Chemosphere 300 (2022) 134453

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Intrapopulation and temporal differences of phthalate concentrations in North Atlantic fin whales (*Balaenoptera physalus*)

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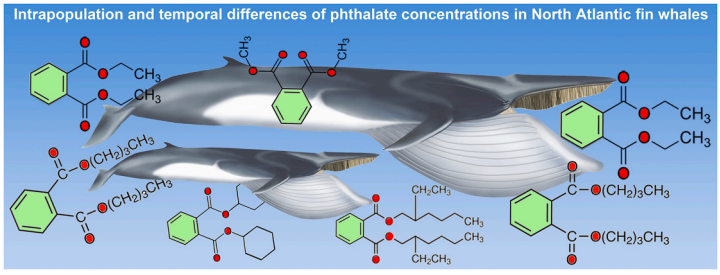
HIGHLIGHTS

- Out of 13 phthalate compounds investigated, 5 were detected.
- DBP, DEP and DEHP were the most abundant forms.
- Phthalate concentrations were not significantly different between sexes.
- Phthalates concentrations were not significantly different between age classes.
- Phthalate concentrations did not show temporal differences.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: James Lazorchak

Keywords:
Plasticizer
Plastic additive
Pollution
Cetacean
Baleen whale

ABSTRACT

The fin whale (*Balaenoptera physalus*) is a migratory filter-feeding species that is susceptible to ingest plastics while lunge feeding across the oceans. Plastic additives, such as phthalates, are compounds that are added to plastics to give them specific characteristics, such as flexibility. These so-called plasticizers are currently raising major concern because of their potential adverse effects on marine fauna. However, little is known about phthalate concentrations in tissues of baleen whales as well as their potential relation with biological variables (*i.e.*, sex, body length and age) and their trends with time. In this study, we assessed the concentration of 13 phthalates in the muscle of 31 fin whales sampled in the feeding grounds off western Iceland between 1986 and 2015. We detected 5 of the 13 phthalates investigated, with di-*n*-butylphthalate (DBP), diethylphthalate (DEP) and bis(2-ethylhexyl) phthalate (DEHP) being the most abundant. None of the biological variables examined showed a statistically significant relationship with phthalate concentrations. Also, phthalate concentrations did not significantly vary over the 29-year period studied, a surprising result given the global scenario of increasing plastic pollution in the seas. The lack of time trends in phthalate concentration may be due in part to the fact that phthalates also originate from other sources. Although no adverse effects of phthalates on fin whales have been detected to date, further monitoring of these pollutants is required to identify potential toxic effects in the future.

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https://doi.org/10.1016/j.chemosphere.2022.134453
Received 1 December 2021; Received in revised form 24 March 2022; Accepted 25 March 2022
Available online 4 April 2022

1. Introduction

Phthalates are broadly used as additives in plastics to give them flexibility and transparency, similarly as in other consumer products, like cosmetics or perfumes (Hansen et al., 2013). They have become ubiquitous environmental chemicals (Net et al., 2015) and, as such, they are frequently detected. Indeed, they have been reported to occur in several different matrices including air (*e.g.*, Hwang et al., 2008), soil (e.g., Zeng et al., 2009), sediments (*e.g.*, Blair et al., 2009), fresh and sea waters (*e.g.*, González-Mariño et al., 2017; Huang et al., 2008; Xie et al., 2007) and the tissues of marine biota (*e.g.*, Güven and Coban, 2013; Routti et al., 2021). It has been hypothesized that despite the rapid metabolism and elimination of most phthalates (Bang et al., 2011), stable tissue concentrations may be maintained through chronic low-level exposure through dietary ingestion (Silva et al., 2004). Due to these properties and their potential toxicity, phthalates are of special concern.

Studies on the adverse health effects of phthalates in laboratory animals (rats and mice), as well as epidemiological studies conducted in humans, indicate that phthalates act as hormone sensitizers and nuclear receptors (Baken et al., 2019; Benjamin et al., 2017; NRC, 2008). Some of these compounds, such as bis(2-ethylhexyl) phthalate (DEHP) and di-*n*-butylphthalate (DBP), appear to impair reproduction, metabolism and development, and to cause neurological and carcinogenic effects (Benjamin et al., 2017; NRC, 2008). Furthermore, in vitro studies showed that DEHP transactivates the thyroid hormone receptor of fin whales (*Balaenoptera physalus*) (Routti et al., 2021). However, the actual impact of these compound on wild animals is yet to be further assessed.

Pollution by marine litter is increasing in all marine basins worldwide (*e.g.*, Lebreton et al., 2018). Since more than 80% of marine litter is composed of plastics (*e.g.*, Garcia-Garin et al., 2020a,b; UNEP/MAP, 2015), and plastics contain between 10 and 60% of phthalates (Fromme, 2011), marine litter can be a major source of phthalate pollution in the sea. Moreover, the release and dispersion of phthalates in the marine environment is facilitated by the fact that these compounds are not chemically bound to plastics (Hahladakis et al., 2018). On the other hand, atmospheric transport is also a relevant pathway for long-range transport and eventual deposition of phthalates in the marine environment (Xie et al., 2007).

However, information on phthalate concentrations in the marine fauna, and especially in the tissues of marine mammals, is scarce. To our best knowledge, fifteen species of cetaceans in ten scientific articles have been investigated on this topic until now, namely: fin whale (Baini et al., 2017; Fossi et al., 2012, 2014, 2016; Routti et al., 2021), bottlenose dolphin (*Tursiops truncatus*) (Baini et al., 2017; Dziobak et al., 2021; Hart et al., 2018, 2020; Montoro-Martínez et al., 2021; Page-Karjian et al., 2020), harbour porpoise (*Phocoena phocoena*) (Rian et al., 2020), Fraser's dolphin (*Lagenodelphis hosei*), Risso's dolphin (*Grampus griseus*), and short-finned pilot whale (*Globicephala macrorhynchus*) (Montoro-Martínez et al., 2021), pygmy sperm whale (*Kogia breviceps*) (Montoro-Martínez et al., 2021; Page-Karjian et al., 2020), striped dolphin (*Stenella coeruleoalba*) (Baini et al., 2017; Montoro-Martínez et al., 2021), melon-headed whale (*Peponocephala electra*), Blainville's beaked whale (*Mesoplodon densirostris*), dwarf sperm whale (*Kogia sima*), pantropical spotted dolphin (*Stenella attenuata*), white-beaked dolphin (*Lagenorhynchus albirostris*), and Atlantic spotted dolphin (*Stenella frontalis*) (Page-Karjian et al., 2020), blue whale (*Balaenoptera musculus*) and bowhead whale (*Balaena mysticetus*) (Routti et al., 2021). The dynamics of these pollutants as related to the species biological variables remains to be clarified.

Baleen whales are filter-feeding, long-lived species that carry out long-range migrations (*e.g.*, Aguilar and García-Vernet, 2018). During lunge feeding, they are liable of ingesting floating plastics (Garcia-Garin et al., 2020c, 2021), and thus they are considered potentially good indicator species to assess the occurrence of microplastics (*e.g.*, Garcia-Garin et al., 2021) or toxic compounds related to plastic pollution, such as organophosphate esters (Garcia-Garin et al., 2020c), in large water masses. Indeed, baleen whales have been previously used to monitor the chemo-physical characteristics of oceanic water masses (Borrell et al., 2018).

In the current study we investigated phthalate concentrations in the muscle of North Atlantic fin whales (*Balaenoptera physalus*) sampled off Iceland along a period of thirty years (1986–2015) with a twofold objective: i) to examine any potential relation between phthalate concentration in muscle and the main biological variables of the sampled individuals (age, sex and body length), and ii) to investigate temporal differences in the concentrations of phthalates in the analysed tissue.

2. Materials and methods

2.1. Study area and sampling

Muscle samples were collected from 31 fin whales (14 males, 17 females) caught off western Iceland and flensed at the Hvalur H/F whaling company (Fig. 1) during the summers of 1986, 2009, 2013 and 2015. The body length of these whales ranged from 16.8 to 20.6 m and their age ranged from 7 to 47 years old (Table 1). Stainless steel material was used to cut through the muscle tissue and manipulate the samples, of which about 40 g per sampled whale were collected and placed in glass bottles. Field blanks were not made, as weather and factory conditions did not facilitate this procedure. To avoid contamination, no plastic material was used. After collection, samples were stored at −20 °C until analysis.

2.2. Ethics statement

Samples were obtained from whales legally caught under Icelandic regulation and were legally imported in Spain. Export/import licenses were obtained from the respective Icelandic and Spanish authorities and the samples transported under the Convention on International Trade in Endangered Species of Wild Fauna and Flora (CITES). Export/import permit numbers are: 13ISO28MA and 15IS017MA/ESBB00222/13I and ESBB00207/15I, respectively. No samples were donated or purchased and all sampled whales were caught with purposes other than research.

2.3. Age determination

Age determination was performed at the Marine and Freshwater Research Institute according to methods described by Lockyer (1984). Growth layers groups (GLG) were counted through a longitudinal section of the ear plug core and each pair of GLGs was assumed to

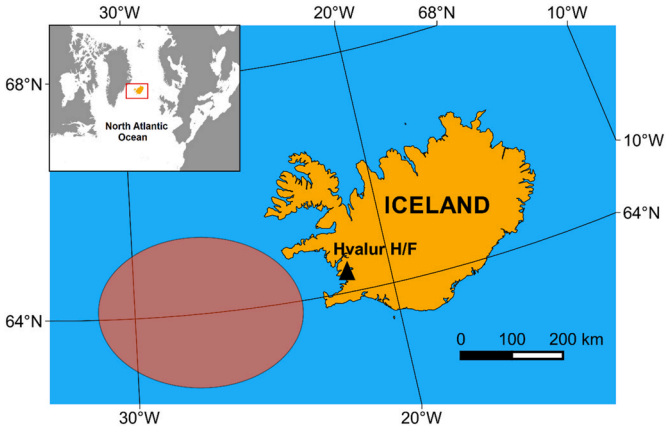

Fig. 1. Area of fin whales catches (red ellipse) and of the whaling factory where fin whales (n = 31) were processed (black triangle). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Biological traits and ∑phthalate concentrations in muscle (expressed in ug g^{-1} lipid weight (lw)) for each fin whale (n = 31) collected off western Iceland. Non detected compounds were computed as 0.

ID	Year	Sex	Length (m)	Age (years)	ΣPAE (μg g^{-1} lw)
1486	1986	F	18.6	16	8.982
1986	1986	M	20.1	23	5.562
2586	1986	F	20.4	27	8.315
3886	1986	M	17.4	14	1.186
4186	1986	F	19.5	35	0.546
4286	1986	F	20.1	17	0.245
4986	1986	F	20.1	26	6.690
F09013	2009	M	17.7	31	2.903
F09022A	2009	F	20.1	17	6.015
F0906	2009	F	17.0	7	2.445
F09093	2009	M	18.2	47	15.058
F09095	2009	F	18.6	21	5.176
F09104	2009	M	19.2	29	5.705
F09112	2009	M	17.8	32	2.656
F09117	2009	F	19.3	23	5.263
F0980	2009	F	16.8	10	34.415
F13002	2013	F	20.0	26	5.384
F13005	2013	F	20.6	28.5	5.574
F13018	2013	F	19.1	24.5	1.301
F13030	2013	M	18.3	15.5	19.289
F13059	2013	M	17.6	25	9.681
F13075	2013	F	18.9	41	6.460
F13099	2013	M	19.0	23	11.018
F15007	2015	M	18.3	30	1.470
F15013	2015	F	20.4	–	13.603
F15017	2015	M	18.0	–	6.089
F15031	2015	M	17.4	–	17.401
F15059	2015	F	19.5	–	37.514
F15071	2015	M	17.1	36	6.332
F15088	2015	M	17.1	32	7.078
F15146	2015	F	20.4	41	4.345
Mean ± SD					8.506 ± 8.706

correspond to one year. Each count was repeated by more than one reader, and for about 70% of samples the count was repeated twice by the same reader. The age of four individuals was not reported because GLGs were not optimal for age determination (Table 1).

2.4. Standards and reagents

A total of thirteen phthalates (Table S1) were analysed, namely: dimethylphthalate (DMP), diethylphthalate (DEP), di-*n*-butylphthalate (DBP), bis(2-methoxyethyl) phthalate (DMEP), dipentylphthalate (DPP), bis(2-ethoxyethyl) phthalate (DEEP), benzyl butyl phthalate (BBP), phthalic acid dicyclohexyl ester (DCHP), bis(4-methyl-2-pentyl) phthalate (BMPP), di-*n*-hexyl phthalate (DHP), bis(2-*n*-butoxyethyl) phthalate (DBEP), bis(2-ethylhexyl) phthalate (DEHP) and di-*n*-octyl phthalate (DNOP). Analytical standards were purchased from Restek (Lisses, France). Labelled phthalic acid diisobutyl ester (d_4-DIBP) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile and ethyl acetate (for HPLC isocratic grade) for trace analysis were purchased from VWR Chemicals BDH. Acetone (SupraSolv®) was sourced from Merck. The extraction salts were purchased from Agilent Technologies.

2.5. Sample preparation

Samples of approximately 20 g of frozen muscle were lyophilised for 48 h. Then, a subsample of 4 g dry weight (dw) was taken from the central part of each sample (to avoid any contamination) and homogenised. Subsequently, 10 mL of acetonitrile, 10 mL Milli-Q water, 100 μL of internal standard (d_4-DIBP) and the extraction salts (1 g of NaCl, 4 g of $MgSO_4$, 1 g of $C_6H_5Na_3O_7{\cdot}2H_2O$ and 0.5 g of $C_6H_6Na_2O_7{\cdot}1.5H_2O$) were added to the sample in a 50 mL centrifuge tube. The mixture was stirred with ceramic homogenizers in a vortex mixer and centrifuged during 5 min at 5000 rpm. Subsequently, 8 mL of extract were transferred to another centrifuge tube containing the salts (400 mg PSA, 400 mg GCB, 1200 mg MgSO4 and 400 mg C18EC) for the dispersive solid phase extraction clean-up step. After vortexing and centrifugation during 5 min at 5000 rpm, 5 mL of supernatant were transferred to a vial. The extraction was carried out twice, the second time using 10 mL of ethyl acetate. Both extracts were combined, reduced under a gentle nitrogen stream to 200 μL, and stored in a glass tube in the freezer until GC-MS/MS analysis was performed.

Lipid weight (lw) was determined gravimetrically from 1 g dw of each sample by sonication using 15 mL of a solution hexane:acetone (1:1) during 15 min, following Garcia-Garin et al. (2020c). The extraction was carried out twice, and both extracts were combined. Then, the solvent was evaporated using a nitrogen stream and the remaining lipids dried at 90 °C until a constant weight was reached.

2.6. Instrumental analysis

All analyses were performed using an Agilent 7890 GC coupled to an Agilent 7000C Triple Quadrupole GC/MS system (Agilent Technologies, France). To provide analyte separation an Agilent DB-17 ms, 30 m × 0.25 mm, 0.25 μm column was used, with helium (99.999% purity) as carrier gas at a constant flow of 1.2 mL/min.

Sample injections were performed in a multimode inlet, operated using the solvent vent injection mode through an ultra-inert inlet liner, with a glass wool frit from Agilent.

The injector operating conditions were as follows: injection volume was 3 μL; the injector temperature was held at 50 °C during the solvent evaporation stage (0.8 min), ramped up to 300 °C at 720 °C/min (hold 5 min), and cooled down to 280 °C (hold 10 min). Helium (99.999% purity) at a flow rate of 2.25 mL/min was used as the quenching gas; and nitrogen (99.999% purity) at a flow rate of 1.5 mL/min as the collision gas. The oven temperature was set as follows: 40 °C for 2 min, programmed to 220 °C at 30 °C/min, then to 260 °C at 5 °C/min and finally to 280 °C at 20 °C/min (hold 7 min). The total run time was 24 min. The triple quadrupole mass spectrometer was operated in electron impact ionisation (EI) with an ionising energy of 70 eV, and in the MRM mode. The temperatures of the transfer line, ion source and quadrupole 1 and 2 were 280 °C, 230 °C and 150 °C, respectively.

2.7. Quality assurance

A blank was included in the analytical run series every 10 samples. If the blank signal did not exceed 25% of sample signals (which was the case for all blanks), the phthalate concentration of the blank was subtracted from the corresponding batch of samples (Net et al., 2015). The procedure was performed in clean laboratory conditions, using glass or metal equipment instead of plastic (both in the field and in the laboratory). All glassware was rinsed with the appropriate solvent (water + detergent, Milli-Q water + HCl, Milli-Q water, and acetone) before use. Sample and standard preparation, as well as extraction and clean-up, were performed in a laminar flow cabinet. Good calibration curves were obtained in the range of 0.1–5000 μg L^{-1} with the correlation coefficients of ≥0.994. Phthalates were non-detected in the solvents. Limits of quantification (LOQs) were determined for each compound based on the average background noise or the concentration in the procedural blanks plus ten times the standard deviation and were verified by the analysis. LOQs were in the range of 0.025–0.125 μg L^{-1} of the extract which correspond to the range of 0.012–0.062 ng g^{-1} dw. The recovery of each phthalate was calculated by spiking the targeted compounds into real matrix of interest. The mean recovery was 92% with the rate of 104, 81, 86, 98 and 76 for DMP, DEP, DBP, DEHP and DCHP, respectively. The repeatability of the analysis procedure, the standard deviations were obtained <5% when the concentration of targeted compound higher than 0.1 ng g^{-1} and ~12% when the concentration of each phthalate was close to LOQs.

All analyses were performed at the LASIRE laboratory (UMR CNRS 8516) of the University of Lille, France.

2.8. Expression of concentrations

As phthalates are lipophilic compounds, it is usually recommended to report their concentrations on a lw basis to compensate for varying lipid content between tissues, individuals and species (Krahn et al., 2003). However, to allow comparison with other studies, here we report the concentrations of phthalates expressed both on an extractable lipid basis (lw) and on a dry weight basis (dw).

2.9. Statistical analysis

The normality and heteroscedasticity of the distributions of phthalate concentrations were preliminarily tested using the Shapiro Wilk and Barlett tests, respectively. As data distribution departed from normality, it was normalized applying a square root transformation. Sex, age and length distributions showed no difference between the two year groups (1986 and 2009–2015) (p-value < 0.05, Kruskal-Wallis rank sum test). PERMANOVAs (Oksanen et al., 2020) were used to explore the potential effect of "year" (*i.e.*, year of sample collection; expressed as a fixed factor: 1986 or 2009–2015), "sex" (*i.e.*, male or female), "length" and "age" on the concentration of phthalates. PERMANOVA equations can be found in Anderson (2001). "Length" and "age" were not correlated (p-value $= 0.42$; Pearson's correlation test). To allow the inclusion of individuals of unknown age in the analysis, additional PERMANOVAs were created by excluding the "age" factor and fitted with "year", "sex" and "length". The most complex model, which included the factors "year", "sex", "length" and "age" (including the biologically relevant interactions), was subjected to sequential, stepwise simplification by deleting one term (whether it was an interaction or a main effect). The information-theoretic approach was used for model selection (Burnham and Anderson, 2002) and models were compared using the AIC (Akaike's Information Criterion) (Akaike, 1974) and the deviance explained. The level of significance was set at $p < 0.05$. Analyses were conducted using the vegan package (Oksanen et al., 2020) in R (R Core Team, 2021).

3. Results

Total phthalate concentrations (*i.e.*, the sum of the single compound concentrations) for each whale are shown in Table 1. At least one phthalate compound was above the limit of quantification in every sample and the total phthalate concentration, in the whales, ranged from 0.245 to 37.514 μg g^{-1} lw (Table 1). The median concentration of each phthalate compound, from all the tested whales, is summarized in Table 2. Out of 13 phthalate compounds investigated, 5 were detected in the fin whale samples. DBP, DEP and DEHP were the most abundant compounds, which were detected in 81%, 100% and 58% of fin whale samples, respectively (Table 2, Fig. 2).

The PERMANOVAs fitted including only the individuals of known

Table 2
Median of individual phthalate-compound concentrations expressed in dry weight (dw) and lipid weight (lw), concentration range, and frequency of occurrence (FO) in the muscle of fin whales (n = 31) collected off western Iceland. Non detected compounds were computed as 0.

	dw (μg g^{-1})	lw (μg g^{-1})	Range (μg g^{-1} lw)	FO (%)
DBP	0.303	2.97	<0.0001–23.04	81
DEP	0.303	2.31	0.17–11.42	100
DEHP	0.010	0.07	<0.0001–3.83	58
DMP	0.008	0.07	0.02–0.25	100
DCHP	<0.0001	<0.0007	<0.0007–0.15	3
ΣPAE	799.39	6.01	0.25–37.51	100

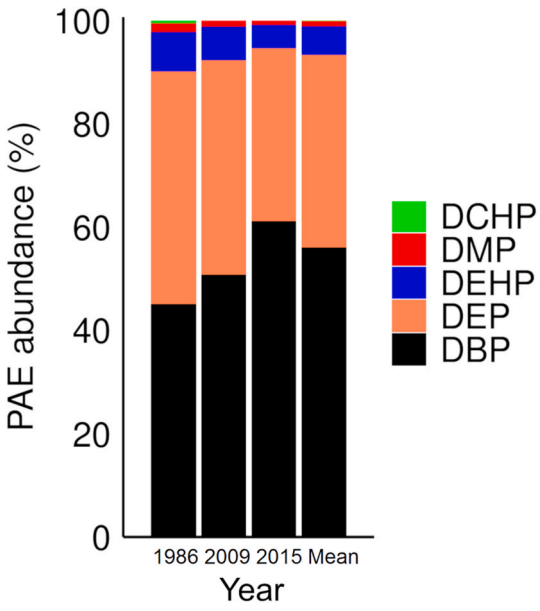

Fig. 2. Percentage contribution of detected PAEs to the total concentration split by year of collection in the muscle of fin whales (n = 31) collected off western Iceland.

Table 3
PERMANOVA results for individual phthalate concentrations (response variables: DBP, DEP, DEHP, DMP, DCHP) ranked by the Akaike information criteria (AIC) including only the fin whales of known age (n = 27) (Type A) or including all the fin whales (n = 31) (Type B) collected off western Iceland. The variables included in the models were: "year" (*i.e.*, year of sample collection; 1986 or 2009–2015), "sex" (*i.e.*, male or female), "length" and "age". The best-fit model for both types is shown in bold. Non detected compounds were computed as 0.

Type	ID	Model	AIC	Explained deviance (%)	Degrees of freedom
A	**MA1**	**Year**	**109.66**	**5.79**	**29**
	MA2	Length	110.36	3.32	29
	MA3	Age	111.05	0.79	29
	MA4	Age + Year	111.10	7.70	28
	MA5	Year + Length	111.15	7.53	28
	MA6	Sex	111.22	0.19	29
	MA7	Year + Sex	111.61	5.93	28
	MA8	Age + Length	112.22	3.79	28
	MA9	Sex + Length	112.26	3.66	28
	MA10	Age + Year + Length	112.67	9.16	27
	MA11	Age + Sex	112.96	1.15	28
	MA12	Year + Sex + Length	113.03	7.93	27
	MA13	Age + Year + Sex	113.06	7.86	27
	MA14	Age + Sex + Length	114.15	4.06	27
	MA15	Age + Year + Sex + Length	114.61	9.38	26
	MA16	Age * Length + Year + Sex	116.21	10.69	25
	MA17	Age * Sex + Year + Length	116.33	10.32	25
B	**MB1**	**Year**	**134.65**	**8.08**	**29**
	MB2	Year + Length	136.38	8.87	28
	MB3	Year + Sex	136.42	8.77	28
	MB4	Length	136.84	1.36	29
	MB5	Sex	137.22	1.36	29
	MB6	Year + Sex + Length	138.07	9.78	27
	MB7	Sex + Length	138.57	2.19	28

age and using all variables plus their interactions did not show any significant effect of age on phthalate concentrations (Table 3; Fig. 3B). As well, the PERMANOVAs fitted including all the individuals showed that none of the explanatory variables (length, sex and year; Fig. 3A, C, D) had a statistically significant effect on phthalate concentrations (Tables 3 and 4), although the variance of phthalate concentrations in the most recent samples (from 2009 to 2015) was higher than that of phthalate concentrations in samples from 1986 (p-value = 0.023, K-squared = 5.158, Barlett test; Fig. 3D).

4. Discussion

This study represents the first investigation on the occurrence and concentration of phthalates in North Atlantic fin whales off western Iceland. We examined the relation between phthalate concentrations and the biological variables of the species and the year of sampling along a period of almost 30 years (from 1986 to 2015).

The only other study on phthalates in North Atlantic fin whales was performed by Routti et al. (2021), who analysed 12 phthalate compounds in the blubber of fin whales from Svalbard, which may transit close to the eastern coast of Iceland during migration (Lydersen et al., 2020). These authors detected only 1 phthalate compound (DEHP) out of the 12 analysed. As these fin whales belong to the same population (Lydersen et al., 2020), differences between studies may be a consequence of comparing different tissues (Sala et al., 2019) or due to analytical methods.

The high incidence of phthalates in the environment (Net et al., 2015) makes it indispensable to control background contamination when analysing biotic phthalate levels. The blank contamination in this study was low (for example <0.012 ng g^{-1} dw for DEHP) compared to other studies (Ikonomou et al., 2012; Routti et al., 2021). Contamination by phthalates can come from many different sources. In the current study, to minimize the potential contamination during the sampling and analysis processes, the use of plastic material was avoided, and all non-volumetric material was rinsed with a suitable solvent just prior to use. Furthermore, the procedure was performed under clean laboratory conditions, using a laminar flow cabinet.

4.1. Intrapopulation differences

Phthalates have only recently gained attention as a potentially important group of pollutants affecting marine fauna. This, added to the analytical challenges involved in the determination of these pollutants have also hindered them to be reported (Ikonomou et al., 2012; Net et al., 2015) and, therefore, studies reporting phthalate concentrations in marine mammals are scarce. Moreover, in most of the few studies available, the relationship between phthalate concentrations and the biological variables of the individuals is not assessed, probably as a consequence of reduced sample size and/or of the difficulties in accessing biological information, particularly from free ranging individuals (*e.g.*, Baini et al., 2017; Fossi et al., 2012, 2014, 2016; Hart et al., 2018; Routti et al., 2021).

To the best of our knowledge, the current study provides the first assessment of intrapopulation differences in phthalate concentrations in baleen whales. According to our results, phthalate concentrations in North Atlantic fin whales do not relate to the biological variables of individuals such as age, body length or sex. If this was the case, the different individual exposure to phthalates could be the main cause behind the highly variable concentration ranges reported in the results of the current study. Although the number of samples is not very high, and it would be advisable to have a larger number in order to obtain more conclusive results, the great difficulty of obtaining these samples must be taken into account.

Three recent studies assessing phthalate concentrations in toothed cetaceans have focused on intrapopulation differences. Dziobak et al. (2021) investigated phthalate metabolites in urinary samples from 51 bottlenose dolphins from Sarasota Bay and concluded that concentrations did not differ between sexes or age classes, a result consistent with the current study. Rian et al. (2020) investigated phthalate metabolites in the liver of 100 harbour porpoises along the coast of Norway and, also consistently with the current study, they did not find any difference between sexes. However, they found a significant negative correlation between the concentration of phthalic acid (a common metabolite of phthalates; Bang et al., 2011) and the body mass and length of the individuals, which was attributed to a more efficient biotransformation process of this metabolite in adult animals (Rian et al., 2020). Page-Karjian et al. (2020) investigated DEP in blubber samples of 46 bottlenose dolphins from Florida and North Carolina and, consistently with the current study, also found no differences between sexes and age classes.

These results appear to be also in line with other studies assessing the relationship between phthalate concentrations and age and body length in other marine vertebrates. Thus, Fourgous et al. (2016) found poor correlations between the concentration of phthalate metabolites in muscle (n = 117) and age and body length of European eels (*Anguilla anguilla*), while Guerranti et al. (2016) found that phthalate concentrations in the muscle of Atlantic bluefin tuna (*Thunnust hynnus*) did not correlate neither to the fish age nor to the fish fork length.

In humans, similarly to what happens in other animals, phthalates do not accumulate in their tissues because they are easily metabolized, and excreted in urine and faeces (Wittassek and Angerer, 2008). However, some authors have reported differences in metabolite concentrations in human populations according to sex and age (*e.g.*, Hartmann et al., 2015; Huang et al., 2015; Silva et al., 2004), which are frequently related to lifestyle and consumer habits (Hartmann et al., 2015; Huang et al., 2015; Parlett et al., 2013), but may also be caused by metabolic differences (Reeves et al., 2019).

However, the absence of bioaccumulation is not necessarily a protection against the deleterious effects of a compound. Although phthalates do not seem to bioaccumulate in fin whale muscles, concern about the potential impact of these compounds on baleen whales should not lessen and monitoring on a medium – large temporal scale is recommended.

4.2. Temporal differences

The concentration of phthalates in fin whale muscle did not show any temporal difference during the 29 years span studied (from 1986 to 2015). This result was rather unexpected considering the increase of production and use of phthalates that has occurred during the last decades. Indeed, Net et al. (2015) calculated that phthalate production raised from 1.8 million tons in 1975 to 8 million tons in 2011. This increment parallels the global increase in plastics production (PlasticsEurope, 2016), which raised from 2 million tons in 1950 to 380 million tons in 2015 (Geyer et al., 2017). As a consequence of these trends, it is estimated that, only in 2010, between 4 and 12 million tons of plastic entered the seas (Jambeck et al., 2015). Once in the sea, plastics travel with ocean currents and tend to concentrate in the five subtropical gyres (Cózar et al., 2014) and the Arctic Ocean (Cózar et al., 2017) and, in other regions, close to highly urbanized and industrialized areas and/or in semi-enclosed seas (*e.g.*, Cózar et al., 2015; Lambert

Table 4
Summary of the outputs of the best-fit PERMANOVA, including the variable "year" (MB1), for individual phthalate concentrations (response variables: DBP, DEP, DEHP, DMP, DCHP) in fin whales (n = 31) collected off western Iceland.

Term	Degrees of freedom	Sum of squares	Mean of squares	Pseudo-F	R2	Pr (>F)
Year		5.95	5.95	2.55	0.08	0.08
Residuals		67.66	2.33		0.92	
Total	29	73.61			1	

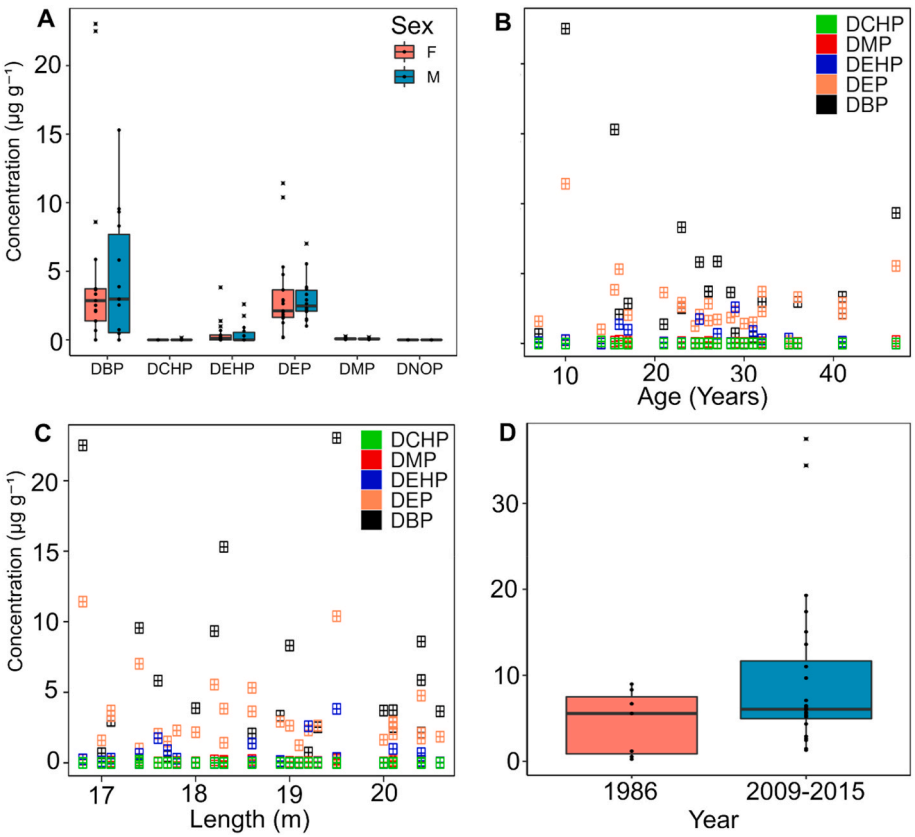

Fig. 3. A: Box-plot illustrating the single phthalate ester (PAE) concentrations in fin whales (n = 31) collected off western Iceland split by sex, B: Scatterplot illustrating the single PAE concentrations in fin whales (n = 27) collected off western Iceland in relation to age of the individual, C: Scatterplot illustrating the single PAE concentrations in fin whales (n = 31) collected off western Iceland in relation to the body length, and D: Box-plot illustrating the total PAE concentrations in fin whales (n = 31) collected off western Iceland split by period of collection (samples from 2009, 2013 and 2015 were grouped). Boxes in A and B subfigures represent the first and third quartiles, lines the median, and vertical bars indicate the most extreme data point which is no more than 1.5 times the interquartile range from the box.

et al., 2020; Ryan, 2014). However, plastics are not the only source of phthalates, as they are present in several materials and products, including building materials, personal-care products, medical devices, detergents and surfactants, packaging, children's toys, printing inks and coatings, pharmaceuticals and food products, textiles, floor tiles, food containers and wrappers, cleaning materials (Net et al., 2015), all of which may contribute to the environmental load of these contaminants.

On the other hand, it can be argued that remote areas, such as the waters off Iceland, are likely to be less polluted by these contaminants, and this might be the cause behind the apparently unnoticeable effects in Icelandic waters of the global trends in plastic and phthalate production. Although the fin whale is an active migrant that undertakes seasonal latitudinal movements spanning large distances Aguilar and García-Vernet, 2018, potentially including areas where phthalate pollution is higher, the results of the current study are consistent with the phthalate concentrations in the atmosphere of the overall North Atlantic Ocean, which in 2017–2018 appear to be similar to that detected during the 1970s (Atlas and Giam, 1981; Bohlin-Nizzetto et al., 2018; Giam et al., 1978). Indeed, Giam et al. (1978) reported DBP and DEHP concentrations ranging 0.4–2.3 and 1.4–4.1 ng m^{-3} respectively in the atmosphere of the North Atlantic Ocean (38°00′N, 69°35′W) during the 1970s, while Bohlin-Nizzetto et al. (2018) reported DBP and DEHP concentrations ranging 0.08–1.01 and 0.29–1.13 ng m^{-3}, respectively, in the Arctic atmosphere, and ranging 0.05–0.20 and 0.15–0.87 ng m^{-3}, respectively, in the North Sea. This would suggest that DBP and DEHP concentrations remained overall constant in the North Atlantic Ocean atmosphere along a period of over 50 years.

Although no significant difference was found between the fin whales sampled in the two distinct periods, the concentration of phthalates in the most recent samples (from 2009 to 2015) included the highest concentrations detected among all the individuals analysed and also showed a higher variance than that of the samples from 1986 (Fig. 3D). It can be hypothesized that the individuals showing the highest concentrations and triggering the increased variance may have visited the North Atlantic subtropical gyre, where marine litter is known to be rapidly accumulating (Cózar et al., 2014). Indeed, the Azores Islands and the south of Portugal, an apparent intermediate stop in autumn destination of fin whales feeding off Iceland in summer (Lydersen et al., 2020; Silva et al., 2013) are located at the margins of the gyre. However, even if the fin whales cross the North Atlantic subtropical gyre during their migratory displacement, the major feeding activity of the species takes place during the summer months in the high-latitude areas such as Iceland (Aguilar and García-Vernet, 2018), where the increase of plastic pollution is less pronounced (Cózar et al., 2015).

The high lability of phthalates may also explain the lack of temporal difference in their concentration in fin whale tissues. These compounds are rapidly degraded in the environment, with photodegradation half-lives (in days) estimated to be 0.38, 0.75, 0.89, 2.39 and 14.41 for DEHP, BBP, DnBP; DEP, and DMP, respectively (Xie et al., 2007). Additionally, the metabolic transformation of phthalates can play an important role on their distribution (Mackintosh et al., 2004), as the metabolic transformation of phthalates in top consumers can cause the consumers to achieve a concentration lower than that in its prey or the environment (Mackintosh et al., 2004). These two factors may combine to determine the environmental availability of phthalates in the ocean and their concentrations in the fin whales' tissues. Whatever the case, the above findings and the hypothesis put forward herein, deserve further research.

From our results we can conclude that: 1) North Atlantic fin whales did not show sex-related differences in phthalate concentrations; and 2) phthalate concentrations did not show temporal differences between the two periods examined (1986 and 2009–2015). Further research is needed to evaluate the pathways of intake and metabolism of phthalates and their potentially toxic effects in this long-lived, filter-feeding and long-range migratory species that, due to these traits, may be highly susceptible to plastic-related pollution.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank the MCIN/AEI/10.13039/501100011033 and FSE "El FSE invierte en tu futuro" for supporting O. Garcia-Garin with a Ph.D. FPU scholarship (FPU17/00073). We also thank the Fundació Montcelimar – Universitat de Barcelona for supporting O. Garcia-Garin with a mobility grant. This study was part of project PID2020-119712 GB-I00 funded by the Ministerio de Ciencia e Innovación of Spain, MCIN/AEI/10.13039/501100011033. Constructive feedback from two anonymous reviewers contributed to improve the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2022.134453.

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