8	0.5	5.9	17	200	270	180	300	95	120	17	57
2002	62	1	9.2	110	3200	2400	37	2.5	28	350	2600	2500	2400	4800	2100	1000	390	1340
2002	68	1	8.6	37	1100	1100	16	1	6.6	94	1200	1300	1100	2500	1100	550	220	1130
2002	74	1	13	2.1	51	95	8.1	0.5	2.8	8.4	50	76	51	110	35	31	11	40
2002	89	1	4.7	2.8	82	170	7	0.5	2	13	91	170	120	270	81	68	27	100
2002	91	1	7.6	0.5	23	64	7.6	0.5	1.6	4.1	22	31	20	41	8.3	10	0.5	3.1
2002	501	1	4.6	2.6	100	46	5.7	0.5	1.9	9.1	100	130	96	140	41	50	11	28
2002	Draget	1	6.7	0.5	26	65	8.4	0.5	1.8	5.5	24	44	29	41	9.4	12	0.5	2.9
2002	Ref Stornäset	1	1.6	1.4	20	41	6.7	0.5	1.7	2.8	17	18	15	24	5.7	6.2	0.5	6.5
2002	Ref X	1	2.6	0.5	17	48	9.1	0.5	1.6	6.1	16	17	11	20	4.7	5.1	0.5	6.5
2019	58	1	42	5.8	41	15	2.9	3.4	1.7	26	28	45	21	47	20	13	4.3	18
2019	58	2	50	6.2	44	15	3.1	3.8	2.4	29	30	45	23	48	21	14	4.9	19
2019	58	3	51	6.2	46	15	3.3	3.7	2.3	30	31	45	23	50	21	14	5	18
2019	62	1	17	12	80	46	1.5	2.7	1.7	24	49	115	56	140	75	39	14	64
2019	62	2	18	12	97	47	1.6	2.7	1.8	25	61	126	62	150	85	40	16	69
2019	62	3	18	12	80	45	1.6	3.4	1.7	26	48	118	58	141	80	41	15	68
2019	91	1	0.5	0.3	2.7	1.3	0.19	0.5	0.19	1.8	2.1	3	1.6	4.6	1.2	2.1	0.53	2.2
2019	91	2	0.5	0.54	3.5	1.7	0.12	0.5	0.3	2	2.8	3.3	2	4.7	2.2	1.3	0.56	2.3
2019	91	3	0.5	0.56	3.2	1.8	0.05	0.5	0.28	1.8	2.6	3.2	2	5.1	2.4	1.4	0.53	2.4
2019	K3	1	9.4	19	118	131	1.1	3	1.8	20	77	257	122	356	225	100	36	185
2019	K3	2	11	21	128	144	1.3	3.9	2.6	26	86	274	132	388	238	98	38	195
2019	K3	3	10	19	119	132	1.3	2.5	1.8	21	78	277	126	350	219	96	37	174
2019	K4	1	5	9.7	43	74	0.76	2.1	1.5	14	33	88	55	197	140	52	22	110
2019	K4	2	3.1	8.6	40	72	0.64	1	1	10	31	85	55	190	134	54	24	101
2019	K4	3	4.2	11	52	79	0.59	3.3	1.9	20	40	95	61	201	141	59	22	114
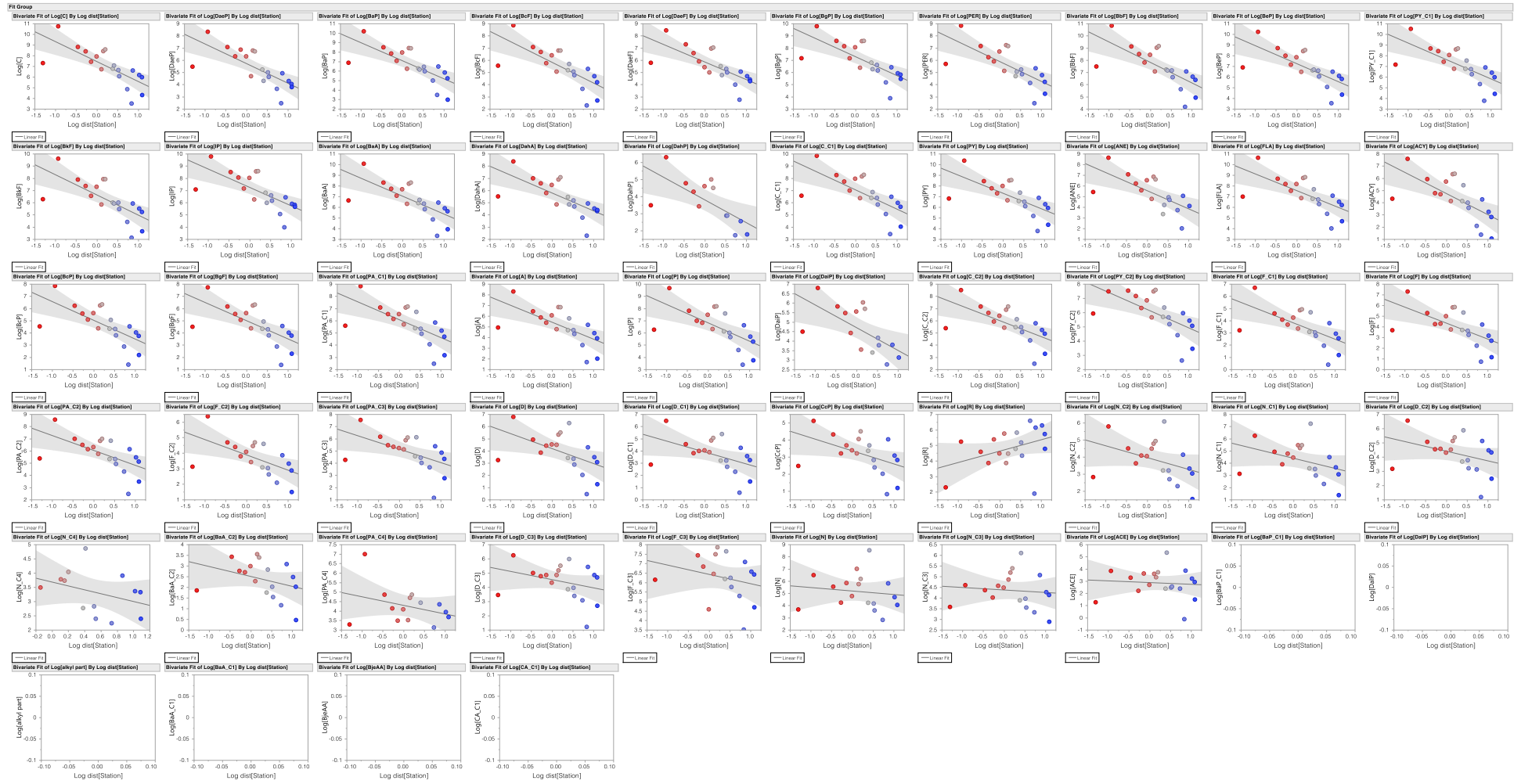
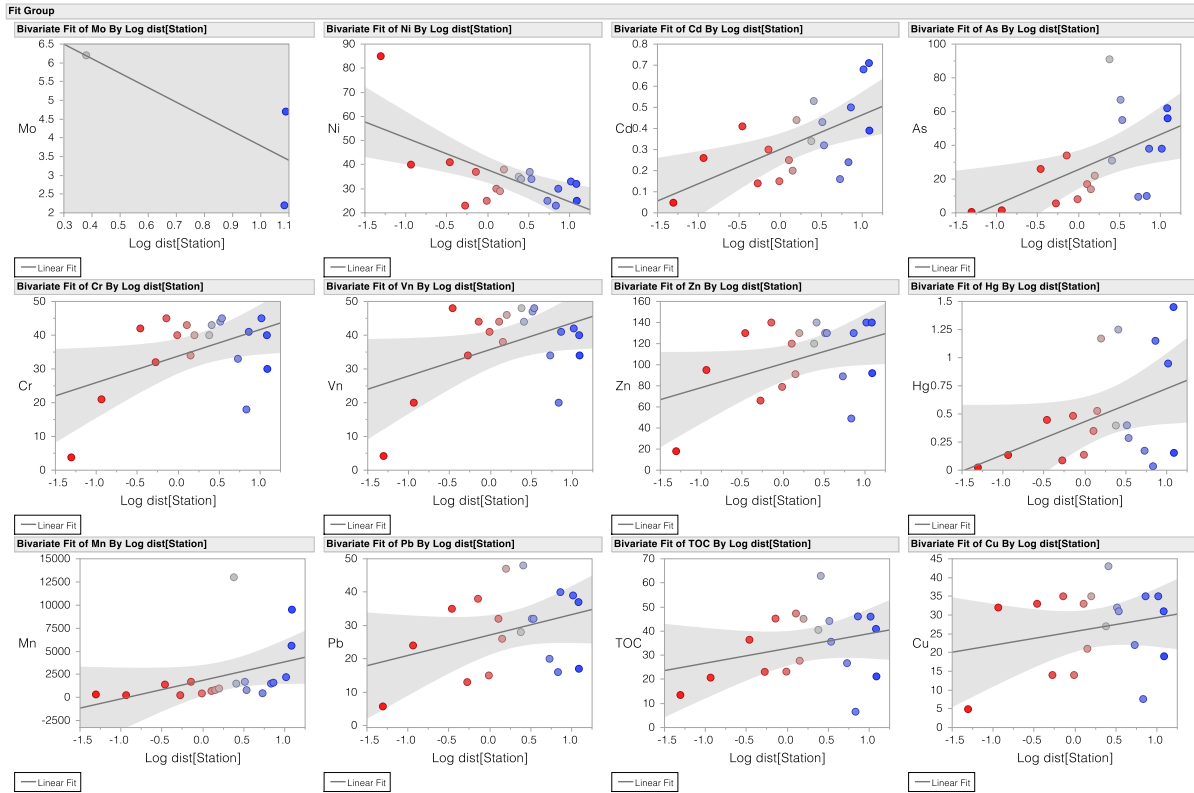Figure 29. Correlations with distance from smelters for all PACs in sediments ordered by the goodness of fit.

Figure 30. Correlation with distance from smelter for all metals in sediments. Concentrations are given in mg/kg dw. The correlations are ordered by the goodness of fit.
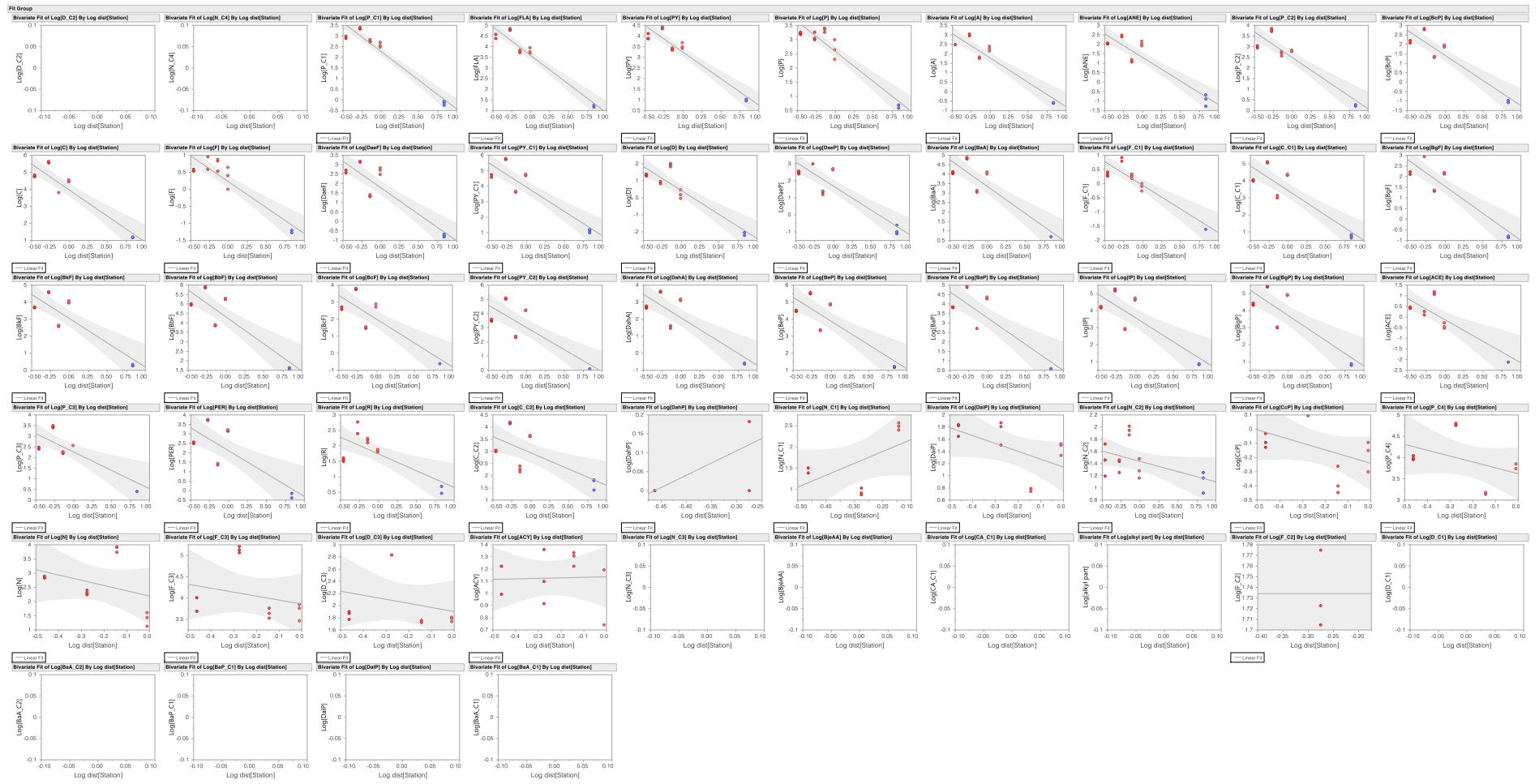
Figure 31. Correlation of all PACs in mussel tissue with distance from smelter.
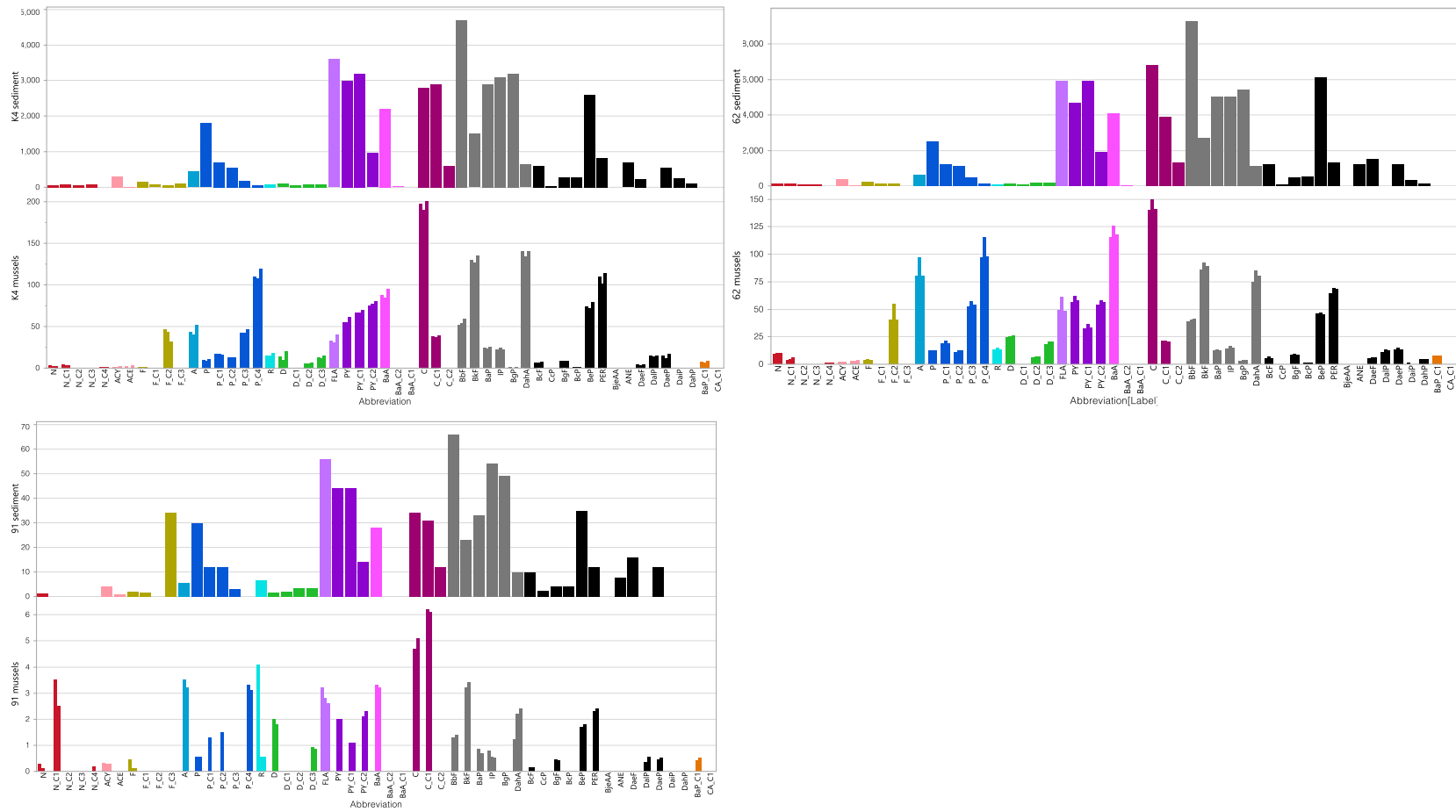
Figure 32. Isomeric pattern of PACs in sediments compared to isomeric pattern of PACs in mussel tissue. The data are presented as µg/kg dw for sediment and µg/kg ww for mussels.
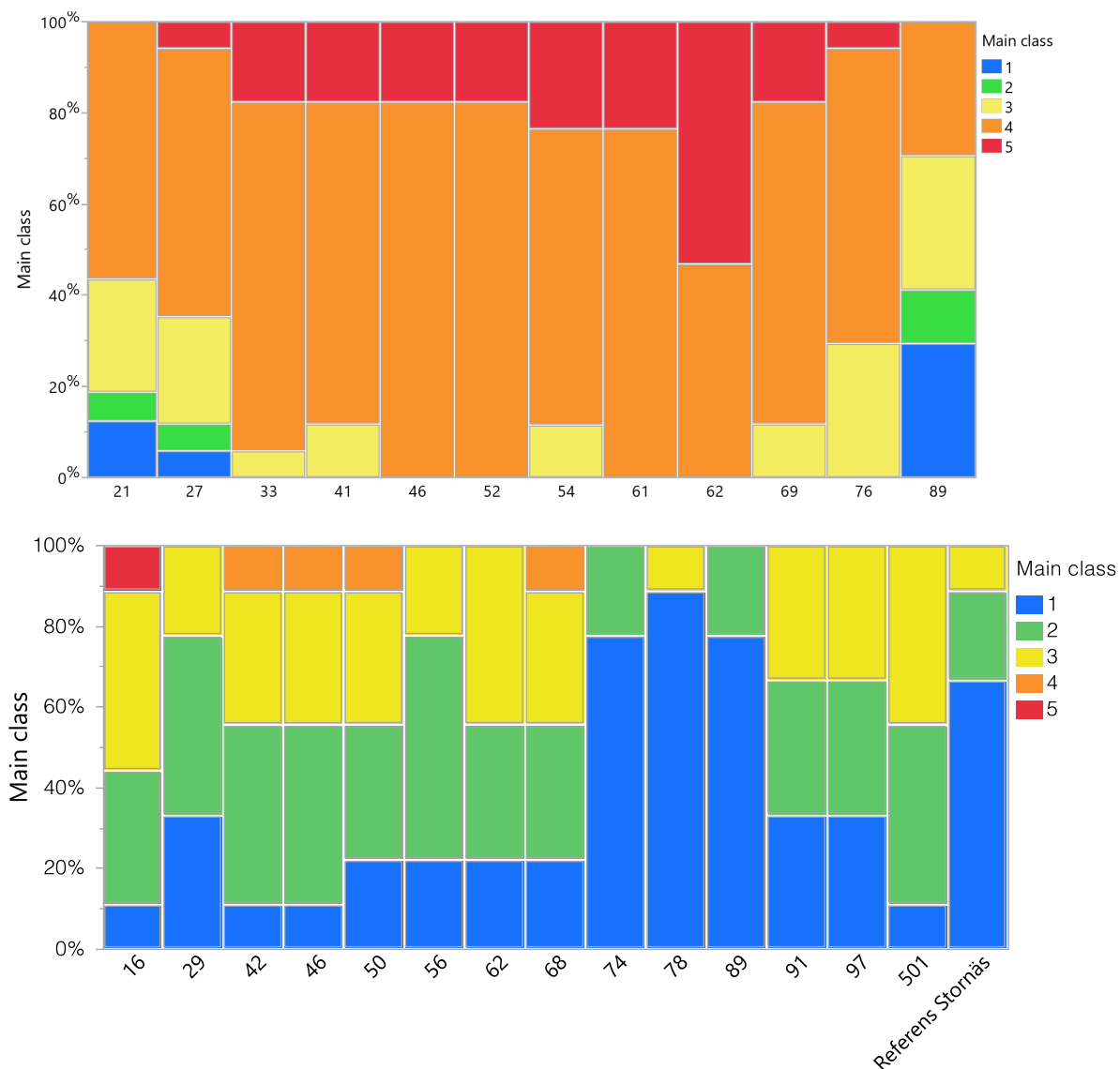
Figure 33. Classification of concentration of PACs in sediments according to EU/Norwegian guidelines for stations investigated in 1988 (upper) and 2002 (lower).
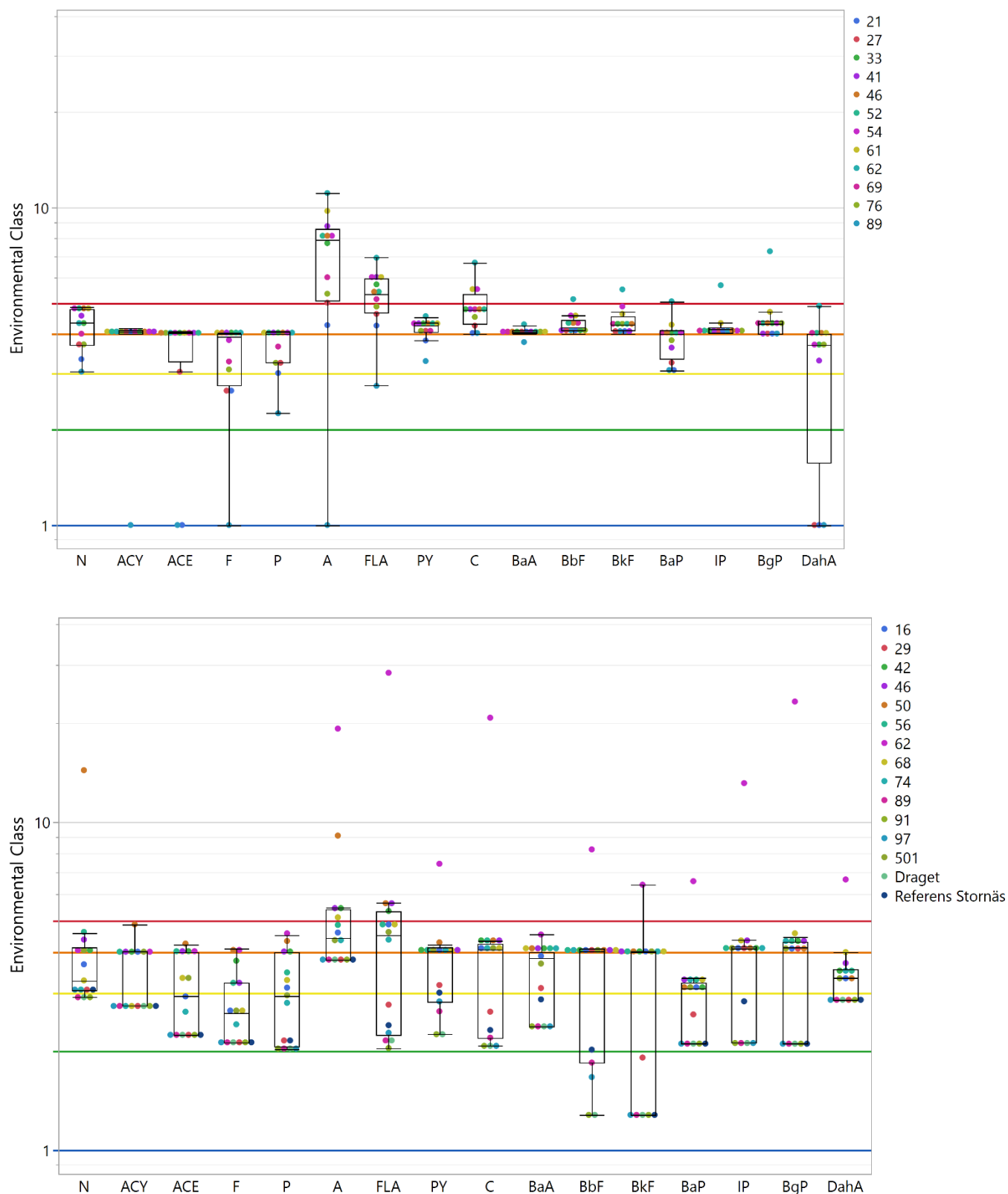
Figure 34. Boxplot of historical environmental class of concentrations of PAC in sediments based on Norwegian guidelines. Upper: 1988, lower: 2002.
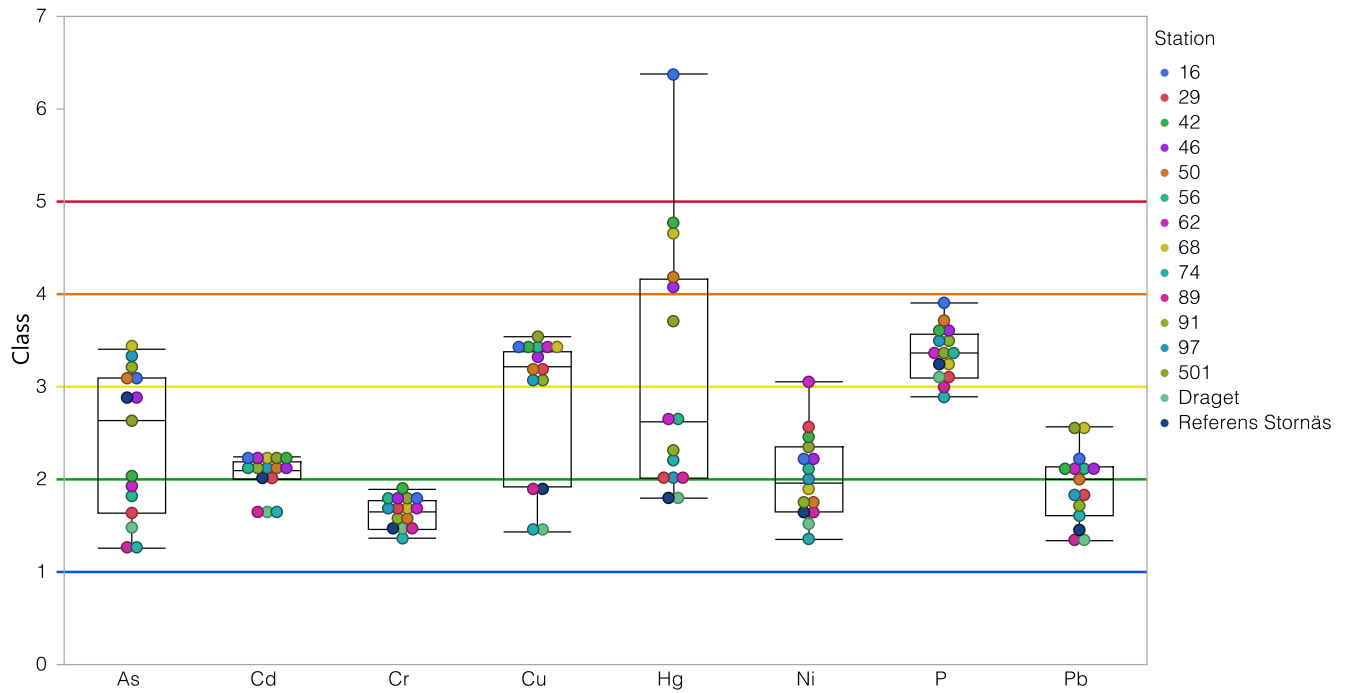
Figure 35. Boxplot of historical environmental class of concentrations of metals in sediments based on Norwegian guidelines (2002)

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