Microplastics and plastic additives in the aquatic environment of the Svalbard

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Abstract

The Svalbard is a remote archipelago far north in the Arctic and not subject to major direct pollution inputs. Although plastics and organic pollutants can be mainly transported to the Svalbard through air- and sea- currents, location sources also exist. This project aimed at evaluating the potential impact of local sources such as wastewater effluents on contaminant levels in the aquatic environment. This was done by screening for the presence of microplastics in water and sediment of the Adventfjord, and in effluents of the human settlements of Barentsburg and Longyearbyen. Extraction and analysis to evaluates the presence of microplastics were undertaken using pyrolysis gas chromatography linked to mass spectrometry (pyroGC/MS). For the Adventfjord sediments specifically, an extraction strategy was tested to extract a range of plastic additives and other hydrophobic organic contaminants from the sediment. Only traces of plastics were found in some fjord water and sediment samples. A signal of polyvinyl chloride (PVC) was consistently found in many samples. Although there may be a genuine presence of PVC microparticles, the presence of coal particles in the Svalbard environment and in our samples may interfere in the detection and quantification of PVC by pyroGC/MS. The globally distributed persistent organic pollutant hexachlorobenzene, the plasticisers dibutyl phthalate, benzylbutyl phthalate and bis(2-ethylhexyl) phthalate and the UV filter ethylhexylmethoxycinnamate (EHMC) were consistently detected in the sediment batches and highest total concentrations were found in sediments from sampling locations closest to Longyearbyen effluent release point. Accessible, freely and density separated concentrations or fractions were in most cases below limits of quantification. For phthalates, these results indicate that these plasticisers could be associated with plastic particles such as PVC and not readily extractable by other means than exhaustive extractions.

Sammendrag

Svalbard er en øygruppe langt nord i Arktis med få store direkte forurensningstilførsler. Selv om plast og organiske miljøgifter hovedsakelig transporteres til Svalbard gjennom luft- og havstrømmer finnes det også lokale kilder. Dette prosjektet hadde som mål å evaluere det potensielle bidraget fra lokale kilder som f.eks. avløpsvann til forurensning i sjøen. Dette ble gjort ved å screene for tilstedeværelse av mikroplast i vann og sedimenter i Adventfjorden og i avløp fra Barentsburg og Longyearbyen. Mikroplast ble analysert ved bruk av en pyrolysegasskromatograf koblet til en massespektrometer (pyroGC/MS). I sedimentprøvene fra Adventfjorden ble en ny ekstraksjons-strategi testet for å ekstrahere plasttilsetningsstoffer og andre hydrofobe organiske forurensninger fra sedimentet. Spor av plast ble funnet i noen av vann- og sedimentprøvene. Det var indikasjoner på polyvinylklorid (PVC) i mange prøver. Selv om det kan være en reell tilstedeværelse av PVC-mikropartikler, kan dette også være forårsaket av kullpartikler som er tilstede på Svalbard, noe som kan forstyrre påvisning og kvantifisering av PVC ved bruk av pyroGC/MS. Den globale miljøgiften heksaklorbenzen samt myknerene dibutylftalat, benzylbutylftalat og bis(2-etylheksyl)ftalat og UV-filteret etylheksylmetoksycinnamat (EHMC) ble påvist i alle sedimentprøver. De høyeste konsentrasjonene

ble målt i prøvene tatt nærmest utslippspunktet av Longyearbyens avløp. Fraksjoner ansett som fritt tilgjengelige var i de fleste tilfeller under kvantifiseringsgrensene. For ftalater indikerer disse resultatene at disse myknerene kan være assosiert med plastpartikler som PVC og ikke lett ekstraherbare på andre måter enn med sterke ekstraksjonsmidler.

1. Introduction

In 2015, over 300 million tons of plastic were estimated to be produced worldwide[1]. It is nowadays widely acknowledged that a proportion of this plastic reaches the aquatic environment in the form of plastic debris of various sizes. While Rochman *et al.,* in the journal *Nature,* suggested to "classify plastic waste as hazardous"[2], the scope of the impact of plastic debris on the aquatic environment and human health remains largely unknown. One significant source of micro and nanoplastics (MNPs) is municipal wastewater sludge and effluents[3] with a direct potential to impact recipient water bodies and land. Microplastics have been the subject of increasing focus over the last decade since they have been found in virtually all waters and oceans around the globe[4]. While rivers are assumed to be a major contributor of microplastic pollution to the marine environment[5], urban wastewater treatment plants are expected to be a significant emission source of not only microplastic particles[6] but also of the less studied nano-size plastic to the environment. This anthropogenic pressure on freshwater and marine ecosystems may be dependent on the type of treatment applied since higher removal efficiencies for MNPs can be expected from plants that implement tertiary treatment rather than primary/secondary treatments only. While nanoplastics can be produced from microplastic particles under natural conditions in seawater[7], it remains unclear whether nanoplastics are only formed in the marine environment[8] or emission to freshwaters are a relevant exposure route for freshwaters.

Another challenge related to plastic contamination of the environment is related to plastic additives. Chemical additives are generally added to plastics during production to enhance certain properties, e.g. flexibility, flame retardancy, or lifetime. The leaching capability of these additives such as plasticisers, flame retardants, UV stabilisers or residual curing agents depends on the type of plastic and the chemical agent itself[9]. The release of chemical additives and fate in the environment is linked to the fate of plastic (emission, particle size or breakdown). It also remains totally unclear whether MNPs release to the environment currently provides an unaccounted-for pathway for the release of chemical additives to the aquatic environment. As part of two previous projects (RIS ID 10583: Establishing an aquatic passive sampling network for the Svalbard and RIS ID 10587: Impact of Arctic urbanization on the occurrence of new "urban" contaminants in the Norwegian Arctic), we have identified a wide range of plastic chemical additives in effluents of Longyearbyen and Barentsburg. Preliminary work has been conducted by other research groups on micro-litter emissions from wastewater effluents in the Svalbard[10].

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[1] Plastic Europe

[2] Rochman et al., 2013. Nature, 494(7436), 169-171.

[3] OECD report; "Science et Avenir" article

[4] Woodall et al., 2014. Royal Society Open Science, 1(4), 140317.

[5] Dailymail article: plastic in the oceans comes from just ten rivers

[6] Murphy et al., 2016. Environmental science & technology, 50(11), 5800-5808.

[7] Gigault et al, 2016. Environmental Science: Nano, 3(2), 346-350.

[8] Andrady, 2011. Marine pollution bulletin, 62(8), 1596-1605.

[9] Valderrama et al, 2016. Environmental Science: Processes & Impacts, 18(1), 87-94.

[10] https://www.ivl.se/download/18.57581b9b167ee95ab9918f0/1551708738424/C373.pdf

The specific objectives of this proposed project are to investigate the release and presence of microplastics in the Adventfjord with this study expanded to evaluate emissions of microplastics from the Barentsburg settlement. A second objective was to evaluate the presence and distribution of selected plastic additives in sediment samples from various sites in the Adventfjord. This combined with modelling can help distinguish whether a significant proportion of additives, if present, is associated with particles of plastics they were added to during production[11]. Chemical additives that may be present in the aquatic environment in the Adventfjord can be from point sources such as the wastewater effluent, or surface run-off in the urban settlement of Longyearbyen, long-range transport with air and water masses as well as possible remobilisation with glacial meltwaters (e.g. from Adventelva).

2. Methods

2.1 Chemicals and materials

All glassware was cleaned in a furnace at 550 °C overnight. Solvents (dichloromethane, methanol, pentane and toluene) were from Rathburn (Walkerburn, Scotland) with the exception of cyclohexane (J.T. Baker, Deventer, Holland) and were of HPLC grade or better. Ultrapure water was obtained from an Option 3, Elga™. Analytical-grade standards and isotopically-labelled standards were from Chiron, Sigma-Aldrich (St. Louis, MO), and Cambridge Isotope Laboratories (Tewksbury, MA, USA). The AlteSil™ silicone rubber (0.5 mm thick) was obtained from Altec (Bude, UK).

2.2 Sediment sampling in the Adventfjord

Sediment sampling in the Adventfjord was conducted at 7 different sites in the Adventfjord. Sampling was undertaken on the 7th and 8th December 2020. A grab sampler was used to sample surface sediments. Multiple grabs were collected at each site and sediments from the top layer (> 5 cm) were placed in solvent-rinsed 2 L metal tins. For each site two 2 L-tins were filled with sediments. Sediments were transported back to Oslo and kept at 4°C until use. Subsamples were collected to measure the water content of the sediment as well as total organic carbon content (% TOC). These are given in Table 1 and Table 2.

Table 1   Details of the sediment and water sampling sites in the Adventfjord.

Sediment ID	Coordinates	Description	Water depth (m)
A	78°15'15N 15°30'50E	Near the airport	35
B	78°14'86N 15°38'95E	Near wastewater emission point	55
C	78°14'84N 15°38'69E	Near wastewater emission point	60
D	Same position as C	Near wastewater emission point	60
E	78°13'10N 15°40'20E	Near outlet of the Advent river	22
F	78°13'84N 15°36'39E	Near Longyearbyen quay	45
G	78°16'62N 15°33'27E	Reference	30-40

2.3 Sediment processing for microplastics measurements

Two strategies were put in place to characterise the microplastic content of the sediment samples with pyrolysis gas chromatography mass spectrometry (pyroGC/MS). The first strategy is based on the

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[11] Allan, Ian John, et al. "Examining the Relevance of the Microplastic-Associated Additive Fraction in Environmental Compartments." *ACS ES&T Water* 2.3 (2022): 405-413.

cryomilling of the sediment while the second uses also uses density separation to separate the microplastics from the matrix prior to pyroGC/MS analysis.

Each sediment batch was sub-sampled and 200 g of wet sediment was placed in clean glass jars. They were then placed at -20 °C. Water was removed by freeze drying the sediment over 48 hours. Once freeze drying complete, sediments were kept at room temperature until further use. Cryomilling was conducted using approximately 45-50 g of sediments placed into the stainless-steel chamber of a 6875D Freezer/Mill® Dual-Chamber Cryogenic Grinder (Spex, New Jersey, USA). The cryomilling programme started with a pre-cooling step (-197 °C) using liquid nitrogen for 15 min. This step was followed by five cycles with a run time of 2 min milling at 12 counts per second followed by 2 min of cooling. Blanks with clean sand were run in between actual sediment samples and the milling cells washed between each sample. Cryomilled sediments were then placed in a new glass jar covered with aluminium foil and a lid.

Density separation was conducted using 10 g of cryomilled sediment placed in a 60 mL glass tube. A sodium iodide (NaI) solution in ultrapure water was prepared by dissolving 800 g of NaI into 1 L of ultrapure water. This solution was filtered using 0.45 µm glass fibre filter prior to use. Thereafter, 25 mL of NaI solution was added to the glass tubes. Tubes were shaken by hand and then placed in ultrasonic bath for 20 min. Tubes were left to settle and were centrifuge at 2700 rpm for 5 min. One tube was used for microplastic measurement while the second one was used for quantification of plastic additives. For microplastics, the suspension was collected through a 1 µm cellulose nitrate filter and the side walls of the glass tube were rinsed with ultrapure water. A blank sample treated in the same way as samples was prepared. Cellulose nitrate filters were placed in a new container for clean-up with kalium hydroxide (KOH; 2M). During KOH treatment to degrade the organic matter present in the samples, the cellulose nitrate filter is destroyed. A similar KOH treatment is undertaken for the cryomilled sediment samples. The KOH solution is centrifuged (4500 rpm) and replaced with fresh KOH (2M). Finally, samples are either freeze dried (sediment samples) or filtered through a 1 µm 13 mm wide glass fibre filter (water samples) for pyroGC/MS analysis.

Table 2   Masses of sediment used during the density separations and total organic carbon content of the sediment.

	Mass vial (g)	Mass vial + sediment (g)	Mass of wet sediment /g	Mass of dry sediment (g)	TOC (%)	Water content (%)
A	31.16	90.51	59.35	27.76	1.8	53
	36.77	96.13	59.36	27.77		
B	30.37	80.90	50.53	14.30	2.1	72
	30.87	96.68	65.81	18.62		
C	30.76	82.69	51.93	16.98	2.2	67
	30.90	89.91	59.01	19.30		
D	36.29	88.92	52.63	14.90	2.2	72
	37.06	90.28	53.22	15.07		
E	36.94	92.89	55.95	10.86	1.6	81
	37.22	101.1	63.87	12.40		
F	36.84	92.81	55.97	14.34	2.1	74
	30.77	84.84	54.07	13.85		
G	31.11	87.89	56.78	10.83	2.0	81
	36.48	97.80	61.32	11.70		

2.4 Water sampling and sample processing for microplastics

Water sampling in the Adventfjord was conducted using a Niskin water sampler. The sampler was deployed and lowered to the appropriate depth, 4-5 m above the seabed. The water samples were transferred to clean glass bottles (2.5 L) prior to further processing.

Table 3 Water sampling of bottom waters of the Adventfjord.

Sample ID	Date	Volume (mL)	
A			
B1	07.12.2020	2100	F10 (7.16)
B2	08.12.2020	2980	
C	07.12.2020	2100	F7 (7.03)
D	08.12.2020	2200	F12 (7.24)
E1	07.12.2020	2250	F9 (7.19)
E2	08.12.2020	2310	F11 (7.23)
F	08.12.2020	1600	F8 (7.22)
G	07.12.2020	2000	F6
Field blank*			F4 (7.30), F5 (7.13)
*1 µm cellulose nitrate filter kept in an open petri dish during sample filtration operations			

Water sampling of the effluent at Barentsburg was conducted on 6 occasions between the 22nd and the 29th of December 2021.

Table 4 Efluent sampling at Barentsburg

Sample ID	Date	Volume (mL)
BAR 1	22.12.2021	1096
BAR 2	23.12.2021	1123
BAR 3	24.12.2021	1116
BAR 4	27.12.2021	1119
BAR 5	28.12.2021	1104
BAR 6	29.12.2021	1123
Blank	-	

Water sampling was also conducted for the effluent from Longyearbyen on 3 occasions from the 20th to the 22nd of April 2022. Since these samples contained relatively large amounts of suspended matter, these were centrifuge at 10 000 rpm for 20 min prior to filtration at 1 µm with cellulose nitrate filters. The supernatant was filtered first and the settled material was resuspended in a small amount of ultrapure water. This was then added to a filter in a smaller container for KOH (2M) clean-up. This clean-up was repeated a second time before pH equilibration and H_2O_2 treatment. The final residue after centrifugation was grinded in a ball grinder prior to analysis by pyroGC/MS.

Table 5   Effluent sampling at Longyearbyen

Sample ID	Date	Volume (mL)	Mass of material (g)	Mass of material analysed (mg)
LYB 1	20.04.2022	1000	0.93	3.55 3.60
LYB 2	21.04.2022	1000	0.28	3.60 3.71
LYB 3	22.04.2022	1000	0.44	4.27 4.21

Blank			0.0393	6.71

2.5 Pyrolysis gas chromatography-mass spectrometry for quantification of microplastics

Two methods were used for the detection and quantification of plastics in environmental samples. The first set of samples that include water samples from the Adventfjord were analysed with first method.

A Frontier lab multi shot pyrolizer and auto shot sampler connected to an Agilent GC/MSD was used for pyrolysis GC/MS analysis of the microplastics. The analytical method for the simultaneous quantification of 10 different polymers was adapted from Ishimura et al.[12] and Matsueda et al.[13] and calcium carbonate was added as catalyst. For the external calibration, deuterated-labelled polybutadiene was added to the calibration mixtures. The samples were also scanned for rubber, originated from car tires. Details of the pyrolysis-GC/MS methods are given in Table 6 and Table 7.

Table 6   Retention time, main and qualifier ions used for the detection and quantification of plastics and calibration range (μg per sample cup) for the first pyroGC/MS method.

	RT (min)	Mz	Qualifiers	Calibration
PE	62	82	55, 83	6-206μg
PET	38.4	163	135, 194	11-340g
PVC	3.37	78	50, 52	17-40 μg
PP	8.4	70	55, 83	19-34μg
PS	68.6	91	117. 207	11-25μg
PA6	26.7	127	55, 70	25-45μg
PA66	63.1	226	55	13-89μg
ISTDdPS	10.4	109	82, 107	

Table 7   Retention time, main and qualifier ions used for the detection and quantification of plastics and calibration range (μg per sample cup) for the second pyroGC/MS method.

	RT (min)	Mz	Qualifiers	Calibration
PMMA	3.4	100	69, 85	0.5 – 21.6
N6.6	4.4	84	55	2.1 – 60
PP	5.0	126	83, 70, 55	2.5 – 91
PVC	8.3	128	127, 129	1.2 – 94.4
N6	8.8	113	85, 55	1.2 – 7
PC	9.1	134	119, 91	0.6 – 11.5
PET	11.3	182	105, 77, 51	1.6 – 42
PE	13.5	82	264, 96	9.2 – 400
ABS	14.1	170	156	0.5 – 41.8

[12] Ishimura, T., Iwai, I., Matsui, K., Mattonai, M., Watanabe, A., Robberson, W., ... & Watanabe, C. (2021). Qualitative and quantitative analysis of mixtures of microplastics in the presence of calcium carbonate by pyrolysis-GC/MS. *Journal of Analytical and Applied Pyrolysis*, *157*, 105188.

[13] Matsueda, M., Mattonai, M., Iwai, I., Watanabe, A., Teramae, N., Robberson, W., ... & Watanabe, C. (2021). Preparation and test of a reference mixture of eleven polymers with deactivated inorganic diluent for microplastics analysis by pyrolysis-GC–MS. *Journal of Analytical and Applied Pyrolysis*, *154*, 104993.

PS	15.4	91	117, 194, 207	0.8 – 48.1
ISTD d-Pb	4.8	60	86	

2.6 Contaminant and plastic additive extraction and analysis

An extraction and analytical strategy was developed to evaluate the distribution of contaminants and additives in sediments collected in the Adventfjord according to the expected distribution reported in the Figure 1. A list of the chemicals of interest is given in Table 8 and includes the compound's name, CAS number, octanol-water partition coefficient (logK$_{ow}$) and silicone rubber-water partition coefficient (logK$_{sw}$). Compounds of interest included a persistent organic pollutant (POP), hexachlorobenzene, some plasticisers (e.g. phthalates), some brominated flame retardants such as pentabromotoluene, and benzotriazole UV filters.

Table 8   Chemical of interest, their CAS numbers, octanol-water partition coefficient (logK$_{ow}$) and silicone-water partition coefficients (logK$_{sw}$)

Compound	Abbreviation	CAS number	logK$_{ow}$*	logK$_{sw}$**	
Hexachlorbenzene	*HCB*	118-74-1	5.7	5.01 (0.02)	Smedes (2018)[14]
Acetyl tributylcitrate	Acetyl tributylcitrate	77-90-7	3.3		
Octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate	Plastic additive 11	2082-79-3	13.8		Smedes (2018)
Dibutylphthalate	DiP	84-74-2	4.7	4.64 (0.09)	Smedes (2018)
Benzylbutyl-phtalate	BBP	85-68-7	4.9	5.20 (0.13)	Smedes (2018)
Bis(2-ethylhexyl) phthalate	DEHP	117-81-7	7.4	4.61 (0.13)	Smedes (2018)
Diiso-nonylphthalate	DINP	28553-12-0	9.6	5.11 (0.14)	Smedes (2018)
Diiso-decyl-phthalate	DIDP	26761-40-0	10.6		
Pentabromotoluene	PBT	87-83-2	5.7	5.68	*Estimated[15]*
Hexabromobenzene	HBB	87-82-1	6.1	5.74	*Estimated*
Benzophenone-3	BP3	131-57-7	3.6	3.08	Pintado-Herrera et al. (2016)[16]
2,4-dihydroxybenzophenone	2,4-dihydroxy-BP	131-56-6	3.2		
2-hydroxy-4-(octyloxy)benzophenone	2-hydroxy-4-(octyloxy)BP	1843-05-6	6.8		
Octocrylene	OC	6197-30-4	7.1	4.95	Pintado-Herrera et al. (2016)
Ethylhexyl methoxycinnamate-Z	EHMC-Z	5466-77-3	5.3	4.77	Pintado-Herrera et al. (2016)
Ethylhexyl methoxycinnamate-E	EHMC-E	5466-77-3	5.3	4.77	Pintado-Herrera et al. (2016)
2-Ethylhexyl-4-dimethyl-aminobenzoate	ODPABA	21245-02-3	5.0	4.49	Pintado-Herrera et al. (2016)
2-(2H-benzotriazol-2-yl)-4,6-di-tert-butyl-phenol	UV-320	3846-71-7	7.3	6.70	*Unpublished****
2-(2'Hydroxy-3'-Tert-Butyl-5'-Methylphenyl)-5-Chlorobenzotriazole	UV-326	3896-11-5	5.6	6.46	*Unpublished*

[14]Smedes, Foppe. "Silicone–water partition coefficients determined by cosolvent method for chlorinated pesticides, musks, organo phosphates, phthalates and more." *Chemosphere* 210 (2018): 662-671.

[15]Sobotka, Jaromír, et al. "Dynamic passive sampling of hydrophobic organic compounds in surface seawater along the South Atlantic Ocean east-to-west transect and across the Black Sea." *Marine Pollution Bulletin* 168 (2021): 112375.

[16]Pintado-Herrera, Marina G., et al. "Determination of silicone rubber and low-density polyethylene diffusion and polymer/water partition coefficients for emerging contaminants." Environmental toxicology and chemistry 35.9 (2016): 2162-2172.

2,4-di-tert-butyl-6-(5-chlorobenzotriazol-2-yl)phenol	UV-327	3864-99-1	6.9	7.04	*Unpublished*
2-(2H-1,2,3-Benzotriazol-2-yl)-4,6-bis(2-methylbutan-2-yl)phenol	UV-328	247-384-8	7.4	6.87	*Unpublished*
2-(2H-benzotriazole-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol	UV-329	3147-75-9	7.3	6.31	*Unpublished*
LogK$_{ow}$ from PubChem ([PubChem (nih.gov)](#))					
**Silicone-water partition coefficients (L kg^{-1}) for AlteSil™ silicone rubber					
***Results from experiments conducted at NIVA but not yet published					

Total concentrations

First, an exhaustive Soxhlet extraction with 250 mL (toluene/dichloromethane) for 8 hr was performed to evaluate total concentration of additives. In short, glass fibre thimbles (from Sigma Aldrich) were clean by placing them in aluminium foil and in the furnace at 550 °C overnight. Between 5.2 and 5.8 g dry sediment was placed in the thimble inserted into the Soxhlet extractor. Replicate extractions of each sediment were conducted. Two blanks composed only of the extraction thimble and solvent were used to evaluate possible contamination during sample work up. Recovery work with chemical additives of interest were tested as part of similar study earlier. Internal standards were pipetted directly onto the sample once placed in the Soxhlet extractor. These included the deuterium-labelled DEHP (d4-DEHP) spiked at a level of 50 ng per sample. For UV filters, internal standards were d$_3$-Benzophenone-3, d$_{15}$-ethylhexyl methoxycinnamate (Z/E), d$_3$-Bumetrizole and ^{13}C-labelled Octocrylene spiked at a concentration level of 25 ng per sample. For the quantification of hexachlorobenzene, the polychlorinated biphenyl congener PCB 30 was added to the extraction vessel (50 ng per sample). These recovery standard concentration levels were the same for all sample types. Once the extraction completed, samples were transferred to a vial for gentle evaporation of the solvent with a stream of nitrogen. The set-up for quantitation is given in Table 9.

Table 9   Set-up for the quantitation of the various compounds

pcb-30	ISTD
pcb-53	ISTD
BP3-d5	ISTD
EHMC-d15 Z	ISTD
EHMC-d15 E	ISTD
pcb-204	ISTD
d3-bumetrizole	ISTD
d4-DEHP	ISTD
13C-OC	ISTD
BP-d10	BP3-d5
HCB	pcb-30
dibutylphtalate	d4-DEHP
BP3	BP3-d5
2,4-dihydroxyBP	pcb-53
EHMC-Z	EHMC-d15 Z
ODPABA	EHMC-d15 E
pentabromotoluene	pcb-204

Tributyl-O-acetylcitrate	pcb-204
EHMC-E	EHMC-d15 E
benzylbutyl-phtalate	d4-DEHP
hexabromobenzene	pcb-204
UV-320	d3-bumetrizole
DEHP	d4-DEHP
UV-326	d3-bumetrizole
UV-329	13C-OC
OC	13C-OC
UV-327	13C-OC
UV-328	13C-OC
2-hydroxy-4-(octyloxy)BP	pcb-204
diiso-nonyl-phtalate	d4-DEHP
diiso-decyl-phtalate	d4-DEHP
Plastic add-11	pcb-204

Accessible concentrations

AlteSil™ silicone rubber was used to extract the accessible fraction of additives that may be present in these sediment batches[17]. The silicone rubber was first cleaned using a soxhlet extractor and ethyl acetate to remove impurities and silicone oligomers. This was followed by further cleaning by soaking in methanol. Batch experiments were conducted in duplicate in 50 mL glass centrifuge tubes to expose 4 g of silicone rubber to 1 g of dry sediment. A 80:20 solution of ultrapure water:methanol (25mL) was added to centrifuge tubes before the silicone rubber strips were added. Centrifuge tubes were placed horizontally on an orbital shaker at 150 rpm for 24 h and 30 d. With 2 % OC carbon on average dry weight in these sediment batches, the nominal mass ratio of silicone rubber to OC was 200. Once the extraction complete, silicone rubber strips were removed, cleaned with ultrapure water and dried prior to extraction using pentane (2x 50 mL). Internal standards were added during the first pentane extraction. Sample volumes were then reduced under a gentle stream of nitrogen.

The accessible concentration represents a concentration of chemicals of interest able to desorb easily from the sedimentary matrix[18].

Measurement of C_{free} in the sediment

The freely dissolved concentration of additives in the sediment was measured with the help of silicone rubber. Instead of using a large mass of silicone rubber for a small amount of sediment as was done with the accessible concentration measurement, here a small silicone rubber strip (100 mg) is placed in a 1 L glass jar containing 900 mL of each of the sediment (wet sediment). The jars were placed horizontally on an orbital shaker at 80 rpm for 6 weeks. One jar per sediment was prepared and two blank silicone strips were used to evaluate possible contamination during experimental procedures.

[17] Allan, I. J., O'Connell, S. G., Meland, S., Bæk, K., Grung, M., Anderson, K. A., & Ranneklev, S. B. (2016). PAH accessibility in particulate matter from road-impacted environments. *Environmental science & technology*, *50*(15), 7964-7972.
[18] Reichenberg, F., & Mayer, P. (2006). Two complementary sides of bioavailability: accessibility and chemical activity of organic contaminants in sediments and soils. *Environmental Toxicology and Chemistry: An International Journal*, *25*(5), 1239-1245.

Then for each compound, C_{free} was estimated from the polymer-water partition coefficient, K_{pw} specific to the compound of interest and the polymer used in the measurement[19].

Extraction of density separated material

In a final set of extractions, density separations of the various batches of sediment were conducted. Ten grams of cryomilled sediment was placed in a 50 mL centrifuge tube and 25 mL of a solution of sodium iodide (density of 1.7 g mL^{-1}) was added. The slurry was vigorously shaken and placed in an ultrasonic bath for 2x 20 min. Vials were then left to settles prior to centrifugation at 2700 rpm for 5 min (same as for the microplastic determination). The supernatant was poured through a glass fibre extraction thimble before an exhaustive extraction of the material in suspension by Soxhlet. The procedure described above for the total concentration measurements was followed.

The Soxhlet extraction is expected to extract most of the chemicals associated with the sedimentary matrix as well as those associated with microplastics.

Sample clean-up and instrumental analysis for phthalates and UV filters by GC/MSMS

The solvent of the extracts (dichlormethane or pentane) was changed to ethyl acetate: cyclohexane (80:20, v:v) and interfering matrix and sulphur was removed by GPC (gel permeation chromatography). Due to very high sulphur contents, the extracts needed to get treated with activated copper prior GC/MSMS analysis. Phthalates and UV filters were quantified by isotopic dilution method. To ensure the validity of the calibration over the hole batch, QC samples were injected approx. after 10 samples.

Modelling

We have shown in previous work that it was possible to apply some relatively simple multiphase equilibrium modelling to evaluate whether a significant proportion of plastic additives are emitted as an integral part of microplastics particles[20]. In many environments such as soils and sediments, non-ionised and hydrophobic plastic additives can be distributed between the dissolved phase, the organic matter (OM) and the plastic particles that may be present. Plastic additives may be in high concentration in plastic particles that they were originally added to and may be released into the environment. These additives may also sorb from the environment to plastic particles that are free of such additives to start with. Sorption to sediments for these compounds is driven by interaction with the organic matter through the organic carbon-water partition coefficient, K_{oc}. The latter will be dependent on the type of organic matter present in the sediment. Black carbon or coal particles such as those that can be found in the Svalbard environment will tend to increase the apparent sediment-water distribution coefficient.

[19] Allan, I. J., Raffard, V., Kringstad, A., & Næs, K. (2021). Assessment of marine sediment remediation efficiency with SPME-based passive sampling measurement. *Science of The Total Environment*, *756*, 143854.

[20] Allan, I. J., Samanipour, S., Manoli, K., Gigault, J., & Fatta-Kassinos, D. (2022). Examining the Relevance of the Microplastic-Associated Additive Fraction in Environmental Compartments. *ACS ES&T Water*, *2*(3), 405-413.
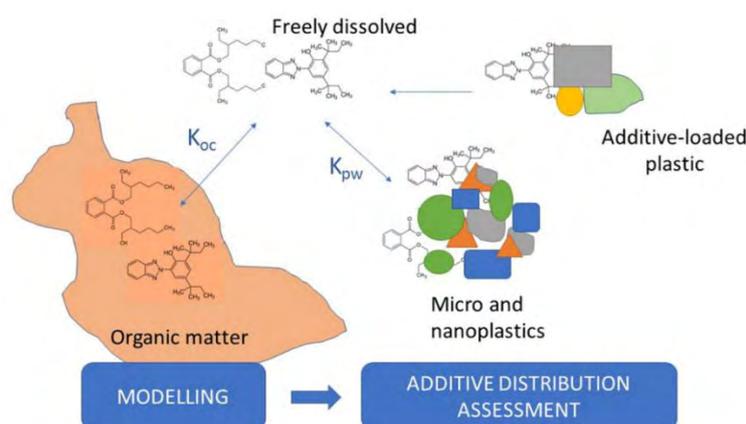
Figure 1   Expected distribution of plastic additives in aquatic sedimentary environments

3. Results and discussion

3.1   Microplastic concentrations in water samples from the Adventfjord

Samples were collected in wintertime with very low suspended particulate matter in water allowing filtration at 1 μm of approx. 2 L of fjord water. Traces of polyethylene, polystyrene, and polypropylene were sporadically found in samples (Table 11). Polyvinyl chloride was more consistently found in the Adventfjord water samples. The highest concentrations of PE and PVC detected were 12-13 μg L^{-1}. That is equivalent to approximately 20 plastic particles with a diameter of 100 μm or 20 000 with a diameter of 10 μm. For PVC, we cannot be certain that the signal is truly from PVC only and may be partly the result of the presence of coal particles in the samples. In general, the calibration range for the pyro-GCMS analyses is in line with other studies[21] but few data exist for this environment. Previous microplastic sampling with manta trawl and pumping in the Adventfjord in 2018 showed low levels of microplastics[22] with less than one particle per m^3.

Table 10   Plastic content of the water samples collected in the Adventfjord (μg L^{-1})

Site	Description	PE	PA66	PA6	PS	PP	PET	PVC
B1	Near wastewater emission point	**1.9**	<LOD	<LOD	<LOD	**1.1**	<LOD	**3.9**
C	Near wastewater emission point	**13.0**	<LOD	<LOD	<LOD	<LOD	<LOD	**12.2**
D	Near wastewater emission point	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.6**
E1	Near outlet of the Advent River	**2.6**	<LOD	<LOD	**2.5**	<LOD	<LOD	**2.2**
E2	Near outlet of the Advent River	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**6.6**
F	Near Longyearbyen quay	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
G	Reference	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**3.0**
LOD close to 1 μg per filter analysed								

3.2   Microplastic concentrations in sediment samples from the Adventfjord

The microplastic content of the sediment batches was assessed and is reported in Table 11. All plastics except for PVC are not detected in the samples. Limits of detections are the lowest for polystyrene

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[21] Dierkes, Georg, et al. "Quantification of microplastics in environmental samples via pressurized liquid extraction and pyrolysis-gas chromatography." *Analytical and bioanalytical chemistry* 411.26 (2019): 6959-6968.

[22] Carlsson, P., Singdahl-Larsen, C., & Lusher, A. L. (2021). Understanding the occurrence and fate of microplastics in coastal Arctic ecosystems: The case of surface waters, sediments and walrus (Odobenus rosmarus). *Science of The Total Environment*, *792*, 148308.

(PS) with LODs below 0.1 $\mu g\ mg^{-1}$. For the other plastics, limits of detection vary between 0.2 and 1 $\mu g\ mg^{-1}$.

Levels of PVC are relatively consistent with values in the range of 1.6-3.9 $\mu g\ g^{-1}$ dw. The concentration for the blanks were lower with an average of 0.9 $\mu g\ g^{-1}$ dw. Overall PVC concentrations may reflect partly some contamination during sample preparation, actual presence of PVC in some of the samples (e.g. in sediment batch C), or a signal from the presence of trace of coal in the samples. The quantification of PVC with pyroGC/MS may be hindered in case coal or black carbon is present in the sample. In general, the direct analysis of some mg of sediment result in limits of detection of plastic particles in mg per gram of sediment. Combining the pyrolysis instrumental analysis with a density separation technique based on using tens of grams of sediment allows to considerably lower limits of detection with LODs well below $\mu g\ mg^{-1}$ dw sediment level. Only polypropylene (PP) was above limits of detection when density separation was applied in samples B and G (Table 10) with concentrations at 0.20 and 0.06 $\mu g\ g^{-1}$. The PVC signal for all samples was well above the calibration curve. However, this is not a surprise since coal particles were buoyant and extracted with the density separation method.

Table 11   Plastic content of the sediment samples collected in the Adventfjord ($\mu g\ mg^{-1}$ dw sediment)

Site	Description	PMMA	N66	PP	PVC*	N6	PC	PET	PE	ABS	PS
A	Wastewater emission point	<0.16	<0.27	<0.40	**1.6 (*18*)**	<0.54	<0.16	<0.54	<0.54	<0.13	<0.05
B	Wastewater emission point	<0.24	<0.40	<0.60	**3.0 (*42*)**	<0.80	<0.24	<0.80	<0.80	<0.20	<0.08
C	Near wastewater emission point	<0.21	<0.35	<0.52	**3.9 (*67*)**	<0.70	<0.21	<0.70	<0.70	<0.17	<0.07
D	Outlet of Advent River	<0.18	<0.29	<0.44	**3.0 (*24*)**	<0.58	<0.18	<0.58	<0.58	<0.15	<0.06
E	Outlet of Advent River	<0.17	<0.28	<0.43	**1.6 (*4.1*)**	<0.57	<0.17	<0.57	<0.57	<0.14	<0.06
F	Longyearbyen quay	<0.19	<0.31	<0.47	**2.2 (*10*)**	<0.63	<0.19	<0.63	<0.63	<0.16	<0.06
G	Reference	<0.20	<0.33	<0.50	**3.3 (*10*)**	<0.66	<0.20	<0.66	<0.66	<0.17	<0.07
	Blank sediment	<0.21	<0.36	<0.54	**0.9 (*11*)**	<0.71	<0.21	<0.71	<0.71	<0.18	<0.07

Average of two pyro-GC/MS analyses (relative percent difference, %RPD in brackets). The blank sediment was prepared from a deep core of marine sediments collected in the North Sea that is not expected to have been in contact with recent plastic contamination. *The PVC signal in these sediments may be related to the presence of coal particles and may or may not be due to the actual presence of PVC microplastic contamination.

Table 12   Plastic content of the sediment samples extracted with density separation ($\mu g\ g^{-1}$ dw sediment)

Site	Description	PMMA	N66	PP	PVC*	N6	PC	PET	PE	ABS	PS
A	Wastewater emission point	<0.02	<0.08	<0.02	**>calib**	<0.04	<0.06	<0.07	<0.19	<0.02	<0.01
B	Wastewater emission point	<0.03	<0.11	**0.20**	**>calib**	<0.06	<0.09	<0.11	<0.27	<0.02	<0.01
C	Near wastewater emission point	<0.03	<0.11	<0.03	**>calib**	<0.06	<0.08	<0.11	<0.26	<0.03	<0.01
D	Outlet of Advent River	<0.04	<0.14	<0.03	**>calib**	<0.07	<0.10	<0.13	<0.33	<0.04	<0.01
E	Outlet of Advent River	<0.04	<0.16	<0.04	**>calib**	<0.08	<0.12	<0.17	<0.41	<0.04	<0.01
F	Longyearbyen quay	<0.04	<0.14	<0.03	**>calib**	<0.08	<0.11	<0.14	<0.36	<0.04	<0.01
G	Reference	<0.05	<0.14	**0.06**	**>calib**	<0.09	<0.12	<0.17	<0.43	<0.04	<0.01

*The PVC signal in these sediments may be related to the presence of coal particles and may or may not be due to the actual presence of PVC microplastic contamination. ">calib" indicates that the signal was above our highest pyrolysis GCMS calibration point.

3.3   Microplastic concentrations in Barentsburg effluent

The microplastic content of the effluents at Barentsburg sampled on six occasions is given in Table 13. Except for the PVC signal, traces of polypropylene were found close to limits of detection (~0.4 $\mu g\ L^{-1}$). Because of the smaller volumes of water (logistically easier), limits of detections tend to be higher than for the Adventfjord water samples.

Table 13 Plastic content of the effluent samples from Barentsburg (µg L^{-1})

Sample	PMMA	N66	PP	PVC*	N6	PC	PET	PE	ABS	PS
BAR 1	<0.46	<1.8	<0.4	<0.91	<0.9	<1.4	<1.8	<4.6	<0.5	<0.1
BAR 2	<0.45	<1.8	<0.4	**4.6**	<0.9	<1.3	<1.8	<4.5	<0.5	<0.1
BAR 3	<0.45	<1.8	**0.4**	**5.1**	<0.9	<1.3	<1.8	<4.5	<0.5	<0.1
BAR 4	<0.45	<1.8	<0.4	**>Calib**	<0.9	<1.3	<1.8	<4.5	<0.5	<0.1
BAR 5	<0.45	<1.8	**0.4**	**8.5**	<0.9	<1.4	<1.8	<4.5	<0.5	<0.1
BAR 6	<0.45	<1.8	**0.4**	**9.5**	<0.9	<1.3	<1.8	<4.5	<0.5	<0.1
Blank 1	<0.45	<1.8	<0.4	**0.1**	<0.9	<1.4	<1.8	<4.6	**0.08**	<0.1
Blank 2	<0.46	<1.8	<0.4	**0.9**	<0.9	<1.4	<1.8	<4.6	**0.46**	<0.1

*The PVC signal in these sediments may be related to the presence of coal particles and may or may not be due to the actual presence of PVC microplastic contamination. ">calib" indicates that the signal was above our highest pyrolysis GCMS calibration point.

3.4   Microplastic concentrations in Longyearbyen effluent

Results of sampling the effluent of Longyearbyen are reported in Table 14. The limits of detection are higher than those for the samples from Barentsburg. The mass of suspended matter recovered after filtration and treatment was much higher for the samples from Barentsburg. Since the mass added to the sample cup for analysis was in the same range of a few mg for both sets of samples, this result in higher LODs for these samples. PET was consistently detected in the samples and duplicate instrumental analyses resulted in low relative percent differences. PVC and Nylon were found in some of the samples. Relative percent differences between duplicate instrumental analyses were low. The presence of PVC is consistent with the PVC signal from the Adventfjord sediments. The presence of nylon, e.g. from clothing in the wastewater effluent is expected since the effluent is primarily from households. The signal of PET and nylon was not observed in the water or the sediment from the Adventfjord. The untreated effluent in Longyearbyen has seldom been monitored for its content of microplastics. Microfibres monitored extensively in 2017 in the effluent showed a content of 0 to over 200 microfibres (> 50 µm) per litre of wastewater[23].

Table 14 Plastic content of the effluent samples from Longyearbyen (µg L^{-1})

Sample	PMMA	N66	PP	PVC	N6	PC	PET	PE	ABS	PS
LYB 1	<65	**767(16)**	<340	<160	<160	<78	**416 (1)**	<1200	<80	<110
LYB 2	<19	8	<100	**917 (14)**	<46	<23	**100 (18)**	<360	<23	<31
LYB 3	<26	**968 (14)**	<135	<62	<62	<31	**240 (1)**	<480	<31	<42
Blank	<2	<1	<8	**3.5**	<4	<2	**5.3**	<27	<2	<3

Relative percent difference (% RPD) of duplicate pyroGC/MS analyses are given in brackets.

3.5   Contaminant presence and distribution in Adventfjord sediments.

3.5.1   Total concentrations

Different analytical strategies were applied to extract selected organic contaminants from the different sediment batches. Compounds of interest included one persistent organic pollutant, hexachlorobenzene (HCB), some plasticisers (e.g. a range of phthalates), some brominated flame retardants such as pentabromotoluene and hexabromobenzene, and a series of benzotriazole UV filters. Total concentrations measured by Soxhlet extraction are given in Table 15. Only a few contaminants are found above limits of detection. The globally distributed HCB[24] was detected in the sediment samples A, B, C, D and G (i.e. the representative of background levels for

[23] Herzke, D., Ghaffari, P., Sundet, J. H., Tranang, C. A., & Halsband, C. (2021). Microplastic fiber emissions from wastewater effluents: Abundance, transport behavior and exposure risk for biota in an arctic fjord. *Frontiers in environmental science*, *9*, 662168.

[24] Allan, Ian John, et al. "Passive sampling and benchmarking to rank HOC levels in the aquatic environment." *Scientific reports* 11.1 (2021): 1-12.

microplastics/effluent transport in the present study). Concentrations in sediments E and F, near the outlet of the Advent River and near Longyearbyen quay, respectively were a factor of 5-6 higher than at the other sites. HCB is stored in glaciers and terrestrial environments and can be emitted during snowmelt or come from the urban environment where surface run-off may be responsible for these higher concentrations. This is however not in line with our previous results showing higher levels of HCB further away from the Adventelva River[25]. However, it is difficult to conclude based on these results solely. A higher proportion of coal particles could result in higher total sediment concentrations.

Certain phthalate plasticisers, namely dibutyl phthalate (DiP), benzylbutyl phthalate (BBP) and bis(2-ethylhexyl) phthalate (DEHP) are consistently detected in the sediments. As can be seen from Table 8, these substances are hydrophobic, exhibiting high $\log K_{ow}$ values and will tend to sorb to sediments. A gradient of concentrations can be seen for these substances with highest concentrations seen for sediment batches C and D, closest to Longyearbyen wastewater emission point. In some cases, relative percent difference (%) of duplicate analyses appear to be high in some cases (e.g. 170 % for duplicate analyses of DiP in sediment C). This variability may be due to the heterogeneity of the distribution of these contaminants in sediment.

The impact of wastewater-based contamination of sediments C and D shown by the presence of plasticisers is reinforced the detection of a number of UV filters often found in urban effluents. Octocrylene and ethylhexyl methoxycinnamate (EHMC) are UV filters often used in personal care products and are found above limits of detection and in highest concentrations in sediments C and D. Levels barely above limits of detection were observed for UV-328.

Table 15 Total sediment concentrations (ng g^{-1} dw)

Compound	Accessible concentrations (ng g^{-1} dw)						
	A	B	C	D	E	F	G
POP							
HCB	**0.18 (6)**	**0.19 (1)**	**0.18 (6)**	**0.18 (1)**	**0.96 (5)**	**1.3 (71)**	**0.20 (9)**
Plasticisers/flame retardants							
Acetyl tributylcitrate	<11	<11	<14	<11	<12	<11	<11
Plastic additive 11	<2000	<2000	<2000	<2000	<2000	<2000	<2000
DiP	<47	<28	**4701 (170)**	**955 (15)**	**220 (32)**	173	<81
BBP	**42 (191)**	**2.3**	**130 (180)**	**22**	**7.0 (65)**	**3.2**	**4.4 (150)**
DEHP	**493 (104)**	**<63**	**5727 (18)**	**1236 (46)**	**143 (126)**	<134	<209
DINP	<2000	<2000	<2000	<2000	<2000	<2000	<2000
DIDP	<2000	<2000	<2000	<2000	<2000	<2000	<2000
PBT	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
HBB	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
UV filters							
BP3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3	<1.3
2,4-dihydroxy-BP	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
2-hydroxy-4-(octyloxy)BP	NA	NA	NA	NA	NA	NA	NA
OC	<1.4	<1.4	**1.7**	**2.5 (30)**	<1.4	<1.4	<1.4
EHMC-Z	<0.12	<0.06	**2.5 (168)**	**0.88 (9)**	**0.64 (3)**	**0.73 (168)**	<0.15
EHMC-E	**0.06**	**0.14 (13)**	**1.1 (160)**	**0.43 (6)**	**0.31 (17)**	**0.31 (142)**	**0.07 (48)**
ODPABA	NA	NA	NA	NA	NA	NA	NA
UV-320	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
UV-326	<0.8	<0.8	<0.8	<0.8	<0.9	<0.8	<0.8
UV-327	**0.03 (130)**	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
UV-328	<0.03	<0.05	**0.50**	**0.05**	**0.05**	<0.02	<0.02

[25] Johansen, Sverre, et al. "Terrestrial inputs govern spatial distribution of polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) in an Arctic fjord system (Isfjorden, Svalbard)." *Environmental Pollution* 281 (2021): 116963.

UV-329	<1.5	<1.5	<1.5	<1.5	<1.6	<1.5	<1.5
Mean of duplicate extractions and analyses (relative percent difference, % RPD in brackets)							

3.5.2   Accessible/easily extractable concentrations

Accessible concentrations were measured through batch extraction experiments using silicone rubber placed in contact with the sediment in water and agitated vigorously for 24 hours and 30 days. As shown in Table 8, polymer-water partition coefficients for AlteSil™ silicone rubber are high. These high $logK_{sw}$ mean that compounds able to desorb will transfer to the silicone rubber[26]. As shown in Table 16, most compounds are found below limits of detection. The only compound consistently found in these sediment samples and in line with total concentrations is the UV filter EHMC. The plasticiser, acetyl tributylcitrate is sparsely well above detection limits in sediments B, F and G. Although laboratory blank levels were low, we cannot exclude the possibility of contamination of the samples during extraction/analysis. Other plasticisers such as DiP, BBP and DEHP and UV filter UV-327 and UV-328 were sporadically found above limits of detection as well.

3.5.3   Freely dissolved concentrations

Freely dissolved concentrations (C_{free}) of these contaminants were also measured using silicone rubber. Small size silicone rubbers were exposed to sediment slurries and agitated for a sufficiently long period of time to establish an equilibrium between the contaminant concentration in the silicone and that in the sediment. Silicone-water partition coefficients provided in Table 8 ($logK_{ow}$ was used as proxy for $logK_{sw}$ for substances for which $logK_{sw}$ are not available). Values of C_{free} were calculated from:

$$C_{Free} = \frac{C_{sil}}{K_{sw}}$$

with C_{sil} the contaminant concentration in silicone at equilibrium. Most freely dissolved contaminant concentrations are below limits of detection with these ranging from tens of ng per litre down to low pg per litre level. Limits of detection are related to the instrumental analysis but also to $logK_{sw}$ values. Limits of detection will be proportionally lower for compounds with higher K_{sw}. Values of C_{free} for EHMC-Z were in the 40-60 pg L^{-1} in sediment batches B, D and E. The detection of this compound is in line with results from total and accessible concentration measurements. It is however surprising not to find some of the other contaminants present at much higher total concentrations above LOD with accessible or freely dissolved concentration measurements. HCB was above LOD in sediment A with an estimated C_{free} of 10 pg L^{-1}.

We can calculate organic carbon-water distribution coefficients ($logK_{oc}$) for these compounds:

$$logK_{oc} = \frac{C_{sed,total}/OC}{C_{Free}}$$

with $C_{sed,total}$ the total contaminant concentration in the sediment and OC the proportion of organic carbon content of the sediment. For both EHMC-Z and HCB, calculated $logK_{oc}$ are close to 6.0. These values are in line but slightly higher than the $logK_{ow}$ values of 5.3 and 5.7 for EHMC-Z and HCB, respectively (Table 8). This may be the result of strong sorption to coal particles present in Adventfjorden sediments.

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[26] Allan, Ian J., et al. "PAH accessibility in particulate matter from road-impacted environments." Environmental science & technology 50.15 (2016): 7964-7972.

3.5.4 Density separated concentrations

Soxhlet extraction of density separated particles was performed for each sediment batch. Particles expected to be separated include micro and nanoplastic particles, perhaps some organic matter loosely bound to sediment and unsurprisingly coal particles. Coal particles were easily distinguishable owing to their colour. EHMC is consistently found in sediments while HCB, BBP and DIDP are only sporadically measured above limits of detection in sediments. Results for EHMC are consistent with other measurements in these sediment batches. The fractions of EHMC extracted by density separation is minor in comparison with total concentrations measured by Soxhlet extraction. This tends to indicate that only a minor fraction of EHMC present in sediment is bound to coal and/or plastic particles. The same conclusion can also be drawn for HCB.

For plastic additives such as the phthalates (DiP, BBP and DEHP) found with total concentration measurements, density separated fraction did not show levels above limits of detection despite suitably low LODs. The presence of phthalates could be associated to the PVC signal observed in the sediments, although it is not clear whether this is due to PVC particles in the samples or coal particles with a similar signal. We could have expected that in the presence of PVC-associated phthalates, these would have been separated from the matrix owing to the density of PVC particles in comparison with the NaI solution.

These discrepancies are difficult to explain but could be related to:

- Homogeneity of the sediments despite the cryomilling. In this case plasticisers-loaded plastic particle are not homogenously distributed in the sediment and this could explain why some additives remain non-detected by certain extraction procedures.
- The limit extractability or accessibility of additives in plastic particles, not able to desorb from the plastic.
- The strong sorption of coal particles able to sorb contaminants during extractions where an agitation of the wet sediment is undertaken. In short, coal particles recently emitted through run-off will not have had the possibility to sorb much contaminants. The agitation during freely dissolved and accessible concentration measurements may promote a desorption of the contaminants from the sediment and preferential/additional sorption to coal particles.

3.5.5 Modelling of the distribution of DEHP in sediment

Considering the amount of DEHP found with total Soxhlet extractions, and assuming it is present as an additive and emitted to the environment associated with the plastic it was added to (e.g. PVC), it is possible to estimate plastic concentration would be needed to obtain such DEHP concentrations in sediment. For example, with an additive concentration in plastic of 1 % in weight, over 500 µg of DEHP-loaded plastic would be needed to reach the DEHP concentration of sediment C. With an additive loading of 10 % this amount reduces to 50 µg. Levels of microplastics observed in sediments were considerably lower than this.

In case DEHP was homogenously distributed in the sediment phase instead of as an additive in plastic, we can calculate a freely dissolved concentration from $\log K_{ow}$ (using K_{ow} as proxy for K_{oc}, Table 8) of approximately 18 ng L^{-1} and similar to limits of quantification shown in Table 17. However, we could expect in this case that the accessible concentration measurement would result in detectable levels of DEHP in the silicone exposed to sediment with a concentration of 5727 ng g^{-1} dw (sediment C). This was not the case. DEHP may be tightly bound to the plastic particle it is part of, or strongly sorbed to black carbon type particles, resulting in negligible easily extractable DEHP.

Table 16 Accessible concentrations of selected contaminants in sediments from the Adventfjord (ng g^{-1} dw).

	A		B		C		D		E		F		G	
	24h	30d	24h	30d	24h	30d	24h	30d	24h	30d	24h	30d	24h	30d
POP														
HCB	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Plasticisers/flame retardants														
Acetyl tributylcitrate	<59	<59	**3333**	<59	<59	<59	<59	<59	<59	<59	<59	**6363**	**5030**	**107**
Plastic additive 11	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000
DiP	<102	**164**	<120	<102	<102	<102	<102	<102	<102	<102	<102	<102	<102	<102
BBP	<3.4	<3.4	<3.4	**4.4 (46)**	<3.4	<3.4	<3.4	<3.4	<3.4	**3.9 (6)**	<3.4	**3.7**	<3.4	<3.4
DEHP	<20	**158**	**46**	**20**	<20	<20	**15**	<20	<20	<20	**16**	<20	<20	**120 (27)**
DINP	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000
DIDP	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000	<10000
PBT	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
HBB	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
UV filters														
BP3	<7	<7	<7	<7	<7	<7	<7	<7	<7	<7	<7	<7	<7	<7
2,4-dihydroxy-BP	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2-hydroxy-4-(octyloxy)BP	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
OC	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2	<7.2
EHMC-Z	<0.3	4.0	<0.3	**0.93**	**1.0**	**0.91**	<0.3	**0.54**	**0.32**	**1.1**	**0.41**	**0.35 (115)**	**0.82**	**1.6 (58)**
EHMC-E	<0.3	0.3	<0.3	**0.16**	**0.11**	**0.42**	<0.3	**0.1**	<0.3	**0.2 (96)**	<0.3	<0.3	<0.3	**0.13 (67)**
ODPABA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
UV-320	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
UV-326	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3	<4.3
UV-327	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**0.38**	<0.1	<0.1	<0.1	<0.1
UV-328	<0.1	**0.27**	<0.1	<0.1	<0.1	**8.2**	<0.1	<0.1	<0.1	**0.43**	<0.1	<0.1	<0.1	<0.1
UV-329	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8	<8
Mean of duplicate extractions and analyses (relative percent difference, % RPD in brackets). For the duplicate 30 day extractions, if concentrations above LOD were found for only one replicate, that value is reported (with no %RPD in brackets)														

Table 17 Freely dissolved contaminant concentrations in sediments from the Adventfjord (ng L^{-1})

Compound	Freely dissolved concentrations (ng L^{-1})						
	A	B	C	D	E	F	G
POP							
HCB	**0.010**	0.0098	0.0098	0.0098	0.0098	0.0098	0.0100
Plasticisers/flame retardants							
Acetyl tributylcitrate	<296	<296	<296	<296	<296	<296	<296
Plastic additive 11	<*	<*	<*	<*	<*	<*	<*
DiP	<24	<24	<24	<24	<24	<24	<24
BBP	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
DEHP	<17	<17	<17	<17	<17	<17	<17
DINP	<777	<777	<777	<777	<777	<777	<777
DIDP	<*	<*	<*	<*	<*	<*	<*
PBT	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
HBB	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
UV filters							
BP3	59	59	59	59	59	59	59
2,4-dihydroxy-BP	NA	NA	NA	NA	NA	NA	NA
2-hydroxy-4-(octyloxy)BP	<0.0032	<0.0032	<0.0032	<0.0032	<0.0032	<0.0032	<0.0032
OC	<0.81	<0.81	<0.81	<0.81	<0.81	<0.81	<0.81
EHMC-Z	<0.051	**0.043**	<0.051	**0.055**	**0.045**	<0.051	<0.051
EHMC-E	<0.051	<0.051	<0.051	<0.051	<0.051	<0.051	<0.051
ODPABA	NA	NA	NA	NA	NA	NA	NA
UV-320	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
UV-326	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
UV-327	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
UV-328	<0.08	**0.07**	<0.08	<0.08	<0.08	<0.08	<0.08
UV-329	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04

*Compounds not detected. The logK$_{sw}$ is not known, LODs are high and therefore estimated freely dissolved concentrations are very unreliable
NA: unreliable quantification

Table 18 Contaminant masses extracted by density separation (ng g^{-1} dw sediment)

Compound	Accessible concentrations (ng g^{-1} dw)						
	A	B	C	D	E	F	G
POP							
HCB	<0.004	<0.005	<0.005	<0.007	<0.008	<0.007	**0.005**
Plasticisers/flame retardants							
Acetyl tributylcitrate	<1	<1.5	<1.4	<1.8	<2.2	<2.0	<2.3
Plastic additive 11	<116	<164	<189	<251	<433	<311	<472
DiP	<1.4	<2.1	<2.12	<2.6	<3.2	<2.9	<3.4
BBP	<0.29	<0.44	<0.42	<0.54	**1.1**	<0.58	<0.69
DEHP	<3.1	<4.6	<4.5	<5.8	<7.0	<6.2	<7.4
DINP	NA	NA	NA	NA	NA	NA	NA
DIDP	<1.3	<1.9	<1.9	<2.4	**32**	**11**	**8.4**
PBT	<0.004	<0.005	<0.005	<0.007	<0.008	<0.007	<0.009
HBB	<0.004	<0.005	<0.005	<0.007	<0.008	<0.007	<0.009
UV filters							
BP3	<0.17	<0.25	<0.24	<0.31	<0.38	<0.34	<0.40
2,4-dihydroxy-BP	<3.6	<5.4	<5.2	<6.7	<8.1	<7.3	<8.6
2-hydroxy-4-(octyloxy)BP	<0.72	<1.1	<1.1	<1.4	<1.7	<1.5	<1.8
OC	<0.15	<0.22	<0.21	<0.27	<0.33	<0.30	<0.35
EHMC-Z	**0.0044**	<0.0054	**0.0029**	**0.0039**	**0.0146**	**0.0046**	**0.0051**
EHMC-E	**0.02**	<0.03	<0.03	<0.03	**0.04**	<0.04	<0.04

ODPABA	<0.01	<0.01	<0.01	<0.01	<0.02	<0.01	<0.02
UV-320	<0.29	<0.43	<0.41	<0.53	<0.65	<0.58	<0.68
UV-326	<0.61	<0.91	<0.88	<1.2	<1.4	<1.3	<1.5
UV-327	<0.10	<0.15	<0.15	<0.19	<0.23	<0.20	<0.24
UV-328	<0.15	<0.23	<0.22	<0.29	<0.35	<0.31	<0.37
UV-329	<0.33	<0.49	<0.48	<0.61	<0.74	<0.66	<0.79
Mean of duplicate extractions and analyses (relative percent difference, % RPD in brackets)							

4. Conclusions

Screening for the presence of microplastics in water and sediment of the Adventfjord, and in effluents of the human settlements of Barentsburg and Longyearbyen was undertaken in this study. Methodologies to quantify microplastics with instrumental analysis using pyrolysis gas chromatography linked to mass spectrometry were applied to water and sediment samples. For the Adventfjord sediments, an extraction strategy was tested to characterise the presence of a range of plastic additives and other hydrophobic organic contaminants.

Only traces of plastics were found either in fjord water or sediment samples. A signal of polyvinyl chloride (PVC) was consistently found in many samples. Although there may be a genuine presence of PVC microparticles supported by the detection of PVC in Longyearbyen effluent samples, the presence of coal particles in the Svalbard environment and in our samples may interfere in the detection and quantification of PVC by pyroGC/MS. This issue requires further methodological developments. Nylon 66 and PET were also found in the untreated effluent samples from Longyearbyen. Procedures used for these measurements are promising but require further development to improve limits of detection and reliability and applicability to various types of water and sediment samples.

The globally distributed persistent organic pollutant hexachlorobenzene, the plasticisers dibutyl phthalate, benzylbutyl phthalate and bis(2-ethylhexyl) phthalate and the UV filter ethylhexylmethoxycinnamate (EHMC) were consistently detected in the sediment batches and highest total concentrations were found in sediments from sampling locations closest to Longyearbyen effluent release point. Accessible, freely and density separated concentrations or fractions were in most cases below limits of detection. For phthalates, these results indicate that these plasticisers could be associated with plastic particles such as PVC and not readily extractable by other means than exhaustive extractions.

Further work may be needed to investigate the presence of other relevant additives in Adventfjord environment. Further studies to understand the fate of microplastics released with untreated effluents into the Adventfjord is also relevant. Since the wastewater treatment process is being upgraded, studying its impact on the release of microplastics into the fjord will be relevant.

Fieldwork: Sediment sampling in December 2020.