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Tributary loading and sediment desorption as sources of PFAS to receiving waters

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23

24 **Abstract**

25 Transport of per- and polyfluoroalkyl substances (PFAS) to the Great Lakes is of great
26 importance as this large freshwater system provides drinking water to over 40 million people.
27 Tributary PFAS loading to the Great Lakes is poorly characterized and the role of sediments as a
28 source or sink of PFAS is largely unknown. We quantified 10 perfluoroalkyl acids (PFAAs) in
29 water (4 – 1,310 ng/L) and sediment (below detection to 3,255 ng/kg) of 41 tributaries to Green
30 Bay of Lake Michigan. We demonstrate that tributary discharge plays a major role in PFAS
31 contribution to receiving waters. In this system, three large rivers (i.e., Fox, Menominee, and
32 Peshtigo Rivers) contribute two-thirds of the total tributary PFAA loading to Green Bay despite
33 their relatively low concentrations and despite the current regulatory focus on sites with high
34 concentrations. Tributary PFAA composition is linked to likely sources, including a fire-fighting
35 foam manufacturer, other industrial activity, and airports. In addition to tributary discharge, we
36 show that tributary sediments can contribute to PFAA transport via desorption.
37 Perfluorooctanesulfonate rapidly desorbs from contaminated riverbed sediments when
38 equilibrated with Lake Michigan water, indicating that sediments may act as a PFAS source if
39 water concentrations are reduced by pollution mitigation methods.

40

41 **Keywords**

42 Perfluorinated substances, Great Lakes, loadings, partitioning, Green Bay

43

44 **Synopsis**

45 PFAA transport in tributaries is largely linked to tributary discharge rate and is impacted by the
46 ability of sediment to act as either a source or a sink of PFAAs.

47 **Introduction**

48 Per- and polyfluoroalkyl substances (PFAS) are a large group of synthetic chemicals that
49 have been used in applications such as cookware and fire-fighting products since the 1950s.¹⁻³
50 Many PFAS are persistent, bioaccumulative, and harmful to humans and wildlife.⁴⁻⁸
51 Perfluoroalkyl acids (PFAAs) are an important class of PFAS compounds that do not degrade
52 naturally and therefore accumulate in the environment.^{1,9-11} PFAS are the active ingredients in
53 many aqueous film-forming foams (AFFF), which are often used at military sites, airports, and
54 flammable storage facilities to extinguish petroleum-based fires.^{12,13} AFFF is a significant source
55 of environmental PFAS contamination as its use dispenses relatively high quantities of PFAS
56 directly into the environment.^{14,15} Other routes of environmental contamination include municipal
57 wastewater treatment facilities either from their effluents^{9,16,17} or from land-spreading of
58 biosolids.¹⁸⁻²⁰

59 Preventing PFAS contamination in the Laurentian Great Lakes of North America is of
60 utmost concern as it is the largest freshwater system in the world, supplies drinking water to 40
61 million people,²¹⁻²³ and supports a vibrant commercial and recreational fishery.^{21,24} The Great
62 Lakes Basin includes Lakes Superior, Michigan, Huron, Erie, and Ontario. PFAS have been
63 detected in water, sediment, and biota of the Great Lakes, with higher concentrations measured in
64 the eastern lakes.²⁵⁻²⁷ Lake Michigan has moderate PFAS concentrations and yet is understudied
65 compared to the other Great Lakes.

66 Green Bay, a major 4,210 km² embayment in the northwest side of Lake Michigan, is of
67 particular concern for contamination given potential PFAS sources in its watershed. A fire-fighting
68 products facility located in Marinette, WI has manufactured, tested, and trained with PFAS-
69 containing AFFF since the 1970s (**Figure 1**). This company started under the name of Ansul,

70 which remains as a major brand of AFFF manufactured by the current company, Tyco Fire
71 Products (Tyco) of Johnson Controls International.²⁸ Tyco first measured PFAS in groundwater at
72 the testing site in 2013, but did not publicly disclose that PFAS had migrated off site until 2017.²⁹
73 PFAS contamination attributed to activities at the Tyco facility is prevalent in the surrounding area
74 including private drinking water wells,³⁰ soil,²⁹ and surface water.³¹ Furthermore, the local
75 wastewater treatment facility has elevated PFAS in its effluent³² and biosolids.³³ Treated
76 wastewater effluent is discharged into the Menominee River, which flows into Green Bay, and
77 biosolids were land-applied on agricultural fields until 2018,³⁴ potentially distributing PFAS
78 contamination throughout the region. Other potential PFAS sources to the bay include the Fox and
79 Menominee Rivers, which both have industrial legacies,³⁵ and small airports that use or used AFFF
80 onsite.

81 The unique properties of PFAS (e.g., both hydrophobic and lipophobic moieties) make
82 their cycling and bioavailability in the environment challenging to predict. PFAS mobility in
83 stream systems can be influenced by partitioning to sediment, but the extent of partitioning
84 depends on several factors, including PFAS chain length, head group chemistry, and differences
85 in water and sediment chemistry (e.g., aqueous cation concentrations and sediment organic carbon
86 content, respectively).^{2,36-40} Sediment-water partition coefficients derived from field
87 measurements are consistently higher than those calculated in laboratory studies,⁴¹ indicating a
88 knowledge gap in partitioning behavior. Previous research shows that soils and sediments readily
89 act as a sink for some PFAS compounds.^{36,39,42,43} Several studies have suggested that irreversible
90 sorption of certain PFAS compounds can occur,⁴⁴⁻⁴⁹ but the ability of contaminated sediments to
91 serve as a PFAS source in tributaries remains unclear.

92 This study quantifies water and sediment PFAS concentrations in 41 Green Bay tributaries
93 to investigate the role of tributaries and sediments as PFAS sources to receiving waters. Green
94 Bay is an ideal location to study PFAS inputs to surface waters due to the extensive groundwater
95 contamination in the region, the variability of tributary sizes and PFAS sources around the large
96 bay, and the critical importance of this freshwater resource. Importantly, we use a mass balance
97 approach to provide the first baseflow estimates of PFAS loadings from tributaries to receiving
98 waters. We also use desorption experiments to demonstrate that riverbed sediments may act as a
99 source of PFASs following remediation efforts. This study provides insight into the fate of PFASs
100 in surface waters and has implications for managing and mitigating PFAS contamination in
101 tributaries of the Great Lakes and other freshwater systems.

102

103 **Methods and Materials**

104 **Materials.** PFAS standards were purchased from Wellington Laboratories. A list of
105 analytes, surrogates, and internal standards is shown in **Supporting Information Table S1**. Other
106 chemicals are described in **Section S1**. Ultrapure water was supplied by a Milli-Q water system
107 maintained at 18.2 M Ω ·cm.

108 **Field Sample Collection.** Samples were collected July 7-10, 2020 at 41 sites under
109 baseflow conditions with no recent storm events (**Figures 1 and S1; Table S2**). Sites included
110 tributaries associated with likely PFAS sources, all major Green Bay tributaries, and sites with
111 anticipated low concentrations to serve as background measurements. We focused on a wide range
112 of sites to assess spatial variability in loadings and sources rather than temporal variability, as
113 aqueous PFAS concentrations in this region exhibit minimal temporal variation.⁵⁰ Water samples
114 for PFAS analysis were collected by submerging a 250 mL polypropylene bottle approximately

115 15 cm below the surface to fill. Samples for other water analyses were filtered (0.45 μm nylon) on
116 site and stored in amber glass vials. A polypropylene dipper was used to retrieve riverbed sediment,
117 which was transferred to 50 mL polypropylene Falcon tubes. Only 34 of the 41 sample locations
118 had accessible sediment. Samples were stored at 4°C prior to analysis. Equipment was chosen to
119 avoid PFAS-containing materials, such as Teflon. Nitrile gloves were worn at all times and only
120 PFAS-free clothing and materials were used. See **Section S2** for quality control measures.

121 **Water Extraction, PFAA Analysis, and Characterization.** Water was analyzed for
122 seven PFCAs and three PFSAAs (**Table S1**) following EPA method 533, modified to use a shorter
123 analyte list.⁵¹ Analytes were chosen based on previous detections in this region,⁵⁰ their importance
124 in surface water regulations, and their known persistence, bioaccumulation potential, and
125 toxicity.⁴⁻⁸ Briefly, 250 mL samples were buffered using 1 g/L ammonium acetate and mass-
126 labeled surrogate standards were added. PFAA compounds were extracted by solid-phase
127 extraction (SPE) onto weak anion exchange cartridges (Phenomenex Strata X-AW) and eluted
128 with 2% ammonium hydroxide in methanol. Extracts were dried under a gentle stream of nitrogen,
129 amended with mass-labeled internal standards, and diluted to 1.0 mL with methanol:Milli-Q water
130 (80:20, v:v). Final extracts were analyzed by liquid chromatography-tandem mass spectrometry
131 (LC-MS/MS; **Sections S1** and **S2**). PFAA concentrations were adjusted based on surrogate
132 standard recovery (**Table S3**). All PFAAs measured in aqueous samples can be assumed to be
133 dissolved due to the low levels of suspended solids (5.3 ± 12.3 mg/L; 70% below detection). Using
134 field-derived partition coefficients, <1% of total aqueous concentrations is expected to be
135 associated with suspended solids in these tributaries. All reported PFAA concentrations are
136 summed linear and branched isomers unless otherwise specified. A separate water sample was

137 used for geochemical characterization, including pH, dissolved organic carbon (DOC), and cation
138 measurements (**Section S1**).

139 **Sediment Extraction, PFAA Analysis, and Characterization.** Sediment samples were
140 analyzed for the same 10 PFAAs following the protocol ASTM D7968-14.⁵² Briefly, 2g of dry
141 sediment was weighed into a 15 mL falcon tube and mass-labeled surrogate standards were added.
142 A 10 mL extraction solution of methanol:Milli-Q water (50:50, v:v) was added and samples were
143 placed on a shaker table for one hour. Samples were adjusted to pH 9-10 using ammonium
144 hydroxide, centrifuged, and filtered (0.2 μm nylon). The filtered supernatant was adjusted to pH
145 3-4 using acetic acid and analyzed by LC-MS/MS (**Section S1** and **S2**). Samples were screened
146 for acceptable surrogate recovery (**Table S4**). Additional sediment was characterized for organic
147 carbon content, point of zero charge (PZC), surface area, and metal content (**Section S1**).

148 **Laboratory PFAA Equilibrium and Desorption Experiments.** Laboratory experiments
149 were performed in sealed 50 mL falcon tubes. For equilibrium experiments, 2 g of dry sediment
150 was added to 50 mL of water from the same site and placed on a shaker table for 10 days. The
151 equilibrium time was based on information from a previous sorption study.³⁹ For desorption
152 experiments, 2 g of sediment was added to 50 mL of Lake Michigan water and placed on a shaker
153 table for up to 10 days. The tubes were centrifuged, supernatant decanted, and refilled with 50 mL
154 of Lake Michigan water every two days. Lake Michigan water served as a low-PFAA surface
155 water surrogate (**Table S8**) and was renewed to ensure it remained low in PFAAs. At the end of
156 each experiment, each tube was centrifuged, supernatant decanted, and sediment was dried at
157 60°C. The sediments were re-weighed to account for loss of colloids, extracted, and analyzed for
158 PFAAs via LC-MS/MS.

159

160 **Results & Discussion**

161 **PFAA Concentrations in Tributary Water.** The sum of measured PFAA concentrations
162 in the water range from 4 ng/L in Renard Creek to 1,310 ng/L in Ditch B (**Figures 2a** and **S2**;
163 **Table S8**). When Ditch B is excluded, the mean and median PFAA concentrations are 27 ± 15
164 ng/L and 23 ng/L, respectively. The summed PFAA concentrations at these sites are similar to
165 other rivers in the area. For example, the average summed PFAA concentrations in the Mississippi
166 and Wisconsin Rivers are 28 ± 12 ng/L (average of the same 10 PFAAs at four sites at three time
167 points) and 38 ± 16 ng/L (average of the same 10 PFAAs at three sites at three time points),
168 respectively.⁵⁰ Concentrations in Green Bay tributaries are generally higher than those reported in
169 Lake Michigan (11 ng/L).²⁵ The majority of the detected compounds are PFCAs, which make up
170 $86 \pm 11\%$ of PFAAs across all sites (**Figure S4**).

171 Aqueous tributary concentrations are below most current and proposed regulatory
172 standards. Only three of the sites (Ditch B, Portage Creek, and Duck Creek) exceed the proposed
173 surface water criteria for Wisconsin for PFOA (20 ng/L) and PFOS (8 ng/L).⁵³ Three sites (Ditch
174 B, Portage Creek, and Thomas Slough) exceed the promulgated drinking water and groundwater
175 standards in Michigan for PFOA (8 ng/L), PFNA (6 ng/L), and PFOS (16 ng/L).⁵⁴ Only Ditch B
176 exceeds the drinking water health advisory level of 70 ng/L combined PFOS and PFOA issued by
177 the U.S. Environmental Protection Agency.⁵⁵

178 We hypothesized that elevated PFAA concentrations would be present in the Marinette
179 area (**Figure S1**) due to the long history of AFFF use in the region. The Tyco Fire Products facility
180 is located between two major rivers, the Menominee and Peshtigo Rivers, and is associated with a
181 large PFAS groundwater plume. These rivers receive wastewater influent from the cities of
182 Marinette and Peshtigo, respectively, which could also serve as PFAS sources. Additionally,

183 several smaller tributaries, including Ditch B, lead directly from the Tyco facility to the bay.
184 Biosolids from the Marinette City Wastewater Plant, which are known to contain high levels of
185 PFAS,³³ were spread on agriculture fields northwest of Marinette until 2018.³⁴

186 Despite these potential distribution pathways, high aqueous PFAA concentrations are only
187 observed in Ditch B. A PFAS treatment system was installed in Ditch B upstream of our sampling
188 site in 2019 but was not operating properly at the time of sampling.^{56,57} The distribution of PFAA
189 compounds (**Figure S3**) in this sample is dominated by PFOA and is consistent with the signature
190 of legacy fluorotelomer-based AFFF. Ansul uses fluorotelomerization in AFFF manufacturing,⁵⁸
191 with 6:2 and 8:2 fluorotelomer thioether amido sulfonates (FtTAoS) as likely active
192 ingredients.^{59,60} FtTAoS compounds can degrade to produce PFCAs including PFPeA, PFHxA,
193 and PFOA as terminal products.⁵⁸ The current AFFF formulation produced by Ansul uses short
194 chain compounds ($C \leq 6$), suggesting that the high amount of PFOA in Ditch B may be attributable
195 to historical manufacture and/or use of C_8 fluorotelomer AFFF.

196 PFAA concentrations measured in the Menominee River are low (16 ng/L) and are similar
197 to concentrations reported by the Wisconsin Department of Natural Resources (WDNR) at the
198 mouth of the river (4 – 7 ng/L summed PFAS in June, July, and September 2019).⁵⁰ Smaller
199 tributaries in this region generally have higher aqueous PFAA concentrations than larger
200 tributaries (**Figure 2a**), which can be attributed to their lower flow rate and proximity to PFAS
201 sources. Two smaller tributaries in the Marinette area have elevated PFAAs: a tributary near the
202 Menominee Regional Airport (Kirby Creek; 71 ng/L) and a creek adjacent to fields that received
203 biosolids (Mudbrook Creek; 60 ng/L).

204 Overall, summed PFAAs levels in the greater Marinette area (Little River through Gravelly
205 Brook in **Figure 2a**) are not elevated compared to other areas. However, the distribution of PFAAs

206 in these sites suggests they are impacted by similar sources. Principal component analysis (PCA)
207 using the PFAA distribution in aqueous samples shows that sites in the Marinette region are closely
208 related (**Figure 3a**), which we attribute to higher percentages of PFHxA and/or PFOA (i.e.,
209 terminal degradation products of 6:2 and 8:2 FtTAoS).^{59,60} An increase in linear isomers could
210 also indicate fluorotelomer AFFF use;^{61,62} however, almost all sites in this study contain high
211 percentage of linear isomers with no notable difference in Marinette (**Figure S5; Table S9**). The
212 PFAA compounds measured in this study are important from a regulatory and toxicity perspective.
213 Given that they represent terminal products associated with fluorotelomer AFFF use, more
214 research, including the quantification of PFCA precursors using total oxidizable precursor (TOP)
215 assay or other methods, is needed to fully assess the extent and potential for long-term release of
216 PFAS in this region.

217 Several sites outside of the Marinette area have notably higher PFAA concentrations
218 (**Figure 2a**). Duck Creek is located in the city of Green Bay and is near the Green Bay Austin
219 Straubel International Airport. Thomas Slough in Oconto, WI does not have any known PFAS
220 sources, but clusters with the Marinette region samples by PCA (**Figure 3a**). Portage Creek
221 receives runoff from the Delta County Airport in Escanaba, Michigan, where significant PFAS
222 contamination has been found,⁶³ and clusters with Green Bay sites due to its high PFHxS content.
223 In all sites that show elevated aqueous PFAAs, the tributary discharge is relatively low (<1 m³/s).⁶⁴
224 Areas with low PFAA concentrations include the eastern and northern shores of the bay (i.e., the
225 Door County peninsula and the upper peninsula of Michigan, respectively), corresponding to a
226 regional background level of 22 ng/L for summed PFAAs (**Table S8**). Areas with elevated aqueous
227 PFAAs tend to be individual tributaries, rather than entire regions around the bay, suggesting that
228 PFAAs are closely associated with nearby sources. However, PCA shows that aqueous PFAA

229 distribution generally clusters by region (**Figure 3a**), indicating that PFAA sources may impact
230 tributaries throughout a region.

231 **PFAA Loading to the Bay of Green Bay from Tributaries.** While concentrations of
232 PFAAs in individual tributaries are important for evaluating the potential for human and ecosystem
233 exposure, stream concentrations do not directly translate into fluxes to receiving waters. Therefore,
234 we calculated baseflow loading of PFAAs to quantify transport to Green Bay by tributaries:

$$235 \quad \text{Loading} = [\text{PFAA}] * \text{tributary discharge} \quad (1)$$

236 where loading is in units of ng/s, [PFAA] is in units of ng/L, and discharge is in units of L/s.
237 Tributary discharge estimates are taken from Mooney *et al.*⁶⁴ where the discharge-watershed area
238 ratio method was used and verified using U.S. Geological Survey stream gauges in the Great Lakes
239 Basin (**Table S2**). All major rivers that drain to the bay, as well as many smaller tributaries, are
240 included in the study. This analysis considers PFAA concentrations measured under baseflow
241 conditions, thus providing a snapshot of loading at the time of sampling. Discharge can range
242 widely (e.g., during snowmelt) and relationships between PFAS concentrations and discharge in
243 these tributaries have not been established. Further work is needed to quantify other loading
244 sources to the bay including groundwater flow (e.g., from the PFAS plume that flows southeast
245 from Tyco) and precipitation.

246 The largest rivers, including the Fox, Peshtigo, and Menominee Rivers, have the largest
247 PFAA loadings (**Figure 2b**), despite having relatively low aqueous concentrations. These three
248 rivers contribute over two-thirds of the total tributary PFAA loading to Green Bay. In total, the
249 sampled tributaries contribute 320 g/day of summed PFAAs into the bay under baseflow
250 conditions. The Fox River contributes 32% of the PFAA loading to the bay from these tributaries,

251 the Peshtigo contributes 12%, and the Menominee contributes 23%. Ditch B, which has high
252 PFAA concentrations but very low discharge, contributes only 4% of the PFAA loading to the bay.

253 PFAA loading from tributaries is strongly correlated with discharge rate, rather than PFAA
254 concentration (**Figure S6**). These results demonstrate that larger rivers dominate PFAA inputs to
255 the bay despite their low concentration relative to many of the smaller tributaries. Current and
256 proposed PFAS regulations focus on concentrations at individual sites,^{53–55} which is critical for
257 protecting human health (e.g., in the context of drinking water or fish consumption). However, the
258 results of this study indicate that regulatory efforts should place greater emphasis on discharge and
259 loadings in order to protect receiving waters. This concept is commonly applied to nutrients and
260 other stressors by applying Total Maximum Daily Loads and should be considered for PFAS.

261 **PFAA Concentrations in Tributary Sediment.** Certain PFAS compounds, like PFOS,
262 exhibit a high potential for sorption and can accumulate in sediments.^{1,40,65} In Green Bay
263 tributaries, as in most fluvial systems, summed PFAA concentrations are much higher in bed
264 sediments than in overlying water, reaching levels of over 1,000 ng/kg in many sites (**Figure 2c**;
265 **Table S10**). Interestingly, PFAA sediment concentrations are more variable than surface water
266 concentrations. Sediment PFAA concentrations range from below detection to 3,255 ng/kg (mean:
267 732 ± 851 ng/kg; median: 304 ng/kg). Lake Michigan open water sediments have reported total
268 PFAA concentrations of 4 ng/kg.²⁵

269 Sediment PFAA concentrations are highest at sites near urban or industrially impacted
270 areas and near airports (**Figures 1** and **2c**). For example, tributaries near the city of Green Bay
271 have elevated sediment PFAA concentrations ranging 258 – 2,508 ng/kg. Portage Creek (2,095
272 ng/kg), which receives runoff from the Delta County Airport, also has very high sediment PFAAs.
273 Near Marinette, there are elevated sediment PFAAs in Ditch B (1,582 ng/kg), which discharges

274 directly off of the Tyco property, and two upstream sites (>2,000 ng/kg) that drain fields that
275 previously received contaminated biosolids.³³

276 Sites outside of the Marinette and Green Bay areas are considered rural or minimally
277 impacted by known point sources. Most of these sites are low in summed sediment PFAAs (below
278 detection to 400 ng/kg), corresponding to a regional background level of 211 ng/kg (**Table S10**).
279 However, several sites have elevated sediment concentrations with no identified PFAS source
280 (**Figure 2c**). Thomas Slough (3,255 ng/kg) is in a rural area between Green Bay and Marinette and
281 contains the highest sediment PFAA concentration in this study. Two large rivers in the upper
282 peninsula of Michigan also have elevated PFAAs: Rapid River (1,309 ng/kg) and Fishdam River
283 (1,101 ng/kg). The source(s) of elevated PFAAs in these three sites are not known.

284 The distribution of specific PFAA compounds in these sediments (**Figure S7**) is dominated
285 by PFOS ($57 \pm 21\%$). Across all sites, PFCAs represented $39 \pm 20\%$ of summed PFAAs (**Figure**
286 **S8**), which is a much lower fraction than in the aqueous samples ($86 \pm 11\%$ PFCAs; **Figure S4**).
287 This difference is likely driven by the high sorptivity of PFOS^{1,40,65} and the increased sorption of
288 PFSAs compared to PFCAs of the same carbon chain length.^{37,39} The percentage of linear isomers
289 is higher in sediments than in the aqueous phase (**Figure S9; Table S11**). For example, $47 \pm 10\%$
290 of PFOS is linear in aqueous samples compare to $85 \pm 10\%$ in sediment samples. This trend is
291 consistent with higher sorption of linear compounds compared to branched compounds observed
292 in the Great Lakes.²⁵

293 Ditch B, Mudbrook Creek, and Gravelly Brook, which are all connected to the Tyco
294 facility, cluster near each other by PCA based on the relative distribution of PFAAs in the sediment
295 (**Figure 3b**) and exhibit elevated levels of PFPeA, PFHxA, and PFOA, which are terminal products
296 of the active ingredients in fluorotelomer-based AFFF.⁵⁸ These three sites contain an average of

297 62% PFCAs, which is much higher than the overall average in sediment. The similarity in
298 compound distributions between Ditch B and the two streams draining biosolids-impacted fields
299 suggests that PFAAs from Tyco-impacted biosolids have impacted nearby streams (**Figure 3b**).
300 According to one analysis, biosolids from the Marinette City Wastewater Plant are elevated in
301 PFHxA and PFOS (290 $\mu\text{g}/\text{kg}$ and 210 $\mu\text{g}/\text{kg}$, respectively) and include some PFOA (10 $\mu\text{g}/\text{kg}$).³³
302 The continued presence of these compounds indicate that agricultural sediments can retain legacy
303 PFAS for years.

304 Sediment-water partition coefficients (**Section S4**) calculated from measured sediment and
305 water PFAA concentrations show that $\log K_d$ values from Green Bay field samples (**Figure S10**)
306 increase with increasing number of carbons in the hydrophobic tail and that PFSA have a higher
307 K_d than PFCA counterparts, in agreement with previous laboratory measurements.^{37,39} While these
308 data indicate that PFAA structure is important for determining the extent of sorption, the high
309 variability in K_d values suggests that other factors may contribute.

310 Variability in PFAS sorption among sediment samples has been largely attributed to
311 organic carbon content,^{1,40,65} although variation in PFAS sorption across sediments cannot be
312 predicted by organic carbon content alone.³⁶ To evaluate the role of organic carbon content on
313 PFAA sorption in Green Bay tributaries, we calculate $\log K_{OC}$ values (**Figure S10; Table S12**)
314 after quantifying organic carbon content in each sediment sample (average = $7.1 \pm 9.7\%$; **Table**
315 **S13**). There is a significant relationship between sorption of individual PFAA compounds and
316 organic carbon content (**Figure S11**; p-values <0.001), indicating that f_{OC} is a factor in PFAA
317 sorption in these tributaries. No significant correlations were found between PFAA sorption and
318 aqueous cations (**Figure S12; Table S14**) or sediment PZC (**Figure S13; Table S15**).

319 Field sediment-water partition coefficients calculated here and in other freshwater field
320 studies⁴¹ are consistently higher than those measured in laboratory studies, suggesting that
321 laboratory studies underestimate PFAS sorption. For example, reported laboratory log K_d values
322 for PFCAs range from -0.75 L/kg for PFPeA to 1.0 L/kg for PFDA,³⁷ which are considerably lower
323 than the values observed here. The log K_d values for PFOA and PFOS in this study agree with
324 published global field averages of 1.9 and 2.3 L/kg, respectively,⁴¹ which are higher than the
325 reported laboratory averages of 0.8 and 1.4 L/kg, respectively.⁶⁶ The difference between laboratory
326 and field partition coefficients may be attributable to the use of water column concentrations rather
327 than porewater or the fact that field samples are not at equilibrium at the time of sampling, as
328 discussed below.

329 **Significance of PFAAs Sorbed to Tributary Sediment.** The large amount of sediment-
330 associated PFAAs identified in tributaries leading to the bay of Green Bay generates questions
331 regarding the mobility of sediment-associated PFAAs. While sorptive compounds like PFOS can
332 accumulate in riverbed sediments if aqueous concentrations are elevated,^{1,40,65} it is unclear if those
333 sediments can later act as a PFAS source once overlying water concentrations decline. Several
334 studies conclude that certain compounds, including PFOS, PFOA, and PFHxS, undergo sorptive
335 hysteresis where sorption to environmental sediments is partially irreversible,⁴⁴⁻⁴⁹ suggesting that
336 sediments primarily act as a sink for certain compounds and do not release them back into the
337 aqueous phase. Alternatively, others propose that the non-ideal, hysteretic desorption of PFOS has
338 minimal effect on its mobility,⁶⁷ suggesting that sediments can act as either a source or a sink of
339 PFOS depending on aqueous phase concentrations. Many studies use high concentration
340 isotherms, which are useful to characterize PFAS behavior, but do not directly address questions
341 about transport under conditions representative of tributaries. Furthermore, the dependence of

342 PFAS sorption and desorption on a wide variety of variables, many of which are unknown, makes
343 transport modeling challenging.⁶⁸ Therefore, simulating environmental conditions as closely as
344 possible is critical for understanding and ultimately modeling PFAS mobility in natural
345 environments.

346 Sediment and water will not be at equilibrium in a riverine system unless either the
347 sorption/desorption processes happen very rapidly or PFAS concentrations in the flowing water is
348 constant over time. In order to test whether PFAAs in these sediments are at equilibrium with the
349 overlying water, we first equilibrate sediment with water from the same site for 10 days. We
350 selected six sites based on their importance (Menominee and Fox Rivers are current or delisted
351 Areas of Concern;³⁵ Peshtigo River and Hay Creek are near a site of high groundwater
352 contamination) and/or high PFAA concentrations (Portage Creek and Thomas Slough have
353 sediment PFAA concentrations >2,000 ng/kg). Sediment PFAS concentrations change by up to
354 150% over the 10-day period, showing that the water and sediments were not at equilibrium when
355 the field samples were collected (**Figure 4a** and **S14a**; **Table S16**). Notably, PFOS concentrations
356 in the bed sediments decrease in four of the six samples, indicating that PFOS is susceptible to
357 desorption from these sediments over time. Initial and final PFOS partition coefficients ($\log K_d$ of
358 1.92 and 1.26 L/kg, respectively; **Table S17**) show that these sediments approach the reported
359 laboratory partitioning coefficient (1.4 L/kg)⁶⁶ after equilibration. This result may support the
360 hypothesis that differing concentrations between water column and porewater drive differences in
361 field and laboratory K_d values. Additionally, PFNA and PFDA decrease in four and one sediment
362 samples, respectively.

363 However, the opposite trend is observed for several other compounds with sediment PFAA
364 concentrations increasing after equilibration. For example, sediment samples increase in

365 concentrations of PFOA (n = 6), PFDA (n = 5), PFNA (n = 2), and PFOS (n = 2). The increase in
366 concentrations of certain PFAAs indicates that the sediment is undersaturated with respect to
367 sorption of these compounds, driving sorption to the sediment. In the case of PFOA, the increase
368 in log K_d from 1.08 to 1.56 L/kg after equilibration (**Table S17**) moves the K_d even further from
369 the global laboratory average of 0.8 L/kg.⁴¹ The reason for this deviation from equilibrium is
370 unknown, but may be related to the low PFOA concentrations in the selected sediment samples
371 (14 – 132 ng/kg). None of the samples increase or decrease in concentrations of all compounds,
372 indicating that the sorptive and desorptive behavior is not inherent to sediment type but rather a
373 function of water and sediment concentrations. Changes in shorter chain compounds were not
374 recorded as either the initial, final, or both concentrations were below the minimum reporting limit.

375 To further quantify the ability of sediment to serve as a PFAA source, we equilibrated site
376 sediment with Lake Michigan water for 10 days. Lake Michigan water was used as an
377 environmentally relevant surrogate for surface water with low PFAA concentrations (**Table S8**),
378 representing the surface water in these tributaries if PFAS sources were substantially reduced. Four
379 sediments were selected based on their high PFAA concentrations (>1,500 ng/kg; **Figure 2c**),
380 while Menominee River sediment was selected based on its proximity to the Tyco facility.
381 Sediment PFAA concentrations decrease in all five samples after 10 days of equilibrium with Lake
382 Michigan water (**Figure 4b** and **S14b**; **Table S18**). Notably, PFOS concentrations decrease in all
383 samples, showing desorption of up to 2,000 ng/kg in one sample. PFOA concentrations decrease
384 in four of the five sediments, with desorption of up to 644 ng/kg in one sample. This further
385 demonstrates that these sediments can act as a source of PFAAs depending on water
386 concentrations. It should be noted that sediment desorption is dependent on further deposition of
387 sediment, as fresh, non-contaminated sediment can potentially cap existing contaminated

388 sediment. PFOS desorption happens rapidly (i.e., within two days; **Figure S15**). Sediment
389 concentrations do not reach zero after desorption experiments, which could be due to either
390 equilibrium with Lake Michigan water or sorption hysteresis.⁴⁴⁻⁴⁹

391 **Conclusions.** This study has implications for both the Green Bay watershed and
392 environmental PFAS contamination as a whole. Baseflow loading calculations for these tributaries
393 demonstrate that rivers with high discharge rates but low concentrations contribute the large
394 majority of PFAAs to the bay. This indicates that tributary discharge must be considered when
395 developing regulations to protect the bay of Green Bay, the Great Lakes, and other receiving
396 waters, an approach markedly different from the current focus on concentrations of individual
397 PFAS on a site-by-site basis.

398 Sediment-water partitioning analyses shows that sediments can act as a source or a sink of
399 PFAAs, but a fraction of PFOS may be irreversibly sorbed. Our findings suggest that tributary
400 sediments with high PFAA concentrations can act as a source of PFAAs if the aqueous
401 concentrations are decreased via pollution mitigation measures.

402 Certain PFAS compounds, including the PFAAs evaluated in this study, can lead to
403 negative health effects in humans and wildlife. Long-chain PFAAs (PFOA and longer, PFHxS and
404 longer) are persistent, bioaccumulative, and toxic.^{3,69,70} The Great Lakes and other waterways are
405 important to protect as they are used as a source of drinking water and food. They are also
406 considered sacred to many indigenous peoples and support the lives of many plant and animal
407 species. Once PFAS compounds have made it into waterways, they are difficult to remove due to
408 their unique lipophobic and hydrophobic characteristics and strong carbon-fluorine bonds.

409 We focused on PFAAs because these terminal compounds are most closely associated with
410 adverse health outcomes. While these PFAA compounds are driving regulations across the United

411 States, including in Wisconsin, future work should focus on fluorotelomers and other precursors
412 in order to more fully assess the potential for long-term release of PFAS in this area.

413

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418 study was provided by the Wisconsin Sea Grant project numbers R/HCE-39 and R/HCE-40.

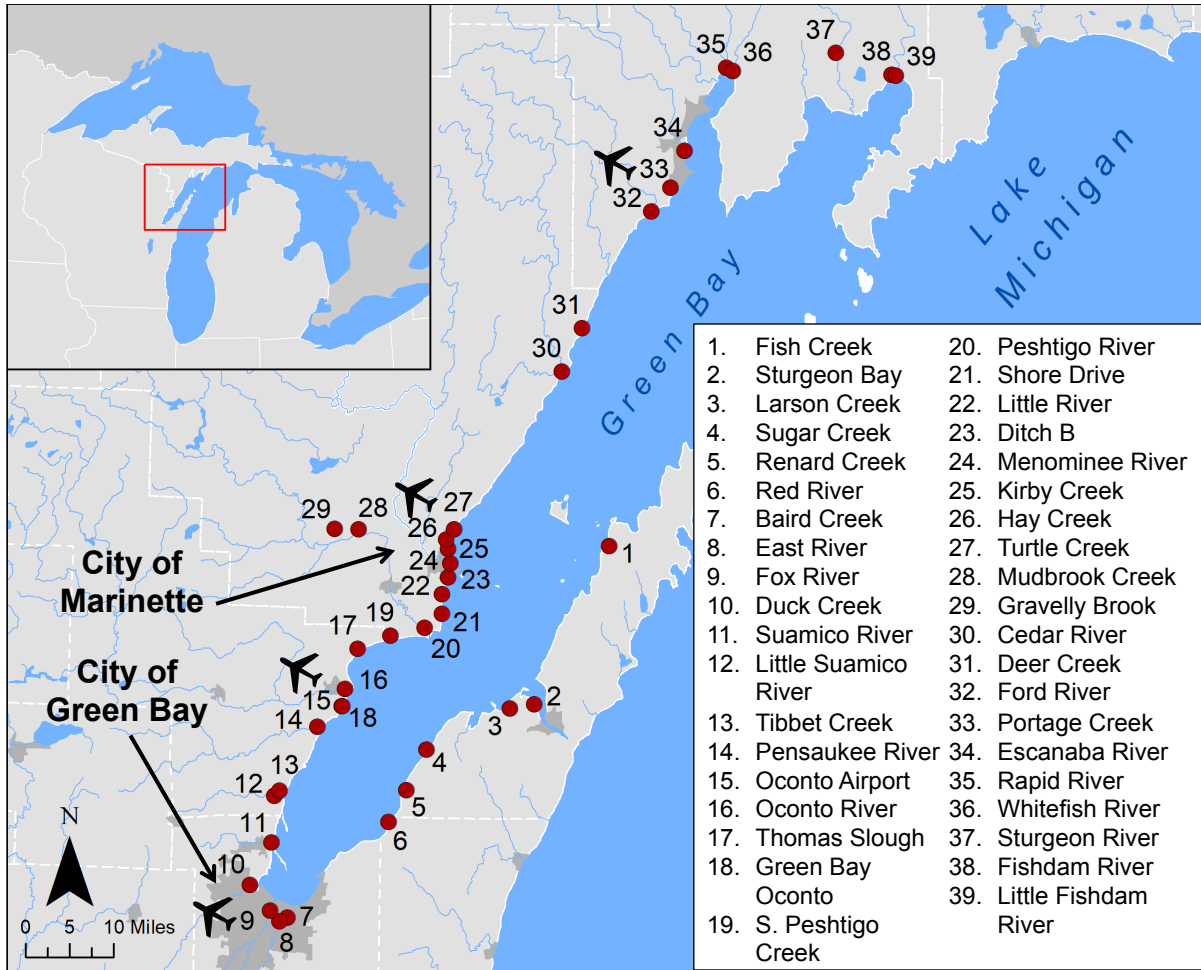
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420 **Supporting Information**

421 The Supporting Information is available free of charge at _____

422 Additional experimental details, quality control information, and supplementary figures
423 and tables (PDF).

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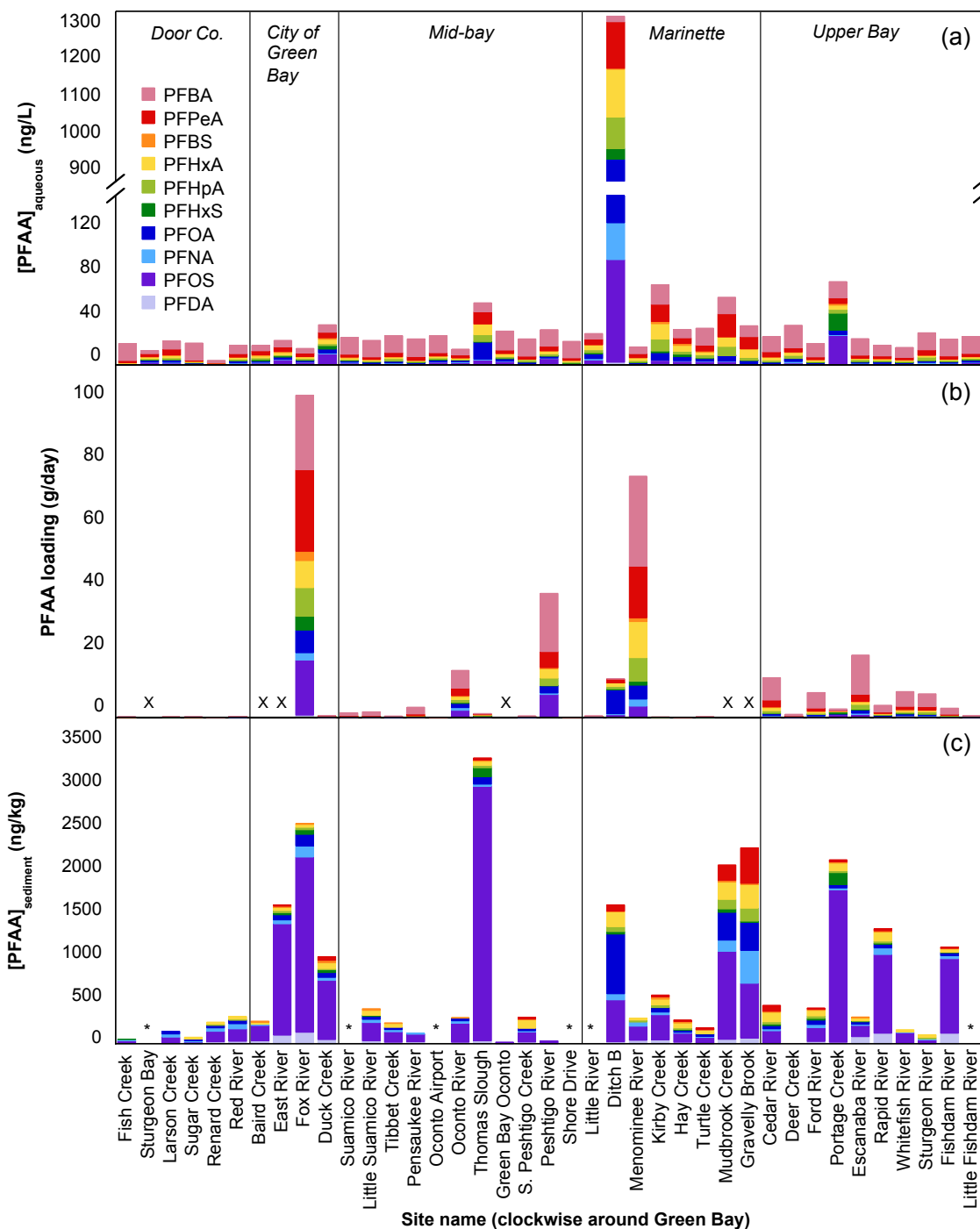


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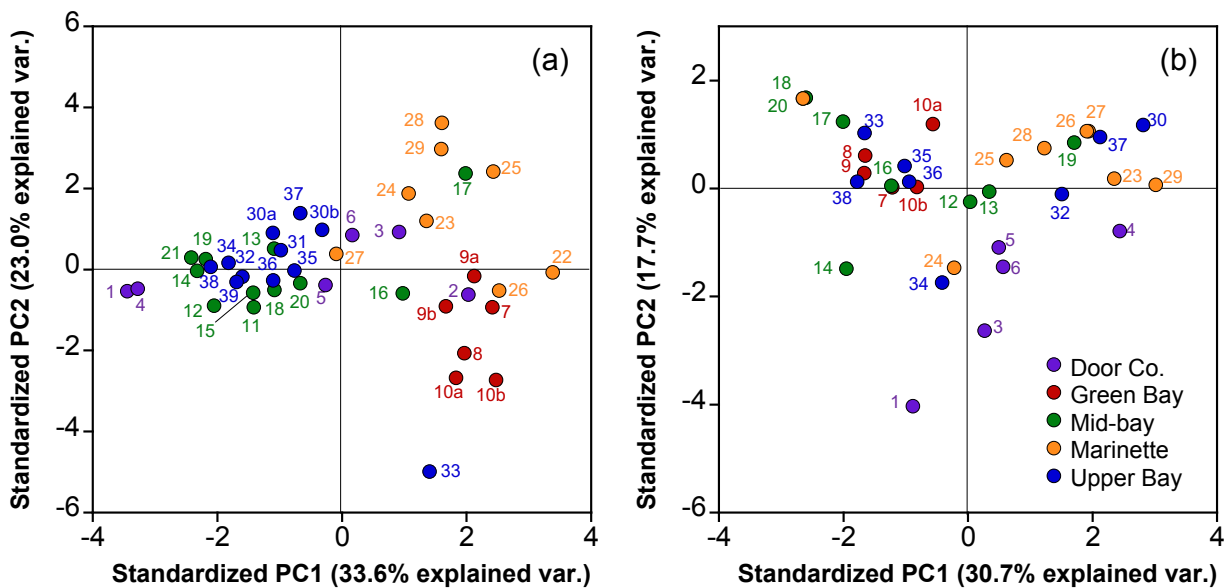
426 **Figure 1.** Map of sites where samples were collected from Green Bay tributaries and in the bay
 427 itself created using ArcGIS software (10.6.1) by Esri. Data provided by the National Atlas of the
 428 United States, USGS. Black airplane symbols show where regional airports are located. Urban
 429 areas, including Green Bay and Marinette, are shaded dark gray. See **Figure S1** in Supporting
 430 Information for a detailed map of the Marinette region, including the Tyco facility.
 431

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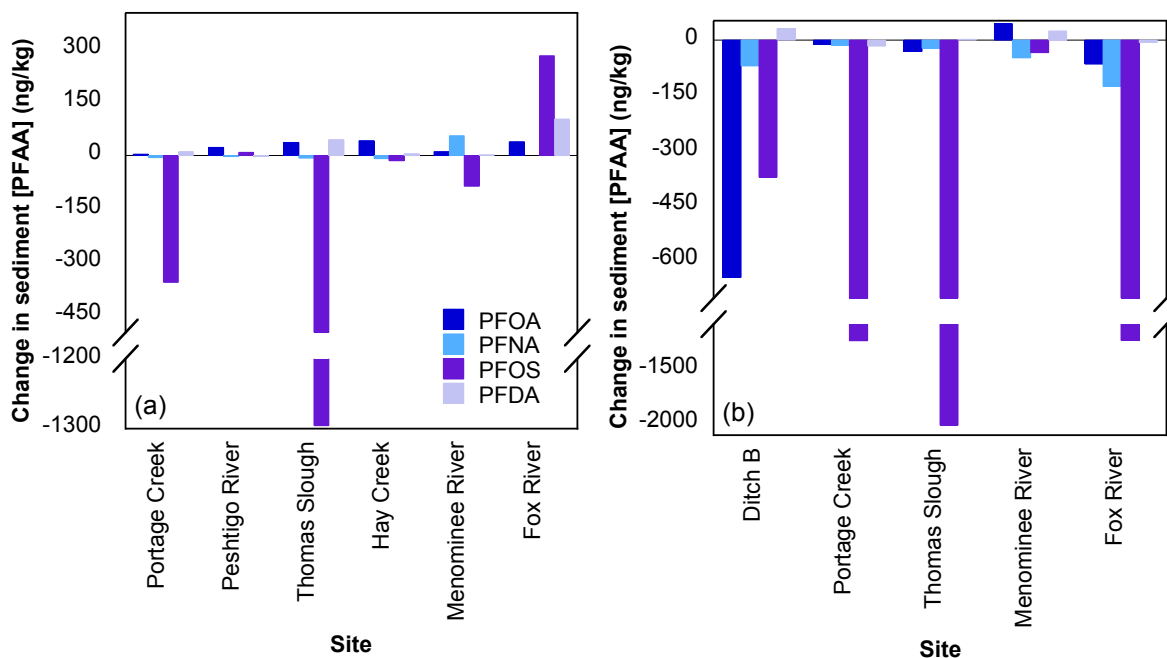
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434
 435 **Figure 2.** PFAA concentrations in Green Bay tributaries including (a) concentrations in the water
 436 column, (b) loading rates into the bay, and (c) concentrations in sediment. Loading is calculated
 437 using aqueous PFAA concentrations and estimated discharge rates.⁶⁴ Loading is not calculated for
 438 sites denoted with an X because these sites do not drain directly into the bay. Sediment data was
 439 not collected for sites denoted by a * due to inaccessibility or rocky riverbeds. See **Figure S2** for
 440 a detailed view of panel (a).
 441



442
 443 **Figure 3.** Principal components analysis of the normalized distribution of 10 PFAAs in (a) aqueous
 444 samples and (b) sediment samples. Labels correspond to site numbers in **Figure 1**.
 445
 446



447
 448 **Figure 4.** Change in PFAA concentrations of sediments that were equilibrated with (a) surface
 449 water from the same site for 10 days, and (b) Lake Michigan water for 10 days. See **Figure S14**
 450 for plots of concentration percent change.
 451
 452

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