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Low organotin contamination of harbour sediment in Svalbard

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Abstract Arctic sea routes are opening up for maritime transport due to sea ice retreat leading to increasing human activities in the Arctic and concomitant pressures on the environment. Organotin compounds are used in antifouling paints of large seagoing vessels and are known to leach into the marine environment and accumulate in sediments and biota. As organotin levels in Svalbard sediments have not been documented in peer-reviewed literature before, this study describes the levels in sediment of harbours around Svalbard (Ny-Ålesund, Longyearbyen, Svea, Pyramiden and Barentsburg). Organotin levels in sediments of Svalbard harbours were low (below the detection limit up to 14 ng Sn/g dw sum-butyltin) compared to other Arctic regions with a longer history of shipping. Levels were below known no effect levels and in accordance, no imposex was found in marine whelks from Ny-Ålesund harbour. Of all other analysed compounds in sediments of Kongsfjorden (polycyclic aromatic hydrocarbon (PAHs), polychlorinated biphenyls, polybrominated diphenylethers and perfluorinated compounds) PAH levels were highest and in one sample above action levels. It is advised to continue monitoring contaminant levels, for which the current results form a good basis. If contaminant levels rise, mitigation measures can be taken in time.

Keywords TBT · Sediment · Spitsbergen · Kongsfjorden · Arctic · Contaminants · Pollution · Shipping

Introduction

Arctic sea routes are opening up for maritime transport due to sea ice retreat. This leads to increasing human activities in the Arctic and concomitant pressures on the environment (Stępień et al. 2014). Local sources of contaminants are

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closely linked to activities in the area such as shipping, mining and harbour activities and may cause local hotspots of contamination. Contaminants are also transported to the Arctic region from diffuse sources far away by evaporation and air currents, or via rivers and ocean currents (AMAP 1998, 2010), causing widespread contamination of pristine areas, and in particular the marine environment (MacDonald et al. 2000; Letcher et al. 2010; Andersen et al. 2015).

Svalbard is an archipelago in the Barents Sea, bordering the Greenland Sea in the west and the Arctic Ocean in the north, about midway between continental Norway and the North Pole. Svalbard has a few human settlements consisting of the main settlement of Longyearbyen, the Russian mining community of Barentsburg, the historical mining settlement of Pyramiden, the research station of Ny-Ålesund, and the Norwegian mining community of Svea. The main industries on Svalbard are coal mining, tourism, education and research.

Local sources of contamination in Svalbard are a consequence of local settlements, shipping and (historical) coal mining (Kozak et al. 2013). Persistent contaminants such as polycyclic aromatic hydrocarbon (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs) and perfluorinated compounds (PFCs) are associated with local settlements and coal mining on Svalbard (Hop et al. 2001; Evenset et al. 2006a, 2009). Contaminants related to shipping include air pollution (such as PAHs, fine particles, S and NOx), waste (solid and liquid) and organotin compounds (OTCs), such as tributyltin (TBT; Van Aardenne et al. 2013; Eckhardt et al. 2013; Matthiessen 2013). Organotin compounds are biocides that are added to paint used on ship hulls to prevent hull fouling and thereby decrease drag and fuel consumption (Lindholdt et al. 2015). These anti-fouling compounds leach into the marine environment and have caused shipping-related accumulation of TBT in sediment resulting in the chronic exposure of aquatic organisms (Matthiessen 2013). A well-known effect of TBT exposure is imposex in gastropod molluscs such as marine whelks (Mensink et al. 2002). Imposex is the formation of male characteristics in female snails. It was estimated that about 150 species showed signs of imposex worldwide (Matthiessen et al. 1999). Since the 1960s, TBT has been applied as anti-fouling biocide in paint, until in 2003, the International Maritime Organization (IMO) banned new application of TBT coatings on ships and since 2008 no TBT is allowed to be present on ships (IMO 2001). Not all countries have ratified the treaty yet. In 2012, some 61 contracting states representing 80 % of the worlds tonnage had ratified the treaty (IMO 2012). New input of TBT from TBT-coated ships cannot be excluded in the Arctic in addition to persistent historical TBT pollution. As TBT slowly degrades over time into dibutyltin (DBT) and finally into monobutyltin (MBT), the relative presence of these three compounds can indicate how recent the TBT input was. For this purpose, the Butyltin Degradation Index (BDI) was developed (Diez et al. 2002).

In Ny-Ålesund harbour, imposex has been reported once for the marine snail *Buccinum undatum* in the mid-1990s (Brick and Bolte 1994). There is, however, no peer-reviewed information available on past or current organotin levels in sediments or biota of Svalbard harbours, nor has imposex been studied further. Organotin contamination and imposex have been studied and identified in other Arctic harbours in Greenland (Jacobsen and Asmund 2000; Strand and Asmund 2003; Strand et al. 2006), Iceland (Skarphéðinsdóttir et al. 1996; Svavarsson 2000) and Alaska (Tallmon 2012).

This study focuses on providing insight into organotin contamination of sediments of Svalbard harbours and the occurrence of imposex in marine whelks (Buccinum sp.) of Ny-Ålesund harbour, Kongsfjorden. In addition, levels of other contaminants (PAHs, PCBs, PBDEs and PFCs) were analysed in the sediment of several locations within Kongsfjorden to get a further understanding of local inputs of contaminants in this Svalbard fjord. This will provide a basis to assess pressures and impacts of current and future activities in Svalbard in order to develop relevant and effective mitigation measures in the future.

Materials and methods

Sediment sampling

Sediment in and near harbours of Svalbard was collected in 2009, 2012 and 2013 using a Van Veen grab (Table 1; Fig. 1). In Kongsfjorden (in 2012 and 2013), sediment was sampled at three sites (Ny-Ålesund harbour, Ny-Ålesund Thiisbukta and Kongsfjorden reference). Sampling location Ny-Ålesund Thiisbukta is located in the intertidal part of a bay adjacent to the west of Ny-Ålesund harbour and close to an abandoned waste dump on land. In Kongsfjorden, the upper 5 cm sediment layer from five grabs was mixed and homogenized on board and two subsamples of 200 ml each of this homogenate were stored in pre-rinsed 250-ml glass jars with aluminium foil between sample and lid. Sediment at Ny-Ålesund Thiisbukta was collected directly from shore during low tide. Five sediment surface samples were mixed and homogenized and two subsamples of 200 ml each from this location were stored. In Longyearbyen and Svea (in 2013), sediment from four grabs was mixed and homogenized on board and two subsamples were stored according to the same procedures used in Kongsfjorden. In Pyramiden and Barentsburg (2009) the sampling procedure

Table 1 Sediment sampling locations in harbours around Svalbard (2009–2013)

Year	Date	Sampling site	Specifics	Fjord	Depth (m)	N coordinate	E coordinate	# Samples OTC analysis	# Samples additional analyses
2009	24-06-2009	Pyramiden	Harbour	Billefjorden	14	78,392	16,231	1	
2009	24-06-2009	Pyramiden	Harbour	Billefjorden	18	78,389	16,234	1	
2009	24-06-2009	Pyramiden	Harbour	Billefjorden	42	78,386	16,246	1	
2009	24-06-2009	Pyramiden	Harbour	Billefjorden	45	78,390	16,252	1	
2009	24-06-2009	Pyramiden	Harbour	Billefjorden	165	783,585	163,080	1	
2009	22-06-2009	Barentsburg	Harbour	Grønfjorden	70	780,380	141,200	1	
2009	22-06-2009	Barentsburg	Harbour	Grønfjorden	40	780,530	141,010	1	
2009	22-06-2009	Barentsburg	Harbour	Grønfjorden	112	780,270	141,165	1	
2009	22-06-2009	Barentsburg	Harbour	Grønfjorden	95	780,570	140,840	1	
2013	12-10-2013	Longyearbyen	Harbour	Adventfjorden	45	781,390	153,630	1	
2013	12-10-2013	Longyearbyen	Harbour	Adventfjorden	45	781,390	153,630	1	
2013	12-10-2013	Longyearbyen	Harbour	Adventfjorden	23	781,374	153,650	1	
2013	12-10-2013	Longyearbyen	Harbour	Adventfjorden	23	781,374	153,650	1	
2013	10-09-2013	Svea	Harbour	Van Mijenfjorden	40	–	–	2	
2013	10-09-2013	Svea	Harbour	Van Mijenfjorden	25	775,137	163,864	2	
2013	10-09-2013	Svea	Harbour	Van Mijenfjorden	18	775,140	163,853	2	
2012	13-06-2012	Ny-Ålesund	Harbour	Kongsfjorden	20	7,855,816	1,156,544	3	1
2012	13-06-2012	Ny-Ålesund	Coal pier	Kongsfjorden	22	7,855,859	1,155,409	3	1
2012	15-06-2012	Reference	Tonsneset	Kongsfjorden	17	7,900,145	1,158,348	2	1
2012	15-06-2012	Reference	Tonsneset	Kongsfjorden	22	7,900,301	1,156,758	2	1
2013	27-06-2013	Ny-Ålesund	Harbour	Kongsfjorden	21	7,855,816	1,156,544	1	1
2013	27-06-2013	Ny-Ålesund	Coal pier	Kongsfjorden	19	7,855,859	1,155,409	1	1
2013	27-06-2013	Ny-Ålesund	West of coal pier	Kongsfjorden	19	7,855,920	1,153,940	1	1
2013	29-06-2013	Ny-Ålesund	Thiisbukta	Kongsfjorden	0	7,855,572	1,154,420	2	1
2013	28-06-2013	Reference	Blomstrand grotten	Kongsfjorden	19	7,859,406	1,158,764	1	1
2013	28-06-2013	Reference	Blomstrand glacier	Kongsfjorden	19	7,900,006	1,158,674	1	1

was slightly different; the upper 0–1 cm from one grab at each sampling station was taken out using a small Plexiglas core and stored directly in pre-cleaned glass jars or polypropylene containers. All sediment samples were frozen to −20 °C immediately after sampling until further analysis.

Sampling of organisms

Nineteen individuals of Buccinum sp. were sampled using baited traps in Ny-Ålesund harbour (near the old coal pier) in July 2013. Snails were kept alive and cool prior to imposex staging. Snails were examined for imposex occurrence using standard procedures (OSPAR Commission 2009).

Chemical analysis

Organotin analysis in sediments consisted of MBT, DBT, TBT, monophenyltin (MPhT), diphenyltin (DPhT) and triphenyltin (TPhT), using an RvA accredited method (Verslycke et al. 2005). In short, tripropyltinchloride was added to the samples as internal standard after which the organotin compounds were extracted by adding methanol, acetic acid and hexane. Compounds were subsequently derivatized using sodium tetraethylborate (4 % in water) after which sodium hydroxide was added to the samples. The hexane layer containing the derivatized compounds was then cleaned by eluting over an aluminium oxide column with pentane. Extracts were concentrated to one ml using a turbovap and subsequently analysed by GC–MS.

PFCs were analysed according to the procedure by Kwadijk et al. (2010). In short, samples were extracted using acetonitrile and cleaned up using hexane and ENVI-Carb. Extracts were analysed using LC–ESI–MS.

PBDEs and PCBs were extracted using the accelerated solvent extraction technique with in-cell clean-up using florisil. Extraction took place over three cycles using a static time of 10 min with a mixture of pentane: dichloromethane (85:15) at 40 °C. Extracts were concentrated to 1 ml.

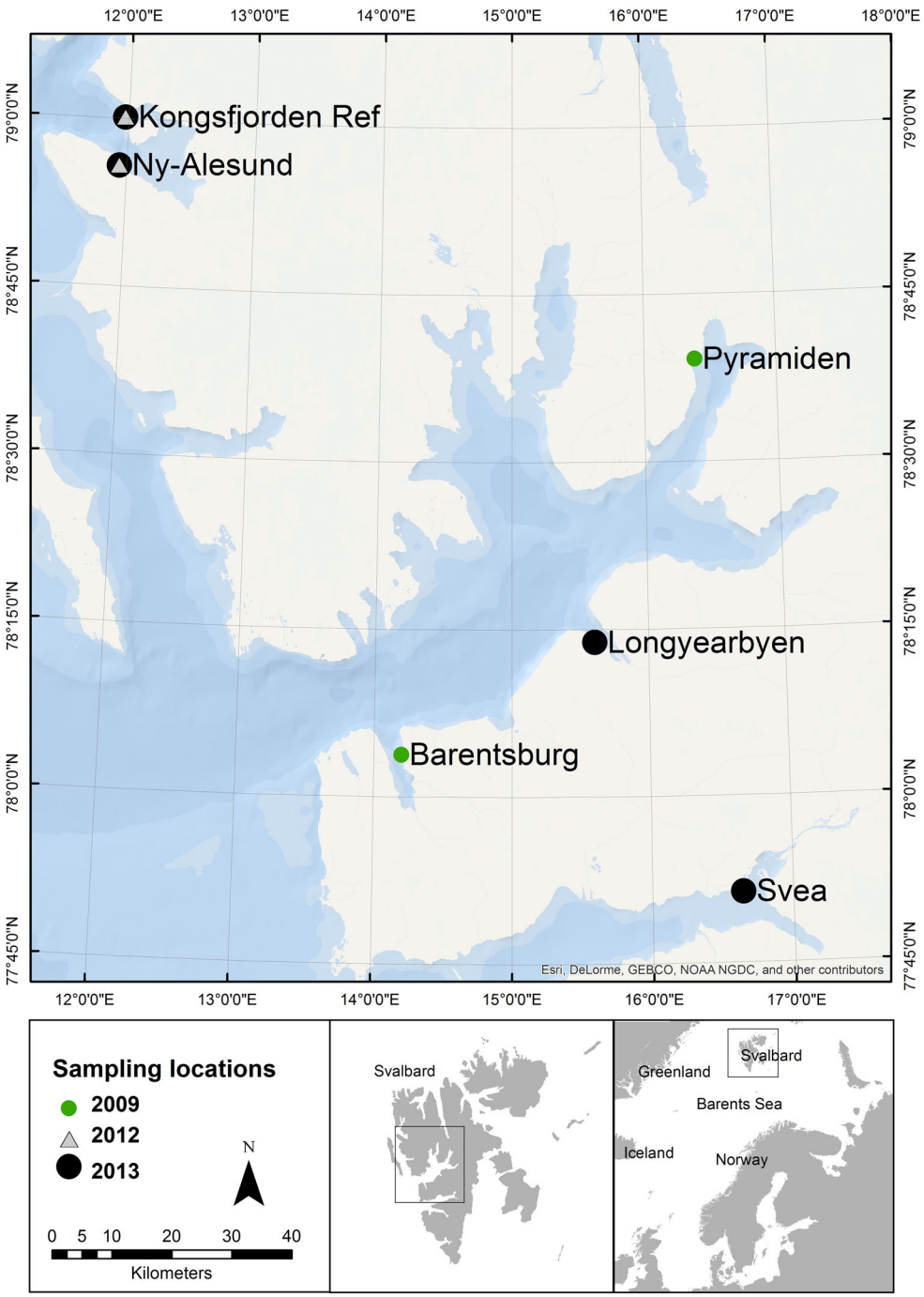

Fig. 1 Sediment sampling locations in harbours around Svalbard (2009–2013)

For PCBs, 1 µl of sample was injected on a Shimadzu GCMS2010 (GC) coupled to a GCMS-QP2010 Ultra (MS) detector (Shimadzu, 's Hertogenbosch, the Netherlands). Column used was a 30 m × 0.25 mm i.d. HT8 with a film thickness of 0.25 µm. Detection was performed using electron impact (EI) in single ion monitoring (SIM) mode. Injection port and source temperatures were 250 and 200 °C, respectively. Oven temperature program started at 90 °C, hold for 3 min, increased by 20 °C/min to 170 °C followed by an increase by 2.5 °C/min to 292 °C. At the end of the program, a column was heated to 320 °C for 10 min. The following quantifier and qualifier ions were monitored, respectively, 256 and 258 for PCB 28, 292 and 290 for PCB 52, 326 and 324 for PCB 101, PCB 112 and PCB 118, 360 and 362 for PCB 138 and PCB 153, 394 and 396 for PCB 180. Recovery was typically between 80 and 110 % for all compounds. Calibration curves consisted of nine points within a range of 1–650 ng/ml. $R^2 \geq 0.999$ was achieved for each calibration curve for all compounds.

For PBDEs, 1 µl of sample was injected on an Agilent 6890 GC–MS (Agilent, Amstelveen, the Netherlands) using a 50 m × 0.25 mm i.d. CPsil8 column with a film thickness of 0.25 µm. Injection port and source temperatures were 275 and 200 °C, respectively. Oven temperature program started at 90 °C, hold for 3 min, increased by 30 °C/min to 210 °C followed by an increase by 5 °C/min to 290 °C. At the end of the program, a column was heated to 325 °C for 25 min. M/z 79 and 81 were used as quantifier and qualifier ions, respectively. Recovery was typically between 80 and 110 % for all compounds. Calibration curves consisted of nine points within a range of 0.1–500 ng/ml. $R^2 \geq 0.999$ was achieved for each calibration curve for all compounds.

PAHs were analysed according to De Boer et al. (2001). In short, PAHs were extracted from the sediments with soxhlet (hexane/acetone 1:1). The extract is concentrated to 10 ml, cleaned over a silica gel–aluminium oxide column and, after addition of 1 ml of acetonitril, concentrated by evaporation to 1 ml of acetonitril. The PAH levels in the acetonitril solution were then analysed by HPLC equipped with fluorescence detection. acenaphthylene was not measured since it was not part of the standard method used for the measurements of PAH in the samples. Naphthalene was excluded from analyses due to fluctuating high background levels in the blanks which would lead to questionable results.

Limit of detection (d limit) was defined as <5 times the method blank or the lowest used calibration point, whichever is highest. Reference materials and method blanks were analysed with each set of samples. All results for blanks and reference materials were within normal limits.

Data treatment

In cases where the TBT concentration was above d limit in a sediment sample, the BDI was calculated as following (Diez et al. 2002):

$$\mathrm{BDI} = \frac{([\mathrm{MBT}] + [\mathrm{DBT}])}{[\mathrm{TBT}]}$$

In case MBT and DBT concentrations were below d limit, the values for these compounds to be included in the calculation were calculated as 0.5 * d limit.

The PAH concentrations were summed as the 16 US EPA PAHs (sum-16-PAH) (naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fl), phenanthrene (Phe), anthracene (An), fluoranthene (Flu), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3 cd]pyrene (Inp), dibenz[a,h]anthracene (DBA) and benzo[ghi]perylene (BgP). Naphthalene and acenaphthylene were, however, not included in the analysis. The PCB concentrations were presented as sum-7-PCB (PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180).

Results

Organotin concentrations

Organotin concentrations in sediments of Svalbard harbours were low (<d limit—14 ng Sn/g dw; Table 2). MBT and DBT were only detected in Kongsfjorden sediment. TBT was present in 20–67 % of the samples, except for samples from Longyearbyen harbour where no TBT was found above d limit. The highest number of samples with TBT was found in Svea harbour (67 % above d limit), whereas highest sum-butyltin concentrations were found in Ny-Ålesund harbour (<d limit—14 ng Sn/g dw). TPhT was only detected in a single sediment sample of Pyramiden harbour (1.4 ng/g dw), whereas MPhT and DPhT were not detected in any of the sediment samples.

A BDI could be calculated for 13 of the sediment samples with a TBT concentration above d limit (Table 3). The BDI for these samples ranged between 0.4 and 8.3.

Table 2 Summarized organotin data in the sediment of Svalbard harbours (2009–2013), dl = d limit

Sampling site	Fjord	N	% > dl MBT	% > dl DBT	% > dl TBT	ng/g dw Range sum-butyltin (Sn)	ng/g dw Range sum-butyltin (Kation)
NA—reference	Kongsfjorden	6	0	33	33	<dl–0.5	<dl–1.2
Ny-Ålesund	Kongsfjorden	9	44	33	44	<dl–14	<dl–24.5
NA—Thiisbukta	Kongsfjorden	2	0	0	50	<dl–2.1	<dl–5.3
Pyramiden	Billefjorden	5	0	0	20	<dl–1.8	<dl–4.4
Barentsburg	Grønfjorden	4	0	0	25	<dl–1.6	<dl–4.1
Longyearbyen	Adventfjorden	4	0	0	0	<dl	<dl
Svea	Van Mijen fjorden	6	0	0	67	<dl–2.1	<dl–4.9

Table 3 BDI scores for the sediment of Svalbard harbours (for all samples with [TBT] > d limit (2009–2013)

Sampling site	Fjord	*N*	*n* > dl TBT	Range BDI	Median BDI
NA—reference	Kongsfjorden	6	2	1.0–1.3	1
Ny-Ålesund	Kongsfjorden	9	4	0.8–8.3	4
NA—Thiisbukta	Kongsfjorden	2	1	1.1	1.1
Pyramiden	Billefjorden	5	1	0.4	0.4
Barentsburg	Grønfjorden	4	1	0.4	0.4
Longyearbyen	Adventfjorden	4	0	–	–
Svea	Van Mijen fjorden	6	4	0.5–0.7	0.7

In case MBT and/or DBT were <d limit, the value was calculated as 0.5*d limit)

Table 4 Imposex scores of *Buccinum* sp. collected at Ny-Ålesund harbour, Kongsfjorden, in 2013

Nr	Length (mm)	Sex	Imposex stage	Penis length (mm)
1	29.1	M	–	15.0
2	23.8	F	0	
3	23.5	M	–	21.0
4	21.3	F	0	
5	19.8	F	0	
6	30.0	F	0	
7	27.0	F	0	
8	28.1	F	0	
9	28.4	F	0	
10	31.9	F	0	
11	33.1	F	0	
12	29.0	F	0	
13	27.4	F	0	
14	27.5	F	0	
15	25.3	F	0	
16	25.6	F	0	
17	25.6	M	–	18.0
18	21.7	F	0	
19	23.6	F	0	

The BDI was <1 in samples of Pyramiden, Barentsburg, Svea and one sample of Ny-Ålesund. The BDI was >1 for most samples of Ny-Ålesund.

Imposex scores

No imposex was found in females of Buccinum sp. of Ny-Ålesund harbour (Table 4). Of the investigated 19 individuals, three were males and 16 were females.

Other contaminants

The sediment sample collected at Thiisbukta contained the highest sum-16-PAH concentration (17,717 g/g dw), about ten times higher than concentrations in Ny-Ålesund harbour and more than a factor 1000 higher than at the Kongsfjorden reference sites (Table 5). PAH concentrations varied within Ny-Ålesund harbour with sum-16-PAH concentrations being almost two times higher in the sediments around the coal pier of the harbour than in sediments at the commercial pier and further westwards of the coal pier.

PCB concentrations in sediment were low in Kongsfjorden (<d.l.—1.613 ng/g dw sum-7-PCB; Table 6). Highest concentrations were found in Ny-Ålesund harbour (two out of five samples), but there were also concentrations above detection levels at Thiisbukta (one out of one sample) and the reference site (one out of four samples) in Kongsfjorden. All PBDE concentrations in sediment of Kongsfjorden were below d limits. PFC concentrations in sediment of Kongsfjorden were all below d limits, except at one sample at Thiisbukta that contained levels of two PFCs just above detection level (0.2 ng/g perfluorodecane

Table 5 PAH concentrations in the sediment of Kongsfjorden, Svalbard (2012–2013), all summed concentrations were above d limit

Location	*N*	µg/kg dw Geometric mean Sum-16-PAH USEPA	µg/kg dw Average Sum-16-PAH USEPA	µg/kg dw SD Sum-16-PAH USEPA	µg/kg dw Range Sum-16-PAH USEPA
NA—reference	4	7	13	12	1–26
Ny-Ålesund harbour	5	1399	1630	859	476–2550
NA—Thiisbukta	1	16,787	16,787	0	16,787

Table 6 PCB concentrations in the sediment of Kongsfjorden, Svalbard (2012–2013), dl = d limit

Location	*N*	% > dl Sum-7-PCB	µg/kg dw Average Sum-7-PCB	µg/kg dw SD Sum-7-PCB	µg/kg dw Range Sum-7-PCB
NA—reference	4	25	0.142	0.284	<dl—0.568
Ny-Ålesund harbour	5	40	0.540	0.762	<dl—1.613
NA—Thiisbukta	1	100	0.330	–	0.330

sulphonate (PFDS) dw and 0.2 ng/g perfluorooctane sulphonate (PFOS) dw).

Discussion

Organotin concentrations

Organotin concentrations in sediment of Svalbard harbours were low (<d.l.—14 ng Sn/g dw/24.5 ng kation/g dw for sum-butyltin; 64 % of all sediment samples had all organotin compounds below d limit). TBT levels above d limit varied from 0.3 to 2.9 ng Sn/g dw. Most of the Ny-Ålesund harbour samples (with TBT levels above d limit) had a BDI of >1 suggesting no recent inputs of butyltins in this harbour (Diez et al. 2002), except for one sample with a BDI of 0.8. The latter, however, consisted of a low TBT concentration of 0.3 ng Sn/g dw, and both MBT and DBT concentrations were below d limit. These low concentrations may have resulted in a deviating BDI value, since the other BDI values in Ny-Ålesund harbour were calculated on OTC concentrations mainly above d limit. The few samples of Pyramiden, Barentsburg and Svea with TBT levels above d limits all had a BDI < 1, showing that there may still be some fresh input of TBT in the area. Pyramiden and Barentsburg only had one sediment sample above d limit with a BDI of <1. Svea had four out of six sediment samples above d limit with all showing a BDI of <1. Shipping traffic to Pyramiden is relatively low with only tourist vessels frequenting the area during summer whereas shipping traffic to Barentsburg and Svea is considerably higher with an active coal mine industry at these places. OTC levels in the sediment of another study in Isfjorden (Pyramiden, Longyearbyen, Barentsburg and Colesbukta) confirm low to non-detectable levels of OTC in Svalbard sediments (Evenset et al. 2006a). In this study, two out of 18 sediment samples in 2005 had TBT concentrations above d limit and contained 1.8 ng Sn/g dw (Longyearbyen) and 3.6 ng Sn/g dw (Barentsburg) (Evenset et al. 2006a). Low levels of TBT were explained by seasonally restricted shipping activities around Svalbard due to heavy ice conditions in winter time and a high sedimentation rate, for example in VanMeijenfjord (Svea), covering and diluting sediment concentrations (Cochrane et al. 2001).

Information on OTC concentrations in sediment of Arctic harbours is very limited. In Nuuk harbour, Greenland, sediment concentrations were reported up to 171 ng Sn/g dw for TBT and 180 ng Sn/g dw for sum-butyltin in 1997 (Jacobsen and Asmund 2000). OTCs were not detected in sediment samples of the coastal area of Thule Air Base and Qaanaaq, West Greenland, in 2002 (Strand et al. 2006). This suggests that OTC levels in Arctic sediment are low compared to more populated regions around the world, where the lowest OTC concentrations were reported in the range of up to 27–124 ng Sn/g dw (along the coasts of Italy in 1999–2000, of Japan in 2003, and of Vietnam in 2003; Antizar-Ladislao 2008). Highest TBT concentrations were reported in sediment of an American harbour in 2001–2003 and a Japanese harbour in 2005 (up to 14,000 ng Sn/g dw; Antizar-Ladislao 2008). Even though decreases of OTC concentrations have been reported in water and biota, sediment does not tend to show clear (>20 %) decreasing trends globally since TBT may not be easily broken down in (especially anaerobic) sediment (Matthiessen 2013; Kim et al. 2014).

More information is available on OTC levels in Arctic benthic invertebrates. TBT concentration varied between 0.5 and 4 ng Sn/g ww in *Nucella lapillus* and 5–65 ng Sn/g ww in *Mytilus edulis* near Reykjavík harbour in 1993–1994, whereas DBT concentrations fluctuated around 5 ng Sn/g ww in *N. lapillus* and between 1 and 6 ng Sn/g ww in *M. edulis* (Skarphédinsdóttir et al. 1996). Concentrations of TBT and degradation products in *M. edulis* of Nuuk harbour in Greenland were close to 1 ng Sn/g ww in 1997 (Jacobsen and Asmund 2000). At one station in West Greenland, low OTC levels were detected in biota in 2002, in whelks (3.1 ng Sn/g dw sum-butyltin) and clams (11 ng Sn/g dw sum-butyltin; Strand et al. 2006). In other southwestern harbours of West Greenland, organotin concentrations were above detection level in biological samples (bivalves) in 66 % of the samples in 1999–2000, with concentrations up to 283 ng/g ww sum-butyltin (Strand and Asmund 2003). In Alaska, evidence of TBT contamination in mussels collected in 2007–2009 was shown in four out of 10 harbours, with a range of 29–54 ng TBT/g ww in mussels at the contaminated harbours (Tallmon 2012). No OTC levels were measured in biota of Svalbard harbours.

All TBT concentrations in the sediment of Svalbard harbours were below the lowest action level of 3 ng Sn/g

dw for dredged materials of OSPAR contracting parties (OSPAR Commission 2004; Schipper et al. 2010) and below no observed effect concentrations (NOEC) of 80 ng Sn/g dw (Stronkhorst and Van Hattum 2003).

A field study in Greenland harbours showed that imposex in gastropods may be a more sensitive biomarker for the presence of TBT in the marine environment than the analysis of TBT in sediment or biota samples (Strand et al. 2006). In the gastropod samples collected in Ny-Ålesund harbour in 2013, none of the 16 female specimen showed any stage of imposex. Imposex occurrence has been found in Ny-Ålesund, Kongsfjorden, in marine snail samples of 1992 (Brick and Bolte 1994). At that time, five out of eight female specimen showed signs of imposex. The BDI in Kongsfjorden suggested that no new sources of TBT were presented in Ny-Ålesund harbour. This may be a further sign that OTC concentrations in Ny-Ålesund harbour have decreased over the past two decades and are currently below effect levels in the harbour. However, other Arctic harbours in Alaska and Greenland did show imposex occurrence (Strand et al. 2006; Tallmon 2012). Imposex development occurred in Buccinum sp. in all five sampled harbours in west Greenland in 1999–2000 (Strand and Asmund 2003) and in *Buccinum finmarkianum* at seven of eight marine stations off Thule Air Base in Northwest Greenland in 2002 (Strand et al. 2006). *Nucella lima* samples from harbour sites in Alaska in 2007–2009 exhibited imposex, with 36–87.5 % females affected per site (Tallmon 2012). Studies on imposex in the dogwhelks (*N. lapillus*) in Icelandic waters in 1998 show that levels of imposex have decreased considerably since the early 1990s after banning the use of TBT-containing paints on small vessels (Svavarsson 2000).

Other contaminants

PAHs concentrations were highest of all compounds analysed in Kongsfjorden sediment (1–16,787 ng/g dw), and below lowest European action levels of 2000 ng/g dw for sum-16-PAH for dredged sediment, except for the sediment sample from Thiisbukta (16,787 ng/g dw; OSPAR Commission 2004). The sediment sample of Thiisbukta fell into category 2 (poor/bad) for sum-16-PAH of 2000–20,000 ng/g dw in Norway and were above action level 1 for sum-6-PAH of 1000 ng/g dw in Germany (OSPAR Commission 2004). The sediment sample of Thiisbukta bay consisted of fine sediment with clear black carbon particles which may explain the elevated PAH levels in this sample. In 1997 PAH levels in Kongsfjorden sediment were 927 ng/g dw (Olsson et al. 1998). There are records of several old oil spills in Ny-Ålesund due to leakage from oil tanks or damaged pipes (Skei 1994) with major spills in 1986 and 1990 (Olsson et al. 1998). Additionally, local coal mining related activities may have caused a further input of PAHs into the harbour.

Low levels of PCBs were detected in Kongsfjorden sediments (d.l.—1.6 ng/g sum-7-PCB dw), both in the harbour area and near the dumpsite. Levels are below lowest European action levels of 20 ng/g dw for sum-7-PCB as set for dredged sediment (OSPAR Commission 2004). Low levels of PCBs in Kongsfjorden sediments have been described before in 1991 (0.32 ng/g sum-7-PCB dw; Skei 1994), 1997 (0.07 ng/g sum-7-PCB dw; Olsson et al. 1998) and 2007 (0.17–0.25 ng/g sum-7-PCB dw; Tessmann 2008). Sum-7-PCB concentrations in sediment of other Svalbard fjords were 0.02–3.50 ng/g (Barentsburg), 0.85–4.30 ng/g (Longyearbyen), 0.03–0.82 ng/g (Pyramiden), and 1.84 ng/g (Isfjorden) in September 1998 (Cochrane et al. 2001), 0.70–6.72 ng/g (Barentsburg), 0.16–0.70 ng/g (Longyearbyen) and 1.91–12.4 ng/g (Pyramiden) in 2005 (Evenset et al. 2006a), and 0.10–0.38 ng/g (Longyearbyen), 0.74–5.41 ng/g (Barentsburg) and 1.8–20.2 ng/g (Pyramiden) in 2009 (Evenset et al. 2009). Flux calculations indicated that local sources are important sources outside these settlements (Governor of Svalbard 2008). Elevated levels outside Pyramiden and Barentsburg were probably due to a flooding event in the summer of 2005. High levels of PCB have been measured in soil from these Russian settlements (Jartun et al. 2009), and flood water probably transported contaminated soil to the marine environment.

Other analysed contaminant groups showed levels below d limit in Kongsfjorden sediment, except for the sediment sample at Thiisbukta that showed low levels of PFCs consisting of PFDS and PFOS concentration just above detection level (0.2 ng/g dw). To our knowledge, PFC levels in Kongsfjorden sediment have not been described in peer-reviewed journals before. PFOS concentrations in sediment of Isfjorden varied between 0.10 and 0.54 ng/g dw, whereas sum-PBDE concentrations were between 0.05 and 1.10 ng/g dw in 2005 (Evenset et al. 2006b).

The fact that, of all Kongsfjorden sediment samples, the sampling location at Thiisbukta often showed levels of contaminants above d limit does not come as a surprise. This site is located directly below an old terrestrial garbage dump and may receive contaminants through run-off from the dumpsite area. In a study from 2000/2001 concentrations of PAHs and PCBs in macrobenthos were highest close to the settlement in Kongsfjorden compared to samples taken further out in the fjord, suggesting a local input of these compounds (Hop et al. 2001). Hop et al. (2001) showed that PAH levels in macrobenthos of the main fjords of Svalbard were quite variable both between and within fjords with highest levels in Isfjorden, followed by Grønfjorden, Billefjorden and Adventfjorden, and lowest

levels in Kongsfjorden (Hop et al. 2001). Based on the Norwegian guide for classification of fjords, Kongsfjorden macrobenthos was judged insignificantly polluted for PAH (Hop et al. 2001).

Sediment is highly heterogeneous in terms of composition (sediment fractions, organic carbon) and contaminant load as is also shown by this study. Often, a considerable number of sediment samples are needed from each location to obtain an acceptable standard error. In order to get a better insight into contaminant load in sediment and temporal trends of contaminants, a reduction in variance may be achieved by sampling sediments using sediment traps in low turbidity areas. This way mainly freshly transported sediment is sampled giving a more representative picture of the contents and contaminant load of freshly formed sediment layers. However, due to glacial run-off Svalbard fjords such as Kongsfjorden, Isfjorden (including Adventfjorden, Grønfjorden and Billefjord) and VanMijenfjorden receive large amounts of sediment every year (Evenset et al. 2006a, b; Governor of Svalbard 2008). This sediment has a low organic content and some of it will accumulate close to the settlements and thus 'dilute' any contaminants that are emitted from the settlements. Therefore, sampling locations should also be carefully selected with knowledge on the sedimentation rates and sources around a settlement.

Future developments

TBT-containing paint has been shown to be highly effective as antifouling paint preventing organisms attaching to ship hulls, thereby preventing the introduction of non-indigenous species and reducing drag on the ship. For the Antarctic region, the best option to prevent the introduction of non-indigenous species is under discussion including the question of whether local sources of TBT contamination may be preferred over the introduction of non-indigenous species with possible catastrophic and non-reversible effects (Lewis et al. 2004). With the predicted increased shipping in the Arctic, the prevention of introduction of invasive species is also a high priority. However, in the meantime, alternative methods to stop fouling have been developed or are under development (for example Müller et al. 2012; Pérez et al. 2016).

Levels of organotin in sediment of Svalbard harbours are currently low and below NOECs based on the results of this study. However, organotin levels below detection level are no guarantee that effects do not occur as TBT may also cause effects below detection level (Strand et al. 2006). A further study on imposex occurrence in all Svalbard harbours may give a more thorough insight into current effects of OTCs in Svalbard.

In the future, with sea ice receding and shipping opportunities in the area rising, more ships may frequent Svalbard shipping lanes and harbours (via the Northern Sea Route and Transpolar Sea Route). As not all countries have ratified the ban on TBT-containing paints for vessels, chances that TBT-containing vessels frequent the area increase. This may result in an elevation of TBT concentrations in areas along shipping lanes and harbours (Ten Hallers-Tjabbes et al. 2003; Schipper et al. 2010). Regular monitoring of sediment organotin concentrations and/or imposex occurrence in gastropods will provide information on organotin trends in the area. If organotin concentrations increase, mitigation is then possible by actively limiting the access of TBT-containing vessels in the Arctic region.

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