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Concentrations of petroleum hydrocarbons in sediments and seawater from the Barents and Norwegian Seas 2003–2005

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PROSJEKTRAPPORT

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Tittel (norsk/engelsk):
Concentrations of petroleum hydrocarbons in sediments and seawater from the Barents and Norwegian Seas 2003-2005.

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Sammendrag (norsk):
I perioden 2003-2005 har det vært gjennomført tokt i Norskehavet og Barentshavet for å samle sediment- og vannprøver for målinger av totalmengde hydrokarboner (THC) og polyaromatiske hydrokarboner (PAH). Rapporten presenterer resultatene fra disse overvåkningsundersøkelsene. THC og PAH konsentrasjonene i sedimenter og vann er generelt lave og ingen betydelig antropogen påvirkning er vist. Naturlige kilder medfører økte konsentrasjoner av THC og PAH i sedimentene sør for Svalbard. THC og PAH i sjøvann viser svært lave bakgrunnskonsentrasjoner.

Summary (English):
During 2003-2005 cruises have been carried out in the Norwegian Sea and the Barents Sea to collect samples of sediments and seawater for analyses of total hydrocarbons (THC) and polyaromatic hydrocarbons (PAH). The report presents the results from these monitoring studies. The THC and PAH concentrations in sediments and water are generally low and no significant anthropogenic influence is apparent. Natural sources contribute to higher concentrations of THC and PAH in sediments south of Svalbard. THC and PAH in seawater show very low background concentrations.

Emneord (norsk):	Subject heading (English):
1. THC/PAH	1. THC/PAH
2. Barentshavet	2. Barents Sea
3. Sedimenter/vann	3. Sediments/water

prosjektleder

forskningsgruppeleder

1. Introduction

Institute of Marine Research (IMR) on a regular basis carry out monitoring of contaminants in the sea areas surrounding Norway. This report presents the results from some of the monitoring activities that took place in the time period 2003-2005 in the Barents Sea and the Norwegian Sea. In this period high priority was given to the analyses of oil hydrocarbons and polyaromatic hydrocarbons (PAHs) in sediments and seawater. One important reason to this was that the secretariat of the Arctic Monitoring and Assessment Programme (AMAP) had taken an initiative to prepare a new assessment report on oil and gas activities in the Arctic (OGA Report). In connection with this there was also a need to get new data on levels of oil hydrocarbons and PAHs in different compartments of the Arctic environment.

Polyaromatic hydrocarbons (PAHs) are a large group of compounds of varying molecular weights (from 128 for the lightest representative of the group, naphthalene, to over 270 for 6-ring compounds), and thus differ in their water solubility, volatility and chemical stability. Lighter compounds are more water-soluble and volatile than the heavier compounds. Some sulphur-containing compounds like dibenzothiophenes are often included in this group of compounds. The presence of some PAHs in the environment may be of concern, due to their toxic properties, including carcinogenicity (Sims and Overcash 1983; Pickering 2000). Benzo[a]pyrene is the best-studied representative of the carcinogenic PAH compounds (Collins *et al.* 1991).

PAHs may have technogenic or natural origin. Origin may be further divided into pyrogenic, petrogenic, biogenic or industrial, i.e. being formed as a result of combustion, as part of fossils, in biological or in industrial processes. There are thus natural sources of PAHs such as seepages of oil at the sea bed, forest fires etc., as well as anthropogenic sources. Far away from point sources, "background levels" of PAHs are normally observed in the marine environment, due to long-range transport with air or water currents. Places close to human-populated areas typically exhibit elevated levels of PAHs. Some places which are point sources of pollution such as oil installations, chemical plants etc. may show strongly elevated levels of PAHs.

It is often difficult to determine the origin of PAHs, since PAHs from different sources may be present in the same place. The relative amounts of certain PAH compounds may be used to distinguish between different types of origin of the local PAH present (see, for example, Budzinski *et al.* 1997). Thus, phenanthrene/anthracene ratio is used to distinguish between combustion and anthropogenic inputs, since these compounds differ in their thermodynamic stability (a low PHE/ANT ratio indicates high temperatures of formation). A predominance of alkylated homologues of naphthalene, phenanthrene and dibenzothiophene over their parent compounds indicates a petrogenic origin of PAHs. Presence of certain PAHs may also indicate the source, such as, for example, biogenic predecessors in case of perylene (Venkatesan 1988).

A large part of PAHs entering the marine environment often ends up in the sediments. In densely populated and industrialized areas PAH levels in marine sediments are often elevated in the surface layer and decrease with the depth in the sediment core. Sediments found at high depths exhibiting low and steady levels of PAHs. For example, the industrial era is apparent in the PAH levels in sediment samples taken in Skagerrak with highest concentrations in surface sediments (NGU 1997). In the Norwegian and Barents Seas, which is remote from populated or industrial areas, this may not be the case and the levels of PAHs remain at low natural background levels, with variations in levels reflecting other processes than those due to anthropogenic inputs.

Since the petroleum industry is now establishing itself in the southern Barents Sea, it is important to have sufficient knowledge about the present background levels of oil/PAHs and to map potential

depocentres for sediments, in order to better be able to judge future effects of the increasing petroleum activity. In the Norwegian Sea there is already ongoing offshore oil and gas production in some few areas.

Scientific cruises in the Norwegian and Barents Seas were carried out using R/V Johan Hjort (2003), Håkon Mosby (2004) and G.O. Sars (2005). The purpose of the cruises was to collect samples of sediments and seawater to get new information about the levels of contaminants like oil (measured as total hydrocarbons - THC) and PAHs, but also presence of persistent organic pollutants, metals and radionuclides were investigated. Sedimentary processes and potential deposition centres for sediments were also studied. Fish were sampled for analyses of different groups of contaminants but this work is not reported here. In this report, only the results of PAH and THC analyses in sediments and water are discussed.

It is also important to study the geological and geochemical processes that can help explain the composition and levels of oil/PAHs in the sediments. For this purpose cooperation with Geological Survey of Norway (NGU) has been established. NGU researchers took part in the sampling at the 2004 cruise, and have performed geological and geochemical analyses to determine sediment characteristics like grain size distributions and total organic carbon content, and to provide other relevant geological and geochemical information on the samples.

Many laboratories are involved in the analyses of PAHs and total hydrocarbons (THC) as a signal of "oil contamination" in marine sea areas. An intercalibration exercise was organised in 2005 to get better knowledge about the comparability in results from some of all laboratories that would deliver results on PAHs and THC to the OGA Report. Laboratories from Denmark, Norway and Russia participated and this report presents the summary and conclusions from the exercise. Six laboratories took part: IMR (Bergen, Norway), DMU (Copenhagen, Denmark), PINRO (Murmansk, Russia), VNIIOkeangeologiya (St. Petersburg, Russia), UNILAB (Tromsø, Norway) and Typhoon (Obninsk, Russia). These laboratories cooperate in providing data for the OGA Report. It is therefore highly important to check the quality and coordinate the analytical part of joint work. Since analytical methods may vary between laboratories, intercalibration of the measurements for same types of contaminants is necessary to be able to compare the data obtained by different laboratories. The following groups of contaminants are routinely analyzed by the participating laboratories:
- Total Hydrocarbons (THC);
- Polyaromatic hydrocarbons (PAHs) including sulfur containing dibenzothiophene and their alkylated derivatives.
- The exact set of compounds may vary from laboratory to laboratory. Only those compounds analysed by all laboratories have been taken for final consideration and comparison of results.

2. Methods

2.1. Sampling and analyses.

In 2003, surface sediment samples were collected at 29 stations in the Western part of the Barents Sea, between ca. 70° and 77° North and 20° and 40° East (Fig. 1). An overview of the sediment samples is given in Table 1.

In 2004, sediment cores were collected at 45 locations along 5 transects each going from the Barents Sea shelf and westwards across the continental slope to a depth of 1500 m in the Norwegian Sea (Fig.

1). Water samples were taken at most of the same locations. Biota samples taken during both cruises are not part of this report.

In 2004, a total of 2021 samples were collected; of these, 1663 were sediment samples and 40 water samples. An overview of the sediment and water samples is given in Table 2.

In 2005, 11 large volume water samples were collected by means of an automatic water sampler in the Norwegian and Barents Seas, between 67° and 72° North and 9° and 21° East (Fig. 2). Geographical coordinates of sampling locations are given in Table 3.
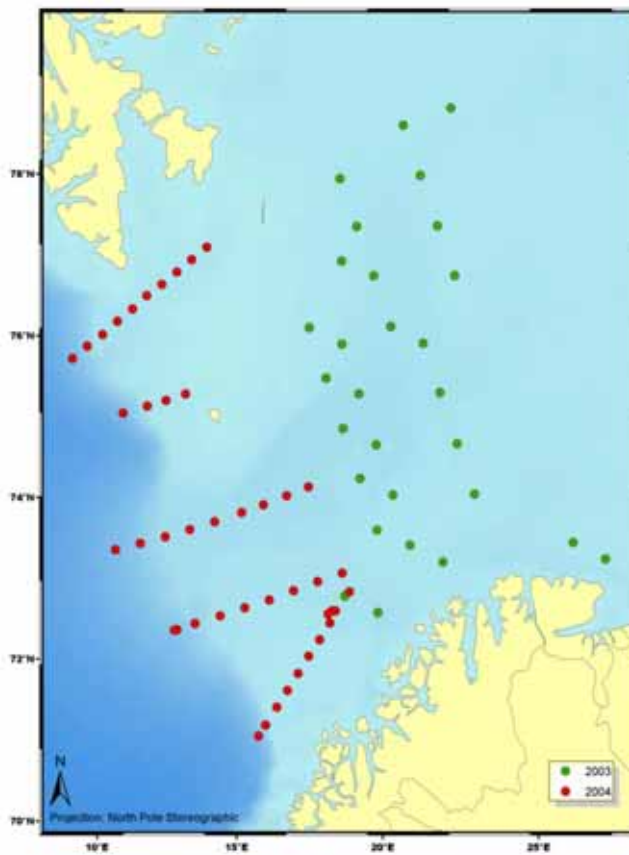
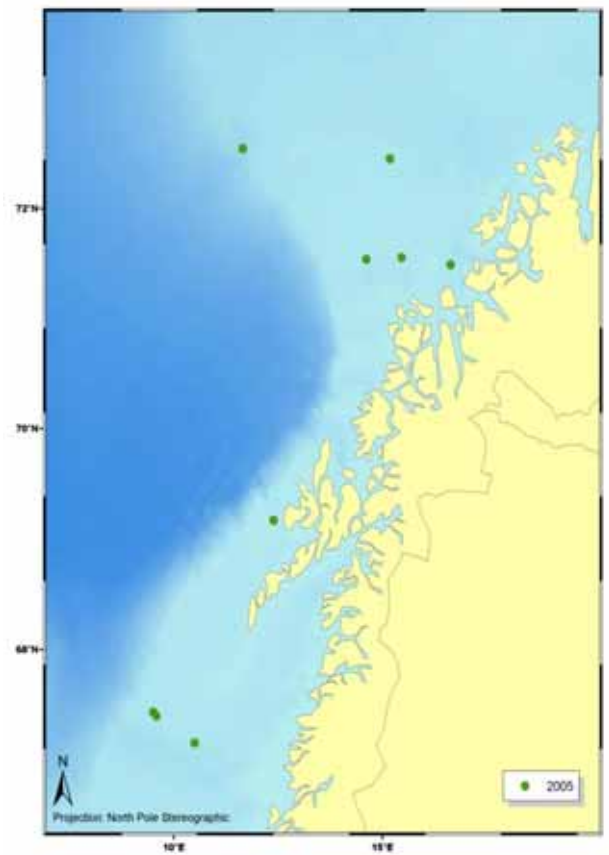

Figure 1. Sampling stations at the 2003 and 2004 cruises.

Figure 2. Sampling stations at the 2005 cruise.

Table 1. Surface sediment samples collected during the cruise in 2003.

Station number	Date	Depth, m	Position			
			Latitude		Longitude	
623	06.08.2003	166	71 02.73	N	021 38.65	E
625	09.08.2003	360	71 43.26	N	021 44.97	E
627	10.08.2003	264	72 19.29	N	024 02.87	E
629	10.08.2003	404	72 59.97	N	024 15.05	E
631	11.08.2003	451	73 39.79	N	024 27.59	E
633	11.08.2003	373	74 19.83	N	024 40.95	E
635	11.08.2003	182	75 00.04	N	024 56.30	E
637	12.08.2003	123	75 39.00	N	025 09.52	E
639	12.08.2003	263	75 33.80	N	027 53.55	E
641	13.08.2003	187	76 18.76	N	025 40.93	E
643	14.08.2003	291	76 29.13	N	029 54.28	E
645	14.08.2003	296	75 51.19	N	029 26.97	E
647	14.08.2003	343	75 12.05	N	028 59.97	E
649	15.08.2003	394	74 32.09	N	028 33.95	E
651	15.08.2003	317	74 37.79	N	026 03.92	E
653	15.08.2003	441	73 58.29	N	025 47.85	E
655	16.08.2003	412	73 17.79	N	025 31.93	E
657	16.08.2003	268	72 38.06	N	025 16.16	E
659	17.08.2003	256	71 58.33	N	025 02.81	E
661	17.08.2003	408	71 22.27	N	022 45.49	E
663	22.08.2003	291	71 35.89	N	25 59.27	E
665	23.08.2003	289	72 10.03	N	28 23.94	E
667	23.08.2003	305	72 49.93	N	28 45.26	E
669	23.08.2003	414	73 30.06	N	29 08.73	E
671	24.08.2003	366	74 08.77	N	29 33.16	E
673	24.08.2003	165	74 40.0	N	32 29.41	E
675	25.08.2003	209	75 18.91	N	33 04.15	E
677	25.08.2003	276	75 58.00	N	33 44.0	E
679	26.08.2003	193	76 37.0	N	34 27.0	E
681	26.08.2003	249	76 26.0	N	37 10.0	E
686	29.08.2003	282	71 14.34	N	26 53.51	E
688	30.08.2003	235	71 07.78	N	28 54.75	E
690	30.08.2003	283	71 00.78	N	30 56.83	E
692	31.08.2003	252	70 37.28	N	31 42.70	E

Table 2. Sediment and water samples collected in 2004.

Station H.Mosby	Date	Latitude N	Longitude E	Water depth m	Core length cm	# Slice samples NGU	# Surface samples NGU	# Surface samples NP	# Gas samples NGU	Core length cm	# Organic chemistry HI	Water samples HI	Location
St.1.	03.08.04	72°00.03'	22°00.09'	367	20	20	1	1	2	17	17	1	Ingøydjupet
St.2.	03.08.04	72°01.24'	20°55.12'	371	21	21	1	1	2	20	20	1	Tromsøflaket
St.3.	03.08.04	72°01.30'	19°51.00'	324	27	27	1	1	2	27	20	1	Tromsøflaket
St.4.	03.08.04	72°01.00'	18°46.00'	315	35	25	1	1	-	33	21	1	Tromsøflaket
St.5.	03.08.04	72°01.30'	17°41.50'	296	31	23	1	1	-	30	21	1	Tromsøflaket
St.6.	04.08.04	72°01.20'	16°36.70'	362	20	18	1	1	-	19	19	1	Upper continental slope
St.7.	04.08.04	72°01.00'	15°31.00'	767	29	22	1	1	-	25	20	1	Bjørnøyvifta
St.8.	04.08.04	72°00.30'	14°43.50'	1260	>60	1	1	1	2	>60	2	1	Håkon Mosby mud volcano
St.9.	04.08.04	72°00.30'	14°37.00'	1317	30	23	1	1	2	30	21	1	Bjørnøyvifta
St.10.	04.08.04	72°00.00'	13°35.00'	1500	-	-	-	-	-	-	-	1	Bjørnøyvifta
St.11.	05.08.04	73°10.00'	12°56.30'	1499	35	25	1	1	-	39	23	1	Bjørnøyvifta
St.12.	05.08.04	73°10.00'	14°05.10'	1030	24	20	1	1	-	23	20	1	Bjørnøyvifta
St.13.	05.08.04	73°10.00'	15°14.00'	485	14	14	1	1	-	13	12	1	Bjørnøyrenna
St.14.	05.08.04	73°00.00'	16°23.00'	475	27	21	1	1	2	33	21	1	Bjørnøyrenna
St.15.	05.08.04	73°10.00'	17°32.20'	460	27	21	1	1	-	27	21	1	Bjørnøyrenna
St.16.	06.08.04	73°10.10'	18°49.00'	423	1	1	1	1	-	1	1	1	Bjørnøyrenna
St.17.	06.08.04	73°10.00'	19°50.90'	441	23	19	1	1	-	33	22	1	Bjørnøyrenna
St.18.	06.08.04	73°10.00'	20°57.00'	463	17	16	1	1	2	19	19	1	Bjørnøyrenna
St.19.	06.08.04	73°10.00'	21°59.90'	444	21	18	1	1	-	20	20	1	Bjørnøyrenna
St.20.	07.08.04	74°48.70'	18°01.00'	296	29	22	1	1	2	25	20	1	Vestbakken
St.21.	07.08.04	74°48.70'	17°00.00'	280	23	19	1	1	-	29	21	1	Vestbakken
St.22.	07.08.04	74°48.70'	16°02.00'	356	20	18	1	1	2	30	21	1	Vestbakken
St.23.	07.08.04	74°48.60'	14°46.80'	1507	33	24	1	1	-	33	22	1	Vestbakken
St.24.	08.08.04	75°38.20'	12°55.20'	1500	31	23	1	1	-	30	21	1	Storfjordrenna
St.25.	08.08.04	75°44.60'	13°49.80'	807	7	7	1	1	-	7	7	1	Storfjordrenna
St.26.	08.08.04	75°50.00'	14°46.00'	370	10	10	1	1	2	11	11	1	Storfjordrenna
St.27.	08.08.04	75°56.70'	15°42.70'	369	27	21	1	1	-	29	21	1	Storfjordrenna
St.28.	08.08.04	76°02.50'	16°40.00'	328	15	15	1	1	-	14	14	1	Storfjordrenna
St.29.	09.08.04	76°08.80'	17°37.00'	309	27	21	1	1	-	24	20	1	Storfjordrenna
St.30.	09.08.04	76°13.20'	18°35.00'	257	19	17	1	1	-	16	16	1	Storfjordrenna
St.31.	09.08.04	76°18.20'	19°34.10'	258	19	17	1	1	2	17	17	1	Storfjordrenna
St.32.	09.08.04	76°23.00'	20°34.50'	228	18	17	1	1	-	21	20	1	Storfjordrenna
St.33.	09.08.04	76°27.70'	21°35.70'	262	21	18	1	1	-	18	18	1	Storfjordrenna
St.34.	12.08.04	71°45.00'	22°00.00'	356	23	19	1	1	-	30	21	1	Ingøydjupet
St.35.	12.08.04	71°36.70'	21°03.80'	319	23	19	1	1	2	25	20	1	Snøhvit (referansest.)
St.36.	12.08.04	71°35.60'	20°51.40'	320	27	21	1	1	-	25	20	-	Snøhvit
St.37.	12.08.04	71°35.70'	21°11.40'	335	25	20	1	1	-	24	20	-	Snøhvit
St.38.	12.08.04	71°28.80'	20°48.60'	310	25	20	1	1	-	26	21	-	Tromsøflaket
St.39.	13.08.04	71°19.80'	20°10.80'	234	14	14	1	1	-	14	14	1	Tromsøflaket
St.40.	13.08.04	71°11.00'	19°33.40'	225	13	13	1	1	-	17	17	1	Tromsøflaket
St.41.	13.08.04	71°01.60'	18°56.60'	199	1	-	1	1	-	-	-	1	Fugløybanken
St.42.	13.08.04	70°52.10'	18°20.20'	173	5	5	1	1	-	-	-	-	Fugløybanken
St.43.	13.08.04	70°42.70'	17°44.70'	273	18	17	1	1	-	20	20	-	Fugløydjupet
St.44.	13.08.04	70°32.60'	17°07.70'	706	1	-	1	1	-	-	-	1	Continental slope
St.45.	13.08.04	70°26.30'	16°44.50'	1500	30	23	1	1	-	28	21	1	Continental slope

Table 3. Geographical position of water sampling stations at the cruise 2005.

Station number	Date	Latitude	Longitude
1	10.06.05	70° 39.3'N	19° 41.9'E
2	10.06.05	70° 45.54'N	18° 39.05'E
3	10.06.05	71° 33.07'N	20° 18.98'E
4	12.06.05	72° 06.44'N	15° 49.83'E
5	14.06.05	70° 25.204'N	21° 01.862'E
6	15.06.05	70° 25.195'N	21° 01.766'E
7	17.06.05	68° 43.762'N	14° 06.216'E
8	19.06.05	66° 55.386'N	10° 53.410'E
9	19.06.05	66° 55.293'N	10° 53.378'E
10	21.06.05	67° 16.384'N	09° 57.909'E
11	22.06.05	67° 13.944'N	10° 01.684'E

The following analyses have been performed on the collected samples:

1. Surface sediment from each station (44 samples NGU), 2004
−   Total carbon and total organic carbon (Method: Leco)
−   Laser granulometry (Method: Coulter)
2. Sliced multicorer sediments from each station (743 samples IMR), 2004
−   IMR performed PAH analyses on a selection of the collected cores.
3. Surface sediment from each station (41 samples IMR), 2003, 2004
−   Analysis of total hydrocarbons (THC).
4. Water samples from each station (40 samples IMR), 2004
−   Analysis of total hydrocarbons (THC).
5. Water samples from each station (11 samples IMR), 2005
−   Analysis of PAHs.

All the chemical analyses of sediments have been carried out according to the accredited methods routinely used at IMR for PAH/THC analyses. Frozen sediment samples were thawed at room temperature, extracted by saponification in methanolic KOH followed by extraction by hexane, removal of sulphur by active copper, clean-up on silica Bond-Elute column and then analysed by GC-MS, with gas chromatograph HP-6890 coupled to Micromass Autospec Ultima mass spectrometer, in SIR-mode, «Selected Ion Recording». The results were quantified with Opus Quan software package. THC have been analysed by gas chromatography with flame ionization detector (GC-FID).

THC has been measured in water samples collected during the 2004 cruise. Sample volumes were 2.8 litres (L) and the samples were cleaned up on a bond-elute column before GC-MS analysis. PAH measurements in water have been carried out on samples collected in 2005. Large volumes of water (between 50 and 200 L) have been filtered by means of an automatic sampler at 6 m depth with a non-ionic polymeric adsorbent, Amberlite® XAD-16, used as the sorbent for PAHs. The analytes were then extracted in the laboratory with dichloromethane and analysed by standard GC-MS technique.

One set of sediment sub-samples was analysed for weight percentages (wt. %) of total carbon (TC), total sulphur (TS) and total organic carbon (TOC) using a LECO CS 244 analyser. For the TOC analyses, aliquots (~200 mg) of the samples were treated with 10 % (volume) hydrochloric acid (HCl) at 60ºC to remove carbonate, and then washed with distilled water to remove HCl. We caution

the reader that the possible loss of organic material by acid leaching is not taken into account. The samples were dried overnight (50ºC) and then analysed. The carbonate content (wt. %) was calculated as $CaCO_3 = (TC - TOC) \times 8.33$.

Grain size analyses of total sediment were obtained from laser diffraction techniques (Coulter LS 2000) (for details, see Xu 2000, and references therein) and wet sieving. The Coulter LS 2000 measured the fractions from 0.4 μm to 2 mm while particles larger than 2 mm were determined by wet sieving. Prior to each analysis, the samples were freeze-dried. The grain size distribution is determined with respect to volume percent and with the assumption of uniform density of the sample.

2.2. Intercalibration experiment.

Two bottom sediment control samples have been used for intercalibration of the analytical techniques used by different laboratories. Sample 1 was collected by IMR during its routine monitoring activity in Skagerrak in 1995. The sample has been freeze-dried, sieved to particle size <0.125 mm and mixed in a mini-cement mixer for 24 h. Sample 2 consisted of samples received from SETOC (International Sediment Exchange for Test on Organic Contaminants) received by IMR in 2000, 2001, 2002 and 2003 and mixed together into one sample, no. 701. Own surrogate isotope-labelled substances have been used by each laboratory for control of recovery of analytes, introduced into samples before extraction. Samples were extracted and cleaned-up in different ways at different laboratories, but the extracts have been analyzed by gas chromatography (THC) and gas chromatrography mass spectrometry (PAHs) at all laboratories. Analytical methods employed by each laboratory are described briefly below (for IMR technique, see section 2.1). Final results from each laboratory have been reported as ng/g dry weight (dw).

2.2.1. Typhoon analytical method.

Extraction of hydrocarbons from bottom sediments was performed in ultrasonic bath using hexane following with alumina clean-up of solvent extracts. Extraction of PAHs from bottom sediments was performed by method of alkaline digestion with methanol and 50% KOH. The analytes in the alkaline solution were extracted with two portions of hexane in a separatory funnel. The clean-up of extracts was carried out by chromatography columns with silica gel.

The determination of hydrocarbons was carried out by GC-FID. Results of analyses were processed with software package MultiChrom. The analyses of PAHs were performed with GC/MS Hewlett Packard 5890/5972. Results of analyses were processed with software package Chemstation.

2.2.2. PINRO analytical method.

Dried bottom sediment samples were extracted by two portions of chloroform using an ultrasonic bath. Chloroform extracts were combined and dried over anhydrous sodium sulphate. Sulphur in the extract was removed with activated copper. Clean-up of the extract was carried out on a silica gel column. The sample was allowed to just soak into the silica gel and then the aliphatic hydrocarbons (aliquots of the hexane) and PAH (aliquots of the hexane and aliquots of the eluent [*n*-hexane in benzene]) are eluted.

Gas chromatographic analyses for PAHs were performed on an Agilent 6890 GC Series N equipped with an Agilent 7683 autosampler. In all analyses, sample extract was injected in splitless mode with helium as the carrier gas. Detection was performed with a 5973 mass selective detector in the selected ion mode (SIM).

2.2.3. VNIIO analytical method.

Sediment samples were dried to constant weight. Samples (100 g dry weight) were extracted in Soxhlet extractor with chloroform during 20 hours. Sample clean-up was achieved by passing extracts through columns containing activated copper. Asphaltene fraction was deposited with petroleum ether. Fraction separation was carried out by preparative column chromatography on silica gel column. Aromatic hydrocarbon fraction in hexane was then taken to analysis on a Hewlett Packard 6850/5973 GC/MS instrument with MS ChemStation. Results of analyses were processed with software package Chemstation.

The laboratory has national accreditation (№ ROSS.Ru. 0001.512785).

2.2.4. UNILAB analytical method.

Sediment samples are extracted by methanolic saponification followed by liquid-liquid extraction with pentane used as solvent. The extracts are then purified by column chromatography using solid phase extraction cartridges containing 500 mg silica. The concentrated sample is quantitatively applied on the column and the petroleum components are eluted with 3x2 ml pentane and subsequently with 2 ml dichloromethane.

The aromatic hydrocarbons are determined by GC/MS operated in the EI/SIM mode. One characteristic ion for each of the compounds of interest is routinely monitored, as are the molecular ions of the internal standards used. THC is analysed by GC/FID using external standard.

2.2.5. DMU analytical method.

Homogenized sediment was Soxhlet extracted with toluene for 24 hrs. (activated copper sheets were added to remove free sulphur). After extraction toluene was exchanged with hexane and the concentrated extracts were further cleaned-up and fractionated using SPE-Si glass columns. Aliphatics were eluted with hexane while aromatics were eluted with DCM. Again solvent was exchanged to toluene and the concentrated eluate analysed by GC-MS/SIM.

3. Results and Discussion.

3.1. PAH and THC measurements in the Barents Sea.

3.1.1. Sediment analyses.

Levels of PAHs and THC in surface sediments (2003-2004) and sediment cores (2004) are presented in Table 4. Time trends for selected compounds are shown as depth profiles in Figg. 3-8.

For 2004 data, levels of PAHs vary from location to location between 37 ng/g dw and 1356 ng/g dw for the sum of 20 individual components in surface sediments, and between 10 ng/g dw and 1417 ng/g dw at 14-15 cm depth. The large difference between various locations may indicate a difference in transport of PAHs in different areas, which results in differences in their deposition. However, local sources such as natural seepages of oil or other organic fossils may also be very important. A more detailed geochemical analysis is necessary to determine the possible origins of the observed PAH present. Most compounds, except dibenzothiophenes and C3-naphthalenes, are found in lower

amounts than has been found in Skagerrak in 1990 (NGU 1997), and heavy-weight PAHs in much lower amounts than in Skagerrak. The mean values for sum of 20 PAHs in the Barents Sea have been measured at 414 ng/g dw in 2004 and 509 ng/g dw in 2003, in contrast to 2025 ng/g dw found in Skagerrak (for 18 compounds). Present data is in good correspondence with the earlier measurements of PAHs in Barents Sea sediments carried out by several institutes in Norway and Russia (Dahle *et al.* 2006).

Depth profiles vary from location to location (see Figg. 3-5), although as a rule exhibiting no significant increase in deposition in modern times. Indeed, in many places there is an obvious decrease in PAH amounts in modern sediments; at other stations the amounts remain at approximately the same level throughout the whole observable time span. Only surface sediments (0-1 cm) exhibit elevated levels of some PAHs, which reflect rather the influence of the outer environment on the surface sediments than the increase in sedimentation of PAHs. Sum of 20 PAHs concentrations at 14-15 cm depth in 2004 samples are similar to surface sediment values. This is contrary to Skagerrak, where there is a clear increase in concentrations in modern times, due to human activities and anthropogenic inputs.

The highest concentrations of benzo[a]pyrene are observed in sediment cores at stations 30 and 32; however, there is no observable increase in the concentrations of this compound in modern times. The levels of benzo[a]pyrene at all stations of the 2004 cruise remained within the limits of insignificant-or-little contamination (below 10 ng/g dry weight) or moderate contamination (10 to 50 ng/g dry weight) by classification of the Norwegian Pollution Authority (SFT 1997).

At all stations, alkylated naphthalenes heavily predominated over the parent compound, naphthalene. Alkylated phenanthrenes predominated at all stations, except station 9 of 2004 cruise where the amounts of the parent compound were comparable to those of its alkylated homologues and exceeding the amount of C1-homologues. The same was observed for dibenzothiophenes at stations 9. 43 and 45, alkylated compounds predominating over the parent compound at all other stations. This indicates the petrogenic origin of PAHs in the studied areas.
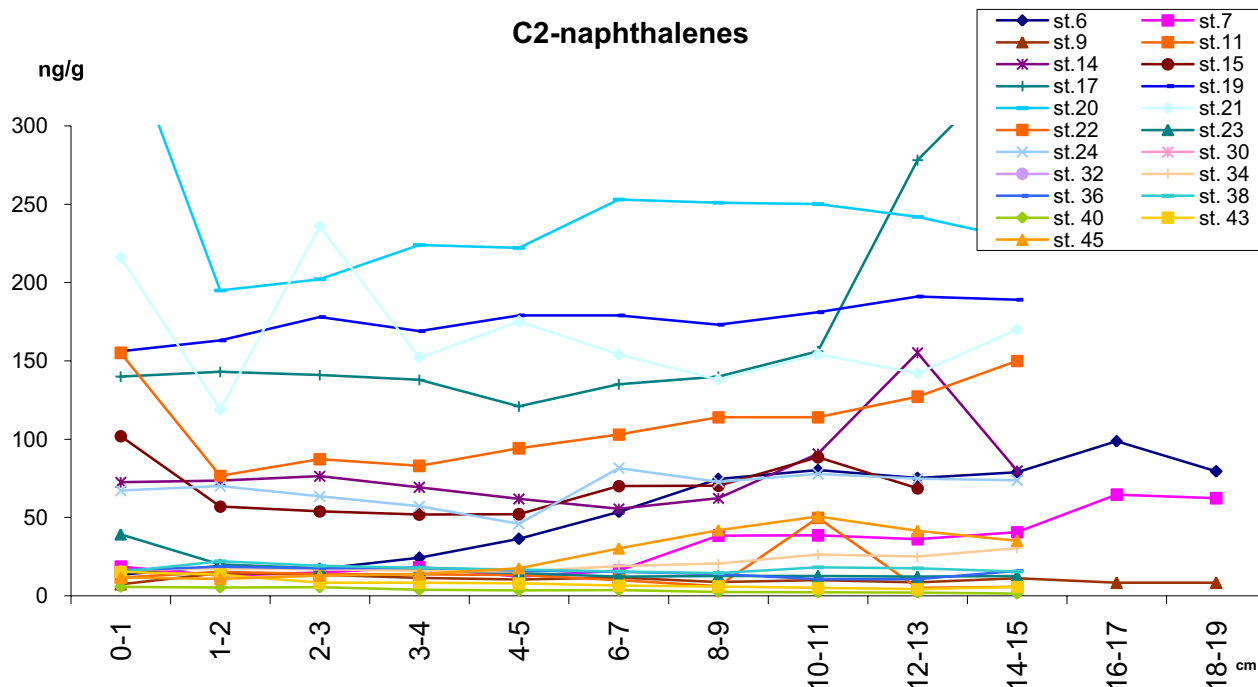
Figure 3. Concentrations of C2-naphthalenes in sediment cores from various stations (only every second centimetre is shown at more than 5 cm depths). Cores longer than 15 cm were taken at stations 6, 7 and 9 only.
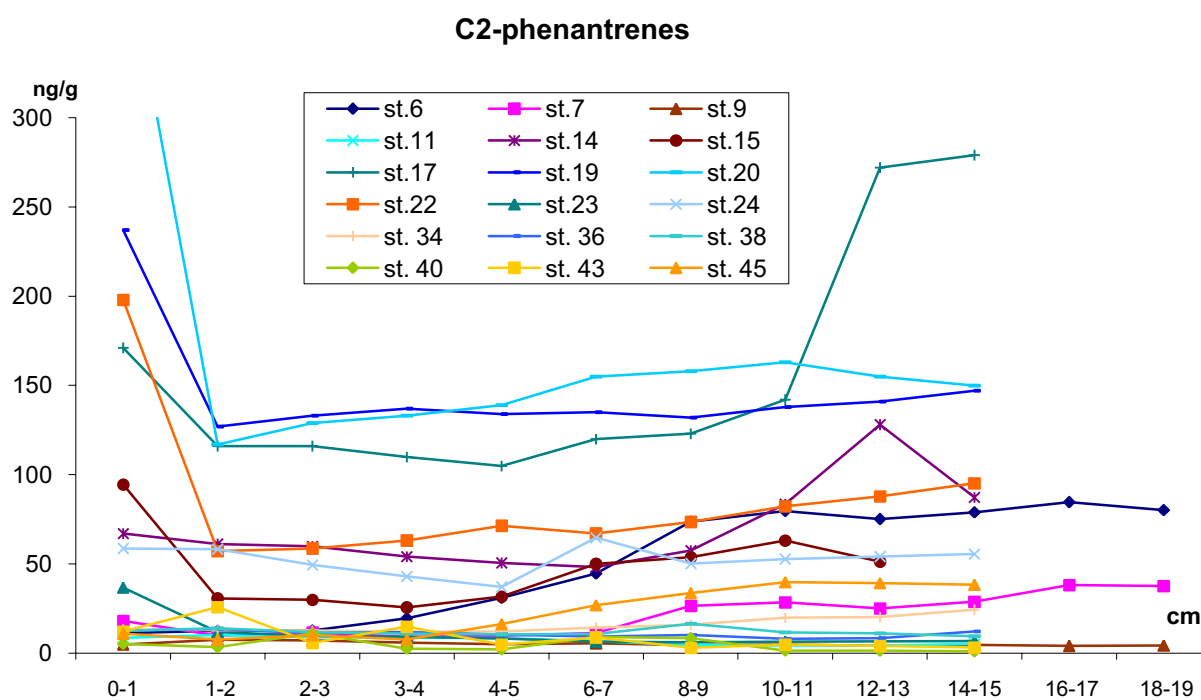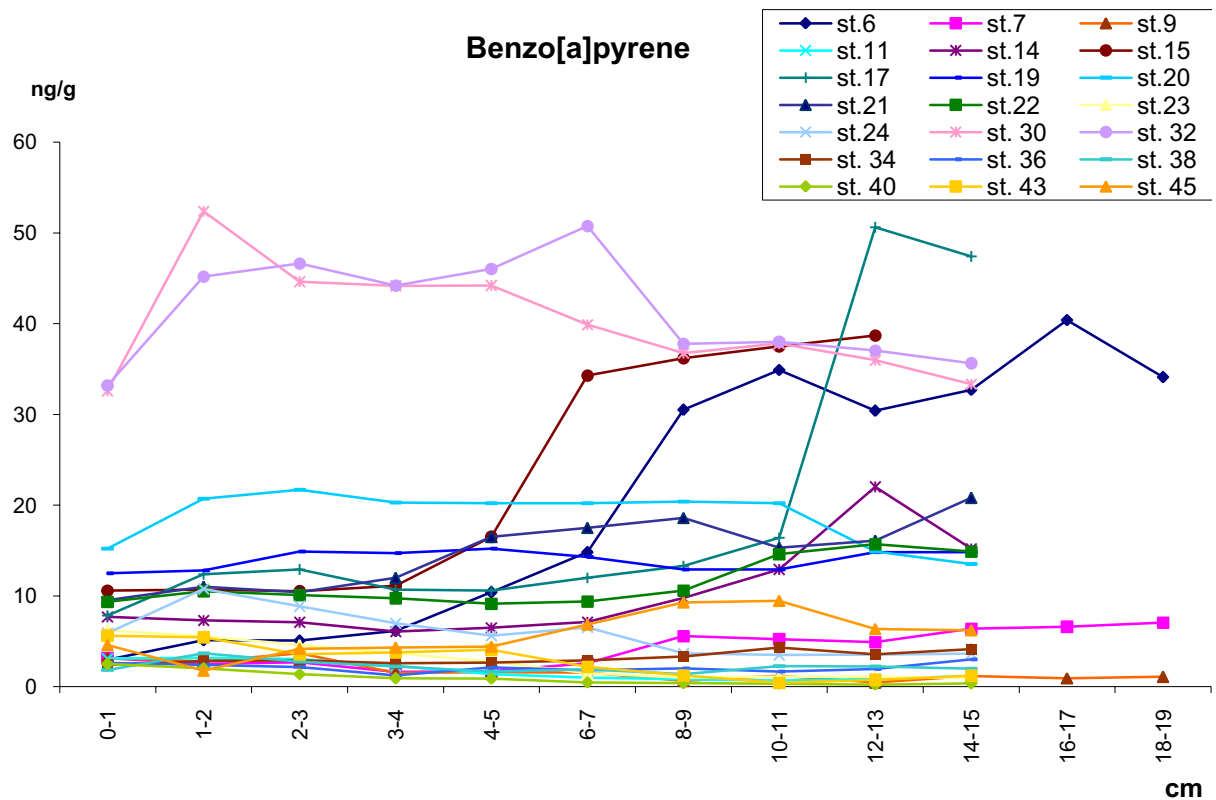

Figure 4. Concentrations of C2-phenantrenes in sediment cores from various stations (only every second centimetre is shown at more than 5 cm depths). Cores longer than 15 cm were taken at stations 6, 7 and 9 only

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Figure 5. Concentrations of benzo[a]pyrene in sediment cores from various stations (only every second centimetre is shown at more than 5 cm depths). Cores longer than 15 cm were taken at stations 6, 7 and 9 only.

The observed depth profiles of PAH concentrations are somewhat different from location to location. Trends for a number of selected compounds at stations 6, 7 and 9, located close to each other, are shown in Figg. 6-8. The decrease in PAH concentrations for most compounds in modern times is obvious at station 6 and is less pronounced but still apparent at station 7. At station 9, on the other hand, the trend is the opposite, levels of most PAHs remaining stable from the end of sediment core up to approximately 5 cm depth, at which a sharp increase in concentrations is observed for most compounds, continuing to modern times (surface sediments again not following the trend). The highest concentrations at all stations are observed for the high-weight compounds due to their higher stability.

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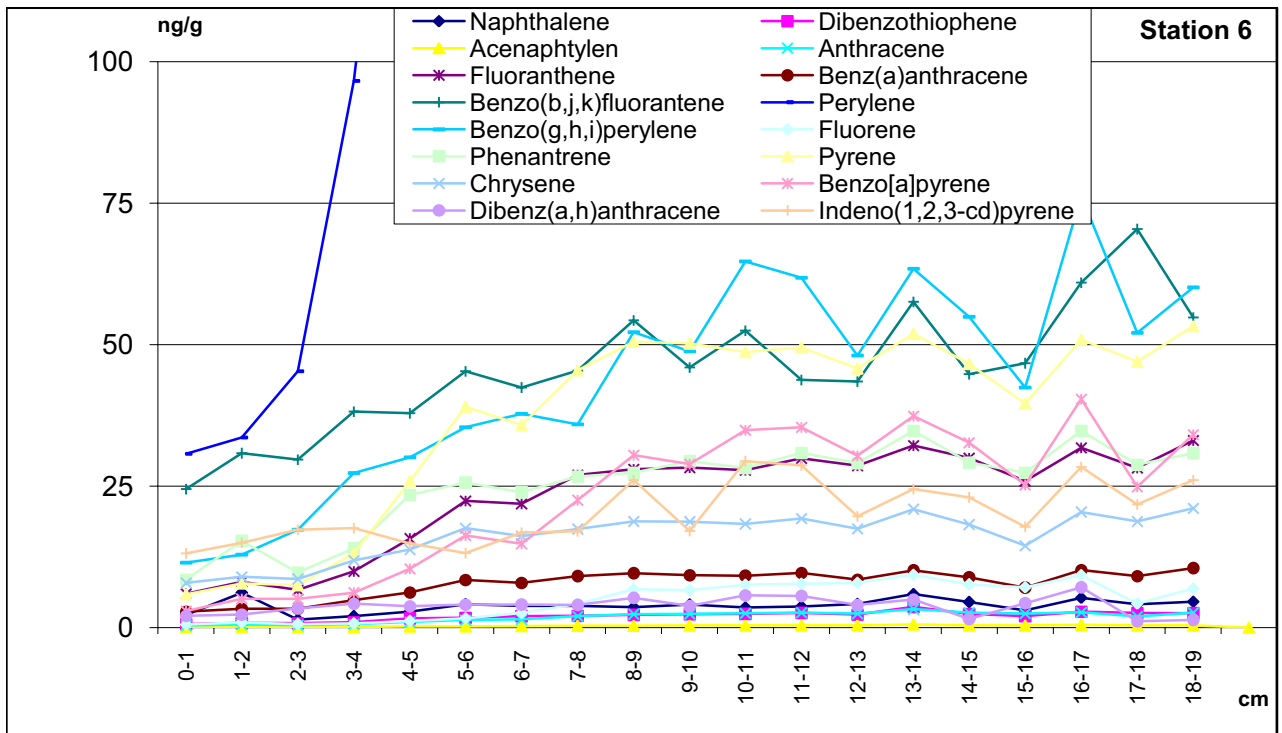
Figure 6. Concentrations of various PAH in sediment cores at station 6.
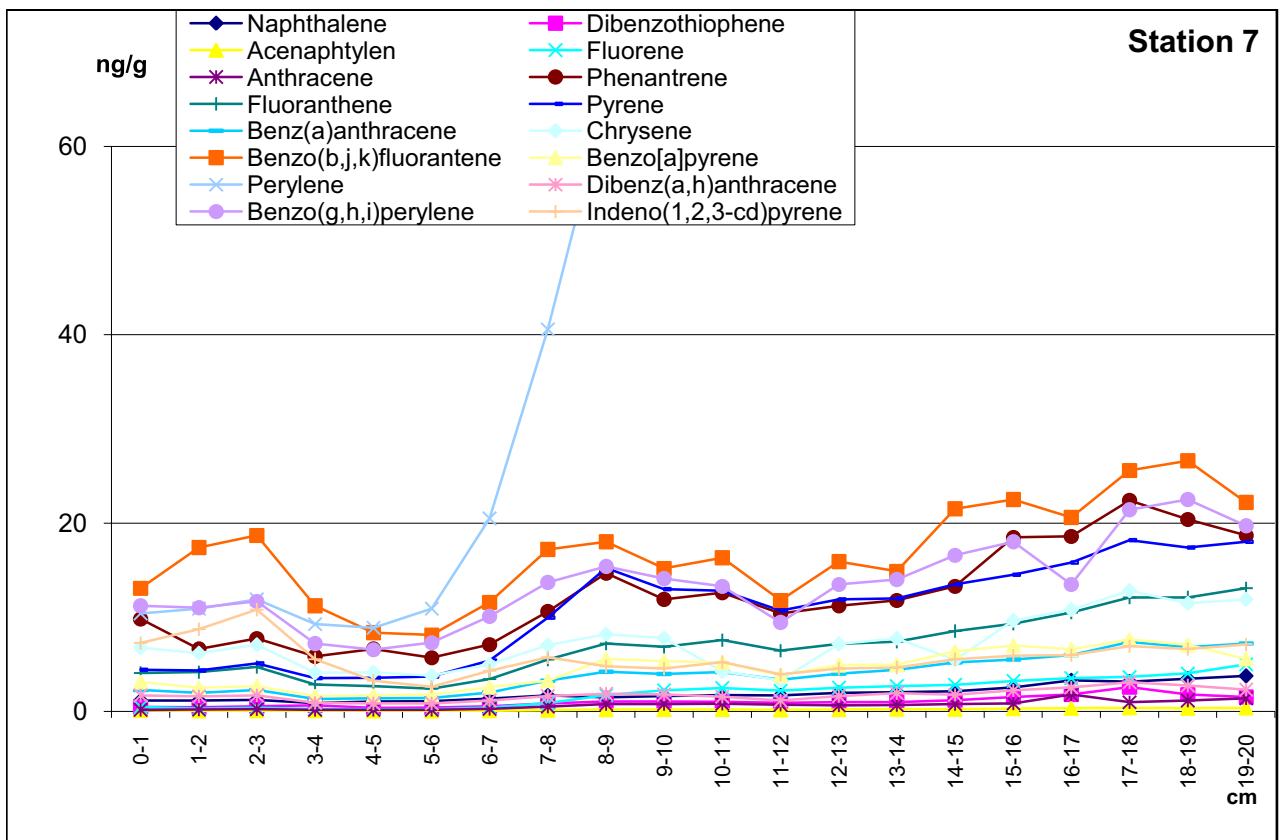
Figure 7. Concentrations of various PAH in sediment cores at station 7.

Stasjon 9

ng/g

Legend:
- Dibenzothiophene
- Acenaphtylen
- Anthracene
- Fluoranthene
- Benz(a)anthracene
- Benzo(b,j,k)fluorantene
- Perylene
- Benzo(g,h,i)perylene
- Naphthalene
- Fluorene
- Phenantrene
- Pyrene
- Chrysene
- Benzo[a]pyrene
- Dibenz(a,h)anthracene
- Indeno(1,2,3-cd)pyrene
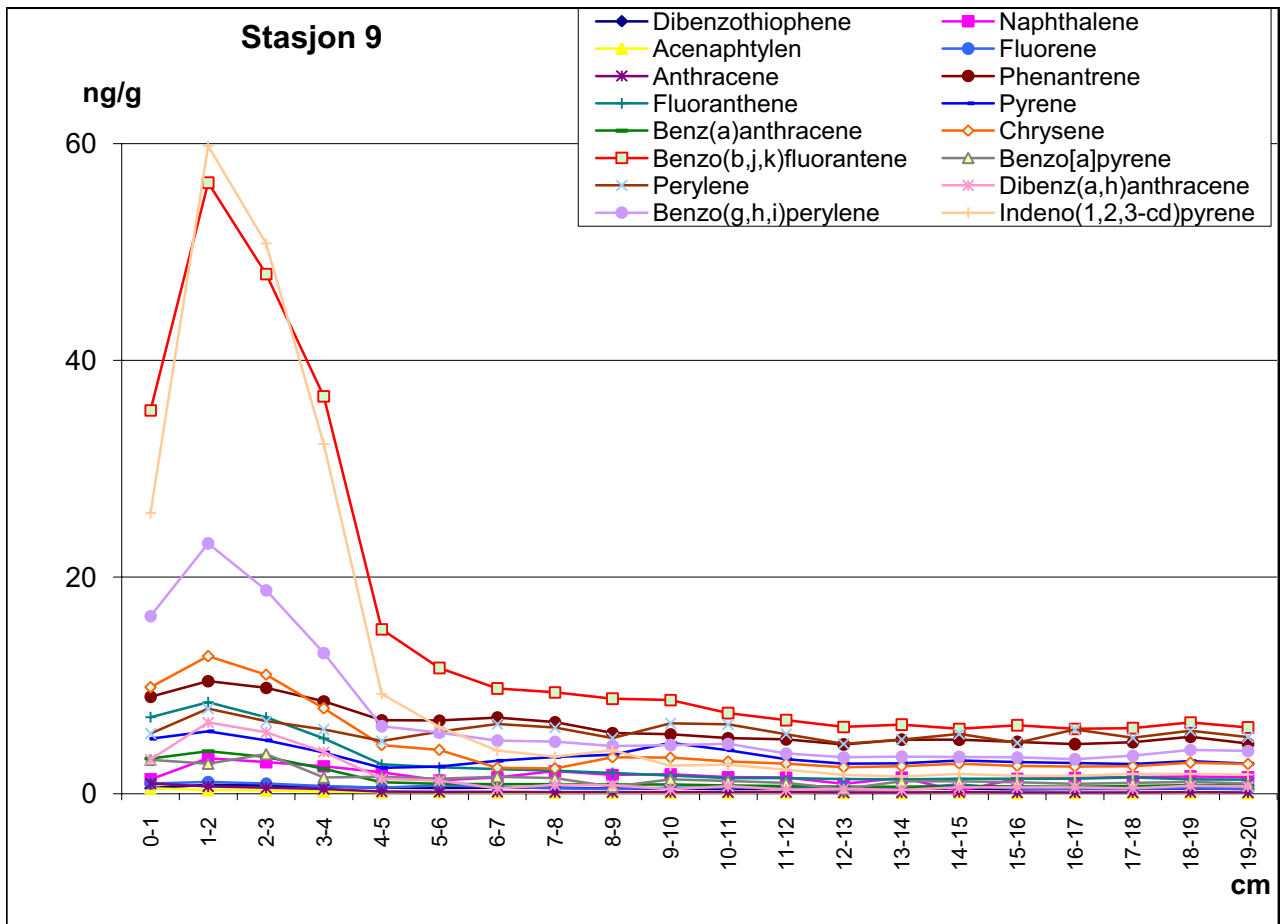
Figure 8. Concentrations of various PAH in sediment cores at station 9.

An overview of PAH levels in surface sediments (0-1 cm) at various stations are given in Fig. 9. Maps with PAH levels in surface sediments for a few representative compounds are shown in Fig. 10. The concentrations of individual compounds at 21 stations (No. 12 and 16-35) exceed 50 ng/g dw, and exceed 100 ng/g dw at 9 stations (No. 22 and 28-25), reaching 236 ng/g for phenanthrene at station 29. Geographically, the highest levels of PAH in surface sediments are observed close to Svalbard, which may be an indication of the natural seeps present in that region. Svalbard is the area with large coal reservoirs, where coal-mining activities have occurred for decades. Some oil and gas activities have been taking place in this region since 1990-s, too. Comparative studies of bottom sediments collected in the Svalbard offshore area and soils from West Spitsbergen Island have demonstrated the predominant source of PAHs to be the erosion of coal-bearing bedrock in Svalbard (Dahle *et al*., 2006). Levels in central Barents Sea and close to the Norwegian coast are low, although an increase is observed for some components in the Eastern part of the transects.
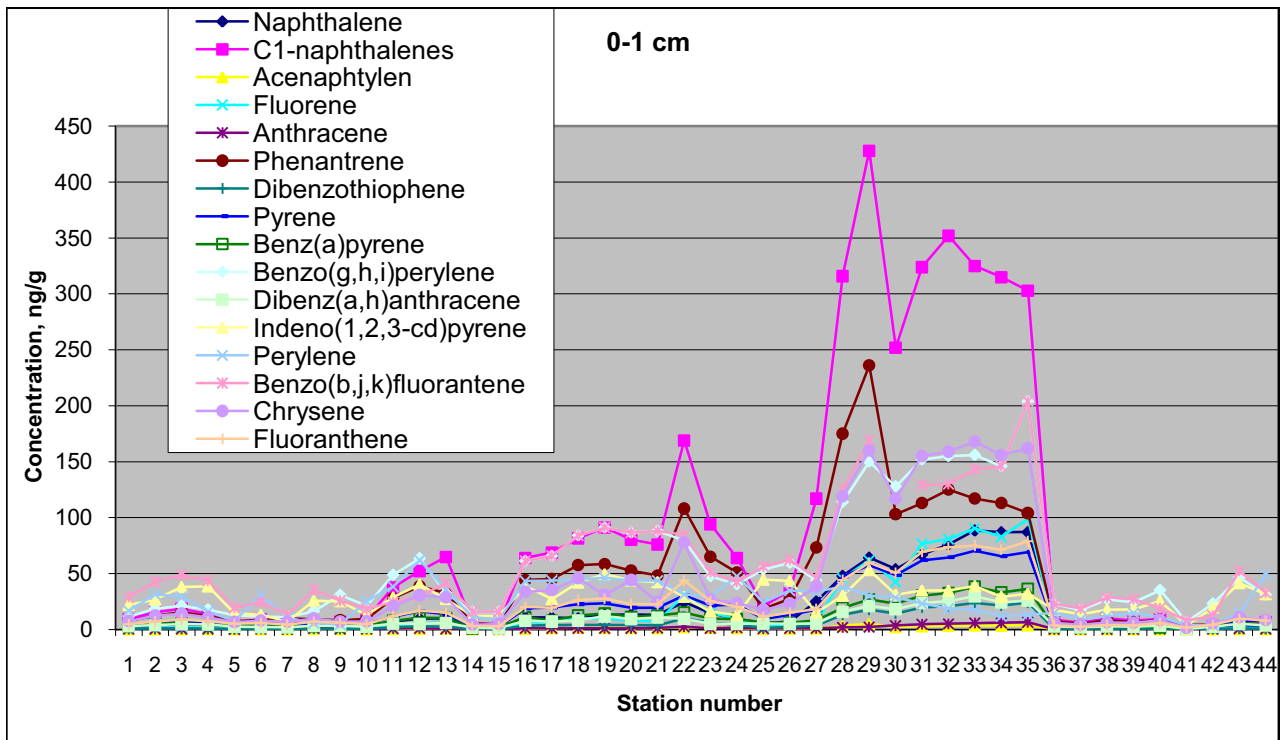
Figure 9. Concentrations of selected PAHs in surface sediments sediment (0-1 cm) at various stations from the 2004 cruise.
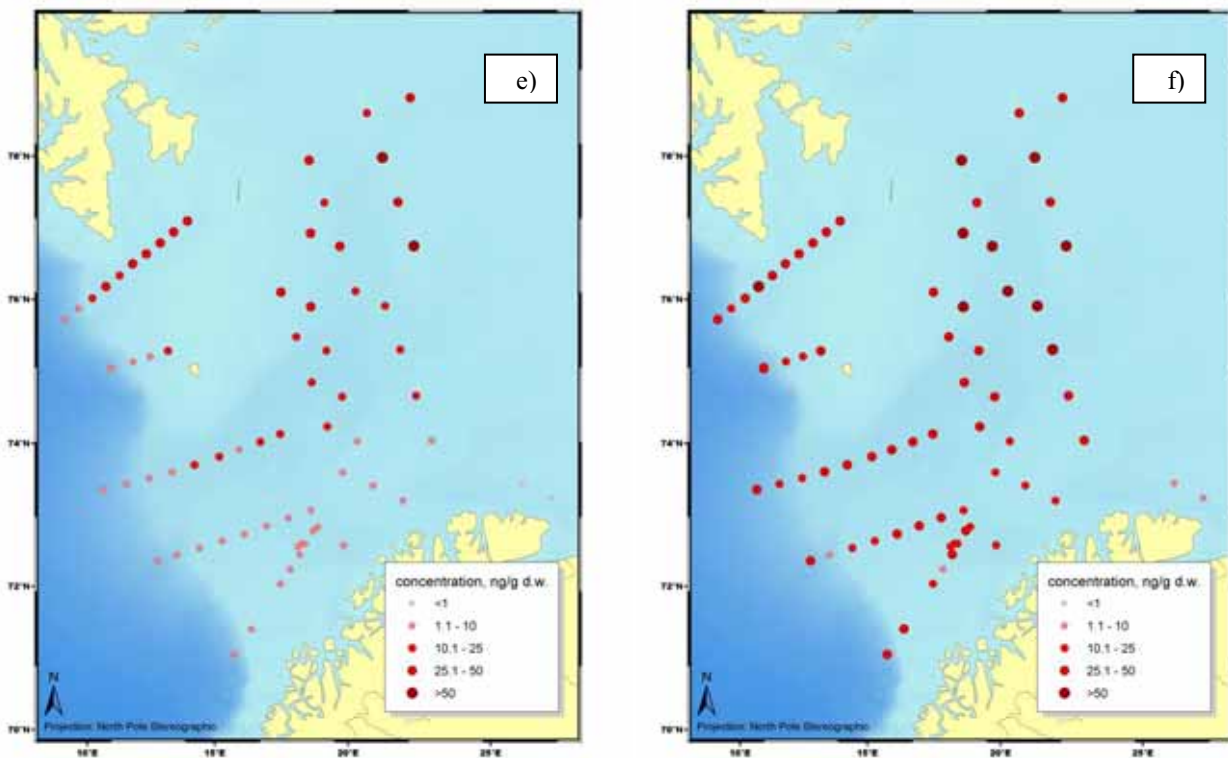
16
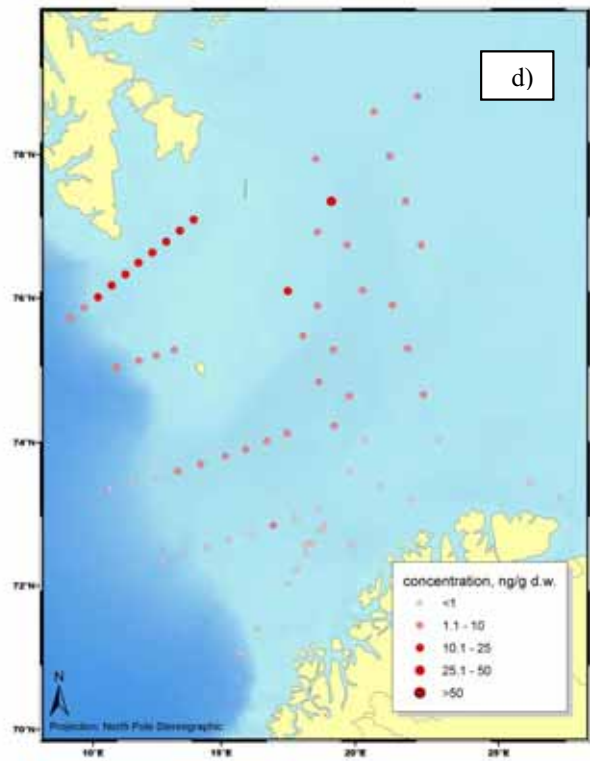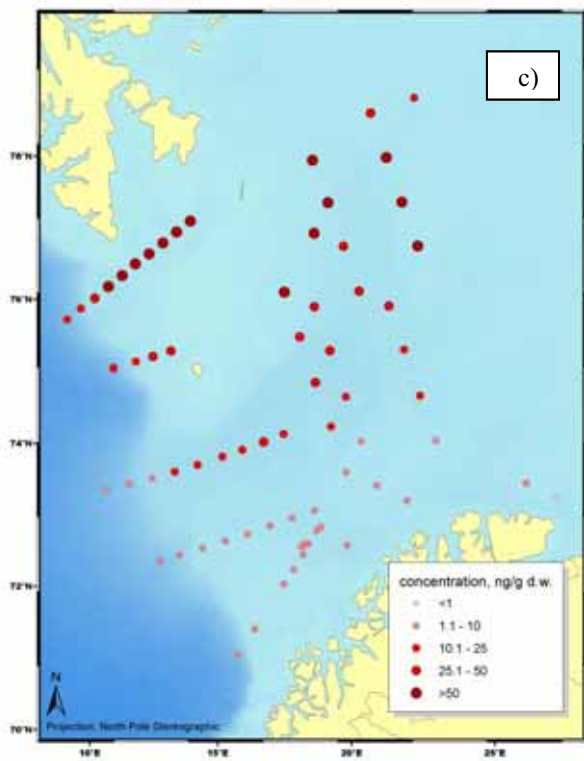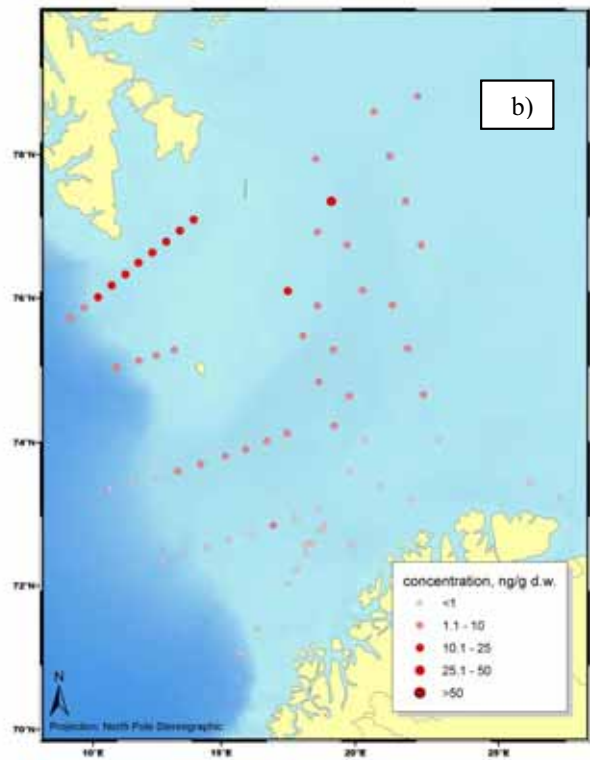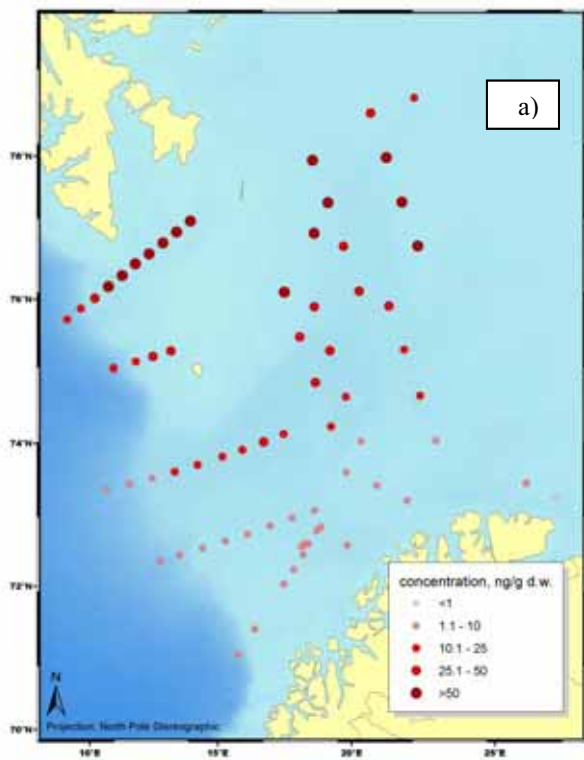
Figure 10: Maps of distribution of selected PAHs in surface sediments (0-1 cm) at various stations from the cruises in 2003 and 2004: a) naphthalene; b) anthracene; c) fluoranthene; d) dibenzothiophene; e) benzo[a]pyrene; f) indeno[1,2,3-c,d]pyrene.

Ranges of PAH levels in surface sediments vary very much from station to station, spanning four orders of magnitude, as shown in the box plot in Fig. 11. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line indicates mean values. Whiskers indicate 10th and 90th percentile, while dots indicate all outliers. The widest range of concentrations is observed for dibenzothiophenes, while anthracene show the most narrow range, having also rather low concentration values. Outliers are shown for all compounds, most of them representing stations 7, 35, 39, 40 (at lowest values) and 27, 31-33 (highest values).
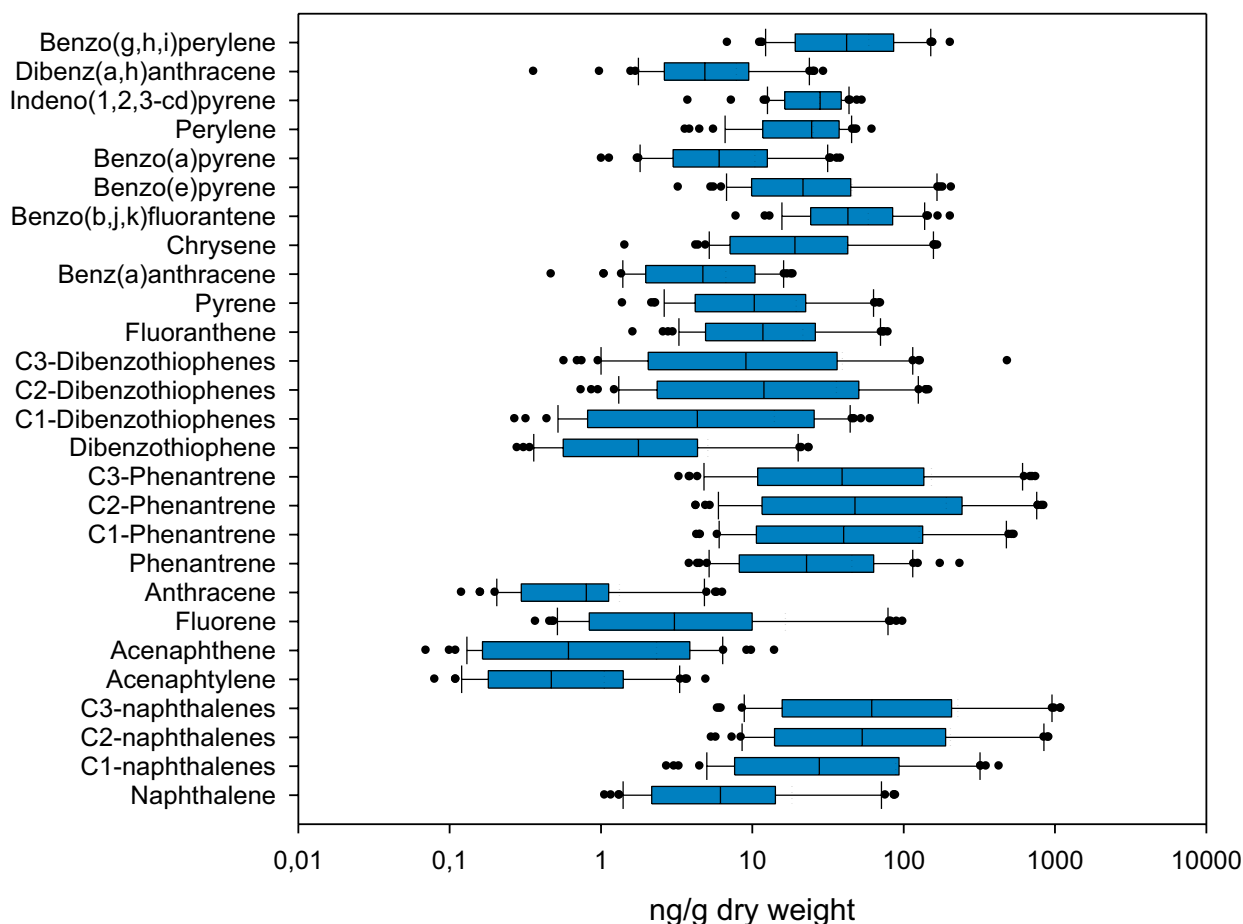
Figure 11. The range of concentrations of selected PAH components in surface layer sediments (0-1 cm) from 2004 cruise
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Trends similar to 2004 data are observed in 2003 data. Only surface sediment samples were collected at that cruise. Maps with PAH levels for a few representative compounds are shown in Fig. 10, while full data for separate components is given in Table 4. As in 2004, highest levels are observed in the north of the sampled area, at stations closest to Svalbard; relatively high levels (above 50 ng/g dw) are observed at the majority of stations in the open sea areas for some heavy-weight components, particularly for perylene, the compound of biogenic origin. The lowest values are observed at stations close to the coastal areas. The levels of benzo[a]pyrene at most stations of the 2003 cruise remained within the limits of insignificant-or-little contamination (below 10 ng/g dw) or moderate contamination (10 to 50 ng/g dw) by classification of the Norwegian State Pollution Control Authority (SFT 1997), slightly exceeding 50 ng/g dw at stations 673 and 677 only and thus falling into the "marked contamination" category at these stations. This classification, however, has been developed for evaluating anthropogenic contaminations in fjords and coastal waters, and is only mentioned here for comparison.

Range of PAH levels in surface sediments collected in 2003 varied even more from station to station than for 2004 samples, spanning five orders of magnitude, as shown in the box plot in Fig. 12. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line indicates mean values. Whiskers indicate 10th and 90th percentile, while dots indicate all outliers. The

widest range of concentrations is again observed for dibenzothiophenes, as well as phenanthrenes and naphthalenes, while acenaphthylene show the most narrow range, having also rather low concentration values. Outliers are shown for all compounds, most of them representing stations 663, 690, 692 (at lowest values) and 635, 639, 645, 647, 651 (highest values).
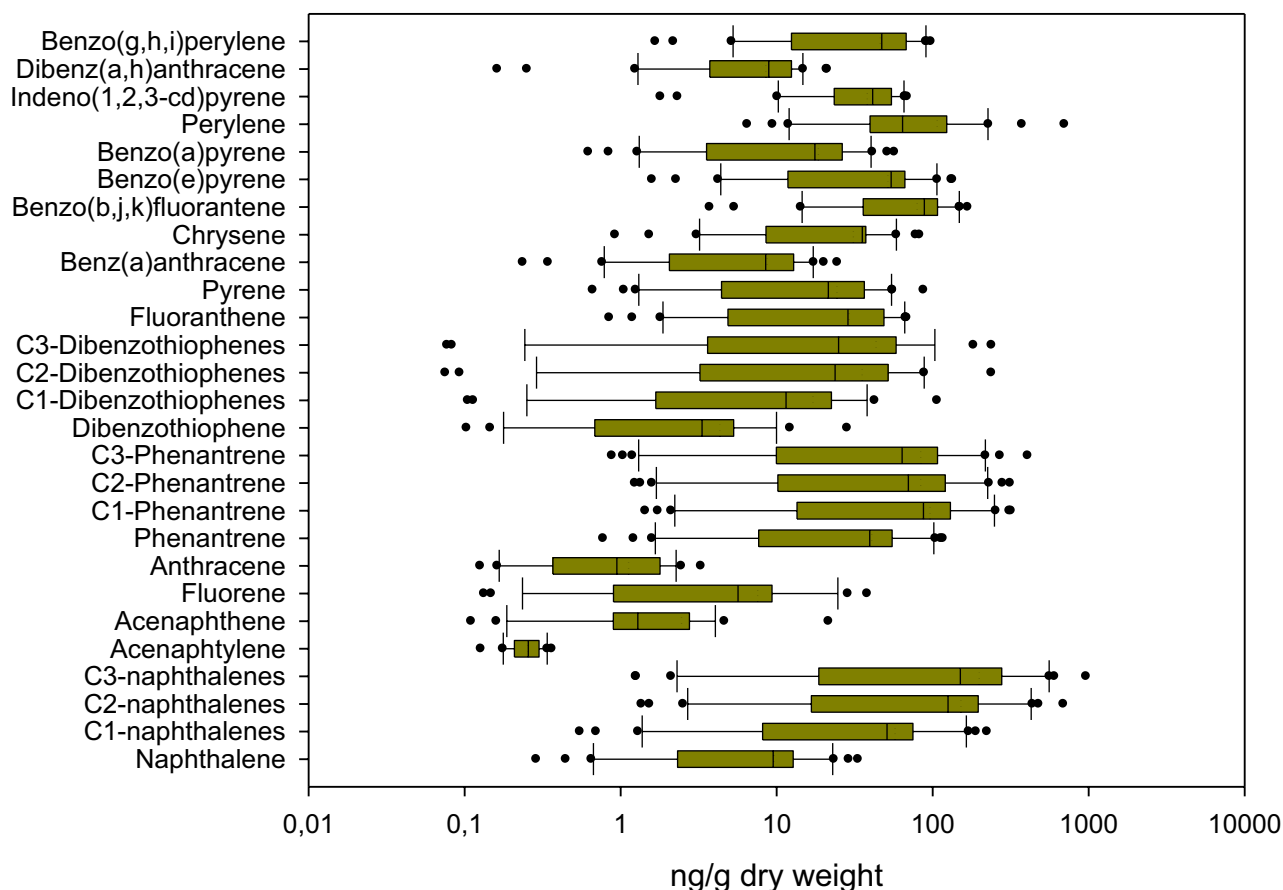

Figure 12. The range of concentrations of various PAHs in surface layer sediments (0-1 cm) from 2003 cruise.

The phenanthrene/anthracene ratio (PHE/ANT) can be used to evaluate the input of combustion PAHs: it is high if there are no significant inputs of organic matter related to high-temperature combustion (i.e. anthropogenic sources), and low (below 10), if such inputs have occurred at a significant scale. In the studied samples, mean PHE/ANT ratio was significantly higher than 10, being 36.2 for 2004 samples and 36.7 for 2003 samples. Only one sample, from station 9 in the 2004 cruise, had the PHE/ANT value below 10 (9.4). Thus, no significant influx of anthropogenic PAHs is observed in the studied samples, or it is masked by the regional PAH pattern.

Levels of total hydrocarbons (THC), measured in surface sediments only, are presented in Figure 13 and Table 4. The levels vary strongly from station to station, generally lying in ppm range both for 2003 and 2004 samples (see Table 4). The highest levels, observed for 2004 samples at stations 26-33 in the vicinity of Svalbard, are in the range of 50-70 µg/g dw, most other stations exhibiting much lower values, below 20 µg/g dw. This is in accordance with the Russian data for the central part of the Barents Sea, where THC concentrations in surface bottom sediments were found to not exceed 80

µg/g dw, while the Russian coastal areas seemed to be more contaminated, with up to 700 µg/g dw concentrations (Ilyin *et al*. 2004).
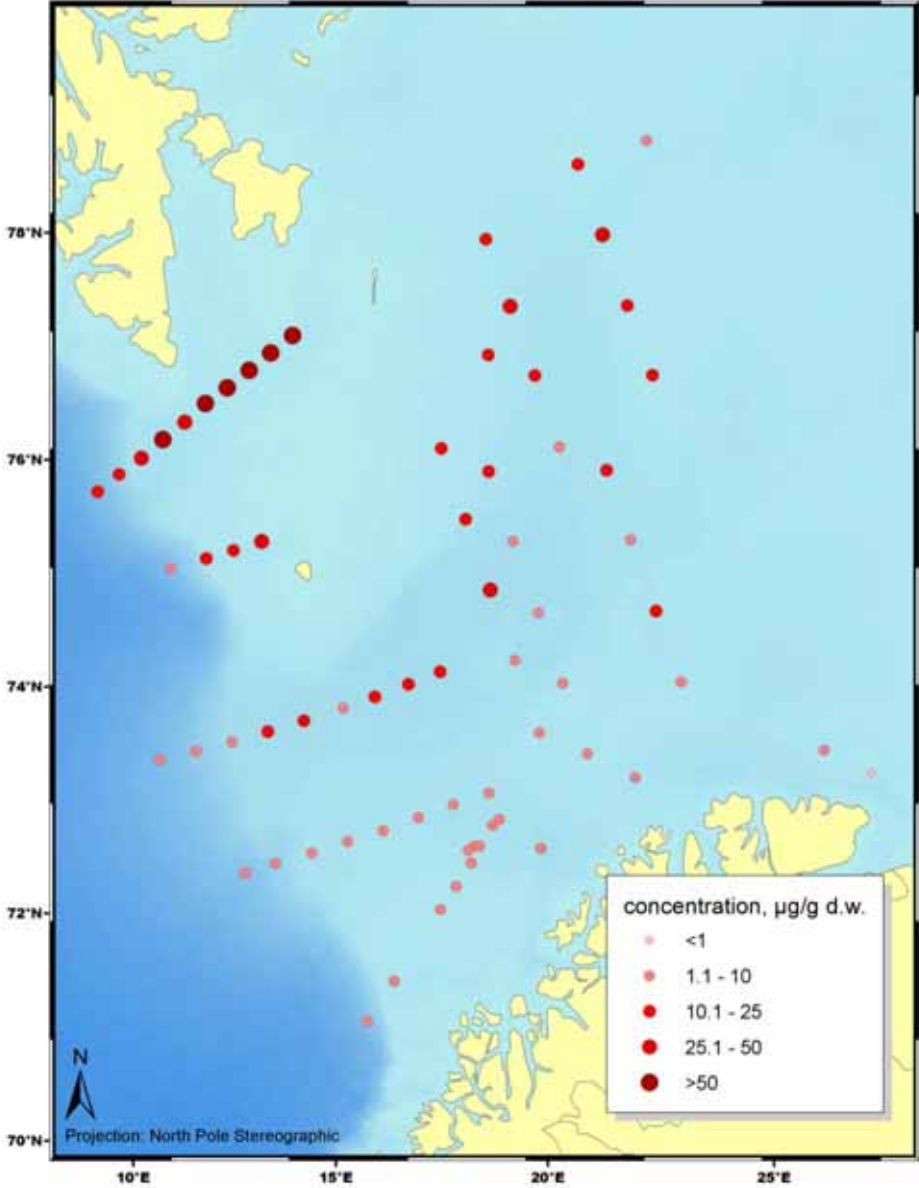

Figure 13. Maps of total hydrocarbon (THC) levels in surface sediments (0-1 cm) at various stations from the cruises in 2003 and 2004.

Table 4. PAH and THC concentrations in sediment samples from sea cruises of 2003 and 2004 (PAHs, ng/g dw, THC, µg/g dw).

Compound	2004				2003	
	Mean 0-1 cm	Range 0-1 cm (40 stations*)	Mean 14-15 cm	Range 14-15 cm (20 stations**)	Mean 0-1 cm	Range 0-1 cm (29 stations***)
Naphthalene	18.3	1.06 - 88.5	16.6	0.27 – 106	9.53	0.29 – 33.3
C1-naphthalenes	88.7	2.72 – 428	97.4	1.22 – 677	57.2	0.55 – 223
C2-naphthalenes	204	5.38 – 911	194	1.47 – 1246	152	1.36 – 689
C3-naphthalenes	228	5.90 – 1095	223	1.12 – 1297	200	1.25 – 963
Acenaphtylene	1.05	0.08 - 4.90	1.20	0.01 - 6.97	0.26	0.13 - 0.36
Acenapthene	2.33	0.07 - 14.1	2.35	0.02 – 11.0	2.52	0.11 - 21.5
Fluorene	16.6	0.37 - 98.8	17.4	0.06 – 113	7.63	0.13 – 38.0
Anthracene	1.33	0.12 - 6.40	1.24	0.03 - 5.40	1.13	0.13 - 3.27
Phenantrene	45.5	3.84 – 236	57.2	1.28 – 271	40.6	0.77 – 117
C1-Phenantrenes	127	4.31 – 538	127	0.95 – 772	96.2	1.44 – 318
C2-Phenantrenes	191	4.25 – 845	151	1.04 – 932	84.2	1.23 – 314
C3-Phenantrenes	153	3.28 – 748	142	0.66 – 752	84.3	0.88 – 407
Dibenzothiophene	5.08	0.28 - 23.8	5.23	0.17 - 24.5	4.36	0.10 - 28.3
C1-Dibenzothiophenes	14.0	0.27 - 60.2	13.4	0.07 – 47.0	17.3	0.11 – 107
C2-Dibenzothiophenes	35.9	0.74 – 147	29.4	0.18 – 131	35.8	0.08 – 238
C3-Dibenzothiophenes	39.4	0.57 – 486	30.0	0.13 – 139	44.1	0.08 – 239
Fluoranthene	21.6	1.63 - 78.9	17.2	0.28 – 54.2	29.1	0.85 - 68.2
Pyrene	19.5	1.39 – 70.4	24.2	0.41 - 80.5	24.5	0.66 - 87.4
Benz(a)anthracene	6.69	0.47 - 18.6	8.02	0.05 - 38.7	8.70	0.24 - 24.5
Chrysene	42.2	1.44 – 168	34.8	0.28 – 175	30.9	0.92 - 82.4
Benzo(b,j,k)fluoranthene♠	58.5	7.82 – 204	32.8	2.14 – 114	78.8	3.72 – 168
Benzo(e)pyrene	45.6	3.25 – 207	43.7	1.42 – 208	51.6	1.59 – 134
Benzo(a)pyrene♠♠	10.4 (II)	1.01 - 38.3 (I-II)	12.9 (II)	0.34 - 47.4 (I-II)	18.6 (I)	0.62 – 56.8 (I-III)
Perylene	25.3	3.61 - 61.9	105	1.69 – 781	109	6.48 – 700
Indeno(1,2,3-cd)pyrene	27.8	3.76 - 53.2	11.6	0.31 - 49.6	38.1	1.80 - 68.6
Dibenz(a,h)anthracene	7.86	0.36 - 29.6	5.25	0.03 - 27.5	8.48	0.16 - 21.1
Benzo(g,h,i)perylene	58.9	6.86 – 204	38.8	1.05 – 146	46.3	1.67 - 97.4
Sum 20 PAH	*414*	*37.4 – 1357*	*435*	*10.2 – 1418*	*510*	*19.8 – 1426*
PHE/ANT	36.2	9.41 - 113	52.5	11.0 - 102	36.8	12.6 – 79.0
THC	19.1	3.17 - 70.5	-	-	12.0	0.86 - 46.5

*   Stations 1,2,3,4,5,6,7,9,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,43,45.

**   Stations 6,7,9,11,14,17,19,20,21,22,23,24,30,32,34,36,38,40,43,45.

*** Stations 625,627,629,631,633,635,639,643,645,647,649,651,653,655,657,659,661,663,665,667,669,671,673,675,677,679,681,690,692.

♠ Sum of benzo(b)fluoranthene, benzo(j)fluoranthene and benzo(k)fluoranthene.

♠♠ Degree of contamination by classification of the State Pollution Control Authority (SFT) is given in brackets (I – insignificant or little contamination; II – moderate contamination; III – marked contamination; IV – strong contamination; V – very strong contamination).

Based on the results of the chemical analyses, principal component analysis (PCA) of the surface sediment data for all stations was carried out on both data sets (2003 and 2004). The analysis reveals correlations between objects and variables of the dataset, i.e. PAH components and cruise stations, by explaining the degree of co-variance between the objects and the variables. For 2004 data, 27 PAH compounds are the objects and 44 stations are the variables, while for 2003 data, 27 PAH compounds are the objects and 30 stations are the variables. All data was block-normalised and weighted to average, and a 3-principal components analysis was run on the datasets.

The first two principal components explain 88% of variance for 2004 data and 74% variance for 2003 data. PCA score plots showing the covariance between the objects, and loading plots showing the covariance between the variables, are shown in Figg. 14 and 15.
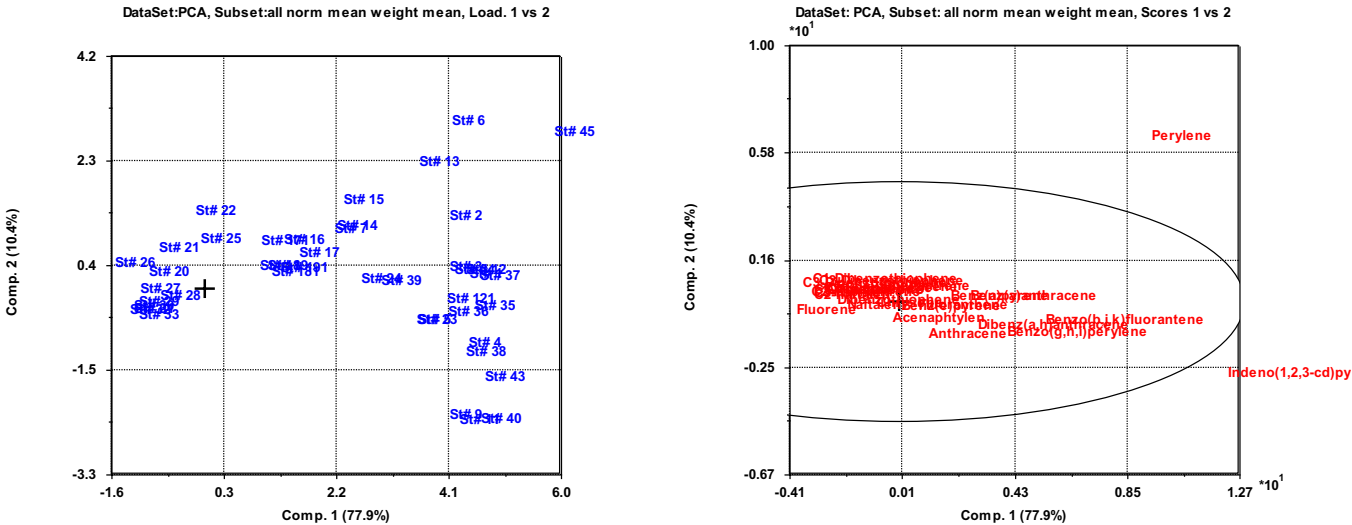
Figure 14. PCA plot for the 2004 cruise data (a: score plot; b: loading plot).
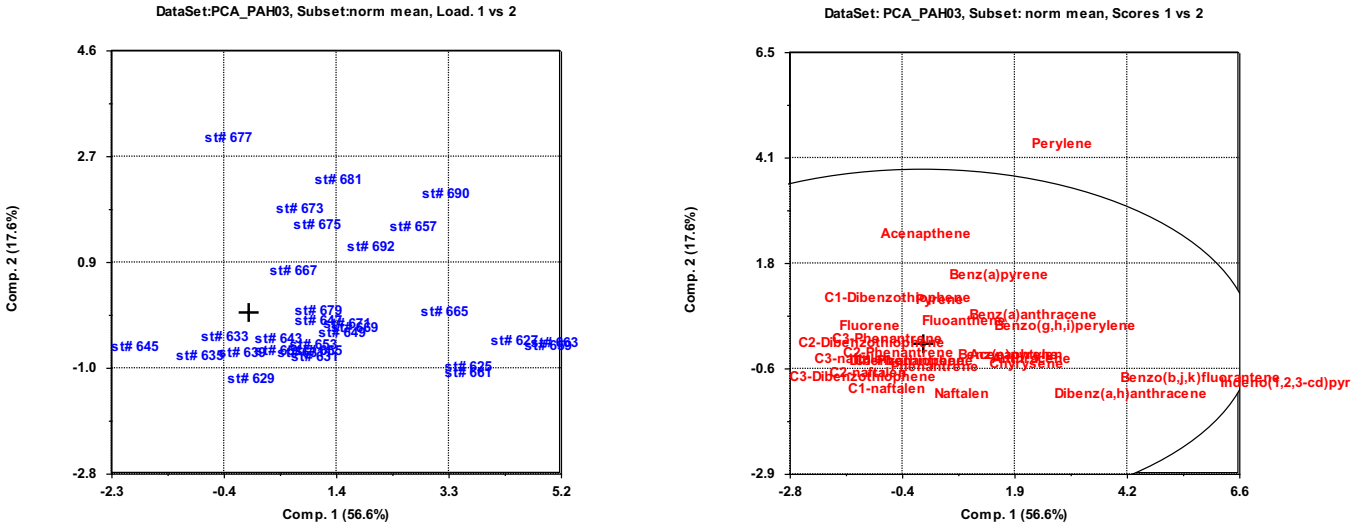
Figure 15. PCA plot for the 2003 cruise data (a: score plot; b: loading plot).

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For the 2004 samples, stations 20-22, 26-33 form a distinct cluster with high levels of alkylated naphthalenes, phenanthrenes and dibenzothiophenes, being also the locations closest to Svalbard region with its fossil resources. An erosion of coal-rich sedimentary rock at Spitsbergen is a probable reason for the elevated PAH levels at these stations. A large part of other stations is at the opposite part of the scale, apparently rich in high-weight combustion PAHs; among these, stations 9, 11 and 40 being low in perylene levels (below 6 ng/g dw). For 2003 data, two groups of stations seem to be differentiated, one with stations 625, 627, 659, 661, 663, 665, all located in the southern part of the studied area off the Norwegian coast to the west of North cape, and the other one with stations 673, 675, 677, 679, 681, 690 and 692 in the eastern part of the studied area (station 657 also falling into the same group).

PCA analysis along the third principal component (Fig. 16) did not reveal new information in case of 2004 data, explaining just under 3% more variance than the first two principal components. However, for 2003 data the analysis along three principal components explains more than 8% extra variance as compared with the first two principal components. The analysis revealed a strong differentiation between station 629 and the rest of the group.
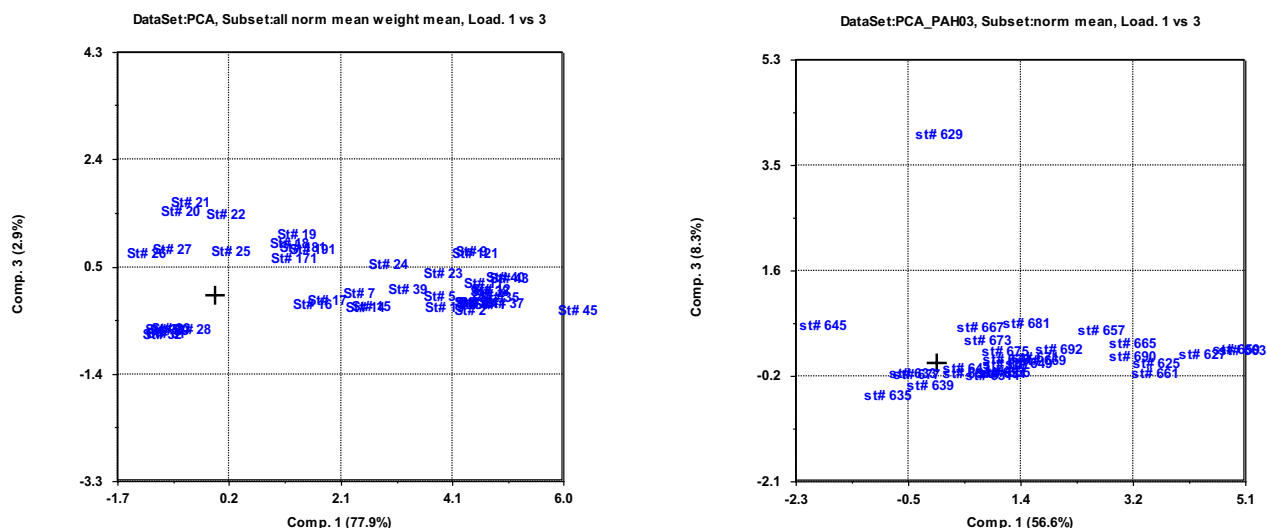

Figure 16. PCA score plots for 2004 (a) and 2003 (b) cruise data analysed along 3 principal components.

3.1.2. Water analyses.

The Atlantic water currents strongly influence the hydrological and ecological conditions in the Barents Sea. Together with the atmospheric transport of contaminants from the northern European industrial centers, this transboundary transfer by ocean currents may influence the contaminant levels of the Barents Sea. This ecosystem may thus be more influenced by human activities outside the Arctic than most other Arctic waters (Ilyin *et al.* 2004). However, the primary concern is normally the persistent organic pollutants which are not easily degraded in the environment (e.g. PCB). PAHs and other non-halogenated hydrocarbons are typically not so persistent, being removed from the environment by evaporation, other physical processes, and chemical and biological degradation in a matter of days to weeks. It is therefore not expected to observe any significant levels of contamination with this type of compounds in the water of the Barents Sea unless a catastrophic release occurs, or regular releases are done throughout long periods of time. It has been reported that on the Russian Barents sea coast (Kola Peninsula) significant releases of wastewater from the industry and households occurs, 71.5 mln. m^3 per year, including 33.7 tonnes of oil hydrocarbons

(Korshenko *et al.* 2005). It is therefore important to monitor the level of contamination in these areas and to check the ability of the environment to handle the influx of anthropogenic pollutants.

THC has been measured in water samples collected during the 2004 cruise in open waters of the Barents Sea. The results showed very low levels in ppb range (μg/L), reaching background values for all stations except station 31 at which a concentration of 23.5 μg/L was observed. The remaining 39 stations had an average THC concentration of 0.9 μg/L, ranging from 0 to 3.8 μg/L. Since these low values are below the limit of quantitation, the results should only be treated as estimates (while better data may be obtained by means of analysing larger volumes of water). These values are significantly lower than what has been reported by Russian researchers who documented THC levels up to 120 μg/L in central and southern parts Barents Sea waters (Ilyin *et al.* 2004). The large discrepancies in the results may be largely due to the differences in analytical methods.

PAH measurements in water have been carried out on samples collected in 2005. PAHs are poorly soluble in water and their concentrations in seawater are typically low, normally at very low background levels. As expected, PAH levels in all samples were at low levels. Unfortunately, a large part of components, particularly naphthalene, were not quantifiable due to impurities present in the sorbent in amounts comparable to those observed for PAH in the seawater (and much higher ones for naphthalene). Therefore, only a few PAH compounds could be quantified. The results for these compounds are shown in Table 5. These values are, like those for THC, significantly lower than what has been reported by Russian researchers for the waters of Eastern Barents sea, ranging from 12 ng/L to 79 ng/L PAH (sum 14 compounds); the highest concentrations were found in coastal waters (Plotitsyna *et al.* 2002; Ilyin *et al.* 2004).

Table 5. PAH levels in water samples collected in 2005, ng/L.

Compound	Mean (N=11)	Range, Min - Max
Acenaphtylene	0.017	0 - 0.057
1-Methylphenantrene	0.086	0 - 0.682
3.6-Dimetylphenantrene	0	0 - 0
Benzo(j)fluoranthene	0.001	0 - 0.006
Benzo(e)pyrene	0.067	0 - 0.197
Benzo(a)pyrene	0.132	0 - 0.346
Perylene	0.221	0.083 - 0.668
Indeno(1,2,3-cd)pyrene	0	0 - 0
Benzo(ghi)perylene	0	0 - 0
Dibenz(a.h)anthracene	0	0 - 0

3.2. Grain size and geochemical analyses.

Composition of sediment material was investigated for all samples collected 2003-2004. For the majority of the samples, the pelite fraction (grain size less than 63 μm, i.e. clay and silt) was predominant, see Fig. 17. Only at 13 stations out of 40 in 2004 and 9 stations out of 29 in 2003, less than 50% of grain size distribution was made by pelites. On average, the percentage of silt and clay in 2004 samples was 62.3%, sand 31.6% and gravel 6.2%; in 2003 samples, correspondingly 68.3%, 27.5% and 4.3%. For more detailed information, see Table 6.

The distribution of grain size composition is also given in Fig. 18. Figure 18 shows the grain-size fractions gravel, sand, silt and clay for the top 1 cm sample in the 73 sample stations. The grain size distribution criteria (>70% of mud, particles ≤ 63μm) for comparison of contaminant levels between

surface sediments in the Barents Sea are not fulfilled. Large variation in the mud content is particularly observed in the south-western part of the Barents Sea and along the upper continental slope (Fig. 17). Here, percentages for mud vary between 5 and 85 %. The grain size distribution in surface sediments is less variable in the central Barents Sea, and mud content ranges between 40 and 80 % (Fig. 17). This pattern holds true for the northernmost transect where low variability of grain size is observed. Sand and gravel (≥ 63μm) is mainly enriched on shallow banks and ridges as well as in coastal settings.
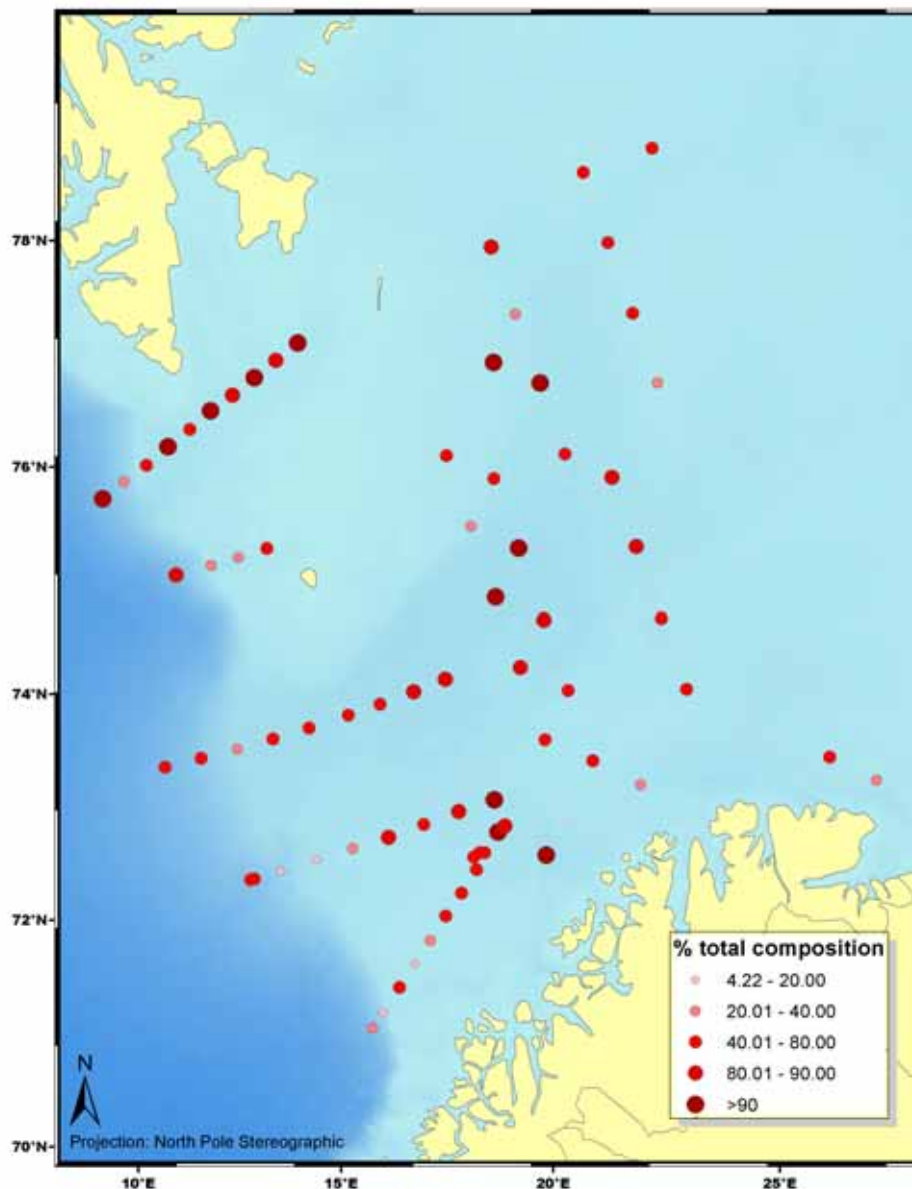
Figure 17. Distribution of sediment material with grain size less than 63 μm (pelites) in the samples collected in 2004.
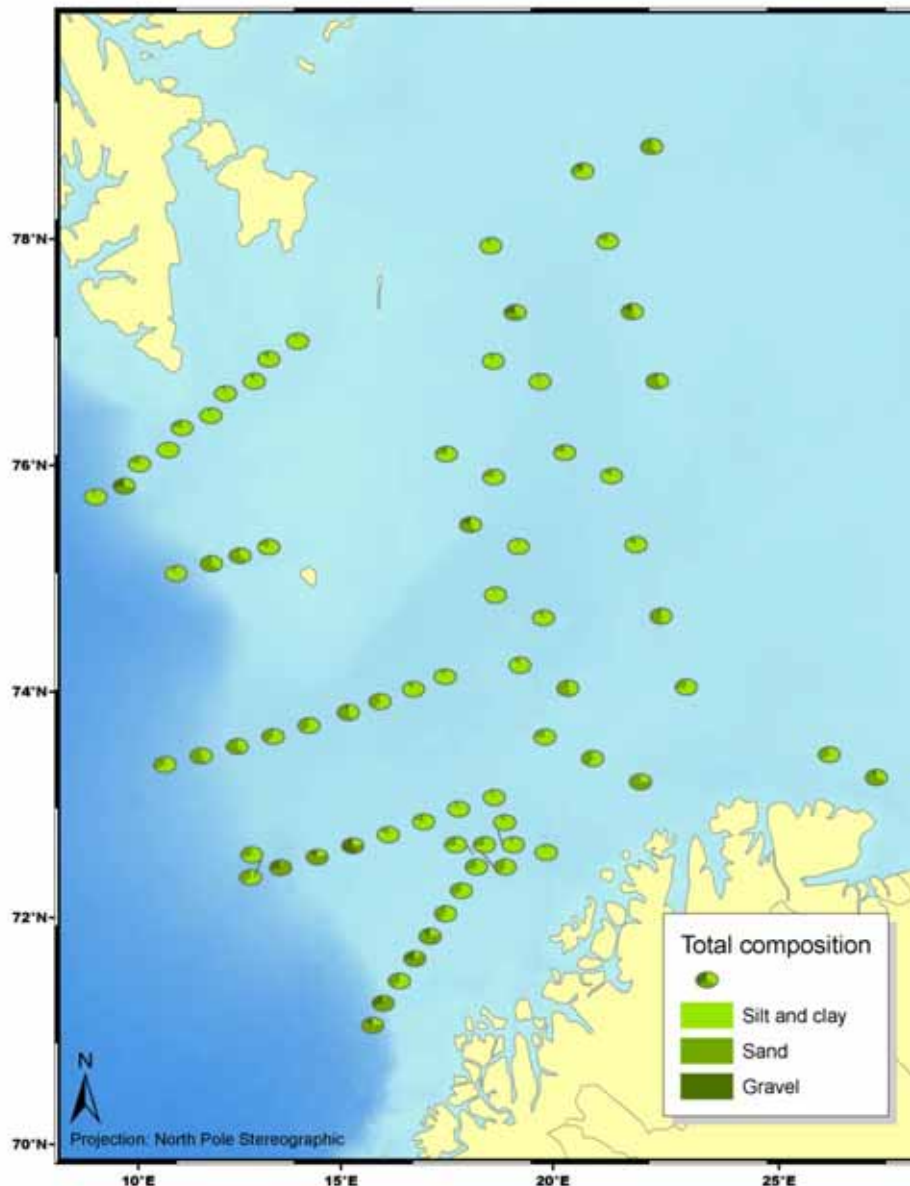
Figure 18. Grain size composition of sediments collected during cruises in 2003 and 2004 (in percent of total sample).

The total organic carbon content (TOC) varies from 0.2 to 2.74 wt. % for the whole investigated area (Fig. 19). There are regional variations with the highest concentrations in the samples taken south of Spitsbergen and the north-eastern Barents Sea with values larger than 1 wt. % in most cases. The TOC-values are generally lower in the southern Barents Sea. Here most of the samples have values less than 1 wt. %, with a few exceptions. The organic carbon source for the sample stations south of Spitsbergen is largely dominated by land-derived organic-rich sedimentary material from Spitsbergen (Winkelmann & Knies 2005), whereas there might be other sources for the TOC-rich samples in the central Barents Sea. Here marine plankton production associated with ice edge effects might play a role for the high TOC-contents in the top 1 cm sediments. However, upcoming analysis on the carbon isotopic composition of the organic matter will help clarifying these assumptions.
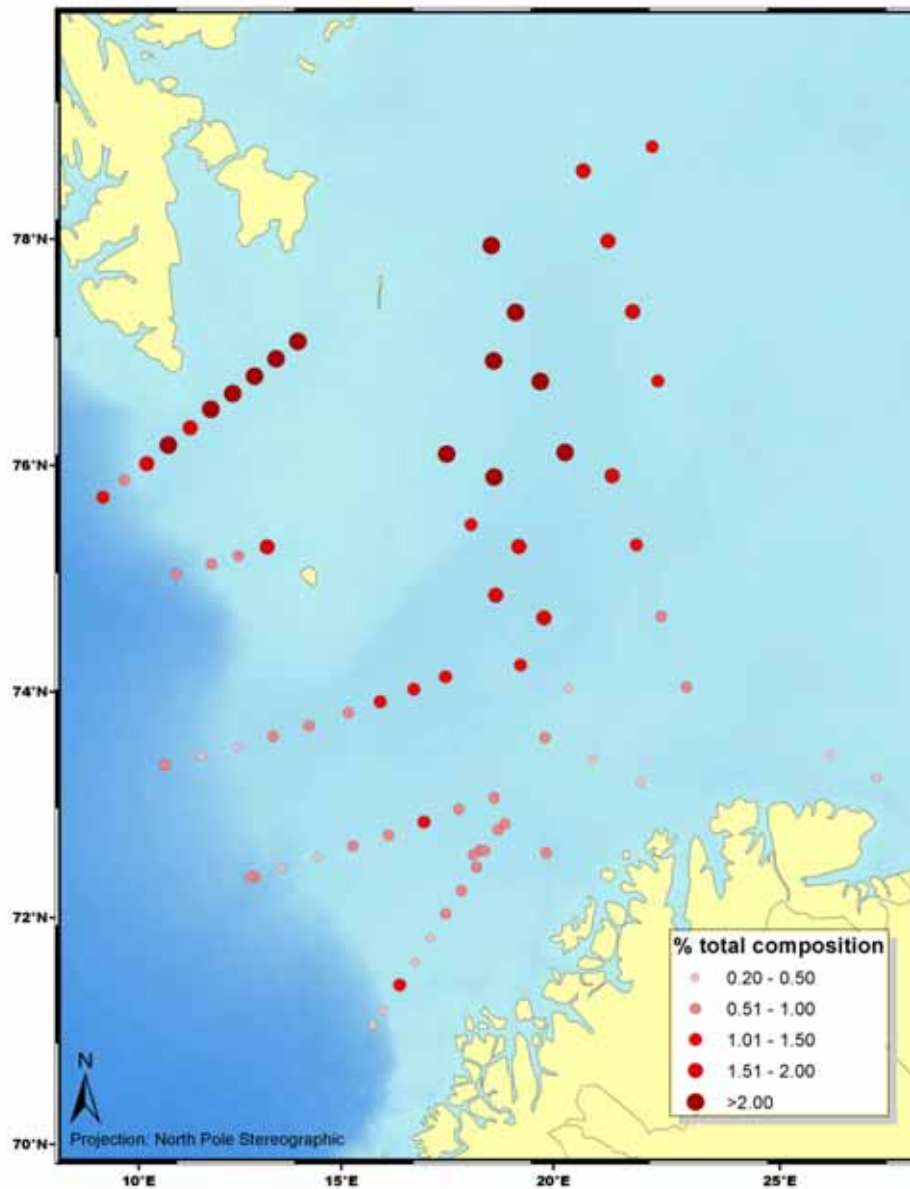
Figure 19. Total organic carbon content (TOC) in the 0 – 1 cm samples, derived from LECO analysis.

Table 6. Distribution of grain size in sediments from cruises of 2003 and 2004 (N is the number of stations).

Grain size class*	2004 (N=40)		2003 (N=29)	
	Mean	SD	Mean	SD
Boulders, cobble, pebble	3.9	9.8	2.1	3.9
Granule	2.2	2.8	2.2	3.3
Very coarse sand	2.1	2.5	1.7	2.2
Coarse sand	2.9	3.9	1.4	1.4
Medium sand	3.6	4.1	2.1	1.9
Fine sand	7.9	7.2	8.2	7.3
Very fine sand	15.1	11.2	14.1	10.3
Silt	55.5	24.0	60.8	19.5
Clay	6.8	3.4	7.5	3.2

*Classification according to Buchanan, 1984.

A dominant part of surface sediments from the Barents Sea is of non-biological (clastic) origin, and the distribution and transport is mainly controlled by bottom water-currents. The main sources for sediments today are concentrated along the southern coast of the Barents Sea. They include the erosion of Quaternary coastal and shallow bank deposits and discharge from rivers. In contrast, complex processes along the marginal ice zone (MIZ) dominate the sedimentation processes in the northern Barents Sea. Large seasonal and inter-annual variations in ice cover in the MIZ directly affect the primary production and release of lithogenic particles in the MIZ. Ice melts during spring and summer give rise to a stratified and nutrient-rich euphotic zone, which supports a pronounced spring bloom (Sakshaug & Skjoldal 1989). The sedimentation is mainly influenced by the water column stratification (strong salinity stratification in the Arctic water; no stratification in the Atlantic water) and also by the activity of plankton organisms. Zooplankton faecal pellets are important constituents of the vertical flux of organic matter (e.g. Olli *et al.* 2002). However, besides the photosynthetic organic matter flux, of the organic carbon content in the Barents Sea sedimentation is also influenced by terrigenous organic matter supply, granulometric composition of bottom sediments and the efficiency of organic matter burial and preservation (Stein & MacDonald 2004).

The variability of total organic carbon (TOC) and grain-size of our dataset give the typical pattern for the recent sedimentological environment in the Barents Sea. Fine-grained sediments rich in TOC occur in shelf depressions/troughs along the polar front where Arctic water encounters Atlantic water. Here, high flux of biologic sediments and terrigenous material is related to the marginal ice zone (MIZ) (Reigstad *et al.* 2002). In addition, organic matter bound to faecal pellets and adsorbed to clay minerals and oxide surfaces is also preserved in surface sediments. Transport of these sediments from MIZ to the western Barents Sea margin may be caused by bottom currents following the bathymetric lows to the west. This is inferred from predominantly fine-grained sediments in the Storfjord Trough enriched in TOC (Fig. 19) pointing to a source in the central Barents Sea (Vogt *et al.* 2001). In contrast, TOC-poor sediments occur in the southern Barents Sea, where most of the organic matter is mineralised in the less productive, ice-free open ocean. In addition, the sediments are generally much coarser, confirming the observation that enhanced wave and current activity favour mechanical differentiation of sediments, which then defines the grain size of sediments and related distribution of TOC in the Barents Sea. Tidal currents in the southern Barents Sea lead to the deposition of mainly coarse-grained sediments in the coastal zones, whereas fine-grained sediments are transported and deposited in the adjacent troughs and depressions in deeper water. Organic carbon-rich mud in these troughs and depressions have the highest potential for accumulation of contaminants (Fig. 19). However, this assumption can only be clarified by going beyond the regional grid and focusing on a small-scale accumulation/erosion centres in the southern Barents Sea. Indeed, levels of hydrocarbons are often normalized to pelite fraction (fine sediments, particle size less than 63 μm) or to total organic carbon contents. The covariance in the current dataset between TOC and PAHs is heavily influenced (dominated) by the samples from Svalbard area, as shown in Fig. 20.
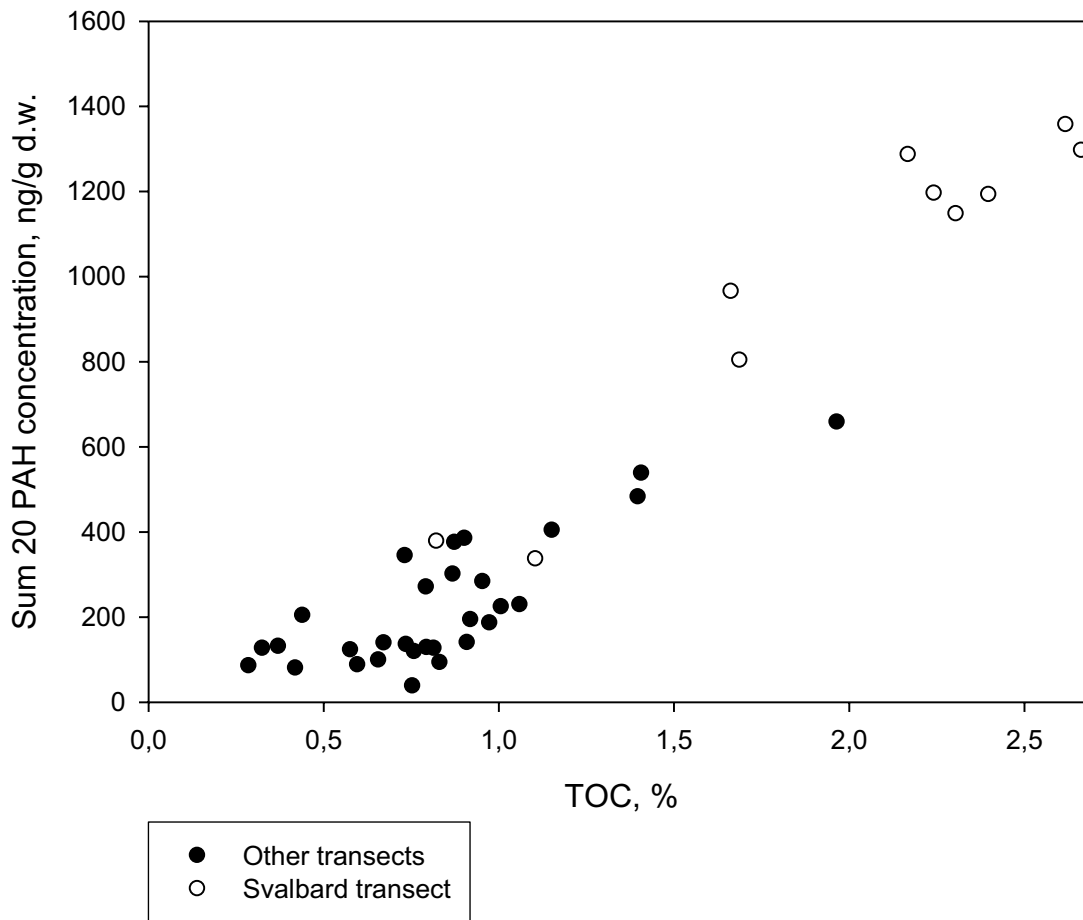
Figure 20. The covariance between PAHs and total organic carbon in surface sediment samples from the 2004 cruise.

3.3. Intercalibration experiment.

The results of the intercalibration study are given in Tables 7 and 8. Data for each lab as compared to all is presented as box plots in Figg. 21-26 for sample 1 and Figg. 27-32 for sample 2. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.

Figs. 21-32. Intercalibration results for the individual institutions as compared to all 6 participant laboratories.
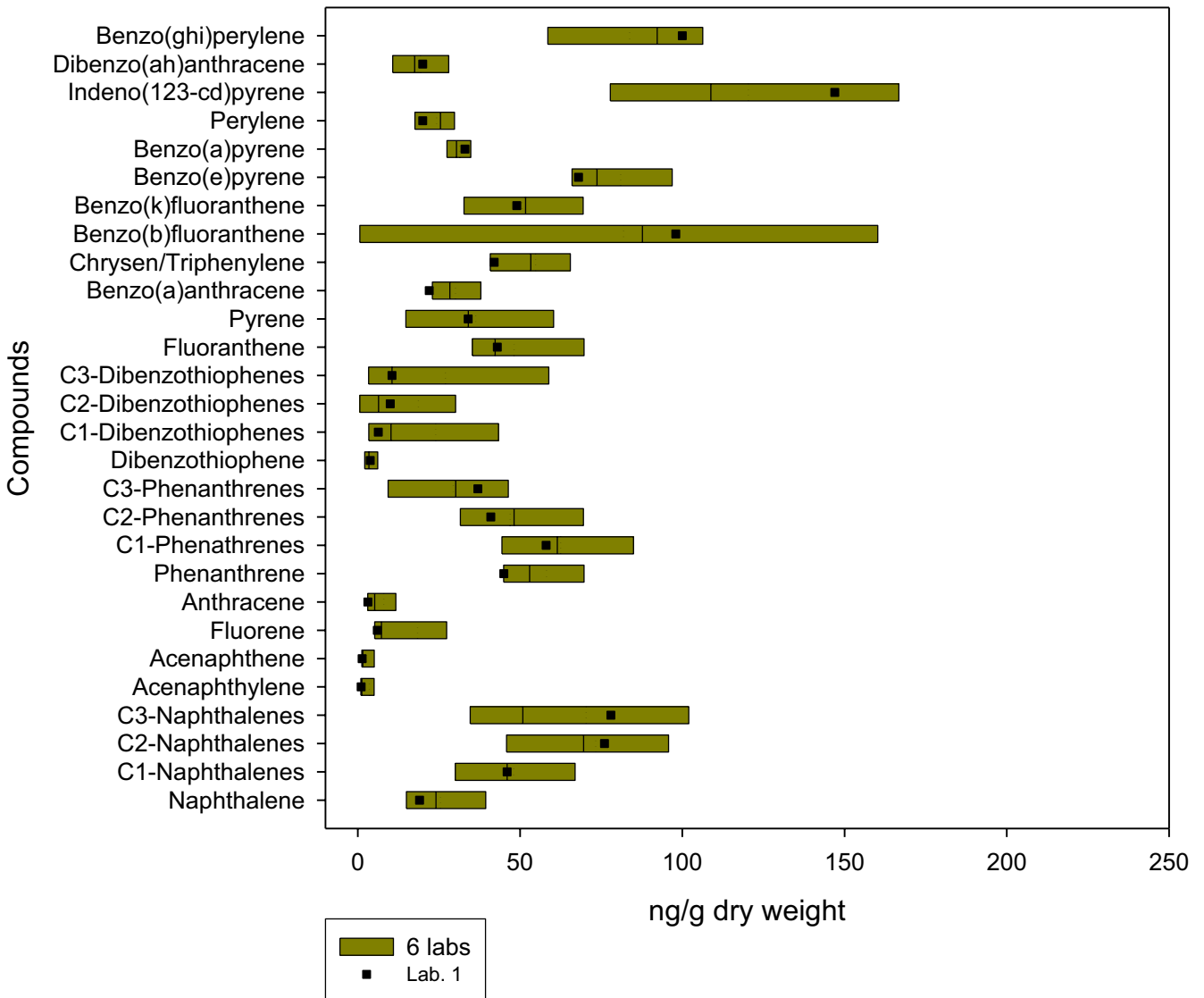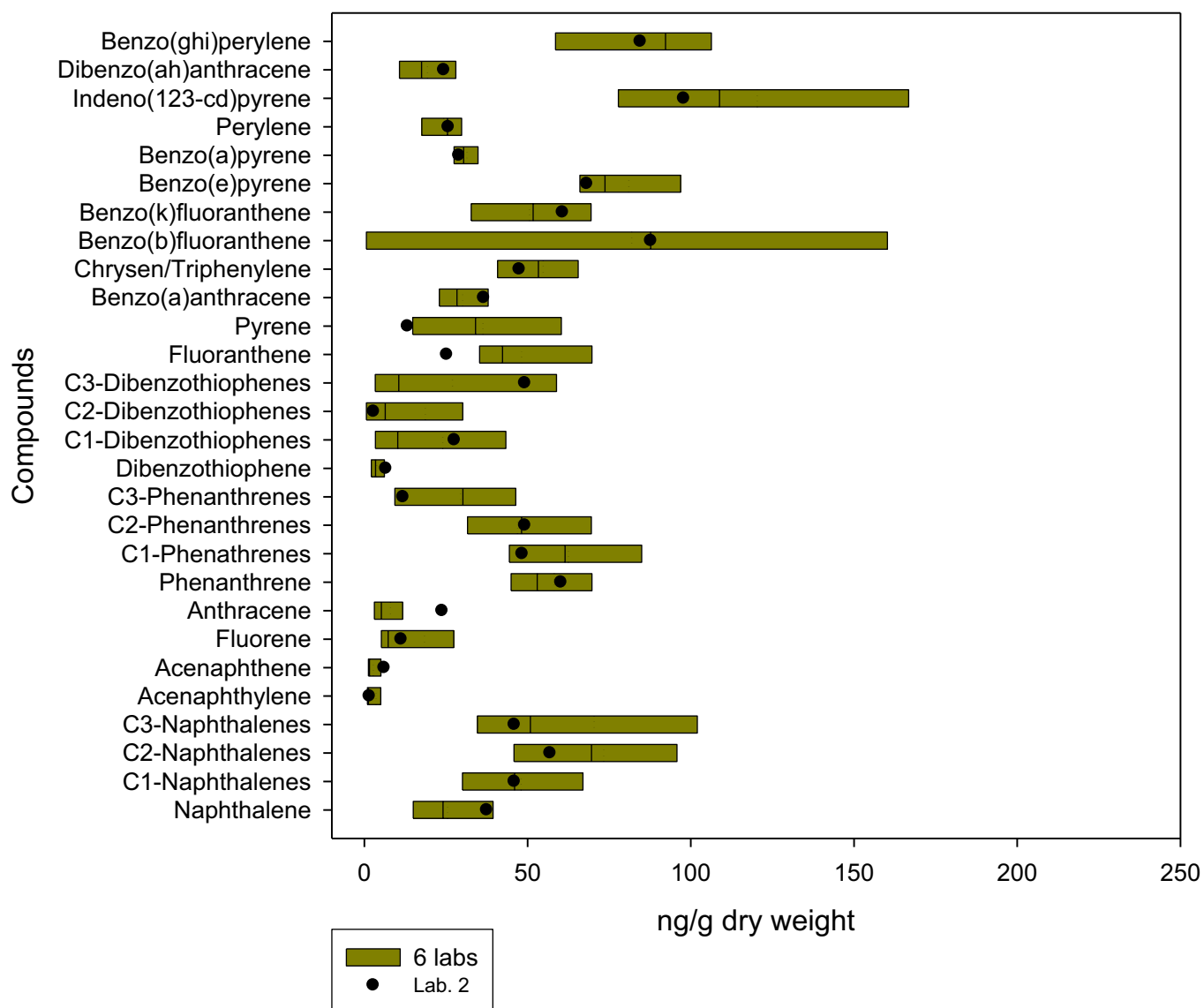
Figure 21. Results for Laboratory 1 on Sample 1 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
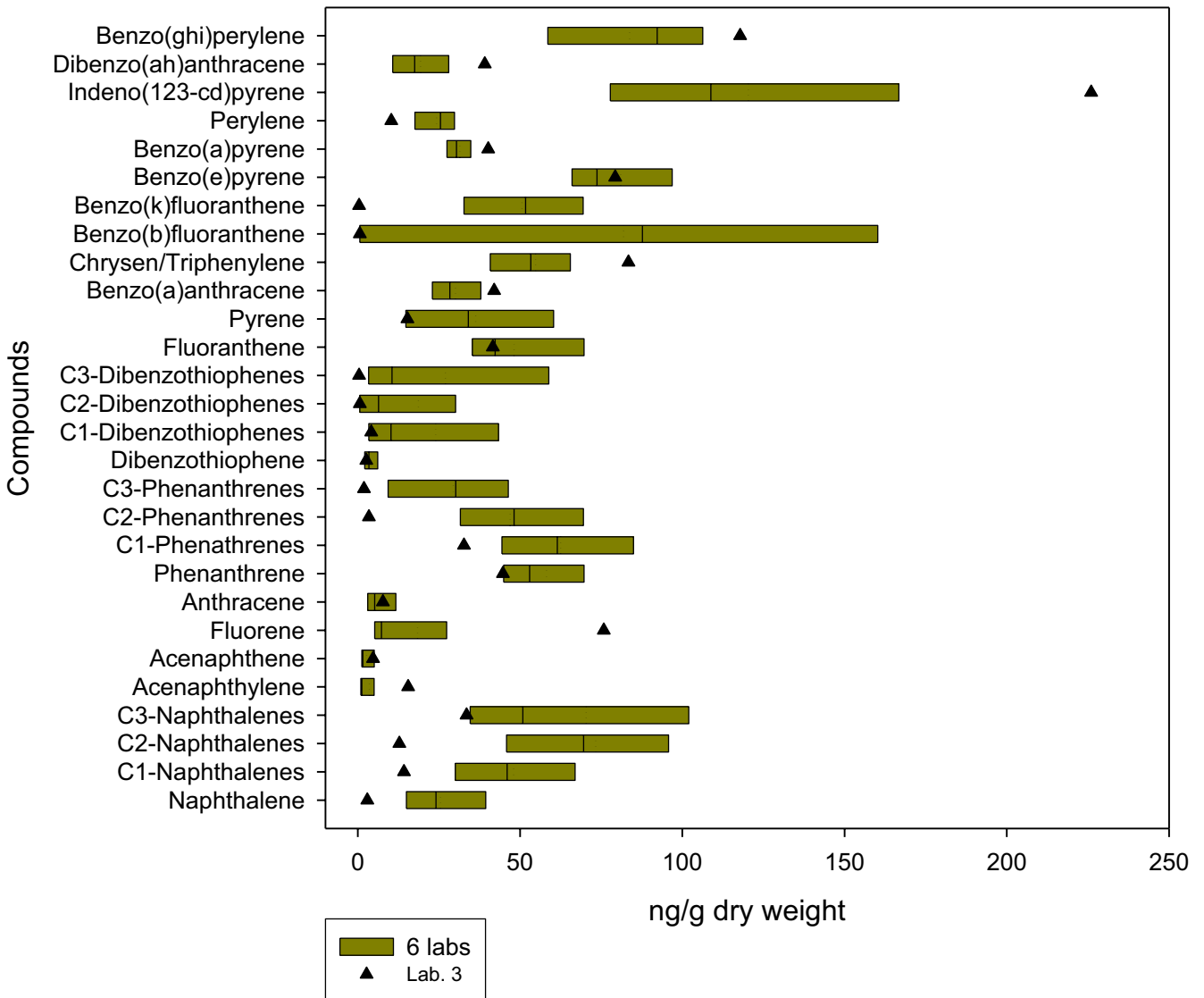
Figure 22. Results for Laboratory 2 on Sample 1 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
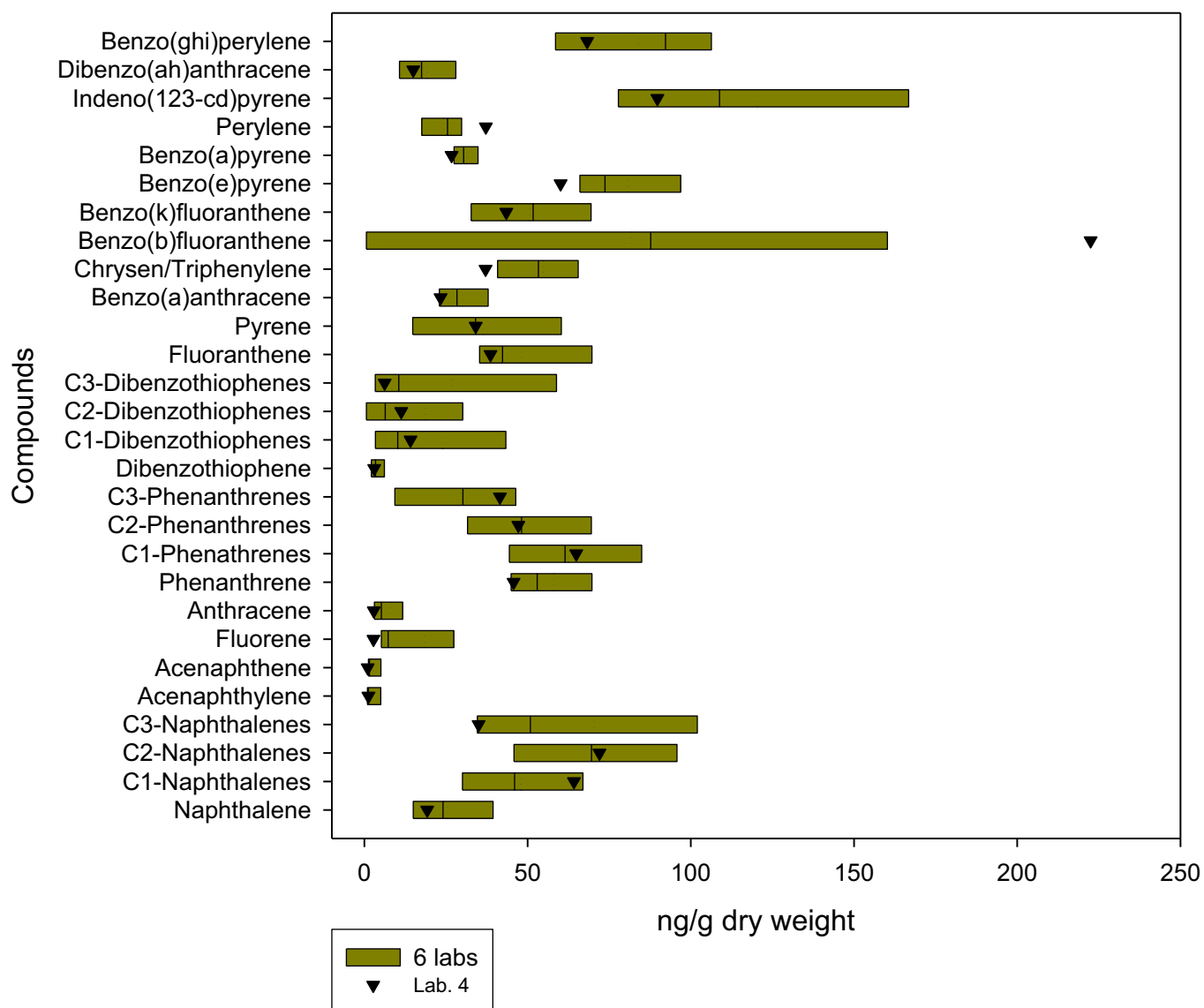
Sample 1

Figure 23. Results for Laboratory 3 on Sample 1 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
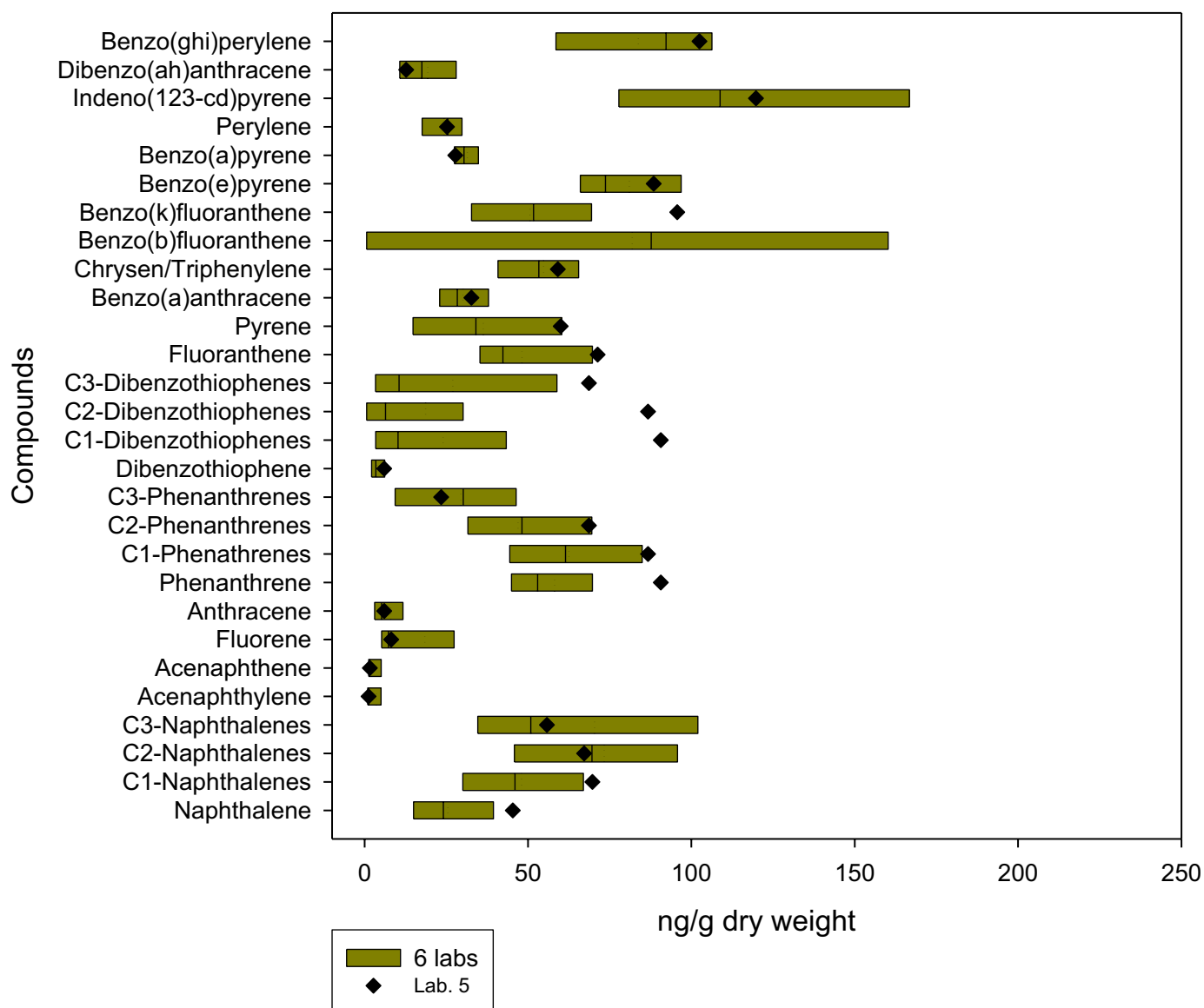
Sample 1

Figure 24. Results for Laboratory 4 on Sample 1 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.

Sample 1

Figure 25. Results for Laboratory 5 on Sample 1 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
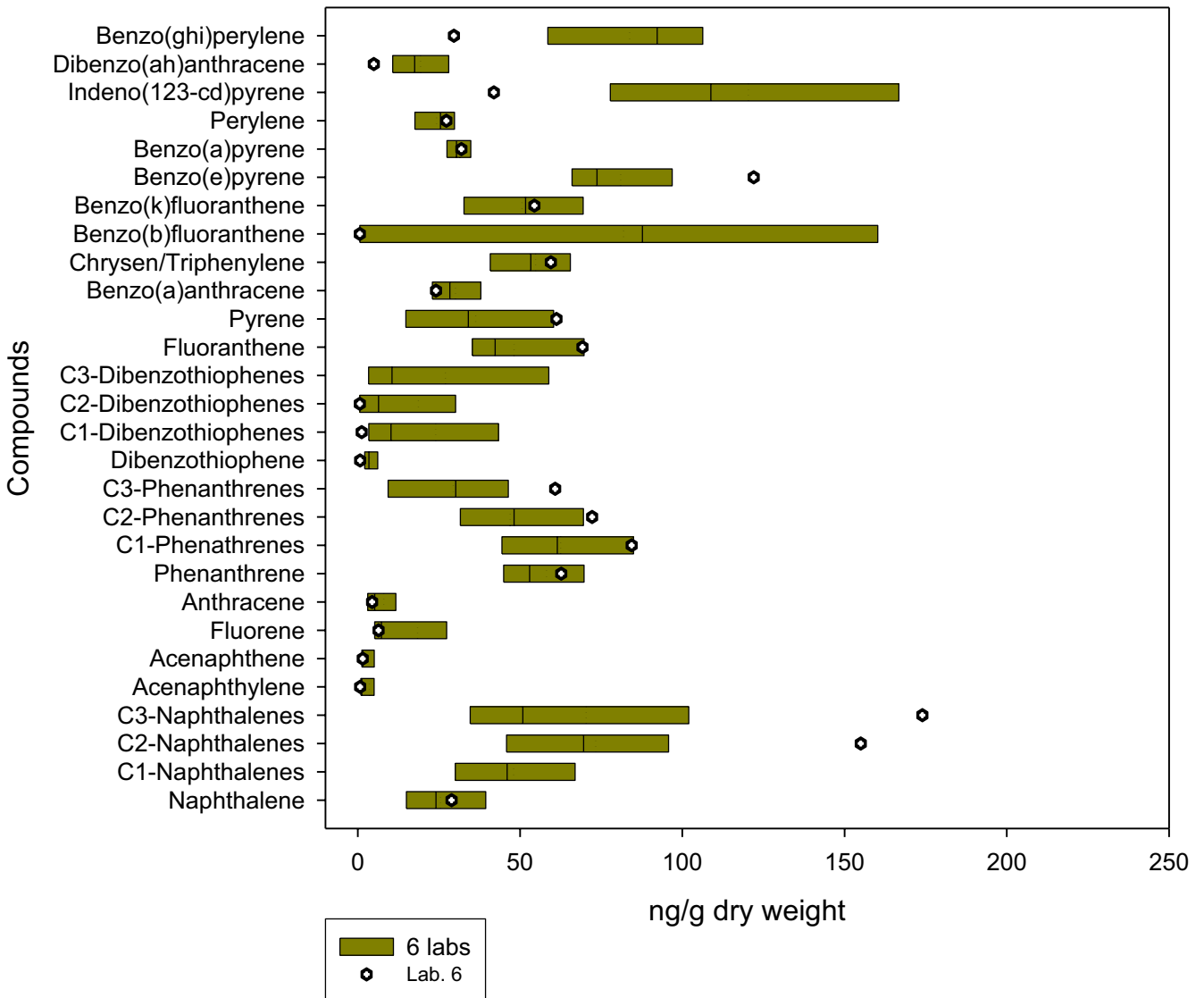
Figure 26. Results for Laboratory 6 on Sample 1 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
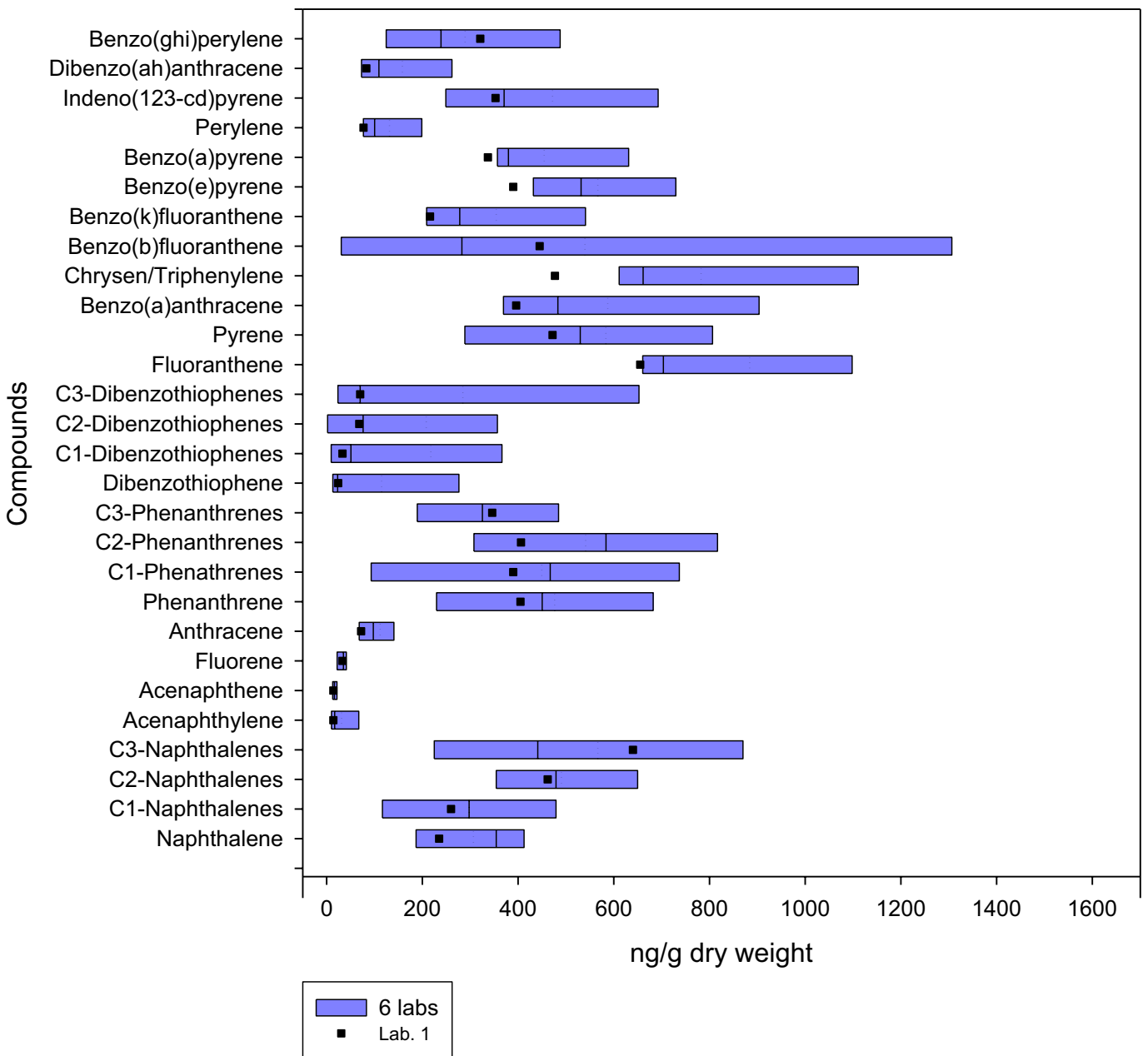
Figure 27. Results for Laboratory 1 on Sample 2 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
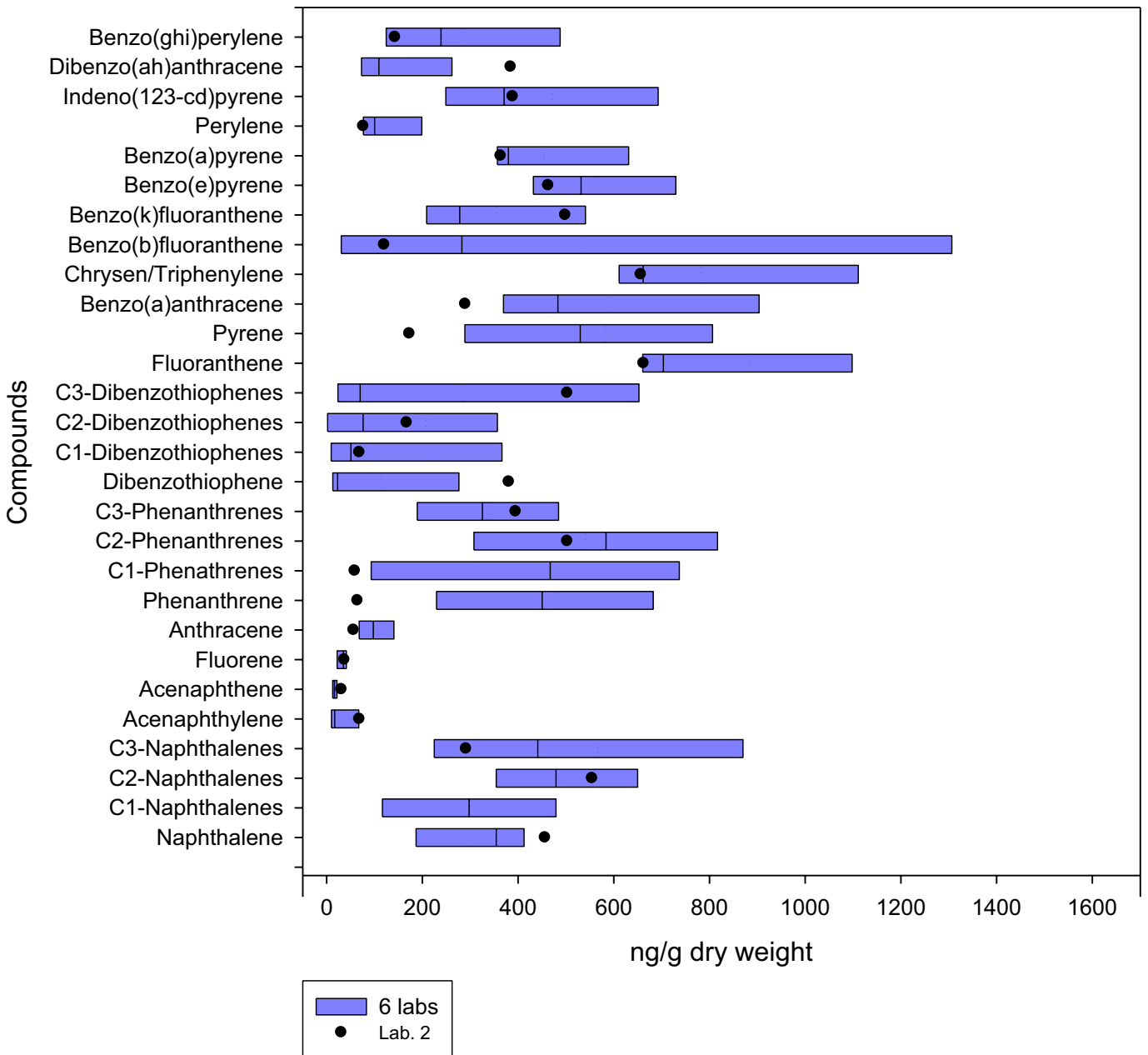
Sample 2

Figure 28. Results for Laboratory 2 on Sample 2 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.

Figure 29. Results for Laboratory 3 on Sample 2 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
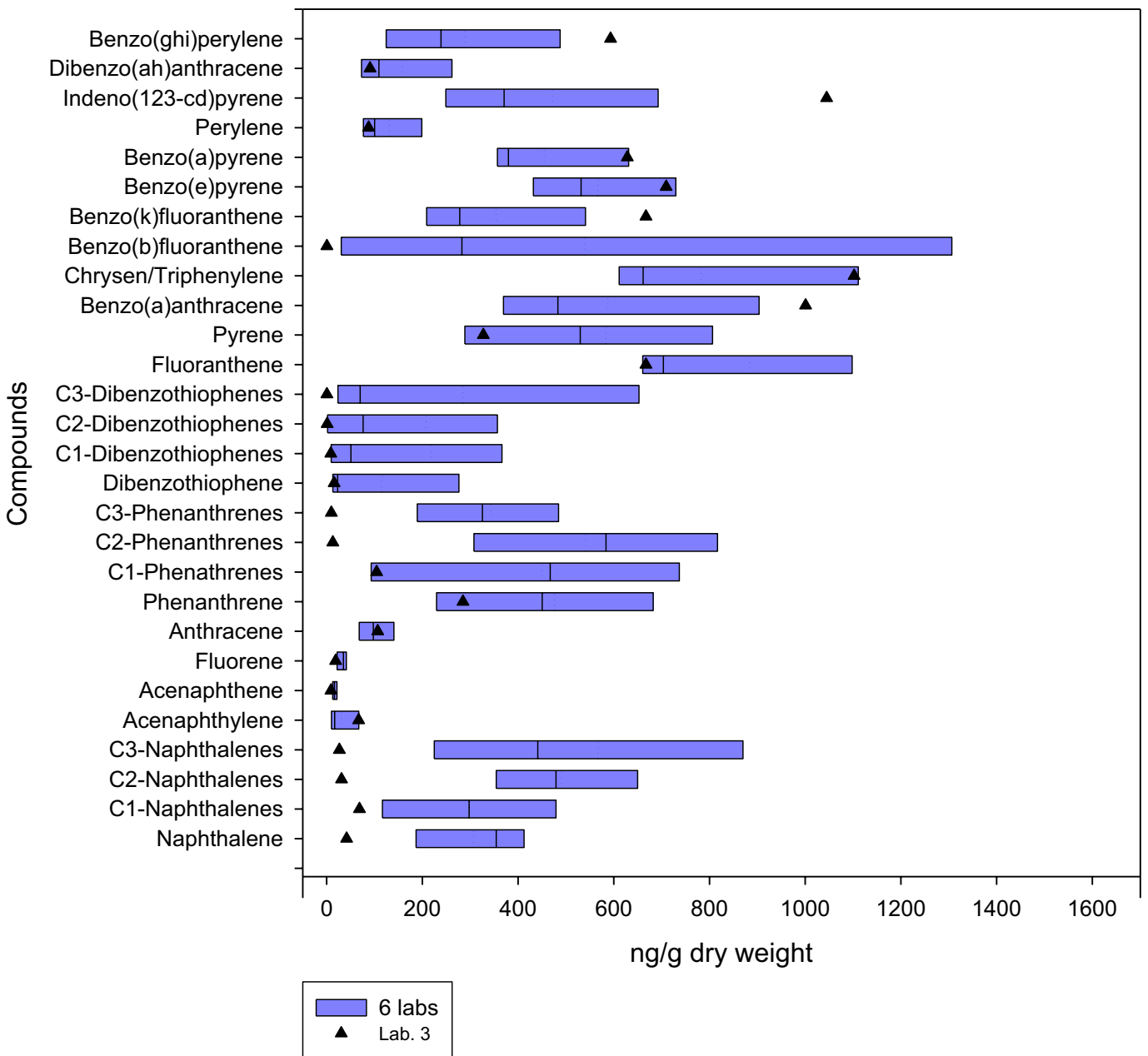
Sample 2

Figure 30. Results for Laboratory 4 on Sample 2 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
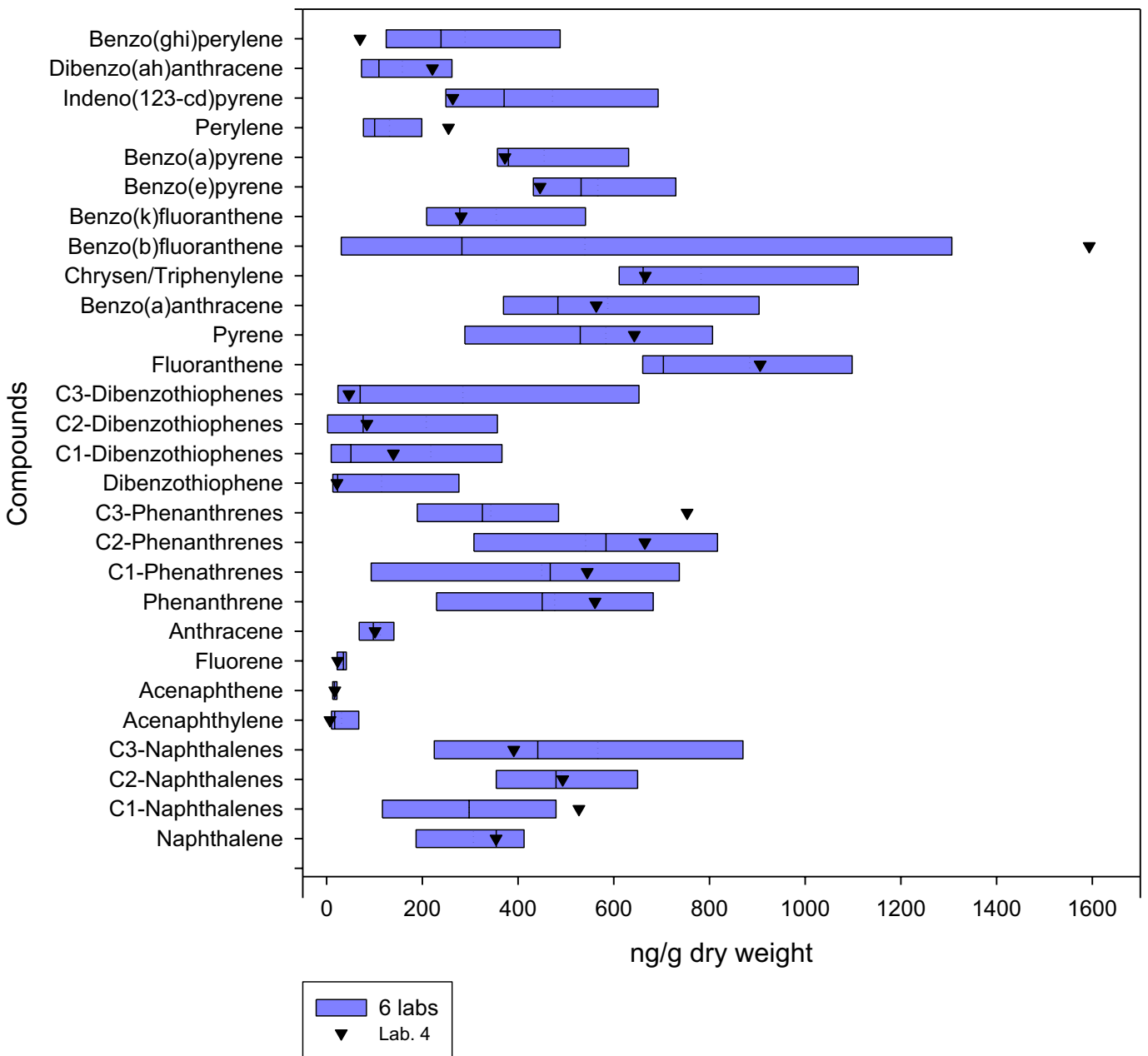
Figure 31. Results for Laboratory 5 on Sample 2 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
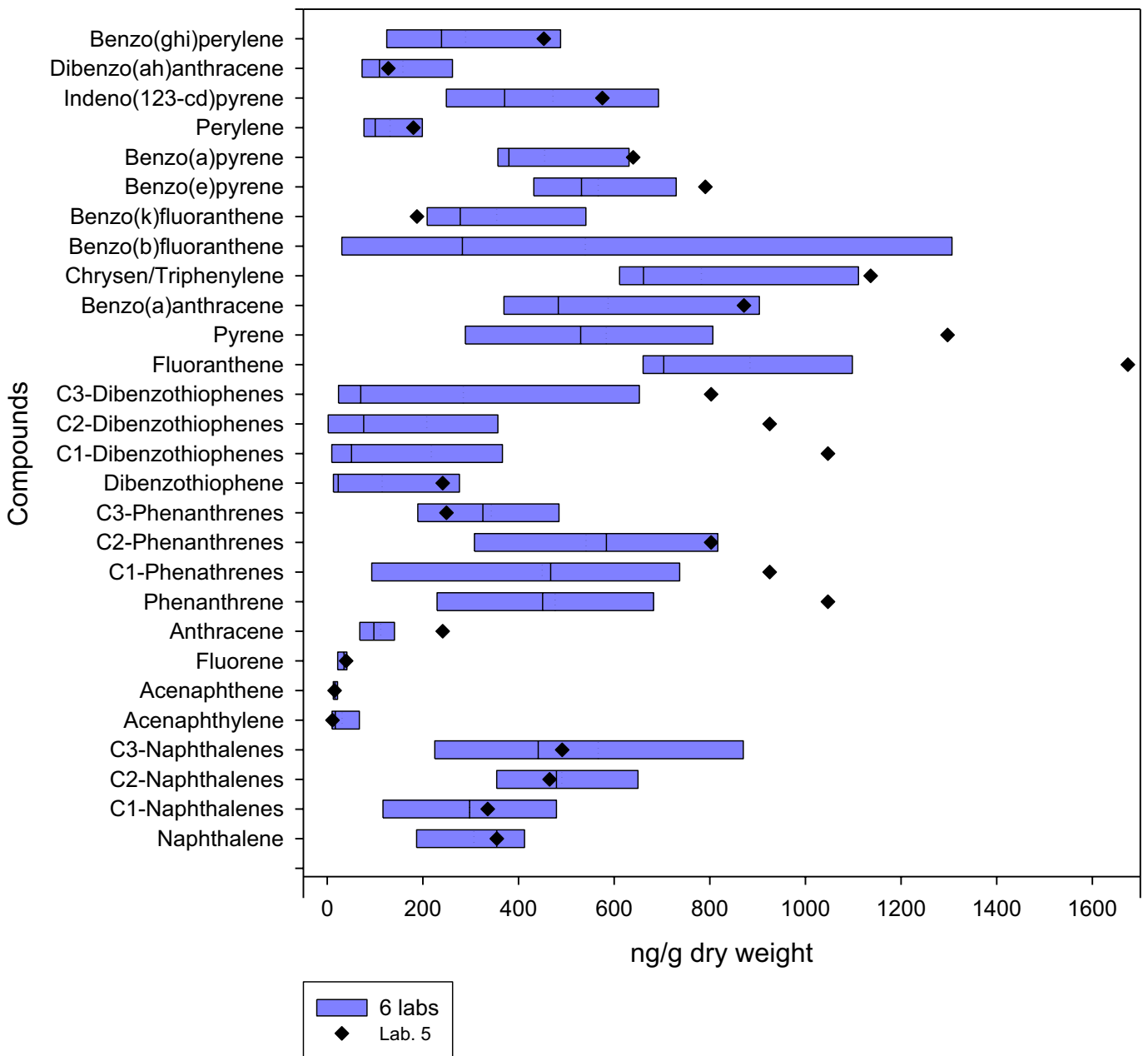
Figure 32. Results for Laboratory 6 on Sample 2 compared to all 6 participant laboratories.

The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Dashed line inside the boxes indicates mean values. Error bars are not shown since not all labs measured each component and there is thus not enough data points for error bars. Only those components are shown which have been measured by more than 2 labs.
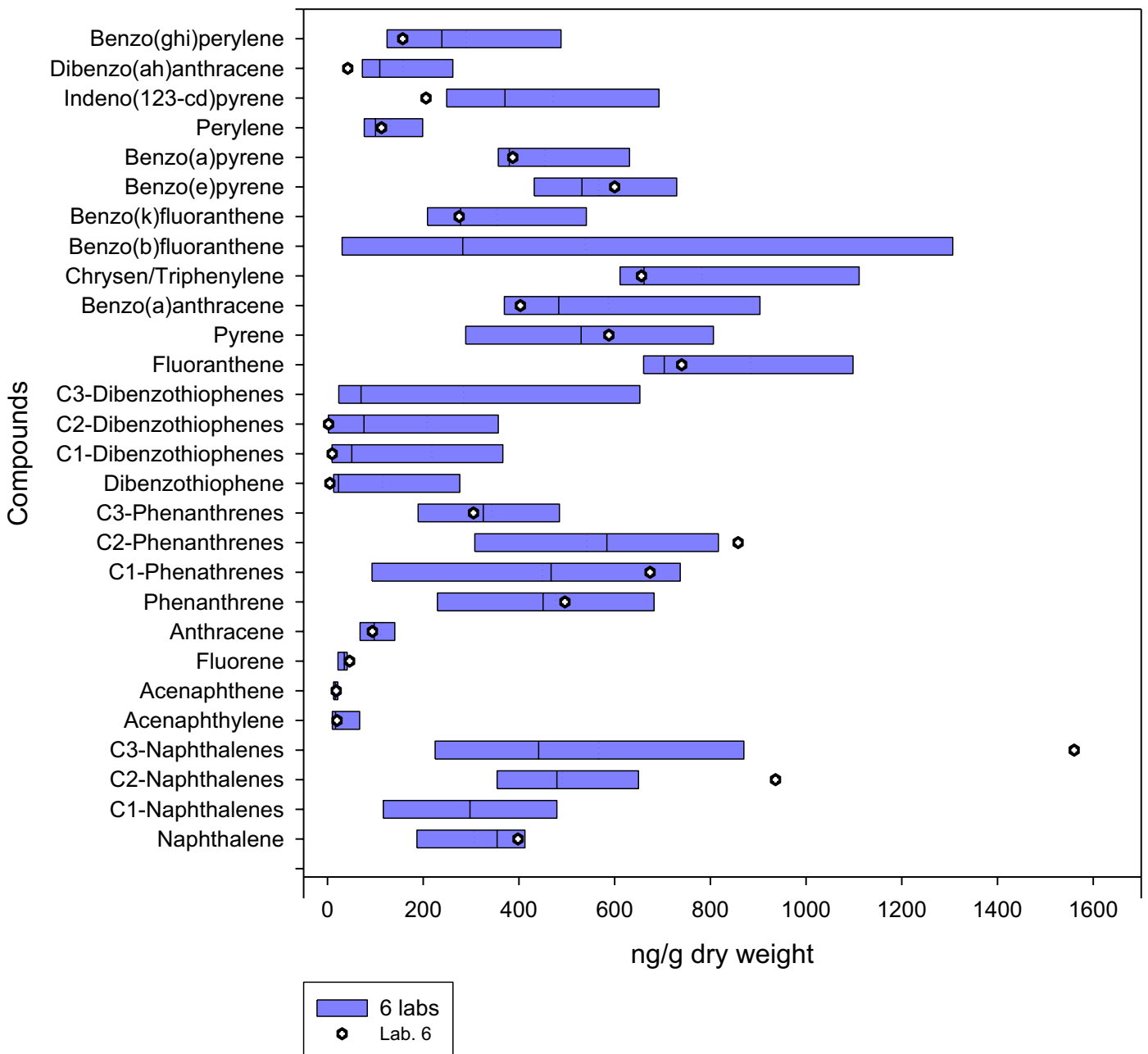
It has to be noted that not all of the components analyzed by the labs were the same. One also has to note that certain components have been analyzed as clusters and reported by the laboratories as sum values (e.g., Sum C1-Chrysenes), and a possibility of difference the clusters analysed at different laboratories cannot be ruled out.

For separate components, the range of resulting values varied significantly, the difference between maximum and minimum values measured by different labs varying from 5 ng/g for acenaphthene to 184.1 ng/g for indeno(1,2,3-cd)pyrene for Sample 1, and from 22 ng/g for acenaphthene to 1124 ng/g for pyrene in Sample 2 (considering only components analyzed by all laboratories). Standard deviation varied accordingly, being, like range, a measure of statistical dispersion. Residual standard deviation, however, was below 100% for all components, the average RSD for Sample 1 being 49.7% and for Sample 2, 54.1%.

It may be concluded that general results from the intercalibration experiment indicate a significant discrepancy in reported values can be expected (cf. Figg. 21-32). This may partly be explained by the novelty of the task for some of the laboratories, which normally face other goals and therefore employ slightly different analytical and quantification methods, reporting fewer PAH components, for example without alkylated PAHs (PINRO) or without lighter compounds (VNIIO), or working in a different concentration range (DMU), etc.

There is, however, an agreement between the results obtained for Sample 1 and Sample 2: RSD is close to 50% for both Samples (values changing slightly depending on whether all components are taken into account or only those analyzed by each lab). This indicates that the difference between the results from different laboratories is consistent with their analytical methods and is not due to external errors. It may also be concluded that the difference in analytical methods for THC is greater than that for PAHs.

Table 7. Intercalibration results for sample N 1.

Compound	Mean (6 labs), *ng/g d.w.*	Range, Max-Min (6 labs)	SD, *ng/g d.w.*	RSD, %
Naphthalene	25.5	2.9 - 45.3	15.1	59.3
C1-Naphthalenes	48.5	14.2 - 69.7	25.0	51.6
2-Methylnaphthalene	43.7	38.6 - 48.8	7.2	16.5
1-Methylnaphthalene	30.9	22.1 - 39.7	12.4	40.2
C2-Naphthalenes	73.3	12.8 - 155.0	46.2	63.0
C3-Naphthalenes	70.4	33.5 - 174.0	53.3	75.8
C4-Naphthalenes	59.0	20.2 - 97.8	54.9	93.0
Acenaphthylene	3.5	0.7 - 15.5	5.9	166.9
Acenaphthene	2.7	1.0 - 6.0	2.1	78.7
Fluorene	18.4	2.8 - 75.8	28.3	153.7
C1-Fluorenes	21.0	21.0 - 21.0	0.0	0.0
C2-Fluorenes	18.8	18.8 - 18.8	0.0	0.0
Anthracene	8.0	2.9 - 23.8	8.0	99.8
Phenanthrene	58.2	44.7 - 90.7	17.8	30.7
C1-Phenathrenes	62.5	32.7 - 86.7	20.9	33.4
C2-Phenanthrenes	46.9	3.4 - 72.2	24.7	52.6
C3-Phenanthrenes	29.4	1.9 - 60.8	21.4	72.8
C4-Phenanthrenes	12.7	12.7 - 12.7	0.0	0.0
Dibenzothiophene	3.3	0.7 - 6.6	2.1	64.1
C1-Dibenzothiophenes	10.7	1.2 - 27.5	10.6	99.4
C2-Dibenzothiophenes	5.0	0.6 - 11.3	5.2	103.0
C3-Dibenzothiophenes	5.7	0.4 - 10.5	5.1	88.9
Fluoranthene	48.2	25.2 - 71.3	18.2	37.9
Pyrene	36.3	13.2 - 61.2	20.8	57.4
C1-Fluoranthenes/Pyrenes	70.2	52.9 - 87.6	24.5	34.9
C2-Fluoranthenes/Pyrenes	40.7	20.1 - 61.2	29.0	71.4
C3-Fluoranthenes/Pyrenes	4.1	4.1 - 4.1	0.0	0.0
Benzo(a)fluorene	23.6	23.6 - 23.6	0.0	0.0
Benzo(a)anthracene	30.1	22.0 - 42.0	8.2	27.3
Chrysen/Triphenylene	54.8	37.1 - 83.4	16.7	30.4
C1-Chrysenes	58.3	44.4 - 72.2	19.7	33.8
C2-Chrysenes	35.9	35.9 - 35.9	0.0	0.0
C3-Chrysenes	11.7	11.7 - 11.7	0.0	0.0
Benzo(b,j)fluoranthene	117.3	94.8 - 139.9	31.9	27.2
Benzo(b,k)fluoranthene	190.6	190.6 - 190.6	0.0	0.0
Benzo(b)fluoranthene	136.1	87.7 - 222.5	75.0	55.1
Benzo(k)fluoranthene	60.6	43.5 - 95.7	20.6	34.0
Benzo(e)pyrene	81.0	60.1 - 122.0	22.4	27.7
Benzo(a)pyrene	31.4	26.7 - 40.2	4.9	15.7
Perylene	24.3	10.3 - 37.2	8.9	36.5
Indeno(1,2,3-cd)pyrene	120.4	41.9 - 226.0	62.4	51.8
Dibenzo(a,h)anthracene	19.3	4.9 - 39.1	11.7	60.6
Benzo(g,h,i)perylene	83.8	29.6 - 117.8	31.5	37.6
THC, *μg/g*	41.2	4.2 - 100.9	43.3	105.1

Table 8. Intercalibration results for sample N 2.

Compound	Mean (6 labs), *ng/g d.w.*	Range, Max-Min (6 labs)	SD, *ng/g d.w.*	RSD, %
Naphthalene	306.6	41.8 - 456.3	148.7	48.5
C1-Naphthalenes	297.8	68.7 - 527.2	189.7	63.7
2-Methylnaphthalene	311.6	267.1 - 356.0	62.8	20.2
1-Methylnaphthalene	141.6	100.1 - 183.0	58.6	41.4
C2-Naphthalenes	490.3	31.1 - 936.0	288.1	58.8
C3-Naphthalenes	566.7	26.5 - 1560.0	528.4	93.3
C4-Naphthalenes	653.4	146.8 - 1160.0	716.4	109.6
Acenaphthylene	31.2	7.1 - 68.2	28.5	91.4
Acenaphthene	17.4	8.9 - 30.9	7.3	42.2
Fluorene	32.9	18.8 - 46.2	10.3	31.4
C1-Fluorenes	95.0	95.0 - 95.0	0.0	0.0
C2-Fluorenes	58.4	58.4 - 58.4	0.0	0.0
Anthracene	111.9	56.2 - 241.5	66.3	59.2
Phenanthrene	476.3	64.4 - 1046.9	330.0	69.3
C1-Phenathrenes	449.5	58.8 - 925.1	334.9	74.5
C2-Phenanthrenes	541.2	12.8 - 858.0	310.8	57.4
C3-Phenanthrenes	343.0	9.8 - 753.3	241.8	70.5
C4-Phenanthrenes	123.8	15.6 - 232.0	153.0	123.6
Dibenzothiophene	89.4	5.1 - 380.7	163.0	182.3
C1-Dibenzothiophenes	51.9	8.8 - 139.6	54.6	105.2
C2-Dibenzothiophenes	64.5	1.2 - 167.3	68.7	106.4
C3-Dibenzothiophenes	39.0	0.6 - 70.0	35.3	90.5
Fluoranthene	884.0	655.0 - 1674.2	398.5	45.1
Pyrene	583.4	172.8 - 1297.2	389.7	66.8
C1-Fluoranthenes/Pyrenes	815.0	784.0 - 846.0	43.9	5.4
C2-Fluoranthenes/Pyrenes	488.4	485.0 - 491.8	4.8	1.0
C3-Fluoranthenes/Pyrenes	83.6	79.3 - 87.9	6.1	7.2
Benzo(a)fluorene	415.4	415.4 - 415.4	0.0	0.0
Benzo(a)anthracene	587.3	289.6 - 1000.7	286.8	48.8
Chrysen/Triphenylene	782.3	477.0 - 1136.4	270.6	34.6
C1-Chrysenes	695.4	632.0 - 758.8	89.7	12.9
C2-Chrysenes	76.3	26.7 - 125.9	70.1	91.9
C3-Chrysenes	20.3	20.3 - 20.3	0.0	0.0
Benzo(b,j)fluoranthene	1036.0	907.0 - 1165.1	182.5	17.6
Benzo(b,k)fluoranthene	1752.5	1752.5 - 1752.5	0.0	0.0
Benzo(b)fluoranthene	719.5	120.1 - 1593.5	774.1	107.6
Benzo(k)fluoranthene	291.7	187.6 - 498.7	122.3	41.9
Benzo(e)pyrene	566.5	390.0 - 790.7	160.1	28.3
Benzo(a)pyrene	454.7	337.0 - 639.8	139.9	30.8
Perylene	131.5	76.4 - 254.6	71.8	54.6
Indeno(1,2,3-cd)pyrene	471.9	206.0 - 1044.7	307.9	65.2
Dibenzo(a,h)anthracene	158.3	42.4 - 384.7	126.3	79.8
Benzo(g,h,i)perylene	289.4	69.6 - 593.2	203.6	70.4
THC, $\mu g/g$	89.0	73.0 - 129.0	26.7	30.0

Conclusion

The Barents and Norwegian Seas remains relatively clean environments only weakly influenced by human activities. Local sources of natural origin contribute to elevated PAH levels in sediments in some areas, in particular close to Svalbard. In the remainder of the studied area, the observed PAH levels are mostly due to complex sedimentation processes, influenced by biotic activities, long-range atmospheric transport, sea currents. No clear anthropogenic influence upon the environment in the Norwegian and Barents Seas has been obvious from the current study. The water column contains only very low background levels of THC and PAHs.

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