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## Flame retardants in dust from the indoor environments of expedition cruise ships

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Flame retardants (FRs) are widely used in indoor environments to meet fire safety requirements. One understudied environment with respect to indoor chemical exposure to FRs is the maritime environment, particularly the indoor environments of cruise ships. This study presents the first comprehensive assessment of FRs in indoor dust collected from three expedition cruise ships of varying ages and refitting histories. Ten polybrominated diphenyl ethers (PBDEs), 23 alternative halogenated flame retardants (AHFRs), and 16 organophosphate esters (OPEs) were analyzed in dust from 12–16 locations per ship. OPEs, especially tris(1-chloro-2-propyl)phosphate (TCIPP), dominated the chemical profile, with concentrations reaching up to 1786  $\mu\text{g g}^{-1}$ . Concentrations of FRs in different areas on the same ships differed greatly, sometimes by an order of magnitude. Older ships exhibited significantly higher FR levels compared to the newer vessel. Estimated daily intake (EDI) modeling indicated that ship crew members—particularly those working in heavily furnished or electronic-rich areas—may experience elevated exposures through ingestion and dermal contact. Strict performance-based fire test procedures are mandatory for all products onboard ships, but no regulations exist concerning the type of FR used or the concentrations thereof. These findings underscore the need for targeted regulation and further monitoring of chemical exposures in maritime environments, especially given the extended periods that crew members spend onboard.

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### Environmental significance

This study offers critical insight into the chemical loads of flame retardants (FRs) present in the unique environment of expedition cruise ship interiors. Given the isolated nature of shipboard environments and the extended durations of crew members' contracts, there is a heightened risk of prolonged exposure to FR chemicals. The findings contribute to advancing our understanding of chemical exposure in the maritime sector and may inform future decisions in ship design, construction, and retrofitting. This could help balance the occupational health of seafarers without compromising essential fire safety standards.

## Introduction

Flame retardants (FRs) have been used in construction materials, textiles, furnishing, plastics, and electronic appliances in indoor spaces since the 1970s.<sup>1–3</sup> Halogenated FRs, particularly brominated compounds such as polybrominated diphenyl ethers (PBDEs), were the primary FR type used for many decades.<sup>4</sup> However, evidence of adverse human and environmental health effects associated with PBDEs resulted in their restriction.<sup>5–7</sup> Organophosphate ester flame retardants (OPEs) and alternative halogenated flame retardants (AHFRs), also known as novel flame retardants, or replacement halogenated

flame retardants have been used as substitutes, *in lieu* of the banned substances.<sup>8,9</sup> However, they have also recently raised health and environmental concerns such as biomagnification through food webs and endocrine disruption in individual organisms.<sup>10,11</sup>

Indoor settled dust is a major exposure vector for many semi- and non-volatile chemicals, and people are exposed to it either through dermal contact or accidental ingestion. Dust from homes, workplaces, public indoor spaces, and transportation infrastructure such as cars, buses, and airplanes has been tested for FRs, and they have been consistently found in quantifiable concentrations.<sup>12–17</sup>

One understudied domain in chemical exposure science is the maritime sector, particularly the indoor environments of cruise ships. Modern cruise ships, due to their size and the inclusion of extensive amenities, resemble small settlements, making them unique and complex exposure settings. Fire safety

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is a critical concern in the maritime industry due to the proximity of fire hazards such as flammable liquids, isolation from external emergency fire services, and limited escape routes and safe zones. According to Allianz Commercial's *Safety and Shipping Review*,<sup>18</sup> fire is the second most common cause of loss for shipping vessels and the most financially damaging. While fires on passenger ships are generally less catastrophic than those on cargo ships carrying volatile materials, they remain surprisingly frequent. For instance, a study analyzing incidents from 2003 to 2010 documented 1521 fire-related events on passenger ships, most of which originated from electronic sparks (excluding static) and primarily occurred in accommodation areas.<sup>19</sup>

To reduce fire risk, the International Maritime Organization (IMO) developed the 2010 Fire Test Procedure (FTP) Code, which sets stringent performance-based criteria for materials used in ship interiors, including limits on flame spread, smoke density, toxicity, and combustibility.<sup>20</sup> However, this regulation does not specify types or concentrations of chemical FRs that manufacturers should use to meet these requirements. This leads to substantial uncertainty in the type and amounts of FRs applied to meet IMO flammability standards, and only one published study has assessed FRs on a maritime vessel,<sup>21</sup> highlighting the need for further investigation. High use of FRs in other transportation infrastructure has been associated with higher FR exposure, *e.g.*, in cars<sup>16,22</sup> and airplanes;<sup>23,24</sup> crew exposure on ships may be uniquely high because ship crew members spend extended periods of weeks to months on board.<sup>25,26</sup>

We analyzed concentrations of legacy- and alternative halogenated and organophosphate FRs (Table S1) in settled dust collected from the indoor environments of three expedition cruise ships, and use these concentrations to estimate exposure for the ship crew in different on-board functions. We hypothesize that, due to strict fire safety standards and the enclosed, climate-controlled nature of ship interiors, FR concentrations in shipboard dust will exceed those typically reported in terrestrial environments, and FR profiles will differ based on ages and design features of the ships.

## Materials and methods

### Dust collection

Indoor settled dust samples were collected from three expedition cruise ships, representing a range of operational ages and refitting, to investigate the FR profiles and concentrations in 2023. Expedition cruise ships are passenger vessels typically cruising in remote regions with the goal of providing passengers an immersive experience into the local culture and environment, as opposed to “resort-based” cruising of traditional cruise ships, where the focus is on onboard amenities. These expedition vessels are typically much smaller (<1000 passengers) than traditional cruise ships. Cruise duration can vary depending on the itinerary and location, but cruise lengths of approximately two weeks are the most common. While electronic dense areas such as theaters and casinos typically found onboard traditional cruise ships were absent, all expedition ships sampled were equipped with a state-of-the-art science

center with multiple microscope setups. All ships were equipped with a sophisticated HVAC and interior heating system. Samples were obtained from 12–16 areas of each ship, including both passenger-occupied and crew-only spaces (Text S1, Table S2; Fig. S1A–H). To maintain confidentiality, the ships are anonymized as follows: Ship 1 (launched in 2003; 570 passengers; 16 000 gross tonnage (GT)); Ship 2 (launched in 2002, refitted in 2020; 530 passengers; 16 000 GT); and Ship 3 (launched in 2020; 530 passengers; 21 000 GT). Ship 2 underwent major refitting, including upgrades to major technical structures such as the onboard wastewater treatment plant, propulsion system, and major interior refitting, such as the inclusion of two restaurants and the science center. All interior furnishings have been replaced. All ships were staffed by approximately 120–160 crew members with different roles and responsibilities, such as housekeeping, officers, engineers, and expedition staff interacting with passengers.

Dust was collected onto a quartz fiber filter (QFF; Whatmann) using a forensic sampling head (VacuumMark, BVDA) with a filter holder (Fig. S2). The sampling head was attached to a commercial vacuum cleaner provided onboard, and sampling areas were vacuumed until a visible dust layer accumulated on the quartz filter. Dust was collected from multiple surfaces in the designated sampling area (*e.g.* carpet, exposed floor, couches or seats where present, and around electronic equipment) to provide a composite sample reflecting general room conditions.<sup>27</sup> After a sample was collected, the filter holder was sealed and placed in a labeled plastic bag. Samples were stored under refrigerated conditions onboard and transferred to a –20 °C laboratory freezer prior to analysis.

Field blanks were prepared by briefly exposing an unused quartz filter and its container to ambient air (30 seconds) without vacuuming, and were then treated as per the samples.

### Sample processing and extraction

Dust samples were homogenized using a Retsch MM 301 mixer mill (Retsch GmbH, Germany) with tungsten carbide grinding jars and a wolframite weight. Prior to homogenization, components were cooled in liquid nitrogen for two minutes to embrittle the dust and facilitate efficient pulverization (full description in Text S2). Homogenized samples were stored in pre-weighed, baked glass vials at –20 °C until analysis.

PBDEs and AHFRs were extracted using supramolecular solvent extraction (SUPRA, following Marcinekova *et al.*<sup>28</sup>). OPEs were extracted using methanol, based on a protocol adapted from Svobodová *et al.*<sup>16</sup> Full extraction protocols are detailed in the SI (Text S2). The full list of internal standards is presented in Tables S3 and S4.

### Instrumental analyses

Out of 16 OPEs that were analyzed for (Table S1), 15 were detected in the samples at least once: TDCIPP, TCIPP, CDP, EHDPP, oTMPP, ip-TPP, m/p TMPP, TBOEP, TCEP, TEHP, TEP, TiBP, TnBP, TnPP, TPHP. The full list of target OPEs with compound names and identifiers is given in Table S1. OPEs were quantified using an Agilent 1290 Infinity high-



performance liquid chromatograph (HPLC) coupled to an Agilent 6495 triple quadrupole mass spectrometer operating in positive electrospray ionization mode (ESI+). Chromatographic separation was achieved on an ACQUITY BEH C18 column (2.1 mm × 100 mm, 1.7 μm) with a mobile phase gradient of 0.1% formic acid in water and methanol at a flow rate of 0.2 mL min<sup>-1</sup>. Quantification was performed in multiple reaction monitoring (MRM) mode using isotope dilution with <sup>13</sup>C- or deuterium-labeled standards for TPHP, TnBP, TDCIPP, and TnPP.

Ten PBDE congeners were detected (BDEs-28, 47, 66, 99, 100, 153, 154, 183, and 209) and 16 out of 23 AHFRs (HBB, BEH-TEBP, PBBZ, PBT, PBEB, TBP-DBPE, EH-TBB, DBDPE, TBP-AE, aDBE-DBCH, bDBE-DBCH, gdDBE-DBCH, BTBPE, sDP and aDP) were detected in the samples. The full list of PBDEs and AHFRs is given in Table S1. PBDEs and AHFRs were analyzed using an Agilent 7890A gas chromatograph equipped with an RTX-1614 column (15 m × 0.25 mm, 0.10 μm) and coupled to a Waters AutoSpec Premier high-resolution mass spectrometer operated in electron impact ionization (EI+) and selected ion monitoring (SIM) mode with a resolving power greater than 10 000. BDE-209 was analyzed at a reduced resolution of >5000 to improve sensitivity. While PBDEs and AHFRs were measured

using the same instrumental setup, distinct GC oven temperature programs and injection conditions were applied for each compound group. Full analytical parameters are provided in the SI (Text S3; Tables S4–S8) and example chromatographs presented in Fig. S3–S7.

### Quality assurance/quality control

Eight field blanks were collected across three vessels. Method detection limits (MDLs) were calculated as the average blank concentration plus three times the standard deviation; for non-detected analytes, instrument detection limits were used. Sample values above MDL were blank-corrected by subtracting the average of the field blanks; those below were reported as <MDL. QA/QC is summarized in SI Text S4. Recovery rates are presented in Tables S9–S11.

### Statistical analysis

Descriptive statistics were calculated using Graphpad Prism 8 (<https://www.graphpad.com>). Because the data sets were not normally distributed, analyses mainly relied on unpaired, two-tailed Mann-Whitney (MW) non-parametric tests with Dunn tests for multiple comparisons. Significance was set at  $p < 0.05$ .

Table 1 Exposure estimate parameters. Parameter values as described in de la Torre *et al.*<sup>29</sup> unless otherwise specified

Parameter	Normal scenario	High exposure scenario
$C_{\text{dust}}$ – concentration in dust	Dust median concentration	Dust 95 <sup>th</sup> percentile concentration
$IR_{\text{dust}}$ – dust ingestion rate	20 mg per day	60 mg per day
DAS – dust adherence to skin	0.01 mg cm <sup>-2</sup> for adults	
ESA – exposed skin area	4614 cm <sup>2</sup> , which is the estimated area of the head, neck, arms, and hands	
$AF_{\text{gastro}}$ – gastrointestinal absorption factor	100%	
$AF_{\text{dermal}}$ – dermal absorption factor	25% for TCIPP, 17% for TBOEP, and 0.05% for BDE-209	
EF – exposure fraction	100%	
BW – body weight	70 kg (ref. 30)	

Table 2 Descriptive statistics of OPEs in dust from three ships<sup>a</sup> (μg g<sup>-1</sup>)

		CDP	EHDPP	m/pTMPP	TBOEP	TCEP	TCIPP	TDCIPP	TiBP	TnBP	TPhP
Ship 1	Average	0.68	15.0	0.053	13.6	2.43	476	0.81	0.19	<MDL	5.52
	SD	1.00	16.5	0.20	22.9	6.59	576	2.07	0.72	<MDL	12.1
	Median	0.26	9.19	<MDL	3.88	<MDL	72.2	<MDL	<MDL	<MDL	<MDL
	Min	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
	Max	3.66	60.6	0.83	79.1	23.6	1786	6.56	3.0	<MDL	46.4
	DF (%)	81.3	75	6.3	93.8	12.5	75	18.8	6.3	0	25
Ship 2	Average	2.56	0.39	0.12	14.5	1.99	556	1.64	0.14	1.21	26.7
	SD	2.94	0.48	0.094	24.0	2.49	537	1.84	0.086	0.83	35.5
	Median	0.91	<MDL	0.10	4.71	1.08	427	0.8	0.15	1.14	5.89
	Min	0.39	<MDL	0.018	3.33	<MDL	14.9	<MDL	<MDL	<MDL	3.27
	Max	9.9	1.40	0.35	91.8	9.1	1689	6.1	0.25	2.68	95.2
	DF (%)	100	41.7	100	100	83.3	100	91.7	75	91.7	100
Ship 3	Average	2.72	1.93	0.22	1.56	<MDL	95.1	<MDL	0.99	<MDL	9.21
	SD	2.23	3.65	0.35	1.34	<MDL	159	<MDL	1.9	<MDL	31.9
	Median	1.34	<MDL	<MDL	1.16	<MDL	45.1	<MDL	<MDL	<MDL	<MDL
	Min	0.43	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
	Max	6.54	10.4	1.27	5.69	<MDL	557	<MDL	5.64	<MDL	120
	DF (%)	100	23.1	38.5	92.3	0	53.8	0	23.1	0	7.7

<sup>a</sup> SD: standard deviation; DF: detection frequency; MDL: method detection limit.



Table 3 Descriptive statistics of PBDEs and AHFRs in dust from the three ships<sup>a,b</sup> (ng g<sup>-1</sup>)

	PBDE47	PBDE100	PBDE99	PBDE153	PBDE183	PBDE209	PBBZ	PBT	HBB	EH-TBB	BEH-TEBP	DBDPE	aDBE-DBCH	bDBE-DBCH	BTBPE	sDP	aDP
Ship 1	Average	3.58	0.874	5.41	9.72	16 900	3.74	3.13	5.59	11.7	378	2250	0.111	0.0637	7.09	2.28	4.77
	SD	4.96	1.19	7.84	32.0	41 800	9.81	6.02	11.3	13.3	514	5660	0.316	0.226	2.65	1.06	2.44
	Median	2.30	0.59	3.70	1.11	1850	0.933	0.819	1.66	5.28	112	77.9	<MDL	<MDL	7.11	2.06	3.98
	Min	0.235	<MDL	0.438	<MDL	221	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	2.47	0.989	2
	Max	21.3	5.06	33.2	129	169 000	40.3	19.2	45.6	46	1540	21 200	1.24	0.904	13.3	4.58	10
Ship 2	DF (%)	100	75	100	75	93.75	75	81.2	81.2	81.2	93.8	93.8	25	16.7	100	100	100
	Average	17.9	3.25	9.54	0.974	894	0.294	3.01	1.75	39	2040	15.5	1.14	0.907	14	14	96.9
	SD	5.78	1.94	4.88	0.493	984	0.347	5.04	0.742	51.1	2650	12.3	1.83	1.45	10.4	159	159
	Median	18.2	3.01	8.90	<MDL	338	<MDL	0.956	<MDL	7.25	386	22.4	0.504	0.406	13.6	20.2	20.2
	Min	8.36	<MDL	4.60	<MDL	148	<MDL	<MDL	<MDL	<MDL	66.7	<MDL	<MDL	<MDL	3.43	3.43	6.56
Ship 3	Max	25.4	6.06	18.9	1.95	2590	1.13	15.1	2.77	129	6670	31.8	5.51	4.35	34.5	443	443
	DF (%)	100	87.5	100	12.5	100	12.5	50	37.5	75	100	62.5	75	75	100	100	100
	Average	2.22	0.535	2.80	0.345	257	1.57	11.8	9.62	11.5	255	541	0.064	0.0323	4.68	2.24	4.83
	SD	2.98	0.651	3.27	0.305	227	4.47	31.7	31.5	12.3	268	1810	0.124	0.0743	2.6	1.42	3.34
	Median	0.91	0.21	1.28	<MDL	224	<MDL	1.43	0.553	4.12	101	19.9	<MDL	<MDL	4.21	1.81	3.86
Ship 3	Min	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	0.822	<MDL	<MDL	21	<MDL	<MDL	<MDL	2.73	1.24	2.26
	Max	10.6	2.15	11.2	1.11	825	15.7	112	110	34	871	6270	0.2	0.2	12.5	6.58	15
	DF (%)	91.7	66.7	91.7	25	91.7	41.7	100	50	75	100	83.3	18.75	12.5	100	100	100

<sup>a</sup> BTBPE was not analyzed in Ship 2 due to instrumental issues. <sup>b</sup> SD: standard deviation; DF: detection frequency; MDL: method detection limit.

Outliers were not excluded from analysis. For statistical analyses, values < MDL were substituted with MDL/2.

### Human exposure assessment calculations

Estimated daily intakes (EDIs) were calculated using eqn (1) and (2), following parameters listed in Table 1:<sup>29</sup>

$$EDI_{\text{ingestion}} = (C_{\text{dust}} \times IR_{\text{dust}} \times AF_{\text{gastro}} \times EF) / BW \quad (1)$$

$$EDI_{\text{dermal}} = (C_{\text{dust}} \times DAS \times ESA \times AF_{\text{dermal}} \times EF) / BW \quad (2)$$

## Results

Of the 49 additives targeted in this study, eight compounds (7 AHFRs and 1 OPE) were not detected above MDL in any sample (Table S12). Of the detected compounds, 10 OPEs, 6 BDEs and 11 AHFRs were found in 75% of samples on at least one ship—these compounds are presented in Tables 2 and 3. A full description of concentrations in different sampling locations on all ships for all compounds is presented in Table S12.

### Comparison between and within ships

Concentrations of total FRs in dust varied significantly between the older ships (Ships 1 and 2) and the newer Ship 3, with the latter having much lower concentrations present in dust (Ship 1 vs. Ship 3  $p = 0.0392$ ; Ship 2 vs. Ship 3  $p = 0.0082$ ).

Within the ships, FR concentrations and profiles varied between different locations onboard (Fig. 1 and 2). Passenger congregation areas, such as restaurants and lounges, typically had the highest concentrations (Fig. 1). Crew spaces typically had lower overall FR concentrations, but a more varied compound composition was detected, with different OPEs and AHFRs than were found in passenger spaces of certain ships (Fig. 1 and 2).

### OPEs

OPEs were the dominant compound class detected across all three ships, with TCIPP emerging as the most abundant compound. TCIPP had the highest median concentration on Ship 2 (427  $\mu\text{g g}^{-1}$ ), followed by Ship 1 (72  $\mu\text{g g}^{-1}$ ), and Ship 3 (45  $\mu\text{g g}^{-1}$ ) (Fig. 3, Table 2). Concentrations of TCIPP were significantly lower on Ship 3 compared with Ship 2 ( $p = 0.0117$ ). In several locations on all three ships, TCIPP accounted for over 90% of the total FR burden (Fig. 2). Despite its elevated concentrations, TCIPP was not ubiquitous in all dust: while TCIPP was detected in 100% of dust from Ship 2, it was only present in 75% of dust on Ship 1, and 54% on Ship 3.

Two other OPEs, CDP and TBOEP, were also frequently detected (DF > 75%) across all vessels, though at much lower concentrations. TBOEP was present in all samples from Ship 2, while CDP was in all areas from both Ships 2 and 3. Median concentrations for these compounds generally remained below 5  $\mu\text{g g}^{-1}$ , with some variation between ships (Table 2).



Fig. 1 Flame retardant concentrations in different locations across the three sampled ships. A similar figure excluding TCIPP can be found as Fig. S8.

CDP was the only OPE where concentrations in the newest ship exceeded those in the other ships. The lowest concentrations of CDP were in the oldest ship that has not been refitted (Ship 1), and these were significantly lower than those in Ship 2 ( $p = 0.011$ ) and Ship 3 ( $p = 0.001$ ).

Other OPEs, such as TCEP and TPhP, had more irregular patterns. For example, TCEP was frequently detected on Ship 2 (83%) but was absent from Ship 3. TPhP was detected in all samples on Ship 2, while on Ship 3 was only detected in dust from the bridge, but at  $120 \mu\text{g g}^{-1}$ , its highest concentration of all dust samples. Several additional OPEs—including *m*/pTMPP, TDCIPP, TiBP, and TnBP—were prevalent on Ship 2 (DFs 75–100%) but largely absent from Ship 1 and Ship 3. For example, TnBP was undetected on the latter two ships but found in 92% of Ship 2 samples, albeit in lower concentrations (median:  $1.14 \mu\text{g g}^{-1}$ ), highlighting strong ship-specific patterns (Table 2).

### PBDEs and AHFRs

PBDEs were most prevalent on Ship 1 and dominated by high concentrations of BDE-209 (median  $1850 \text{ ng g}^{-1}$ ), far exceeding levels on Ship 2 ( $338 \text{ ng g}^{-1}$ ) and Ship 3 ( $224 \text{ ng g}^{-1}$ ) (Fig. 4A). The highest BDE-209 concentration was found in the engine control room of Ship 1, with  $169\,000 \text{ ng g}^{-1}$ . BDE-47 and BDE-99 were detected frequently across all ships (DF > 91%), indicating a background presence, though concentrations were highest on Ship 2 (Fig. 4A; Table 3).

Among the AHFRs, BEH-TEBP and EH-TBB were widely detected (>75% DF on all ships, Table 3). BEH-TEBP had the highest median concentrations on Ship 2 ( $386 \text{ ng g}^{-1}$ ), followed by Ship 1 ( $112 \text{ ng g}^{-1}$ ) and Ship 3 ( $101 \text{ ng g}^{-1}$ ). EH-TBB concentrations were moderate across ships, with median values of  $7.25 \text{ ng g}^{-1}$  on Ship 2,  $5.28 \text{ ng g}^{-1}$  on Ship 1, and  $4.12$

$\text{ng g}^{-1}$  on Ship 3. DBDPE was the AHFR found at the second-highest concentrations ( $20\text{--}78 \text{ ng g}^{-1}$ ) (Fig. 4B).

Other AHFRs showed heterogeneity in detection and profiles similar to what was noted for the OPEs: PBT was found in all samples from Ship 3, 81% from Ship 1, but only in 50% of samples from Ship 2. PBT was one of the few chemicals where Ship 3 had the highest concentrations amongst the three ships. aDBE-DBCH and bDBE-DBCH were present primarily on Ship 2, with detection frequencies of 75% for both isomers, but at low concentrations (medians:  $0.38 \text{ ng g}^{-1}$  and  $0.30 \text{ ng g}^{-1}$ , respectively). In contrast, BTBPE was quantified 75% of dust from Ship 1, but not detected in Ship 3 (Table 3).

Dechlorane Plus (*syn*- and *anti*-DP) were the only compounds detected at 100% DF across all three ships. Ship 2 had the highest median concentrations of both sDP ( $13.6 \text{ ng g}^{-1}$ ) and aDP ( $20.2 \text{ ng g}^{-1}$ ) compared with Ships 1 and 3 where median concentrations ranged between  $1.8 \text{ ng g}^{-1}$  and  $4 \text{ ng g}^{-1}$ .

## Discussion

The most striking result in our study was dominance of TCIPP in dust from the indoor environment of expedition cruise ships, with levels exceeding  $1000 \mu\text{g g}^{-1}$  in some samples on Ships 1 and 2. While TCIPP is frequently one of the OPEs with the highest detection frequencies and concentrations (*e.g.*, 21–40% of FR profile in indoor dust from China<sup>31</sup>) our results are notable for the extremely high contribution of TCIPP to total FRs, clearly indicating this FR as a major additive FR in the sampled ships.

Within each ship, concentrations of FRs varied greatly – sometimes up to an order of magnitude between different functional spaces *e.g.* crew cabins and restaurants (Fig. 1). The spatial distribution of OPEs, specifically TCIPP, within the ships



## A) Ship 1



## B) Ship 2



## C) Ship 3



Fig. 2 Relative compositions of major flame retardants in different areas of three expedition ships (A–C). A similar figure excluding TCIPP can be found as Fig. S9.

supports the hypothesis that upholstered furnishings are a substantive source of FRs to indoor dust. In most cases, the highest concentrations were found in restaurants and lounge areas—spaces heavily furnished with couches and seating containing polyurethane foam (PUF). Following the phase-out of PBDEs, TCIPP is commonly used as a primary FR in PUF, comprising up to 12% of the foam's weight.<sup>32</sup> A recent study

reported median concentrations of  $300 \mu\text{g g}^{-1}$  (max  $34\,000 \mu\text{g g}^{-1}$ ) and  $220 \mu\text{g g}^{-1}$  (max  $40\,000 \mu\text{g g}^{-1}$ ) in furniture fabrics and furniture foam, as well as consistent high concentrations in carpets and curtains (maximum concentrations of  $1600 \mu\text{g g}^{-1}$ ),<sup>33</sup> supporting the hypothesis that TCIPP concentrations are linked with areas containing upholstery and textile furnishings.





Fig. 3 Median OPE concentrations across different ships. A similar figure excluding TCIPP can be found as Fig. S10.

The concentrations of TCIPP found in this study are some of the highest concentrations found in literature,<sup>34</sup> especially the recently refitted Ship 2. The most comparable concentrations from literature are mostly from indoor environments in the United Kingdom,<sup>35,36</sup> which has a strict furniture flammability standard and high concentrations in indoor dust.<sup>37</sup>

AHFRs were generally lower on ships than in most terrestrial indoor spaces when compared with literature.<sup>38</sup> The same is true for legacy BDEs.<sup>39</sup> However, BDE-209 was elevated in the oldest unaltered ship (Ship 1), where concentrations on onboard dust (especially from technical areas such as the engine control room) were higher than many previous studies.<sup>39</sup>

### FR differences according to ship age reflecting global regulatory changes

The elevated concentrations of FRs found in ship dust are particularly significant when considering the regulatory framework for fire safety on ships. The IMO mandates performance-based standards for fire safety under the International Convention for the Safety of Life at Sea (SOLAS) and the 2010 FTP Code,<sup>20</sup> but does not require specific FR chemicals as long as combustibility, smoke, and toxicity thresholds are met.

The relatively higher presence of lower brominated (legacy) PBDEs on Ships 1 and 2 and their near-complete absence on Ship 3 (Fig. 1 and 2) is consistent with global phase-out and restrictions on PBDEs over the past two decades. Dust from Ship 3 had significantly lower legacy BDEs than either Ship 1 ( $p = 0.043$ ) or Ship 2 ( $p = 0.0001$ ), and significantly lower BDE-209 than Ship 1 ( $p < 0.0001$ ). The use of lower brominated PBDE congeners was restricted in Europe in 2004 and they were added to the international Stockholm Convention on Persistent Organic Pollutants in 2009. BDE-209 was similarly listed in 2017,<sup>40</sup> after Ships 1 and 2 were constructed. While the Stockholm Convention prohibits the use of PBDEs in the production of new products, existing products containing these FRs are allowed to be used for their full life cycle.<sup>41</sup>

According to the Stockholm Convention, BDE-209 may be applied to selected aviation and automotive parts until 2036.<sup>4,42</sup> The elevated concentration of BDE-209 on Ship 1 (especially in technical areas such as the engine control room; Fig. 2A and Table 3) suggests that the compound was used in certain technical parts. This is plausible given that the ship was constructed prior to the implementation of relevant regulations and has not undergone significant refitting since.

Almost all FRs had lower concentrations in the newest ship (Ship 3) compared to the two older ships (Fig. 1, Tables 2 and 3). For PBDEs, the differences observed across the ships are likely



Fig. 4 Median (A) PBDE and (B) AHFR concentrations across three ships.



driven by global bans and restrictions new PBDE use, particularly in upholstery, electronics, and insulation, rather than any maritime-specific legislation. Similar trends of decreasing PBDE concentrations have been observed in terrestrial environments<sup>43</sup> and in human matrices.<sup>44</sup>

Although OPEs are considered replacements for legacy brominated FRs and clearly have more substantial use across all ships, their lower concentrations in the newer ship has a few possible explanations. One possibility is a general reduction in the use of chemical FRs, in favour of other methods to enable ship materials to meet flammability standards. Notably, Ship 3 was built with advanced fire suppression systems not present on the older vessels, which may have reduced the need for chemical FRs in interior materials. While AHFRs and OPEs have been thought to be a safer alternative to BDEs, some OPEs and AHFRs have been associated with environmental and health concerns similar to the legacy compounds they have replaced, such as endocrine disruption, potential carcinogenicity, and neurological effects.<sup>10,45</sup> Another strong possibility is that the newer ship relies on flame retardants that were not included in our target list. The lower levels of FRs in Ship 3 may be due to a transition away from FRs included in our suite of analytes, particularly the chlorinated trialkyl phosphates, including TCIPP, which have been recommended for restriction under the EU FR strategy.<sup>46</sup> Flammability requirements may now be met by newer and/or polymeric FRs that are not typically included in standard environmental monitoring methods, including bisphenol S and DOPO derivatives, melamine-based FRs, and polymeric FRs, which have been suggested for use in transportation foams.<sup>47,48</sup>

### Comparison with other transport sectors

Flammability requirements vary significantly across transport sectors, reflecting differences in evacuation times and fire risk. Generally, aircraft are subject to the most stringent flammability standards, followed by ships, trains, buses, and lastly cars.<sup>47</sup> These differences strongly influence the types and quantities of FRs used in interior materials.

There is a limited set of data from other ships with which our results can be compared. Corsolini *et al.*<sup>21</sup> analyzed FRs in dust from the UK research vessel RRS James Clark Ross (built in 1991),<sup>49</sup> focusing on selected PBDEs and AHFRs in storage, laundry, and laboratory areas only, with limited from living or command spaces, aside from 2 cabins. Overall, BFR concentrations reported in that study were comparable to those found in Ship 1. The highest concentration was reported for BTBPE (maximum 905 ng g<sup>-1</sup>, median 4.52 ng g<sup>-1</sup>), whereas we quantified BTBPE up to 13.3 ng g<sup>-1</sup> on Ship 1 (median 7.11 ng g<sup>-1</sup>). Various shipping categories exist with distinct functional spaces that will result in different flammability rules. Further research is recommended and FR composition and concentrations across different ship types.

Chemical data on dust collected from aircraft focused primarily on PBDEs, with minimal coverage of AHFRs and OPEs. In one of the most comprehensive studies, dust collected from the interiors of nine international aircraft contained five PBDE congeners (BDE-47, -99, -153, -183, and -209) in 100% of

samples.<sup>24</sup> PBDE concentrations were substantially higher than those found in our study (mean 450 µg g<sup>-1</sup>); our study identified a maximum concentration of 170 µg g<sup>-1</sup> in dust from the engine control room of Ship 1. Other studies have also reported BDE-209 as the dominant congener in aircraft dust with median concentrations of 10 µg g<sup>-1</sup>,<sup>14</sup> and 17 µg g<sup>-1</sup>.<sup>23</sup>

Similarly, AHFRs quantified in aircraft dust by Allen *et al.*<sup>24</sup> were substantially higher than in our data, with aDP, sDP, and HBB median concentrations of 330 ng g<sup>-1</sup>, 110 ng g<sup>-1</sup> and 100 ng g<sup>-1</sup>, respectively. To our knowledge, TDCIPP was the only chlorinated OPE quantified in dust from aircraft, and was present at higher concentrations in aircraft floor dust (2 µg g<sup>-1</sup>) compared with the ships from this study (Ship 2: 0.8 µg g<sup>-1</sup>). Multiple studies have found several OPEs at high concentrations in automobile dust. TDCIPP, TCIPP, and TCEP are typically present at µg g<sup>-1</sup> concentrations<sup>16,50-52</sup> and even up to mg g<sup>-1</sup> levels; *e.g.*, TDCIPP was found at 1.4 mg g<sup>-1</sup> concentrations in car dust.<sup>16</sup> Along with elevated OPEs, BDE-209 was also very prevalent at high concentrations in cars.<sup>16,50,51</sup> It is clear that many transportation indoor environments, including ships, have high FR burdens in dust, but the specific compounds and levels are highly heterogeneous due to differences in the ages of the environments sampled as well as differences in target compounds across studies. Where ships differ from other indoor environments is that they represent living and working spaces for crew members, leading to potential for continuous elevated exposures.

### Occupational exposure of ship crew members

Crew members face elevated exposure to indoor chemicals due to the isolated nature of the ship, long working hours, and long contracts which require them to remain onboard. The IMO and Maritime Labor Convention<sup>25</sup> specify a maximum continuous period onboard of 11 months without leave. Contract duration differs significantly between different positions onboard and according to the type of vessel.<sup>26</sup> Wolff *et al.*<sup>53</sup> stated that the majority of cruise ship employees work onboard for ten months, followed by a two-month holiday.

To evaluate potential health risks associated with long-term on-board exposures, EDI *via* accidental dust ingestion for adults was calculated for three FRs: TBOEP, TCIPP, and BDE-209. These were selected based on both high measured concentrations and the availability of oral reference doses (RfDs) in the CompTox database.<sup>54</sup> The lack of RfDs for many OPEs highlights a broader challenge in chemical exposure assessment. Exposure *via* inhalation was not considered, as it is generally minor for FRs compared to exposures from dust.<sup>55</sup>

Across all ships and scenarios, EDIs remained below health-based reference doses, even under high exposure scenarios. TCIPP exposure was pronounced on the older ships (Ships 1 and 2), with EDIs exceeding those found in UK and Norwegian homes under both average and high exposure scenarios (Table 4). Estimated TCIPP exposure on Ship 3 were comparable to those in UK homes, while TBOEP exposure was an order of magnitude lower than on the other ships, and BDE-209 concentrations resembled those found in Norwegian homes.<sup>45</sup>



Table 4 EDI (ng per kg per day) by non-dietary ingestion of chemicals from ships compared with UK and Norwegian homes<sup>35</sup>

	Ships			UK homes			Norwegian homes		
	TBOEP	TCIPP	BDE-209	TBOEP	TCIPP	BDE-209	TBOEP	TCIPP	BDE-209
<b>Average exposure scenario: EF 100%; P50; normal IR (20 mg g<sup>-1</sup>)</b>									
Ship 1	1.1	20.6	0.52	2.3	18.4	0.95	5.2	0.56	0.046
Ship 2	1.3	121	0.09						
Ship 3	0.3	12.8	0.061						
<b>High exposure scenario: EF 100%; P95; high IR (60 mg g<sup>-1</sup>)</b>									
Ship 1	67.7	1530	145	42	721	36.1	34.3	24.2	2.2
Ship 2	78.6	1447	2.2						
Ship 3	4.8	477	0.7						
<b>RfD</b>	<b>90 000</b>	<b>10 000</b>	<b>7000</b>	<b>90 000</b>	<b>10 000</b>	<b>7000</b>	<b>90 000</b>	<b>10 000</b>	<b>7000</b>

Table 5 Cumulative EDI (sum of ingestion and dermal contact) (ng per kg per day) of different positions onboard the different ships. The colour scale emphasizes the occupational sectors' EDI of the respective compounds, with red indicating the highest EDI, followed by orange, yellow, and green indicating the lowest

	TCIPP			TBOEP			BDE-209		
	Ship 1	Ship 2	Ship 3	Ship 1	Ship 2	Ship 3	Ship 1	Ship 2	Ship 3
R1 waiter	247	334	8.37	3.3	13.1	0.68	2.5	0.4	0.049
R2 waiter	216	195	0.06	3.5	13	0.46	2.4	0.81	0.058
R3 waiter	19	300	103	5.7	13.7	1.21	2.4	0.51	0.036
Bartender	225	88	60.5	3.5	12.9	0.43	2.6	0.33	0.073
Reception	15	143	0.06	14.9	14.6	0.37	2.6	0.33	0.066
Shop	80	121	0.06	4.6	12.8	0.37	2.6	0.39	0.066
Housekeep	20	101	8.37	3.5	13.1	0.37	2.6	0.39	0.075
Officer	14		0.06	17.4		0.28	3		0.039
Technician	21			3.0			33.5		

We further investigated the impact of differences in concentrations across dust from different areas of the ships by constructing exposure scenarios based on the working areas of different crew members. For these scenarios, we considered both non-dietary ingestion and dermal contact of different crew positions (Table 5). Full ingestion and dermal EDI values are presented in Table S13. The Marine Labor Convention limits working hours on ships to 14 per day.<sup>25</sup> However, a questionnaire conducted by Oldenburg *et al.*<sup>26</sup> revealed that 10-hour shifts are closer to reality. For modeling purposes, a 10-hour shift in specific working environments was assumed, with 8 hours in the cabin, and the remaining 6 hours for recreation. For each of the timeframes, specific working environments, generalized crew cabins, and crew mess halls, respectively, were used for modeling purposes.

EDI values varied across crew roles based on activity-based exposure modeling. Roles involving greater indoor time in heavily furnished areas (*e.g.*, waiters and bartenders) had relatively elevated intakes, particularly of TCIPP. None of the EDI values exceeded the RfDs. On Ship 2, restaurant waiters were estimated to have the highest TCIPP exposure, with a cumulative EDI of  $\geq 300$  ng per kg per day for two of the restaurants

(those with upholstered seating). Technicians working in the engine room and engine control room of Ship 1 had a modelled BDE-209 intake of 33.5 ng per kg per day. Unfortunately, these technical spaces were not sampled on the other two ships, which is a limitation, which should be considered in future studies. As expected, Ship 3 consistently showed the lowest exposures across all roles (with the sole exception of TCIPP in Restaurant 2), reflecting the lower concentrations of these target chemicals in dust.

## Conclusion

Fire safety at sea is of paramount importance to the maritime industry. As such, many interior materials on ships are treated with halogenated or organophosphate FRs. These compounds are present in indoor dust where passengers and crew members are exposed *via* inhalation, dermal contact, and accidental ingestion.

Within the three expedition cruise ships studied, chlorinated OPEs, most prominently TCIPP, were found at very high concentrations, in some spaces in the mg g<sup>-1</sup> range. While it is not unexpected for an enclosed space such as a ship to have elevated concentrations of FRs, as has been seen in dust from



other modes of transport, such as cars and airplanes, the fact that crew members often spend months at a time onboard presents a unique occupational exposure scenario.

This study provides an important baseline for future studies on FR and other chemical exposure in the maritime sector. The concentrations of FRs, especially TCIPP, on these expedition ships were very elevated compared concentrations reported in other indoor spaces. However, more research is needed to assess different maritime indoor environments. These were relatively small ships (approximately 500 passengers), with fewer restaurants, lounges, and amenities compared to the larger cruise ships, which may impact observed concentrations. Other categories of ships should also be studied—it is unknown whether military ships or cargo ships will exhibit the same pattern or concentrations of FRs as expedition ships.

From a regulatory perspective, the maritime sector occupies a unique space. While performance-based fire safety standards are mandated under international conventions such as SOLAS and the 2010 FTP code, there are no explicit requirements or restrictions regarding the chemical identity or quantity of FRs used. This stands in contrast with terrestrial regulations, where legacy PBDEs and similar compounds have been phased out or banned under frameworks such as the EU REACH Regulation and the Stockholm Convention. Based on these findings, a more coordinated regulatory approach that includes maritime indoor environments and accounts for cumulative occupational exposure is urgently needed. Without such oversight, regrettable substitution and over-application of FRs may occur, posing long-term health risks to crew members.

## Author contributions

Veronica van der Schyff: conceptualization, funding acquisition, methodology, investigation, data curation, writing – original draft, writing – review & editing; Verena Meraldi: conceptualization, resources, writing – review & editing; Andrew Luke King: conceptualization, writing – review & editing; Simona Rozárka Jílková: validation, writing – review & editing; Ondřej Audy: investigation, writing – review & editing; Petr Kukučka: investigation, writing – review & editing; Jiří Kohoutek: investigation, writing – review & editing; Lisa Melymuk: conceptualization, supervision, validation, writing – original draft, writing – review & editing.

## Conflicts of interest

There are no conflicts of interests to declare.

## Data availability

The authors confirm that the data supporting the findings of this study are available within the supplementary information (SI) accompanying this manuscript.

Supplementary information is available. See DOI: <https://doi.org/10.1039/d5va00257e>.

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