



Baseline

Phthalate contamination in marine mammals off the Norwegian coast



Clare Andvik^{a,*}, Pierre Bories^{b,1}, Mikael Harju^c, Katrine Borgå^a, Eve Jourdain^{a,d},
Richard Karoliussen^d, Audun Rikardsen^e, Heli Routti^f, Pierre Blévin^g

^a Department of Biosciences, University of Oslo, Norway

^b INRS, Eau Terre Environnement center, Quebec City, Canada

^c The Climate and Environmental Research Institute NILU, Fram Centre, Tromsø, Norway

^d Norwegian Orca Survey, Andenes, Norway

^e Department of Arctic and Marine Biology, UiT - The Arctic University of Norway, Tromsø, Norway

^f Norwegian Polar Institute, Fram Centre, Tromsø, Norway

^g Akvaplan-niva AS, Fram Centre, Tromsø, Norway

ARTICLE INFO

Keywords:

Toothed whales
Arctic
Emerging contaminants
Plasticizer
Maternal transfer

ABSTRACT

Phthalates are used in plastics, found throughout the marine environment and have the potential to cause adverse health effects. In the present study, we quantified blubber concentrations of 11 phthalates in 16 samples from stranded and/or free-living marine mammals from the Norwegian coast: the killer whale (*Orcinus orca*), sperm whale (*Physeter macrocephalus*), long-finned pilot whale (*Globicephala melas*), white-beaked dolphin (*Lagenorhynchus albirostris*), harbour porpoise (*Phocoena phocoena*), and harbour seal (*Phoca vitulina*). Five compounds were detected across all samples: benzyl butyl phthalate (BBP; in 50 % of samples), bis(2-ethylhexyl) phthalate (DEHP; 33 %), diisononyl phthalate (DiNP; 33 %), diisobutyl phthalate (DiBP; 19 %), and dioctyl phthalate (DOP; 13 %). Overall, the most contaminated individual was the white-beaked dolphin, whilst the lowest concentrations were measured in the killer whale, sperm whale and long-finned pilot whale. We found no phthalates in the neonate killer whale. The present study is important for future monitoring and management of these toxic compounds.

1. Introduction

Phthalates, also known as diesters of phthalic acids, are a group of chemicals added to plastics to enhance their flexibility and durability (EPA, 2023). These plasticisers are often used in order to turn polyvinyl chloride (PVC) into a flexible material, as well as in cosmetics (e.g. hairspray and nail polish), plastic clothing, adhesives and lubricants (ECHA, 2023a). The annual worldwide production of phthalates was estimated to exceed 5 million tonnes per year in 2018 (Holland, 2018). Phthalates have been identified as persistent and potentially toxic for living organisms since the late 1970s (Dillingham and Autian, 1973; Giam et al., 1978; Peck and Albrot, 1982). Therefore, the European Chemicals Agency (ECHA) has listed 14 phthalates on the REACH Authorisation List (Annex XIV), and several compounds including the *ortho*-phthalates diisobutyl phthalate (DiBP), dibutyl phthalate (DBP), benzyl butyl phthalate (BBP), bis(2-ethylhexyl) phthalate (DEHP) and dicyclohexyl phthalate (DCHP) are on the Candidate List of substances

of very high concern due to their toxicity to the endocrine system and reproduction (ECHA, 2023b).

Phthalates are ubiquitous and even present in remote areas such as the Arctic (Xie et al., 2007; Routti et al., 2021), where they may enter through air deposition and leaching from plastics carried by air and ocean currents (Xie et al., 2007). Most phthalates are lipophilic, with the potential to bioaccumulate in lipid-rich tissues and biomagnify in food chains (Cousins and Mackay, 2000). Given their large fat stores, marine mammals typically accumulate high concentrations of lipophilic pollutants in their blubber (Dietz et al., 2019). Only a handful of studies have investigated phthalate concentrations in Arctic marine mammals (Routti et al., 2021; Vorkamp et al., 2004). Blue whales (*Balaenoptera musculus*) and fin whales (*Balaenoptera physalus*) from the Norwegian Arctic, that ingest large amounts of krill, had considerably higher concentrations of phthalates than polar bears that feed at the top of the Arctic marine food web (Routti et al., 2021). In Greenland, DEHP concentrations in sediment were similar to concentrations in birds, fish and

* Corresponding author.

E-mail address: clarem@uio.no (C. Andvik).

¹ Contributed equally, shared first authorship.

seals, and only slightly higher in polar bears (Vorkamp et al., 2004). Such trophic dilution of phthalates in marine mammal food webs is also supported by both field and modelling studies in aquatic food webs (Kim et al., 2016; Mackintosh et al., 2004) likely due to metabolic transformation and/or elimination in higher trophic level species (Goutte et al., 2020; Hu et al., 2016). Phthalate concentrations in many marine mammal species remain unknown, especially in apex predators such as toothed whales, known to bioaccumulate high concentrations of legacy POPs (Sonne et al., 2018; Jepson and Law, 2016; Andvik et al., 2021).

The aim of our study was to provide information about contamination to phthalates in marine mammals from the Norwegian coast. We measured blubber concentrations of 11 compounds in 16 samples from stranded and/or free-living killer whale (*Orcinus orca*), sperm whale (*Physeter macrocephalus*), long-finned pilot whale (*Globicephala melas*), white-beaked dolphin (*Lagenorhynchus albirostris*), harbour porpoise (*Phocoena phocoena*), and harbour seal (*Phoca vitulina*). To our knowledge, this is the first documentation of phthalate contamination in killer whale and sperm whale, and the first to detect di-isononyl phthalate (DiNP) and dioctyl phthalate (DOP) in marine mammal blubber. The present work focused mainly on killer whales, which is one of the most polluted species on Earth (Jepson and Law, 2016), and contributes to filling the gap of knowledge on phthalate contamination in marine mammals from Norway (Routti et al., 2021; Rian et al., 2020).

2. Materials and methods

2.1. Field sampling

Blubber samples were collected from dead marine mammals that had stranded along the Norwegian coast between 2016 and 2020, and from live killer whales that were taken by biopsy sampling in northern Norway in 2020 (Fig. 1).

Sampling of the stranded specimens ($n = 7$) was coordinated by Norwegian Orca Survey (NOS) (Table 1, Fig. 1). A minimum of 10*10*10 cm piece of skin-blubber-muscle was collected from the mid-

dorsal region of the body for each stranded animal. The two killer whales (ID OO4 and OO6 – a neonate) and one harbour seal (2SB) were sampled by NOS directly, whilst samples from the sperm whale (SW1), harbour porpoise (HP1), long-finned pilot whale (PW2) and white-beaked dolphin (D1) were collected by volunteers. Morphometrics and photographs were also collected. Each carcass was also assigned a code reflecting its decomposition state, from 2 (freshly deceased and no bloating) to 4 (advanced decomposition with major bloating / organs beyond recognition) (Kuiken and García-Hartmann, 1991) (Table 1). Prior to sampling, equipment was cleaned with soap and water, boiled for 5 min and sterilized with 95 % ethanol. All samples were wrapped in aluminium foil and stored at $-20\text{ }^{\circ}\text{C}$ until analysis.

Sampling from free-living killer whales ($n = 9$) was carried-out by the Arctic University of Norway (UiT) in northern Norway (Table 1; Fig. 1). A biopsy of skin and blubber (~4 cm long) was collected using the ARTS darting system operated from a Rigid Inflatable Boat, and targeting the region directly below or posterior to the dorsal fin (Kleivane et al., 2022). Adult males were identified based on observable secondary sexual characteristics (overall body size and height of the dorsal fin), per Ford et al. (2014), and other individuals classed as “Unknown” due to adult females and subadult individuals being indistinguishable from observations of size / dorsal fin. The biopsies were immediately removed from the dart to separate skin, dermis, and blubber on a glass petri dish using disposable scalpels and sterile scissors. Blubber samples were immediately stored in glass vial with a polypropylene top cap, with septum lined with polytetrafluoroethylene (PTFE) foam urethane (National Scientific, Austin, Texas, USA). Glassware used in the field were rinsed using cyclohexane and acetone and heated in an oven at $450\text{ }^{\circ}\text{C}$ for 8 h prior to the field season.

All samples were stored at $-20\text{ }^{\circ}\text{C}$ upon sampling and until analysis.

2.2. Phthalate analyses

Phthalate analyses were conducted at the Norwegian Institute for Air Research in Tromsø (NILU), Norway. Samples of stranded individuals

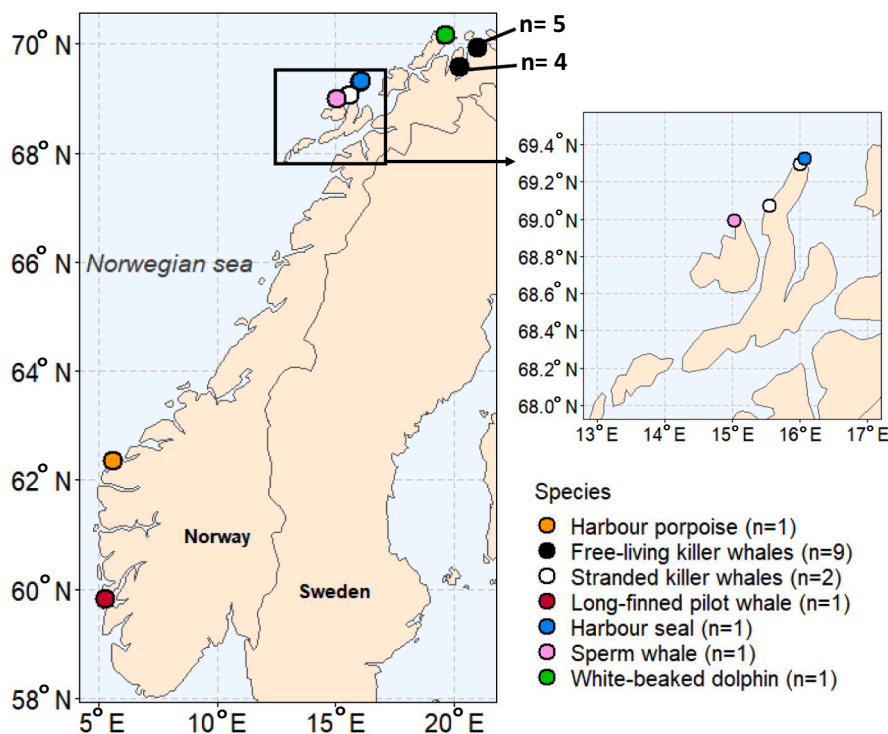


Fig. 1. A map of Norway showing the sampling location of each stranded and free-living marine mammal and the number of individuals. Biopsies were collected from free-living killer whales in two locations and n indicates the number of biopsies performed at each sample site.

Table 1

Sampling information and concentrations of phthalates expressed as ng/g wet weight (ww) and lipid weight (lw) in blubber of stranded and free-living marine mammals from the Norwegian coast 2016–2020. NA = not applicable, UNK = unknown and n.a. = not analysed. Samples under the limit of detection (LOD) are indicated by a less-than sign (<), and samples over the LOD are shaded light grey. The LOD and limit of quantification (LOQ) for each sample is also provided in the supplementary dataset. Samples between LOD and LOQ are indicated with an asterisk (*).

	Sample information							Phthalate concentrations (ng/g)															
	ID	Species	Year	Sex	Age class	Code ^a	Lipid %	BBP ^b		DEHP ^c		DiBP ^d		DiNP ^e		DOP ^f		DEP ^g	DHxP ^h	DCHP ⁱ	DiDcP ^j	DNP ^k	DnBP ^l
								ww	lw	ww	lw	ww	lw	ww	lw	ww	lw	ww	lw	ww	ww	ww	ww
Stranded	PW2	Long-finned pilot whale	2016	UNK	Subadult	3	57	1.7	2.9	<45	<78	<5.0	<8.7	54*	94*	<3.0	<5.2	<14	<5.0	<5.0	<28	<1.4	<16
	OO6	Killer whale	2017	Male	Neonate	2	80	<0.6	<0.8	n.a.	n.a.	<5.0	<6.3	n.a.	n.a.	n.a.	n.a.	<14	<5.0	<5.0	n.a.	n.a.	<16
	HP1	Harbour porpoise	2018	Female	Adult	2	98	<0.2	<0.2	23	24	<0.2	<0.2	1800	1800	65	66	<3.0	<0.2	<0.1	<2.4	<0.7	<0.7
	SW1	Sperm whale	2020	UNK	UNK	3	27	<0.2	<0.7	4.1*	15*	<0.2	<0.7	<3.1	<11	<0.3	<1.1	<3.0	<0.2	<0.1	<2.4	<0.7	<0.7
	OO4	Killer whale	2020	Male	Adult	3	55	<0.2	<0.4	3.3*	5.9*	<0.2	<0.4	<3.1	<5.6	<0.3	<0.5	<3.0	<0.2	<0.1	<2.4	<0.7	<0.7
	D1	White-beaked dolphin	2019	UNK	UNK	3	89	<0.2	<0.2	120	130	35	39	7020	7900	205	230	<3.0	<0.2	<0.1	<2.4	<0.7	<0.7
	2SB	Harbour seal	2018	UNK	UNK	2	79	<0.2	<0.3	<1.3	<1.6	7.4	9.3	720	910	<0.3	<0.4	<3.0	<0.2	<0.1	<2.4	<0.7	<0.7
Free-living	KW01	Killer whale	2020	UNK	UNK	NA	41	2.8	6.8	<45	<110	<5.4	<13	<29	<71	<3.0	<7.3	<15	<0.3	<0.1	<28	<2.0	<16
	KW04	Killer whale	2020	Male	Adult	NA	15	3.6	25	55*	380*	<5.4	<37	<29	<200	<3.0	<21	<15	<0.3	<0.1	<28	<2.0	<16
	KW05	Killer whale	2020	UNK	UNK	NA	38	5.3	14	<45	<120	<5.4	<14	240	640	<3.0	<8.0	<15	<0.3	<0.1	<28	<2.0	<16
	KW06	Killer whale	2020	UNK	UNK	NA	43	4.1	9.6	<45	<100	<5.4	<13	<29	<68	<3.0	<7.0	<15	<0.3	<0.1	<28	<2.0	<16
	KW07	Killer whale	2020	UNK	UNK	NA	55	3.9	7	<45	<81	<5.4	<9.8	<29	<53	<3.0	<5.5	<15	<0.3	<0.1	<28	<2.0	<16
	KW08	Killer whale	2020	UNK	UNK	NA	20	2.6	13	<45	<220	10.6*	52	<29	<140	<3.0	<15	<15	<0.3	<0.1	<28	<2.0	<16
	KW10	Killer whale	2020	UNK	UNK	NA	48	<0.6	<0.6	<45	<92	<5.4	<11	<29	<60	<3.0	<6.7	<15	<0.3	<0.1	<28	<2.0	<16
	KW14	Killer whale	2020	UNK	UNK	NA	18	<0.6	<1.6	<45	<250	<5.4	<31	<29	<160	<3.0	<17.0	<15	<0.3	<0.1	<28	<2.0	<16
	KW15	Killer whale	2020	UNK	UNK	NA	52	2.8	5.4	<45	<87	<5.4	<11	<29	<56	<3.0	<5.8	<15	<0.3	<0.1	<28	<2.0	<16

^aDecomposition code, *per* Kuiken and Garcia-Hartmann (1991); ^b Benzyl butyl phthalate (CAS: 85-68-7); ^c Bis(2-ethylhexyl)phthalate (CAS: 117-81-7); ^d Diisobutyl phthalate (CAS: 84-69-5); ^e Di-iso-nonyl phthalate (CAS: 28553-12-0); ^f Di-n-octyl phthalate (CAS: 117-84-0); ^g diethylphthalate (CAS: 84-66-2); ^h di-n-hexyl phthalate (CAS: 84-75-3); ⁱ dicyclohexyl phthalate (CAS: 84-61-7); ^j di-iso-decyl phthalate (CAS: 26761-40-0); ^k di-n-nonyl phthalate (CAS: 84-76-4); ^l di-n-butylphthalate (CAS: 84-74-2).

were sent whole to the laboratory, where a subsample was taken from the inside of each sample to minimise contamination. 11 phthalates were analysed in all samples: DiBP, BBP, DEHP, DCHP, DiNP, DOP, diethyl phthalate (DEP), di-n-butyl phthalate (DnBP), di-hexylphthalate (DHxP), dinonyl phthalate (DNP) and diisodecyl phthalate (DiDcP). Due to possible degradation of lipids / interference from matrix, DEHP, DOP, DiNP, DNP and DiDcP could not be screened in the neonate killer whale (OO6). The limit of detection (LOD) and limit of quantification (LOQ) for each phthalate and sample are provided in Table 1 and the Supplementary dataset.

2.2.1. Chemicals

Chemicals used were acetonitrile (Rathburn, LCMS grade), n-Hexane (Merck, Suprasolv), acetic acid (ReagentPlus, >99 % purity, Sigma Aldrich Co LLC), milli-Q (Advantage, A10, Merck KGaA), florisil (J.T. Baker, activated at 675C, Avantor Performance materials, Inc.), acetone (Merck KGaA, Suprasolv) and methanol (Merck KGaA, Lichrosolv). All phthalate standards were from Accustandard Inc., New-Havens, United States.

2.2.2. Sample preparation

Samples were prepared based on Guerranti et al. (2013) and Fossi et al. (2014). 0.3 g of blubber was added to a 15 mL centrifuge glass with 100 ng of surrogate standard (d4-DEHP). The sample was vortexed, and extracted by ultrasound twice for 10 min with acetone and centrifuged.

The supernatant was evaporated to dryness and lipid content determined. Acetic acid/water (9/1) and 1 mL n-hexane was added to the extract, vortexed and centrifuged. n-hexane was transferred to a new glass and the procedure was performed three more times. The n-hexane extract was evaporated to dryness and 1 mL acetonitrile and 100 ng of internal recovery standard (d4-DOP) was added and the sample was vortexed. 0.5 mL was taken for analysis on UPLC/MS/MS. The instrumental analysis was performed using the Thermo Fisher Scientific TSQ Vantage LC/MS/MS fitted with an analytical column (100 mm × 2.1mmID, 1.8 µm; Acquity UPLC HSS T3, Waters Inc) and a pre-column (50 mm × 2.1 mm, 5 µm; XBridge C18, Waters Inc) fitted between pump and injector to offset system background. 10 µL sample was injected and mobile phase was 0.1 % aqueous formic acid (A) and methanol with 0.1 % formic acid (B) starting at 90/10 (A/B) with a gradient to 85/15 and finally to 100 % B at 0.3 to 0.4 mL/min. The ESI-MS was operated at 380 °C and a capillary voltage of 4.0 kV in negative mode identifying parent/daughter ions.

2.2.3. Quality assurance

All glassware were washed with acetone and n-hexane and burned at 450 °C for 8 h the day before use, and again rinsed with n-hexane immediately before use. All work was conducted in a clean room. n-hexane was precleaned before use by adding Florisil into the flask and shaken to absorb contaminants. The acetic acid/water (9/1) mix was purified in a separatory funnel with precleaned n-Hexane and put in

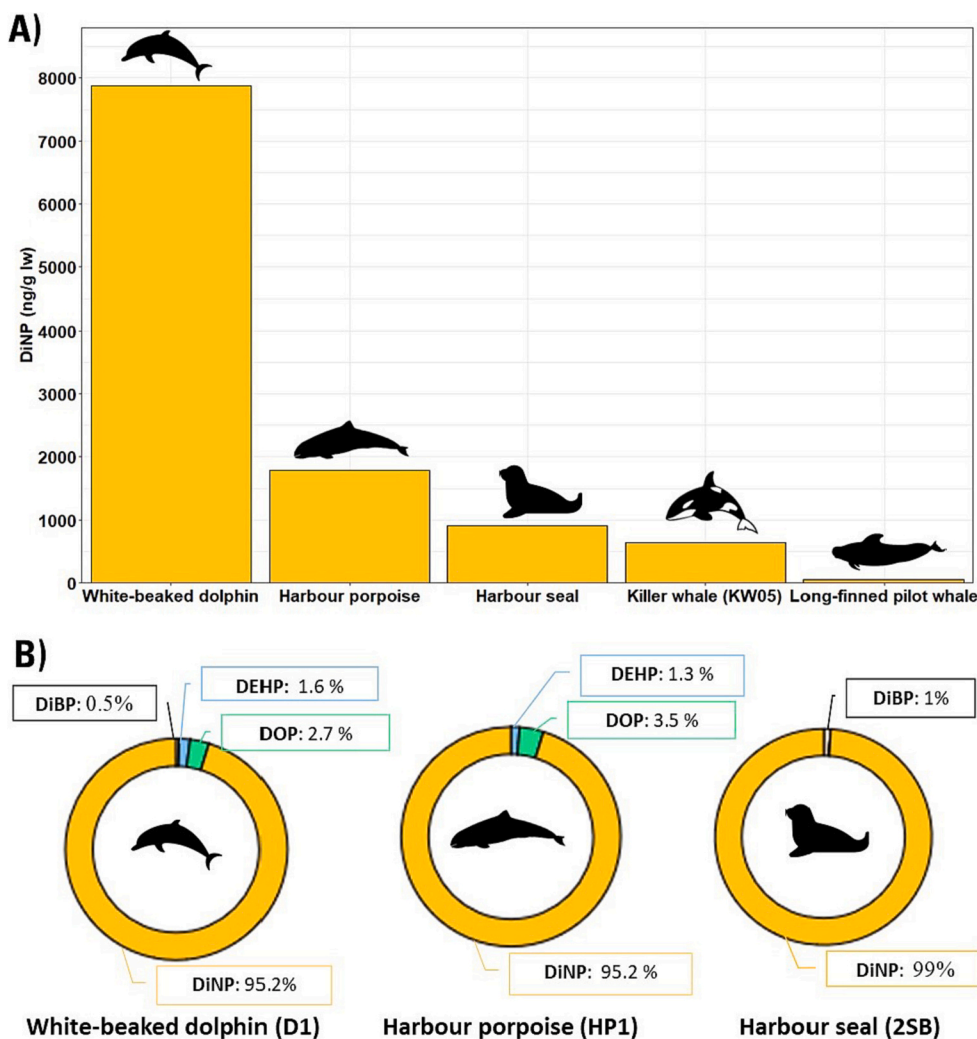


Fig. 2. A) Di-iso-nonyl phthalate (DiNP) concentrations (ng/g lw) in blubber of four stranded marine mammals and one free-living biopsied killer whale (KW05). B) Proportions of phthalates in blubber of the three most contaminated individuals.

shaker at 200 min⁻¹ for 30 min, and the n-hexane was discarded. Milli-Q water was generated through a Milli-Q unit with an additional polishing cartridge to remove contaminants. To assure the quality of the sample preparation and analysis, three laboratory blanks were used and a certified reference material (NIST 3074, phthalates in methanol) was added to seal blubber samples in three replicates and a reference sample without addition of NIST 3074 giving a standard deviation for DEHP of 6.6 % between replicates and 82–96 % recovery of the actual certified value. The instrument was run on a 6-point calibration curve from 10 to 1000 ng/mL. LOD and LOQ (Supplementary dataset) were determined by 3xSD and 10xSD in laboratory blanks respectively, and all samples were blank corrected. The LOD for DEHP is higher for the long-finned pilot whale (PW2) and the free-living killer whales, compared to the stranded marine mammals, as the d4-DEHP standard was contaminated with DEHP and there was not enough material to repeat analysis.

2.3. Data treatment

No statistical analyses were conducted due to the low sample size and low occurrence of phthalates in the dataset.

3. Results

Of the 11 screened phthalates, we found five compounds across all the samples: BBP (detected in 50 % of samples), DEHP (33 %), DiBP (19 %), DiNP (33 %) and DOP (13 %) (Table 1). The most phthalate-contaminated individual was the white-beaked dolphin, followed by the harbour porpoise and the harbour seal (Table 1, Fig. 2A). Concentrations of phthalates were systematically < LOD for all compounds in the neonate stranded killer whale.

DiNP was the most abundant phthalate and made up over 90 % of the total phthalate load in the white-beaked dolphin, harbour porpoise, harbour seal and long-finned pilot whale (Fig. 2B). Concentrations of DiNP in the white-beaked dolphin were approximately 4, 7, 80 and 2000 times higher than in the harbour porpoise, seal, long-finned pilot whale and both the stranded sperm whale and killer whale, respectively (Table 1; Fig. 2A). Amongst the free-living killer whales, DiNP was detected in only one individual (Table 1).

BBP was only detected in one stranded specimen, the long-finned pilot whale, whilst it was the most frequently detected phthalate in free-living killer whales (7 out of 9). DEHP was detected in four of the stranded marine mammals, the harbour porpoise, the sperm whale, a killer whale (OO4) and the white-beaked dolphin. DiBP was detected in two stranded marine mammals, the white-beaked dolphin and the harbour seal. DOP was detected also in two stranded individuals, the harbour porpoise, and the killer whale (Table 1). DEHP and DiBP were detected in only one free-living killer whale each (different individuals) (Table 1). DOP was not detected in free-living killer whale samples.

4. Discussion

Our results showed that the killer whale, sperm whale and long-finned pilot whale had the lowest concentrations of phthalates compared to the white-beaked dolphin, harbour porpoise and harbour seal. Whilst information about their diet is not available in the literature for all the species in this study area, it is known that killer whales off the Norwegian coast eat a range of prey including (primarily) herring, but also other fish and marine mammal prey (Jourdain et al., 2019), and that sperm whales from Norway and long-finned pilot whales from the North Atlantic feed on deep-sea benthic prey (Christensen et al., 1992; Desportes and Mouritsen, 1988; Mendes et al., 2007; Similä et al., 2022). The stable isotope ratios of nitrogen in sperm whales were higher than baleen whales in the Barents Sea (Mackenzie et al., 2022), and there are indications that they are high trophic species due to the trophic level of their prey being comparable to top vertebrate predators in the Arctic (Golikov et al., 2018). Harbour seal, harbour porpoise and white-beaked

dolphins along the Norwegian coast are thought to be opportunistic feeders feeding primarily on small pelagic fish (Berg et al., 2002; Bjørge, 2003; Fall and Skern-Mauritzen, 2014), indicating that they are mid-trophic species. Whilst we cannot directly compare the trophic position of these species, and our sample size is small, there are indications that our results support a trophic dilution of phthalates in the marine mammal food web. This is in line with recent works reporting higher concentrations of DEHP in baleen whales than polar bears from the Norwegian Arctic (Routti et al., 2021), and similar concentrations of DEHP in sediment, birds, fish and seals, and only slightly higher in polar bears from Greenland (Vorkamp et al., 2004).

Feeding habitat may also influence phthalate concentrations in marine mammals. In the Mediterranean sea, baleen whales in areas with high amounts of plastic pollution accumulate higher concentrations of phthalates through the ingestion of microplastics and direct exposure to seawater (Baini et al., 2017; Fossi et al., 2014, 2012). White-beaked dolphins, harbour porpoises and seals are pelagic and coastal feeders, and therefore, potentially, more exposed to plastics than the deep-diving sperm and pilot whales. However, this is heavily dependent on the types of plastics in the local environment, with different densities determining if they float or sink (GESAMP, 2015).

With the exception of the white-beaked dolphin and one free living killer whale (KW04), DEHP concentrations measured in our study were lower than those found in blue and fin whale blubber from the Norwegian Arctic (Routti et al., 2021). DEHP concentrations measured in common bottlenose dolphin blubber from the Brittany gulf (90–160 ng.g⁻¹ ww) (Zanuttini, 2019) were similar to the blubber concentrations we have measured in the white-beaked dolphin. Concentrations in different species from different environments are likely correlated to local sources and/or transport of phthalates. For example, there was a strong influence of location on phthalate metabolite concentrations in harbour porpoises from coastal Norway, with lower concentrations in individuals from lesser populated areas than those sampled closer to active oil and gas fields (Rian et al., 2020).

The differences in concentrations and proportions of phthalates between the free-living killer whales and stranded marine mammals might be explained by differences in sample collection, area and depth of blubber sampled, chemical degradation, as well as in LODs for the same phthalate between different analyses batches. For example, the LOD for DEHP in the long-finned pilot whale and all the free-living killer whales was 44.6 ng/g ww, whereas for the stranded marine mammals it was 1.3 ng/g ww. Due to the ubiquitous presence of phthalates in the environment, blank levels are often high and can vary widely between batches, despite best efforts to minimise background contamination. This also makes comparison to other studies challenging, with different procedures used to account for contamination. For example, in Vorkamp et al. (2004) samples were not blank-corrected despite high blank levels. The LOD levels in the present study are, however, within the ranges, and in many cases lower, than that reported in the existing literature (e.g. Routti et al., 2021; Baini et al., 2017; Vorkamp et al., 2004).

The absence of phthalates in the neonate killer whale suggests an inefficient maternal transfer of phthalates in killer whales and/or absence of phthalates in the mother. These results are consistent with other studies indicating a lack of maternal transfer of phthalates in common bottlenose dolphin (*Tursiops truncatus*) from the Brittany Gulf in France (Zanuttini, 2019) and from Florida (Dziobak et al., 2021), as indicated from blubber and urine samples. This is in contrast with maternal transfer of other lipophilic pollutants confirmed for this same specimen in a previous study (Andvik et al., 2021). Given that this neonate had died only a few hours before sampling, degradation of phthalates is unlikely.

The high concentrations of DiNP in our study, in comparison to DEHP, may be representative of the shift in the overall industrial use and production of phthalates, with a replacement of DEHP with DiNP following regulations (ECHA, 2013). DEHP was placed on the Norwegian Priority List of chemicals that should be phased out in 2002

(Norwegian Priority List, 2023), and has been regulated in Europe under REACH Annex XVI since 2015 and Annex XVII since 2018 (ECHA, 2023b). Subsequently, a simultaneous increase of DiNP and decrease of DEHP concentrations has been highlighted in time series from the freshwater environment (Nagorka et al., 2022; Nagorka and Koschorreck, 2020) and humans (Reyes and Price, 2018) in the period mid-2000s to late-2010s. Whilst a recent study on Icelandic fin whales did not report any variation in total concentrations of phthalates over three decades, the contribution of DEHP within the phthalate profile decreased over the study period, although DiNP was not quantified (Garcia-Garin et al., 2022). DiNP was not, however detected in baleen whales from the Norwegian Arctic suggesting species- and/or location-specific differences in its bioaccumulation (Routti et al., 2021). This may, however, also be due to the higher LOD value for DiNP (100 ng/g ww), as opposed to the present study (3.1–39 ng/g ww).

The small contribution of BBP, DIBP and DOP in the phthalate profile may be attributed to a low regional production and exposure, and/or a more efficient metabolism/elimination of these compounds in the marine mammals sampled for the present study. BBP has been previously detected in polar bear, common minke whale (*Balaenoptera acutorostrata*), ringed seal (*Pusa hispida*) and long-finned pilot whale liver from Greenland, in concentrations two to ten times higher than the blubber concentrations reported here (Vorkamp et al., 2004). These differences could be tissue related (blubber vs liver) or could be representative of lower background concentrations of BBP along the Norwegian coast. DiBP has previously been detected in a stranded common dolphin blubber from the French coast at 30 times higher concentrations than the seal from the present study (Zanuttini, 2019), although two other stranded dolphins had concentrations <LOD.

Ocean plastic pollution is expected to significantly rise in the next decade (Jambeck et al., 2015; Mai et al., 2020) leading to increased leaching of phthalates in the marine environment. The present study provides knowledge on the occurrence of phthalates in marine mammals from the Norwegian coast, which is important for future monitoring and management of these toxic compounds. Further studies on marine mammals from a range of trophic levels, and other organisms in the food web, are needed to deepen our understanding of phthalate contamination routes in the marine environment.

Ethic statement

All fieldwork was approved by the Norwegian Animal Research Authority (FOTS ID 13639 and 14135) and carried out by experienced scientists.

CRediT authorship contribution statement

Clare Andvik and Pierre Bories contributed equally to this work and should be regarded as joint first authors. **Clare Andvik:** Conceptualization, Formal analysis, Funding acquisition, Project administration, Visualization, Writing – original draft. **Pierre Bories:** Conceptualization, Formal analysis, Visualization, Writing – original draft. **Mikael Harju:** Investigation, Resources, Writing – review & editing. **Katrine Borgå:** Funding acquisition, Project administration, Resources. **Eve Jourdain:** Funding acquisition, Resources, Writing – review & editing. **Richard Karoliussen:** Resources. **Audun Rikardsen:** Funding acquisition, Resources. **Heli Routti:** Funding acquisition, Resources, Writing – review & editing. **Pierre Blévin:** Conceptualization, Funding acquisition, Project administration, Resources, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare no competing interests.

Data availability

All data is available in the Supplementary Dataset.

Acknowledgements

This study was funded by the Hazardous Substances” flagship program (462/602019 and 602018 - H. Routti), the Norwegian Environment and Climate Agency’s Arktis 2030 programme (grant number QZA-15/0137 – K. Borgå), the Research Council of Norway (COPE RCN #287114 - Ingjerd Sunde Krogseth, SLICE RCN #335489 - Pierre Blévin) and the research program ‘Cumulative Impact of Multiple Stressors in High North Ecosystems (CLEAN)’ of the Fram Centre, Tromsø, Norway. Emma Vogel, Lars Kleivane and Juni Bjørneset helped with biopsy sampling.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.marpolbul.2023.115936>.

References

- Andvik, C., Jourdain, E., Lyche, J.L., Karoliussen, R., Borgå, K., 2021. High levels of legacy and emerging contaminants in killer whales (*Orcinus orca*) from Norway, 2015 to 2017. *Environ. Toxicol. Chem.* 40, 1848–1858. <https://doi.org/10.1002/etc.5064>.
- Baini, M., Martellini, T., Cincinelli, A., Campani, T., Minutoli, R., Panti, C., Foino, M.G., Fossi, M.C., 2017. First detection of seven phthalate esters (PAEs) as plastic tracers in superficial neustonic/planktonic samples and cetacean blubber. *Anal. Methods* 9, 1512–1520. <https://doi.org/10.1039/C6AY02674E>.
- Berg, I., Haug, T., Nilssen, K.T., 2002. Harbour seal (*Phoca vitulina*) diet in Vesterflen, North Norway. *Sarsia* 87, 451–461. <https://doi.org/10.1080/0036482021000155735>.
- Björge, A., 2003. The harbour porpoise (*Phocoena phocoena*) in the North Atlantic: variability in habitat use, trophic ecology and contaminant exposure. *NAMMCO Scientific Publications* 5, 223–228. <https://doi.org/10.7557/3.2749>.
- Christensen, I., Haug, T., Oien, N., 1992. Seasonal distribution, exploitation and present abundance of stocks of large baleen whales (*Mysticeti*) and sperm whales (*Physeter macrocephalus*) in Norwegian and adjacent waters. *ICES J. Mar. Sci.* 49, 341–355. <https://doi.org/10.1093/icesjms/49.3.341>.
- Cousins, I., Mackay, D., 2000. Correlating the physical-chemical properties of phthalate esters using the ‘three solubility’ approach. *Chemosphere* 41, 1389–1399. [https://doi.org/10.1016/S0045-6535\(00\)00005-9](https://doi.org/10.1016/S0045-6535(00)00005-9).
- Desportes, G., Mouritsen, R., 1988. Diet of the pilot whale, *Globicephala melas*, around the Faroe Islands. In: *International council for the Exploration of the Sea, 1988/N:12*.
- Dietz, R., Letcher, R.J., Desforges, J.-P., Eulaers, I., Sonne, C., Wilson, S., Andersen-Ranberg, E., Basu, N., Barst, B.D., Bustnes, J.O., Bytingsvik, J., Ciesielski, T.M., Drevnick, P.E., Gabrielsen, G.W., Haarr, A., Hylland, K., Jenssen, B.M., Levin, M., McKinney, M.A., Norregaard, R.D., Pedersen, K.E., Provencher, J., Styrishave, B., Tartu, S., Aars, J., Ackerman, J.T., Rosing-Asvid, A., Barrett, R., Bignert, A., Born, E. W., Branigan, M., Braune, B., Bryan, C.E., Dam, M., Eagles-Smith, C.A., Evans, M., Evans, T.J., Fisk, A.T., Gamber, M., Gustavson, K., Hartman, C.A., Helander, B., Herzog, M.P., Hoekstra, P.F., Houde, M., Hoydal, K., Jackson, A.K., Kucklick, J., Lie, E., Loseto, L., Mallory, M.L., Miljeteig, C., Mosbech, A., Muir, D.C.G., Nielsen, S. T., Peacock, E., Pedro, S., Peterson, S.H., Polder, A., Rigét, F.F., Roach, P., Saunes, H., Sinding, M.-H.S., Skaare, J.U., Søndergaard, J., Stenson, G., Stern, G., Treu, G., Schuur, S.S., Vikiingsson, G., 2019. Current state of knowledge on biological effects from contaminants on arctic wildlife and fish. *Sci. Total Environ.* 696, 133792. <https://doi.org/10.1016/j.scitotenv.2019.133792>.
- Dillingham, E.O., Autian, J., 1973. Teratogenicity, mutagenicity, and cellular toxicity of phthalate esters. *Environ. Health Perspect.* Jan3, 81–89.
- Dziobak, M.K., Wells, R.S., Pisanski, E.C., Wirth, E.F., Hart, L.B., 2021. Demographic Assessment of Mono(2-ethylhexyl) Phthalate (MEHP) and Monoethyl Phthalate (MEP) Concentrations in Common Bottlenose Dolphins (*Tursiops truncatus*) From Sarasota Bay, FL, USA. *GeoHealth* 5, e2020GH000348. <https://doi.org/10.1029/2020GH000348>.
- ECHA (European Chemicals Agency), 2013. Evaluation of new scientific evidence concerning DNP and DIDP. Accessed 17 October 2023, retrieved from: <https://echa.europa.eu/documents/10162/31b4067e-de40-4044-93e8-9c9ff1960715>.
- ECHA (European Chemicals Agency), 2023a. Phthalates. Accessed 08 June 2023, Retrieved from: <https://echa.europa.eu/hot-topics/phthalates>.
- ECHA (European Chemicals Agency), 2023b. Substance restricted under reach. Accessed 26 September 2023, Retrieved from: <https://echa.europa.eu/substances-restricted-under-reach>.
- EPA (United States Environmental Protection Agency), 2023. America’s children and the environment (ACE), biomonitoring phthalates. Accessed 08 June 2023, Retrieved from: <https://www.epa.gov/americaschildrenewenvironment/biomonitoring-phthalates>.

- Fall, J., Skern-Mauritzen, M., 2014. White-beaked dolphin distribution and association with prey in the Barents Sea. *Mar. Biol. Res.* 10, 957–971.
- Ford, M.C., Coppola, D., Bains, M., Giannetti, M., Guerranti, C., Marsili, L., Panti, C., de Sabata, E., Clò, S., 2014. *Killer Whales: The Natural History and Genealogy of Orcinus orca* in British Columbia and Washington State, 2nd ed. UBC Press, Vancouver, BC, Canada.
- Fossi, M.C., Panti, C., Guerranti, C., Coppola, D., Giannetti, M., Marsili, L., Minutoli, R., 2012. Are baleen whales exposed to the threat of microplastics? A case study of the Mediterranean fin whale (*Balaenoptera physalus*). *Mar. Pollut. Bull.* 64, 2374–2379. <https://doi.org/10.1016/j.marpolbul.2012.08.013>.
- Fossi, M.C., Coppola, D., Bains, M., Giannetti, M., Guerranti, C., Marsili, L., Panti, C., de Sabata, E., Clò, S., 2014. Large filter feeding marine organisms as indicators of microplastic in the pelagic environment: the case studies of the Mediterranean basking shark (*Cetorhinus maximus*) and fin whale (*Balaenoptera physalus*). *Mar. Environ. Res.* 100, 17–24. <https://doi.org/10.1016/j.marenvres.2014.02.002>.
- Garcia-Garin, O., Sahyoun, W., Net, S., Vighi, M., Aguilar, A., Ouddane, B., Vikingson, G.A., Chosson, V., Borrell, A., 2022. Intrapopulation and temporal differences of phthalate concentrations in North Atlantic fin whales (*Balaenoptera physalus*). *Chemosphere* 300, 134453. <https://doi.org/10.1016/j.chemosphere.2022.134453>.
- GESAMP, 2015. Sources, fate and effects of microplastics in the marine environment: a global assessment. In: Kershaw, P.J. (Ed.), Rep. Stud. GESAMP 2015, No. 90.
- Giam, G.S., Chan, H.S., Neff, G.S., Atlas, E.S., 1978. Phthalate ester plasticizers: a new class of marine pollutant. *Science* 199, 419–421. <https://doi.org/10.1126/science.413194>.
- Golikov, A.V., Ceia, F.R., Sabirov, R.M., Zaripova, Z.I., Blicher, M.E., Zakharov, D.V., Xavier, J.C., 2018. Ontogenetic changes in stable isotope ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) values in squid *Gonatus fabricii* (Cephalopoda) reveal its important ecological role in the Arctic. *Mar. Ecol. Prog. Ser.* 606, 65–78. <https://doi.org/10.3354/meps12767>.
- Goutte, A., Alliot, F., Budzinski, H., Simonnet-Laprade, C., Santos, R., Lachaux, V., Maciejewski, K., Le Menach, K., Labadie, P., 2020. Trophic transfer of micropollutants and their metabolites in an urban riverine food web. *Environ. Sci. Technol.* 54, 8043–8050. <https://doi.org/10.1021/acs.est.0c01411>.
- Guerranti, C., Sbordoni, I., Fanello, E.L., Borghini, F., Corsi, I., Focardi, S.E., 2013. Levels of phthalates in human milk samples from central Italy. *Microchem. J.* 107, 178–181. <https://doi.org/10.1016/j.microc.2012.06.014>.
- Holland, M., 2018. Socio-economic assessment of phthalates. In: OECD Environment Working Papers No. 133, 91 pp.
- Hu, X., Gu, Y., Huang, W., Yin, D., 2016. Phthalate monoesters as markers of phthalate contamination in wild marine organisms. *Environ. Pollut.* 218, 410–418. <https://doi.org/10.1016/j.envpol.2016.07.020>.
- Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., Narayan, R., Law, K.L., 2015. Plastic waste inputs from land into the ocean. *Science* 347, 768–771. <https://doi.org/10.1126/science.1260352>.
- Jepson, P.D., Law, R.J., 2016. Persistent pollutants, persistent threats. *Science* 352, 1388–1389. <https://doi.org/10.1126/science.aaf9075>.
- Jourdain, E., Ugarte, F., Vikingson, G.A., Samarra, F.I.P., Ferguson, S.H., Lawson, J., Vongraven, D., Desportes, G., 2019. North Atlantic killer whale *Orcinus orca* populations: a review of current knowledge and threats to conservation. *Mammal Rev.* 49, 384–400.
- Kim, J., Gobas, F.A.P.C., Arnot, J.A., Powell, D.E., Seston, R.M., Woodburn, K.B., 2016. Evaluating the roles of biotransformation, spatial concentration differences, organism home range, and field sampling design on trophic magnification factors. *Sci. Total Environ.* 551–552, 438–451. <https://doi.org/10.1016/j.scitotenv.2016.02.013>.
- Kleivane, L., Kvadsheim, P.H., Bocconcelli, A., Øien, N., Miller, P.J.O., 2022. Equipment to tag, track and collect biopsies from whales and dolphins: the ARTS, DFHorten and LK Dart systems. *Anim. Biotelemetry* 10, 32. <https://doi.org/10.1186/s40317-022-00303-0>.
- Kuiken, T., García-Hartmann, M., 1991. Cetacean pathology: Dissection techniques and tissue sampling. In: ECS Newsletter No. 17, Special Issue, 39 pp.
- Mackenzie, K.M., Lydersen, C., Haug, T., Routti, H., Aars, J., Andvik, C.M., Borgå, K., Fisk, A.T., Meier, S., Biuw, M., Lowther, A.D., Lindström, U., Kovacs, K.M., 2022. Niches of marine mammals in the European Arctic. *Ecol. Indic.* 136, 108661.
- Mackintosh, C.E., Maldonado, J., Hongwu, J., Hoover, N., Chong, A., Ikonou, M.G., Gobas, F.A., 2004. Distribution of phthalate esters in a marine aquatic food web: comparison to polychlorinated biphenyls. *Environ. Sci. Technol.* 38 (7), 2011–2020. <https://doi.org/10.1021/es034745r> (PMID: 15112801).
- Mai, L., Sun, X.-F., Xia, L.-L., Bao, L.-J., Liu, L.-Y., Zeng, E.-Y., 2020. Global riverine plastic outflows. *Environ. Sci. Technol.* 54, 10049–10056. <https://doi.org/10.1021/acs.est.0c02273>.
- Mendes, S., Newton, J., Reid, R.J., Zuur, A.F., Pierce, G.J., 2007. Stable carbon and nitrogen isotope ratio profiling of sperm whale teeth reveals ontogenetic movements and trophic ecology. *Oecologia* 151, 605–615. <https://doi.org/10.1007/s00442-006-0612-z>.
- Nagorka, R., Koschorreck, J., 2020. Trends for plasticizers in German freshwater environments – evidence for the substitution of DEHP with emerging phthalate and non-phthalate alternatives. *Environ. Pollut.* 262, 114237. <https://doi.org/10.1016/j.envpol.2020.114237>.
- Nagorka, R., Birmili, W., Schulze, J., Koschorreck, J., 2022. Diverging trends of plasticizers (phthalates and non-phthalates) in indoor and freshwater environments—why? *Environ. Sci. Eur.* 34, 46. <https://doi.org/10.1186/s12302-022-00620-4>.
- Norwegian Priority List, 2023. Den norske prioritetslista. Retrieved from. <https://www.miljodirektoratet.no/ansvarsomrader/kjemikalier/prioritetslista/>. (Accessed 26 September 2023).
- Peck, C.C., Albro, P.W., 1982. Toxic potential of the plasticizer Di(2-ethylhexyl) phthalate in the context of its disposition and metabolism in primates and man. *Environ. Health Perspect.* 45, 11–17. <https://doi.org/10.2307/3429378>.
- Reyes, J.M., Price, P.S., 2018. Temporal trends in exposures to six phthalates from biomonitoring data: implications for cumulative risk. *Environ. Sci. Technol.* 52 (21), 12475–12483. <https://doi.org/10.1021/acs.est.8b03338>.
- Rian, M.B., Vike-Jonas, K., Gonzalez, S.V., Ciesielski, T.M., Venkatraman, V., Lindström, U., Jenssen, B.M., Asimakopoulos, A.G., 2020. Phthalate metabolites in harbor porpoises (*Phocoena phocoena*) from Norwegian coastal waters. *Environ. Int.* 137, 105525. <https://doi.org/10.1016/j.envint.2020.105525>.
- Routti, H., Harju, M., Lühmann, K., Aars, J., Ask, A., Goksøy, A., Kovacs, K.M., Lydersen, C., 2021. Concentrations and endocrine disruptive potential of phthalates in marine mammals from the Norwegian Arctic. *Environ. Int.* 152, 106458. <https://doi.org/10.1016/j.envint.2021.106458>.
- Similä, T., Haug, T., Lindblom, L., Lockyer, C., O'Callaghan, S.A., 2022. Stomach contents of three sperm whales (*Physeter macrocephalus*) stranded on Andøya, Northern Norway. *Aquat. Mamm.* 48, 449–455. <https://doi.org/10.1578/AM.48.5.2022.449>.
- Sonne, C., Jepson, P.D., Desforges, J.-P., Alstrup, A.K.O., Olsen, M.T., Eulaers, I., Hansen, M., Letcher, R.J., McKinney, M.A., Dietz, R., 2018. Pollution threatens toothed whales. *Science* 361, 1208. <https://doi.org/10.1126/science.aav2403>.
- Vorkamp, K., Dam, M., Riget, F., Fauser, P., Bossi, R., Hansen, A.B., 2004. Screening of New Contaminants in the Marine Environment of Greenland and the Faroe Islands. National Environmental Research Institute, Denmark - NERI Technical Report No 525, 97 pp.
- Xie, Z., Ebinghaus, R., Temme, C., Lohmann, R., Caba, A., Ruck, W., 2007. Occurrence and air–sea exchange of phthalates in the Arctic. *Environ. Sci. Technol.* 41, 4555–4560. <https://doi.org/10.1021/es0630240>.
- Zanuttini, C., 2019. Les contaminants chez les grands dauphins (*Tursiops truncatus*) du golfe normand-breton. GECC Report [in French] (49 pp).