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1 **Mechanistic insight into the uptake and fate of persistent organic pollutants in sea ice**

2

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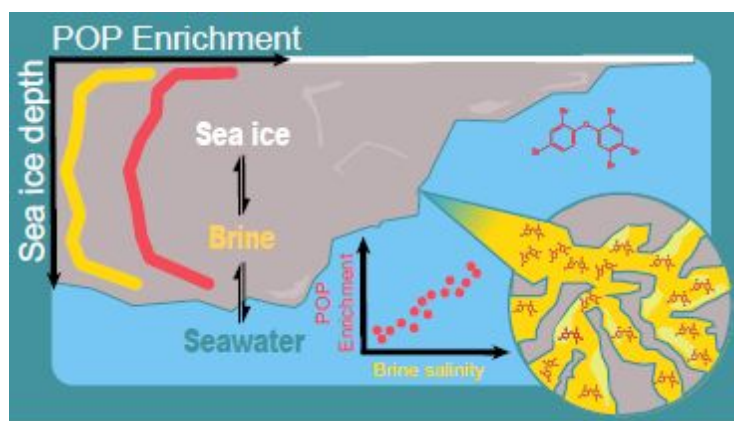
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12

13 **Abstract**

14

15 The fate of persistent organic pollutants in sea ice is a poorly researched area and yet ice
16 serves as an important habitat for organisms at the base of the marine foodweb. This study
17 presents laboratory-controlled experiments to investigate the mechanisms governing the fate
18 of organic contaminants in sea ice grown from artificial seawater. Sea ice formation was
19 shown to result in the entrainment of chemicals from seawater, and concentration profiles in
20 bulk ice generally showed the highest levels in both the upper (ice-atmosphere interface)
21 and lower (ice-ocean interface) ice layers, suggesting their incorporation and distribution is
22 influenced by brine advection. Results from a 1-D sea ice brine dynamics model supported
23 this, but also indicated that other processes may be needed to accurately model low-polarity
24 compounds in sea ice. This was reinforced by results from a melt experiment, which not only
25 showed chemicals were more enriched in saltier brine, but also revealed that chemicals are
26 released from sea ice at variable rates. We use our results to demonstrate the importance of
27 processes related to the occurrence and movement of brine for controlling chemical fate in
28 sea ice which provides a pathway for exposure to ice-associated biota at the base of the
29 pelagic food web.

30 1. Introduction

31 Persistent organic pollutants (POPs) comprise a large group of mainly synthetic, toxic
32 chemicals that have long environmental half-lives and are subject to long-range transport by
33 global atmospheric and oceanic circulation currents¹. As such, these chemicals are present
34 in the marine environment of polar regions and have been shown to bioaccumulate and
35 biomagnify in Arctic food webs^{2,3}. The role of snow and sea ice in the fate and transfer of
36 both older 'legacy' and contemporary 'emerging' chemicals to biological systems has not
37 been well studied despite their occurrence in Arctic seawater. There are now a number of
38 observational studies that have reported relatively high POP concentrations in the remote
39 sea ice snow pack⁴⁻⁶ and their presence in sea ice itself⁷⁻¹⁰.

40 A warming climate is resulting in substantial changes to the volume and properties of sea
41 ice¹¹. There is a strong declining trend in the areal extent of Arctic sea ice cover, which
42 currently ranges between 4 and 16 million km² over the annual seasonal cycle¹².
43 Furthermore, the nature of sea ice is also changing, with the Arctic Ocean now dominated by
44 first-year sea ice (FYI)¹³. As sea ice forms, most of the salts present in the freezing sea
45 water are rejected into the underlying ocean, leaving only small amount entrapped within a
46 network of highly saline brine pockets. As ice continues to grow, more salts are expelled and
47 seasonal meltwater at the surface often 'flushes' the sea ice, reducing its bulk salinity
48 further. Multi-year sea ice (MYI) therefore has a lower bulk salinity and a lower salt flux to
49 the ocean during melt¹⁴. Compared to older MYI, young ice contains more brine per unit
50 volume, and this appears to influence the behaviour and fate of organic micro-pollutants
51 present in the sea ice system⁸. Importantly, many organisms situated at the base of the
52 pelagic food web are abundant in sea ice and inhabit the network of brine inclusions. As the
53 Arctic environment is rapidly changing, there is a rising motivation to understand the
54 biogeochemical cycling of these toxic chemicals in sea ice.

55 Whilst the presence of POPs such as polychlorinated biphenyls (PCBs) has been
56 established in sea ice⁷ most of the recent knowledge on chemical behaviour in sea ice and
57 interactions with seawater and the overlying snowpack has been established through the
58 field observations of Pućko et al.,^{5, 6, 8, 9, 15, 16} who examined the α - and γ -isomers of
59 hexachlorocyclohexane (HCH) in FYI in the Amundsen Gulf of the Canadian Arctic. The key
60 findings from these studies showed sea ice to have some of the highest concentrations of
61 HCHs measured anywhere in the Arctic. The majority of the HCHs were present in brine,
62 and brine advection influenced the transfer of HCHs between the sea ice, overlying
63 snowpack and underlying seawater.

64 The aim of this study was to better understand the basic mechanisms governing the
65 uptake and release of organic pollutants in growing and melting sea ice, respectively. We

66 hypothesize that chemical uptake and distribution is strongly influenced by the formation of
67 brine during sea ice growth and melt. To test this, we performed sea ice growth experiments
68 under controlled laboratory conditions where an artificial ‘ocean’ was spiked with several
69 persistent organic pollutants. To assess the role of brine in determining their fate, we
70 measured vertical profiles of pollutant concentrations through bulk sea ice samples and
71 made comparisons to predictions from a sea ice brine dynamics model during sea ice
72 formation. We also conducted an experiment to extract brine and assess its composition to
73 examine how organic chemicals are released from sea ice during melt.

74 **2. Materials and methods**

75

76 2.1. Experimental facility and conditions

77 The study was conducted in the Roland von Glasow Air-Sea-Ice Chamber (RvG-ASIC) at
78 the University of East Anglia, UK. In essence, the facility consists of a glass-walled tank
79 (approximately 3.5m³; height: 1.2m; width 1.2m; length 2.5m) located inside an enclosed
80 chamber that can be chilled to –55°C (see [https://www.uea.ac.uk/environmental-](https://www.uea.ac.uk/environmental-sciences/sea-ice-chamber)
81 [sciences/sea-ice-chamber](https://www.uea.ac.uk/environmental-sciences/sea-ice-chamber)). The tank was filled with artificial sea water (de-ionised water
82 with NaCl – (AksoNobel Sanal-P; purity > 99.5%)). A submerged pump (flow rate: 1000 L h⁻
83 ¹) was used to mix the seawater (SW; we refer to it as seawater even though it only contains
84 NaCl). The tank was equipped with an *in-situ* conductivity-temperature sensor (SeaStar DST
85 CTD) along with a series of automated *in-situ* thermistors spanning the depth of the ice
86 profile to measure the ice temperature throughout the experimental periods. Table 1
87 presents an overview of the experimental conditions for two freeze periods (1 & 2). For the
88 main experiment (Freeze - 1), the air temperature of the chamber was chilled to –35 °C for 3
89 days resulting in rapid ice growth and the formation of an ice layer 17±1 cm in depth
90 (uncertainty reflects ice thickness variations across the tank). The ice was subsequently
91 sampled to establish the presence of chemicals in the ice and their distribution throughout
92 the ice column. After the ice had completely melted, ‘Freeze - 2’ was undertaken with the air
93 temperature set to -18°C but for a longer duration (7 days) resulting in slower ice growth but
94 with a thicker final ice layer 26±1 cm. The ice sampled during ‘Freeze - 2’ was also subject
95 to an additional slow-melt experiment to assess chemical behaviour during melt (see Section
96 2.4.).

97 Table 1. Experimental conditions and sea ice physical properties for two freeze experiments.
98 Sea ice samples used to assess chemical release in the slow-melt experiment were taken
99 from Freeze - 2 (see section 2.4).

	Freeze - 1	Freeze - 2
Initial NaCl concentration (g L ⁻¹)	35.4 ± 0.1	35.4 ± 0.1
Air temperature during freezing phase (°C)	-35	-18
Air temperature during melting phase (°C)	5	0
Maximum sea ice depth (cm)	17 ± 1	26 ± 1
Freezing duration (days)	3	7
Coldest recorded temperature in ice (°C)	-13.8	-11.3
Maximum modelled brine salinity (g L ⁻¹)	178.2*	154.8*
Average ice growth rate (cm d ⁻¹)	5.7	3.7
Melting phase (days)	6	3

100 * Derived using the recorded minimum temperature in the sea ice using Equation S1¹⁷.

101

102 An array of chemicals that have been previously observed in the Arctic marine
 103 system (see Table 2) and that cover a wide range of physical-chemical properties (Table S1)
 104 were spiked into the tank using a stock solution (0.2 to 1.4 μM in 1 L ethanol) to give
 105 concentrations between 0.1 and 0.4 nM (Table S2). This was undertaken once the
 106 temperature of the seawater had cooled to -1°C to ensure minimal loss of chemicals by
 107 volatilisation. The chemical concentrations were up to two orders of magnitude below the
 108 estimated aqueous solubilities in seawater (see Table S1), but also up to two orders of
 109 magnitude greater than those typically observed in Arctic seawater. The freeze experiments
 110 conducted in the facility were performed in darkness to limit the growth of algae and reduce
 111 any photochemical loss of the compounds.

112

113 2.2. Sampling procedures

114 Prior to the introduction of chemicals into the chilled seawater, a short period (2 days) of ice
 115 growth at -35 °C permitted samples of seawater (*SW*) (0.2 L; *n* = 3) and bulk ice (*BI*) (3.5 L;
 116 *n* = 1) to be collected for the purpose of method blanks. After the ice had melted, the
 117 chemical stock spike solution was added and mixed under pumping. A seawater sample (0.2
 118 L, *n* = 1) was taken daily, and triplicate samples (0.2 L; *n* = 3) were obtained on three key
 119 days of Freeze - 1 (start: day 1 (before any ice formation); middle: day 4 (once maximum ice
 120 had formed);, end: day 11 (after complete ice melt)) to assess analytical precision. Seawater
 121 was taken via a pre-installed silicone hose (I.D. 8 mm) with an inlet set at 0.5 m above the
 122 base of the tank to avoid interference with any forming ice layer. Bulk ice samples (*n* = 2)
 123 were taken once the ice had reached a suitable handling depth using techniques developed
 124 by Cottier et al.,¹⁸ to limit brine loss and displacement during sampling. Following sampling,
 125 ice samples were immediately wrapped in pre-cleaned polyethylene (PE) sheets and

126 transferred to a freezer ($-40\text{ }^{\circ}\text{C}$) where they were stored prior to further processing. Bulk ice
127 samples were subsequently sectioned into horizontal layers (0.4 to 1.2 L each; $n = 9$) using
128 a grease-free electric band saw in a cold room ($-25\text{ }^{\circ}\text{C}$), transferred to individual PE bags
129 and melted at room temperature. Frost Flowers (0.2 L; $n = 1$) present on the surface of the
130 ice were carefully collected using a polyethylene spatula and stored in a freezer before
131 melting for analysis.

132

133 2.3. Sample processing and analysis

134 Salinity was measured in melted sea ice samples, 'slow-melt' aliquots, and melted frost
135 flowers using a calibrated conductivity probe (Hach HQd40 logger with CDC401 probe) after
136 50 μL of surrogate standard ($(^{13}\text{C})\text{PCB-28}$, $(^{13}\text{C})\text{PCB-52}$, $(^{13}\text{C})\text{PCB-180}$ at 60 $\text{pg } \mu\text{L}^{-1}$ in
137 ethanol) was added to each solution. Samples were then subject to solid phase extraction
138 (SPE) using a 12-port vacuum manifold system. Briefly, SPE cartridges (30 mg of 3 cc
139 OASIS HLB) were conditioned using 5 mL of methanol followed by 5 mL of chemical-free
140 purified water (MilliQ; $>18\text{ M}\Omega\text{ cm}$) and then loaded with sample at a rate of 1 to 2 drops per
141 second. Subsequently, the cartridges were centrifuged for 5 minutes at 2000 rpm and later
142 air-dried for a further 40 minutes whilst fitted with an additional cartridge as a precaution
143 against airborne contamination. Cartridges were then soaked with 3 mL of
144 hexane:dichloromethane (1:1) for 5 minutes and eluted with a further 3 mL of this solvent
145 mix. Each sample extract was then subject to a clean-up procedure involving elution through
146 an alumina/silica column followed by gel permeation chromatography (GPC). Samples were
147 then transferred to amber GC vials containing 50 μL of recovery standard (IS) ($[^{13}\text{C}]\text{PCB-141}$
148 [$25\text{ pg } \mu\text{L}^{-1}$] and BDE-69 [$75\text{ pg } \mu\text{L}^{-1}$]) in *n*-dodecane was then added before being reduced
149 under N_2 to a final volume of 50 μL .

150 Analysis of extracts was performed using a Thermo GC-MS (Trace GC Ultra - DSQ)
151 (Xcalibur software Version 1.4.x) operating in electron impact mode (70 eV) and equipped
152 with an Agilent CP-Sil 8 CB 50 m x 0.25 mm capillary column with 0.12 μm film thickness. A
153 10-point mixed calibration standard in *n*-dodecane was used for quantification (10 to 450 $\text{pg } \mu\text{L}^{-1}$
154 for OCPs, 10 to 120 $\text{pg } \mu\text{L}^{-1}$ for PCBs and 10 to 1250 $\text{pg } \mu\text{L}^{-1}$ for PBDEs, respectively).
155 Chemical concentrations presented in this study were corrected for recovery, but not blank
156 corrected. Method detection limits (MDL) were calculated from method blanks ($\text{MDL} = \bar{x}_{\text{method blank}} \pm 3 \cdot \text{SD}_{\text{method blank}}$) (see Table S3).

157

158 2.4. Slow-melt experiment

159 Following Freeze 2, a separate experiment was conducted (outside of the glass tank but
160 within the coldroom) to examine the release of chemicals from ice during thaw, and to
161

162 determine how strongly associated each chemical was with brine. Sea ice cores ($n = 8$) were
 163 sampled from across the ice slab using a pre-cleaned titanium manual corer (75 mm I.D.).
 164 These were individually split into top (T) and bottom (B) sections of approximately equal
 165 length, with each section placed into a separate pre-cleaned PE bag, which were
 166 subsequently kept at 0 ± 1 °C to induce melt, as described by Pućko, et al.,⁸ and others¹⁹⁻²².
 167 Sequential meltwater (MW) fractions (0.1 to 1.2 L; $n = 8$) were collected from the respective
 168 top and bottom sections and analysed separately (Table S4).

169

170 2.5. Calculations and data analysis

171 Enrichment factors (EF) were calculated using Equation 1 to assess the accumulation of
 172 chemicals in a particular compartment, relative to seawater. The average chemical
 173 concentration of all seawater samples over the experimental period was used for the
 174 denominator for each chemical (SW ; day 1 to day 11). The brine (BR) assessed in this study
 175 was operationally defined using the average of the first meltwater (MW) fraction from both
 176 the top and bottom ice sections (MW_{F1T} & MW_{F1B} ; $n = 2$) and FF is a frost flower sample
 177 (taken in Freeze 1). Hence, EF values >1 and <1 indicate specific enrichment or depletion,
 178 relative to seawater, respectively.

179

$$180 \quad EF = \frac{[\text{chemical}]_{\text{e.g. bulk ice (BI); brine (BR); frost flower (FF); meltwater (MW)}}}{[\text{chemical}]_{\text{seawater (SW)}}} \quad (1)$$

181

182 Sea ice depths were normalised to the total sea ice thickness in that experiment (i.e.
 183 in Freeze - 1 & 2) to aid comparison between modelled and measured data. A mass-balance
 184 calculation was used to assess chemical loss from the system (e.g. volatilisation and/or
 185 chamber-side sorption) and evaluate the fraction of chemical present in the various
 186 compartments i.e. seawater, bulk ice and brine (at maximum ice depth). Average sea ice
 187 concentrations were used to calculate the mass fraction of chemical in the bulk ice, with
 188 respect to the total measured mass in the seawater at day 1. The relative standard deviation
 189 (RSD) of triplicate seawater samples were used to calculate conservative estimates of the
 190 variability of some samples (e.g. frost flowers) (see Table S3). For more information on
 191 calculations and data analysis, refer to Equations S1 - S5).

192

193 2.6. Brine dynamics model

194 A 1-dimensional sea ice growth and desalination model was used to predict brine dynamics
 195 in a forming sea-ice layer, using the gravity drainage parameterisation presented by¹⁷. The
 196 model is presented in detail in Thomas, et al.,^{23, 24} where it has been shown to have
 197 predictive capability for the dynamics of brine in sea ice. The brine dynamics

198 parameterization has also been evaluated previously ¹⁷. The model was initialised by
 199 prescribing an initial seawater salinity, concentration of a dissolved solute in seawater (e.g.
 200 an organic chemical), sea ice thickness, and ocean mass. For this study, the initial salinity
 201 and chemical concentrations were taken from the measured values in the seawater at the
 202 beginning of the experiment (i.e. day 1). The model was run with ± 2 s.d. of the initial starting
 203 conditions, based on the precision of the measurements of the chemical concentrations in
 204 the seawater. The initial sea ice thickness was set to 1cm, and the bulk sea ice salinity and
 205 chemical concentrations were set to initial ocean concentrations for all model sea ice layers.
 206 The model was forced using measured sea ice temperature profiles, and sea ice
 207 thicknesses calculated by extrapolating those profiles back to the measured seawater
 208 temperature. In this case, measurements were used instead of a thermodynamic model to
 209 minimise errors. Full details including the key equations governing brine salinity (derived
 210 using the ice temperature), and how the model simulates brine dynamics (gravity drainage)
 211 are presented in the SI.

212

213 3. Results and Discussion

214

215 3.1. Quality controls & mass-balance

216 Average recoveries of the surrogate standards were 42 ± 17 % and did not vary significantly
 217 between sample type (Table S3). Some blanks contained low levels of several target
 218 analytes (e.g. α -HCH γ -HCH, PCB-28, PCB-52) thereby increasing the method detection
 219 limits (MDLs) for these compounds. The relative standard deviation (RSD) of triplicate
 220 seawater analyses demonstrated precisions of 8 to 40% between all test compounds (see
 221 Table S3). Table 2 shows the relative distribution of chemicals in the various compartments
 222 of the experimental system on selected days. By day 11, all of the ice had melted and a
 223 comparison of the relative mass in the seawater on the initial (day 1) and final (day 11) days
 224 of the experiments showed that there was no significant difference ($p > 0.05$; student t-test)
 225 for any of the chemicals, indicating negligible losses during the experimental period. Hence,
 226 all of the chemicals in the system can be accounted for and are not subject to an artefact of
 227 the experimental set-up.

228

229 Table 2. Chemical mass (± 1 .s.d) apportionment for the experimental compartments on day
 230 1, day 4 and day 11 of Freeze - 1.

Experimental day	Start (day 1)	Middle (day 4)			End (day 11)
Compartment	Seawater	Seawater	Bulk ice	Frost flowers	Seawater
Volume fraction of	$100 \pm <1$	$83 \pm <1$	$17 \pm <1$	$<<1\%$	$100 \pm <1$

compartment					
NaCl (% _{mass})	100 ± <1	93 ± <1	7 ± <1	<<1%	100 ± <1
α-HCH (% _{mass})	100 ± 15	96 ± 18	4 ± 1	<<1%	97 ± 14
γ-HCH (% _{mass})	100 ± 22	97 ± 34	3 ± 1	<<1%	83 ± 2
PCB-28 (% _{mass})	100 ± 18	93 ± 10	7 ± 1	<<1%	116 ± 17
PCB-52 (% _{mass})	100 ± 12	96 ± 14	4 ± 1	<<1%	108 ± 11
Chlorpyrifos (% _{mass})	100 ± 29	96 ± 32	4 ± 1	<<1%	156 ± 42
BDE-47 (% _{mass})	100 ± 16	94 ± 64	6 ± 2	<<1%	114 ± 32
BDE-99 (% _{mass})	100 ± 17	91 ± 48	9 ± 3	<<1%	80 ± 5

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241 3.2. Entrainment of POPs in sea ice.

242 A time-series for the concentration of NaCl and chemicals in seawater throughout the

243 experiment (day 1 – day 11) can be seen in Figure S1. During the period of sea ice

244 formation (day 1 – day 4) an increase in sea ice thickness and decrease in seawater volume

245 was accompanied by solute rejection from the sea ice, and an increase in the underlying

246 NaCl concentration (from around 35 to 39 g L⁻¹). Given the experimental precision of the

247 measurements made for the organic chemicals seawater (8 to 40 %), it was not possible to

248 establish whether they followed a similar trend to the salt. However, the measured

249 concentrations of salt and all chemicals were markedly lower in bulk ice than seawater, as

250 indicated by the Enrichment Factors ($EF_{BI-SW} < 1$) presented in Table 3. This finding

251 suggests that organic chemicals are rejected from sea ice throughout ice growth.

252 Interestingly, $EF_{BI-SW} [NaCl] > EF_{BI-SW} [POPs]$ which may indicate preferential rejection of organic

253 chemicals during sea-ice growth.

254

255 Despite the low chemical concentrations present in bulk ice, results presented in

256 Table 3 show that $EF_{BR-SW} > EF_{BI-SW}$ ($p < 0.05$; student t-test), indicating that the chemicals are

257 more strongly associated with the brine fraction and are entrained within the complex

258 network of brine inclusions which extends throughout the ice ²⁵. Pućko et al., ⁸ quoted the
 259 mean depth-averaged salinity of bulk ice to be 11.6g L⁻¹ which gave $EF_{BI-SW} = 0.4$ for NaCl.
 260 Similarly, values for EF_{BI-SW} were obtained for α -HCH and γ -HCH at 0.4 and 0.5,
 261 respectively. The resemblance between this calculated index for NaCl and the two HCH
 262 isomers suggests that the levels of HCH in FYI are probably governed by processes that
 263 function to conservatively distribute brine in sea ice. In our study, EF_{BI-SW} of NaCl resulted in
 264 a value of 0.4, although there is a larger range (0.1 – 0.4) between the index for all of the
 265 chemicals presented in our study. Natural sea ice is a highly complex medium with marked
 266 heterogeneity in physical features over relatively narrow spatial scales (i.e. cms). The
 267 chamber ice is markedly younger and thinner than the mid/late-winter Arctic sea ice
 268 measured in the field studies above, but the ice formation processes and physical features
 269 such as brine channels and frost flowers etc are similar ²³. Some of the differences between
 270 our enrichment factors and previous field studies could be due to different temperature and
 271 sea-ice growth regimes. However, the higher brine salinity concentrations observed in the
 272 Arctic sea ice could have affected organic chemical occurrence and distribution, and is likely
 273 to account for differences between the field studies and the chamber ice of this study.

274

275 Table 3: Enrichment factors (± 1 .s.d) for NaCl and chemical contaminants in the different
 276 sea ice system compartments. BI=bulk ice; BR=brine; SW=seawater; FF=frost flower; L1=
 277 uppermost sea ice layer sampled.

278

Enrichment Factor	Bulk ice depth(cm)	NaCl	α -HCH	γ -HCH	PCB-28	PCB-52	Chlorpyrifos	BDE-47	BDE-99	Reference	
EF_{BI-SW}	17 \pm 1	0.4 \pm <0.1	0.1 \pm <0.1	0.1 \pm 0.1	0.2 \pm 0.1	0.2 \pm <0.1	0.2 \pm 0.1	0.1 \pm 0.1	0.4 \pm 0.2	Freeze - 1	
EF_{BI-SW}	26 \pm 1	0.3 \pm <0.1	0.2 \pm 0.1	0.3 \pm 0.2	0.2 \pm 0.1	0.1 \pm <0.1	0.3 \pm 0.2	0.2 \pm 0.1	0.4 \pm 0.2	Freeze - 2	
EF_{BI-SW}	30	0.4	0.4	0.5	n/m					8	
EF_{BI-SW}	90	0.2	0.3	0.3	n/m					9	
EF_{BI-SW}	5	0.3	0.3	0.4	n/m					9	
EF_{BR-SW}	26 \pm 1	1.4 \pm <0.1	0.6 \pm 0.2	1.0 \pm 0.8	1.3 \pm 0.5	1.2 \pm 0.3	1.2 \pm 0.7	0.7 \pm 0.5	0.9 \pm 0.6	Freeze - 2	
EF_{BR-SW}	90	4.4	3.9	4	n/m					8	
EF_{FF-SW}	n/a	2.3 \pm <0.1	0.2 \pm 0.1	0.2 \pm 0.2	0.2 \pm 0.1	0.4 \pm 0.1	0.3 \pm 0.2	6.6 \pm 4.4	24 \pm 15	Freeze - 1	
EF_{FF-SW}	n/a	< 2.0	0.7	2.1	0.0 – 38.9 Δ					10	
EF_{FF-L1}	n/a	5.0 \pm <0.1	1.5 \pm 0.5	2.0 \pm 1.5	2.5 \pm 0.9	3.0 \pm 0.7	2.4 \pm 1.4	30 \pm 20	50 \pm 31	Freeze - 1	
EF_{FF-L1}	n/a	< 0.7	1.7 – 68.0 Δ								10

279

280 n/a=not applicable; n/m=not measured; Δ =different organic chemical used other than that
 281 analysed in this study. See Table S5 for values that were used in this literature analysis.

282

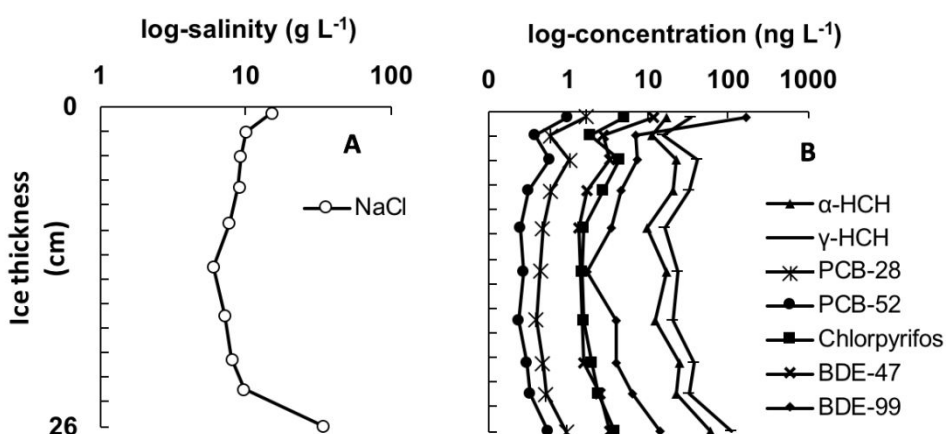
283 Brine salinity is set by the appropriate *liquidus* relationship ²⁶ and is usually at its
 284 respective freezing-point. Changes in the local thermal conditions will cause a corresponding
 285 phase-change following this temperature-salinity relationship. Brine salinity measured in

286 Pućko et al.,⁸ and in this study was 128 g L^{-1} and 58 g L^{-1} , respectively. Hence, the brine
 287 collected in our study was much less concentrated and this is likely to be attributed to
 288 differences in sea ice properties (given the age and thickness of the chamber ice) as well as
 289 the brine sampling techniques which limited our ability to obtain enough brine for analysis
 290 with a salinity $>58 \text{ g L}^{-1}$. These factors most likely contribute to the slightly lower *EFs*
 291 measured in this study compared to those calculated from Arctic sea ice^{8, 9}. Furthermore,
 292 additional pollution sources such as the transfer of chemicals from the overlying snowpack
 293 into sea ice and the incorporation of other seawater constituents such as organic matter
 294 (dissolved and particulate) may also affect the quantity and distribution of POPs in natural
 295 sea ice.

296

297 3.3. Distribution of chemicals within sea ice

298 Figure 1 shows the vertical distribution of salt and chemicals in our chamber-grown sea ice.
 299 Data were plotted on a log-scale to show all chemicals and account for their wide range in
 300 concentrations. A 'c-shape' profile for bulk salinity (Panel A) is typical for first-year sea ice,
 301 whereby elevated concentrations exist at the ice-atmosphere and ice-ocean interfaces. The
 302 processes governing the distribution of NaCl in sea ice have been reviewed by Notz and
 303 Worster¹⁴. Due to the crystal structure and the close-packing arrangement of water
 304 molecules in ice, there is limited inclusion of solutes (e.g. dissolved ions, particulates etc)
 305 within the ice itself²⁵, but are retained within liquid inclusions between the ice lamellae. Due
 306 to surface cooling, brine at the surface of sea ice is colder, more saline, and denser than that
 307 below, driving convection currents and facilitating the downward movement of salt-rich brine.
 308 This process is better known as gravity drainage and is believed to be the predominant
 309 mechanism controlling the removal of salts from the bulk sea ice¹⁴.



310

311 Figure 1: Chemical concentrations in a vertical section of sea ice grown at $-18 \text{ }^{\circ}\text{C}$ to a depth
 312 of 26cm. Zero on the y-axis represents the upper most surface of the ice in contact with the
 313 chamber atmosphere

314

315 We are confident that the NaCl profile provided in Figure 1 is driven by brine gravity
316 drainage processes ²³. As the profiles for each organic chemical (Panel B) display a similar
317 shape, we suggest that their distribution in young sea ice is strongly influenced by brine
318 advection during ice growth.

319

320 3.4. Accumulation of POPs in frost flowers

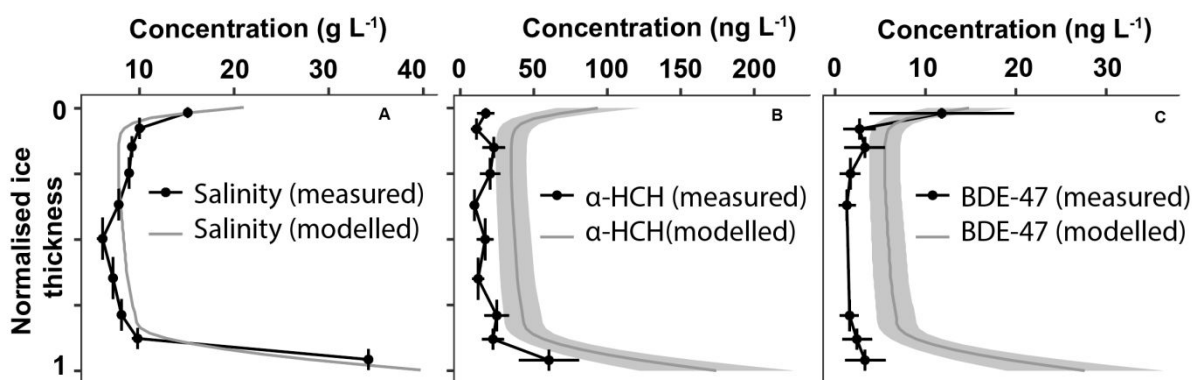
321 Frost flowers (*FF*) are highly saline ice structures that develop on the surface of newly
322 formed sea ice, typically refreezing leads ²⁷. The salinity of frost flowers sampled in polar
323 environments have been measured up to 110 g L⁻¹ (i.e. $EF_{FF-SW} = 3$) ²⁸ and are typically
324 enriched in other sea-salt ions as well ^{29, 30}. The leading mechanism proposed for this
325 enrichment suggests that freezing water vapour located at the sea ice surface forms an ice
326 skeleton, causing salts and other solutes to be advected from the surface layer through
327 capillary action ²⁹. In our study, frost flowers covered around 10% of the surface area of the
328 ice (Freeze - 1) and melted samples measured a salinity of 83 g L⁻¹, representing a
329 significant enrichment of NaCl from the upper layer layer ($EF_{FF-L1} = 5.0 \pm <0.1$). Results
330 displayed in Table 3 show that $EF_{FF-L1 [POPs]} > 1$, indicating they too are advected with brine
331 from the surface layer, but to a lesser degree. However, chemical enrichment factors (EF_{FF-L1})
332 for BDE-47 and BDE-99 were 30 ± 20 and 50 ± 31 , respectively, indicating selective
333 fractionation of organic chemicals in frost flowers. Douglas et al. ¹⁰ observed similar
334 enrichments ($EF_{FF-L1} = 2 - 68$) for a number of analogous chemicals, including higher-
335 chlorinated-PCBs, in frost flowers sampled on coastal sea ice close to Barrow, Alaska.

336 The relatively large surface area of frost flowers has been suggested as an important
337 feature that enhances the atmospheric scavenging of airborne chemicals ¹⁰. However,
338 atmospheric scavenging is unlikely to be significant in our experiments because the blanks
339 revealed negligible levels of the chemicals in the chamber air (Table S3). A possible
340 mechanism for observing enrichment in frost flowers involves evaporation of chemicals from
341 the relatively warmer surface ice layer, and subsequent condensation to the colder frost
342 flowers ¹⁰. However, we propose that organic solutes may be advected from the ice at
343 different rates and related to factors controlled by their individual physicochemical
344 properties. The high enrichment observed for some of these chemicals suggests that frost
345 flowers may play an important role in the ice-atmosphere exchange of POPs in polar marine
346 environments.

347

348 3.5. Simulated chemical behaviour in sea ice

349 The initial NaCl and chemical concentrations measured in the seawater were used
350 as input parameters for the brine dynamics model. The model predicts the convection of
351 brine, driven by gravity drainage, assuming that: (i) the chemicals are perfectly dissolved
352 and are advected with the moving brine; (ii) the chemicals are well-mixed in the underlying
353 seawater. Figure 2 shows an example of a comparison between the predicted and
354 measured chemical distribution of NaCl (Panel A), α -HCH (Panel B) and BDE-47 (Panel C)
355 (see Figures S3 and S4 for other chemical profiles), normalised by ice thickness. The model
356 produced a predictable 'c-shape' concentration profile for NaCl and organic chemicals,
357 where concentrations were generally highest at the upper and lower sea ice interface.



358
359 Figure 2: Modelled and measured bulk concentration profile for salinity, α -HCH and BDE-47
360 in sea ice grown at -18°C to a depth of 26 cm. Vertical bars indicate layer thickness.
361 Horizontal bars represent ± 2 s.d. for modelled (grey shade) and measured data.

362
363 Although a qualitative comparison between the measured and modelled chemical
364 profiles in the sea ice was reasonable, the model tended to overestimate the concentrations
365 of the organic chemicals. A ratio of the modelled and measured bulk ice concentrations
366 (integrated vertically over all the sea ice layers) showed a ratio for NaCl of around 1,
367 whereas a ratio of 9 was observed for BDE-47 (see Table S6 for other chemicals). The
368 comparison suggests that low-polarity organic compounds may not be transported
369 conservatively with respect to salt. Rather, additional factors other than gravity drainage may
370 also play a role in the degree of chemical incorporation during sea ice growth.

371 The extreme environment (i.e. low temperatures and high brine salinity) in sea ice
372 causes large uncertainties regarding the physical-chemical properties of organic solutes in
373 brine inclusions. We derived simple salinity-temperature dependent relationships for each
374 chemical to estimate whether the aqueous solubility was exceeded at the minimum recorded
375 temperature and highest modelled brine salinity within the sea ice (listed in Table 1). Our

376 basic approach indicated that the aqueous solubility was not exceeded for each chemical at
377 these conditions. While we can not state conclusively that this factor did not affect the
378 distribution of chemicals in our experiments, our results suggest that another process(es)
379 currently not described by the physics incorporated within the brine dynamics model may
380 also be at play. Given the dynamic nature of our artificial sea ice, chemical solutes are
381 unlikely to attain equilibrium between the seawater, ice surfaces and ice brine
382 compartments. As sea ice grows thicker (late season Arctic sea ice may be several metres
383 thick), the rate of ice growth generally decreases, allowing more time for exchange of
384 organic chemicals between these compartments and affecting their accumulation in sea ice.
385 We therefore propose that thermodynamic factors such as the partitioning of low polarity
386 organic contaminants between these different ice compartments ³¹ (processes which do not
387 feature in the model) may account for the discrepancy between the observed and modelled
388 values.

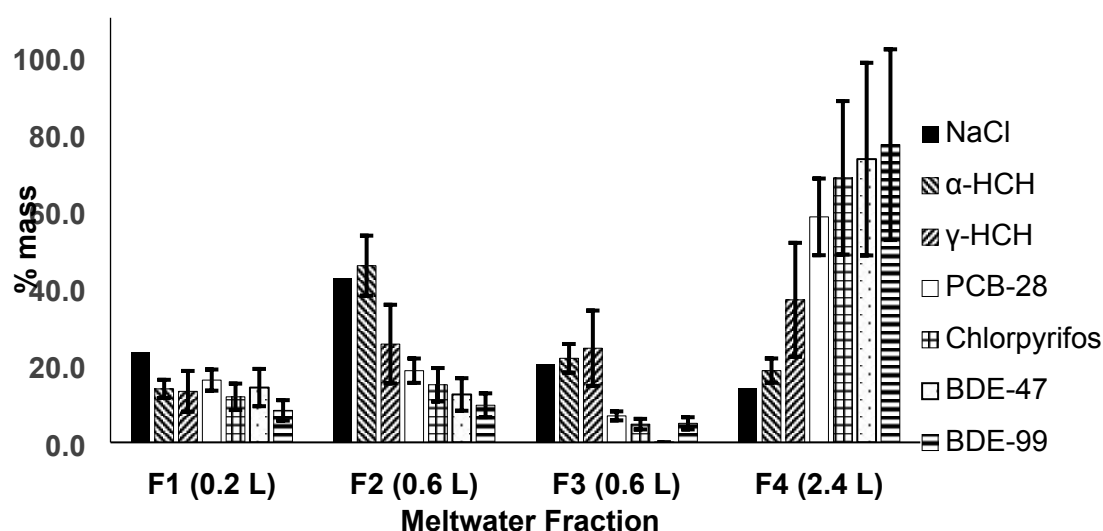
389

390 3.6. Brine composition and chemical dynamics

391 The thermodynamic state controls the fluid dynamics of sea ice and plays a crucial role in
392 the biogeochemical cycling of sea ice constituents ^{8, 21, 32, 33}. As the brine volume of sea ice
393 approaches around 5%, it is generally accepted that sea ice becomes sufficiently permeable
394 to permit brine to move freely ³⁴. However, the melting of natural sea ice and hence its
395 desalination during seasonal thaw is a complex process that is governed by the properties of
396 the sea ice and the thermal regime (i.e. basal melt or surface melt). We conducted a slow-
397 melt experiment (see section 2.4.) to investigate the association of organic chemicals with
398 different meltwater fractions of varying NaCl concentrations. This enabled us to observe the
399 composition of brine and therefore infer the temporal behaviour of organic contaminants in
400 sea ice during the transition from FYI to older MYI.

401 The experiment resulted in brine-rich meltwater being released first (e.g. NaCl; MW_{F1}
402 = 58 g L⁻¹), followed by a supply of fresher meltwater due to the melting of the ice-matrix
403 itself (e.g. NaCl; MW_{F4} = 1.9 g L⁻¹), indicating that brine release is governed by
404 thermodynamically controlled phase-changes within the sea ice pores. Figure S2 shows that
405 the level of chemical enrichment in meltwater (i.e. EF_{MW-SW}) was positively correlated (n=48,
406 $r^2=0.507$, $p<0.01$) with the concentration of NaCl in the sea ice meltwater. Therefore, saltier
407 brine can be expected to contain higher concentrations of chemicals. Our results are
408 consistent with field studies investigating inorganic ^{21, 32} and organic ^{8, 9} chemical behaviour
409 in sea ice.

410 Despite earlier meltwater fractions showing a higher degree of chemical enrichment,
 411 the volumes of meltwater that were collected varied from 0.2 to 2.4 L (see Table S7). To
 412 further investigate the dynamics of chemicals during melt, the percentage mass of chemical
 413 in each meltwater fraction was calculated (see Table S8) and shown in Figure 3. The results
 414 show that the highest mass of the most hydrophobic chemicals (PCB-28, chlorpyrifos, BDE-
 415 47, BDE-99) was present in the final meltwater fraction (MW_{F4}), unlike NaCl which has the
 416 lowest mass in MW_{F4} . The results indicate that organic chemicals can be retained within the
 417 bulk sea ice even after the brine has drained and implies that more hydrophobic chemicals
 418 are preferentially retained within the sea ice.



419 Figure 3: The percentage mass of individual chemicals in the sequential meltwater fractions.
 420 Bracketed values are the actual volumes for each meltwater fraction. PCB-52 was <MDL in
 421 several fractions and so was not included in this plot. Error bars calculated from RSD.

422
 423 The three initial meltwater fractions (MW_{F1-F3}) show that chemical mass loss from the
 424 ice is lower than salt, but highest for the more water soluble chemicals (i.e. around 75% of α -
 425 HCH and γ -HCH is lost in F1 to F3, compared to only around 20% of BDE-99). The final melt
 426 fraction (MW_{F4}) contained >50 % of the mass of (in increasing order) PCB-28, chlorpyrifos,
 427 BDE-47 and BDE-99, initially present in the ice prior to the onset of melt. The results
 428 suggest that chemicals are released at variable rates, possibly due to thermodynamic
 429 factors associated with the aqueous solubility and the rate of dissolution³⁵, which may affect
 430 the phase distribution and rate of transfer between the solid fresh ice matrix to the mobile
 431 liquid brine solution. This observation is comparable to studies performed in environmental
 432 and laboratory snow, whereby soluble ions are generally released in initial meltwater
 433 fractions (i.e. “type I elution” see references^{36, 37}), whereas very hydrophobic organic

434 compounds (possibly associated with particles), are retained in the snow until final meltwater
435 elution associated with complete melting (i.e. “type II elution”).

436 Our results show that brine dynamics play an important role in the distribution of
437 persistent chemicals in young sea ice, supporting our hypothesis that chemical uptake and
438 distribution is strongly influenced by the formation of brine during sea ice growth. However,
439 chemical specific processes may remove these chemicals from the dissolved phase,
440 decoupling them from the NaCl within the sea ice system. Support for this assertion comes
441 from our melting experiments where chemicals were released from the sea ice at varying
442 rates. The most hydrophobic chemicals were preferentially retained within the sea ice
443 relative to the more water soluble chemicals, and to NaCl. Physical-chemical processes
444 such as adsorption to brine inclusion walls or precipitation within brine inclusions are
445 promising explanations for this behaviour. Our results have several important implications for
446 the biogeochemical cycling of persistent organic pollutants in natural sea ice, by: (i) altering
447 the input rate of different contaminants to surface waters from melting sea ice; (ii) affecting
448 the level and retention rates of chemical contaminants in FYI and subsequent MYI, and; (iii)
449 controlling the spatial and temporal exposure of chemicals to ice-associated biota.

450

451 Tables S1 – S7 show chemical data along with associated Equations S1 – S5 and Figures
452 S1 – S4 which is available as Supporting Information (SI) to this manuscript.

453

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POP Enrichment

Sea ice depth

Sea ice

Brine

ACS Paragon Plus Environment
Seawater

POP Enrichment

Brine salinity

