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Occurrence and chemical characteristics of microplastic paint flakes in the North Atlantic Ocean

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| 4 | microplastic paint flakes in the North Atlantic Ocean |
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26 Abstract

27 Non-fibrous microplastics sampled by the Continuous Plankton Recorder (CPR) 28 Survey throughout the North Atlantic Ocean during 2018 have been recorded and a 29 selection (n = 17, or 16.7 % of non-fibrous particles collected) physically and 30 chemically characterized. The average abundance of flakes captured by the plankton silks and detectable by microscopy was estimated to be around 0.01 m⁻³, with the 31 highest concentrations evident in shelf seas of northwest Europe. Amongst the 32 33 samples analysed, median size was 180 µm and, based on visible properties (e.g., 34 brittleness, layering) and infra-red spectra, all but one were identified as flakes of 35 paint. Semi-quantitative analysis by energy-dispersive X-ray fluorescence 36 spectrometry with a collimated beam revealed that six flakes from European shelf 37 seas were Cu-based antifouling formulations (without evidence of organo-Sn 38 compounds), and five with a broader geographical distribution were Pb-based 39 formulations of likely marine origin. Other elements regularly detected included Cr, 40 Fe, Ti and Zn that were present in pigments or as contaminants from the underlying 41 substrate. After fibres, paint flakes appear to be the most abundant type of 42 microplastic in the oceans that, because of the abundance and mobility of metallic 43 additives, deserve closer scientific attention. 44 45 46 Keywords: energy-dispersive XRF; paint flakes; microplastics; pigments; Atlantic 47 Ocean; metals 48

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52 Introduction

53 Microplastics as marine contaminants have come under intense scientific scrutiny 54 over the past two decades (Ng and Obbard, 2006; do Sul et al., 2013; Ruiz-Orejon et 55 al., 2016; Burkhardt-Holm and N'Guyen, 2019; Tanhua et al., 2020). Primary and 56 secondary microplastics of sub-mm dimensions are derived from an array of land-57 based and offshore sources and encompass a variety of shapes (e.g., fibres, fragments, 58 flakes, films, pellets), materials (or polymers), structures (e.g., rigid, flexible, foamed) 59 and properties (e.g., density, crystallinity, hardness). Microplastics may also exhibit 60 different surface morphologies depending on the polymer and its structure and any 61 impacts of weathering and chemical- and bio-fouling (Richard et al., 2019; Liu et al., 62 2020).

63

64 One type of microplastic that has received relatively little attention is microscopic 65 paint flakes that are generated by weathering or abrasion of coatings. Paint particles 66 are typically more angular, brittle and layered than most other types of microplastic 67 because of a relatively low polymer content (and relatively high functional additive 68 and filler content) and the application of multiple coatings to a substrate. These 69 properties result in a physico-chemical composition that is typically much more 70 heterogeneous than other plastics and one that more readily enables the migration of 71 additives from the matrix (Turner, 2021). Significantly, many contemporary and 72 historical paint additives are potentially harmful because they have antifouling or anti-73 corrosive properties (del Amo et al., 2002; Takahashi et al., 2012). 74

75 In the recent literature, paint flakes have been identified amongst microplastics

sampled in the marine environment and from the digestive tracts of marine animals

(Cardoza et al., 2018; Aliabad et al., 2019; Herrera et al., 2019; Lacerda et al., 2019),
with some studies suggesting that paint might be the dominant form of microdebris at
or near the sea surface (Lima et al., 2014; Kang et al., 2015). It is generally assumed
or implied that paint particles are derived from shipping activities, although this is
difficult to establish without chemical characterisation of the material by, for example,
pyrolysis-gas chromatography-mass spectrometry (Dibke et al., 2021; Lee et al.,
2021).

84

85 An alternative means of non-destructively characterising microscopic paint flakes is 86 to determine the elemental (e.g., pigment) content of samples by energy-dispersive X-87 ray techniques. X-ray spectroscopy coupled with scanning electron microscopy (EDS-88 SEM) can be used to semi-quantitatively characterise elements of relatively low 89 secondary X-ray energies at the 0.1% level, but the higher excitation energies and 90 larger irradiation areas make X-ray fluorescence (XRF) spectroscopy more suited to 91 analysing heavier metals at lower concentrations in more inhomogeneous samples. 92 93 In the present study, microplastics retrieved from plankton trawls towed throughout 94 different regions of the North Atlantic region are examined to determine the presence 95 and significance of microscopic paint flakes, and information on the chemical 96 characteristics and origin of the particles is gained by Fourier transform infrared 97 (FTIR) and energy-dispersive XRF analyses. The more general capability of the latter 98 technique to quantify the metal (hence, pigment) content of microplastic paint flakes 99 is also explored in a series of tests in which paint particle diameters are successively 100 reduced.

101

102 Materials and methods

103 Sampling and the CPR

104 Microplastic samples were collected by analysts recording and cataloguing the 105 contents of silks as part of the Continuous Plankton Recorder (CPR) Survey at the 106 Marine Biological Association. The majority of microplastics identified within the 107 CPR Survey in the past have been fibrous in nature, partly because of their ease of 108 identification (Thompson et al., 2004; Sadri, 2015). Here, however, analysts were 109 instructed to record plastics that were non-fibrous (that is, fragments or flakes, and 110 hereafter referred to as "flakes") during their routine examinations, and to retrieve 111 selected samples for further characterisation.

112

113 The CPR is described comprehensively by Richardson et al. (2006). Briefly, the 114 device itself is approximately 1 m in length and is towed behind commercial vessels throughout the North Atlantic and farther afield at a speed of up to 10 m s^{-1} and a 115 depth of about 7 m. Seawater passes through a square aperture of 1.6 cm^2 and 116 117 plankton (and microplastics) are filtered onto a slowly moving band of silk (270-µm 118 mesh size) driven by a propeller-gearbox. The silk is covered with a second band of 119 moving silk and the contents are spooled into a storage tank containing formalin. In 120 the laboratory, the filtering silk is unwound and divided into sections representing 10 121 nautical miles of tow (equivalent to approximately 3 m³ of water filtered), with the 122 time and location of a section derived from the ship's route and speed and the rate of 123 silk advance within the device. Sections of silk are examined on a mobile sliding glass 124 stage housed inside a ventilated fume cupboard, using a binocular compound bright field microscope at 50 x and 500 x magnification coupled with a circular counting 125 126 reticule measuring 2 mm and 0.295 mm in diameter, respectively (Sadri, 2015).

127 Larger planktonic organisms (and microplastics) are inspected under a lower128 magnification stereo dissecting microscope.

129

| 130 | Although the CPR sampling method is described as semi-quantitative due to the |
|-----|---|
| 131 | relatively large mesh-size and small aperture, it captures a consistent fraction of |
| 132 | particles within the water column (Richardson et al., 2006). Currently there is not a |
| 133 | standardised NMBAQC (NE Atlantic Marine Biological Analytical Quality Control |
| 134 | Scheme) protocol for microplastic enumeration. However, the skilled team of CPR |
| 135 | analysts follow the OSPAR (Oslo-Paris Convention for the Protection of the Marine |
| 136 | Environment of the North-East Atlantic) guidelines recording the size, shape and |
| 137 | colour (Maes et al., 2017). Compared to a Manta net trawl (typically used for |
| 138 | sampling microplastics), the CPR captures fewer particles when assessed by number |
| 139 | of items. However, when standardised by the volume of water sampled, CPR samples |
| 140 | and Manta trawl samples yield values that are not significantly different from each |
| 141 | other (Sadri, 2015). |
| | |

142

143 Microplastic analysis

144 Seventeen microplastic flakes from various tows conducted in different regions of the North Atlantic in 2018 (and mainly during late summer) were retrieved using a pair of 145 146 stork-billed, fine-pointed forceps and placed in the centre of individual 47-mm 147 diameter Whatman filter papers. Filters were folded twice and stored in petri dishes 148 that were sealed with clear adhesive tape. Flakes were first examined and 149 photographed while on their filter papers under a Nikon SMZ800 stereo-microscope 150 in order to estimate particle size and observe any surface or structural features. Samples removed from their filters were subsequently characterised for chemical 151

152 composition by energy-dispersive XRF spectrometry and as described below, before 153 the polymers were identified by FTIR spectroscopy. For FTIR analysis, flakes were 154 clamped down on to the diamond crystal of a Bruker ALPHA Platinum attenuated 155 total reflection QuickSnap A220/D-01 spectrometer. Measurements consisted of 16 156 scans in the range 4000 to 400 cm⁻¹ and at a resolution of 4 cm⁻¹. Polymer 157 identification involved a comparison of sample transmittance spectra with libraries of 158 reference spectra and a hit quality criterion of > 70%. 159

160 XRF analysis

161 Analysis by energy-dispersive XRF was accomplished using a Niton XL3t 950 He 162 GOLDD+ portable instrument housed, nose upwards, in a laboratory accessory stand and activated remotely by a laptop. With the aid of stainless steel precision tweezers, 163 164 flakes were placed centrally over the detector window on 3.6 µm Mylar polyester film 165 (Chemplex Industries, FL). Positioning was facilitated and particle size independently 166 estimated with the aid of real-time imagery generated by a CCD camera within the detector window and a central, circular reticule of 3 mm that were both projected to 167 168 the laptop via Niton software.

169

The XRF spectrometer was operated in a low density 'plastics' mode through a standard-less, fundamental parameters-based alpha coefficient correction model. This mode incorporates a thickness correction algorithm that accounts for the limited mass absorption of X-rays by polymers (flakes in the present study were assumed to have a thickness of 100 µm) and is able to detect 18 elements. The instrument's small-spot facility was employed throughout, whereby the primary X-ray beam is collimated to a diameter of 3 mm at the detector window (and defined by the circular reticule).

177 Secondary sample X-rays were counted for a period of 90 seconds, and during

178 successive periods of irradiation at 50 kV and 40 μA (70 seconds) and 20 kV and 100

179 μA (20 seconds). Spectra were quantified by fundamental parameters to yield

180 elemental concentrations on a dry weight basis (in mg kg⁻¹) and a counting error of

181 2σ (95% confidence).

182

183 XRF performance testing on microplastics

184 Given that the area of the flakes analysed by XRF (up to ~ 0.2 mm^2) are considerably smaller than the reticule and collimated beam area of the detector window (7.1 mm²), 185 186 the performance of the instrument was evaluated by determining elemental 187 concentrations in plastics whose sizes encompassed this range. The results of tests 188 undertaken on polyethylene and polyvinyl chloride cut to different sizes are reported 189 elsewhere (Turner, 2017) while tests specifically performed on paint flakes are 190 described as follows. Three samples of marine paint were acquired from the wooden 191 hulls of two abandoned boats and the deck of a third abandoned boat in Hooe Lake 192 (Plym estuary, SW Devon), and one sample of external decorative paint was sourced 193 from a metal downpipe attached to the side wall of a domestic property in the city 194 centre of Plymouth. Individual flakes that completely covered the reticule were 195 analysed by XRF according to the operating conditions above before they were placed 196 on Mylar film on a white benchtop and crushed with the handle of a pair of stainless 197 steel tweezers. The tweezers were then used to pick out flakes of different sizes (n = 4198 to 6) which were transferred, on the polyester film, to the steel base plate of the 199 accessory stand. Each flake was analysed after carefully moving the film to align the 200 central point of the sample into the centre of the reticule and detector window (Figure 201 1).



209 Figure 1: (a) A sample of boat paint on the XRF detector window and covering

210 $\,$ the area defined by the 3-mm reticule, and (b) a flake of about 700 μm in

211 diameter generated by crushing the sample and centred in the 3-mm reticule.

212

213 **Results and Discussion**

214 Distribution of flakes

Figure 2 shows the routes of the CPR tows undertaken during 2018, along with the

216 distribution of microplastic flakes that were recorded and flakes that were retrieved

217 for characterisation. Flakes were observed in all tows and all regions sampled, but

appeared to be more densely distributed around the shelf seas of northwest Europe.

219 Overall, flakes were reported in about 2.8% (102) of all silks (3611) analysed. This

compares with fibres or stands observed in 48.8% (1763) of silks.



Figure 2: CPR samples in the North Atlantic for the year 2018 (overlapping and
continuous yellow circles), locations where flakes were observed (red circles),
and location of flakes analysed within this study (black stars).

226

236

227 Physical and polymeric characteristics of microplastic flakes

228 The locations and dates of the silks capturing the 17 flake samples characterised in the 229 present study are shown in Table 1, along with the size of each particle (d, defined as230 the average of the largest and smallest diameter measured under the microscope) and, 231 where recorded or evident, its colour. Median particle size was 180 µm, and the 232 majority of particles were smaller than the mesh size of the silks (270 μ m). This may 233 be attributed to the variable aspect ratios of some flakes and, more generally, the 234 gradual clogging of the mesh by gelatinous forms of phytoplankton and zooplankton 235 that act to reduce the effective pore size of the silk (Richardson et al., 2006).

237 Table 1: Characteristics of the flake samples and locations and dates of collection

| sample # location | | latitude | longitude | date | <i>d</i> , μm | type | colour | polymer |
|-------------------|--------------------------|----------|-----------|--------|---------------|---------|-------------|----------------------------|
| 1 | Labrador Sea | 50.827 | -46.888 | Sep-18 | 1100 | plastic | white | polyethylene terephthalate |
| 2 | Southern North Sea | 53.247 | 1.127 | Aug-18 | 230 | paint | black | alkyd |
| 3 | Skagerrak | 56.81 | 7.97 | Aug-18 | 230 | paint | silver | |
| 4 | Labrador Sea | 57.067 | -36.853 | Aug-18 | 100 | paint | black | |
| 5 | Barents Sea | 74.64 | 15.837 | Sep-18 | 90 | paint | blue | alkyd |
| 6 | Skagerrak | 57.635 | 9.853 | Aug-18 | 210 | paint | blue | ероху |
| 7 | Southern North Sea | 52.83 | 3.807 | Aug-18 | 320 | paint | pink-yellow | chlorinated rubber |
| 8 | Northern North Sea | 60.628 | -3.602 | Sep-18 | 110 | paint | nd | |
| 9 | Norwegian Sea | 70.525 | 19.175 | Apr-18 | 190 | paint | nd | |
| 10 | Northeast Atlantic Ocean | 61.828 | -6.057 | Aug-18 | 80 | paint | black | |
| 11 | Central North Sea | 54.837 | 5.737 | Aug-18 | 230 | paint | black | alkyd |
| 12 | Southern North Sea | 54.267 | 5.14 | Aug-18 | 160 | paint | blue | |
| 13 | Irish Sea | 53.517 | -5.082 | Aug-18 | 200 | paint | blue | |
| 14 | Nova Scotia coast | 44.14 | -63.718 | Aug-18 | 180 | paint | blue | chlorinated rubber |
| 15 | Faroe-Iceland Rise | 64.688 | -12.063 | Aug-18 | 70 | paint | black | |
| 16 | Skagerrak | 57.765 | 10.407 | Aug-18 | 180 | paint | blue | |
| 17 | Nova Scotia coast | 43.4 | -64.897 | Aug-18 | 60 | paint | blue | |

238 (**nd** = **not** determined).

240

239

| 241 | Visual inspection of microplastic flakes and their response to handling with tweezers |
|-----|---|
| 242 | or clamping onto the diamond crystal of the FTIR allowed ready discrimination |
| 243 | between thermoplastics and paints, with the latter distinctly brittle, more angular and |
| 244 | irregular, and often multi-coloured and layered. Overall, and as indicated in Table 1, |
| 245 | just one sample was thermoplastic (a white fragment of polyethylene terephthalate; # |
| 246 | 1) and the remainder were paint flakes of various colours whose resins were alkyd-, |
| 247 | epoxy- or chlorinated rubber-based. (Note that FTIR analysis of paints was |
| 248 | incomplete as many samples were too small or fragile to withstand clamping on the |
| 249 | crystal.) |
| 250 | |
| 251 | XRF performance on microplastic paint flakes |
| 252 | Because the majority of microplastics retrieved from the North Atlantic region were |

253 paint-based, a critical component of the study was an evaluation of the response of the

- 254 XRF spectrometer to paint particles of a comparable size. Figure 3 shows the
- concentration of different elements in four paints reported by the instrument as flake

| 256 | size (d) is reduced from > 4 mm to < 250 μ m. Thus, as the area occupied by the |
|-----|--|
| 257 | sample within the X-ray beam area was reduced, the counts registered by the detector |
| 258 | decreased and the counting error (and detection limit) increased, but variable changes |
| 259 | in elemental concentrations were returned by fundamental parameters that appeared to |
| 260 | be sample- and element-specific. In many cases, a decreasing concentration occurs |
| 261 | with a reduction in flake size that is either continuous (e.g. Cl and Fe in paint a, Sn in |
| 262 | paints b and c, Cu and Zn in paint c) or occurs over a relatively small size range (e.g. |
| 263 | Cr and Ti in paint a, Cu and Zn in paint b). In other cases, concentration appears to be |
| 264 | independent of particle size (e.g. Fe and Pb in paint c, Ba, Pb, Zn in paint d) or |
| 265 | increases with decreasing flake size (Ba in paints a and b). The precise causes of these |
| 266 | different responses are unknown but could be related to variations in sample |
| 267 | thickness, layering, binder content or absolute (true) elemental concentrations |
| 268 | (measured at $d > 4$ mm), or to differences in secondary X-ray energies amongst the |
| 269 | elements considered. Nevertheless, the results of this experiment reveal that no false |
| 270 | positives arise as flake size is reduced, and that a semi-quantitative assessment of |
| 271 | elemental composition of microscopic paint particles can be gained from the data |
| 272 | returned and the trends observed in Figure 3. |









277 paints as flake size is reduced. Black = Pb; white = Ti; grey = Ba; green = Zn;

278 blue = Cu; red = Sn; yellow = Fe; brown = Cr. Error bars represent two

279 counting errors and < denotes not detected (and shown above the circle defining



- 281
- 282

Table 2: Results of XRF analysis of the microplastic flakes retrieved from the

284 plankton silks. Concentrations (in bold) and detection limits (<) are in mg kg⁻¹

and errors represent one standard deviation about the mean of five

286 determinations undertaken at different positions and orientations within the 3-

287 mm reticule (an asterisk denotes that the element was detected once amongst the

288 replicates).

| | sample # | Ва | Cu | Cr | Fe | Pb | Sn | Ti | Zn |
|---|----------|--------|------------------|-------------------|-------------------|---------------------|-------|-------------------|-------------------|
| | 1 | <2060 | <56.4 | <10.5 | 93.9 | <46.8 | 387 | 24500 | 87.2 |
| | 2 | <10800 | 3210 | <71.0 | 2290 | <782 | <1250 | 1560 | 37400 |
| | 3 | 7900* | <435 | <42.6 | 2850 <u>+</u> 810 | <206 | <1210 | 5440 <u>+</u> 413 | 2000 <u>+</u> 357 |
| | 4 | <1770 | <65.4 | 41.9 | <74.7 | <51.3 | <278 | <7.0 | 139 |
| | 5 | <18600 | <956 | <201 | 31700 | <321 | <1900 | 71400 | <1030 |
| | 6 | 9770 | 1310 | 81.9 | 783 | 2670 | <875 | <36.6 | 6970 |
| | 7 | <30000 | 2060 | 121 | 4970 | 1220 | <421 | 407 | 11400 |
| | 8 | <2670 | <114 | 51.6 | 1220 | <84.5 | <428 | 1220 | <60.8 |
| | 9 | <11700 | <548 | <77.1 | <808 | <675 | <1450 | 8240 | <427 |
| | 10 | <3010 | <130 | 68.9 | <104 | 4690 | <427 | 30.0 | <95.1 |
| | 11 | 7510* | 824 <u>+</u> 265 | 617 <u>+</u> 78.6 | 3720 <u>+</u> 580 | 264* | <825 | 3900 <u>+</u> 384 | 4550 <u>+</u> 620 |
| | 12 | <1980 | <75.2 | 57.0 | <61.6 | <51.6 | <281 | 7.5 | 972 |
| | 13 | <1860 | <58.6 | 64.8 | <70.9 | <55.2 | <273 | 23.4 | 218 |
| | 14 | 1630 | <52.9 | 33.3 | 426 | <27.5 | <216 | 2140 | 201 |
| | 15 | 2320* | <86.0 | 65.1 <u>+</u> 8.1 | <56.7 | 17300 <u>+</u> 3650 | <261 | 15.7 <u>+</u> 6.4 | <38.2 |
| | 16 | <4800 | 6960 | 34.8 | 1060 | 29000 | <738 | 31.3 | 5530 |
| _ | 17 | <1800 | <67.9 | 56.1 | 161 | <42.9 | <263 | <6.6 | 272 |

290

289

291 Elemental profiles of microplastic flakes

The results of the XRF analysis of the microplastics retrieved from CPR tows in the North Atlantic are shown in Table 2. The data reveal the heterogeneity of the analyte concentrations and detection limits, both between elements and, for a given element, between samples, but a repeatability when the same sample is positioned differently that is usually better than 20%. Copper was detected in five paint samples at concentrations up to about 7000 mg kg⁻¹, with the information in Figure 3 suggesting that the true concentrations are likely to be significantly higher. Tin was only detected

| 300 | are variable but, according to Figure 3, are likely to be representative of true values. |
|-----|---|
| 301 | Chromium, Fe, Ti and Zn were detected in at least 11 samples with concentrations |
| 302 | that are likely to be underestimates. |
| 303 | |
| 304 | By comparison, Song et al. (2014) report concentrations of Cu, Fe, Pb and Zn of |
| 305 | 29,000, 129,000, 73,000 and 17,000 mg kg ⁻¹ , respectively, in alkyd-based paint |
| 306 | particles retrieved from the sea surface microlayer of coastal Korea. However, while |
| 307 | the authors mention screening by "energy dispersive X-ray", no analytical details or |
| 308 | constraints are provided and it is not clear whether concentrations represent an |
| 309 | average of multiple samples or a single value arising from the analysis of a composite. |
| 310 | |
| 011 | |

in the thermoplastic sample and Pb was detected in six paints at concentrations that

Table 3: Chemical characteristics of the paint flakes inferred from the

312 information in Table 2. Filler and pigments are defined by concentrations

313 exceeding 1000 mg kg⁻¹.

| | antifouling | antifouling | | | | | | |
|----------|-------------|-------------|-----------|-------------|------------|------------|------------|------------------|
| sample # | (Cu-based) | (TBT-based) | Ba filler | Fe pigment* | Pb pigment | Ti pigment | Zn pigment | Cr contamination |
| 2 | ✓ | | | ✓ | | ✓ | ✓ | |
| 3 | | | ✓ | ✓ | | ✓ | ✓ | |
| 4 | | | | | | | | ✓ |
| 5 | | | | ✓ | | ✓ | | |
| 6 | ✓ | | ✓ | | ✓ | | ✓ | ✓ |
| 7 | ✓ | | | ✓ | ✓ | | ✓ | ✓ |
| 8 | | | | ✓ | | ✓ | | ✓ |
| 9 | | | | | | ~ | | |
| 10 | | | ~ | | ~ | | | ~ |
| 11 | ~ | | ~ | ✓ | | ~ | ~ | ~ |
| 12 | | | | | | | | ✓ |
| 13 | | | | | | | | ✓ |
| 14 | | | ~ | | | ~ | | ✓ |
| 15 | | | ~ | | ~ | | | ✓ |
| 16 | ~ | | | ~ | ~ | | ~ | ✓ |
| 17 | | | | | | | | ✓ |

314

- 315 *It is suspected that Fe may also be present as a contaminant from the
- 317

318 Types of microplastic paint flakes

underlying (metallic) substrate.

319 Despite the uncertainties in the absolute metal concentrations reported here, coupled 320 with variable analytical performances for different elements, the XRF data enable the 321 broad chemical characteristics of the samples to be defined. Table 3 provides these 322 characteristics for the paint particles, with the assumptions that a pigment or filler is present at a measured concentration of $> 1000 \text{ mg kg}^{-1}$ and the detection of Cu or Sn 323 324 denotes an antifouling formulation based on compounds of Cu(I) and/or organotin. 325 Note that presence of Cr is indicated as evidence of contamination by a Cr-based 326 primer, and while Fe is included as a pigment, it is possible that the presence of this 327 element also reflects contamination of the paint from corroded fragments of an

328 underlying steel substrate.

329

330 Overall, we infer that six flakes of various colours and sampled from the shelf seas 331 around northwest Europe are Cu-based antifouling flakes, with none of these samples 332 exhibiting evidence of organotin-based antifouling agents. The highest concentrations 333 of Zn were associated with detectable Cu, consistent with the common use of ZnO in 334 Cu-based antifouling paints to improve performance and control erosion rates 335 (Lindgren et al., 2018), but its presence in other samples suggests a wider use as a 336 pigment in primers and topcoats. Five paint samples contained appreciable quantities 337 of Pb, including three antifouling fragments (sample #s 6, 7, 16), that exhibited a 338 broad distribution throughout the Atlantic. Lead associated with Cu may represent 339 historical antifouling formulations in which inorganic or organo-lead compounds were

340 combined with Cu(I) (Cardarelli, 1976). However, it is more likely that the co-341 existence of these elements reflects distinct layers of a Cu-based antifouling 342 formulation and a Pb-based anticorrosive steel primer (e.g., red lead). Sample #7 was 343 sufficiently large and flat to analyse both faces by XRF and the results revealed 344 distinctly different Cu:Pb concentration ratios (about 1.8 and 0.6). Clearly, X-ray 345 attenuation is limited in paint of this thickness but the results suggest that layering 346 was present in this case. More generally, it is suspected that the presence of small but 347 variable quantities of Cr arise from the heterogeneous contamination of antifouling 348 layers and other surface coatings by underlying basic chromated primers. Lead in the 349 absence of Cu is consistent with the presence of leaded marine paint used above the 350 water-line on wood or steel. Booher (1988) reports a geometric mean concentration of Pb in ship paints of 2500 mg kg⁻¹ and, although Pb pigments have since been 351 352 restricted, historical, extant formulations in various conditions are still likely to be 353 present (Hall, 2006; Driscoll et al., 2016).

354

355 Origin and abundance of microplastic paint flakes

356 The implication of the discussion above is that the microscopic paint flakes retrieved 357 from the plankton silks are derived from the hulls and other painted components of 358 ships mobilised in the Atlantic region. Without information on the types of 359 formulations employed on the commercial ships towing the CPR devices, it is not 360 possible to ascertain whether samples were derived from these or other vessels. 361 However, the visual and chemical characteristics of paint applied to the steel frame of 362 a CPR device in storage (silver flakes with measurable Ba, Fe, Ti and Zn but no 363 detectable Cr) suggest that one sample (# 3) was derived from material shed from the 364 structure itself during sampling or silk retrieval. Inferences in the marine literature

365 regarding paint sources are varied, with some investigations matching sample colours

and infra-red spectra to those of paint flaking from the trawl frame or research vessel

367 (Bagaev et al., 2017; Lacerda et al., 2019) and other studies highlighting the

importance of pre-existent paint particles (Song et al., 2014; Dibke et al., 2021).

369

370 Another potential source of paint samples trawled from the ocean is land-based inputs of weathered building and road coating particles via rivers, treated municipal sewage, 371 372 untreated road runoff and the atmosphere. Estimates based on paint usage suggest that 373 inputs to surface waters from this source should exceed inputs from marine paints 374 (Hann et al., 2018). However, it is unlikely that particles as dense as dried paint formulations (up to about 3 g cm⁻³; Ruble, 2002; Brockenbrough, 2009) and of the 375 376 sizes typically trawled from the marine environment (a few hundred microns; Kang et 377 al., 2015; Bagaev et al., 2017; Aliabad et al., 2019) are able to undergo long-range 378 transportation in the surface of the ocean. For example, experiments performed by 379 Soroldoni et al. (2018) showed that antifouling paint particles exceeding 1 mm in 380 diameter settle in estuarine water according to density and size, and below 180 µm in 381 diameter remain at the surface without agitation but settle after the surface tension is 382 broken. In theory, therefore, and based on chemical characteristics of trawled particles 383 reported here and elsewhere (Song et al., 2014; Dibke et al., 2021), shipping activities 384 (including hull corrosion, and weathering and abrasion of ship paints above the 385 waterline and paints applied to containers) would appear to be the dominant source of 386 paint flakes in the ocean.

387

388 The data obtained in the present study allow us to estimate the absolute and relative389 abundance of paint flakes in the North Atlantic Ocean. Thus, during 2018, a total of

390 102 flakes were recorded amongst 3611 silk samples, with each silk filtering about 3 m^3 of seawater. This is equivalent to a mean concentration of about 0.01 paint flakes 391 392 per m³, assuming that all non-fibrous microplastics are paint-based, and compares 393 with an estimated concentration of about 0.16 microplastic fibres per m³. It must be 394 appreciated that both estimates are subject to uncertainty because of constraints on 395 silk efficiency (Richardson et al., 2006) and, with respect to flakes, underestimation 396 because of difficulties in their identification, the existence of finer particles that evade 397 capture and the negative buoyancy of most paint formulations. Regarding size 398 distribution, for example, Kang et al. (2015) found a two-order of magnitude increase 399 in paint particle abundance off the Korean coast when a 330 µm Mantra net was 400 replaced with a 50 µm hand net. Nevertheless, the observations of this study add to 401 the emerging literature in the area suggesting that paint particles represent a 402 significant, yet understudied fraction of the microplastic stock suspended in the ocean 403 (Dibke et al., 2021; Gaylarde et al., 2021).

404

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