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Data sheet

Title:	Screening of “new” contaminants in the marine environment of Greenland and the Faroe Islands
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Abstract:	Blubber and liver samples of biota from the marine environment of Greenland and the Faroe Islands were analysed for a variety of “new” contaminants: Perfluorinated alkylated substances (PFAS), brominated flame retardants (PBDE and PBB), polychlorinated naphthalenes (PCN), synthetic musk compounds and phthalates. All compounds were detected in the top-predator species polar bear (East Greenland) and pilot whale (Faroe Islands). Compared with other findings from the Arctic, high concentrations were found for PFAS in polar bear (1300 ng/g wet weight) and PBDE in pilot whale (400-1000 ng/g lipid weight). For the other compound groups, little information is available for comparisons. Increasing concentrations with increasing trophic levels indicated biomagnification of the halogenated compound groups, while the concentrations of the main phthalate DEHP were within the range of 60-140 ng/g wet weight in all samples. In Greenland, the same geographical pattern with higher concentrations in East than in West Greenland was found for PFAS and PBDE as had previously been found for the better-studied organochlorine compounds.
Keywords:	Biomagnification, brominated flame retardants, Faroe Islands, food chain, Greenland, marine biota, phthalates, polybrominated biphenyls, polybrominated diphenyl ethers, polychlorinated naphthalenes, polyfluorinated alkylated substances, synthetic musk compounds.
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Summary

As part of the Arctic Monitoring and Assessment Programme (AMAP), persistent organic pollutants (POPs) are regularly monitored in Greenland and on the Faroe Islands, with a particular focus on the marine environment. Among the information obtained from these activities, biomagnification of POPs has been identified as a crucial issue, since animals at higher trophic levels are important food items in the traditional diet.

The objective of this study was to screen biota samples from the Greenland and Faroese marine environment for "new" contaminants, i.e. compounds that have been identified as potential POPs and of which little knowledge exists with regard to their occurrence in Greenland and on the Faroe Islands. Particular focus was on potential biomagnification of the compounds. Therefore, the Greenland samples selected for analysis included sediment and species of different trophic levels of the food chain: shorthorn sculpin, black guillemot, ringed seal, minke whale and polar bear. The Faroese samples included high-trophic level animals: pilot whale (juveniles, males and females) and fulmar.

In accordance with the national and international AMAP recommendations, the following compounds and compound groups were selected for this screening project: Perfluorinated alkylated subtances (PFAS), polychlorinated naphthalenes (PCN), the brominated flame retardants polybrominated diphenyl ethers (PBDE), polybrominated biphenyls (PBB), tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD) as well as synthetic musk compounds and the plasticizers phthalic acid esters (phthalates). New analytical methods were developed within this project for PFAS, PCN, PBB, musk compounds and phthalates. Due to the different physical-chemical properties of TBBPA and HBCD, it was not possible to develop a method for these two compounds.

In agreement with information available on monitoring of PFAS in biota, perfluorooctane sulfonate (PFOS) was the predominant fluorochemical in most samples, followed by PFOSA, which was found at relatively high concentrations in pilot whales (43-62 ng/g wet weight) and minke whales (29 ng/g wet weight). PFOS was found at concentrations above the limit of quantification (9.6 ng/g wet weight) in 13 out of 16 samples. The results from Greenland showed increasing concentrations of PFOS: shorthorn sculpin<ringed seal<polar bear, indicating biomagnification of PFOS along the marine food chain. The concentrations in polar bear were within the range observed in Alaska and Hudson Bay, Canada. Given the high concentrations of PFOS, a retrospective time trend analysis is recommended. Besides, it is recommended to follow the development of PFAS concentrations in key species from Greenland and the Faroe Islands, since PFOS-related compounds are still in use and not regulated at present.

The results for PCN showed that these compounds occured and biomagnified in Greenland and Faroese biota. Higher PCN levels were observed in marine biota from the Faroe Islands than in marine biota from Greenland. The concentrations in juvenile pilot whales from the Faroe Islands (4068 pg/g lipid weight) were an order of magnitude higher than in beluga from the Canadian Arctic. The toxic equivalent (TEQ) concentrations based on PCN were in the same order of magnitude as the dioxin TEQ concentrations in pilot whales. The main PCN congener in pilot whale and fulmar was CN-66/67, while the main congener in polar bear was CN-68. On the basis of the screening results it is recommended to screen for PCNs in species from the Faroe Islands with dioxin TEQ concentrations close to the regulatory limits. The Greenland samples ought to be re-analysed with a more sensitive analytical method prior to recommendations for further studies.

Both PBDE and PBB biomagnify along the marine food chain, in a similar manner to polychlorinated biphenyls (PCBs). PBBs showed indications of a higher biomagnification potential than PBDEs. The PBB concentrations were lower than those of PBDEs, however, the PBDE/PBB ratio increased in the order ringed seal<pilot whale< minke whale<fulmar<polar bear, leading to almost equal concentrations of PBDEs and PBBs in polar bear.

The highest concentrations of PBDEs were found in pilot whale samples, which were about 15 times higher than the concentrations in polar bear (52 ng/g lipid weight). This confirmed that the concentrations in pilot whale are among the highest concentrations ever found in Arctic marine mammals. The PBDE concentrations in East Greenland were similar to concentrations on Svalbard, while concentrations in West Greenland were similar to concentrations in the Canadian Arctic. Thus, the geographical distribution of PBDEs is similar to the distribution of PCBs. The main congeners were BDE-47 and BDE-99, except for polar bear, which contained higher percentages of BDE-153 than of BDE-99. Of the PBB congeners analysed, BB-153 generally was the dominant congener.

The recommendations for PBDEs include a retrospective time trend analysis as well as basic monitoring in the future, given the ongoing production and use of PBDEs in North America. Due to their biomagnfication potential, PBBs should be analysed in other high trophic level animals from Greenland and the Faroe Islands in order to obtain more data on their occurrence and concentrations in biota.

The synthetic musk compounds were only detected in quantifiable concentrations in polar bear liver. However, indications of the presence of musk compounds in all matrices but sediments were noted. Since the compounds were detected, it is recommended to analyse existing samples of high trophic animals, but more sensitive and robust analytical methods are needed to analyse these compounds at trace levels. If the occurrence of musk compounds in top-predators is confirmed, follow up monitoring on the development of the concentrations may be needed since the compounds are still in use.

Phthalates and one adipate were detected in almost samples, with highest concentration in polar bear liver from East Greenland, fulmars from the Faroe Islands and ringed seals from East and West Greenland. Of the compounds analysed, levels were highest for DEHP (75-161 ng/g wet weight) and DEHA (2.5-144 ng/g wet weight) It is remarkable that phthalates were also detected in sediment and in species at lower trophic levels. Thus, possible biomagnification processes are apparently not as pronounced as for the halogenated compounds. It is therefore recommended to conduct a food web study in order to obtain more information on the occurrence of phthalates in the marine environment and to assess the question of biomagnification. Similarly to the musk compounds, the analytical method ought to be improved with regard to sensitivity and robustness.

Correlation analysis was applied to identify similarities in occurrence patterns between the compound groups. A statistically significant correlation was found for most pairs of the halogenated compound groups, such as PBDE/PBB and PFAS/PBDE, and a weaker correlation was found for PCN/PBDE and PCN/PBB. The phthalates were not correlated with any of the halogenated compound groups, but showed an internal correlation. The main reason for the correlation is seen in similar biomagnification patterns.

Resumé

Svært nedbrydelige organiske stoffer (POPs) er regelmæssigt overvåget i Grønland og på Færøerne som en del af det internationale program ”Arctic Monitoring and Assessment Programme (AMAP)”. Overvågningen har fokus på det marine miljø. Bioakkumuleringen af POPs op gennem den marine fødekæde har vist sig at være en vigtig faktor, idet dyr i de højere trofiske niveauer er vigtige i den traditionelle kost.

Formålet med dette studie var at scanne biologiske prøver fra det grønlandske og færøske marine miljø for ”nye” kontaminanter, dvs. stoffer som er identificeret som potentielle POPs og for hvilke den nuværende viden om deres forekomst i det grønlandske og færøske miljø er meget begrænset. Fokus var på stoffernes potentielle bioakkumulering. De udvalgte grønlandske prøver omfatter derfor sediment og dyr fra forskellige trofiske niveauer i fødekæden, almindelig ulk, tejst, ringsæl, vågehval og isbjørn. De færøske prøver omfatter dyr højt placeret i fødekæden: grindehval (hanner, hunner og juvenile) og mallemuk.

De følgende stofgrupper er blevet udvalgt i scanningsprojektet i overensstemmelse med de nationale og internationale AMAP rekommandationer: Perfluorerede alkylerede stoffer (PFAS), polychlorerede naphthalener (PCN), de bromerede flammehæmmere polybromerede diphenyl ethere (PBDE) og polybromerede biphenyler (PBB), tetrabromobisphenol A (TBBPA), hexabromocyclododecan (HBCD), og syntetiske muskforbindelser og phthalater. Gennem nærværende projekt er der udviklet nye analytiske metoder for PFAS, PCN, PBB, musk-forbindelser og phthalater. Det har ikke været muligt at udvikle analysemetoder for TBBPA og HBCD på grund af disse stoffers forskellige fysisk-kemiske egenskaber.

I overensstemmelse med den eksisterende viden om PFAS i biologisk materiale var perfluoroctane sulfonat (PFOS) den dominerende fluorerede forbindelse i de fleste prøver, efterfulgt af PFOSA som blev fundet i relativ høje koncentrationer i grindehvaler (43-62 ng/g våd vægt) og vågehvaler (29 ng/g våd vægt). PFOS blev fundet i koncentrationer over kvantificeringsgrænsen (9.6 ng/g våd vægt) i 13 ud af 16 prøver. Resultaterne fra Grønland viste stigende koncentrationer af PFOS; almindelig ulk<ringsæl<isbjørn, hvilket indikerer bioakkumulering op gennem fødekæden. Koncentrationen i isbjørn var indenfor det interval som er observeret i Alaska og Hudson Bay, Canada. Med baggrund i de høje PFOS koncentrationer anbefales det at foretage retrospektive tidstrend analyser. Derudover anbefales det at følge udviklingen af PFAS koncentrationen i nøglearter fra Grønland og Færøerne, idet PFOS relaterede stoffer stadig er i anvendelse og ikke er reguleret på nuværende tidspunkt.

Resultaterne for PCN viste at disse stoffer forekom og bioakkumulerede i grønlandske og færøske marine dyr. Højere PCN niveauer blev fundet i marine dyr fra Færøerne end i dyr fra Grønland. Koncentrationen i juvenile grindehvaler fra Færøerne (4068 pg/g lipid vægt)

var en størrelsesorden højere end i hvidhvaler fra den arktiske del af Canada. I grindehvaler var den toksicitetsekvivalente (TEQ) koncentration baseret på PCN i samme størrelsesorden som dioxin TEQ koncentrationen. Den dominerende PCN congener i grindehval og malemuk var CN-66/67, mens det var CN-68 i isbjørn. På basis af disse resultater er det anbefalet at scanne for PCN i færøske arter med dioxin TEQ koncentrationer tæt på reguleringsgrænserne. De grønlandske prøver bør re-analyseres med en mere følsom analytisk metode før yderligere anbefalinger kan gives.

Både PBDE og PBB bioakkumulerer op gennem fødekæden i lighed med polychlorerede biphenyler (PCB). PBB viste tendenser til et højere bioakkumulerings potentiale end PBDE. PBB koncentrationen var lavere end PBDE koncentrationen, men PBDE/PBB forholdet steg i rækkefølgen ringsæl<grindehval<mallemuk<isbjørn, med stort set samme koncentration af PBDE og PBB i isbjørn.

De højeste koncentrationer af PBDE blev fundet i grindehval prøverne, som var omkring 15 gange højere end koncentrationen i isbjørn (52 ng/g lipid vægt). Dette bekræfter at koncentrationen i grindehval er blandt de højeste koncentrationer fundet i arktiske marine pattedyr. PBDE koncentrationerne i Østgrønland var i samme størrelsesorden som på Svalbard, mens koncentrationerne i Vestgrønland var ens med koncentrationerne i den arktiske del af Canada. Det geografiske mønster af PBDE er derfor ens med mønsteret af PCB. De dominerende congenere var BDE-47 og BDE-99, undtagen for isbjørn, som havde højere andele af BDE-153 end BDE-99. BB-153 var generelt den dominerende PBB congener blandt de undersøgte congenere.

Anbefalingerne for PBDE inkluderer en retrospektiv tidstrend analyse samt en fremtidig basis overvågning, idet PBDE stadig produceres og anvendes i Nordamerika. På grund af PBB's bioakkumuleringspotentiale bør PBB analyseres i dyr fra Grønland og Færøerne placeret højt i fødekæden for at opnå et bedre data grundlag for PBB's forekomst og koncentrationsniveau.

De syntetiske muskforbindelser blev kun påvist i kvantificerbare koncentrationer i lever fra isbjørn. I næsten alle matricer undtagen sediment er der imidlertid fundet tegn på tilstedeværelsen af muskforbindelser. Idet stofferne er påvist, anbefales det at analysere eksisterende prøver af dyr placeret højt i fødekæden, men det er nødvendigt med mere følsomme og robuste analysemetoder for at detektere stofferne på sporstofniveau. Såfremt tilstedeværelsen af muskforbindelser kan bekræftes, kan det være nødvendigt med overvågning af koncentrationsudviklingen, idet disse forbindelser stadig anvendes.

Phthalater og en adipatforbindelse blev påvist i alle prøver med de højeste koncentrationer i isbjørn fra Østgrønland, mallemuk fra Færøerne og ringsæl fra Øst- og Vestgrønland. De højeste niveauer blandt de undersøgte stoffer blev fundet for DEHP (75-161 ng/g våd vægt) og DEHA (2,5-144 ng/g våd vægt). Det er bemærkelsesværdigt, at pththalater også blev fundet i sediment og i arter lavt placeret i fødekæden. En eventuel bioakkumulering er åbenbart ikke så tydelig som for halogenerede forbindelser. Det er derfor anbefalet at foretage et fødenet studie for at opnå større viden om tilstedeværel-

sen af phthalater i det marine miljø og vurdere en eventuel bioakkumulering. Analysemetoden må i lighed med musk-forbindelser forbedres med hensyn til følsomhed og robusthed.

Korrelationsanalyser er gennemført for at identificere ligheder i forekomsten af stofgrupperne. Statistisk signifikante korrelationer er fundet mellem de fleste par af de halogenerede stofgrupper, f.eks. PBDE/PBB og PFAS/PBDE og en svagere korrelation mellem PCN/PBDE og PCN/PBB. Phthalaterne er ikke korreleret med de halogenerede stofgrupper, men viser en inbyrdes korrelation. Hovedårsagen for korrelationerne anses for at være lignende bioakkumuleringsmønstre.

Naalisagaq

Kalaallit Nunaanni Savalimmiunilu nunarpassuit pilersaarutaannut ”Arctic Monitoring and Assessment Programme (AMAP)”-imut atatillugu stoffit uumassuseqartuneersut arrortikkuminaatsorujussuit (POP-iit) akuttunngitsumik misissorneqartarput. Misissuisarneq immamut tunngatinneqarneruvoq. POP-iit uumasuni annertusiartortarnerat uumassut nerisareqatigiinneratigut pisarnera pingaaruteqartoq paasineqarpoq, tassami POP-iit nerisareqatigiinni uumasuni anginerusuni annertunerusarnerat ileqquusumik nerisannaajusunut pingaaruteqartarmat.

Misissuinermi tassani kalaallit savalimmiullu imartaanni misissugassatut tigusani mingutitsisut ”nutaat” nassaariniarneqarnissaat siunertaavoq, imaappoq stoffit POP-nngorsinnaasutut pasinartut suuneri paasiniarlugit aammalu kalaallinut savalimmiorniunullu imartaannut tunngatillugu tamakkuninnga ilisimasat killilerujussuummata. Pingaartillugu sammineqarneruvoq stoffit tamakkua uumasunut akuliullutik annertusiartortarnerat. Kalaallit Nunaanniit misissugassanut ilaapput kinnerit ujaranngortut aamma uumasut nerisareqatigiinnermi assigiinngtsumik inissisimasut, kanassut, serfat, natsiit, tikaagulliit nannullu. Savalimmiunniit misissugassat ilagaat uumasut nerisareqatigiinnermi qaffasissumut inissisimasut: niisarnat (angutivissat, arnavissat nutaqqallu) aamalu malamuk.

Stoffit makkua misissuinermi sammisassatut toqqarneqarput AMAP-imiit nunamut pineqartumut nunanullu amerlasuunut tunngatillugu inassutaasut malillugit: Perfluorerede alkylerede stoffer (PFAS), polychlorerede naphthalener (PCN), ikuallannaveersaatit bromitallit polybromerede diphenyl ethere (PBDE) aamma polybromerede biphenyler (PBB), tetrabromobisphenol A (TBBPA), hexabromocyclododecan (HBCD), aamma inuit atortussialiaat muskforbindelser aamma phthalater. Misissuinermut uunnga atatillugu PFAS-imik, PCN-imik, PBB-mik, musk-forbindelsenik phthalatenillu misissueriaatsit nutaat pilersinneqarput. TBBPA-mik aamma HBCD-mik misissueriaatsit pilersinneq ajornarsimapput stoffit taakkua fysisk-kemiskimik periaasiisa assigiinnginnerat pissutigalugu.

PFAS-imik uumasuniittumik ilisimasat malillugit perflurooctane sulfonat (PFOS) misissukkani fluoritalinni amerlanerpaani malunnarnerpaavoq, tulleralugu PFOSA, taannami niisarnani annertujaartorujussuarmik (43-62 ng/g misissugassami masattumi) tikaagullinnilu (29 ng/g misissugassami masattumi) akuusoq nassaarineqarmat. PFOS nassaarineqarpoq killissaliutaasoq (9.6 ng/g misissugassami masattumi) misissukkani 16-init ilaanni 13-ini taanna sinneralugu sinnerlugu annertussuseqartoq paasineqarmat. Misissukkani Kalaallit Nunaanneersuni paasineqarpoq PFOS uumasuni ukunani annertusiartuaartoq, tassa kanajoq<natseq<nanoq; tassuunalu erserpoq akuliukkiartortarnera nerisareqatigiinnikkut annertusiartortartoq. Nannumi akuunera nunani allani, Alaskami Canadamilu Hudson Bay-imi, akuusut annertussusiisa iluannippoq. PFOS-it akkusut annertussusiat tunngavigalugu kingumut qiviarluni piffissani assigiinngitsuneersunik misissuinissaq inassutigineqassaaq. Tamatuma sania-

tigut PFAS-ip annertusiartornerata uumasuni Kalaallit Nunaannut Savalimmiunullu pingaaruteqarnerni malittarineqarnissaa inassutigineqassaaq, stoffimmi PFAS-imut attuumassutillit suli atorneqarmata ullumikkullu killilersuiffigineqaratik.

PCN-imik paasisat takutippaat stoffit tamakkua akuusut uumasunilu Kalaallit Nunaanni Savalimmiunilu uumasuni imarmiuni akuunerat annertusiartorluni. PCN-ip Savalimmiuni immami uumasuni akuunera Kalaallit Nunaanninngarnit annertuneruvoq. Savalimmiuni niisarnani inuusukaani akuunera (4068 pg/g arrortillugu piikkamit) annertuneruvoq Canadap issittortaani qilalukkani qaqortaniittumit. Niisarnani toqunartoqarnerup annertussusianik naleqqiussinermi (TEQ) atorneqarpoq dioxin-ip TEQ-a PCN-imut taamaaqataanut naleqqiullugu. Niisarnani malamunnilu PCB congenerinit malunnarnerpaaq CN-66/67-iuvoq, nannumili CN-68-iulluni. Inernerit taakkua tunngavigalugit Savalimmiuni uumasut PCN-imik dioxin-imut TEQ-rlugu misissuiffigeqqullugit inassutigineqarpoq inernerit killilersuiffissamut qaneqimmata. Misissukkat Kalaallit Nunaanneersut inassuteqaateqarfigitinnagit misikkarinnerusumik misissueriaaseqarluni misissuiffigineqaqqittariaqarput.

PBDE PBB-lu nerisareqatigiitsigut polychlorerede biphenyler (PCB) assigalugit annertusiartortarput. Malunnarpoq PBB uumasutigut nerisareqatigiitsigut PBDE-minngarnit annertusiartorumanerussoq. PBB-p akuunera PBDE-mit annikinneruvoq, kisianni PBDE/PBB-llu akuunerat annertusiartorpoq uumasuni ukunani natseq<niisarnaq-<malamuk<nanoq, kisianni PBDE-p PBB-llu nannumi akuunera assigiingajalluinnarpoq.

Niisarnamit misissugassani PBDE-p akuunera annertunerpaaq nassaarineqarpoq, taannalu nannumi akuusumit 15-iaat tikillugu annertuneruvoq (52 ng/g arrortillugu piikkamit). Tamtumuunalu uppernarsarneqarpoq issittup uumasuini imarmiuni akuusut annertunerpaat niisarnamiimmata. Tunumi PBDE akuusoq Svalbardimisut annertutigaaq Kitaanili akuusut Canadap issittortaanisut illutik. Taamaalilluni PBDE-p sumiinnera PCB-ip sumiinneratut ippoq. Congenere-t malunnarnerpaat tassaapput BDE-47 aamma BDE-99, taamaallaat nannuni pinnani, taakkunanimi BDE-153 BDE-99-imut naleqqiullugu malunnarnerummat. Ataatsimut isigalugu congenerini misissukkani BB-153 malunnarnerpaavoq.

PBDE-mut tunngatillugu inassuteqaatinut ilaavoq kingumut qiviarluni piffissani assigiinngitsuneersunik misissuinissaq aammalu tunngaviusumik siunissami nakkutilliinissaq inassutigineqassaaq, tassami PBDE suli Amerikami Avannarlermi sanaartorneqarlunilu atorneqarmat. PBB-p nerisareqatigiitsigut annertusiartortarsinnaanera pissutigalugu Kalaallit Nunaanneersuni Savalimmiuneersunilu PBB uumasuni nerisareqatigiinni qutsissumiittuni misissorneqartariaqarpoq PBB-qarneranik annertussusianillu misissuinermi pitsaanerusunik tunngavissarsiumalluni.

Muskforbindelse-t inuit sanaavineersut uuttorneqarsinnaasut taamaallaat nannup tinguini malugineqarput. Misissukkani tamarluinnangajanni, kinnernit ujaranngortuneersut kisimik pinatik, malunnarpoq muskforbindelse-qartoq. Stoffittaamaattut akuusut paasine-

qarmata nerisareqatigiinni uumasunit anginerusuniit misissuinissaq inassutigineqarpoq, kisiannili pisariaqarpoq misikkarinner-usumik misissueriaaseqarnissaq stoffit akuunerat malugineqarneqassappat. Muskforbindelse-qarnera uppernarsineqarsinnaappat akuusut annertusiartornerannik nakkutilliinissaq pisariaqarsinnaavoq, tamakkuami suli atugaammata.

Phthalater aamma adipatforbindelse Tunumi nannuni, Svalimmiuni malamummi aammalu Tunumi Kitaanilu natsermi misissukkani tamani akuusoq marlugineqarpoq. Misissukkani annertunerpaamik akuusut ilagaat DEHP (75-161 ng/g misissugassami masattumi) aamma DEHA (2,5-144 ng/g misissugassami masattumi). Eqqumiigisassaavoq pththalater kinnerni ujaranngortuni nerisareqatigiinnilu appasissumut inissisimasuni aamma nassaarineqarmata. Uumasutigut akuusut annertusiartortarsinnaanerat halogenerede forbindelser-nisut erseqqitsiginngilaq. Taamaattumik nerisareqatigiinnik misissuinissaq inassutigineqarpoq phthalater-it immami avatangiisinut ilaanerannik ilisimasatamerlanerusut pissarsiariumallugit uumasutigullu annertusiartortarsinnaanerat nalilersorsinnaajumallugu. Muskforbindelse-nut tunngatillugu oqaatsigineqartutut misissueriaaseq pitsanngorsartariaqarpoq misikkarinnerullunilu erseqqinne-ruleqqullugu.

Ataqatigiinnernik misissuinerit ingerlanneqarput stofruppit akuunerminni assigiissutaat paasiumallugit. Ataqatigiinnerit malunnaatillit nassaarineqarput halogenerede stofgruppini marlukkuuttaani amerlanerni, soorlu PBDE/PBB aamma PFA/PBDE-ni aammalu erseqqinnginnerugaluartumik PCN/PBDE aamma PCN/PBB-ni. Phthalaterne halogenerede stofgrupper-nut ataqatigiinngillat kisiannili imminnut ataqatigiisssut malunnarluni. Ataqatigiinnernut pissutaanerpaatut assigiimmik uumasutigut annertusiartoriaaseqarnerat isigisariaqarpoq.

Úrtak

Kannað verður, um “nýggj” dálkingarevni eru í grønlendskum og føroyskum havumhvørvi

Mannaskapt lívfrøðilig evni, sum niðurbrótast seint (POPs), eru undir regluligari eftiransing í Grønlandi og í Føroyum sum partur av altjóða verkætlanini ”Arctic monitoring and Assessment Programme (AMAP)”. Henda eftiransing er fyrst og fremst við havumhvørvinum. Ein lýsing av upphópingini av POPs upp gjøgnum føðiketuna í sjógvi er ein týdningarmikil táttur í kanningini, við tað at djór í teimum ovaru føðiliðunum hava stóran týdning sum døgurðamatur.

Endamálið við hesi kanning var at vita, um ”nýggj” dálkingarevni vóru at finna í lívfrøðiligum sýnum frá grønlendska og føroyska havumhvørvinum. Hesi dálkingarevni eru evni, sum eru eyðmerkt sum møgulig POPs, og sum sera avmarkað vitan er um, um tey koma fyri í grønlendskum og føroyskum umhvørvi. Høvuðsdentur varð lagdur á møguliga upphóping av evnunum. Tey útvaldu grønlendsku sýnini fata um botnsetur og djór úr ymsum stigum í føðiketuni, vanliga ulku, teista, ringkóp, sildreka og ísbjørn. Tey føroysku sýnini eru tikin av djórum, sum eru ovarlaga í føðiketuni: grindahvali (hannhvalum, honhvalum og hvølpum) og havhesti.

Fylgjandi evnisbólkar eru vorðnir útvaldir í kanningarverkætlanini í samsvari við tjóðar- og altjóða AMAP-tilmælini: Perfluorerað alkylerað evni (PFAS), polychloreraðir naphthalenar (PCN), bromeraðir logatálmar sum polybromeraðir diphenyl etharar (PBDE) og polybromeraðir biphenylar (PBB), tetrabromobisphenol A (TBBPA), hexabromocyclododecan (HBCD) og syntetiskar musksambindingar og phthalatar. Í hesi verkætlanini eru ment nýggj greiningarháttaløg fyri PFAS, PCN, PBB, musksambindingar og phthalatar. Tað hevur ikki verið gjørligt at menna greiningarháttaløg fyri TBBPA og HBCD, tí hesi evni hava serstakar alis- og evnafrøðiligar eginleikar.

Í samsvari við ta vitan, ið er tøk nú um PFAS í lívfrøðiligum tilfari, var perflurooctane sulfonat (PFOS) tann ráðandi fluoreraða sambindingin í flestum sýnum, síðan kom PFOSA, sum varð funnið í rættiliga stórum megni (konsentratiónum) í grindahvali (43-62 ng/g vátvekt) og sildreka (29 ng/g vátvekt). PFOS varð funnið í megni oman fyri mátingarmarkið (9.6 ng/g vátvekt) í 13 av 16 sýnum. Úrslitini úr Grønlandi vístu økt megn av PFOS í røðini; vanlig ulka < ringkópur < ísbjørn, sum bendir á lívfrøðiliga upphóping upp gjøgnum føðiketuna. Megnið í ísbjørn var innan fyri tað, sum er funnið í Alaska og Hudson Bay, Kanada. Við støði í tí stóra PFOS-megninum verður mælt til at gera afturlítandi tíðarrákgreiningar. Harumframt verður mælt til at fylgja við gongdini í PFAS-megni í lyklasløgum úr Grønlandi og Føroyum, við tað at PFOS-líknandi evni enn eru í nýtslu og ikki verða stýrd við avmarkingum sum nú er.

Úrslitini fyri PCN vístu, at hesi evni vóru til og vóru upphópað í grønlendskum og føroyskum sjódjórum. Hægri PCNinnihald vórðu funnin í sjódjórum úr Føroyum enn í djórunum úr Grønlandi.

Megnið í grindahvølpum úr Føroyum (4068 pg/g lipid vekt) var 10 ferðir størri enn í hvítfiski úr arktiska partinum av Kanada. Í grindahvalum var toksisitetsekvivalenta (TEQ) megnið grundað á PCN á sama støddarstigi sum dioxin TEQ-megnið. Tann ráðandi PCN-congenurin í grindahvali og havhesti var CN-66/67, og í ísbjarnum var hann CN-68. Við støði í hesum úrslitum verður mælt til at kanna fyri PCN í føroyskum sløgum, ið hava dioxin TEQ-megn nær við markvirði í EU. Grønlendsku sýnini eiga at verða endurkannað við einum neyvari greiningarháttalag, áðrenn fleiri tilmæli verða gjørd.

Bæði PBDE og PBB hópast upp ígjøgnum føðiketuna eins og polychloreraðar biphenylir (PCB). PBB hevði helling til at upphópast í størri mun enn PBDE. PBB-megnið var minni enn PBDE-megnið, men lutfallið millum PBDE og PBB øktist í raðfylgjuni ringkópur < grindahvalur < havhestur < ísbjørn við sum heild sama megni av PBDE og PBB í ísbjørn.

Størsta PBDE-megnið varð funnið í sýnunum av grindahvali, og tað var uml. 15 ferðir størri enn megnið í ísbjørn (52 ng/g lipid vekt). Hetta váttar, at megnið í grindahvali er millum tey størstu megnini, sum eru funnin í arktiskum sjósúgdjórum. PBDE-megnið í Eysturgrønlandi var á sama støddarstigi sum í Svalbarð, og megnið í Vesturgrønlandi var tað sama sum megnið í arktiska partinum av Kanada. Geografiska mynstrið av PBDE er tí tað sama sum PCB-mynstrið. Teir ráðandi congenarnir vóru BDE-47 og BDE-99, undantikið í ísbjørn, sum hevði størri partar av BDE-153 enn BDE-99. BB-153 var sum heild tann ráðandi PBB-congenurin av teimum kannaðu congenunum.

Tilmælini fyri PBDE fata eisini um eina afturlítandi tíðarrákgreining og eina framtíðar støðiseftiransing, við tað av PBDE enn verður framleitt og nýtt í Norðuramerika. Orsakað av upphópingarmøguleikunum hjá PBB eigur tað at verða kannað í grønlendskum og føroyskum djórum, ið eru ovarlaga í føðiketuni fyri at fáa eitt betri dátugrundarlag fyri, hvar PBB kemur fyri, og hvussu stórt megnið er.

Tær syntetisku musksambindingarnar eru bert funnar í mátandi megni í ísbjarnalivur. Tó er í næstan øllum sýnisdømunum uttan í botnsetri funnið tekin um, at musksambindingar eru til staðar. Við tað at evnini eru ávíst, verður mælt til at greina tey verandi sýnini av djórum, ið eru ovarlaga í føðiketuni, men tað er neyðugt við neyvari og dyggari greiningarháttaløgum fyri at raka við evnini á sporevnisstigi. Um so er, at váttast kann, at musksambindingar eru til staðar, kann vera neyðugt at hava eftiransing við megnisgongdini, við tað at hesar sambindingar enn verða nýttar.

Phthalatar og ein adipatsambinding vórðu ávíst í øllum sýnum við størstum megni í ísbjørn úr Eysturgrønlandi, havhesti úr Føroyum og ringkópi úr Eystur- og Vesturgrønlandi. Tey størstu megnini millum tey kannaðu evnini vórðu funnin fyri DEHP (75-161 ng/g vátvekt) og DEHA (2,5-144 ng/g vátvekt). Tað er merkisvert, at phthalatar eisini eru funnir í botnsetri og í sløgum, sum eru niðarlaga í føðiketuni. Ein møgulig upphóping er eftir øllum at døma ikki so týðilig sum fyri halogeneraðar sambindingar. Tað verður tí mælt til at gera eina føðinetakanning fyri at fáa meiri vitan um, um phthalatar eru til

staðar í havumhvørvinum, og metast má um eina møguliga upphóping. Greiningarháttalagið má eins og í sambandi við musksambindingarnar betrast viðvíkjandi neyvleika og dyggleika.

Korrelatiónsgreiningar eru gjøgnumførdar fyri at eyðmerkja líkleikar í fyrikomingini av evnisbólkunum. Hagfrøðiliga frámerkjandi korrelatiónir eru funnar millum tey flestu pør av teimum halogeneraðu evnisbólkunum, t.e. PBDE/PBB og PFAS/PBDE og ein veikari korrelatión millum PCN/PBDE og PCN/PBB. Phthalatarnir broytast ikki samsvarandi teimum halogeneraðu evnisbólkunum, men vísa eina sínámillum korrelatión. Høvuðsorsøkin til korrelatiónirnar verður roknað at vera líknandi upphópingarmynstur.

1 Introduction

Since 1991, the Arctic Monitoring and Assessment Programme (AMAP) has provided information on persistent organic pollutants (POPs) in the Arctic. The initial activities were centred on organochlorine compounds that were transported from distant sources to the Arctic, where they accumulate in animals with lipid-rich tissues. As a consequence of persistence and biomagnification, chronic exposure of the indigenous peoples depending on traditional food sources has been observed. These findings contributed to the establishment of a global agreement on POPs which was concluded in 2001 at the Stockholm Convention.

At the same time, other compounds have been identified that may be potential POPs, for instance perfluorinated compounds including perfluorooctane sulfonate (PFOS), brominated flame retardants such as polybrominated diphenyl ethers (PBDEs) and polychlorinated naphthalenes (PCNs). First results from the Arctic showed that their concentrations in Arctic air and biota were much lower than in temperate regions. Nevertheless, temporal trend studies of PBDEs have demonstrated increasing concentrations (AMAP, 2004).

These compounds have often been referred to as new or emerging compounds although they have been in use for decades. However, the awareness of these compounds as potential pollutants of the Arctic is new and more information on their occurrence in the Arctic has been requested. The emerging compounds were emphasised in the recommendations of the second AMAP assessment of POPs as well as the Danish assessment report on the environment of Greenland:

“Additional research and monitoring of “new” chemicals is needed, in particular for brominated compounds that are increasing in concentration. An understanding of circumpolar trends of these “new” chemicals is needed, in particular for the Russian Arctic. Work on persistent organic compounds in current industrial, consumer and agricultural uses should be encouraged, even for chemicals that are not considered to have potential for atmospheric transport to the Arctic based on their physical properties.” (AMAP, 2004; p.197)

“An exponential increase in PBDE levels has been reported elsewhere, therefore it is recommended to incorporate this group of compounds in time trend studies for marine key species. A screening of the Greenland environment for the compounds PFOS, synthetic musks, polychlorinated naphthalenes, other brominated flame retardants (HBCD, TBBPA and PBB), polybrominated dibenzodioxins and dibenzofurans, aromatic amines and the biocide triclosan is recommended.” (Riget et al., 2003; p.171).

Based on these recommendations, a screening project was initiated for Greenland and the Faroe Islands. Samples from the marine environment were chosen since previous monitoring activities had indicated that the main health risks were linked with the biomagnifica-

tion of POPs in the marine food web. The chemicals analysed in this project are listed in Table 1. In accordance with the international recommendations, the compounds cover a wide range of physical-chemical characteristics, which might be rather dissimilar to polychlorinated biphenyls (PCBs) and other POPs. All compounds had or have widespread application as high volume chemicals in industrial and consumer products. The occurrence of these compounds in the environment, mainly close to production sites, has been shown previously.

The objective of this study was to screen marine samples from Greenland and the Faroe Islands for a variety of "new" contaminants in order to give preliminary information on their concentrations in the marine food web. Based on these results, recommendations regarding future monitoring are given. Futhermore, the project contributes to the circumpolar assessment of these compounds as requested in the international recommendations.

Table 1: Compounds selected for analysis

Compound group	Acronym	Congeners and analytes
Perfluorinated alkylated substances	PFAS	Perfluorooctane sulfonate (PFOS), Perfluorooctane sulfonamide (PFOSA), Perfluorooctanoic acid (PFOA), Perfluorohexane sulfonate (PFHS)
Polychlorinated naphthalenes	PCN	CNs 36, 42, 48, 52, 53, 54, 66/67, 68, 70, 72, 73, 74
Polybrominated diphenyl ethers	PBDE	BDEs 17, 28, 47, 49, 66, 99, 100, 153, 154, 183
Polybrominated biphenyls	PBB	BBs 15, 49, 52, 101, 153
Hexabromocyclododecane	HBCD	
Tetrabromobisphenol A	TBBPA	
Nitro musks		Musk ambrette (MA) Musk ketone (MK) Musk moskene (MM) Musk tibetene (MT) Musk xylene (MX)
Polycyclic musks		Cashmeran (DPMI) Celestolide (ADBI) Galaxolide (HHCB) Phantolide (AHMI) Tonalide (AHTN) Traseolide (ATII)
Phthalates		Dimethyl- (DMP) Diethyl- (DEP) Dibutyl- (DBP) Butylbenzyl- (BBP) Di-n-hexyl- (DnHP) Di(2-ethylhexyl)- (DEHP) Di-n-octyl- (DnOP) Di(2-ethylhexyl)-adipat (DEHA)

2 Samples

Table 2 lists the samples analysed in this project; more detailed sample information is given in chapter 11.1. The Greenland samples represent different trophic levels and cover different locations, while the Faroese samples include representatives of two high-trophic level marine species: Pilot whale and fulmar. It has to be noted that the limited data material might indicate trends, but does not allow a comprehensive fate study. With regard to the screening objective of this study, pooled samples were analysed to obtain mean concentrations of several individuals.

Table 2: Samples analysed in the project. N: Number of pooled samples analysed, each consisting of at least 4 individuals.

Sample	Tissue	N	Compounds	Location (see Figure 1 and Figure 2)
Greenland:				
Polar bear *(Ursus maritimus)*	blubber	2	PCN; BFR	Ittoqqortoormiit
	liver	2	PFAS; Musk; Phthalates	
Minke whale *(Balaenoptera acutorostrata)*	blubber	2	PCN; BFR	Central West Greenland *)
	liver	2	PFAS; Musk; Phthalates	
Ringed seal *(Phoca hispida)*	blubber	2	PCN; BFR	Ittoqqortoormiit
	liver	2	PFAS; Musk; Phthalates	
Ringed seal	liver	2	PFAS	Avanersuaq
Ringed seal	blubber	2	PCN; BFR	Qeqertarsuaq
	liver	2	PFAS; Musk; Phthalates	
Black guillemot *(Cepphus grylle)*	liver	2	PFAS	Qeqertarsuaq
	liver	2	PFAS	Ittoqqortoormiit
Shorthorn sculpin *(Myoxocephalus scorpius)*	liver	2	PCN; BFR; Musk; Phthalates; PFAS	Ittoqqortoormiit
	liver	2	PFAS; PCN; BFR; Musk; Phthalates	Qeqertarsuaq
Sediment		2	PFAS; PCN; BFR; Musk; Phthalates	Qeqertarsuaq
Faroe Islands:				
Longfinned pilot whale *(Globicephala melas)*	blubber	3	PCN; BFR	Miðvágur and Bøur
	liver	3	PFAS; Musk; Phthalates	
Fulmar *(Fulmarus glacialis)*	fat	2	PCN; BFR; Musk; Phthalates	Nólsoy and Viðareiði
	liver	2	PFAS	

*) One pooled blubber sample and one pooled liver sample contained one individual from East Greenland. See Table 19 for details.

2.1 Samples from Greenland

The samples from Greenland were pools of five individuals, based on equal amounts of wet weight. Individuals of the same sex and of similar age were chosen for the pooled samples. Different tissues were provided since PFAS analysis uses liver samples, while PCN and BFR were analysed in lipid-rich material, i.e. blubber of marine mammals and liver of fish. Originally, these tissues had also been chosen for the phthalates and musk compounds. The method development showed, however, that despite an effective purification of the samples, a high lipid content would produce less reliable data. Therefore, liver samples instead of blubber samples of marine mammals were used for analysis. For the sediment samples, the dry matter content was determined and the samples were pooled on the basis of equal amounts of dry matter. Two samples of each species and sediment were analysed.

Besides the samples originally selected for this screening project, additional samples from Greenland were analysed for perfluorinated compounds. The rationale for the selection of the additional samples was as follows: Liver samples of shorthorn sculpin from East Greenland were chosen to complement the previous analyses from West Greenland. Ringed seal samples originated from a different location on the west coast. Minke whale samples were included in the remaining analyses and were therefore also picked for the additional measurements of perfluorinated compounds. POP and Hg concentrations are monitored regularly in black guillemot eggs and livers. Therefore, this species was introduced into the sample catalogue.

Samples of polar bears were collected by Inuit hunters from Ittoqqortoormiit (70°30'N / 22°W) between 1999 and 2002 (Fig. 1). Most samples of minke whale were obtained from central West Greenland (between 60°-70°N) in 1998 during licensed whaling operations. One individual originated from central East Greenland (65°38'N / 37°45'W), which was caught during licensed whaling operations in 1998. Ringed seal samples were collected at Ittoqqortoormiit and Qeqertarsuaq (68°59'N / 53 °18'W) in 2002 and at Avanersuaq (77°29'N / 66° 75'W) in 1998. Seals from Ittoqqortoormiit and Qeqertarsuaq were all males, while the seals from Avanersuaq were all females. Samples of black guillemot and shorthorn sculpin were obtained from Ittoqqortoormiit and Qeqertarsuaq. Black guillemot and shorthorn sculpin were collected in 2000 and 2002, respectively. All samples were kept at outdoor temperature (-5 to -20° C) until frozen storage (-20° C).

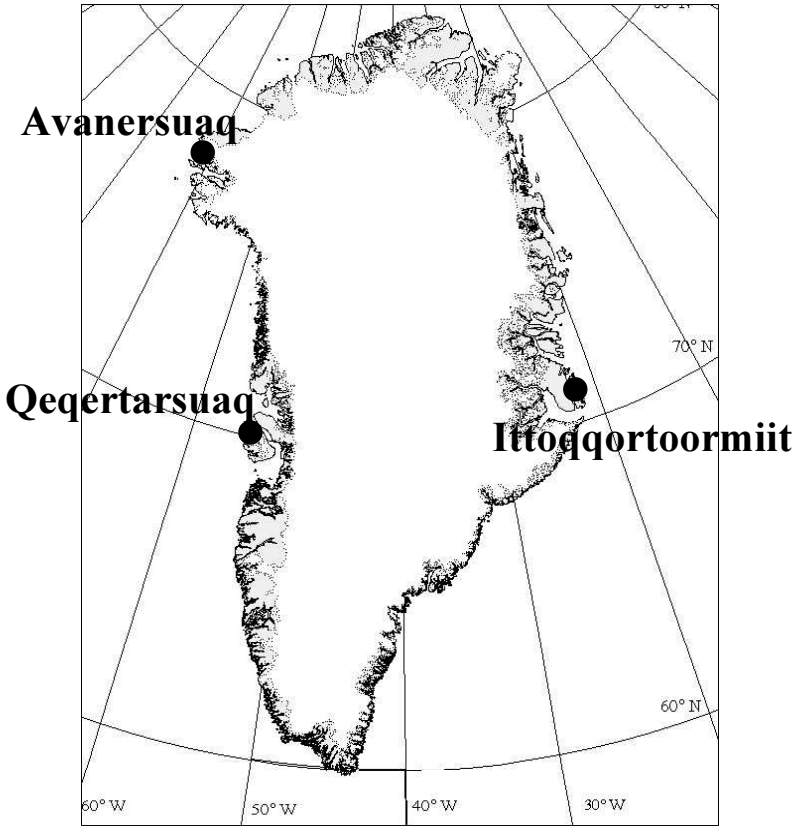

Figure 1: Sampling locations in East and West Greenland

2.2 Samples from the Faroe Islands

The samples from the Faroe Islands included pooled samples of juvenile, male and female long-finned pilot whale as well as male and female juvenile fulmar. The pooled blubber samples of pilot whale originated from 14 juvenile, 34 female and 5 male individuals, while liver samples were pooled from 11 juvenile, 16 female and 3 male individuals. Subcutaneous fat samples were taken from 6 male and 8 female fulmars, while liver samples were taken from 9 male and 9 female fulmars. All pooled samples were prepared on the basis of equal wet weight. The analysis of juvenile, female and male samples was chosen to elucidate possible differences due to age and sex, which had often been seen in similar studies, in particular on POPs.

Samples of long-finned pilot whale liver were collected during a traditional hunt event at Miðvágur (Fig. 2) in July 2001. Due to the limited number of adult males in this hunt, the samples were fortified with adult male samples taken in the hunt at Bøur a few days after the Miðvágur hunt. Samples were taken within approx. 4 hours after death and kept frozen (-20° C) from a few hours after the sampling until further sample preparation. Fulmars were taken during two different sampling events on the islands Nólsoy and Viðareiði in April 1998 (n=6) and September 1999 (n=12), respectively (Fig. 2). The birds were frozen shortly after the hunt, and kept frozen (-20° C) until dissection.

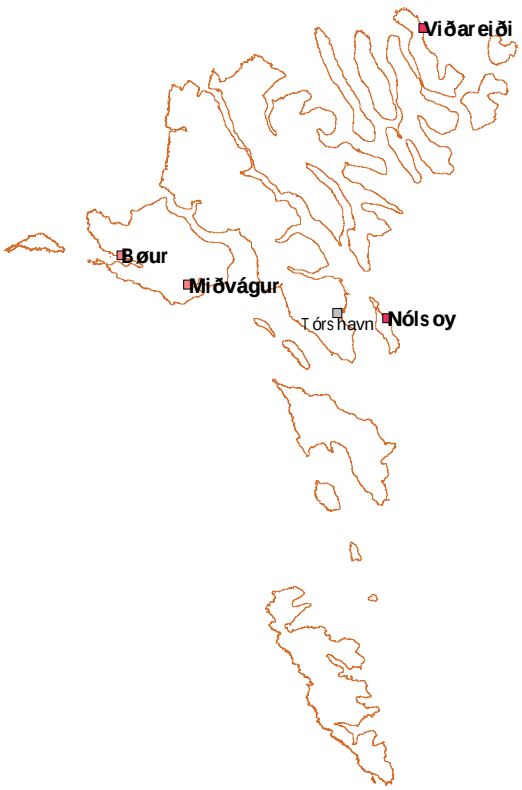

Figure 2: Sampling locations on the Faroe Islands.

3 Perfluorinated alkylated substances (PFAS)

3.1 Introduction

Sulfonyl-based fluorocompounds have been produced and used for over 40 years as refrigerants, surfactants and polymers in for instance textiles, upholstery, carpeting and in particular fire-fighting foams. In 2000, the production of sulfonyl-based fluorochemicals was estimated to be 29 tons (Kannan et al., 2002). A major manufacturer of these compounds announced a phase-out of their production from December 2000, due to concerns about the persistence of PFOS in the environment and potentially harmful effects on the environment (Taniyasu et al., 2003).

Because of the high-energy carbon-fluorine bond, PFOS and related fluorochemicals are stable in the environment and resist hydrolysis, photolysis and biodegradation (Kannan et al., 2001a). They are non-volatile, have high molecular weights and can repel both water and oils (Kannan et al., 2001b). In contrast to the more lipophilic halogenated compounds, their analysis requires high performance liquid chromatography / mass spectrometry (Giesy and Kannan, 2001).

Extensive screening analyses in biota samples from all over the world have identified PFOS and some related compounds as global pollutants and shown their bioaccumulation to higher trophic levels of the food chain (Giesy and Kannan, 2001). Studies on birds have shown highest exposure in urbanised areas (Kannan et al., 2001b). The primary sources of PFOS and other fluorochemicals are consumer products, thus, highest concentrations are likely to occur close to discharges of industrial and municipal wastewater (Kannan et al., 2001a; Taniyasu et al., 2003).

Samples from the Arctic included ringed seals from Svalbard, grey seals from Sable Island, Canada, and northern fur seals, stellar sea lions and polar bears from Alaska. Due to their amphipathic nature, PFAS do not accumulate in the blubber, but are mainly found in blood and liver. Therefore, the tissues analysed were liver of polar bears, liver and blood of northern fur seals and blood of seals (Kannan et al., 2001a; Giesy and Kannan, 2001). PFOS was below the detection limit in most northern fur seals and stellar sea lions, but was detected in polar bear, ringed seals and grey seals. This confirms the ubiquitous distribution of the perfluorochemicals beyond industrialised areas.

A Swedish monitoring study has found increasing levels of PFOS in eggs of Baltic guillemot (Cederberg et al., 2004). The concentrations were 36 ng / g in eggs from 1968 and increased to 600 ng / g in eggs from 2003. The toxicity of perfluorinated compounds has not been well characterized, but recent studies have shown a potential effect on metabolism (peroxisome proliferators) and intercellular communi-

cation (Hu et al., 2002; Berthiaume et al., 2002). Laboratory tests have also raised speculation about the hepatic toxicity of PFOS (Hoff et al., 2003).

3.2 Analytical methods

Perfluorinated compounds were analysed in liver samples by high performance liquid chromatography (HPLC) and tandem mass spectrometry (MS-MS) using electrospray ionisation (ESI). The extraction method and the chromatographic method are based on the method by Hansen et al. (2001) with partial modification of the LC method. The extraction method for sediment was developed in this project and has not been fully validated.

3.2.1 Extraction and purification

Liver tissue was homogenised and 5 grams were weighed. Deionised water (25 ml) was added and the sample was thoroughly mixed for 15 seconds with a vortex mixer. The homogenate (1 ml) was transferred to a polypropylene centrifuge tube and the internal standard (perfluorododecanoic acid) was added. Teflon or glass containers were avoided through the whole extraction procedure. 1 ml of a 0.5 TBA (tetrabutylammonium hydrogen sulphate) solution (pH 10), 2 ml of sodium carbonate/sodium bicarbonate buffer and 5 ml MTBE (methyl-tert-butyl-ether) were added to each sample. The samples were shaken for 20 minutes and then centrifuged for 25 minutes at 3500 rpm. The MTBE layer (4 ml) was transferred to a polypropylene tube and the solvent was evaporated to dryness. The extract was reconstituted in 500 µl methanol and vortex mixed for 15 seconds.

3.2.2 Instrumental analysis

Sample extracts were analysed by LC-MS-MS with electrospray ionisation (ESI) operated in negative ionisation mode. The methanol extracts (10 µl injection volume) were chromatographed on a C8 Luna 5 µm, 150 x 2.00 mm analytical column (Phenomenex, Torrance, CA, USA) using a PE Series 200 HPLC (Perkin Elmer, Norwalk, CT, USA). The mobile phase A was 2 mM ammonium acetate and the mobile phase B was methanol. The flow rate was 0.3 ml/min. The mobile phase gradient started at 45 % A, 55 % B and ended at 5 % A, 95 % B after 4.5 minutes. After that, the mobile phase composition was constant for 7.5 minutes. The total run time was 16 minutes with an equilibration time of 10 minutes between injections.

The HPLC was interfaced to a triple quadrupole API 2000 (Sciex) equipped with a TurboIon Spray source maintained at 375° C. Analyses were performed in multiple reaction monitoring (MRM). The values of the voltages applied to the sampling cone, focusing lenses, collision cell and quadrupoles were optimized in MRM mode by direct infusion of a solution containing the analytes. One or two product ions were chosen for each compound for LC-MS-MS analysis. The precursor and product ions for each analyte, together with the applied collision energy are summarised in Table 3.

Table 3: Precursor and product ions for the compounds analysed in negative ionisation mode, method limit of detection (LOD) and limit of quantification (LOQ) for biota (ng / g wet weight) and sediment (ng / g dry weight)

Compound	Precursor ion (m/z)	Product ions (m/z)	Collision energy (V)	LOD biota	LOQ biota	LOD sediment
PFOS	499	80; 99	-79; -70	5.8	9.6	2.0
PFOSA	498	78	-50	2.7	4.4	0.2
PFOA	413	169; 369	-26; -14	7.3	12.2	2.0
PFHS	399	80	-64	4.2	6.9	1.0

3.2.3 Quality assurance and quality control

Blank samples were prepared using bovine liver previously checked for the target analytes. Calibration standards and QC samples were prepared by spiking the blank samples with the analytes covering the concentration range between 10 and 1000 ng / g wet weight. The limits of detection (LOD) and quantification (LOQ) are summarised in Table 3. For the liver samples, the LOD is calculated as 3 times the standard deviation of 8 replicate samples spiked at 25 ng / g wet weight. For the same samples the LOQ is defined as 5 times the standard deviation. The value obtained as LOQ is verified by spiking 3 samples at the determined LOQ concentration. For the sediment samples, the LOD was estimated as 3 time the signal-to noise ratio of sediment samples spiked with the target analytes. Concentrations of the analytes in samples were not corrected for recovery as the calibration was performed with extracted samples.

3.3 Results and Discussion

The concentrations of perfluorinated compounds measured in animals from Greenland and the Faroe Islands are summarised in Figure 3 and Figure 4. Sediments were not included in Figure 3 since all concentrations were below the limit of detection. A detailed overview of all concentrations measured is given in Table 4. Values below the limit of quantification were substituted by half the LOQ in the calculation of total PFAS concentrations. Concentrations below the LOD were regarded as zero. In agreement with information available on monitoring of perfluorinated surfactants in biota, PFOS was the predominant fluorochemical in the biota analysed, followed by PFOSA. PFOS was found at concentrations above LOQ (9.6 ng / g wet weight) in 13 out of 16 samples.

3.3.1 Samples from Greenland

The results from Greenland showed increasing concentrations of PFOS: shorthorn sculpin<ringed seal<polar bear, indicating biomagnification of PFOS along the marine food chain. The concentrations of the other fluorochemicals were below LOQ or not detected for all samples, with the exception of a shorthorn sculpin sample (8.6 ng / g wet weight PFOSA) and a minke whale sample (28.9 ng / g wet weight PFOSA).

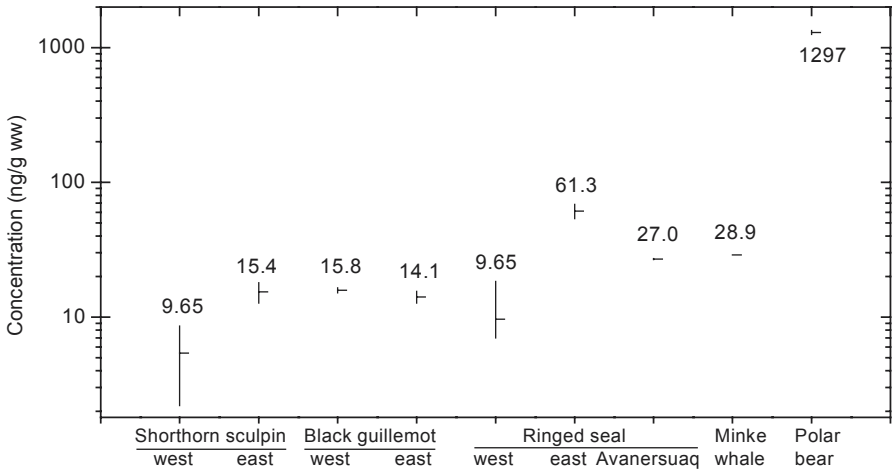

Figure 3: Mean concentrations of total PFAS in liver samples of biota from Greenland. Values below the LOQ were substituted by half the LOQ. Concentrations < LOD were regarded as zero.

The highest concentration of PFOS was found in liver of polar bear from East Greenland (mean: 1285 ng / g wet weight for 2 samples of 5 pooled individuals each). These levels are significantly higher than the mean level (350±33 ng / g) reported in Alaskan polar bear liver by Kannan et al. (2001a) (t-test, $p<0.05$). The concentrations in the Greenland samples are lower than the levels found in bears from the southern Hudson Bay reported by Martin et al. (2004) (3100±878 ng / g wet weight), however, the difference was not statistically significant. The Hudson Bay subpopulation is at lower latitude compared to the Greenland subpopulation, and the increased levels in the former may be due to proximity to regional sources. The PFOS concentrations in polar bears from East Greenland are comparable to those found in liver of fish eating mammals (mink and otter) from industrialised and urbanised regions (Kannan et al., 2002b).

The concentration of PFOS in ringed seals and shorthorn sculpins from East Greenland was generally higher than that of the respective samples from West Greenland, however, this was only statistically significant for ringed seals (t-test, $p<0.05$). This observation of higher concentrations on the east compared to the west coast of Greenland has been made repeatedly for PCBs and other organochlorine compounds in marine mammals (e.g. Cleemann et al., 2000; Riget et al., 2004). The East Greenland concentrations were about 10 times lower than the mean concentration found in liver of ringed seals (460 ng / g wet weight) from the Baltic Sea (Kannan et al., 2002a).

The average concentrations of PFOS in liver of black guillemot were similar when comparing East and West Greenland, which is in contrast to the observations for ringed seals and shorthorn sculpin. For other organohalogens (PCBs, DDTs, chlordanes, PBDEs), Vorkamp et al. (2004a) found somewhat higher concentrations in black guillemot liver and egg samples from East Greenland than from West Greenland.

This preliminary study on perfluorochemicals in the Arctic environment shows that the level of contamination is quite high, especially

for marine mammals and polar bears and confirms the biomagnification suggested by Giesy and Kannan (2001).

3.3.2 Samples from the Faroe Islands

The samples from the Faroe Islands (Figure 4) included only two species, pilot whale and fulmar. The concentration of PFOS in juvenile pilot whale (27.9 ng / g wet weight) was similar to the concentration measured in adult females (38.7 ng / g wet weight), but lower than the concentration measured in adult males (64.8 ng / g wet weight). However, Kannan et al. (2001) did not find a positive correlation between liver concentrations of PFOS and age in marine mammals, presumably due to accumulation patterns different from those observed for organochlorine compounds (e.g. PCBs and DDTs). Kannan et al. (2002b) compared the accumulation of PFOS to that of butyltin. Due to their ionic nature, both compounds bind to proteins and are therefore likely to undergo entero-hepatic circulation rather than accumulation in lipid reservoirs with time. Studies in mink did not show a correlation of PFOS concentration with lipid content (Kannan et al., 2002b).

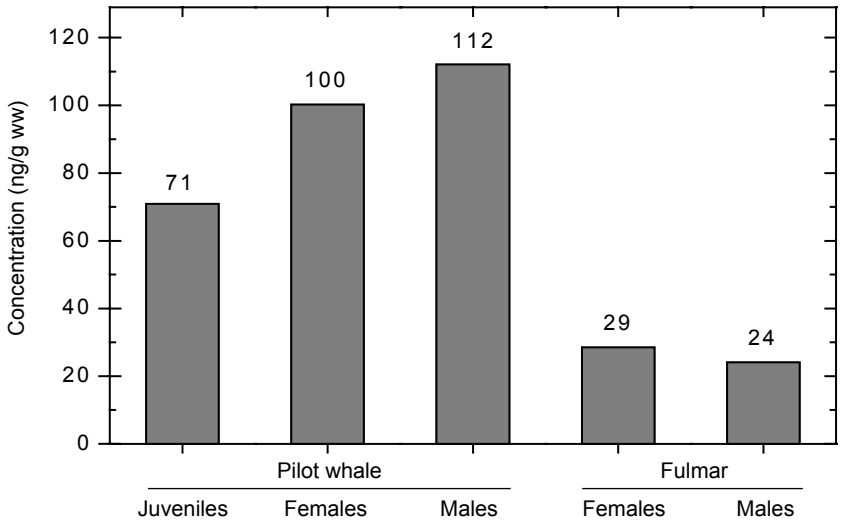

Figure 4: Concentrations of total PFAS in liver samples of biota from the Faroe Islands. Values below the LOQ were substituted by half the LOQ. Concentrations < LOD were regarded as zero.

PFOSA was found in all samples of pilot whale at concentrations similar to or higher than those of PFOS. The overall concentrations of PFOS and PFOSA in the Faroese samples, however, were substantially lower than those found in a similar study on pilot whale samples from the Faroe Islands collected in 2002 (Kallenborn et al., 2004). For PFOS, the concentrations in the 2002 samples were about twice the concentrations in this study, while concentrations of PFOSA in the 2002 samples exceeded the results of this study by a factor of 3 times for females and up to 10 times for males. Differences in POP levels between pilot whale schools have been observed before and are presumably related to the foraging area and preferences (Aguilar et al., 1993; Dam and Bloch, 2000; Dam et al., 2002).

Of all the samples analysed, relatively high concentrations of PFOSA were also found in minke whale samples, where PFOS was detected but not quantified, and the concentration of PFOSA was 28.9 ng/g wet weight. These data are in accordance with Kannan et al. (2002a,b), who found concentrations of PFOSA 1-5-fold greater than those of PFOS in liver of cetaceans from the Mediterranean Sea. In general, PFOSA was distributed sporadically in certain species and locations and was usually found in 10-15% of the samples analysed. Kannan et al (2002a) also pointed out that PFOSA was an intermediate in the production of several perfluorinated compounds and also a metabolic product in mammals of n-ethyl perfluorooctanesulfonamide (sulfluramid), an insecticide used for the control of cockroaches, termites and ants. The presence of PFOSA at high concentrations in certain samples and locations may indicate different sources of exposure of PFOS and PFOSA, respectively (Kannan et al., 2002a).

Table 4: Concentrations of perfluorinated surfactants in liver samples from Greenland and the Faroe Islands. All concentrations are in ng/g wet weight (sediments in ng/g dry weight). n.d.: not detected (below LOD). <LOQ: detected, but below the limit of quantification.

Species	Reg. no.	PFOS	PFOSA	PFOA	PFHS
Greenland:					
Polar bear	03-0129	1245	n.d.	< 12.2	< 6.9
	03-0164	1325	4.6	< 12.2	< 6.9
Ringed seal, East Greenland	03-0123	66.5	< 4.4	n.d.	n.d.
	03-0165	51.6	< 4.4	n.d.	n.d.
Ringed seal, West Greenland	03-0126	< 9.6	< 4.4	n.d.	n.d.
	03-0166	10.1	< 4.4	< 12.2	n.d.
Shorthorn sculpin, West Greenland	03-0119	n.d.	< 4.4	n.d.	n.d.
	03-0120	n.d.	8.6	n.d.	n.d.
Sediment	03-0267	n.d.	n.d.	n.d.	n.d.
	03-0268	n.d.	n.d.	n.d.	n.d.
Faroe Islands:					
Pilot whale, Juveniles	02-1755	27.9	43.0	n.d.	n.d.
Pilot whale, Females	02-1756	38.7	61.6	n.d.	n.d.
Pilot whale, Males	02-1757	64.8	47.3	n.d.	n.d.
Fulmar, Females	02-1760	28.5	n.d.	n.d.	n.d.
Fulmar, Males	02-1761	24.1	n.d.	n.d.	n.d.
Additional samples for PFAS analysis:					
Minke whale	03-0207	< 9.6	28.9	n.d.	n.d.
Ringed seal; Avanersuaq	03-0205	27.2	n.d.	n.d.	n.d.
	03-0206	26.8	n.d.	n.d.	n.d.
Black guillemot, West Greenland	03-0201	12.9	< 4.4	n.d.	n.d.
	03-0202	14.3	< 4.4	n.d.	n.d.
Black guillemot, East Greenland	03-0203	12.7	n.d.	n.d.	n.d.
	03-0204	15.5	n.d.	n.d.	n.d.
Shorthorn sculpin East Greenland	03-0185	18.0	n.d.	n.d.	n.d.
	03-0186	12.7	n.d.	n.d.	n.d.

4 Polychlorinated naphthalenes (PCN)

4.1 Introduction

PCNs had numerous industrial applications similar to those of PCBs, for instance in capacitor dielectrics, cutting oils, engine oil additives, ship insulation, dye carriers, wood and paper preservatives and cable insulation (Yamashita et al., 2000). Having been produced since the beginning of the 20th century, they preceded PCB application in the United States and Europe. Their production was discontinued in the 1980s, at a total production volume of 150 000 tons (Falandysz, 1998). Beside the direct industrial application, PCNs can be formed during waste incineration or emitted from metallurgical and chlor-alkali processes (Benfenati et al., 1991; Kannan et al., 1998). PCNs have also been identified as impurities in PCB formulations. However, the PCN emitted from the use of PCB mixtures are estimated to be less than 1% of the PCNs produced as technical preparations (Yamashita et al., 2000).

Several PCN congeners exhibit dioxin-like effects through the Ah-receptor mediated mechanism. These include induction of aryl hydrocarbon hydroxylase and EROD, chloracne and liver damage (Kannan et al., 2001). PCNs have been assigned TEF values similar to the coplanar PCBs (Blankenship et al., 2000; Villeneuve et al., 2000). Model calculations based on persistence, bioaccumulation and toxicity have shown that PCNs meet all the criteria for candidates according to the UN-ECE protocol for POPs (Lerche et al., 2002). PCN are listed on the OSPAR list of chemicals for priority action, as chemicals without current production or use interest (OSPAR, 2002). Monitoring data for PCNs have confirmed the presence in organisms high in the food chain as a result of bioaccumulation and biomagnification (e.g. Farlandysz, 1998). The penta- and hexa-CNs in particular have bioaccumulative and biomagnifying potential, with log K_{ow} values from 6.8-7.7 (Helm et al., 2002).

Helm et al. (2002) analysed PCNs in ringed seal and beluga blubber from the eastern Canadian Arctic. TEQ contributions from PCNs in beluga were of the same order as or greater than found for PCDD/Fs. PCNs were also analysed in ringed seal blubber from Svalbard collected in 1981 (Jansson et al., 1993). The sum of tetra-CNs and penta-CNs was similar to the more recent levels from Canada. Corsolini et al. (2002) found PCNs in polar bear liver from Alaska at a mean concentration of 370±390 pg/g ww and observed a strong correlation between concentrations of PCBs and PCNs.

4.2 Analytical methods

An analytical method for PCNs was developed in this project, based on the existing method for extraction and purification of PCBs. This method was described in detail by Cleemann et al. (1999) and updated by Vorkamp et al. (2004a). Samples were analysed by gas chroma-

tography (GC) and mass spectrometry (MS). A method validation was conducted prior to analysis of the samples and will briefly be described here.

4.2.1 Extraction and purification

After homogenisation, defined sample amounts were dried with Chem Tube-Hydromatrix and spiked with the recovery standard CB-198. The samples were Soxhlet extracted using 350 ml of a mixture of n-hexane and acetone (4:1, v/v) and concentrated by rotary evaporation to a volume of 1 ml. For extraction of sediment samples, Cu was added to the solvent. The extracts were cleaned on a multilayered glass column packed with 5 g deactivated aluminium oxide containing 10 % water, 1 g activated silica (24 h at 160°C), 5 g activated silica impregnated with concentrated sulphuric acid and 1 cm anhydrous Na_2SO_4, and eluted with 200 ml n-hexane. The cleaned extracts were concentrated to about 1 ml by rotary evaporation with iso-octane as keeper and under nitrogen. After defined amounts of the internal standard CN-27 were added, the samples were adjusted to a precise volume of 1 ml.

4.2.2 Instrumental analysis

A chromatogram of a standard (20 ng/ml) is shown in Figure 5. The extracts were analysed by GC-MS with negative chemical ionisation (NCI) in the single ion monitoring mode (SIM). Methane was used as the ionisation gas. The temperature programme was as follows: 0.5 min at 120°C followed by an increase to 160°C at a rate of 25°C/min, increase to 270°C at a rate of 2°C/min and a further increase at 25°C/min to 270°C, which are kept isothermic for 7 min. Other instrumental parameters are identical to the method for PBDEs described by Christensen et al. (2001). The m/z values of target and qualifier ions are listed in Table 5. CN-66/67 co-elute and can only be determined in the summed concentration. Quantification was based on a duplicate 9-point calibration.

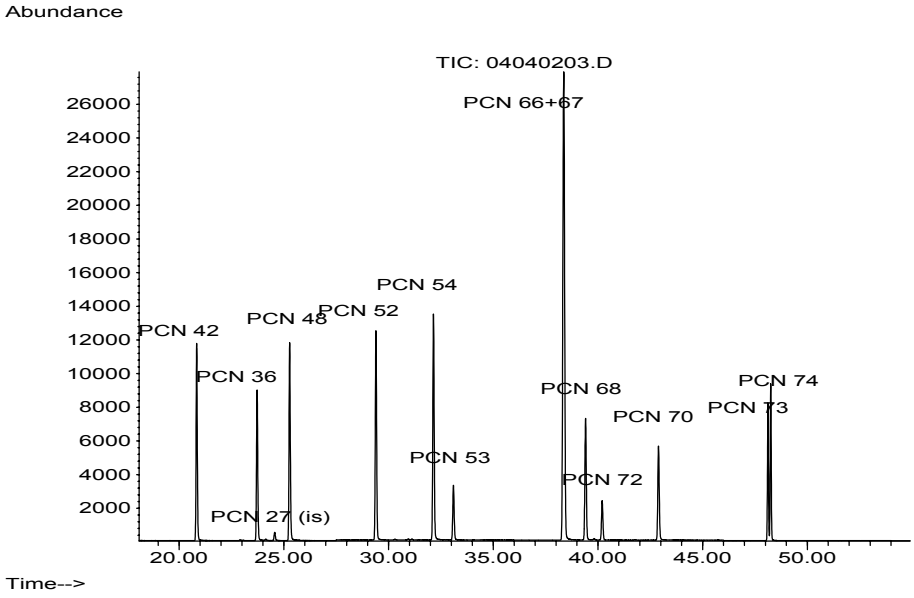

Figure 5: Chromatogram of a PCN-standard (20 ng/ml)

4.2.3 Method validation

The following parameters were investigated for PCNs in the method validation:

- Linear response ranges
- Limit of detection and limit of quantification
- Precision
- Recovery
- Blank values

It has to be noted that the method validation was based on biota samples only and was not further optimised with regard to the sediment analyses. However, the validation of PBDEs showed that the same method could be used for both biota and sediment, if sulphur removal from sediments is considered, for instance by addition of cupper during sample extraction.

The linear response ranges were tested by duplicate analysis of nine standards, covering a concentration range from 0.1 ng/ml to 20 ng/ml. Linear calibration curves could be chosen for the whole concentration range, with r^2 values given in Table 5. Limit of detection (LOD) is defined as the signal to noise (S/N) ratio equal to 3, and LOQ as S/N = 5. The values were found by extrapolating results from spiked samples, according to recommendations by Covaci et al. (2003). LOD and LOQ for environmental matrices can be obtained by dividing the values in Table 5 by the sample amount. The values in Table 5 are not referred to the sample weight as a variety of matrices with different sample amounts are included in this project. In the analysis of shorthorn sculpin, for example, about 2.5 g sample were extracted, which means that the LOD and LOQ values of Table 5 have to be divided by 2.5 to obtain the LOD and LOQ of the sample.

Table 5: Parameters in the instrumental analysis of PCNs.

Compound	m/z Target ion	m/z Qualifier ion	r^2 Linear response	LOD (ng/ml)	LOQ (ng/ml)
CN-27 (IS)	266	264			
CN-36	266	264	0.999	0.060	0.100
CN-42	266	264	0.999	0.060	0.100
CN-48	266	264	0.999	0.060	0.100
CN-52	300	266; 302	0.999	0.060	0.100
CN-53	266	300; 302	0.998	0.120	0.200
CN-54	300	266; 302	1.000	0.060	0.100
CN-66/67	334	332; 336	1.000	0.120	0.200
CN-68	334	332; 336	0.996	0.060	0.100
CN-70	334	332; 336	0.998	0.240	0.400
CN-72	334	332; 336	0.998	0.120	0.200
CN-73	368	370	0.997	0.060	0.100
CN-74	368	370	0.999	0.060	0.100

Precision was determined at repeatability conditions, i.e. at the same operating conditions within a limited period of time. Thus, the test describes the precision (or uncertainty) within the same analytical batch. 6 samples of internal reference material (sand launce oil) were spiked at two concentration levels (1 ng/ml and 10 ng/ml). Previous experiments had shown that the reference material did not contain detectable amounts of PCNs and that no interference occurred. After an equilibration time of minimum 4 hours, the test samples were analysed as described above. The results are summarised in Table 6.

Between-batch uncertainty or long-term precision will be monitored in control charts, which document the concentration development in a reference material. The long-term precision will be used to define warning and action limits. Results outside these limits indicate problems with the analytical methods, which may affect the overall quality of the results. Control charts were established in connection with the validation experiments.

Recovery was determined on the basis of the six replicates spiked at either low or high concentration of PCNs. The recovery values range from 87-113 %, which has to be considered satisfactory. However, recoveries from spiked samples tend to be higher than recoveries from "real" samples since the contaminants are not incorporated in the matrix and may be extracted more easily (Covaci et al., 2003).

The recoveries are calculated in relation to so-called archives, which are standard solution of the same compounds. In this case, the archives were evaporated under nitrogen in order to change the solvent, which might have led to small losses of the PCN compounds. This would explain the tendency of recoveries above 100%. The standard deviations within the recovery experiment are low, ranging between 2.6-5.6% at the low concentration and 2.1-4.5% at the high concentration.

A variety of other halogenated compounds was analysed using the PCN-method to exclude the possibility of co-elution with other compounds. This test included PCBs, PBBs and PBDEs and did not show any co-elution of the congeners included in our methods. Two blanks were extracted and analysed in the same way as the biota samples and did not show any peaks at the retention times of the PCNs.

Table 6: Uncertainty (expressed as relative standard deviation from target value) and recovery for PCNs in spiked sand launce oil (six replicates per concentration), expressed as percent of the concentration in the archive spikes. All data are given in percent. Low concentration level: 1 ng / ml. High concentration: 10 ng / ml.

Compound	Low concentration			High concentration		
	Uncertainty	Average recovery	Recovery range	Uncertainty	Average recovery	Recovery range
CN-36	4.92	104	97-110	3.13	106	102-110
CN-42	4.92	105	97-110	2.52	110	105-113
CN-48	5.48	103	95-112	2.42	102	97-104
CN-52	3.91	106	102-111	2.92	103	100-107s
CN-53	7.55	95	87-106	3.93	101	98-104
CN-54	3.90	102	96-109	2.25	101	95-105
CN-66/67	2.85	101	98-106	3.71	104	100-108
CN-68	3.38	102	96-105	5.02	98	91-104
CN-70	4.83	102	97-109	4.61	93	87-99
CN-72	5.69	108	97-114	3.25	100	95-103
CN-73	4.17	109	101-113	4.09	100	94-104
CN-74	4.11	104	97-110	4.69	98	93-105

4.2.4 Quality assurance and quality control

The quality assurance procedure for the analysis of environmental samples followed the QA / QC system established for PCBs (Asmund et al., 2004). The analyses were performed in a batch of 19 samples two of which were analysed in duplicate. Furthermore, the batch contained one blank and two samples of the internal reference material, sand launce oil. As described above, the sand launce oil was spiked with PCNs, and the concentrations were plotted in control charts. For each batch, three samples are prepared without addition of internal or recovery standards, which are used to test interference of the matrix with the standards. Relative retention times are calculated to verify the identification of the compounds. The overall quality of the trace analyses is monitored by intercalibrations, such as PCBs and organochlorine pesticides in biota arranged by QUASIMEME. The results of the time period 1999-2002 are described by Asmund et al. (2004).

4.3 Results and Discussion

Summed concentrations of the PCN congeners in the samples from Greenland and the Faroe Islands are shown in Figure 6 and Figure 7, respectively. Sediments are not included in Figure 6 since all concentrations were below the limit of detection, except for the concentration of CN-73, which was below the limit of quantification. The detailed results of the individual congeners are given in Table 7 and Table 8.

TEQ were calculated on the basis of the toxic equivalent factors given by Kannan et al. (2001c). Among the most toxic and bioaccumulative CN congeners are CN-66 and CN-67, but they typically co-elute in most GC analysis (Helm et al., 2002). In this study, a TEF of 0.0024 was used for the co-eluting congeners, according to Kannan et al. (2001c). Blankenship et al. (2000) determined relative potency factors (REP) of 0.004 for CN-66 and 0.001 for CN-67. This indicates a certain variation in the TEQs published, depending on the analytical method and on the TEF/REP chosen for TEQ calculation. Helm et al. (2002) showed that the co-eluting congeners could be separated on a Rt-βDEXcst column, which may be recommendable for more detailed analyses.

In general, several PCN congeners were below the limit of detection in all samples analysed. These congeners (CNs 36, 53, 54, 70, 72) were regarded as zero in the sum calculation. Concentrations below LOQ were substituted with half the limit of quantification. For comparisons with literature data and a more detailed assessment of the PCN concentrations in Arctic biota, lower limits of detection will be advisable.

4.3.1 Samples from Greenland

The summed PCN concentrations in the biota samples from Greenland range from 124 pg/g lw in ringed seal blubber from West Greenland to 640 pg/g lw in polar bear. However, due to the high number of congeners below the limit of quantification, these concentrations have to be regarded as indicative.

Only a few PCN measurements exist from the Arctic. Helm et al. (2002) analysed PCNs in ringed seals and beluga blubber from the eastern Canadian Arctic. The samples were collected off Baffin Island in Nunavut Territory in 1993 and contained ΣPCN concentrations between 35-71 pg/g lw. Thus, the summed concentrations in ringed seals appear lower than those observed in this study, which, however, are uncertain and might in fact be close to the concentrations obtained in the Canadian Arctic. PCNs were also analysed in ringed seal blubber from Svalbard collected in 1981 (Jansson et al., 1993). The sum of tetra-CNs and penta-CNs was 38 pg/g lw, thus being similar to the more recent levels from Canada. Hexa-CNs were not detected in the ringed seals from Svalbard.

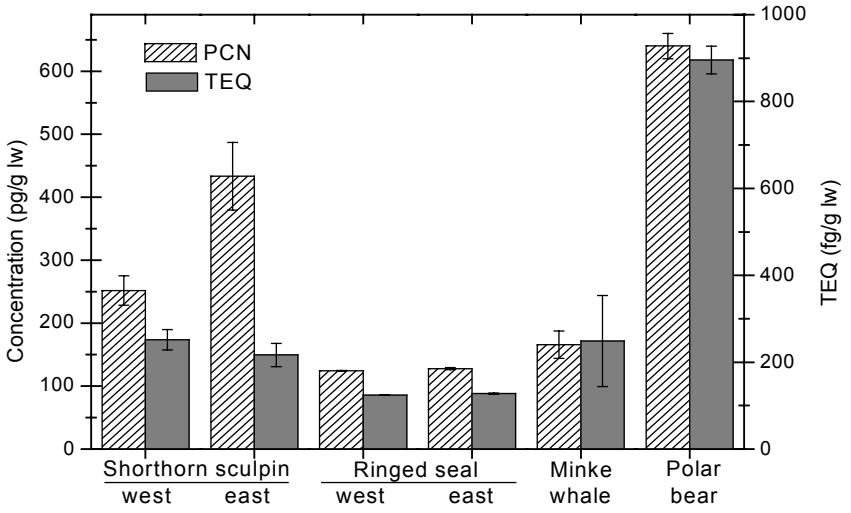

Figure 6: Summed PCN concentrations and TEQ for the samples from Greenland. The concentrations are averages of the two samples analysed. The error bars indicate the difference from the concentrations in the two samples. Concentrations < LOQ are substituted with ½ LOQ. Values < LOD are not considered in the sum.

Data available from the Baltic Sea had similar PCN levels in ringed seals as those observed in Canada and on Svalbard (Koistinen, 1990). Corsolini et al. (2002) also noted that the PCN levels in remote marine environments such as the Antarctic only were slightly lower than in biota from other locations. They detected PCNs in all samples analysed, even at low trophic levels of the food web, for instance in krill. Their method was based on very low limits of detection, which allowed the detection of hexa-CNs above 0.043 pg/g wet weight.

ΣPCN concentrations in 5 samples of polar bear liver from Alaska ranged from < 0.1 pg/g wet weight to 945 pg/g ww, with a mean concentration of 370 pg/g ww (Corsolini et al., 2002). On a wet weight basis, the two polar bear samples from East Greenland contained 436 and 478 pg/g ww of CN 68. Including the congeners below the limit of quantification as half LOQ, the concentration will raise to 554 and 591 pg/g ww, respectively. Since Corsolini et al. (2002) analysed all tri- through octa-CNs, the values from Greenland represent minimum values in this comparison. However, different tissues were analysed and cannot be compared directly. Corsolini et al. (2002) found a strong correlation between concentrations of PCBs and PCNs.

TEQ contributions from PCNs in beluga from the Canadian Arctic (30-426 fg/g lw) were of the same order as or greater than found for dioxins and furans. They contribute up to 11% relative to the mono- and non-ortho-PCBs even though their concentrations were <1% of summed coplanar PCB concentrations (Helm et al., 2002). The TEQ concentrations in the polar bear samples from Greenland were higher (Figure 6). Even when compounds below the limit of quantification were not considered, TEQ concentrations in the two samples were 802 and 732 fg/g lw.

4.3.2 Samples from the Faroe Islands

The samples from the Faroe Islands contained considerably higher concentrations of PCNs than the samples from Greenland. The concentrations in pilot whale ranged from 1496 pg/g lw to 4068 pg/g lw, with the highest concentrations in the juvenile samples and the lowest concentrations in the female samples. These summed concentrations will only be slightly reduced if values below the limit of quantification are excluded (see Table 8). This is mainly due to the high concentrations of the hexa-CN congeners 66/67 in the pilot whale samples, which account for 62-76 % of the summed PCN concentration.

Apparently, concentrations of PCN are high in predatory animals such as polar bear and pilot whale, suggesting biomagnification in the food web. The tendency of highest concentrations in juvenile pilot whales from the Faroe Islands was also found for PBDEs (Lindström et al., 1999a,b) and was attributed to the uptake of contaminants during suckling. Consequently, concentrations are lowest in the female animals, which transfer the contaminants to their offspring. More analyses will be necessary, however, to confirm that this trend also is valid for PCNs.

The highest concentration is about an order of magnitude higher than found for beluga blubber from the Canadian Arctic (Helm et al., 2002). The homologue distribution pattern also varies, with the penta-CNs accounting for approximately 50% of the summed PCN concentration in the beluga. Homologue distributions have also been found to vary in other marine mammals: Harbour porpoises from Sweden and the southern Baltic Sea were dominated by hexa-CNs and tetra-CNs, respectively (Ishaq et al., 2000; Falandysz and Rappe, 1996). However, it has to be taken into consideration that the congener spectrum analysed usually differs.

The fulmar samples also had higher concentrations than all samples from Greenland, with 2960 pg/g lw in female and 4072 pg/g lw in male fulmars (Figure 7). Concentrations in the same order of magnitude as those in fulmars were also detected in livers of south polar skua (*Catharacta maccormicki)* from the Antarctic (2550 pg/g lw) (Corsolini et al., 2002). The concentrations in fulmar were also comparable to the concentrations in gulls eggs from the Faroe Islands when the same ratio between egg and subcutanuous fat concentration for PCN as for CB 153 and pp-DDE is assumed (Pusch, 2004).

While all Faroese samples were dominated by the CN-66/67 congeners, these were below the limit of detection in the polar bear samples from Greenland, which contained higher concentrations of CB-68. Besides differences in PCN exposure due to different feeding habits, selective metabolism may be of importance. In the more detailed study by Helm et al. (2002), various differences in contaminant pattern were found between beluga and ringed seal, including differences in occurrence of contaminants, concentrations and homologue distribution, which were explained by selective metabolism.

The TEQ values found for pilot whales in the present study were compared with TEQ concentrations for dioxins and non-ortho PCBs (Mikkelsen et al., 2002). The TEQ concentrations in the pilot whales

based on PCN were similar to the dioxin TEQ concentrations. Male pilot whales contained dioxin TEQ concentrations of 8-10 pg/g lw, while female pilot whales had dioxin TEQ concentrations of 11-13 pg/g lw. Total TEQs including dioxins and non-ortho PCBs, but no PCN concentrations, ranged from 46 pg/g lw to 71 pg/g lw.

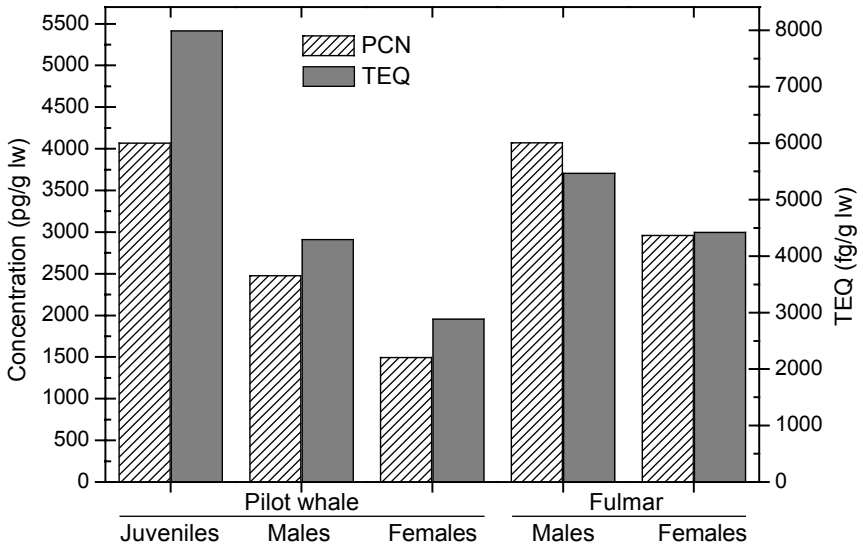

Figure 7: Summed PCN concentrations and TEQ for the samples from the Faroe Islands. Concentrations < LOQ are substituted with ½ LOQ. Values < LOD are not considered in the sum.

The results from Greenland and the Faroe Islands suggest a wide-spread distribution of PCNs even in remote areas. In general, the concentrations appear only slightly lower than those observed in ringed seals from the Baltic Sea and increase by several orders of magnitude in top predators, probably due to biomagnification. More sensitive analytical methods would allow a more certain assessment of the concentrations in the Arctic. The TEQ values are lower than those considered to elicit toxicological effects in birds and marine mammals (Kannan et al., 2001c). However, as most of the animals analysed in this study are part of the traditional local diet, they have to be considered as a route of human exposure to PCNs, which exhibit dioxin-like toxicity (Helm et al., 2002).

Table 7: PCN Concentrations (pg/g lipid weight (lw) unless stated otherwise) in samples from Greenland.
[a)] Values < LOQ are substituted by half LOQ. [b)] Values < LOQ are not included in ΣPCN

Species	Reg. no.	CN-36	CN-42	CN-48	CN-52	CN-53	CN-54	CN-66/67	CN-68	CN-70	CN-72	CN-73	CN-74	ΣPCN [a)]	ΣPCN [b)]	TEQ (fg/glw)
Polar bear	03-0127	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	534	n.d.	n.d.	< 252	n.d.	660	534	928
	03-0128	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	488	n.d.	n.d.	< 265	n.d.	620	488	864
Minke whale	03-0130	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 353	n.d.	177	n.d.	177
	03-0131	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 288	n.d.	144	n.d.	144
Ringed seal, East Greenland	03-0121	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 252	n.d.	126	n.d.	126
	03-0122	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 259	n.d.	129	n.d.	129
Ringed seal, West Greenland	03-0124	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 250	n.d.	125	n.d.	125
	03-0125	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 247	n.d.	124	n.d.	124
Shorthorn sculpin, East Greenland	03-0117	n.d.	n.d.	n.d.	< 380	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 380	n.d.	380	n.d.	190
	03-0118	n.d.	n.d.	n.d.	< 487	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 487	n.d.	487	n.d.	244
Shorthorn sculpin, West Greenland	03-0119	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 457	n.d.	228	n.d.	228
	03-0120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 550	n.d.	275	n.d.	275
Sediment	03-0267	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 8.23	n.d.	4.12	n.d.	4.12
	03-0268	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< 8.30	n.d.	4.15	n.d.	4.15

Table 8: PCN Concentrations (pg/g lipid weight (lw) unless stated otherwise) in samples from the Faroe Islands
[a)] Values < LOQ are substituted by half LOQ. [b)] Values < LOQ are not included in ΣPCN

Species	Reg. no.	CN-36	CN-42	CN-48	CN-52	CN-53	CN-54	CN-66/67	CN-68	CN-70	CN-72	CN-73	CN-74	ΣPCN [a)]	ΣPCN [b)]	TEQ (fg/glw)
Pilot whale, Juveniles	02-1754	n.d.	n.d.	< 269	n.d.	n.d.	n.d.	3086	298	n.d.	n.d.	< 269	281	4068	3664	7987
Pilot whale, Females	02-1758	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	990	253	n.d.	n.d.	< 253	< 253	1496	990	2883
Pilot whale, Males	02-1759	n.d.	n.d.	< 259	n.d.	n.d.	n.d.	1544	305	n.d.	n.d.	< 259	367	2475	2216	4293
Fulmar, Females	02-1762	n.d.	< 410	n.d.	793	n.d.	n.d.	1756	n.d.	n.d.	n.d.	< 410	n.d.	2960	2550	4421
Fulmar, Males	02-1763	n.d.	566	n.d.	1175	n.d.	n.d.	2008	322	n.d.	n.d.	< 322	n.d.	4072	3749	5465

5 Brominated flame retardants (BFR)

Brominated flame retardants (BFR) are a chemically diverse group of brominated organic compounds. This study includes the chemical groups polybrominated diphenyl ethers (PBDE) and polybrominated biphenyls (PBB) as well as the compounds tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD). With the exception of TBBPA, these BFRs are added to polymers without forming covalent bonds and can therefore leach into the environment during production, use and disposal of the products (Sjödin et al., 2001).

All BFR included in this project are listed on the OSPAR list of chemicals for priority action (OSPAR, 2002). PBDEs are on the list of priority substances under the Water Framework Direktive of the European Union (EP, 2001). Penta-BDE is identified as a priority hazardous substance on this list.

The analytical method for PBDEs in biota and sediment was developed and validated by Christensen et al. (2001). PBBs were included in this method, after test runs and a method validation. A method development was attempted for TBBPA and HBCD, however, given the more polar character of TBBPA, the results were not satisfactory. Details of the method development and possible alternatives are described in sections 5.2.2 and 11.2.

5.1 Polybrominated diphenyl ethers (PBDE) and Polybrominated biphenyls (PBB)

5.1.1 Introduction

PBDEs are high volume chemicals used as flame retardants in electric and electronic equipment, textiles and paint. Tetra- and penta-BDEs have logK_{ow}-values of 5.9-7.0 and have been shown to bioaccumulate similarly to PCBs. For octa- through deca-BDE, logK_{ow}-values of 8.4-10 have been estimated, but little is known about the bioaccumulation potential (AMAP, 2004).

The use of Penta-BDE was voluntarily withdrawn from the Japanese market and has been banned in Europe, but production and use continues in North America (Alaee et al., 2003). The European Union also announced a ban on marketing of octa-BDE (EP, 2002). The regulatory measures taken in Europe are considered as the main reason for declining BDE congener concentrations observed in Swedish human milk samples during the last 5 years (Meironyte et al., 1999).

Since the early 1980s, PBDEs have been detected in all compartments of the environment word-wide, making them global and ubiquitous contaminants. So far, their occurrence and fate in the Arctic have not been studied as extensively as for PCBs, however, the knowledge available of PBDEs is increasing. Jansson et al. (1987) and Sellström et al. (1993) were the first to report the presence of PBDEs in the Arctic, studying ringed seals on Svalbard. A recent study on ringed seals

from the Canadian Arctic indicated an exponential increase of PBDEs during the last 20 years (Ikonomou et al., 2002). The authors predicted that the levels of PBDEs would surpass PCBs if present trends of use and release continued.

BDEs in fish and mussels from Southwest Greenland were studied by Christensen et al. (2002). In addition to the long range atmospheric transport from more industrialised areas in mid-latitudes to the remote areas of the Arctic, they also found an indication of local sources of PBDEs in Greenland. Vorkamp et al. (2004a) showed the presence of BDEs in black guillemot liver and eggs in Greenland. Similar to the spatial trend observed for PCBs and organochlorine pesticides (e.g. Cleemann et al., 2000; Riget et al., 2004), the ΣBDE levels were higher in East Greenland than in West Greenland.

In a recent study on PBDEs in Greenland biota collected in 2001, concentrations were obtained for black guillemot eggs, ringed seal blubber, shorthorn sculpin liver and Arctic char muscle from East Greenland. PBDE levels correlated with PCB, DDT and chlordane-concentrations in the same samples, indicating similar mechanisms of uptake, bioaccumulation and biomagnification (Vorkamp et al., 2004b).

Samples of pilot whales from the Faroe Islands have revealed high concentrations of some of the tetra and penta-brominated diphenylethers. The most abundant congener BDE-47 was found at concentrations up to 1.7-1.8 µg/g lipid weight in juvenile animals (Lindström et al., 1999a).

PBBs were produced and applied in clearly smaller amounts than PBDEs, and the production in the USA was discontinued in the 1970s, following the accidental feeding of dairy cattle with the PBB-product firemaster FF-1 (Silberhorn et al., 1990). The characteristics of PBBs are similar to those of polychlorinated biphenyls (PCBs). However, their volatility is clearly lower than that of PCBs and resembles the volatility of polychlorinated terphenyls (PCTs) (de Boer, 1999). Most PBBs have a $\log K_{OW} > 7$.

The detection of PBBs in sperm whales, whitebeaked dolphins and harbour seals has shown that PBBs have to be considered as global pollutants (de Boer et al., 1998). PBBs have also been detected in birds and seals preying on fish, which indicates that the compounds are transferred from prey to predator (Jansson et al., 1993; Pijnenburg et al., 1995). Three PBB congeners (PBB-15, -52, and -153) were part of a polar bear study from Svalbard analysing archived samples from 1967. All brominated flame retardants were below the detection limit (Derocher et al., 2003).

5.1.2 Analytical methods

In addition to the BDE congeners described by Christensen et al. (2001), the hepta-BDE BDE-183 was included in the PBDE method. A more recent description of the analytical method was published by Vorkamp et al. (2004a). Briefly, the samples were homogenised, dried with anhydrous Chem Tube-Hydromatrix and spiked with the recovery standard BDE-77 prior to Soxhlet extraction using glass-distilled

n-hexane and acetone. The extracts were cleaned using a multilayered glass column packed with 5 g deactivated aluminium oxide containing 10 % water, 1 g activated silica (24 h at 160°C), 5 g activated silica impregnated with concentrated sulphuric acid and 1 cm anhydrous Na_2SO_4. The column was eluted with 250 ml n-hexane. After preconcentration of the eluates, the quantification standard BDE71 was added, and the samples were adjusted to a precise volume of 1 ml.

PBDEs and PBBs were analysed by GC-MS in the negative chemical ionisation (NCI) mode. Methane was used as the chemical ionisation gas at a pressure of 1.9×10^{-4} torr. The transfer line was held at 280°C, and the ion source temperature at 150°C. All samples were analysed in the selected ion monitoring (SIM)-mode, recording signals for the m / z values -79, -81 and -161. Quantification of PBDEs was based on a duplicate 8-point-calibration, with the exception of BDE-183, which was quantified on the basis of a duplicate 7-point-calibration. The quantification of PBBs included duplicates of nine standards.

BB-153 and BDE-154 co-elute on a DB-5 capillary colum (Covaci et al., 2003). Therefore, a J&W Scientific DB-1701 capillary column (length 60 m, 0.25 mm internal diameter, 0.3 µm film thickness) was chosen for the combined method. Furthermore, a longer temperature programme with a low temperature rate gave better results (2 min at 90°C followed by an increase to 180°C at a rate of 25°C / min, followed by an increase to 300°C at a rate of 1.5°C / min, finally held for 9.4 min at 300°C). With these changes, it was possible to overcome the problem of co-elution. A chromatogram of all PBDE and PBB congeners is shown in Figure 8.

The procedure in the method validation was identical to the PCNs and included the following parameters:

- Linear response ranges
- Limit of detection and limit of quantification
- Precision
- Recovery
- Blank values

The linear response ranges were tested by duplicate analysis of nine standards, covering a concentration range from 0.125 ng / ml to 25 ng / ml. Linear calibration curves through the origin could be chosen for the whole concentration range, with the r^2 values given in Table 9. LOD and LOQ were determined in the same way as described for PCNs (chapter 4.2.3). In order to calculate the LOD or LOQ of the individual sample, the values in Table 9 have to be divided by the sample amount. Two blanks were extracted and analysed in the same way as the biota samples and did not show any peaks at the retention times of the PBBs.

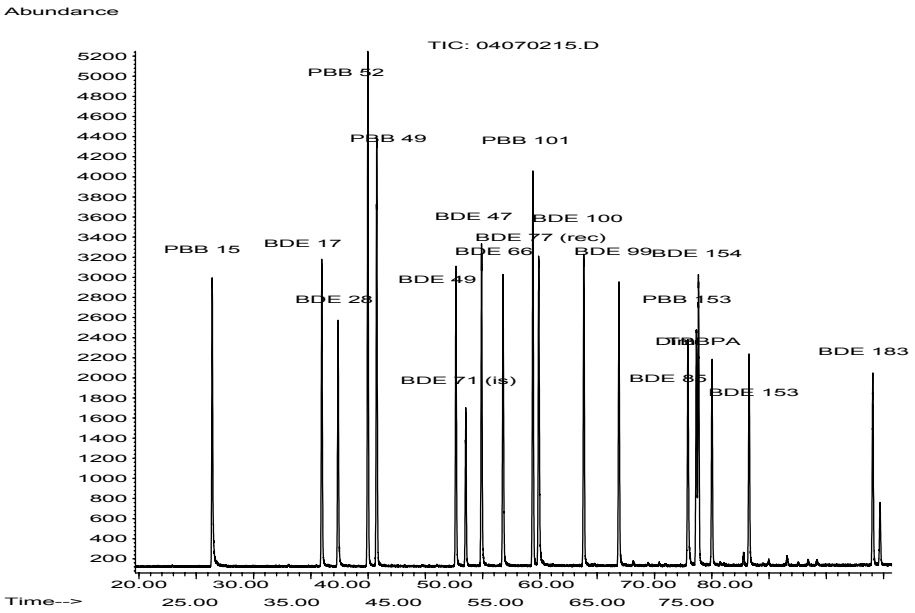

Figure 8: Chromatogram of a standard of PBDEs and PBBs (15 ng / ml)

For the determination of the analytical precision, 12 samples of sand launce oil were spiked with PBBs at two concentration levels. The standard deviation between the six samples of identical concentration gives the uncertainty in Table 9. As described for PCNs, the long-term precision will be monitored in control-charts, which were established as part of the method development. However, as PBBs do not occur in detectable amounts in the internal reference material, the control charts will have to be based on spiked samples.

The recovery describes the concentration of the PBB congeners in relation to so-called archives spikes. These spikes are solutions of the recovery and internal standards prepared at the same time as the recovery and internal standards were added to the samples. At the high concentration level of 10 ng / ml the recovery rates range from 89-107%, which is well within the acceptable range of 80-120%. At the low level of 1 ng / ml, however, the recovery rates generally were higher and exceeded the 120 % for BB-15 and BB-153.

The high recoveries might be related to losses of the archives spikes which were evaporated for a solvent change. The standard deviations within the recovery experiment are low, between 2.06-5.33 at the low concentration and 2.41-5.14 at the high concentration. It has to be noted that spiked contaminants do not bind to the matrix in the same manner as in environmental samples and might therefore be extracted more easily (Covaci et al., 2003). Thus, the recovery rates are likely to be maximum values.

After the successful separation of BB-153 and BDE-154 on a DB-1701 capillary column, no other co-elution occurred for the compounds tested (PCNs, PBDEs and PCBs). Interference of the matrix with the recovery or internal standards is tested for each run as part of the routine quality assurance. Three samples are analysed that do not contain internal standards and can thus show other peaks at their retention times.

The analysis of the samples from Greenland and the Faroe Islands included the quality assurance elements described for PCNs (chapter 4.2.4). The laboratory participated in the QUASIMEME development exercise on Brominated Flame Retardants in 2002 and 2003. The results are summarised by Asmund et al. (2004).

Table 9: Parameters in the instrumental analysis of PBBs. Target ion: m/z=79 and qualifier ion: m/z=81 for all compounds. Low concentration: 1 ng/ml. High concentration: 10 ng/ml. "Uncertainty" gives the relative standard deviations of PBBs in six samples of sand launce oil. For corresponding details for PBDEs, see Christensen et al. (2001).

Compound	r^2 Linear response	LOD (ng/ml)	LOQ (ng/ml)	Low concentration			High concentration		
				Uncertainty (%)	Average recovery (%)	Recovery range (%)	Uncertainty (%)	Average recovery (%)	Recovery range (%)
BB-15	0.995	0.0743	0.124	3.19	120	117-127	5.59	98	90-107
BB-49	1.000	0.0675	0.113	3.96	106	101-110	4.12	98	90-101
BB-52	0.999	0.0750	0.125	2.25	106	103-108	3.90	98	91-101
BB-101	0.999	0.0750	0.125	3.07	108	105-113	2.64	101	97-104
BB-153	0.998	0.0750	0.125	5.25	114	106-122	5.63	99	89-104

5.1.3 Results and discussion

Summed concentrations of the PBDE and PBB congeners in the samples from Greenland and the Faroe Islands are shown in Figure 9 and Figure 10, respectively. The concentrations presented for the Greenland samples are an average of the two analysed samples. The detailed results of the individual congeners in the two samples are given in Table 10 to Table 13. BDE-85 was not detected in any of the samples. BDE-17 and BDE-183 could be detected in the pilot whale samples from the Faroe Islands, but were below the limits of quantification or detection in the remaining samples. In the calculation of the summed concentrations, values below the LOQ were substituted by half LOQ, while concentration below the LOD were considered zero.

Sediments are not included in Figure 9 since all concentrations were below the limit of detection. In a study on ΣPBDE concentrations from Denmark, the sum of the BDEs 47, 99, 100 and 153 only exceeded 1 ng/g dry weight in samples from Randers Bay and Copenhagen Harbour (Christensen and Platz, 2001). However, BDE-209 levels were considerably higher, with maximum values of 21.5 ng/g dry weight in Copenhagen Harbour. The fully brominated congener BDE-209 is unstable at high temperatures and has to be analysed separately. Thus, it was not part of the current project. Its occurrence in Greenland biota has been shown for peregrine falcon eggs (Sørensen et al., 2004). Thus, BDE-209 might also be present in Greenland sediment.

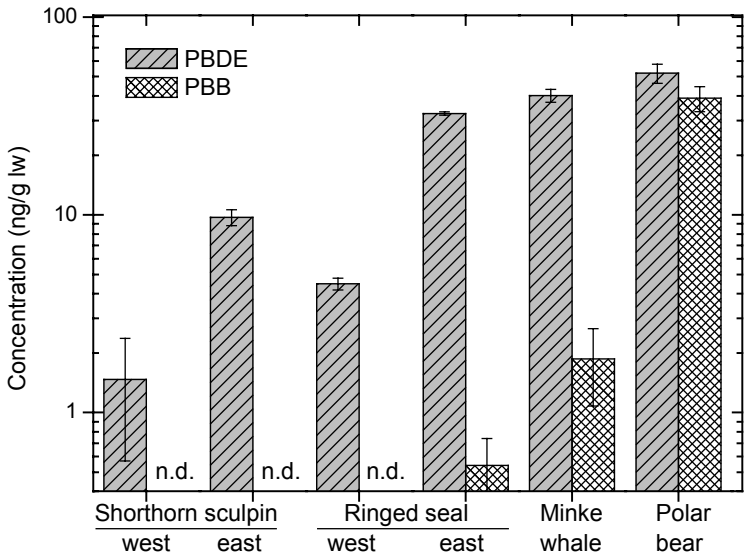

Figure 9: Concentrations of PBDEs and PBBs in the samples from Greenland. The concentrations are averages of the two samples analysed. The error bars indicate the difference from the concentrations in the two samples analysed. Concentrations < LOQ are substituted with ½ LOQ. Values < LOD are not considered in the sum. n.d.: < LOD.

The summed PBDE concentrations range from 1.5 ng/g lw in shorthorn sculpin liver from West Greenland to 52 ng/g lw in polar bear from East Greenland. A clear concentration increase can be seen in the order shorthorn sculpin < ringed seal < polar bear, which indicates biomagnification of PBDEs along the Greenland marine food chain. This tendency is more pronounced for PBDEs than observed for PCNs (Figure 6). Boon et al. (2002) showed biomagnification in ΣPBDE concentrations of more than an order of magnitude from gadoid fish sampled in 1999 to marine mammals of the North Sea. ΣPBDE data from the St. Lawrence Estuary collected in 1999/2000 were reviewed by Law et al. (2003) and showed a concentration range of more than three orders of magnitude between invertebrates and marine mammals.

Table 10: PBDE concentrations (ng/g lipid weight (lw)) in samples from Greenland. BDE-85 (penta-BDE) and BDE-183 (hepta-BDE) are not included in the table since all samples were below the limit of detection. The homologue group is given for each congener.
[a)] Values < LOQ are substituted by half LOQ. [b)] Values < LOQ are not included in ΣPBDE

Species	Reg. no.	BDE-17	BDE-28	BDE-47	BDE-49	BDE-66	BDE-99	BDE-100	BDE-153	BDE-154	ΣPBDE [a)]	ΣPBDE [b)]	Rec. (%)
		tri-	tri-	tetra-	tetra-	tetra-	penta-	penta-	hexa-	hexa-			
Polar bear	03-0127	n.d.	< 0.63	34.57	n.d.	n.d.	2.05	1.47	18.35	1.09	57.85	57.53	89
	03-0128	n.d.	n.d.	26.17	n.d.	n.d.	2.98	1.21	14.90	1.02	46.28	46.28	109
Minke whale	03-0130	< 0.37	0.95	23.33	0.57	0.88	8.41	2.99	1.78	3.20	41.96	41.45	86
	03-0131	< 0.29	0.76	20.12	1.11	< 0.72	8.73	2.84	1.17	1.88	37.12	36.61	95
Ringed seal, East Greenland	03-0121	n.d.	1.53	24.19	0.34	< 0.63	2.83	1.61	0.66	0.44	31.92	31.60	88
	03-0122	n.d.	0.93	26.43	0.26	n.d.	2.90	1.41	0.81	0.39	33.14	33.14	88
Ringed seal, West Greenland	03-0124	n.d.	n.d.	3.36	n.d.	0.44	0.36	n.d.	n.d.	n.d.	4.16	4.16	84
	03-0125	n.d.	n.d.	4.10	n.d.	0.40	0.29	n.d.	n.d.	n.d.	4.79	4.79	85
Shorthorn sculpin, East Greenland	03-0117	n.d.	n.d.	8.23	n.d.	< 0.38	0.78	n.d.	n.d.	0.59	9.79	9.60	100
	03-0118	n.d.	n.d.	8.54	n.d.	n.d.	0.56	n.d.	n.d.	0.52	9.62	9.62	91
Shorthorn sculpin, West Greenland	03-0119	n.d.	n.d.	< 1.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.57	n.d.	88
	03-0120	n.d.	n.d.	< 1.76	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.37	2.37	97
Sediment	03-0267	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	89
	03-0268	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	102

PBDE concentrations in 20 ringed seals (females and males) and 20 shorthorn sculpins (females) from the east coast of Greenland collected in 2001 were published by Vorkamp et al. (2004b). The concentrations cover a range of 21-51 ng/g lw for ringed seals and 4.2-17 ng/g lw for shorthorn sculpins. The median values were 35 and 8.9 ng/g lw, respectively, and thus very close to the concentrations obtained in this study. The concentrations in shorthorn sculpins are similar to concentrations observed in samples from a reference station in Southwest Greenland collected in 2000 (Christensen et al., 2002).

Lower concentrations in samples from the west coast compared to the east coast of Greenland can be noted for shorthorn sculpins and ringed seals. PBDE concentrations in black guillemot eggs from East Greenland were three times higher than those found in black guillemot eggs from the west coast of Greenland, collected in the same year (Vorkamp et al., 2004a,b). In this study, the east/west ratio was 7-8 for ringed seals and 4-16 for shorthorn sculpin. Previous studies in Greenland have consistently shown higher concentrations of organochlorine compounds to occur in marine animals from East Greenland than in those from West Greenland probably as a result of their transport pathways (Riget et al., 2004). Apparently, the same tendency is seen for PBDEs in the marine animals of Greenland.

Concentrations of ΣPBDE in ringed seals from the Canadian Arctic were similar to the levels in ringed seals from West Greenland, but clearly lower than those from East Greenland (Ikonomou et al., 2002). ΣPBDE in ringed seal blubber from the Canadian Arctic was based on 13 congeners, but the concentrations could be re-calculated by summing concentrations for the same congeners as were analysed in this study. Male seals aged 0-15 years collected in 2000 contained about 4.6 ng/g wet weight ΣPBDE on average. The individuals from West Greenland analysed in this study were males aged 0.5-3.5 years, and their summed concentrations were 4.1 and 4.8 ng/g ww. The ringed seals from East Greenland were males aged 3.5-7.5 years and contained ΣPBDE concentrations which were about 7 times higher than those found in the Canadian seals.

In a study including ringed seals collected on Svalbard in 1981, BDE-47, BDE-99 and an unknown penta-BDE compound were detected at a summed concentration of 51 ng/g lw (Sellström et al., 1993). Today's knowledge on PBDE patterns in biota samples suggests that the unknown penta-BDE compound could be BDE-100. Including BDE-100 in the sum calculation, the corresponding summed concentration would be 30 ng/g lw (East Greenland) and 4.5 ng/g lw (West Greenland) in the ringed seal samples of the present study.

In Europe, the penta-mix PBDE formulation was used to a lesser extent than in the United States and was banned recently in the European Union (Alaee et al., 2003). While the sources of PBDEs in the Canadian Arctic are likely to be from usage in North America, Svalbard and the east coast of Greenland mainly receive contaminants from Europe and Asia (Gregor et al., 1998). Still, higher levels were found in ringed seals from East Greenland and on Svalbard than in the Canadian Arctic.

The pilot whale samples from the Faroe Islands contained the highest ΣPBDE concentrations of all the samples analysed, ranging from 372 ng/g lw in female pilot whales to 1018 ng/g lw in juvenile pilot whales (Figure 10). PBDEs had previously been analysed in pilot whales from the Faroe Islands, which contained even higher levels, with 840 ng/g lw in females and 3160 ng/g lw in juveniles (Lindström et al., 1999). Higher concentrations in juveniles than in adults were attributed to lactational transfer of PBDEs, which also explains the comparably low concentrations found in the female animals. The same tendency in the contaminant distribution between juveniles, females and males was also observed for organochlorines (Dam and Bloch, 2000).

Table 11: PBDE Concentrations (ng / g lipid weight (lw)) in samples from the Faroe Islands. BDE-85 is not included in the table since all samples were below the limit of detection. The homologue group is given for each congener. [a)] Values < LOQ are substituted by half LOQ. [b)] Values < LOQ are not included in ΣPBDE

Species	Reg. no.	BDE-17	BDE-28	BDE-47	BDE-49	BDE-66	BDE-99	BDE-100	BDE-153	BDE-154	BDE-183	ΣPBDE [a)]	ΣPBDE [b)]	Rec. (%)
		tri-	tri-	tetra-	tetra-	tetra-	penta-	penta-	hexa-	hexa-	hepta-			
Pilot whale, Juveniles	02-1754	0.84	29.59	561.00	8.34	25.67	216	89.12	36.16	50.10	0.86	1017.70	1017.70	86
Pilot whale, Females	02-1758	0.52	11.42	173.10	4.68	12.08	87.06	33.18	22.60	26.69	1.09	372.42	372.42	82
Pilot whale, Males	02-1759	0.85	30.09	535.80	9.13	25.18	180.15	83.42	39.10	42.52	1.03	950.27	950.27	94
Fulmar, Females	02-1762	n.d.	n.d.	8.24	< 0.41	n.d.	5.72	1.26	4.32	1.83	n.d.	21.56	21.36	83
Fulmar, Males	02-1763	n.d.	1.22	28.78	1.50	1.12	16.33	4.33	16.28	4.83	n.d.	74.39	74.39	85

The results for ΣPBDE in fulmar also show a large concentration difference between female and male birds, with 22 ng/g lw in females and 74 ng/g lw in males. Thus, the summed concentration in male fulmars is in the same order of magnitude as that in polar bear (Figure 9). Analyses of black guillemot livers from Greenland gave PBDE concentrations an order of magnitude below the concentrations in fulmars (Vorkamp et al., 2004a).

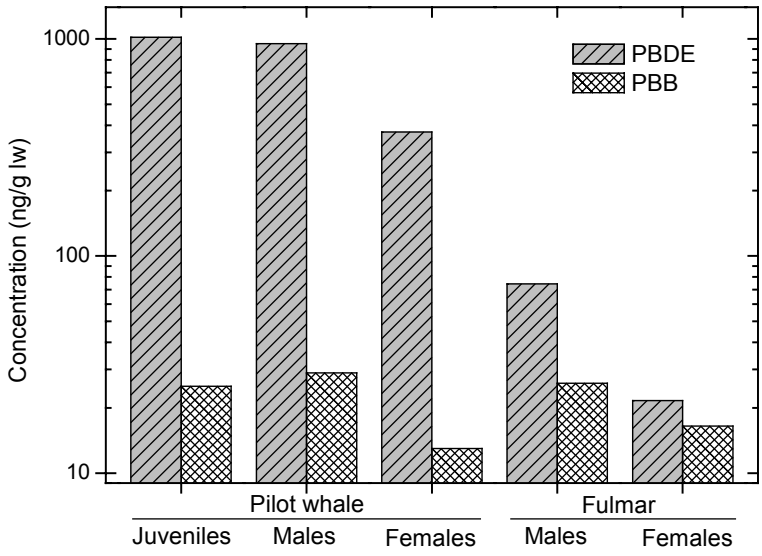

Figure 10: Concentrations of PBDEs and PBBs in the samples from the Faroe Islands. Concentrations < LOQ are substituted with ½ LOQ. Values < LOD are not considered in the sum.

Little information is available on PBBs in the environment. de Boer et al. (1998) detected PBBs in sperm whales, whitebeaked dolphins and harbour seals. The concentration in sperm whale blubber was approximately 2 ng/g wet weight, which was about 50 times lower than the concentrations of PBDEs. The concentrations in minke whale blubber was almost identical, with about 2 ng/g wet weight, while pilot whale blubber from the Faroe Islands contained ΣPBB concentrations an order of magnitude higher, with up to 26 ng/g wet weight in males. The ratios between PBDE and PBB are similar to those observed by de Boer et al. (1998).

The PBDE/PBB ratio in pilot whales is intermediate when compared to ringed seals and minke whales. The PBDE concentrations in minke whales and ringed seals are similar, but the minke whales contain relatively more PBBs. This is reflected by PBDE/PBB ratios of 22 in minke whales and 60 in the ringed seals. However, for some of the other animals analysed, this ratio varies considerably: In polar bear, the summed PBB concentration was 75 % of the ΣPBDE (PBDE/PBB ratio of 1.34). Fulmars also had a higher relative content of PBBs, which was 35 % and 76 % of the PBDE concentrations in male and female fulmars, respectively (PBDE/PBB ratios of 2.87 and 1.31, respectively). Thus, the ΣPBB concentration is in the same order of magnitude as the PBDE concentration.

Jansson et al. (1993) studied the accumulation of the hexabrominated biphenyl BB-153 from Baltic herring to grey seal and compared the biomagnification of hexa-BB, PBDEs and the PCB congener CB-153. They found that BB-153 biomagnified to the same extent as CB-153 and more than PBDEs.

Concentrations of BB-153 in freshwater and marine fish ranged between < 0.1 – 0.4 ng/g lipid weight, being 50-1000 times lower than the concentration of BDE-47 in the same animals (Jansson et al., 1993). Unfortunately, the concentrations of PBBs were below the limit of detection in the shorthorn sculpins analysed in this study. It would be interesting to study whether or not they have an equally large PBDE/PBB ratio. Ringed seals from Svalbard collected in 1981 contained BB-153 at a concentration of 0.42 ng/g lipid weight, which is comparable with the concentration of BB-153 found in the ringed seal samples from East Greenland. In the samples from West Greenland, PBBs could not be detected, which may reflect the trend of higher levels in East than in West Greenland. In grey seals and osprey from the Baltic Sea, BB-153 was 26 and 22 ng/g lipid weight, respectively (Jansson et al., 1993). Thus, the concentration in osprey was similar to the concentration measured in the fulmar samples from the Faroe Islands.

Table 12: PBB concentrations (ng/g lipid weight (lw)) in samples from Greenland. [a)] Values < LOQ are substituted by half LOQ. [b)] Values < LOQ are not included in ΣPBB. For recovery, see Table 10.

Species	Reg. no.	BB-15	BB-49	BB-52	BB-101	BB-153	ΣPBB [a)]	ΣPBB [b)]
Polar bear	03-0127	n.d.	n.d.	n.d.	< 0.30	33.11	33.26	33.11
	03-0128	n.d.	n.d.	n.d.	0.31	44.26	44.57	44.57
Minke whale	03-0130	n.d.	n.d.	0.55	0.51	1.21	2.27	2.27
	03-0131	n.d.	< 0.36	< 0.32	< 0.36	0.56	1.08	0.56
Ringed seal, East Greenland	03-0121	n.d.	n.d.	n.d.	n.d.	0.34	0.34	0.34
	03-0122	n.d.	< 0.32	n.d.	< 0.32	0.42	0.74	0.42
Ringed seal, West Greenland	03-0124	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0125	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Shorthorn sculpin, East Greenland	03-0117	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0118	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Shorthorn sculpin, West Greenland	03-0119	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sediment	03-0267	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0268	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 13: PBB concentrations (ng/g lipid weight (lw)) in samples from the Faroe Islands. [a)] Values < LOQ are substituted by half LOQ. [b)] Values < LOQ are not included in ΣPBB. For recovery, see Table 11.

Species	Reg. no.	BB-15	BB-49	BB-52	BB-101	BB-153	ΣPBB [a)]	ΣPBB [b)]
Pilot whale, Juveniles	02-1754	n.d.	3.10	3.74	5.67	12.60	25.11	25.11
Pilot whale, Females	02-1758	n.d.	1.17	1.12	1.99	8.71	12.99	12.99
Pilot whale, Males	02-1759	n.d.	3.05	3.24	5.72	16.93	28.94	28.94
Fulmar, Females	02-1762	n.d.	< 0.46	n.d.	n.d.	16.25	16.48	16.25
Fulmar, Males	02-1763	n.d.	0.37	n.d.	n.d.	25.54	25.91	25.91

The BDE congener profiles of the samples from Greenland and the Faroe Islands as well as the composition of the commercial Penta-BDE mixture Bromkal 70-5DE are shown in Figure 11 to 13. The pattern in the technical product was determined by Sjödin et al. (1998). The main congeners are BDE-47 (tetra-BDE) and BDE-99 (penta-BDE), which account for more than 70% on a weight basis. BDE-183 is the major congener found in commercial Octa-BDE, but has not been detected in the samples of this project, except for the pilot whale samples from the Faroe Islands. It is therefore not included in Figure 12 and Figure 13.

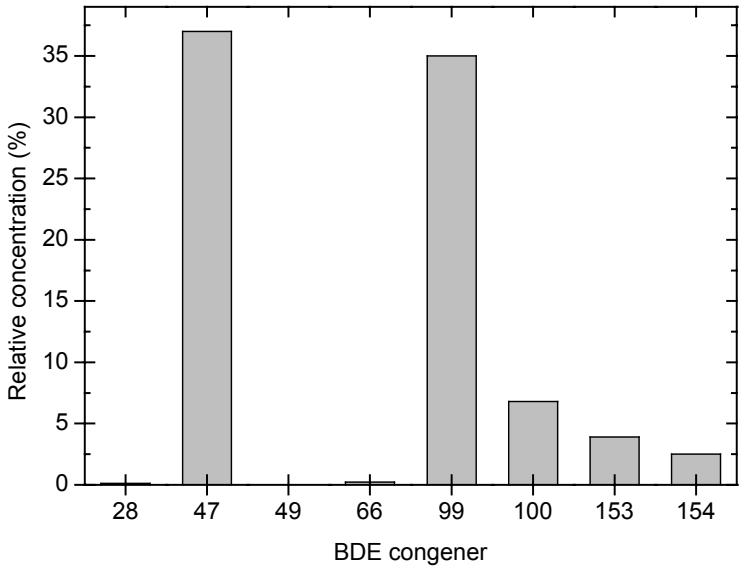

Figure 11: PBDE congener pattern in the commercial Penta-BDE mix BromKal 70-5DE according to Sjödin et al. (1998)

Biota samples are usually dominated by the tetra- and penta-BDEs. Ikonomou et al. (2002) presented the congener profile of ringed seals from the Canadian Arctic, which was very similar to the PBDE composition in the Greenland seals (Figure 12). Both the Canadian samples and the ringed seal samples of the present study were depleted in the contribution of BDE congeners with five or more bromine atoms as compared to the commercial Penta-mix. This observation was partly explained by an "atmospheric distillation", meaning that com-

pounds with low levels of bromination are more likely to be transported by air and water. Furthermore, high dietary uptake efficiencies were shown for BDE-47, BDE-99 and BDE-153. On the other hand, BDE-99 and BDE-153 were also eliminated rapidly, indicating that these congeners may accumulate to a lesser degree than BDE-47 (Ikonomou et al., 2002).

However, animals from higher trophic levels had a considerable contribution of penta-BDE or even the hexa-BDE congeners BDE-153 and BDE-154. All samples from the Faroe Islands contained approximately 20% BDE-99 (Figure 13). The pattern in the pilot whale samples was similar to that presented for harbour porpoise from British Columbia (Ikonomou et al., 2002). The higher content of the penta-BDE compared to that of the ringed seal samples was explained by a more direct impact from industrialised regions.

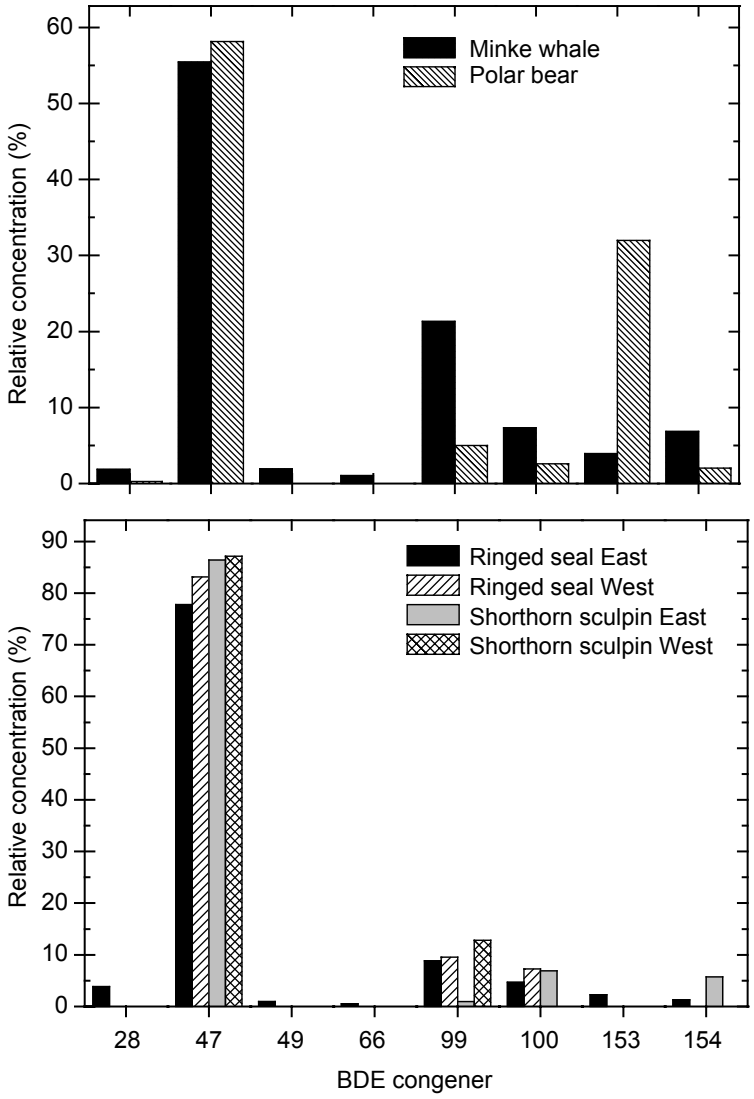

Figure 12: PBDE congener pattern in samples of polar bear, minke whale, ringed seal and shorthorn sculpin from Greenland

BDE-153 accounted for about 20% in the fulmar samples and even more than 30% in the polar bear samples (Figure 12). The high abundance of BDE-153 was also observed in peregrine falcon eggs from Sweden and from Greenland (Lindberg et al., 2004; Sørensen et al., 2004).

In the present study, differences in exposure may explain some of the differences in the BDE patterns since the samples originate from the Faroe Islands as well as East and West Greenland. The animals studied represent predator and prey at different trophic levels. Thus, differences in diet are unlikely to explain all the variation in PBDE patterns. More detailed studies will be needed to clarify the large differences in BDE congener composition.

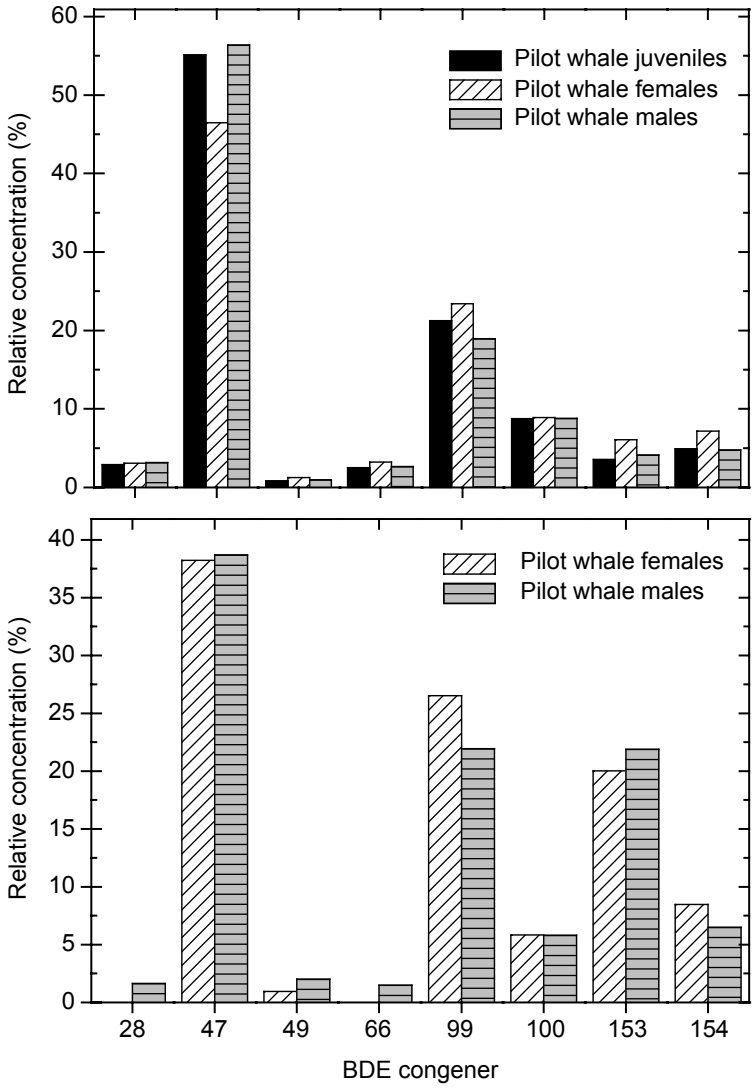

Figure 13: PBDE congener pattern in pilot whale and fulmar samples from the Faroe Islands

Summarising the results obtained for PBDEs and PBBs in this screening project, it can be noted that both compound groups seem to biomagnify along the marine food chain, in a similar manner to PCBs. PBBs show indications of a higher biomagnification potential than

PBDEs. Even though their absolute concentrations are lower than those of PBDEs, the PBDE/PBB ratio increases in the order ringed seal<pilot whale<minke whale<fulmar<polar bear, leading to almost equal concentrations of PBDEs and PBBs in polar bear. Thus, PBB should not be neglected in the overall contaminant assessment.

Apparently, the compounds follow the same spatial trend as previously observed for organochlorine compounds, with higher concentrations in East Greenland than in West Greenland. It is recommended to establish monitoring of PBDEs in order to study whether the regulatory measures taken in Europe to ban the Penta-BDE will have an effect on the concentrations in Greenland and on the Faroe Islands. As both pilot whale and fulmar are part of the traditional diet on the Faroe Islands, human exposure of PBDEs with the food will have to be taken into account.

5.2 Tetrabromobisphenol A (TBBPA) and Hexabromocyclododecane (HBCD)

5.2.1 Introduction

TBBPA is the most abundant brominated flame retardant currently in use (Hakk, 2001). Between 1992 and 1998, the global demand for TBBPA had increased from 50 000 to 145 000 tons per year and is expected to keep increasing. In Europe, the annual demand for TBBPA is estimated to be 40 000 tons (RIKZ, 2000). About 90% of TBBPA use is for the production of resins used in printed circuit boards (Hakk, 2001). TBBPA has a very low vapour pressure (< $133x10^{-6}$ Pa at 20°C). The water solubility is reported as 720 µg/l at 20°C, but increasing to 4.2 mg/l at 25°C. The log K_{OW} has been determined as 4.5-5.3 (RIKZ, 2000).

Information about TBBPA in the environment is still rare. In water and air, TBBPA was only found in traces, even near production sites, probably as a consequence of sorption to sediment and soil (WHO, 1995). A Swedish study showed increasing TBBPA levels downstream a plastic-pro-ducing plant (Sellström and Jansson, 1995). In soils, TBBPA has half-lives of 50-100 days and is degraded both aerobically and anaerobically. The phenolic groups might be methylated, changing the rather polar nature of the parent compound to the lipophilic characteristics of dimethyl-TBBPA. This compound has been found in sediment, fish and shellfish (WHO, 1995) and has also been detected in peregrine falcon eggs from Southern Greenland (Sørensen et al., 2004).

HBCD is a non-aromatic brominated flame retardant mainly used in polystyrene resins and textiles (Lund et al., 2001). Its demand in the European Union is estimated to be about 10 000 tons per year. HBCD has a vapour pressure of $62.7x10^{-6}$ Pa at 20°C and low water solubility (3.4-8 µg/l). The log K_{OW} is 5.8-7.0 (RIKZ, 2000). HBCD has been detected at levels of about 8000 ng/g lw in pike in a Swedish river receiving wastewater from several industries (Sellström et al., 1998). The compound appears to be bioavailable and can potentially bioaccumulate. HBCD was also included in a Swedish study on peregrine

falcon eggs, yielding concentrations in a range of 34-2400 ng / g lw in Swedish study and <0.1-230 ng / g lw in a study from Greenland (Sellström et al., 2001; Sørensen et al., 2004).

5.2.2 Analytical methods

The project included the attempt to develop an analytical method for TBBAP and HBCD in biota and sediment. A detailed report on the method development is attached in chapter 11.2.

The extraction and purification of TBBPA and HBCD was based on two different methods: (1) The methods for PCBs and PBDEs as described by Cleemann et al. (1999) and Christensen et al. (2001). (2) A fractionated analysis separating polar and non-polar analytes as described by Sellström and Jansson (1995). In order to optimise the extraction efficiency, method (1) was varied using different combinations of solvents. Finally, soxhlet extraction with hexane:acetone (4:1) and the fractionated analyses as described by Sellström and Jansson (1995) were chosen for further experiments.

The purification procedures tested were based on adsorption chromatography with different solid and mobile phases. The initial experiments were conducted with standard solutions. Best results were obtained for packed columns, consisting of activated alumnium oxide, silica gel and acid-impregnated silica gel, and elution with hexane:dichloromethane. It has to be noted that the application of dichloromethane in the laboratory should be minimised due to the risk of health impacts.

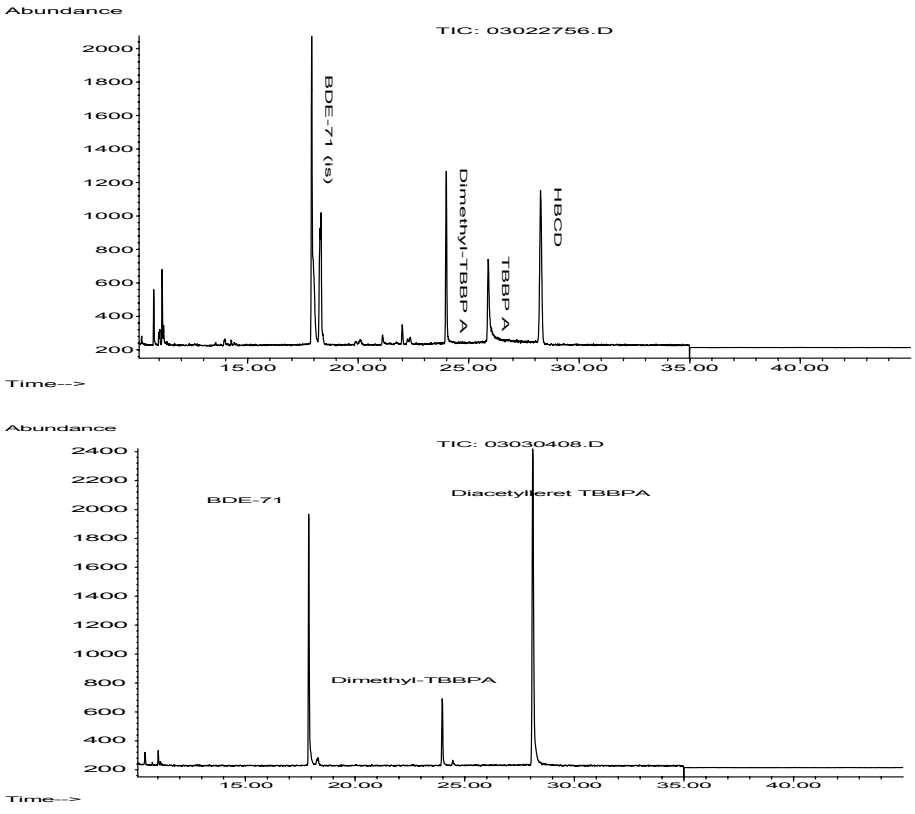

Figure 14: Chromatograms of TBBPA, dimethyl-TBBPA, HBCD and diacetyl-TBBPA

However, problems occurred when the purification was repeated with sand launce oil, the internal reference material, as TBBPA could no longer be eluted from the packed column. Further experiments were conducted to overcome this problem, for instance by reducing the amount of aluminium oxide in the packed columns, but they did not give satisfactory results. Therefore, different clean-up methods will have to be considered, possibly based on size exclusion chromatography.

The extracts were analysed by GC-MS with negative chemical ionisation (NCI). The method was identical to the analytical method for PBDEs (Christensen et al., 2001). Single ion monitoring (SIM) was chosen with the ions m/z=79 and m/z=81 for both compounds. Additionally, m/z=160 was monitored for HBCD and m/z=544 was monitored for TBBPA. Due to the rather polar character of TBBPA, the GC-analysis yielded a very low response with tailing peaks. Therefore, TBBPA was derivatised to diacetyl-TBBPA which was monitored at m/z=505. Chromatograms of the compounds are shown in Figure 14. Another drawback of the GC-method is that the three HBCD isomers cannot be distinguished. Thus, the GC-MS method gives acceptable, but not optimal results for the analysis of TBBPA and HBCD.

It has to be concluded that it was not possible to analyse TBBPA and HBCD in the sediment and biota samples from Greenland and the Faroe Islands. The main obstacle was the purification method. Different approaches for the clean up of the extracts will have to be considered. Furthermore, separate analyses of TBBPA and HBCD might be recommendable to take into account their different physical-chemical characteristics.

6 Synthetic musk compounds

6.1 Introduction

Synthetic musk compounds impart desirable odours and are used as fragrances in personal care and household products, such as cosmetics, soaps, laundry detergents, fabric softeners, household cleaning products, air fresheners etc. (Rimkus, 1999). The two main groups of synthetic musk compounds are nitro musks and polycyclic musks. Initially, nitro musks were used as synthetic musk fragrances, however, toxicological concerns led to restrictions on the use of musk ambrette and a partial phase out of musk xylene in some West European countries (Rimkus, 1999). According to Kallenborn et al. (1999a), the main toxicological risk potential is attributed to the amino metabolites that are formed by microbial degradation.

Thus, the production and use of polycyclic musk compounds has increased. In 1996, the world-wide production volume of polycyclic musks was 5600 t/year and accounted for 70% of the world market (Gebauer and Bouter, 1997). The main compounds are Galaxolide (HHCB) and Tonalide (AHTN). Little is known about toxicological threats, but Kallenborn et al. (1999a) assume a connection between polycyclic musks and endocrine induction. Musk xylene is included on the OSPAR list of chemicals for priority action (OSPAR, 2002).

Due to their occurrence in consumer products, musk compounds primarily enter the environment through wastewater and sewage sludge. Consequently, the highest concentrations in the environment have been found close to industrial sites and urban areas (Rimkus, 1999). To our knowledge, no data have been obtained from the Arctic or other remote areas. However, surveys in Europe, Japan and Canada have demonstrated the ubiquitous distribution of the musk compounds, which reflects the persistence of these compounds (Yama-gishi et al., 1983; Rimkus, 1999). The detection of musk compounds in air indicates that air is an important transport medium for synthetic musk compounds (Kallenborn et al., 1999a; 1999b).

Musk compounds have been detected in aquatic biota from the freshwater environment and in blue mussels and shrimps from the North Sea. In the latter case, however, the polycyclic compounds were below the detection limit, and only musk ketone was detected (Rimkus and Wolf, 1997; Rimkus, 1999). In general, the concentrations of HHCB and AHTN exceed those of the nitro musks. In many fish samples, the following order of concentration was observed: HHCB > AHTN > musk ketone > musk xylene (Rimkus, 1999). These findings are generally supported by a recent Nordic study on the presence of synthetic musks in abiotic matrices (rainwater, sewage sludge) and biota (fox liver, blue mussels) (Mogensen et al., 2004). However, in biota samples from the Canadian aquatic ecosystem, musk ketone was the dominant compound, while the levels of HHCB, AHTN and musk xylene were 1-2 orders of magnitude lower (Gatermann et al., 1999; Rimkus, 1999). This difference is pro-bably

caused by the continuing use of nitro musks in Canada, which have been replaced by polycyclic musks in Europe (Rimkus, 1999).

The $\log K_{OW}$ values of HHCB and AHTN range between 5.7-5.9, which is in the same order of magnitude as lipophilic compounds such as PCBs, while those of musk xylene and musk ketone are 4.9 and about 4.3, respectively (reviewed by Rimkus, 1999). Bioconcentration experiments have indicated that HHCB and AHTN are metabolised to more polar compounds in fish. The metabolisation seems to be species-dependent, yielding varying bioconcentration factors for different species (reviewed by Rimkus, 1999).

6.2 Analytical methods

Synthetic musk compounds were analysed in biota, including liver and fat tissues, and sediment samples by gas chromatography (GC) and mass spectrometry (MS) in selected ion monitoring (SIM) mode. The applied extraction, clean-up and chromatographic techniques used in this project are modified versions of methods described in the literature, but so far the applied method has not been fully optimised and validated.

6.2.1 Extraction

Aliquots of approximately 2 g of homogenised liver or fat tissue were weighed. For sediments, approximately 2 g of drained, homogenised sample were weighed. Using a mortar and a piston, each sample was thoroughly ground with 10-15 g of pre-cleaned sodium sulphate to give an almost dry powder. The samples were then transferred to 33 ml stainless steel ASE (accelerated solvent extraction) cells that already had been partly filled with 20-25 g of pre-cleaned alumina oxide (neutral). The samples were then spiked with a mixture of internal recovery standards (deuterium labelled musk and phthalate compounds), and on top of the sample another approximately 5 g of sodium sulphate were added and the cells were carefully closed. The use of ASE for the extraction of musk compounds from environmental samples has recently been described by Draisci et al. (1998) and by Osemwengie and Gerstenberger (2004). The role of the bottom layer of alumina oxide was to act as a fat retainer (Sporring and Björklund, 2004). The filled cells were then loaded into the Dionex ASE unit (ASE 200 incl. solvent controller) and extracted in 2 x 20 min. cycles at 75°C (1500 psi) using pentane/dichloromethane (90/10, v/v) as solvent. After the extraction, extracts were concentrated to 4 ml using a rotary evaporator.

6.2.2 Clean-up

To free the concentrated sample extracts of remaining lipid and other high-molecular-weight material they were purified by gel permeation chromatography (GPC). This technique has been applied for the clean-up of synthetic musk compounds in other types of biota (Rimkus, Rummler and Nausch, 1995) and in municipal sewage effluent (Osemwengie and Steinberg, 2001). A preparative Gilson HPLC instrumentation comprising a dual piston pump, a dual channel UV/

Vis-detector, a syringe piston pump and a combined injector/fraction collector was used. The chromatographic clean-up was obtained by a combination of a PLgel Prep Guard column (25 mm x 25 mm ID) and a PLgel GPC column (60 mm x 25 mm ID) loaded with 10 µm/50 Å polystyrene material. The system was operated at 7 ml/min using a mixture of 2% (v/v) methanol in dichloromethane as eluent. Eluents were detected by simultaneously monitoring the UV absorption at 225 and 254 nm. Solutions of synthetic musk standards were analysed using the same conditions to establish the appropriate time window for collection of fractions of desired analytes. A clean-up run included the injection of 1000 µl and the subsequent collection of 38.5 ml eluent. Typical GPC chromatograms of synthetic musk standards and a liver sample extract are shown in Figure 15. For each extract, two runs were completed to process a total of 2 ml. 1 ml toluene was added to the collected GPC fractions as keeper, the fractions were concentrated to 1 ml and spiked with 100 µl internal standard comprising three fluorinated polycyclic aromatic hydrocarbons (F-PAHs), 1-fluoronaphthalene, 3-fluorophenanthrene and 1-fluoropyrene, at approximately 1000 ng/ml.

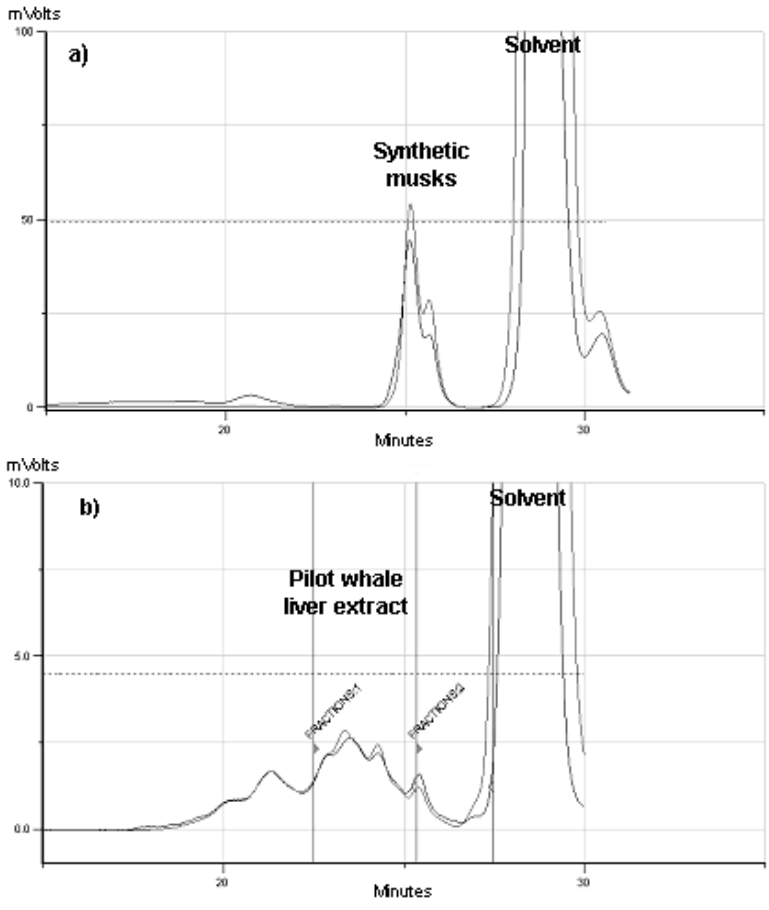

Figure 15: GPC chromatograms of a) mix of synthetic musk standards and b) pilot whale liver extract.

6.2.3 Instrumental analysis

Sample extracts were analysed by GC-MS/SIM with electron impact ionisation (EI). The toluene extracts were chromatographed on a J&W DB5-MS capillary column (60 m x 0.25 mm ID x 0,25 µm film column using an Agilent GC-MS system comprising a 6890 GC, a 5973 MSD (mass selective detector) and 7683 injector. Helium was used as carrier gas, and the temperature programme was as follows: 1.0 min at 90°C followed by an increase to 140°C at 25°C/min, increase to 195°C at 5°C/min, increase to 205°C at 1°C/min, increase to 240°C at 5°C/min, and a further increase at 10°C/min to 280°C, which are kept iso-thermal for 5 min. Other instrumental parameters were as follows: injection/flow: 2 µl injected using the pulsed splittless mode at 250°C and 50 psi dropping to about 28 psi after 2 min to maintain a con-stant flow of 1.5 ml/min.; MSD transfer line and ion source: 280°C and 250°C, respectively. The analytes were grouped in four SIM windows with each ion having a dwell time of about 50-70 msec. The m/z values of target and qualifier ions of each analyte are listed in Table 14, and the selected ions are in accordance with those described by e.g. Osemwengie and Steinberg (2001). Figure 16 shows a TIC (total ion) GC-MS chromatogram of the synthetic musk compounds analysed in this project.

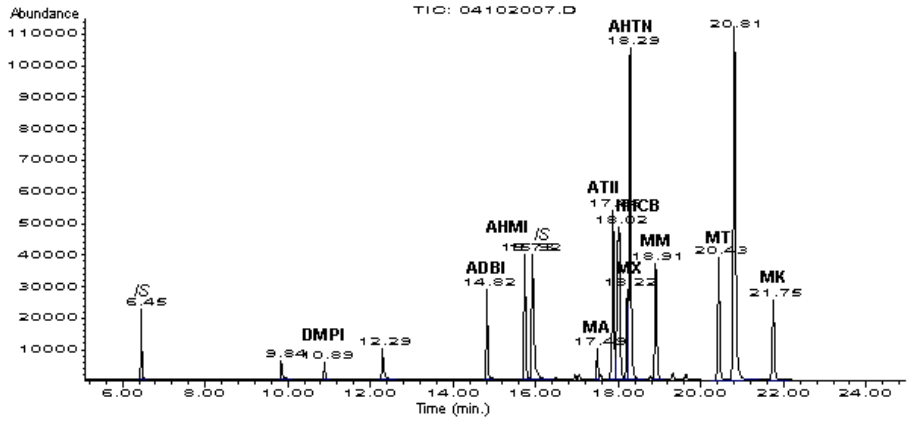

Figure 16: GC-MS/SIM total ion chromatogram of synthetic musk standards. See Table 14 for a list of compound abbreviations; *IS* denotes internal standards (F-PAHs).

Quantifications were based on a duplicate 5-point calibration ranging from approximately 1.5 to 150 ng/ml. In most cases it did not seem possible to impose a proper linear fit to the calibration data, and quadratic fits were generally used.

6.2.4 Method evaluation

Method blanks were prepared by filling ASE cells with similar amounts of alumina oxide and sodium sulphate as for the biota samples and spiking them with the mix of recovery standards and treating them as real samples. However, the variation between the method blank samples was substantial and not appropriate for determining detection and quantification limits (LOD and LOQ, resp.). Instead, an estimate of LOD was chosen as the level of the lowest

calibration standard (1.5 ng / ml), which generally gave S / N > 3 for all analytes during calibration; for LOQ, an estimate of three times this LOD has been chosen (3 * 1.5 ng / ml ≈ 5 ng / ml). The LOQ is relatively high, but as the applied method has not been fully optimised and validated, and as linear calibration curves did not give satisfactory fits, this conservative estimate has been considered appropriate.

The applied method for the analysis of synthetic musk compounds in various biota (liver and fat) and sediment samples comprised three different steps: ASE extraction, preparative GPC clean-up and GC-MS detection with subsequent quantification based on internal standards. Both the extraction and clean-up steps were based on techniques previously described in the literature. As both types of biota contained considerable amounts of lipid, an ASE technique involving the *in situ* use of alumina oxide as fat retainer was applied. Sporring and Björklund (2004) reported that a high fat-to-fat retainer ratio (FFR) of at least 0.05 and a low extraction temperature (50°C) was most efficient. Due to smaller cell volumes (33 ml) and higher sample amounts in this project, FFR smaller than 0.1 was not possible. Additionally, a somewhat higher extraction temperature was used (75°C). As can be seen from the GPC chromatogram in Figure 15b (pilot whale liver extract) and Figure 17b (polar bear liver extract), the extracted lipid phase was not completely removed by the application of an *in situ* fat retainer, but as the extraction method was not fully optimised it is not possible to conclude to what extent the fat retainer actually worked.

Regarding the preparative GPC clean-up, this is a slight modification of the techniques previously described by Rimkus et al. (1995) and Osemwengie and Steinberg (2001). Due to the high amount of lipids in most extracts, they would become too viscous for the GPC injector to sample and inject the preselected amount of extract if they were concentrated to less than 4 ml. Additionally, no more than 1 mL extract could typically be injected in one run, otherwise the lipid content could influence retention times and subsequently the recovery of analytes. Hence, each extract was analysed in duplicate to process a total of 2 ml. For several of the biota samples, the lipid content in the extracts was still significant and of such a composition that the applied GPC method was incapable of separating the analytes properly from the lipid phase, and some co-elution generally occurred. Again, as the method has not been fully optimised and validated it is not possible to evaluate to what extent the coelution with low-molecular-weight lipids influenced the recoveries of analytes.

Table 14: Target and qualifier ions used for the compounds analysed and estimated limit of quantification (LOQ).

Compound (trivial name)	CAS-No.	Chemical formula	Target ions (m/z)	Qualifier ions (m/z)	LOQ (ng/mL)
Cashmeran (DPMI)	33704-61-9	$C_{14}H_{22}O$	191	206	5.0
Celestolide (ADBI)	13171-00-1	$C_{17}H_{24}O$	229	244	5.0
Phantolide (AHMI)	15323-35-0	$C_{17}H_{24}O$	229	244	5.0
Galaxolide (HHCB)	1222-05-5	$C_{18}H_{26}O$	243	213	5.0
Traseolide (ATII)	68140-48-7	$C_{18}H_{26}O$	215	258	5.0
Tonalide (AHTN)	1506-02-1	$C_{18}H_{26}O$	243	258	5.0
Musk Xylene (MX)	81-15-2	$C_{12}H_{15}N_3O_6$	282	297	5.0
Musk Ambrette (MA)	83-66-9	$C_{12}H_{16}N_2O_5$	253	268	5.0
Musk Moskene (MM)	116-66-5	$C_{14}H_{18}N_2O_4$	263	278	5.0
Musk Tibetene (MT)	145-39-1	$C_{13}H_{18}N_2O_4$	251	266	5.0
Musk Ketone (MK)	81-14-1	$C_{14}H_{18}N_2O_5$	279	294	5.0

With respect to the evaluation of the recovery of analytes, the application of recovery standards gave inconclusive results. Two deuterium-labelled musk compounds, AHTN-d3 and MX-d15, were spiked to all samples at levels of approximately 50 ng/g prior to extraction. Only MX-d15 was recovered, and at highly varying amounts, while the AHTN-d3 practically remained undetected in all samples. The recovery of MX-d15 varied not only between extracts from different biota species but also between extracts from the same species. A rough estimate from average values gave an average recovery for MX-d15 of 50% for all samples (range: 10-90%), but due to the variation between samples it does not seem possible to conclude whether the relatively low to poor average recoveries are due to method deficiencies (poor extraction and clean-up) or the degradation of compounds during sample preparation. However, no data in the open literature seems to indicate that synthetic musk compounds in general, or musk xylene and tonalide in particular, should be labile to degradation during extraction and clean-up from biological matrices using techniques similar to those applied in this study, i.e. ASE extraction and clean-up by alumina oxide and GPC.

6.3 Results and discussion

The results of the measured concentrations of synthetic musk compounds in the various biota and sediments samples from Greenland and the Faroe islands are given in Table 15. The samples that are listed twice are analysed in duplicate. As can be seen from the table hardly any compounds were detected. Only in the polar bear liver extracts two musk compounds, cashmeran (DPMI, 5.5 ng/g ww) and musk tibetene (MT, 6.0 ng/g ww), were detected. In one polar bear liver sample, a relatively high value (31.1 ng/g ww) of tonalide (AHTN) was observed, but as this value could not be confirmed by the second sample of the duplicate extraction, the value is suspected to be caused by contamination or co-elution of lipid, which deteriorates the integration of the corresponding peak in the SIM chromatogram. Traseolide (ATII) was detected in all polar bear liver extracts, but the values were below the estimated LOQ and therefore assigned a value of ½ * LOQ, *i.e.* 2.5 ng/g ww.

Of the other samples, only one ringed seal liver sample contained detectable amounts of tonalide (AHTN, 6.2 ng/g ww), but again this level could not be confirmed by the duplicate analysis of this sample. For several other samples peaks were detected, but as signals were below the estimated LOD of 1.5 ng/ml, the results have been reported as < 1.5 ng/g ww. For the remaining samples, signals were absent or below ⅓ *LOD and hence reported as “not detected” (n.d.).

Although the available data are rather limited they seem to indicate that polar bears from East Greenland are the wildlife species studied here that experience the highest exposure to the group of synthetic musk compounds. On the basis of the limited data it is difficult to judge whether this is a consequence of biomagnification. Clearly, more data are needed for insights into the relevant processes. According to recent studies on synthetic musk compounds in aquatic biota samples, the polycyclic musks seem to exeed the nitro musks (Gatermann et al., 1999; Rimkus, 1999). In the polar bear samples analysed in this study, this trend is not really confirmed as cashmeran and musk tibetene are found at the same levels. This may indicate that polars bears are exposed to different sources of musk than the aquatic fauna. The proximity to emission sources of musk compounds may also be of importance.

Table 15: Synthetic musk concentrations (ng / g wet weight) in liver samples from various Greenland and Faroe Islands wildlife species.
[a)] Fulmar: fat samples. Values < LOQ (5 ng / g) are substituted by ½*LOQ.
n.d.-values < ⅓ *LOD.

Species	DMU No.	DPMI	ADBI	AHMI	ATII	HHCB	AHTN	MA	MX	MM	MT	MK
Polar bear (Greenland)	03-0164	**2.5**	n.d.	n.d.	**2.5**	< 1.5	n.d.	n.d.	n.d.	n.d.	< 1.5	n.d.
	03-0129	**2.5**	n.d.	n.d.	**2.5**	< 1.5	**(31.0)**	n.d.	n.d.	n.d.	**2.5**	n.d.
	03-0129	**5.5**	n.d.	n.d.	**2.5**	n.d.	n.d.	n.d.	n.d.	n.d.	**6.0**	n.d.
Minke whale (Greenland)	03-0132	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Pilot whale (Faroe Islands)	02-1755	< 1.5	n.d.	n.d.	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	02-1757	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	02-1756	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	02-1756	< 1.5	n.d.	n.d.	n.d.	< 1.5	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.
Ringed seal (East Greenland)	03-0123	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0165	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ringed seal (West Greenland)	03-0166	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0126	< 1.5	n.d.	n.d.	n.d.	< 1.5	**(6.2)**	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0126	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Shorthorn sculpin, (East Greenland)	03-0118	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0117	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0117	< 1.5	< 1.5	< 1.5	n.d.	< 1.5	< 1.5	< 1.5	< 1.5	n.d.	n.d.	n.d.
Shorthorn sculpin, West Greenland)	03-0119	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0120	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Northern fulmar[a)] (Faroe Islands)	02-1761	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	02-1760	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	02-1760	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sediment (Greenland)	03-0267	< 1.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0268	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	03-0268	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

7 Phthalates

7.1 Introduction

Phthalates are esters of phthalic acid. They are used as additives to plastics in order to make the material softer and more flexible. They "swim" among the plastic polymers without a true chemical bond to the plastic structure and are therefore, similarly to PBDEs, likely to leach out of the product (Domininghaus, 1988). 77% of the phthalates produced are used for turning polyvinyl chloride (PVC) into a flexible material. In PVC, the phthalate plasticizers may provide up to 67% (w / w) of the final product (Giam et al., 1984). The majority of all phthalates are used in the construction, automobile and textile industries (Bauer, 1997). Besides, they have been used in paints, glue, lubricants, varnish, pharmaceutics, cosmetics, perfume, pesticides and printing ink (BUA, 1988).

The most frequently used compounds are di(2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DBP) (Lützel, 1987). According to VKE (1992), 50% of all applications of plasticizers include DEHP. The low-molecular-weight phthalates have been used in insect repellents, cosmetics, textiles and medical devices (Giam et al., 1984). The industrial use of phthalates has led to a ubiquitous distribution in the environment.

The acute toxicity of phthalates is known to be low (Furtmann, 1994), however, some studies have shown carcinogenic potential in rodents (Morgenroth, 1993; Page and Lacroix, 1995). DEHP as well as its metabolite mono-(2-ethylhexyl) phthalate have shown teratogenicity (Morgenroth, 1993). Dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, butylbenzyl phthalate (BBP), DEHP and dioctyl phthalate (DOP) are among the priority pollutants listed by the US Environmental Protection Agency.

The log K_{OW} values vary according to the chain length of the alcohol and are for example 1.53 (DMP), 5.61 (DBP) and 7.48 (DEHP). Thus, some phthalates resemble PCBs with regard to their hydrophobicity and are therefore likely to accumulate in biota in a similar manner. To our knowledge, no data are available on phthalates in biota from the Arctic region. Most studies from Europe, North America and Japan concentrate on the effects of local pollution sources on aquatic organisms, as reviewed by Giam et al. (1984). Previous analyses of fish from the North Atlantic Ocean gave DEHP concentrations of up to 135 ng / g (Giam et al., 1978). In a recent review, Clark et al. (2003) compiled data on phthalates in the environment. For sediments levels are in the order of 0.1-20 µg / g, and it seems that levels are generally higher in the USA than in Europe, except for DEHP of which levels are two times higher in Europe; in the USA, DBP has the highest level.

In this study, di(2-ethylhexyl) adipate (DEHA) was included together with the phthalates. It belongs to another group of plasticizers, the

adipates – esters of adipic acid, which also are frequently used and often mixed with other plasticizers for the processing of PVC and other polymers. It is also frequently used as a solvent in lubricants, cosmetics and sanitary products just as it is applied as a plasticizer in food storage wraps, from where it has been shown to migrate into stored food (US EPA). Thus, a recent study has shown that DEHA is present in retail foods together with phthalates and other plasticizers (Tsumura et al., 2002).

Sources of adipates are fly ash from municipal waste incineration, wastewater effluents and chemical plants. If released to soil or water, adipates are expected to biodegrade relatively rapidly. Estimated log K_{OC} values of 3.70-4.68 suggest that adipates will be relatively immobile in soil, and should partition from the water column to sediment in the aquatic environment (US EPA).

Having a log $K_{OW} \geq 6.11$, DEHA is expected to bioaccumulate in aquatic biota. However, some studies have shown a much lower bioconcentration factor than expected (BCF = 27 for blue-gill fish), and bioconcentration is therefore only expected to be environmentally important in aquatic organisms that are unable to metabolise adipates (US EPA).

7.2 Analytical methods

Phthalates and one adipate (DEHA) were analysed in liver, fat and sediment samples by gas chromatography (GC) and mass spectrometry (MS) in selected ion monitoring (SIM) mode. The applied extraction, clean-up and chromatographic techniques used for this group of compounds are similar to those previously described for the synthetic musk compounds as the two groups of compounds were analysed together from the same set of biota and sediment samples. As phthalates are commonly present in the laboratory environment due to frequent use of plastic, detergents etc. only glassware that had been carefully cleaned and annealed at 450°C was used during laboratory operations.

7.2.1 Extraction

The same extraction techniques as described for the synthetic musk compounds applies here. As the phthalates are sensitive to hydrolysis at pH < 7 (US EPA, 1996), only neutral alumina oxide was used as *in*-situ fat retainer during ASE extractions.

7.2.2 Clean-up

The GPC clean-up technique described for the synthetic musk compounds also applies here as the two groups of compounds were processed together. As for the synthetic musk compounds, solutions of phthalate standards were analysed using the same conditions to establish the appropriate time window for collection of fractions of desired analytes (Figure 17). As can be seen from this figure, some extracts from the ASE extraction still contain considerable amounts of

lipid, and that this is not sufficiently separated from the phthalate analytes.

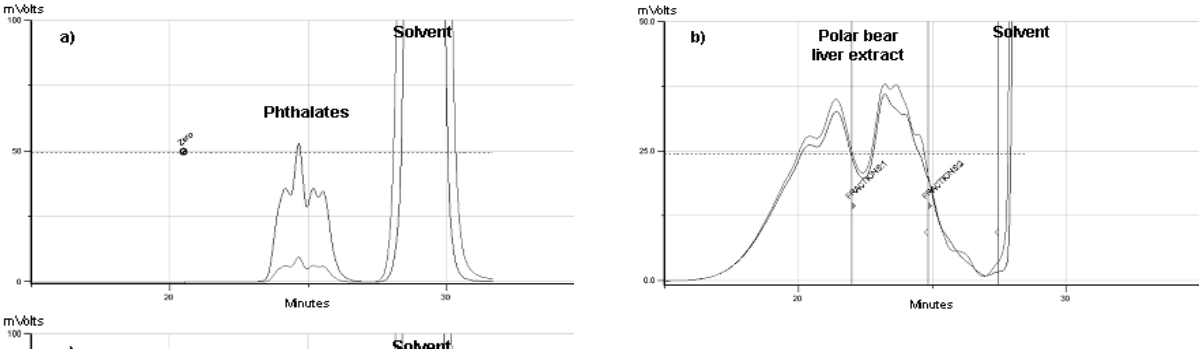

Figure 17: GPC chromatograms of a) mix of phthalate standards and b) polar bear liver extract.

Table 16: Target and qualifier ions used for the compounds analysed, and the estimated limit of quantification (LOQ). [a)]Phthalate and [b)]Adipate, derivative of adipic acid.

Compound (trivial compound name)	CAS-no.	Chemical formula	Target ions (m/z)	Qualifier ions (m/z)	LOQ (ng/mL)
Dimethyl-Ph[a)] (DMP)	131-11-3	$C_{10}H_{10}O_4$	163	194	5.0
Diethyl-Ph[a)] (DEP)	84-66-2	$C_{12}H_{14}O_4$	149	177	5.0
Di-n-butyl-Ph[a)] (DBP)	84-74-2	$C_{16}H_{22}O_4$	149	223	5.0
Di-n-hexyl-Ph[a)] (DnHP)	84-75-3	$C_{20}H_{30}O_4$	149	251	5.0
Butylbenzyl-Ph[a)] (BBP)	85-68-7	$C_{18}H_{18}O_4$	149	206	5.0
Di-(2-ethylhexyl)-Ad[b)] (DEHA)	103-23-1	$C_{22}H_{42}O_4$	129	147	5.0
Di-(2-ethylhexyl)-Ph[a)] (DEHP)	117-81-7	$C_{24}H_{38}O_4$	149	167	5.0
Di-n-octyl-Ph[a)] (DnOP)	117-84-0	$C_{24}H_{38}O_4$	149	279	5.0

7.2.3 Instrumental analysis

Sample extracts were analysed using the same method as for the synthetic musk compounds described in Chapter 6 as the two groups of compounds were analysed together. The phthalate analytes were grouped in five SIM windows with each ion having a dwell time of about 50-70 msec. The m/z values of target and qualifier ions of each analyte are listed in Table 16; the selected ions are in accordance with those reported elsewhere (David et al., 2003). Figure 18 shows a TIC (total ion) GC-MS chromatogram of a mix of phthalate standards.

Quantifications were based on a duplicate 5-point calibration ranging from approximately 2 to 150 ng/ml. As for the musk compounds, in

most cases it did not seem possible to fit a proper linear curve to the calibration data, and quadratic fits were generally used.

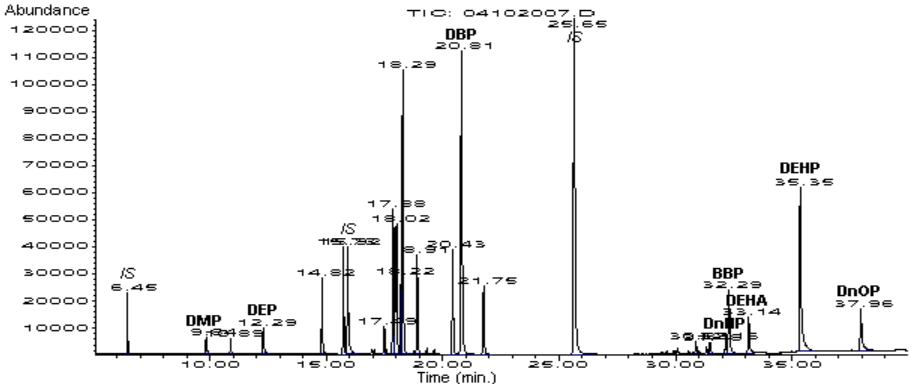

Figure 18: GC-MS/SIM total ion chromatogram of phthalate standards. See Table 16 for a list of compound abbreviations; *IS* denotes internal standards (F-PAHs).

7.2.4 Method evaluations

The applied method for the analysis of phthalates/adipate in various biota (liver and fat) and sediment samples are the same as that described for the synthetic musk compounds as the two group of compounds were processed together from the same samples. Thus, the remarks given earlier for the musk compounds regarding extraction and clean-up also apply for the phthalates/adipate. As mentioned earlier, background levels of phthalates from glassware etc. may be significant. Evaluated from the analyses of a series of laboratory blanks this was not a general problem. Only DEHP had a significant average background levels (> 25 ng/ml extract), while for the other analysed compounds average background levels were close to or below LOQ, i.e. 5 ng/mL extract. Due to the varying background levels of DEHP in blank samples no background correction has been performed on the real samples.

Regarding the evaluation of the recovery of analytes, the application of labelled recovery standards also gave inconclusive results for the phthalates. Three deuterium-labelled phthalates, DBP-d4, BBP-d4 and DEHP-d4, were spiked to the samples at levels of approximately 50 ng/g prior to extraction. Only BBP-d4 was recovered, and at highly varying amounts, while the other two labelled compounds remained undetected in most samples. The recovery of BBP-d4 varied not only between extracts from different biota species, but also between extracts from the same species. A rough estimate from average values gave an average recovery for BBP-d4 of 10% (range 2-50%), but due to the variation between samples it does not seem possible to conclude whether the relatively low average recoveries are due to method deficiencies (poor extraction/clean-up) or the degradation of compounds during sample preparation. Phthalates are known to be susceptible to acid hydrolysis, and the use of acidic alumina oxide for column clean-up is not recommended. Recoveries better than 90% of phthalates using neutral alumina oxide clean-up have been documented by the US EPA recently (US EPA, 1996). In this study, thus, only neutral alumina oxide was used as fat retainer during ASE extrac-

tions to avoid hydrolytic breakdown of phthalates, but it has not been studied in more details whether this was achieved or not. The duplicate analyses show some variation for the analysed phthalates.

7.3 Results and discussion

The levels of analysed phthalates / adipate in various biota (liver and fat tissues) and sediment samples from Greenland and the Faroe Islands are summarised in Figure 19, while a detailed overview of recorded concentrations for all compounds in all sample types is listed in Table 17. The samples that are listed twice are analysed in duplicate. In contrast to the results for synthetic musk compounds, phthalates and adipate were detected in almost all samples above the LOQ level.

Table 17: Phthalate concentrations (ng / g wet weight) in liver samples from various Greenland and Faroe Islands wildlife species; [a)] Fulmar: fat tissue samples; values < LOQ (5 ng / g) are substituted by ½*LOQ; n.d.-values <⅓ *LOD; n.a.: data not available.

Species	DMU no.	DMP	DEP	DBP	DnHP	BBP	DEHA	DEHP	DnOP
Polar bear (Greenland)	03-0164	53.8	16.9	13.2	10.1	24.7	n.a.	n.a.	45.0
	03-0129	44.1	24.1	10.9	107.4	37.0	60.5	151.2	18.5
	03-0129	56.5	24.2	14.2	6.4	31.4	144.3	133.9	2.5
Minke whale (Greenland)	03-0132	2.5	15.2	10.7	7.2	29.7	63.1	86.2	6.7
Pilot whale (Faroe Islands)	02-1755	2.5	17.0	15.7	2.5	32.5	65.5	81.2	15.0
	02-1757	2.5	31.4	19.3	2.5	29.3	41.2	95.7	2.5
	02-1756	2.5	23.4	7.7	2.5	18.0	56.6	133.9	2.5
	02-1756	2.5	20.9	17.7	5.5	32.3	64.2	n.a.	2.5
Ringed seal (East Greenland)	03-0123	8.4	31.6	10.5	15.4	30.5	93.0	136.2	14.0
	03-0165	2.5	15.1	2.5	7.3	17.5	32.8	99.8	7.6
Ringed seal (West Greenland)	03-0166	2.5	16.4	10.3	8.8	30.0	93.1	160.7	5.2
	03-0126	2.5	28.6	7.6	25.7	44.2	71.2	74.6	5.5
	03-0126	2.5	13.2	5.4	9.7	32.6	23.2	114.5	5.7
Shorthorn sculpin (East Greenland)	03-0118	< 1.5	35.7	5.5	2.5	15.7	83.1	121.9	11.6
	03-0117	< 1.5	19.5	10.8	5.4	21.7	37.5	119.8	6.9
	03-0117	< 1.5	76.9	8.6	10.7	22.2	43.4	107.5	15.3
Shorthorn sculpin (West Greenland)	03-0119	2.5	44.8	5.6	6.1	15.1	92.7	n.a.	2.5
	03-0120	2.5	15.6	2.5	2.5	11.9	21.0	91.8	2.5
Northern fulmar[a)] (Faroe Islands)	02-1761	< 1.5	29.5	13.2	2.5	18.2	56.8	120.0	2.5
	02-1760	5.8	23.0	28.7	47.7	68.6	45.3	145.2	40.4
	02-1760	< 1.5	20.4	13.5	5.9	58.5	94.2	137.4	10.7
Sediment (Greenland)	03-0267	< 1.5	48.9	9.6	2.5	14.0	29.9	120.3	2.5
	03-0268	< 1.5	42.6	2.5	< 1.5	6.3	2.5	118.6	< 1.5

Figure 19a shows how each analysed compound is distributed between the different sample types. DEHP and DEHA have the highest levels in all samples, except for the sediment samples where DEP exeeds the level of DEHA. Only polar bear samples had quantifiable amounts of DMP. For DEP, the highest concentration is observed in sediment samples, and a similar level is observed in liver samples of shorthorn sculpin, a bottom dwelling fish. Generally, the overall trend for all sample types seem to be: DEHP > DEHA > BBP ≈ DEP > DnHP ≈ DBP ≈ DnOP > DMP. It has to be noted that the analyses were based on liver samples, with the exception of fulmer. Due to the lipophilic character of the phthalates, they may also be detected in blubber samples.

Figure 19b shows the distribution of the compounds within each sample type. For most compounds highest concentrations are observed in polar bear liver and fulmar fat samples. Considering the average concentration of all measured analytes, the general trend seems to be: polar bear > fulmar > ringed seal ≥ shorthorn sculpin ≥ pilot whale > minke whale ≥ sediment. However, the concentration differences between the species are small, usually smaller than observed for the halogenated compounds studied in this project. Futhermore, the duplicate analyses show relatively large variations, which introduce uncertainty into the comparison of the species. The DEHP concentration in shorthorn sculpin is similar to concentrations found in fish from the North Atlantic Ocean (Giam et al., 1978).

The similar concentrations between the biota samples analysed in this project indicate that phthalates biomagnify to a lesser extent than the halogenated compounds studied in this project. Since the concentrations are highest in polar bear, biomagnification processes cannot be ruled out, but the biomagnification factors are clearly smaller than for the halogenated compounds, due to relatively high concentrations in the abiotic media (sediment) and animals at lower trophic levels (shorthorn sculpin). These elevated concentrations may be related to the widespread presence of phthalates in all kinds of products, which could lead to emissions close to the sampling locations.

Fulmars were also observed to have relatively high overall levels, but here lipid samples were analysed, and hence these levels may not be directly comparable with levels in liver samples. For some types of biota (ringed seal and shorthorn sculpins) samples had been collected both in East and West Greenland, but no substantial differences were observed in measured concentrations between the two locations.

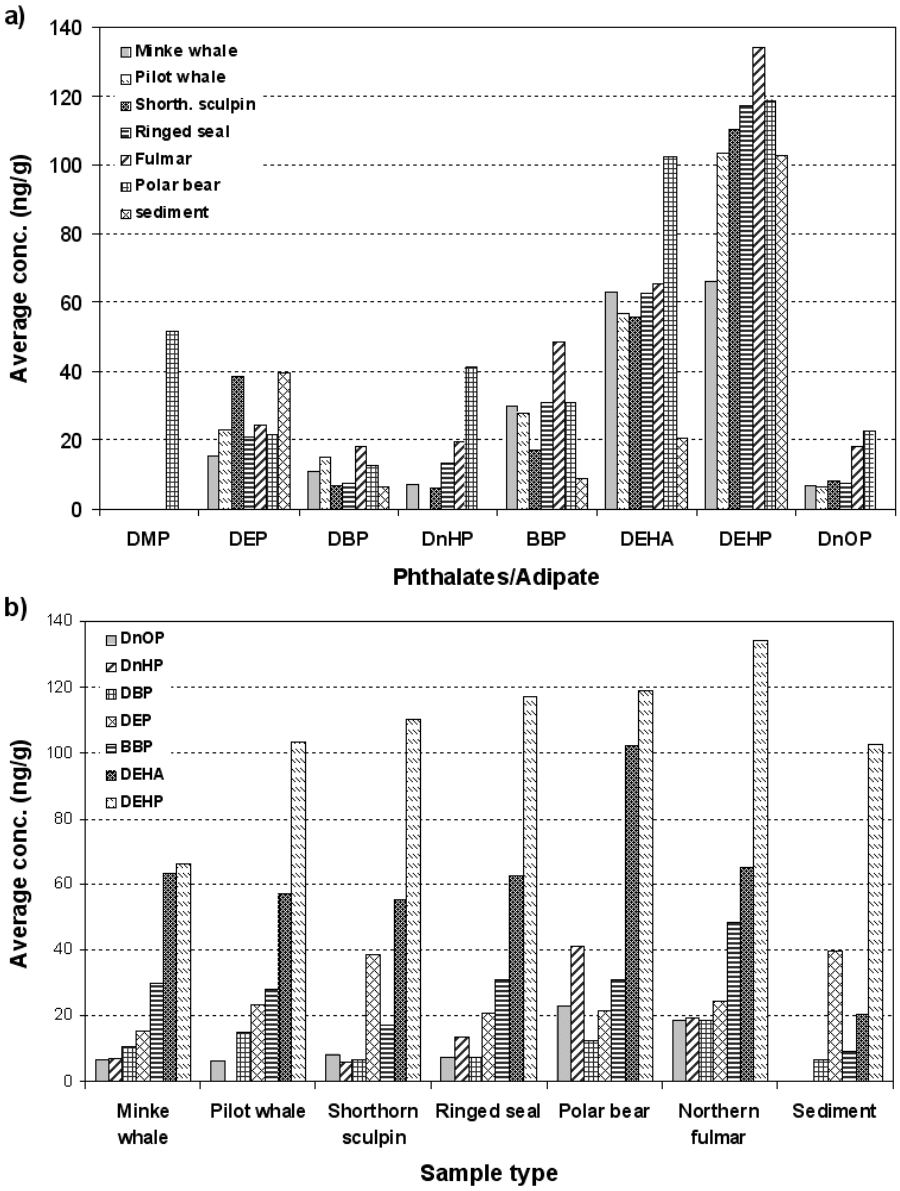

Figure 19: Bar charts showing the average concentrations (ng / g wet weight) of selected phthalates / adipate analysed in this study in wildlife (liver and fat tissues) and sediment samples from Greenland and the Faroe Islands:
a) differences in concentration of analysed compounds between the different sample types;
b) distribution of analysed compounds within each sample type.

8 Correlation

Correlation analysis was applied to identify similarities in occurrence patterns between the compound groups. The summed concentrations were calculated for each compound group, including values below the limit of quantification as half the limit of quantification. Besides the summed concentrations of all phthalates, the compounds with the highest concentrations, DEHA and DEHP, were included. The non-parametric Spearman correlation was applied in order to avoid assumptions of normality and linear relationships and because the concentration levels of the different compounds differ with an order of magnitude.

The results are presented in Table 18. A statistically significant correlation was found for most pairs of the halogenated compound groups, such as PBDE/PBB and PFAS/PBDE. The correlation between PCN/PBDE and PCN/PBB was somewhat weaker. PCN/PFAS is the only pair of the halogenated compound groups that is not significantly correlated. The main reason for the correlations is that the compound groups are found to biomagnify. Since the samples cover a broad spectrum of the food chain (fish, seabirds, seals, whales and polar bear), similar trends will be found due to biomagnification.

However, the phthalates seem to follow a different pattern since they are not correlated with any of the groups of halogenated compounds. This seems to confirm the observation that they do not biomagnify in the same way as the halogenated compounds. The phthalates are only correlated internally, with significant correlations between sum phthalates/DEHA, sum phthalates/DEHP and DEHA/DEHP. This internal correlation probably reflects their similar use as plasticizers and a similar fate in the environment. Their widespread use as plasticizers may lead to different patterns of emissions when compared to the halogenated compounds. Besides, phthalates are known to be subject of degradation in the environment, which probably makes them less persistent than the halogenated compounds studied in this project.

Table 18: Results of Spearman correlation analyses. N=15 in correlations including PFAS, N=12 in correlations including phthalates, otherwise N=17. PFAS (ng/g ww), PCN (pg/g lw), PBDE and PPB (ng/g lw), phthalates (ng/g ww). * denotes $p<0.05$. ** denotes $p<0.01$

	PCN	PBDE	PBB	Phthalates	DEHA	DEHP
PFAS	0.41	0.81**	0.85**	0.25	0.24	0.36
PCN		0.63**	0.67**	0.10	0.08	0.10
PBDE			0.86**	-0.05	0.03	0.03
PBB				0.16	0.22	0.27
Phthalates					0.83**	0.88**
DEHA						0.70*

Correlation analyses on the basis of individual halogenated compounds or congeners showed strong correlation within each group of compounds. An exception was BDE-183 which was inversely correlated with the other BDE congeners. However, this observation is only based on the three pilot whale samples from the Faroe Islands, which were the only samples with BDE-183 at detectable concentrations.

9 Conclusions and recommendations

Various phenomena have been described for the compounds studied, such as differences in concentrations or compound patterns between species as well as geographical differences or differences between the age groups of pilot whale. It should be kept in mind, however, that the number of samples is small, and the results can only be considered as indicative. The observed phenomena are likely to be a consequence of a variety of conditions, such as

- Transport pathways of the chemicals
- Bioavailability
- Biology of the animals (e.g. migration pattern and feeding habits)
- The ability of the animals to metabolise the chemicals

Combinations of these conditions are likely to affect the concentrations and compound patterns in biota. The compounds included in this studied are all less-studied compounds in the Arctic and the knowledge of the factors described above is rather limited, in particular with regard to transport pathways and metabolisation of the chemicals. It is therefore not possible to point at one particular explanation for the phenomena observed in this study.

Beyond the conclusions of this study, recommendations will be given regarding further analyses of the compounds analysed in this project. The recommendations will be based on the following aspects:

- International conventions and regulations of the chemicals in questions
- Need for further monitoring

Other studies may have pointed at additional aspects of importance, for instance knowledge gaps in the fate of the chemicals or their toxicity and effects. However, these questions are not addressed in the recommendations. If follow up studies and further monitoring confirm the problematic issues indicated in this project, i.e. biomagnification, ubiquitous occurrence and relative high concentrations of the “new” contaminants, more comprehensive risk assessments will be needed.

9.1 PFAS

9.1.1 Conclusions

- An analytical method has been developed for trace analysis of biota and sediment. Quality assured chemical analysis at trace level will thus be possible in the future.
- The concentrations in polar bear are within the range observed in Alaska and Hudson Bay.
- PFOS and PFOSA biomagnify.

- The highest PFAS concentrations were found in polar bear from East Greenland, followed by pilot whale from the Faroe Islands and ringed seal from East Greenland.
- There is a tendency of higher PFAS levels in marine biota from East Greenland than from West Greenland.
- PFOSA was found at relatively high concentrations in pilot whales and minke whales.

9.1.2 Recommendations

- A retrospective time trend analysis of the last two decades is recommended in order to identify the concentration development of PFAS in Greenland.
- Since PFOS-related compounds are still in use and not regulated at present, it is recommended to follow the development of PFAS concentrations in key species (polar bear, ringed seal, pilot whale) from Greenland and the Faroe Islands.

9.2 PCN

9.2.1 Conclusions

- An analytical method has been developed and validated for trace analysis of biota and sediment. Given the low concentrations in the environment, the limits of detection ought to be lower.
- The PCN concentrations in juvenile pilot whales were an order of magnitude higher than in beluga from the Canadian Arctic.
- Higher PCN levels were observed in marine biota from the Faroe Islands than in marine biota from Greenland.
- PCNs seem to biomagnify. The highest concentrations in the Greenland samples were found in polar bear.
- CN-66/67 is the dominant congener in the Faroese samples while CN-68 is the dominant congener in the polar bear samples.
- The TEQ concentrations for PCN in pilot whales were similar to or slightly lower than the dioxin TEQ concentrations in pilot whales.

9.2.2 Recommendations

- Screening of species with dioxin TEQ concentrations close to regulatory limits is recommended for the Faroe Islands, for instance of marine fish. Additional TEQ contributions based on PCN concentrations could exceed the regulatory limits.
- The samples from Greenland ought to be re-analysed with a more sensitive analytical method prior to recommendations.

9.3 BFR

9.3.1 Conclusions

- An analytical method has been developed and validated for trace analysis of PBB in biota. Quality assured chemical analysis at trace level will thus be possible in the future.

- PBDE concentrations in East Greenland were similar to concentrations on Svalbard, while concentrations in West Greenland were similar to concentrations in the Canadian Arctic.
- The study confirmed that the concentrations in pilot whales are higher than in any other Arctic marine mammal examined to date (AMAP, 2004).
- The highest concentrations of PBDEs were found in pilot whales from the Faroe Islands, which were about 15 times higher than PBDE concentrations in polar bear from East Greenland.
- The PBDE concentrations in biota from East Greenland were higher than in biota from West Greenland, with a factor of approximately 7 times (ringed seal and shorthorn sculpin).
- Thus, the geographical distribution of PBDEs is similar to the distribution of PCBs.
- PBB concentrations are generally lower than PBDE concentrations. However, for polar bear and fulmar, PBB concentrations are similar to PBDE concentrations.
- PBDE and PBB biomagnify.
- BDE-47 is the main PBDE congener in all samples, usually followed by BDE-99. Polar bears are an exception with higher percentages of BDE-153 than of BDE-99.
- BB-153 is the main PBB congener in all samples.

9.3.2 Recommendations

- A retrospective time trend analysis of the last two decades is recommended in order to identify the concentration development of PBDEs in Greenland.
- Given the increasing concentrations of PBDEs and the ongoing production and use in North America, it is recommended to include PBDEs in the next sampling round of the basic monitoring programmes for Greenland and the Faroe Islands.
- Further analyses of PBBs in existing samples of high trophic level animals, such as beluga, narwhale, walrus and polar bear, are recommended for Greenland. Similarly, for the Faroe Islands, further analyses of PBBs in black guillemot and gulls eggs, grey seal and white-sided dolphins are recommended.

9.4 Synthetic musk compounds

9.4.1 Conclusions

- An analytical method has been developed, but needs improvements with regard to sensitivity and robustness for trace analysis of biota samples.
- Due to the high number of analyses below the limit of detection, it is not possible to identify potential biomagnification processes.
- DPMI, ATII and MT were detected in polar bear liver. DPMI was detected in most samples, but was below the limit of quantification.

9.4.2 Recommendations

- The analytical method should be optimised, with a focus on low limits of detection and quantification, and validated.
- Further analyses of musk compounds in existing liver or blubber samples of high trophic level animals are recommended.
- If the occurrence of musk compounds in high trophic level animals is confirmed, it is recommended to follow the development of musk concentrations in key species, since the compounds are still in use and not regulated.

9.5 Phthalates

9.5.1 Conclusions

- An analytical method has been developed, but needs improvements with regard to sensitivity and robustness for trace analysis of biota samples.
- Phthalates and one adipate were detected in all samples. The highest concentrations were found in polar bear liver from East Greenland, fulmars from the Faroe Islands and ringed seals from East and West Greenland.
- It is remarkable that phthalates were detected in sediment and in species at lower trophic levels. In general, only small concentration differences were found between the sample types.
- Levels were highest for DEHP and DEHA, generally above 50 ng/g ww, and the general trend was: DEHP > DEHA > BBP ≈ DEP > DnHP ≈ DBP ≈ DnOP > DMP.
- The concentration of DEHP in shorthorn sculpin from Greenland was similar to the concentration in fish from the North Atlantic Ocean.
- No geographical trends between East and West Greenland could be observed.

9.5.2 Recommendations

- The analytical method should be optimised and validated.
- A more comprehensive food web study is recommended, including liver and blubber samples, in order to obtain more information on the occurrence of phthalates in the marine environment and to assess the question of biomagnification.

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11 Appendices

11.1 Additional sample information

Table 19: Samples from Greenland analysed in this project, additional information. N: Number of individuals pooled.

Species	Tissue	Reg.no.	Location	Sampling years	N	Age (years)	Sex	Length/ Weight	Lipid (%)	Dry matter (%)
Polar bear	Blubber	03-0127	Ittoqqortoormiit	1999-2001	5	3-15	M + F	-	89.48	87.53
Polar bear	Blubber	03-0128	Ittoqqortoormiit	2000-2002	5	5.5-28	M + F	-	89.40	88.64
Polar bear	Liver	03-0129	same individuals as sample 03-0127		5				-	-
Polar bear	Liver	03-0164	same individuals as sample 03-0128		5					
Minke whale	Blubber	03-0130	Central West Greenland	1998	5	-	M + F	600-830 cm	68.32	81.14
Minke whale	Blubber	03-0131	4 from Central West Greenland, 1 from Central East Greenland	1998	5	-	F	740-800 cm	83.78	89.20
Minke whale	Liver	03-0132	same individuals as sample 03-0130		5				-	-
Minke whale	Liver	03-0207	4 from Central West Greenland, 1 from Central East Greenland	1998	5	-	F	750-965 cm	-	-
Ringed seal, East Greenland	Blubber	03-0121	Ittoqqortoormiit	2002	5	4.5-5.5	M	-	96.70	98.55
Ringed seal, East Greenland	Blubber	03-0122	Ittoqqortoormiit	2002	5	3.5-7.5	M	-	96.28	98.62
Ringed seal, East Greenland	Liver	03-0123	same individuals as sample 03-0121		5				-	-
Ringed seal, East Greenland	Liver	03-0165	same individuals as sample 03-0122		5				-	-
Ringed seal, West Greenland	Blubber	03-0124	Qeqertarsuaq	2002	5	0.5-1.5	M	-	97.45	97.55
Ringed seal, West Greenland	Blubber	03-0125	Qeqertarsuaq	2002	4	0.5-3.5	M	-	97.07	98.37
Ringed seal, West Greenland	Liver	03-0126	same individuals as sample 03-0124		5				-	-
Ringed seal, West Greenland	Liver	03-0166	same individuals as sample 03-0125		4				-	-
Shorthorn sculpin, East Greenland	Liver	03-0117	Ittoqqortoormiit	2002	5	-	F	29-35 cm	15.47	33.53
Shorthorn sculpin, East Greenland	Liver	03-0118	Ittoqqortoormiit	2002	5	-	F	29-38 cm	12.53	29.31
Shorthorn sculpin, West Greenland	Liver	03-0119	Qeqertarsuaq	2002	5	-	F	30-36 cm	12.27	33.18
Shorthorn sculpin, West Greenland	Liver	03-0120	Qeqertarsuaq	2002	5	-	F	33-40 cm	10.43	30.24
Sediment	-	03-0267	Qeqertarsuaq	2002	5	-	-	-	-	76.72
Sediment	-	03-0268	Qeqertarsuaq	2002	5	-	-	-	-	66.67

Table 20: Samples from the Faroe Islands analysed in this project, additional information. N: Number of individuals pooled.

Species	Tissue	Reg.no.	Location	Sampling years	N	Age (years)	Sex	Length/ Weight	Lipid (%)	Dry matter (%)
Pilot whale, Juveniles	Blubber	02-1754	Miðvágur	2001	14	Juveniles	M + F	186-445 cm	91.27	87.55
Pilot whale, Juveniles	Liver	02-1755	Miðvágur	2001	11	Juveniles	M + F	186-445 cm	-	-
Pilot whale, Females	Blubber	02-1758	Miðvágur	2001	34	Adult	F	400-498 cm	93.47	87.60
Pilot whale, Females	Liver	02-1756	Miðvágur	2001	16	Adult	F	400-498 cm	-	-
Pilot whale, Males	Blubber	02-1759	Miðvágur and Bøur	2001	5	Adult	M	540-578 cm	90.33	88.38
Pilot whale, Males	Liver	02-1757	Miðvágur and Bøur	2001	3	Adult	M	540-578 cm	-	-
Fulmar, Females	Fat	02-1762	Nólsoy and Viðareiði	1998-1999	8	Juveniles	F	605-762 g	56.90	82.84
Fulmar, Females	Liver	02-1760	Nólsoy and Viðareiði	1998-1999	9	Juveniles	F	471-762 g	-	-
Fulmar, Males	Fat	02-1763	Nólsoy and Viðareiði	1998-1999	6	Juveniles	M	731-948 g	69.31	86.10
Fulmar, Males	Liver	02-1757	Nólsoy and Viðareiði	1998-1999	9	Juveniles	M	731-948 g	-	-

11.2 Method development of TBBPA and HBCD

11.2.1 Introduction

In this project, TBBPA was to be analysed in a variety of biota and sediment samples from Greenland and the Faroe Islands. It was attempted to combine the analysis of TBBPA with analyses of hexabromocyclododecane (HBCD) and dimethyl-TBBPA, a degradation product of TBBPA. The methods tested were based on the analytical method for PBDEs (Christensen et al., 2001) and on the method by Sellström and Jansson (1995) who analysed TBBPA and dimethyl-TBBPA in river sediments upstream and downstream of plants using TBBPA.

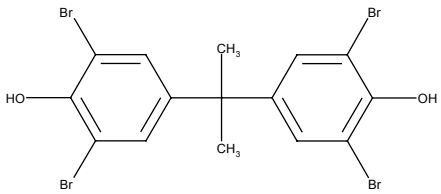

Figure 20: Tetrabomomisphenol A (TBBPA).

11.2.2 Sample preparation and extraction

According to the method for PBDEs, the samples were dried with sodium sulphate. Different extraction methods were tested on standard mixtures of TBBPA, dimethyl-TBBPA and HBCD, which were added to the sodium sulphate prior to extraction:

- Method 1: Soxhlet extraction with hexane:dichloromethane (1:1)
- Method 2: Soxhlet extraction with hexane:diethyl ether (1:1)
- Method 3: Extraction with acetone, hexane and water, fractionated analyses of organic and water phases, according to Sellström and Jansson (1995).
- Method 4: Soxhlet extraction with hexane:acetone (4:1), according to Christensen et al., 2001.

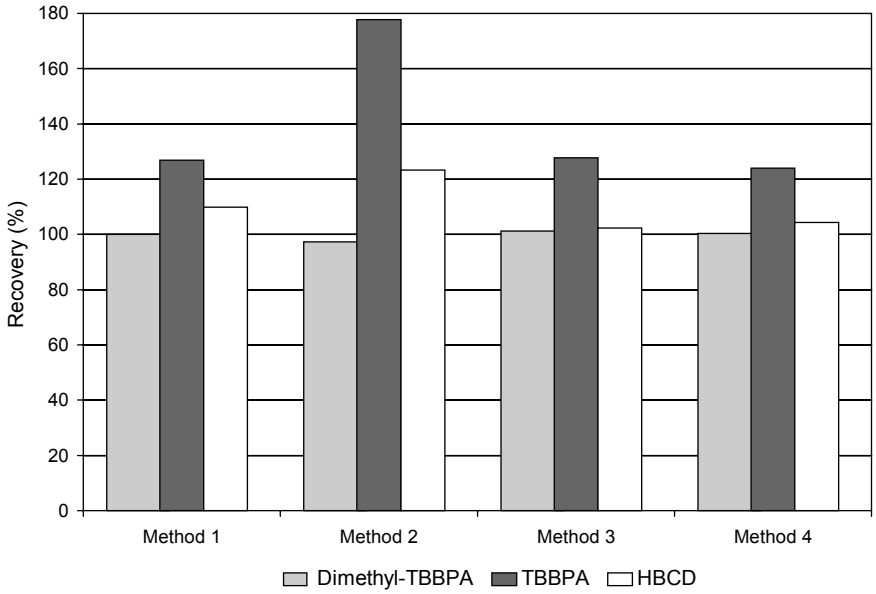

Figure 21: Recovery rates (%) of TBBPA, dimethyl-TBBA and HBCD after different extraction methods.

The recovery rates shown in Figure 21 show problems with too high values for method 2, while the other three methods yielded acceptable results. Given the toxicity of dichloromethane, it was decided to continue with the methods 3 and 4.

11.2.3 Sample purification

The purification method for PBDEs includes treatment with sulphuric acid for lipid removal. The stability of the compounds towards acid treatment was tested prior to the actual purification experiment. A standard mixture of TBBPA, dimethyl-TBBPA and HBCD was treated with concentrated sulphuric acid. The ranges of 5 replicates are summarised in Table 21 and show certain instability for all compounds, in particular HBCD. It was decided to accept this loss if it proved to be reproducible and if other steps in the method came close to complete recovery.

Table 21: Recovery rates of TBBPA, dimethyl-TBBA and HBCD after treatment with H_2SO_4

	TBBPA	Dimethyl-TBBPA	HBCD
Recovery (%)	70-82	70-80	63-75

In a first purification test, standard mixtures with defined amounts of the TBBPA, dimethyl-TBBPA and HBCD were added to the following four materials:

- Aluminium oxide
- Activated aluminium oxide (10% H_2O)
- Silica gel
- Silica gel with H_2SO_4

Each material was eluted with the following three solvent mixtures:

- Hexane:dichloromethane (1:1)
- Hexane:diethyl ether (1:1)
- Hexane:toluene (1:1)

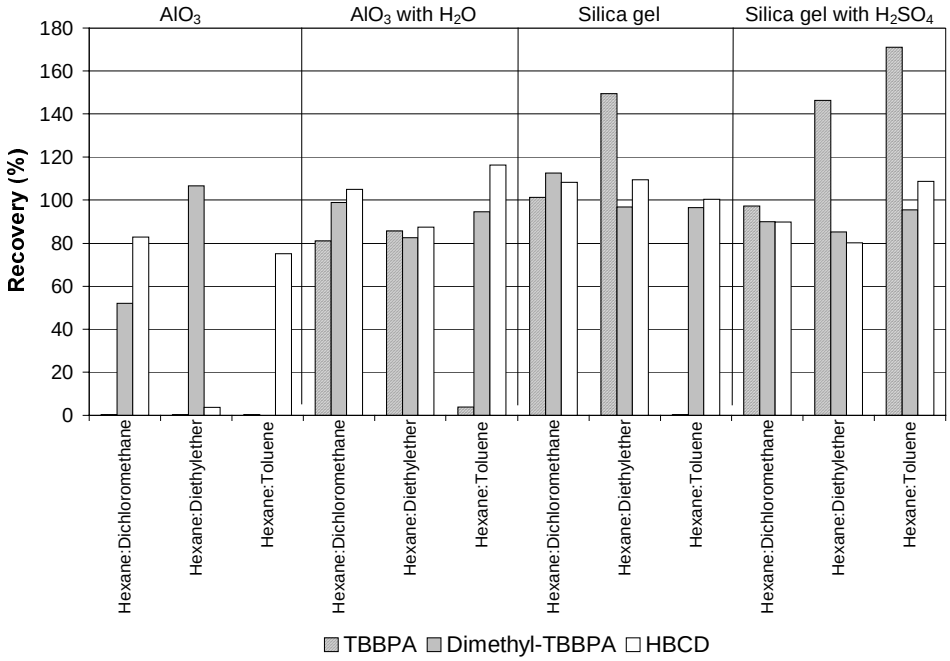

Figure 22: Recovery rates of TBBPA, dimethyl-TBBA and HBCD after purification

The results presented in Figure 22 show that aluminium oxide cannot be used without water. The other materials gave the best results when combined with hexane:dichloromethane. Therefore, the conclusion was to continue with packed columns, consisting of activated alumnium oxide, silica gel and acid-impregnated silica gel, and to elute the columns with hexane:dichloromethane.

On the basis of these results, the spiked samples of sand launch oil were extracted with the extraction methods 3 and 4 (11.2.2) and were purified on the multi-layer columns which were eluted with 200 ml of hexane:dichloromethane. Unfortunately, the results for the standard mixtures could not be repeated, in fact, neither TBBPA nor HBCD could be detected in the chromatogram. First, it was suspected that the elution volume of 200 ml had been insufficient. Therefore, extraction of sand launch oil was repeated, but solely by extraction method 4, and the extraction volume was increased to 250 ml. Still, TBBPA was hardly recovered (Table 22) and the recoveries for HBCD were > 100%.

Table 22: Recovery rates of TBBPA, dimethyl-TBBA and HBCD after extraction (method 4) and purification on the multi-layer column.

	TBBPA	Dimethyl-TBBPA	HBCD
Recovery (%)	0.15-0.17	82-90	126-151

Apparently, the sample matrix affects TBBPA during the clean up procedure, so the promising results obtained for the standard mixtures cannot be reproduced for real samples. It was suspected that aluminium oxide might retain TBBPA. Therefore, new experiments were conducted with reduced amounts of aluminium oxide and without aluminium oxide. In these samples, the recovery of TBBPA was slightly increased, however, the amount was still far too low to be acceptable.

11.2.4 Derivatisation

As far as possible, TBBPA should be included in the existing method for PBDEs. Due to the rather polar character of TBBPA, however, the GC-analysis yielded a very low response with tailing peaks. This was less crucial in method development where samples could be spiked with high concentrations of TBBPA, but it would have meant high detection limits and high uncertainty in quantification for the samples to be analysed. Therefore, it was chosen to derivatise TBBPA prior to GC-analysis in order to turn it into a more apolar molecule. The derivatisation is based on a reaction of TPPBA with pyridine:eddikesyre anhydride (1:1) and a subsequent treatment with sulphuric acid. The reaction product is diacetyl-TBBPA (Figure 23).

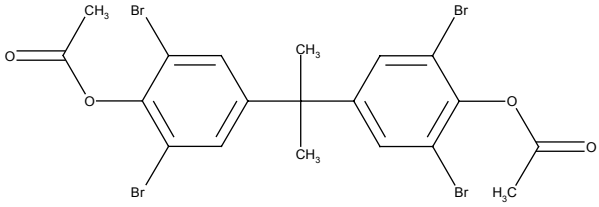

Figure 23: Diacetyl-TBBPA

The derivatisation was tested on standard mixtures of TBBPA, HBCD and dimethyl-TBBPA at two different concentrations. Table 23 shows that the derivatisation can be carried out without loss for TBBPA. The results for dimethyl-TBBPA are acceptable, too. HBCD, however, was not detectable after derivatisation. If the derivatisation is chosen in a combined method for the three compounds, it will have to take place after analysis of HBCD.

Table 23: Recovery rates for TBBPA, dimethyl-TBBA and HBCD after derivatisation of TBBPA.

	TBBPA	Dimethyl-TBBPA	HBCD
Recovery (%)	81-101	99-131	n.d.

11.2.5 Analysis by GC-MS

The samples were analysed by GC-MS with negative chemical ionisation (NCI). The method was identical to the analytical method for PBDEs (Christensen et al., 2001). Single ion monitoring (SIM) was chosen with the ions m/z=78.9 and m/z=80.8 for all compounds. Furthermore, m/z=159.8 was monitored for dimethyl-TBBPA and HBCD, m/z=504.7 was monitored for diacetyl-TBBPA, and m/z=543.7 was monitored for TBBPA.

As stated above, the response was very low for TBBPA (Figure 24). The different HBCD-isomers cannot be distinguished in the GC-MS analysis. Therefore, a total HBCD-amount was calculated. Due to the low response on the usual DB-5 GC-column, the standards were also analysed on a DB-1701 column, but no improvement could be observed. As a possible alternative, standards were also analysed by high pressure liquid chromatography (HPLC) with UV-detection. With the solvent gradient chosen preliminarily, HBCD and TBBPA co-eluted. As the response did not indicate better detection limits, work on the separation of the two compounds was not continued.

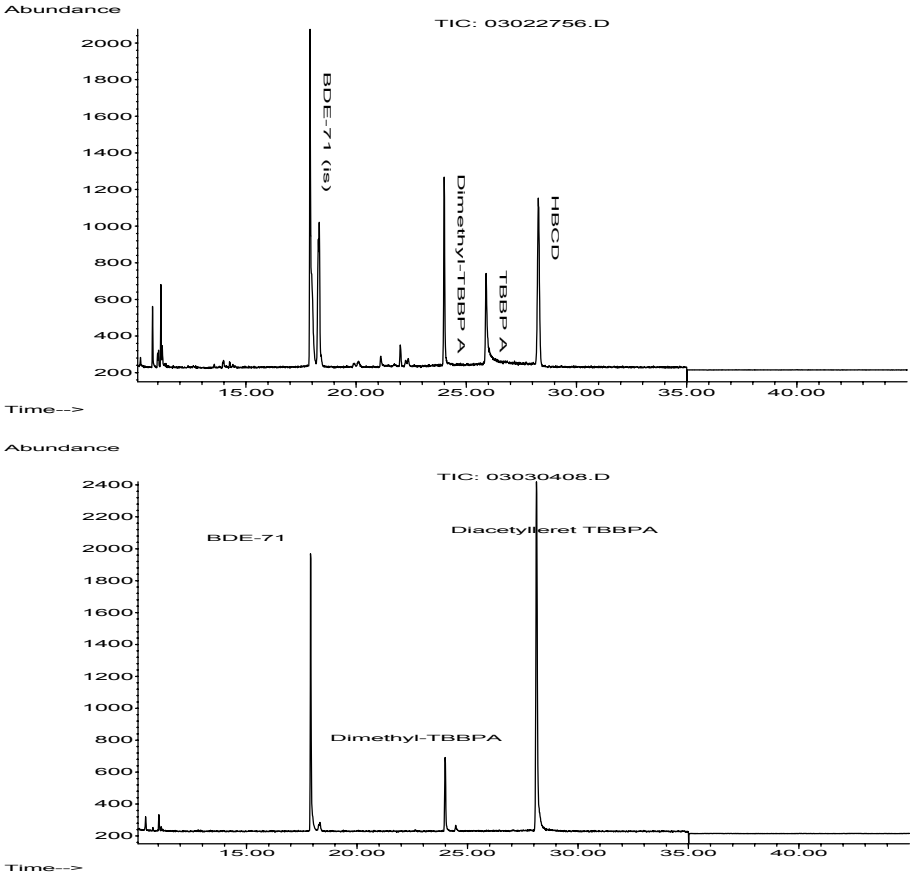

Figure 24: Chromatogrammes of TBBPA, dimethyl-TBBPA, HBCD and diacetyl-TBBPA

11.2.6 Conclusions

At present, it is not possible to analyse TBBPA in the sediment and biota samples from Greenland and the Faroe Islands. The main obstacle has been the purification method. The tests have been based on a traditional clean up by adsorption chromatography, which gave good results for the standards, but could not be used for real samples. Therefore, different methods will have to be considered, possibly based on size exclusion chromatography. The previous and subsequent steps have not shown any unacceptable loss of TBBPA and may be kept in the final analytical method.

HBCD and dimethyl-TBBPA showed satisfactory results for all the methodological steps tested. It might therefore be a more suitable approach to include HBCD and dimethyl-TBBPA in the existing

method for PBDEs and analyse TBBPA separately. However, a final method validation will have to be conducted for HBCD and di-methyl-TBBPA prior to a possible extension of the existing PBDE-method.

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Blubber and liver samples of biota from the marine environment of Greenland and the Faroe Islands were analysed for a variety of »new« contaminants: Perfluorinated alkylated substances (PFAS), brominated flame retardants (PBDE and PBB), polychlorinated naphthalenes (PCN), synthetic musk compounds and phthalates. All com-pounds were detected in the top-predator species polar bear (East Greenland) and pilot whale (Faroe Islands). Compared with other findings from the Arctic, high concentrations were found for PFAS in polar bear (1300 ng / g wet weight) and PBDE in pilot whale (400-1000 ng / g lipid weight). For the other compound groups, little infor-mation is available for comparisons. Increasing concentrations with increasing trophic levels indicated biomagnification of the halo-genated compound groups, while the concentrations of the main phthalate DEHP were within the range of 60-140 ng / g wet weight in all samples. In Greenland, the same geographical pattern with higher concentrations in East than in West Greenland was found for PFAS and PBDE as had previously been found for the better-studied organochlorine compounds.

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