

## 36 Instrumental analyses

- 37 *PIGE Data normalization.*
- 38 Several measures were taken to ensure that data acquired at Hope College in 2016, and at the
- 39 University of Notre Dame in 2020 are compatible. Sets of data from each time period were
- 40 normalized to one another by comparing the total F counts given from sets of fluorinated paper
- 41 samples analyzed at both locations/times. Samples with total F counts near or below the LOD for
- 42 PIGE (highlighted gray in Table S3) were excluded from the average calculation. The coefficient
- 43 of determination for 2016 vs 2020 was  $r^2 = 0.9628$  and for 2018 vs 2020  $r^2 = 0.9976$ , signaling a 44 small variance between the total F counts of samples taken at separate time points. The average
- 45 conversion factor for each set revealed that PIGE total F counts from ND2020 were  $2.7\pm0.4$
- 46 times higher than Hope2016 and  $2.2\pm0.2$  times higher than ND2018 (see Table S3) as detector
- 
- 47 efficiency and beam optimization occurred. These factors were used to normalize PIGE counts
- 48 from Hope2016 and ND2018 to the same scale as ND2020.
- 49 50 *PIGE Analysis*
- 51 Additional information on PIGE instrumentation and analysis is reported elsewhere.<sup>1-4</sup> At both
- 52 facilities/times a blank target frame was measured for each batch of  $\sim$  50-60 samples to confirm a
- 53 clean background. Each sample was irradiated with approximately 10-50 nanoamperes of 3.4 or
- 54 3.9 megaelectron-volts (MeV) protons for 180 seconds. The beam was extracted *ex vacuo*
- 55 through a thin (8 µm) Kapton® foil and impinged on each target in air, through the center hole of
- 56 each target frame. The characteristic gamma-rays emitted from the de-excitation of <sup>19</sup>F at 110
- 57 keV and 197 keV had background-subtracted integrations summed for each sample irradiation. 58 In addition, all the data collected in a day (typically one or two batches) were normalized to the
- 59 770 keV gamma ray that comes from the interaction of the beam on air before it strikes the
- 60 target.<sup>2</sup> In order to transform the argon-normalized integrated gamma-ray counts in the 110 and
- 61 197 keV peaks per microcoulomb of beam on target (counts/ $\mu$ C) into a F concentration in  $\mu$ g
- 62 F/cm<sup>2</sup> , a set of paper-based external inorganic fluorine standards were utilized. Solutions of
- 63 sodium fluoride were prepared at concentrations from 0-750 µg/mL. 0.3 mL of prepared
- 64 solutions were pipetted onto 42.5 mm diameter Whatman 1 filter papers (Cat No. 1001-042). The 65 papers were allowed to dry and the amount of fluorine added was calculated as the µg of fluorine
- 66 added per the area of the paper circles. The concentrations in  $\mu$ g F/cm<sup>2</sup> were plotted against the
- 67 argon-normalized counts per microcoulomb for each standard and a linear fit was applied. The
- 68 LINEST function was used on these standards to determine the limit of detection (LOD) and
- 69 limit of quantification (LOQ) for PIGE analysis of total F (see Figure S1). The LOD was
- 70 calculated as 3.3 times the standard error in the response divided by the slope. LOQ was
- 71 calculated as 10 times the standard error in the response divided by the slope. The LOD and
- 72 LOQ were found to be 0.127 and 0.384  $\mu$ g F/cm<sup>2</sup> respectively and these values were utilized to
- 73 define a sample as containing low F (<0.127  $\mu$ g F/cm<sup>2</sup>), moderate F (>0.127, <0.384  $\mu$ g F/cm<sup>2</sup>
- 74 ), and high F  $>0.384 \,\mu g \,$  F/cm<sup>2</sup>).
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## 76 *Targeted Analysis using LC-MS/MS and GC-MS*

- 77 50-100 mg of product was spiked with surrogate standards before sonicating twice with 3 mL of
- 78 4:1 hexane-isopropanol and twice with 3 mL of 1:1 methanol-acetonitrile. Supernatants were
- 79 combined and concentrated to a final volume of 5 mL under nitrogen. Concentrates were
- 80 vortexed and centrifuged with 100 mg of Envi-Carb for clean-up, concentrated again under
- 81 nitrogen, and filtered. Filtrate was transferred to polypropylene vials and spiked with internal

82 standards for quantitation. LC-MS/MS analysis was done using an ultrahigh performance LC

- 83 coupled with a triple-quadrupole MS (Agilent 1290 Infinity II UPLC 6470 QQQ-MS) in
- 84 negative electrospray ionization mode. GC-MS analysis was performed on an Agilent 7890 GC –
- 85 5977B PCI-MS operated in the positive chemical ionization mode. Additional instrumental 86 parameters can be found in the Supporting Information of Wu *et al.* (2020).<sup>5</sup> A procedural blank
- 87 and a matrix spike sample were processed along with each batch samples to evaluate possible
- 88 contamination from laboratory operations and the performance of our method. The recoveries of
- 89 surrogate standards were all in the range of 60-130%. Samples were corrected for recovery using
- 90 the appropriate surrogate standards (see Table S7). After this correction, matrix spike recoveries
- 91 of individual analytes were all within 80-115%. Additionally, data reported in this study were
- 92 blank corrected by subtracting the corresponding average blank on a mass basis. The Method
- 93 Detection Limits (MDLs) were defined as the average procedural blank  $+3 \times$  standard deviation 94  $(n = 5)$  or the amount of chemical generating a signal-to-noise of 5 if the compound was not
- 95 detected in the procedural blanks.
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## 98 *Collection and analysis of ingredient labels chosen for targeted analysis*

99 Ingredient lists were collected for the U.S. products chosen for targeted analysis. Ingredient lists 100 for each product were accessed online in 2020-2021 from the retailers where products were 101 purchased. Information on the chemical structures, properties and described uses of ingredients 102 were determined using INCIDecoder.com and EWG's Skin Deep database.<sup>6, 7</sup> Publicly available 103 industrial reports and brochures were also utilized. All ingredients were tabulated, including 104 those listed as "may or may not be present". Tables S14-S16 below focus on these results. Table 105 S14 lists the 62 ingredients and their described use in cosmetics that were reported at least two 106 times on the ingredient lists of U.S. products selected for targeted analysis. The remaining 104 107 ingredients were only detected once and are given in Table S15. Table S16 gives a heatmap 108 relating all ingredients listed in the U.S. products selected for targeted analysis to the number of 109 times the ingredient was found in each category of F concentrations identified by PIGE. This 110 heatmap reveals both fluorine-free and fluorinated ingredients that were found in nearly all 111 products surveyed. Ingredients such as water, isododecane, and phenoxyethanol were commonly 112 found in all categories of F concentrations but are unlikely to be fluorinated. These represent 113 ingredients that are likely essential to the composition of cosmetic products. Probable inorganic 114 sources of fluorine include disteardimonium hectorite and synthetic fluorphlogopite, both of

- 115 which were more commonly found in products with high F concentrations. Ingredients such as
- 116 methicone and dimethicone, acrylate and methacrylate, and silicone polymers were commonly
- 117 reported. Fluorinated versions of these ingredients have been reported in literature as shown in
- 118 Table S14. Many ingredient labels contained polymeric compounds unique to that product but
- 119 have chemical structures similar to the generalized methicone, dimethicone, acrylate,
- 120 methacrylate, and silicone polymers reported on multiple products.

121 Table S1. Breakdown of cosmetic categories tested based on the category description and the types of products surveyed in that category. Products were assigned to a category based on the 122 types of products surveyed in that category. Products were assigned to a category based on the

123 intended use of the product as defined by the manufacturer.

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126 Table S2. List of cosmetic brands and cosmetic category of the products selected for PIGE

127 analysis. See Table S1 for a breakdown of cosmetic category codes. Brands for all products are

128 shown below, including those for products that showed low, moderate, and high fluorine levels.

129 On some occasions one cosmetic category contained multiple products from the same brand for

130 analysis. The table below does not contain information on the frequency any individual brand

131 was tested, or the individual product names or shades selected for analysis. Brands with 132 individual products that were entirely collected in Canada are highlighted in green. Brands with

133 individual products collected in both Canada and the U.S. are highlighted in yellow.

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138 Table S3. Data utilized to normalize PIGE data sets collected at Hope College (2016), and Notre<br>139 Dame at two different time points (2018 and 2020). Samples where the conversion factor is

139 Dame at two different time points (2018 and 2020). Samples where the conversion factor is given as N/A are those whose counts are below the detection limit for PIGE.

given as  $N/A$  are those whose counts are below the detection limit for PIGE.

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147 Figure S1. Plot of fluorine concentrations in  $\mu$ g F/cm<sup>2</sup> versus the argon-normalized counts per 148 microcoulomb with a linear regression. The regression function was used to determine the LOD 149 and LOQ. 5 replicate runs of a paper standard at 2.87 µg F/cm<sup>2</sup> were used to determine the 150 precision and accuracy. The relative standard deviation among these samples was 18.6% and the 151 measured concentration was found to be 0.8% different than the expected concentration.  $152$ 



157 Table S4. List of analytes included in targeted analysis for both LC-MS/MS and GC-MS along with their Instrument Detection Limits (IDL). A description of the calculation of Method Detection Limits (MDLs) are given in t

158 (IDL). A description of the calculation of Method Detection Limits (MDLs) are given in the Instrumental Analyses section above. The

159 MDLs ranged from 0.01 ng/g for pefluoropentanesulfonic acid (PFPeS) to 12.0 ng/g for 2-perfluorooctyl ethanol (8:2) (8:2 FTOH

















## Table S6: List of targeted PFAS measured by GC-MS. 164<br>165



Native PFASs SS for correction IS for quantitation Surrogate standards IS for quantitation PFPrA M3PFBA MPFBA M3PFBA MPFBA PFBA | M3PFBA | MPFBA | MPFHxA | M8PFOA PFPeA M3PFBA MPFBA MPFOA M8PFOA PFHxA | MPFHxA | M8PFOA | MPFUnDA | M7PFUnDA PFHpA MPFHxA M8PFOA M2PFTeDA M7PFUnDA PFOA | MPFOA | M8PFOA | M3PFBS | M3PFHxS PFNA | MPFOA | M8PFOA | MPFHxS | M3PFHxS PFDA | MPFUnDA | M7PFUnDA | MPFOS | M8PFOS PFUnDA | MPFUnDA | M7PFUnDA | M2-8:2 FTCA | M8PFOA PFDoDA M2PFTeDA M7PFUnDA M2-8:2 FTSA M8PFOS PFTrDA | M2PFTeDA | M7PFUnDA | dMeFOSA | M8PFOS PFTeDA | M2PFTeDA | M7PFUnDA | M4-4:2 FTOH | M4-8:2 FTOH PFHxDA | M2PFTeDA | M7PFUnDA | M2-8:2 FTOH | M4-8:2 FTOH PFPrS M3PFBS M3PFHxS dMeFOSE M4-8:2 FTOH PFBS M3PFBS M3PFHxS M2-8:2 PAP M4-6:2 diPAP PFPeS | MPFHxS | M3PFHxS PFHxS | MPFHxS | M3PFHxS PFHpS | MPFOS | M3PFHxS PFOS | MPFOS | M8PFOS PFNS | MPFOS | M8PFOS PFDS | MPFOS | M8PFOS PFECHS | MPFOS | M8PFOS Cl-PFOS | MPFOS | M8PFOS 6:2 CI-PFESA | MPFHxS | M8PFOS 8:2 CI-PFESA | MPFOS | M8PFOS  $4:2$  FTSA  $\parallel$  M2-8:2 FTSA  $\parallel$  M3PFHxS  $6:2$  FTSA  $\parallel$  M2-8:2 FTSA  $\parallel$  M3PFHxS 8:2 FTSA | M2-8:2 FTSA | M8PFOS  $6:2$  FTCA  $\parallel$  M2-8:2 FTCA  $\parallel$  M8PFOA 8:2 FTCA | M2-8:2 FTCA | M8PFOA 10:2 FTCA | M2-8:2 FTCA | M8PFOA FBSA | M3PFBS | M3PFHxS FHxSA MPFHxS M3PFHxS FOSA MPFOS M8PFOS MeFOSA dMeFOSA M8PFOS EtFOSA | dMeFOSA | M8PFOS 4:2 FTOH M4-4:2 FTOH | M4-8:2 FTOH 6:2 FTOH M2-8:2 FTOH | M4-8:2 FTOH 8:2 FTOH M2-8:2 FTOH | M4-8:2 FTOH 10:2 FTOH | M2-8:2 FTOH | M4-8:2 FTOH MeFOSE | dMeFOSE | M4-8:2 FTOH EtFOSE dMeFOSE M4-8:2 FTOH 6:2 FTAc  $\blacksquare$  M4-4:2 FTOH  $\blacksquare$  M4-8:2 FTOH 8:2 FTAc M2-8:2 FTOH | M4-8:2 FTOH 10:2 FTAc M2-8:2 FTOH | M4-8:2 FTOH 6:2 FTMAc | M2-8:2 FTOH | M4-8:2 FTOH 8:2 FTMAc | M2-8:2 FTOH | M4-8:2 FTOH 6:2 PAP M2-8:2 PAP M4-6:2 diPAP 8:2 PAP M2-8:2 PAP M4-6:2 diPAP 6:2 diPAP M2-8:2 PAP M4-6:2 diPAP

6:2/8:2 diPAP | M2-8:2 PAP | M4-6:2 diPAP 8:2 diPAP | M2-8:2 PAP | M4-6:2 diPAP

167 Table S7: Surrogate (SS) and internal (IS) standards used to calculate PFAS concentrations.

169 Table S8. Comparison of the minimum, maximum, median, and average  $\mu$ g F/cm<sup>2</sup> value from 170 PIGE analysis of each cosmetic category.

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Category Minimum Maximum Median Average Lips (Li)  $< 0.127$  33.9 0.495 2.37 Eyes (E)  $\leq 0.127$  44.0 0.734 5.73 Foundation (F)  $\leq 0.127$  54.7 1.06 3.50 Mascara (M)  $\leq 0.127$  1140 0.120 132 Face (Fa)  $\leq 0.127$  152 0.232 6.22 Concealer (C)  $\leq 0.127$  25.7 0.113 3.67 Eyebrow (Eb)  $\leq 0.127$  15.4 0.027 3.11 Miscellaneous (Mi) <0.127 12.0 0.282 2.38

174 Figure S2. Distribution of log µg F/cm<sup>2</sup> measured using PIGE for each cosmetic category. Red 175 bars indicate the median  $\log \mu$ g F/cm<sup>2</sup> value for that category.



176 Table S9. Trends in PIGE results for cosmetic subcategories. Lip products can be split into many

177 sub-categories but primarily belong to either solid formulas (lipsticks and balms) or liquid

178 formulas (glosses, stains, and cremes). Roughly 70% (42 of 60) of lip products tested were liquid

179 formulas and of the 29 lip products determined to have high fluorine concentrations, 26 of them 180 were liquid formulas. One sub-category of mascaras is waterproof mascaras. Of the 32 mascaras

181 tested 11 (34%) were waterproof formulas. From the 15 mascaras determined to have high total

- 182 fluorine concentrations, 60% were waterproof formulas.
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187 Table S10. Comparison of the concentrations in  $\mu$ g F/cm<sup>2</sup> determined from PIGE to the

188 concentrations in µg F/g product. To calculate this, a 1cm x 1cm was chosen to approximate the

189 size of the beam from PIGE. 3 products from each cosmetic product category selected for

190 targeted analysis (lip products, foundations, and mascaras) giving a total of 9 cosmetic products. 191 For all 9 products, five 1 cm by 1 cm Whatman 1 filter paper squares were weighed both before

192 and after the addition of one layer of the cosmetic product. The difference in the before and after

193 weight was used to determine the amount of product applied, which was averaged for each

194 cosmetic product and for all products within the same cosmetic product category. For the 7

195 products that had quantifiable concentrations of total fluorine the micrograms of F per grams of

196 product were determined using the  $\mu$ g F/cm<sup>2</sup> determined from PIGE, the known 1 cm<sup>2</sup> area, and

197 the calculated average applied mass.



200 Table S11. Full results for all 12 U.S. cosmetic samples selected for targeted analysis using LC-MS/MS and GC-MS. Concentrations 201 of each analyte are given in ng/g (ppb). Cells containing values <MDL are left empty.

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204 Table S12. Full results for all 17 Canadian cosmetic samples selected for targeted analysis using LC-MS/MS and GC-MS.

205 Concentrations of each analyte are given in ng/g (ppb). Cells containing values <MDL are left empty. Samples highlighted in orange 206 do not have a replicate U.S. product.





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218 Table S14. List of ingredients and their described use in cosmetics that were reported at least two times on the ingredient lists of U.S. products selected for targeted analysis. Ingredient names highlighted green are

219 products selected for targeted analysis. Ingredient names highlighted green are those that are possible or likely a source of inorganic F. 220 Ingredient names highlighted yellow are those where industrial reports, brochures, or patents (references given) describe the use of

221 organic F (PFAS) as a treatment or that the listed ingredient has a fluorinated alternative.





![](_page_25_Picture_125.jpeg)

226 Table S15. List of ingredients cosmetics that were reported just once on the ingredient lists of U.S. products selected for targeted 227 analysis.

![](_page_26_Picture_155.jpeg)

![](_page_27_Picture_263.jpeg)

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261 Table S16. Heatmap relating all ingredients listed in the U.S. products selected for targeted analysis to the number of times the ingredient was found in each category of F concentrations identified by PIGE. The number 262 ingredient was found in each category of F concentrations identified by PIGE. The number of maximum times an ingredient could be given in each category were 4, 1, and 7 times each for Low F, Moderate F, and High F resp given in each category were 4, 1, and 7 times each for Low F, Moderate F, and High F respectively.

![](_page_28_Picture_216.jpeg)

![](_page_29_Picture_324.jpeg)

![](_page_30_Picture_336.jpeg)

![](_page_31_Picture_252.jpeg)

![](_page_32_Picture_246.jpeg)

![](_page_33_Picture_252.jpeg)

![](_page_34_Picture_85.jpeg)

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