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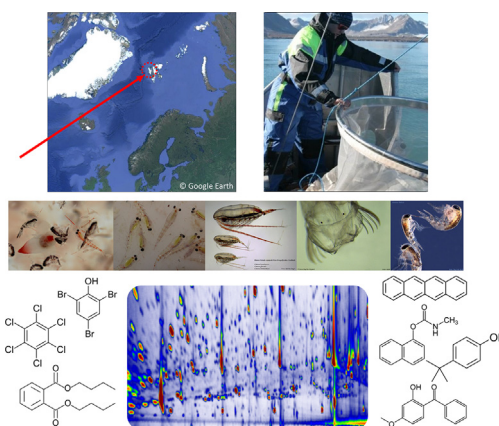
# Non-target and suspect screening reveal complex pattern of contamination in Arctic marine zooplankton

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## HIGHLIGHTS

- A method for NTS of small biotic samples was developed and applied to Arctic invertebrates.
- Several currently untargeted chemicals were identified across species.
- Both POPs and select contaminants of emerging concern were quantified by target analysis.
- Benthic species had a higher body burden of traditional POPs.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Although increasing, there is still limited knowledge of the presence of ‘contaminants of emerging concern’ in Arctic marine biota, particularly in lower trophic species. In the present study, we have applied a novel pipeline to investigate the presence of contaminants in a variety of benthic and pelagic low-trophic organisms: amphipods, copepods, arrow worms and krill. Samples collected in Kongsfjorden in Svalbard in 2018 were subject to extraction and two-dimensional gas chromatography coupled to high-resolution mass spectrometry (GC × GC-HRMS). Tentatively identified compounds included plastic additives, antioxidants, antimicrobials, flame retardants, precursors, production solvents and chemicals, insecticides, and pharmaceuticals. Both legacy contaminants (PAHs, PCBs, PBDEs, hexachlorobenzene) as well as novel and emerging contaminants (triclosan, bisphenol A, and ibuprofen) were quantified in several species using target analysis by GC-MS/MS. The significance of these discoveries is discussed considering the potential for detrimental effects caused by these chemicals, as well as suggested local and distant sources of the components to the Arctic environment.

## 1. Introduction

The accumulation of persistent organic pollutants (POPs) in Arctic food chains is by now well known. More recently, focus is being given to so-called ‘chemicals of emerging concern’ (CECs) (Sonne et al., 2021). These chemicals are not necessarily “new”, but their persistency, bioaccumulation,

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and toxicity (PBT) properties have not been given focus previously and thus they have typically gone under the radar of routine environmental monitoring. However, recent studies have shown that several organic pollutants are present in different Arctic environmental compartments, including water, sea ice, sediments and biota (Kallenborn et al., 2018; Sonne et al., 2021; Xie et al., 2022). In addition to legacy contaminants – such as heavy metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), dioxins and organophosphorus flame retardants (OPFRs), CECs – including perfluorinated alkylated substances (PFAS), bisphenol A (BPA), phthalates, nonyl- and octyl-phenols, pharmaceuticals and personal care products (PPCPs) – have recently been detected in environmental samples from Svalbard and other Arctic locations (Ademollo et al., 2021; Choi et al., 2020; Evensen et al., 2018; Kallenborn et al., 2018; Lee et al., 2019; Muir et al., 2019; Vorkamp et al., 2019). Current-use pesticides and novel flame retardants have also been detected in Arctic samples, most of which are high production volume chemicals and suspect sources include long-range transport (Balmer et al., 2019b; Vorkamp and Rigét, 2014). Wastewater treatment is often inefficient or lacking in Arctic regions (Gunnarsdóttir et al., 2013). Pharmaceuticals and personal care products (PPCPs) are therefore expected and detected in Arctic environments (Kallenborn et al., 2018). Yet, to date, only limited data is available regarding the presence of emerging contaminants in the Arctic food chain, and in particular in lower trophic levels such as invertebrates.

For screening of environmental samples, a combination of target analysis with suspect and non-target screening is becoming an increasingly popular approach, both using LC- and GC-based methods (Fu et al., 2022; Lee et al., 2019; Simonnet-Laprade et al., 2022).

The aim of the present study was to investigate the diversity of organic contaminants in benthic and pelagic low-trophic organisms in an Arctic environment. Samples of Arctic marine invertebrates were collected in Kongsfjorden (Svalbard, Norway) in 2018 and subject to chemical extraction and analysis using two-dimensional gas chromatography coupled to mass spectrometry (GC × GC-MS) aiming to provide an initial non-target screening of organic, GC-amenable compounds. Sensitive GC-MS/MS was further applied to quantify select compounds, including a selection of POPs. Results of this study show accumulation of several, both legacy and ‘new’, compounds in Arctic benthic and pelagic invertebrates.

## 2. Materials and methods

### 2.1. Chemicals and materials

Analytical grade reference standards were purchased from Chiron AS (Norway) and Sigma-Aldrich (Germany). Calibration, spike, surrogate, and recovery standards were all prepared by dilution of compounds in dichloromethane (DCM). All solvents were of analytical grade and the purity was verified in-house prior to use.

### 2.2. Zooplankton sampling

Sampling was performed in Kongsfjorden, Svalbard in July 2018. Pelagic zooplankton was sampled by vertical net hauls from 200 m depth (N 78° 55.28, E 011° 59.86) using a WP3 net (1000 µm mesh) fitted with a closed cod end (KC Denmark). The bulk zooplankton samples were transferred unsorted to 50 L buckets. Benthic amphipods were collected in traps with encapsulated bait near Prince Heinrich Islands (N 78° 55.33, E 011° 58.10), and transferred to holding containers. Samples were kept at 4 °C and transported to the onshore laboratory where they were sorted by genus using a stereomicroscope. The samples (pooled individuals of the different species) were frozen and stored at –20 °C in pre-cleaned Kimax® glass vials used directly in the extraction process to reduce handling and contamination risks. Field blanks (empty vials,  $N = 5$ ) were taken to the sampling sites, opened, and collected to account for contamination during the sampling procedure.

### 2.3. Sample extraction and purification

Samples of zooplankton were thawed and accurately weighed without subsampling (sample weight range 50–700 mg). After addition of *n*-hexane-DCM (1:1 v/v, 4 mL), sodium sulfate and surrogate standards (250.8 ng naphthalene-*d*8, 50.0 ng phenanthrene-*d*10, 48.6 ng chrysene-*d*12, 50.8 ng perylene-*d*12, 2533.4 ng phenol-*d*6, 104.2 ng *p*-cresol-*d*8, 137.4 ng 4-*n*-propylphenol-*d*12), the samples were homogenized using a disperser (IKA 10 basic ULTRA-TURRAX®), vortexed and centrifuged (720 g, 2 min) at ambient temperature. The supernatant was collected, and the extraction step repeated two additional times. Combined extracts were volume reduced (40 °C under a gentle flow of N<sub>2</sub>) to approximately 1 mL, and further subject to clean-up by gel permeation chromatography (GPC) where 0.5 mL of the extract was injected on an Agilent 1200 LC system with a 1260 series fraction collector. Separation was achieved using an Envirogel column (19 × 300 mm, 15 µm; Waters Milford, MA, USA) with DCM as a mobile phase (5 mL/min). Chromatograms were monitored at 210, 254 and 280 nm UV. The fraction for analysis was collected from 10.5 to 15 min with pre-added *n*-hexane as a keeper in the collection vials. The sample volume was adjusted to 0.5 mL by solvent evaporation (40 °C under a gentle flow of N<sub>2</sub>) and recovery internal standards (98.4 ng fluorene-*d*10 and 106.4 ng acenaphthene-*d*10) were added prior to analysis. One laboratory blank sample was included approximately for each five samples ( $N = 9$  total) and subject to the same sample preparation as described.

### 2.4. Non-target screening

Comprehensive two-dimensional gas chromatography mass spectrometry (GC × GC-MS) analyses were performed using a 7890B GC coupled with a 7250 quadrupole time of flight mass spectrometer interfaced with a Zoex ZX2 cryogenic modulator. The first-dimension column was a Zebron ZB-1 (30 m × 0.25 mm × 0.25 µm) followed by a 1 m × 0.25 mm deactivated fused silica modulation loop. The second-dimension column was a DB17-MS (1.5 m × 0.25 mm × 0.25 µm). The carrier gas was high purity helium at constant flow (1.2 mL/min). Samples (1 µL) were injected at 250 °C splitless. The oven temperature was kept at 90 °C (1 min hold), ramped by 5 °C/min to 300 °C (5 min hold). The hot jet was constantly offset at +50 °C. The modulation time was 4 s with a 350 ms pulse length. The transfer line temperature was 300 °C, the ion source temperature was 200 °C and the EI source was operated at 70 eV. Scan speed was 50 Hz, and the recorded mass range 50–450 *m/z*. Chromatograms were first investigated in GCImage®, and further data processing was performed using a semi-automated pipeline as described in SI.

### 2.5. Target compound analysis

Samples were analyzed by an Agilent 7890 gas chromatograph coupled with an Agilent 7010B triple quadrupole mass spectrometer fitted with an EI source and collision cell (Agilent Technologies, Santa Clara, CA, USA). Two Agilent HP-5MS UI GC-columns (30 m × 0.25 mm × 0.25 µm) were coupled in series through a purged ultimate union. The carrier gas was high purity helium at constant flow (1.2 mL/min). For analysis of PAHs and alkyl PAHs, samples (1 µL) were injected at 310 °C in pulsed splitless mode. The oven temperature was kept at 40 °C for 1 min, then ramped to 110 °C by 40 °C/min, to 220 °C by 6 °C/min and finally to 325 °C by 4 °C/min. For the other target compounds, samples were injected at 250 °C, the oven temperature was kept at 40 °C for 1.5 min, then ramped to 110 °C by 40 °C/min, to 310 °C by 5 °C/min and held for 20 min. For both methods, the temperature was finally raised to 330 °C for 5 min, while the first column was backflushed. The transfer line temperature was 300 °C, the ion source temperature was 230 °C and the quadrupole temperatures were 150 °C. The EI source was operated at 70 eV. Nitrogen was used as collision gas at a flow of 1.5 mL/min and helium was used as a quench gas at a flow of 2.25 mL/min. Target analytes were identified by two unique MRM transitions and quantified by the most intense peak. PAHs and alkyl PAH MRMs

are previously described (Sørensen et al., 2015, 2016). MRM transitions for other target compounds are detailed in SI (Table S1). PAHs were quantified by linear regression of a calibration curve (0.01–10 ng/mL) after normalization to fluorene-*d*10, while other compounds were quantified by quadratic regression (0.1–1000 ng/mL) after normalization to chrysene-*d*12.

## 2.6. Method validation and quality control

The sample preparation protocol described above has previously been validated and applied for quantification of PAHs and alkylated phenols from fish eggs (Hansen et al., 2022; Oppegård et al., 2020; Sørensen et al., 2019). However, the invertebrates analyzed herein represent a more challenging matrix in terms of fat content, and the range of compounds represent a greater diversity in terms of physical-chemical properties. For method performance testing we here used *Calanus* oil. Samples of oil (100 mg) were transferred to a glass tube followed by addition of spike standards (10, 100 and 1000 ng) and internal standards (as above), and made up to a volume of 1 mL using DCM:*n*-hexane (1:1 v/v) followed by brief vortexing. Control spike sample were prepared the same way, without the addition of matrix. All spike samples were purified by GPC as described above. These samples were analyzed using GC–MS/MS as described above to determine recovery during sample purification, detection limits and method repeatability. Spiked samples were also analyzed by GC×GC–MS, both for the purpose of obtaining retention indexes, and to validate the data processing protocol.

## 2.7. Statistics

Limits of detection (LOD) were calculated as the average of blank samples added three times the standard deviation. Other validation parameters were calculated as described in (Sørensen et al., 2015). Due to the varying invertebrate sample size (50–700 ng), some target compounds were found to be below the method LOD in the samples of lower size. To avoid confounding, these samples were omitted when calculating averages. Comparisons between species were by one-way ANOVA test followed by Tukey's multiple comparisons test in the R software (R Development Core Team, 2008). Multivariate statistics was performed in R using the mixOmics package (Rohart et al., 2017) and the pls package (Mevik and Wehrens, 2007). Further details are described in SI.

## 3. Results and discussion

A total of 43 samples of Arctic marine invertebrates was analyzed using the described pipeline (SI). Pelagic amphipods (*Themisto abyssorum*, *T. libellula*), copepods (*Calanus finmarchicus*, *C. glacialis*, *C. hyperboreus*), arrow worms (*Sagitta elegans*) and krill (*Thysanoessa inermis*) as well as benthic scavenging amphipods (*Onisimus* sp., *Anonyx* sp) were among the collected and studied species. The benthic amphipods and lipid-rich copepods contained the highest abundance of identified and tentative compounds in comparison to the other test species.

### 3.1. Method suitability

A suite of selected emerging contaminants (Table S1, SI) spiked in samples with and without matrix (*Calanus* oil) was analyzed both by GC–MS/MS for quantification method validation and by GC×GC–MS for verification of the automated identification pipeline.

Method performance was tested by comparison of levels analyzed in spiked matrix and no-matrix samples (10, 100 and 1000 ng) prepared according to the described sample preparation protocol. All validation parameters are summarized in Table S2 (SI). Quantification of some compounds was challenging due to high instrumental LODs. A selection of compounds with low instrumental LODs, were still not recovered even at the highest spike (1000 ng) concentration. These included all phthalates and organophosphates, hexachlorobenzene and *n*-butylbenzenesulfonamide. A combination of factors, such as volatile losses and poor recovery over the GPC step

could possibly explain losses leading to them not being detected in prepared samples. Some compounds (notably triclosan, bisphenol A, ibuprofen, and 17 $\beta$ -estradiol) suffered high recoveries due to matrix effects. Given the unfortunate lack of deuterated internal standards to account for these factors, quantified concentrations of these compounds must be viewed as having relatively high uncertainty (Fu et al., 2022).

In terms of GC×GC–MS analysis, with the exception of BDE-183, TCEP and DEHP, all spiked compounds were identified in at least one of the validation samples or by direct injection of the spike mixture using the automated pipeline (Table S3, SI). BDE-183 was the only compound that could not be identified by manual peak picking. Neither of the organophosphates or phthalates could be found in the samples subject to sample preparation, by either GC×GC–MS or GC–MS/MS analysis. The hypothesized reason for these losses is loss due to size in the GPC purification step. Furthermore, these compounds have a poor UV-signal so during initial testing of the GPC protocol, their elution time could not be verified. However, their losses could of course be due to other factors not controlled for (low partitioning to the solvents applied, or sorption to vessel wall). Based on these observations, tentatively identified organophosphate or phthalate structures from the NTS pipeline must be regarded as uncertain.

Retention time shifts in both dimensions during GC×GC-analysis was monitored by the spiked internal standards. With few exceptions, the range of first dimension retention times across all samples was <0.5 min, and the range of second dimension retention times was <0.25 s for all internal standard peaks.

### 3.2. Non-target screening pipeline and results

Investigation of such complex chromatograms as those obtained by GC×GC–MS manually are not feasible for larger sample sets. Therefore, a semi-automated approach as described was applied (Fig. S1). For primary investigation, principal component analysis (PCA) was performed on the GC×GC–MS total ion chromatograms (TICs). None of the species or blank groups showed separation (as visualized by ellipses representing standard deviation) (Fig. S2). PC1 showed the largest standard deviation for the benthic amphipod group which separated some of the samples from that group from the rest of the samples. The group was not separated from the other groups. Investigation of the features contributing to PC1 showed that it was mainly the biogenic material co-eluting in these samples that contributed to this difference (Fig. S3).

Initial, automated, evaluation of the complete data set, including all invertebrate samples, field, and laboratory blank samples, yielded 2154 tentatively identified compounds (unique combination of retention position and CAS number of the best NIST17 library match identity (lower cut-off 80 % match) across invertebrate samples, field blanks and laboratory blanks (Schymanski et al., 2014). Of these compounds, 213 were assigned as siloxanes and 23 as TMS-derivatives. The former may originate from column bleed, and the latter are unlikely due to no sample derivatization. These compounds were thus omitted from further sample treatment. Further, a limit of detection (LOD) was approximated based on responses in laboratory blank samples. The LOD was set to the average of responses in the nine blank samples added three times the standard deviation. If the compound was only detected in one blank sample, this value was used as the LOD. Compounds in invertebrate and field blank samples were removed from the data set if they were below this LOD. Further, compounds only detected in field blanks were also removed. This left 1488 tentatively identified compounds. Manual investigation was then applied to remove compounds identified as biogenic or of most likely biogenic origin (e.g. fatty acids), leaving 214 tentatively identified compounds of potential anthropogenic origin. To further support these identifications, first dimension retention indexes (RI) were compared to predicted indexes based on compound properties retrieved from PubChem (as detailed in SI). 18 of the proposed structures could not be found in PubChem using the automated query, and they were omitted from further data processing. Within the remaining 196 compounds, there were several duplicate identities, found at differing retention times. For several of these, the likely explanation was that



structure was assigned to an isomer of the true structure. These were not removed from the data set. Of the remaining duplicates, the identity with the poorest RI fit was omitted from the data set. Where structural isomers (e.g., 2,6- and 1,7- dimethylnaphthalene) were identified at the same RI in different samples, these results were merged under one identity. Finally, to limit the data assessment, only the structures identified in at least two invertebrate samples (regardless of species) were selected for reporting (Table S5, SI). A total of 127 tentative structures were found across the 43 invertebrate samples, of which 106 were identified in copepod samples, 82 in benthic amphipods, 54 in pelagic amphipods, 41 in arrow worms and 32 in krill samples. 41 of the features were also identified in field blank samples, but were left in the data set at this stage.

A large group of compounds could be assigned to likely petrogenic origin, including methylated naphthalenes, hydrogenated naphthalenes, fluorenes, phenanthrenes, biphenyls and alkyl substituted benzenes (Sørensen et al., 2019). In Table 1, we present a sub-set of tentatively assigned compounds of non-petrogenic origin. Identity of some compounds (marked \* in Table 1) were confirmed by verification of retention position through co-injection of analytical standards, and these are also quantitated using target GC-MS/MS (discussed below).

Tentatively identified compounds included high production volume chemicals such as plastic additives, solvents, and synthesis pre-cursors, as well as antioxidants, antimicrobials, insecticides, PPCPs, and flame retardants. Only five compounds (4-methyl-5-thiazolethanol, 1H-indole-3-carboxaldehyde, dicyclopentadiene diepoxide, benzeneacetamide, and 2-phenylpropenal) were identified in >50 % of the invertebrate samples. Several of the peaks were also identified in one or more field blank samples. Further discussion will focus on tentatively identified compounds primarily detected only in invertebrate samples.

Among the most frequently detected compounds, several were registered as natural products, with potential applications as fragrance or flavor ingredients or synthesis precursors (Api et al., 2020; Zhang et al., 2016). Among these, were also several compounds commonly acknowledged as pollutants, for which anthropogenic sources are likely. 2,4-Di-*tert*-butylphenol, is a precursor and degradation product of UV-stabilizers commonly used in plastic polymers, but it also has natural sources (Fiege et al., 2000; Zhao et al., 2020). 2,4,6-Tribromophenol, while noted that it can be produced as a metabolite of marine fauna (Fielman et al., 2001), it is mainly recognized as a fungicide and 'novel' flame retardant (Vorkamp and Rigét, 2014).

Most peaks were detected in several species, both pelagic and benthic, with some notable exceptions. The wide-spread insecticide carbaryl (Derbalah et al., 2020) was detected in samples of all pelagic invertebrates, but not in any benthic amphipods. Several compounds were found only in pelagic invertebrate samples. This included 2,4,6-tribromophenol, the semiconductor additive naphthacene (Takahashi et al., 2007), the polymer UV stabilizer bumetrizole (also known as Tinuvin 326 or UV-326) and antioxidant 7,9-di-*tert*-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione. Both of the latter are commonly found in environmental plastic, and the former seen to transfer to biological oils in laboratory experiments (Kühn et al., 2020).

2,4-Di-*tert*-butylphenol, 2,4,6-tribromophenol, carbaryl and naphthacene are classified as environmental hazards according to international guidelines. 2,4,6-tribromophenol and bumetrizole are currently undergoing assessment as PBT chemicals. Neither of these chemicals are readily biodegradable according to the US EPA EpiSuite™ software (U.S. EPA, 2012).

### 3.3. Suspect screening and quantified concentrations of a selection of emerging contaminants and POPs

A suite of selected emerging contaminants (Table S1, SI) were analyzed by target GC-MS/MS and quantified. Of the compounds tentatively identified in samples by the non-target screening protocol described above; phthalide, benzothiazole, benzophenone, 2-(methylthio)benzothiazole and *n*-butylbenzenesulfonamide were quantified and found in levels >LOD in only one each of the invertebrate samples (Table S6, SI). Phthalimide was quantified in single samples from three separate species

(Table S6, SI). Acetophenone was quantified in several samples of copepods and benthic amphipods, as well as in a single sample of arrow worms.

In addition to the selected compounds based on the non-target screening, the target analysis also factored in a selection of emerging contaminants of interest that did not show up on the GC×GC-MS screening. These included triclosan, ibuprofen, 17β-estradiol, 4-*tert*-octylphenol, 4-*n*-nonylphenol and bisphenol A. Due to their polarity and structural properties, instrumental detection limits are higher than most other compounds, and this may also explain why they were not detected during the untargeted screening. Levels of 4-*tert*-octylphenol, 4-*n*-nonylphenol were not quantified >LOD in any sample. 17β-estradiol was quantified at high levels (250 µg/kg) in a single sample of pelagic amphipods (Table S6, SI). Triclosan, bisphenol A and ibuprofen were quantified in almost all invertebrate species, and in levels well above what was detected in both field and laboratory blank samples (Fig. 1). The antimicrobial biocide triclosan has been used extensively as an antiseptic, preservative and disinfectant in consumer products and healthcare (Shrestha et al., 2020). Bisphenol A is a high-production volume chemical, most known for its presence in various plastic consumer products (Corrales et al., 2015). Levels of bisphenol A quantified in water samples from Kongsfjorden (sampled 2016–2017) were up to 1.4 ng/L. An estimated bioconcentration factor (BCF) of bisphenol A is 72.03 L/kg wet weight (U.S. EPA, 2012). The concentrations reported in invertebrate samples here are thus several orders of magnitude above what would be expected based on simple bioconcentration from water. Ibuprofen is an analgesic and non-steroidal anti-inflammatory drug that is widely used, and is known to be present in Arctic environmental compartments (Kallenborn et al., 2018), but to our knowledge this is the first report of presence and concentration levels in Arctic biota. Environmental concentrations of ibuprofen reported globally range from ng-mg/L magnitudes (Chopra and Kumar, 2020). An estimated BCF of ibuprofen is 3.162 L/kg wet weight (U.S. EPA, 2012), which implicates that water concentrations observed by the sampled invertebrates in the current study would be in the higher end (100–1000 µg/L) of those reported worldwide, but no water concentrations of ibuprofen from Kongsfjorden are yet available to verify this. The impact of such elevated concentrations must be considered, for while acute toxicity is not expected for this chemical (U.S. EPA, 2012), long-term exposure to low concentrations has previously demonstrated behavioral effects in the amphipod *Gammarus pulex* (De Lange et al., 2006).

A suite of POPs (seven PCBs, nine PBDEs 16PAHs) were analyzed in all invertebrate samples. For the samples with concentrations above methodological LOD, the levels were generally exceeding concentrations in laboratory and field blank samples. PBDEs (mainly BDE-47, BDE-100, BDE-85 and BDE-154) as well as PAHs were found in significantly higher concentrations in benthic amphipods than the other sampled species ( $p < 0.005$  and  $p < 0.000005$ , respectively) (Fig. 2). Apart from PCB-138 in one single sample, arrow worms appeared to have accumulated less POPs by wet weight than other species, but the difference was not significant. It is also worth to note that the lipid content of arrow worms, although not analyzed within the current study, is generally low compared to copepods, amphipods, and krill, all of which are known to have relatively high lipid content. PBDEs have previously been detected in the Arctic food chain, including in pelagic copepods and amphipods (Hallanger et al., 2011; Sørmo et al., 2006). The concentrations of PBDEs were generally in the same range as observed in the current study, despite a difference in target congeners. Benthic amphipods were not investigated in the cited study, but the omnivorous amphipod *Gammarus wilkitzkii* was found to contain a ten-fold higher concentration of PBDEs than the other invertebrate species. PAHs have previously been quantified in benthic bivalves from Kongsfjorden, and the concentrations were generally in line with the concentrations found in the current study (Szczybelski et al., 2016).

The persistent insecticide hexachlorobenzene (Barber et al., 2005). was quantified in samples from all invertebrate categories (Fig. 1). Although not significant, concentrations of hexachlorobenzene were generally higher in the pelagic species than in the one sample of benthic amphipods it was detected in. The overall range of concentrations are in line with those reported in benthic bivalves from Kongsfjorden (Szczybelski et al., 2016).

Table 1

Tentatively identified compounds and their detection frequencies (% , number of samples in parenthesis). Compounds labelled \* were verified by co-injection of analytical standards.

CAS	Name	RT	RI	RI deviation from predicted	Biota samples (N = 43)	Benthic amphipods (N = 9)	Copepods (N = 20)	Krill (N = 4)	Arrow worms (N = 3)	Pelagic amphipods (N = 7)	Field blanks (N = 5)
137-00-8	4-Methyl-5-thiazoleethanol	10.89	1370	74	88 (38)	77 (7)	95 (19)	100 (4)	33 (1)	100 (7)	20 (1)
487-89-8	1H-Indole-3-carboxaldehyde	22.24	1883	341	72 (31)	77 (7)	60 (12)	100 (4)	66 (2)	85 (6)	
81-21-0	Dicyclopentadiene diepoxide	11.68	1403	207	69 (30)	55 (5)	75 (15)	75 (3)	66 (2)	71 (5)	20 (1)
103-81-1	Benzeneacetamide	13.30	1471	135	60 (26)	77 (7)	45 (9)	75 (3)	33 (1)	85 (6)	
4432-63-7	2-Phenylpropanal	8.35	1265	-71	53 (23)	33 (3)	40 (8)	75 (3)	100 (3)	85 (6)	20 (1)
103-82-2	Benzeneacetic acid	10.25	1344	-33	44 (19)	55 (5)	30 (6)	75 (3)	66 (2)	42 (3)	
90-15-3	1-Naphthalenol	11.09	1378	-181	39 (17)	11 (1)	55 (11)	75 (3)	33 (1)	14 (1)	20 (1)
7175-47-5	1-Isocyano-4-methylbenzene	7.75	1240	-76	37 (16)	77 (7)	40 (8)	25 (1)			
615-13-4	1,3-Dihydro-2H-inden-2-one	8.30	1263	-87	32 (14)	44 (4)	20 (4)	50 (2)	33 (1)	42 (3)	
90-15-3	1-Naphthalenol	12.32	1430	-129	32 (14)	11 (1)	50 (10)	50 (2)		14 (1)	20 (1)
122-78-1	Benzeneacetaldehyde	6.28	1179	3	30 (13)	55 (5)	10 (2)	75 (3)	33 (1)	28 (2)	
63-25-2	Carbaryl	12.33	1430	-496	30 (13)		40 (8)	50 (2)	33 (1)	28 (2)	
	1,3-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	39.21	2947	214	30 (13)	33 (3)	40 (8)			28 (2)	20 (1)
5062-30-6	Phenacylidene diacetate	13.54	1481	-488	27 (12)	55 (5)	15 (3)	25 (1)	33 (1)	28 (2)	
532-55-8	Benzoyl isothiocyanate	6.61	1193	-444	25 (11)	11 (1)	35 (7)		33 (1)	28 (2)	20 (1)
3319-31-1	Tri(2-ethylhexyl) trimellitate	49.68	3662	-173	25 (11)	11 (1)	30 (6)		33 (1)	42 (3)	20 (1)
65-85-0	Benzoic acid	8.41	1268	-77	23 (10)		25 (5)	50 (2)	66 (2)	14 (1)	20 (1)
62,108-16-1	2,3-Dihydro-4-methyl-1H-indole	15.12	1549	88	20 (9)	33 (3)	20 (4)		66 (2)		
96-76-4	2,4-Di-tert-butylphenol	16.82	1624	-375	20 (9)	44 (4)	10 (2)		66 (2)	14 (1)	
84-77-5	Didecyl phthalate	40.30	3032	-165	20 (9)	11 (1)	20 (4)		33 (1)	42 (3)	
13,679-41-9	3-Phenylfuran	11.09	1378	-26	20 (9)	22 (2)	30 (6)	25 (1)			20 (1)
57,147-25-8	3,4-Dihydro-2(1H)-pyridinone	6.86	1203	37	18 (8)	88 (8)					
10,468-64-1	1-Isocyano-2-methylbenzene	7.79	1242	-81	18 (8)	55 (5)	15 (3)				
334-68-9	1-Fluorododecane	12.70	1446	-16	18 (8)	22 (2)	15 (3)		33 (1)	28 (2)	60 (3)
1241-94-7	Octicizer	34.16	2583	-66	18 (8)		20 (4)	25 (1)	33 (1)	28 (2)	60 (3)
118-79-6	2,4,6-Tribromophenol	19.40	1744	-210	16 (7)	78 (7)					
529-19-1	2-Methylbenzotrile	7.78	1241	-87	16 (7)	33 (3)	20 (4)				
98-88-4	Benzoyl chloride	10.15	1339	0	16 (7)		20 (4)	50 (2)	33 (1)		
532-27-4	2-Chloro-acetophenone	6.68	1196	-170	16 (7)	11 (1)	25 (5)			14 (1)	20 (1)
140-29-4	Benzyl nitrile	7.75	1240	-6	13 (6)	33 (3)	15 (3)				
84-16-2	Hexestrol	22.14	1878	-499	13 (6)		20 (4)		33 (1)	14 (1)	
92-83-1	9H-Xanthene	19.56	1751	-4	13 (6)		20 (4)			28 (2)	20 (1)
98-54-4	p-tert-Butylphenol	11.52	1396	-143	13 (6)	22 (2)	5 (1)		33 (1)	28 (2)	20 (1)
122-99-6	2-Phenoxyethanol	9.72	1321	46	11 (5)	22 (2)	10 (2)		33 (1)		
23,069-99-0	N-(2-Phenylethyl)-formamide	15.33	1558	159	11 (5)			50 (2)		42 (3)	20 (1)
13,779-41-4	Di fluorophosphoric acid	6.56	1191	145	9 (4)	11 (1)	10 (2)	25 (1)			
83-34-1	3-Methylindole	13.53	1480	10	9 (4)		20 (4)				
135-67-1	Phenoxazine	20.91	1816	-66	9 (4)	11 (1)		25 (1)	66 (2)		
13,674-84-5	2-Propanol, 1-chloro-, phosphate (3:1)	22.72	1907	109	9 (4)	33 (3)				14 (1)	20 (1)
2944-47-0	o-Isopropylanisole	12.72	1446	46	9 (4)		10 (2)	50 (2)			20 (1)
1620-98-0	3,5-Di-tert-butyl-4-hydroxybenzaldehyde	18.20	1687	-467	9 (4)	11 (1)	10 (2)			14 (1)	
136-36-7	1,3-Benzenediol, monobenzoate	17.70	1664	-342	6 (3)		10 (2)		33 (1)		
83,834-59-7	2-Ethylhexyl trans-4-methoxycinnamate	32.48	2472	234	6 (3)		5 (1)		33 (1)	14 (1)	
14,035-33-7	3,5-Di-tert-butyl-4-hydroxyacetophenone	23.35	1940	-351	6 (3)	11 (1)	10 (2)				
98-86-2	Acetophenone*	6.74	1198	-26	6 (3)	11 (1)	5 (1)	25 (1)			
55-21-0	Benzamide	11.88	1411	125	6 (3)	33 (3)					
946-80-5	(Phenoxyethyl)-benzene	12.71	1446	-191	6 (3)			25 (1)	66 (2)		
98-91-9	Benzenecarbothioic acid	6.93	1206	-194	6 (3)		15 (3)				
3622-84-2	n-Butylbenzenesulfonamide*	22.06	1874	5	6 (3)	22 (2)				14 (1)	
485-31-4	Binapacryl	4.98	1126	-1701	6 (3)		15 (3)				
78,134-83-5	Isoparvifuran (1-Hydroxycyclohexyl) phenyl-methanone	25.11	2034	-328	6 (3)	11 (1)	5 (1)		33 (1)		
947-19-3	phenyl-methanone	20.57	1799	-128	6 (3)		10 (2)		33 (1)		
23,950-04-1	2-(1-Methyl-2-pyrrolidinyl)-pyridine	12.93	1455	56	6 (3)	33 (3)					
108-88-3	Toluene	13.40	1475	414	6 (3)	11 (1)	5 (1)			14 (1)	
834-97-9	1-Acetyl-4,6,8-trimethylazulene	21.61	1851	-191	6 (3)	22 (2)	5 (1)				20 (1)
58-08-2	Caffeine	23.22	1934	82	6 (3)	11 (1)	10 (2)				40 (2)
120,928-09-8	Fenazaquin	12.59	1441	-1179	6 (3)		10 (2)			14 (1)	40 (2)
10,075-50-0	5-Bromo-1H-indole	18.84	1717	82	4 (2)	22 (2)					
19,212-27-2	3-Oxo-4-phenylbutyronitrile	10.37	1348	-179	4 (2)		5 (1)			14 (1)	
	7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,9-diene-2,8-dione	27.33	2158	-551	4 (2)		5 (1)		33 (1)		
100-83-4	3-Hydroxybenzaldehyde	12.70	1446	130	4 (2)		10 (2)				
588-67-0	(Butoxymethyl)-benzene	6.13	1173	-184	4 (2)	22 (2)					
95-16-9	Benzothiazole*	9.93	1330	18	4 (2)		5 (1)	25 (1)			
100-51-6	Benzyl alcohol	6.09	1172	24	4 (2)		10 (2)				
3896-11-5	Bumetrizole	36.23	2727	-122	4 (2)		5 (1)		33 (1)		
28,029-89-2	Didecan-2-yl phthalate	42.90	3243	144	4 (2)		10 (2)				
13,679-41-9	3-Phenylfuran	12.32	1430	25	4 (2)		5 (1)			14 (1)	
120-72-9	Indole	11.31	1387	39	4 (2)		10 (2)				

(continued on next page)

Table 1 (continued)

CAS	Name	RT	RI	RI deviation from predicted	Biota samples (N = 43)	Benthic amphipods (N = 9)	Copepods (N = 20)	Krill (N = 4)	Arrow worms (N = 3)	Pelagic amphipods (N = 7)	Field blanks (N = 5)
611–70-1	Isopropyl phenyl ketone	20.41	1792	362	4 (2)		10 (2)				
92–24-0	Naphthalene	34.67	2618	439	4 (2)		5 (1)		33 (1)		
95–47-6	<i>o</i> -Xylene	4.35	1099	–65	4 (2)		5 (1)			14 (1)	
119–47-1	2,2'-Methylenebis[6-(1,1-dimethylethyl)-4-methyl-phenol]	33.96	2569	–510	4 (2)		5 (1)			14 (1)	
31,570–04-4	Phosphite (3:1)	49.48	3653	–1542	4 (2)	11 (1)	5 (1)				
85–41-6	Phthalimide*	14.87	1538	–69	4 (2)		5 (1)			14 (1)	
526–55-6	Tryptophol	21.55	1849	191	4 (2)		10 (2)				
93–56-1	1-Phenyl-1,2-ethanediol	11.51	1395	93	4 (2)		10 (2)				20 (1)
89,876–55-1	2- Bromopropionic acid, octadecyl ester	32.59	2479	–50	4 (2)		10 (2)				20 (1)
128–37-0	Butylated hydroxytoluene	27.09	2144	67	4 (2)				33 (1)	14 (1)	20 (1)
105–60-2	Caprolactam	10.12	1338	144	4 (2)		5 (1)		33 (1)		20 (1)
616–55-7	4,6-Di(1,1-dimethylethyl)-2-methylphenol	16.98	1631	–493	4 (2)		5 (1)	25 (1)			20 (1)

### 3.4. Comparison of species

In general, a higher number of tentatively identified compounds were found in benthic amphipods and copepods compared to the other species. The tentatively identified compound data set (Table S5) was subject to inspection by multivariate statistics using PCA, sparse PCA (sPCA) and partial least squares discriminant analysis (PLSDA) (Fig. S4). None of the groups showed separation from the others based on the standard deviation (visualized by ellipses), with one exception. The benthic amphipod group showed a non-significant separation from the other groups in PC3 (10 % of variance, compared to 16 and 10 % for PC1 and PC2, respectively) for both PCA and sPCA models. For these data a sparse PLSDA model was generated to test if a supervised approach could differentiate between the groups. Based on the two first latent variables (LV), the benthic amphipods and arrow worm groups were separated from the other samples as visualized by standard deviation ellipses along LV1 and LV2 respectively, but not with a confidence level of 0.95.

Although varying greatly between seasons and life stages, the relative lipid content (by wet weight) of the studied species, is generally expected to be higher in copepods and krill than in arrow worms and pelagic amphipods (Hallanger et al., 2011). In general, copepods and amphipods have a higher relative content of storage lipids (respectively wax esters and triglycerids) while arrow worms have a higher relative content of phospholipids (Connelly et al., 2012). Lipid content did not clearly influence the body concentrations of contaminants in the present study. Quantified levels of bisphenol A, hexachlorobenzene, ibuprofen and triclosan were generally higher in pelagic species than in the benthic amphipods, although the difference was not significant. This is contrary to the PAHs, PCBs and PBDEs, where benthic amphipods generally had higher concentrations (significant for PAHs and PBDEs). Differences in solubility, again affecting transport pathways, may explain this. While PAHs, PCBs and PBDEs are generally more lipophilic and more prone to accumulation in sediments and species with higher fat content, the other compounds (as many other compounds of emerging concern) are more water soluble and thus more likely present in the water column where pelagic species dwell. Thus, while benthic species may have been exposed to more POPs, the pelagic species may be more likely to be exposed to CECs that are transported to, and accumulate in, the Arctic. Metabolism in Arctic species is often slower than in their relatives from temperate regions, as shown e.g. for PAHs in *Calanus hyperboreus* (Agersted et al., 2018; Øverjordet et al., 2018). Slow elimination of contaminants in lower trophic levels result in elevated risk for a transfer to predators and magnification along the food chain (Fisk et al., 2001).

Hallanger et al. (2011) showed correlation between feeding strategy and concentration of halogenated organic compounds, with higher concentrations found in predatory species (arrow worms and pelagic amphipods) compared to herbivore/omnivore species (copepods and krill). This is not in line with the current data, where no clear difference is seen between

predators and herbivores. However, the concentrations of contaminants were in general higher in the benthic amphipods which can be explained by their scavenging behavior (Nygård, 2011). These species will feed on any organic matter including dead fish, birds, and mammals if available. It is likely that the main source of the more persistent and less biodegradable POPs found in the benthic amphipods are their feed.

### 3.5. Sources of contamination

Long-range transport of POPs to the Arctic has been studied for decades (Bottenheim et al., 2004; Oehme and Ottar, 1984), and more recently evidence of long-range transport of CECs has been demonstrated (Vorkamp and Rigét, 2014). However, both POPs and CECs are expected to have both local and long-range sources (Hung et al., 2022).

Hexachlorobenzene and PCBs is well known to be subject to long-range transport and accumulation in the Arctic (Johansen et al., 2021). Previous studies have shown that PCB-28 is the predominant PCB in water and sediments in Kongsfjorden (Ademollo et al., 2021; Pouch et al., 2017). In contrast, in the current study, PCB-28 was not found above LOD in any of the samples. In the benthic amphipods, levels of PCBs 152, 138 and 118 were in the same order (high variability in the data set) as in the sediments for deposition year 2009 (Pouch et al., 2017). It has been suggested that the source of these PCBs are mainly transport through marine currents and sea ice, rather than atmospheric transport (which is more likely for 'lighter' PCBs) (Ademollo et al., 2021; Pouch et al., 2017). Sources of hexachlorobenzene in sediments from Kongsfjorden have been suggested to arise from a combination of long-range transport and secondary discharge from melting glaciers as the key contributors, and local primary sources as less significant in terms of contribution (Pouch et al., 2018).

Sources of PAHs to the Arctic are difficult to distinguish, and include both local and long-range transported pyrogenic PAHs as well as petrogenic PAHs from seeps and maritime traffic (Balmer et al., 2019a). A recent study with data from 2016 to 2017 showed seasonal and spatial variations in the PAH profile detected, and confirmed contribution from a variety of sources, including local ship traffic (Ademollo et al., 2021). Pouch et al. (2017) used relative distribution of lighter and heavier PAHs as an indication of main contributing source to sediment pollution observed in Kongsfjorden. The same cannot be done for concentrations in biota as interference from various factors affecting bioaccumulation confound the interpretation. However, due to their internally similar expected accumulation (Wassenaar and Verbruggen, 2021), the ratios phenanthrene/anthracene and fluoranthene/pyrene can be used to assess whether the dominant source is likely pyrogenic or petrogenic. Based on sediment analysis in Kongsfjorden, it was suggested that the main source of PAHs was pyrogenic (local coal combustion) (Pouch et al., 2017). In the study by Szczybelski et al. (2016), PAH contamination in benthic bivalves from Kongsfjorden were found to be of mixed pyrogenic and petrogenic origin. In the current study, ratios of

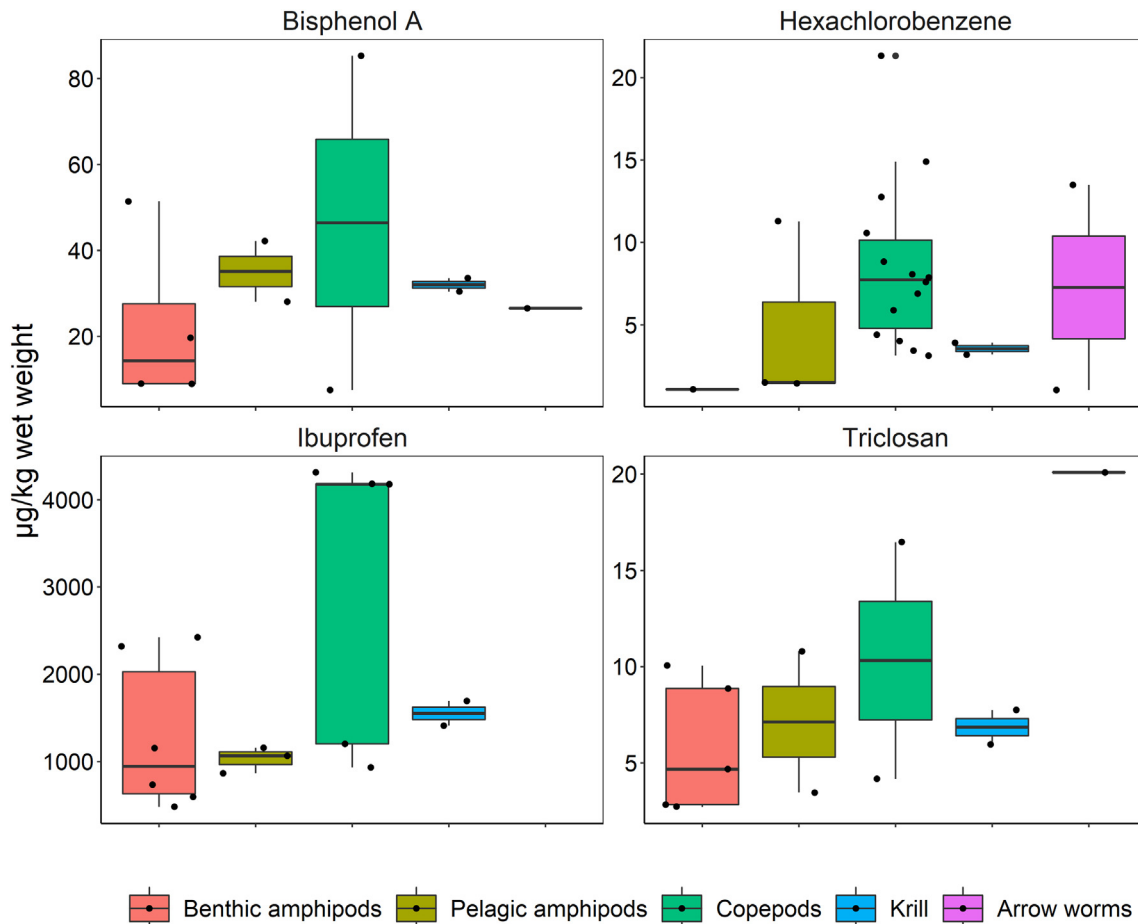


Fig. 1. Quantified levels of bisphenol A, hexachlorobenzene, ibuprofen, and triclosan in tissues of invertebrates ( $\mu\text{g}/\text{kg}$  wet weight). Only concentrations  $>$  LOD (determined by laboratory blank samples) are shown. Jitters represent individual samples.

phenanthrene, anthracene, fluoranthene and pyrene in pelagic species suggest a pyrogenic source. However, for benthic amphipods the fluoranthene/pyrene ratio is  $\sim 1$  and the phenanthrene/anthracene ratio is  $>10$ , suggesting a predominantly petrogenic source. Several alkylated PAHs (e.g., dimethylnaphthalenes, methylphenanthrenes, methyl- and dimethylfluorenes), as well as other compounds of likely petrogenic origin (alkyl substituted benzenes and hydrogenated naphthalenes) were tentatively identified from GC  $\times$  GC-MS NTS (Table S5), and further support the contribution of petrogenic pollution in the area (Andersson and Achten, 2015).

'Novel' brominated flame retardants, such as 2,4,6-tribromophenyl, which herein was found in invertebrate samples using the non-target approach, has previously been detected in biota samples from Arctic areas, and long range transport was suggested as the pre-dominant source (Vorkamp and Rig  t, 2014). Bisphenol A has also been detected in both seawater and Arctic species, and hypothesized sources include long-range atmospheric transport as well as transport by plastic debris (Ademollo et al., 2018, 2021). The insecticide carbaryl is commonly found in water samples worldwide. While it has been banned in several countries, it is still in use elsewhere, such as in the US. While it is expected to photodegrade rapidly, it degrades slowly in dark seawater (Derbalah et al., 2020). While likely sourced from long-range transport, it may thus accumulate in Arctic environments.

Pharmaceuticals and personal care products (PPCPs), examples identified here triclosan and ibuprofen, may arise from long-range transport (Kallenborn et al., 2018), but it has been proposed that local sources are most significant (Hung et al., 2022). In Svalbard, local sources of PPCPs are increasing in significance. Between 2007 and 2019, cruise tourism to Svalbard nearly tripled in number of passengers (PortLongyear, 2020), and mainland tourist overnight stays increased by over 80,000 during the same decade (Epinion, 2019).

Due to the scarcity of wastewater treatment in the Arctic, untreated greywater and blackwater (including raw sewage) are commonly discharged to the marine environment (Jensen et al., 2018). A recent study confirmed that sewage effluents is an important source of pollution to Kongsfjorden specifically (Choi et al., 2020). Pharmaceuticals are only partly removed in wastewater treatment (Verlicchi et al., 2012), meaning local sources may remain important even with improved water treatment. With regards to similar discharges from ships, sewage dumping is currently allowed outside the 12-mile zone around Svalbard whereas treated sewage effluent and greywater can legally be dumped closer to shore (Cowan et al., 2022).

#### 4. Conclusions

In the presented study, it has been demonstrated that marine Arctic invertebrates contain a complex chemical profile. While concentrations of POPs (hexachlorobenzene, PAHs, PCBs and PBDEs) were in line with observations in species at higher trophic levels, a range of previously less studied chemicals was identified and/or quantified in samples from several invertebrate species for the first time. Surprisingly high levels of the pharmaceutical ibuprofen are reported, and this warrants further investigation of key sources, and environmental effects. While contamination from long-range transport cannot be mitigated locally, the increase in tourism and maritime activity in Svalbard and the Arctic in general, warrants preventive action to minimize impacts from the increase in load of contamination from local sources.

#### Data availability

Data will be made available on request.



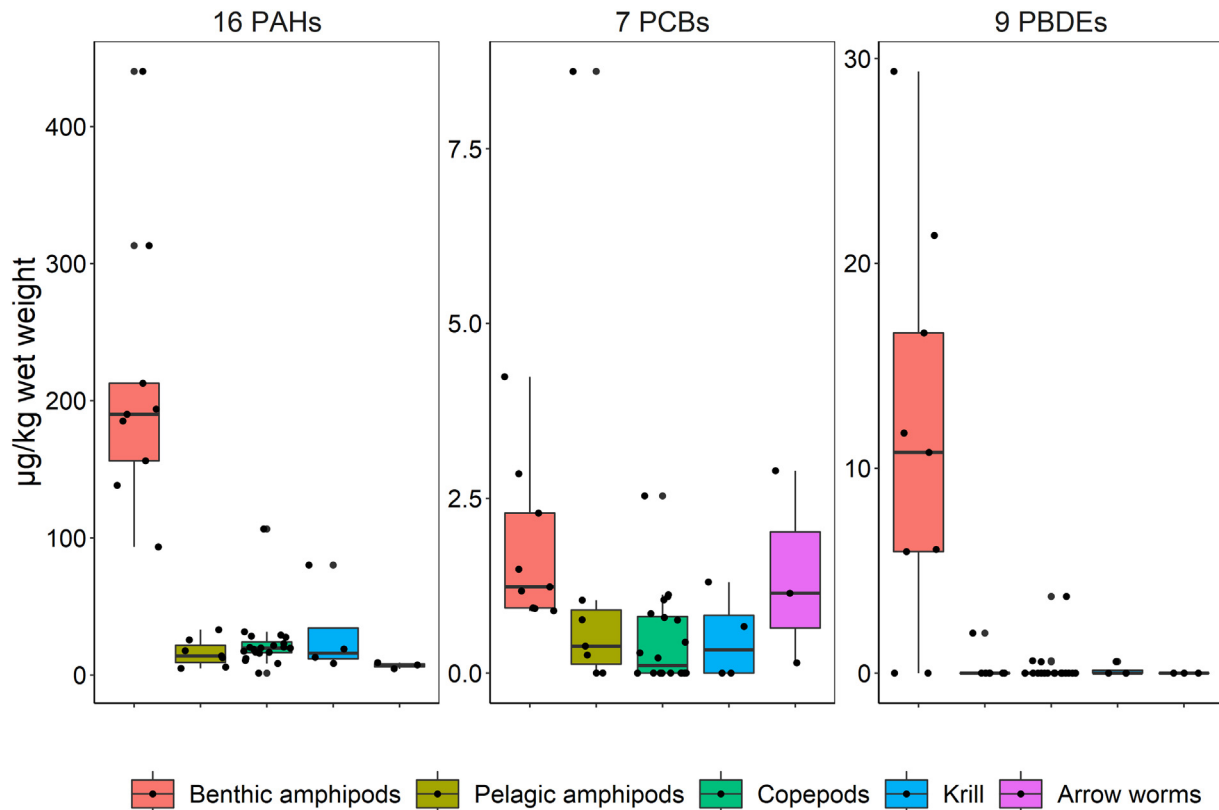


Fig. 2. Quantified levels of  $\Sigma 16$ PAHs,  $\Sigma 7$ PCBs,  $\Sigma 9$ PBDEs in tissues of invertebrates ( $\mu\text{g}/\text{kg}$  wet weight). Only concentrations  $>$  LOD (determined by laboratory blank samples) are shown. Jitters represent individual samples.

### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ida-Beathe Overjordet reports financial support was provided by Svalbard Environmental Protection Fund. Ida-Beathe Overjordet reports financial support was provided by High North Research Centre for Climate and the Environment. Amaia Igartua reports financial support was provided by NoviaSalcedo Fundación, Spain.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2022.161056>.

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