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► To cite this version:

D. Bertin, B. Ferrari, P. Labadie, A. Sapin, J. Garric, et al.. Bioaccumulation of perfluoroalkyl compounds in midge (*Chironomus riparius*) larvae exposed to sediment. *Environmental Pollution*, 2014, 189, p. 27 - p. 34. 10.1016/j.envpol.2014.02.018 . hal-01058508

HAL Id: hal-01058508

<https://hal.science/hal-01058508v1>

Submitted on 27 Aug 2014

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Bioaccumulation of perfluoroalkyl compounds in midge (*Chironomus riparius*) larvae exposed to sediment

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1 **Abstract**

2 Midge larvae (*Chironomus riparius*) were exposed to sediments from a deposition
3 sampled at a site along the Rhône River (France) downstream of an industrial site
4 releasing various perfluorinated chemicals. This sediment is characterized by high
5 concentrations of perfluoroundecanoic acid (PFUnA) and perfluorotridecanoic acid
6 (PFTrDA) and a low perfluorooctane sulfonate (PFOS) concentration. Concentrations
7 of 23 perfluoroalkyl compounds, including C₄-C₁₄ carboxylate acids, C₄-C₁₀ sulfonates,
8 and seven precursors, were analyzed in overlying and pore water, sediment, and larvae.
9 Midge larvae accumulated carboxylate acids (C₁₁-C₁₄), PFOS, and two precursors
10 (perfluorooctane sulfonamide: FOSA and 6:2 fluorotelomer sulfonic acid, 6:2 FTSA).
11 These substances accumulated mainly during the fourth instar larvae exponential growth
12 phase. Accumulation of 6:2 FTSA, PFUnA, and PFOS occurred via trophic and
13 tegumentary routes. Other compounds mainly accumulated from food. Kinetics
14 followed a partition model, from which uptake and elimination constants were derived.

15

16 **Keywords:** Perfluoroalkyl compounds, sediment, *Chironomus riparius*,
17 bioaccumulation.

18

19 **Capsule:** *Chironomus riparius* mainly bioaccumulates long-chain PFASs via trophic
20 and/or tegumentary routes during the fourth instar larvae growth phase.

21

22 **1. Introduction**

23 Polyfluoroalkyl and perfluoroalkyl substances (PFASs) have been produced
24 since the early 1950s. The production and use of these compounds have resulted in their

25 global distribution in the environment (Houde et al., 2011; Houde et al., 2006;
26 Prevedouros et al., 2006). In 2000, the 3M company voluntarily phased -out C₈-based-
27 chemicals (i.e., sulfonamide based polymers), at the base of the formation of
28 perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), and replaced
29 them with shorter- chain chemicals (e.g., perfluorobutane sulfonate, PFBS) (Renner,
30 2006; Lindstrom et al., 2011). In 2009, PFOS was listed under Annex B of the
31 Stockholm convention (United Nations Environmental Program -UNEP) on Persistent
32 Organic Pollutants (POPs) (Lindstrom et al., 2011).

33 PFASs have been found in all aquatic media (Houde et al., 2011; Houde et al.,
34 2006). On the basis of global modelling, marine sediments have been designated as the
35 ultimate containment for PFASs (Armitage et al., 2006). Several studies have shown the
36 presence of PFASs in sediment with concentrations ranging from 0.5 ± 0.1 to $38.3 \pm$
37 $16.8 \text{ ng.g}^{-1} \text{ dw}$ (Ahrens et al., 2009; Bao et al., 2009; Bao et al., 2010; Higgins et al.,
38 2005; Labadie and Chevreuil, 2011; Myers et al., 2012; Zushi et al., 2010). Sediment
39 has been suggested as a major source of contamination of aquatic organisms (Martin et
40 al., 2004). However, the distribution of water, sediment, and biota as well as the role of
41 the sediment compartment in biota contamination is still poorly understood. The length
42 of the fluorocarbon chain is an important criterion for PFAS distribution in the
43 environment (Ahrens et al., 2009; Higgins and Luthy, 2006; Myers et al., 2012). PFASs
44 with eight or more carbon atom backbones are known to be bioaccumulative (Kannan et
45 al., 2005; Kelly et al., 2009; Loi et al., 2011; Tomy et al., 2004).

46 In France, PFASs were found in fish from the Rhône River near Lyon (Miège et
47 al., 2012). Highest levels of PFASs were found in fish from this latter river (mean total
48 PFAS concentration: $241.5 \text{ ng.g}^{-1} \text{ dry weight (dw)}$), the Rhône River was therefore

49 chosen as the study site for this research which aimed to better understand the origin of
50 PFAS contamination in aquatic organisms by evaluating the transfer of these
51 compounds from sediment to invertebrates.

52 A benthic invertebrate, the non-biting midge *Chironomus riparius*, is found in
53 sediment from the Rhône River and is recommended by the OECD for toxicity testing
54 (OECD, 2004). Midges are holometabolous, that is they go through complete
55 metamorphosis consisting of egg, larva, pupa, and adult stages. *C. riparius* mates in
56 aerial swarms. After mating, the female deposits the eggs on the water surface. Larvae
57 undergo four instars; the first (L1) is planktonic and the second to fourth larval stages
58 (L2, L3, L4) are in direct contact with sediment (Fig. S1). Larvae L2 to L4 are collector-
59 gatherers, feeding mainly on detritus and its associated bacteria and fungi. This species
60 represents an important food source for fish, making it a useful species for documenting
61 the bioaccumulation of perfluoroalkyl compounds (Armitage et al., 1995).

62 The objectives of the present study were (i) to experimentally determine the role
63 played by sediment in the accumulation of eleven carboxylic acids (from 4 to 14
64 carbons), five sulfonates (ranging from 4 to 10 carbons), and seven precursors by *C.*
65 *riparius* larvae and (ii) to describe the kinetics of the bioaccumulation process.

66

67 **2. Materials and Methods**

68 The study site, Beurre Island (BER), is a fluvial annex of the Rhône River
69 (eastern central France, N45°28'17,0"E4°46'43,4", Fig. 1) and located downstream of a
70 fluoropolymer manufacturing plant that has been found to be an important source of
71 PFAS contamination with a typical profile (Dauchy et al., 2012).

72 **2.1 Sediments**

73 In 2012, 50 L of natural sediments were collected from the river bed with a Van-
74 Veen grab, kept on ice and brought to the laboratory, where they were sieved at 2 mm,
75 pooled in a polypropylene (PP) jar, and stored at 4°C. Six aquaria (38 × 20 × 24.5 cm in
76 polystyrene) were prepared with 4 L of homogenized sediment and 15 L of groundwater
77 mixed with treated water via an osmosis system in order to reach a conductivity of 300
78 $\mu\text{S}\cdot\text{cm}^{-1}$. Each aquarium was allowed to settle for 1 week before introducing the
79 chironomids. Three control aquaria were prepared in the same manner with silica sand
80 (particle size distribution: 90% 50-200 μm , 10% <50 μm) (Péry et al., 2002).

81 The sediment was characterized for water content, nitrogen, carbonate using a
82 Bernard calcimeter, and loss on ignition (LOI) (AFNOR, 1994, 2000, 2007; Vatan
83 1967) and showed a water content of 43.4%, an organic carbon content of 4.3%, a
84 carbonate content of 27.4%, and a nitrogen content of 0.19%. The particle size
85 distribution was determined by laser diffractometry (Cilas 1190, France) and found to
86 be 10% clay -silt (< 5.83 μm), 40% silt (5.83 - 52.24 μm), and 50% of silt -very fine
87 sand (>52.24 μm).

88 2.2 *C. riparius* exposure

89 Chironomids were obtained from laboratory cultures made according to standard
90 methods (AFNOR, 2010; OECD, 2004). Chironomids were exposed to the BER
91 sediment at standard temperature (21°C). Two experiments were conducted to examine
92 the extent to which developmental stage influences the amount of accumulated
93 chemicals in *C. riparius* (experimental designs shown in Fig. S2). The first experiment
94 (E1) started with L2 larvae until the end of the L4 stage and lasted for 9 days. The
95 second experiment (E2) started directly with L4 larvae.

96 In experiment E1, 2400 L2 larvae (2-day-old larvae post-hatching) were added
97 to three study aquaria, and to three control aquaria (400 in each aquarium). In
98 experiment E2, 1200 early L4 larvae (7-day-old larvae post-hatching) were exposed in
99 three aquaria. Overlying water (OW) was continuously renewed (four times a day) to
100 maintain adequate water quality and oxygenated under a 16:8-h light: dark photoperiod
101 during the experiment. Larvae were fed ad libitum each day with 1mg commercial food
102 (Tetramin[®]) per organism per day. We decided to feed the chironomids during the
103 experiment because previous experiments showed that larvae did not survive without an
104 external supply of food in this sediment. A quantity of 1mg Tetramin[®] per organism per
105 day was selected because preliminary tests (data not shown) conducted with 0.6mg
106 Tetramin[®] per organism per day showed low survival and growth. E1 organisms were
107 sacrificed after 11 post-hatching days, i.e., 9 days (T_{final}, T_f) after being introduced in
108 the aquaria. E2 organisms were sacrificed at 2 (T₁), 3 (T₂), and 4 (T₃) days,
109 respectively, after introducing L4 chironomids. The water quality parameters (pH,
110 concentration of dissolved oxygen, conductivity, NO₂⁻, and NH₄⁺) were monitored once
111 a week and at the beginning and the end of the exposure period (Fig. S2).

112 2.3 Sample collection and chironomid measurements

113 Overlying water (OW), pore water (PW), and sediment were sampled at T₁, T₂,
114 T₃, and T_f. E1 organisms were sampled only at T_f. E2 chironomids were sampled at T₀
115 (fourth instar larvae), T₁, T₂ and T₃, and T_f. The overlying water was sampled directly
116 in a 1L polyethylene (PE) bottle. For pore water, we used a Rhizon[®] system (SDEC,
117 Reignac-sur-Indre, France), which consists of one porous polymer part inside a
118 fiberglass rod. Organisms were collected by sieving the upper layer of sediment at
119 500µm; sub-samples from deeper sediment were deposited in PE tubes. Organisms were

120 split into two different batches for PFAS analysis (about 800 mg ww, representing
121 about 200 larvae) and $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ isotopic analysis (about 5 mg dw of larvae). Biota
122 samples were cryopreserved in liquid nitrogen and stored at -21°C and abiotic samples
123 frozen and kept at -21°C (Fig S2).

124 Chironomid survival, length, and weight were determined for all aquaria. To determine
125 length, four groups of ten larvae were photographed and mean sizes assessed using
126 digital image analysis software (Jmicrovision, freely available via
127 <http://www.jmicrovision.com/>). The same groups were then weighed (weighing scales:
128 Sartorius CPA225D, France) to obtain mean weights.

129 2.4 PFAS extraction

130 2.4.1 Overlying and pore water samples

131 Water samples were each spiked with 2 ng of IS and processed using Srata X-
132 AW cartridges as described by Labadie and Chevreuil (2011).

133 Eluates were concentrated to 400 μL under a nitrogen stream at 40°C and transferred
134 into PP vials (final volume: 250-300 μL). Extracts were stored at -20°C until analysis.

135 2.4.2 Sediment sample

136 Sediment samples were extracted by sonication, using a method adapted from
137 Sun et al. (2011). Samples (1 g dw) were spiked with ISs (1.8 ng each) and extracted
138 with 5 mL of MeOH for 20 min, prior to centrifugation for 3 min (20°C , 2900 g). This
139 procedure was repeated with 2.5 mL of MeOH and the two extracts were combined and
140 concentrated to 800 μL under a nitrogen stream at 40°C . Samples were purified using
141 ENVI-Carb cartridges previously conditioned with 4 mL of MeOH and eluted with 2×4
142 mL of MeOH. Eluates were concentrated to 400 μL under a nitrogen stream at 40°C and
143 transferred into injection vials.

144 2.4.3 *C. riparius* samples and Tetramin[®] samples

145 Extraction of PFASs in 120 mg dw *C. riparius* (800 mg wet weight (ww)) and in
146 540 mg Tetramin[®] followed the same protocol used for the sediment samples. Extract
147 clean-up was adapted from Ballesteros-Gomez et al. (2010). Extracts were diluted 20
148 times with ultra-pure water (5% extract in water) and then passed through a Strata X-
149 AW cartridge previously conditioned as described above. After extract loading,
150 cartridges were washed with 5 mL of sodium acetate buffer (pH=4.5, 25 mM). They
151 were vacuum-dried (30-40 min) and connected via a polyethylene adaptor cap to an
152 ENVI-Carb cartridge previously conditioned with 8 mL of MeOH. Neutral PFASs were
153 eluted with 8 mL of MeOH (fraction A). The ENVI-Carb cartridge was then replaced
154 and a second fraction (fraction B) containing acidic analytes was eluted with 8 mL of
155 MeOH containing 0.2% NH₄OH. Fraction A eluates were concentrated to 300 µL and
156 then transferred into PP injection vials. Fraction B eluates were processed almost to
157 dryness before adding 200 µL of acetonitrile and 200 µL ultrapure water. Extracts were
158 then passed through MeOH-rinsed centrifuge tube filters and transferred into PP
159 injection vials.

160 2.5 Isotopic analysis

161 Isotopic analysis (¹³C and ¹⁵N) was performed by the INRA-Nancy laboratory
162 (PTEF-isotopy pole, France) on decarbonated sediment, Tetramin[®], and chironomids
163 (i.e., chironomids that have eliminated their gut content following 48h in a beaker
164 containing silicate, overlying water with food, and chironomids with gut content).

165 2.6 LC-MS/MS analysis

166 PFAS analyses were performed using an Agilent 1200 LC system (Agilent
167 Technologie, Massy, France) interfaced with an Agilent 6460 triple quadrupole mass
168 spectrometer (details in Table S2).

169 2.7 Quality control and performance methods

170 Analyte recoveries were determined using spiked samples for each matrix
171 (surface and pore water, sediment, and chironomids). Native PFAS recoveries ranged
172 from 50 to 110% (except for PFTeDA, MeFOSA and EtFOSA), with a relative standard
173 deviation below 15% (Table S3).

174 Mean IS recoveries, estimated by external calibration, were in the range 70 -
175 135% for the different matrices. Replicate procedural blanks were analyzed for each
176 series of samples. The predominant compounds in surface water blanks were PFHpA
177 (mean level: 166 pg) and PFHxA (115 pg). For solid samples, the prevailing analytes in
178 blanks were PFOA (63 pg) and PFPA (26 pg). PFAS concentrations were therefore
179 blank-corrected. For compounds present in blanks, the limits of detection (LDs) were
180 defined as three times the standard deviation, and the limits of quantification (LQs)
181 were set at ten times the standard deviation of the blank. For analytes not detected in the
182 blanks, LDs and LQs were determined as the concentration with a signal-to-noise ratio
183 of 3 and 9, respectively. This calculation was performed on matrices spiked at 2-5 ng.g⁻¹
184 (sediment and *C. riparius*) and 2-3 pg.L⁻¹ (Vittel[®] mineral water samples) (Table S4).

185 2.8 Data processing

186 Data were analyzed using the Student' *t*-test. All data were checked for normality and
187 homogeneity of variance using the Shapiro-Wilk test and the Bartlett test, respectively.
188 For all statistical tests, the significance level (alpha) was set at 0.05 and calculations

189 were performed using the software package R (version 2.11.0) (R Development Core
190 Team, 2013). For calculating data below the LQ, 0.5*LQ was used.

191 When relevant, accumulation data were fit to an exponential rise model (Eq.1)
192 with Sigma Plot 10.0 software (Systat software Inc., Point Richmond, CA, USA-
193 www.systat.com).

$$194 \quad C_{\text{org}}(t) = a.(1-e^{-bt}) \quad \text{Eq. (1)}$$

195 Where C_{org} is the concentrations in chironomids ($\text{ng. g}^{-1} \text{ ww}$), t the time in (h), a and b
196 are defined in the discussion.

197 This model has been adapted to existing bioaccumulation models, including the model
198 described by Spacie and Hamelink (1985) and Landrum (Landrum, 1989).

199 **3. Results**

200 **3.1 PFAS distribution in water, sediment, food, and *C. riparius***

201 Short- (PFBA to PFHxA) and long-chain PFCAs (PFOA, PFNA, PFDA,
202 PFUnA, and PFTTrDA), short- and long-chain PFSAAs (PFBS, PFHxS, and PFOS) and
203 one precursor (6:2 FTSA) were detected in OW test aquaria. PFBA, PFPA, PFHxA,
204 PFNA, PFDA, PFBS, PFHxS, and PFOS were also detected in OW control aquaria, at
205 levels comparable to those observed in test aquaria. Concentrations were consistent
206 throughout the replicates (test and control) (Table S5). The same compounds were
207 observed in pore water, except PFDA and PFTTrDA; PFHpA was also measured in this
208 compartment. In PW samples from control aquaria, PFBA, PFPA, PFHxA, PFHpA, and
209 PFHxS were detected at levels lower than PW from test aquaria ($n = 3$, p -value < 0.001).
210 In sediment, short- (PFBA to PFHpA) and long-chain (PFOA to PFTTeDA) PFCAs,
211 PFOS, and two precursors (6:2 FTSA and FOSA) were detected > LQs and EtFOSAA
212 were detected < LQs. Concentration of long-chain PFCAs were higher in sediment:

213 PFTrDA ($2.54 \pm 0.23 \text{ ng.g}^{-1}\text{dw}$), PFUnA ($1.70 \pm 0.22 \text{ ng.g}^{-1}\text{dw}$), PFDoA (1.54 ± 0.63
214 $\text{ng.g}^{-1}\text{dw}$), PFTeDA and PFDA ($0.99 \pm 0.58 \text{ ng.g}^{-1}\text{dw}$ and $0.91 \pm 0.43 \text{ ng.g}^{-1}\text{dw}$
215 respectively), whereas PFOS was lower ($0.26 \pm 0.02 \text{ ng.g}^{-1}\text{dw}$). In sediment control
216 samples, only PFPA and PFOA results were between LDs and LQs; the other
217 compounds were <LDs.

218 The analysis of Tetramin[®] indicated the presence of 4 PFASs: PFNA ($0.20 \pm$
219 $0.05 \text{ ng.g}^{-1}\text{dw}$), PFUnA ($0.34 \pm 0.32 \text{ ng.g}^{-1}\text{dw}$), PFOS ($1.43 \pm 0.17 \text{ ng.g}^{-1}\text{dw}$), and
220 FOSA ($0.39 \pm 0.03 \text{ ng.g}^{-1}\text{dw}$). The range of PFAS concentrations in chironomids at the
221 end of E1 and E2 exposures are presented in Table 1, PFAS concentrations in
222 chironomids control were <LDs.

223 3.2 Growth and accumulation kinetics

224 Survival throughout the experiments (E1 and E2) was greater than 80%.
225 Chironomid weight was significantly different ($p < 0.001$) between growth in sediment
226 (two at fourth instar larvae: $7.15 \pm 0.60 \text{ mg}$) and in silica ($5.84 \pm 0.83 \text{ mg}$) at 11 days
227 post-hatching (Fig. S3). However, no adverse effect of contaminated sediment on
228 chironomid growth was observed. In addition, fourth instar larvae weight data (E2) fit
229 an exponential growth curve well ($R^2 = 0.999$, $p < 0.0001$); growth rate (g) $0.0148 (\pm$
230 $0.0001)$.

231 The results indicated that *C. riparius* accumulated four long-chain PFCAs (> 10
232 carbons: PFUnA, PFTrDA, PFDoA, and PFTeDA), PFOS, one precursor (FOSA), and
233 one fluorotelomer (6:2 FTSA); the other compounds were all <LDs (Fig. 2). Fourth
234 instar chironomid larvae accumulated PFASs as early as the second day of exposure and
235 a steady state was observed at the end of exposure for most of the accumulated
236 compounds, except for PFTeDA (LD < PFTeDA concentration < LQ) and perhaps for

237 6:2 FTSA. No differences in accumulation were observed between organisms exposed
238 only at the fourth instar and those exposed from the second to the fourth instar (Fig. 3,
239 Table 1).

240 The chironomids were not depurated before PFAS analyses; therefore the gut
241 content estimation was based on Brooke et al. (1996). According to this calculation
242 there was no difference in PFAS concentrations between chironomids in which gut
243 content was or was not estimated. Therefore, the data without gut content correction
244 were kept for further interpretation.

245 The biota-to-sediment accumulation factor (BSAF) between organisms was
246 calculated according to (Higgins et al., 2007):

$$247 \text{BSAF}_{\text{ww}} = C_{\text{org}} / C_{\text{sed,oc}} \quad \text{Eq. (2)}$$

248 where C_{org} ($\text{ng}\cdot\text{g}^{-1}$ ww) is the PFAS concentration in the organism (at steady state) and
249 $C_{\text{sed,oc}}$ ($\text{ng}\cdot\text{g}_{\text{oc}}^{-1}$ dw) is the PFAS concentration in sediment normalized by the organic
250 carbon content (Table 2).

251 3.3 Isotopic analysis

252 $\delta^{13}\text{C}$ signatures of $-27.57 \pm 0.005\text{‰}$ and -23.11‰ and $\delta^{15}\text{N}$ signatures of $4.12 \pm$
253 0.64‰ and 7.58‰ were found in sediment and chironomid food (Tetramin[®])
254 respectively. No differences were observed between depurated or non-depurated
255 chironomids: the $\delta^{13}\text{C}$ signature was $-20.37 \pm 0.42\text{‰}$ and the $\delta^{15}\text{N}$ signature $11.61 \pm$
256 0.80‰ (Fig. S4).

257 4. Discussion

258 4.1 PFAS distribution in water, sediment, food, and *C. riparius*

259 The sediment from the study site was characterized by high concentrations of
260 PFNA, PFUnA, and PFTrDA, whereas PFOS concentrations remained low as compared

261 with the data reported in the literature (Table S6). This pattern of PFAS contamination
262 may be characteristic of the upstream industrial discharge from a fluoropolymer and
263 polyvinylidene fluoride facility (Dauchy et al., 2012). In most published studies from
264 other sites, PFUnA and PFDA were usually below 1 ng.g⁻¹dw (Clara et al., 2009;
265 Higgins et al., 2005; Higgins et al., 2007; Labadie and Chevreuil, 2011), except for the
266 Coosa River in Alabama (3.80 ng.g⁻¹dw) and Tennessee, USA (4.66 ng.g⁻¹dw) (Lasier et
267 al., 2011). Detection of other long-chain PFCAs was scarce: a maximum value of 1.19
268 ng.g⁻¹dw for PFTTrDA was reported in Tokyo Bay, Japan (Zushi et al., 2010), and
269 PFDoA and PFTTeDA values were below 1 ng.g⁻¹dw in the Orge River (near Paris,
270 France) (Labadie and Chevreuil, 2011), whereas in the Coosa River, USA,
271 concentrations above 1 ng.g⁻¹dw (1.7 and 4.64 ng.g⁻¹dw respectively) were found
272 (Lasier et al., 2011). For PFOS, BER sediment concentrations (0.247 - 0.294 ng.g⁻¹ dw)
273 were in the same range as reported in other studies around the world (Table S6) (Bao et
274 al., 2009; Benskin et al., 2012; Nakata et al., 2006) and lower than PFOS levels in the
275 Orge River (France), Coosa River (USA), Sydney Harbor (Australia), and the North and
276 Baltic Seas (Labadie and Chevreuil, 2011; Lasier et al., 2011; Theobald et al., 2012;
277 Thompson et al., 2011).

278 Comparison of the respective concentration ranges for the PFASs measured in
279 control and test aquaria make it possible to design a conceptual diagram of PFASs
280 transport between compartments (Fig. 4). Since PFBA, PFPA, PFHxA, PFNA, PFDA,
281 PFBS, and PFHxS display the same concentrations on overlying waters in control and
282 test aquaria, we inferred that sediment is not a source for these compounds to water.
283 Conversely, PFUnA, PFTTrDA, and 6:2 FTSA, which were present only in OW test
284 aquaria and therefore were clearly released from the sediment. Similarly, PFBA, PFPA,

285 PFHxA, PFOA, PFNA, PFUnA, PFOS, and 6:2 FTSA associated with test sediments
286 were in much higher concentrations in PW from test aquaria than in PW from controls.
287 Therefore, their presence in PW cannot be related to OW. PFNA and PFOS were
288 measured in both food (Tetramin[®]) and OW controls aquaria. As a consequence, it
289 could not be exclude that PFNA and PFOS in Tetramin[®] were dissolved into OW.
290 However, all the PFASs measured were <LD in control chironomids; therefore
291 Tetramin[®] is not a source of PFASs. PFUnA, PFOS, and 6:2 FTSA were present in
292 sediment, PW, and chironomids: both PW (respiration) and sediment (food) contribute
293 to the contamination. Conversely, PFDoA, PFTrDA, PFTeDA, and FOSA present only
294 in sediment and chironomids contributed to the contamination by the ingestion of
295 sediment particles.

296 4.2 PFASs in benthic invertebrates

297 Chironomids bioaccumulated four PFCAs, one PFSA (PFOS), and two PFASs
298 precursors. Among these, 6:2 FTSA was found to bioaccumulate poorly in fish and rats
299 (DuPont, 2008). Reported concentrations were generally higher for benthic
300 invertebrates than chironomids, especially for PFOS; ranges of PFOS in Capitellidae
301 and Nereidae were 0.82 -12.6 ng.g⁻¹ww and 0.26 - 0.67 ng.g⁻¹ww (Loi et al., 2011).
302 Mean PFAS concentrations reported for lugworm were 0.41 ng.g⁻¹ww (Nakata et al.,
303 2006) and 280 ± 33 ng.g⁻¹ww for *Diporeia hoyi* (Martin et al., 2004). The latter study
304 also reported that concentrations of PFUnA, PFDoA, PFTrDA, and PFTeDA were
305 higher in *Diporeia hoyi* than in chironomids (Martin et al., 2004). In Nereidae and
306 Capillidae worms, concentrations of PFUnA were lower than in chironomids (Loi et al.,
307 2011). Compared to chironomids from the present study, lower concentrations were also
308 reported for PFDoA in Capillidae (Loi et al., 2011), for PFOS in clams (Nakata et al.,

309 2006; Nania et al., 2009), for FOSA in clams and lugworms (Nakata et al., 2006), and
310 for PFTeDA in Nereidae worms (Loi et al., 2011). However, comparisons between
311 freshwater and marine organisms should be interpreted with caution because salt may
312 affect the chemical activity (Jeon et al., 2010a; Jeon et al., 2010b).

313 4.3 Accumulation kinetics

314 The biota-to-sediment accumulation factors (BSAFs; Eq. 2) indicated values for
315 FOSA > PFTTrDA > PFOS > PFUnA > 6:2 FTSA > PFTeDA > PFDoA, and no trend
316 was observed between BSAF and PFAS chain length. In contrast, Higgins et al. (2007)
317 observed that BSAF values tended to decrease with increasing chain length and Lasier
318 et al. (2011) reported that BSAF values increased with increasing chain length. BSAF
319 values in the present study were lower than BSAFs reported by Higgins et al. (2007)
320 and Lasier et al. (2011) (e.g., PFUnA BSAF_{ww} chironomid = 0.020; BSAF_{ww} = 0.44 ±
321 0.11; BSAF_{ww} = 0.29, CV = 40, respectively). This might be explained by the fact to the
322 food added during the present experiment, in contrast to the absence of feeding in
323 previous studies (Higgins et al., 2007 and Lasier et al., 2011). Adding food may
324 decrease the exposure and dilute the contamination because without this addition the
325 chironomids would have fed only on sediment organic matter. Our experiment was
326 conducted in this manner because preliminary trials showed that survival rates were too
327 low when no food was added to the aquaria.

328 In the Higgins et al. (2007) study, *Lumbriculus variegatus* reached steady state
329 for PFOA and PFDS but not for PFNA, PFOS, PFDA, PFUnA, and PFDoA. In this
330 experiment *C. riparius* reached a steady state both for PFCAs > C₁₁ (PFUnA, PFDoA,
331 PFTTrDA) and PFOS and FOSA. However, in Lasier et al. (2011), *L. variegatus*
332 accumulated other compounds that were not accumulated by chironomids such as

333 PFHpA, PFOA, PFNA, and PFDA, although they were measured in sediment. This
334 could be explained by the difference in feeding habits between the two organisms
335 (Nogaro et al., 2009). In addition, chironomid growth during the accumulation phase is
336 not negligible, unlike for *L. variegatus*, which lost weight (because it went unfed), as
337 growth dilutes contamination. PFAS accumulation in chironomids was as effective
338 when exposure started at 2nd instar as when it started at 4th instar. PFASs concentrations
339 were the same between the end of E1 and E2 exposures (Table 1, Fig. 3). At the latter
340 stage, growth is more rapid than at previous stages (Péry et al., 2002). These results
341 suggest that the sole use of the 4th instar in could be included in the design of future
342 experimental studies with this organism.

343 For PFTrDA, PFUnA, PFOS, and FOSA, accumulation data obtained in the present
344 study fit an exponential rise model well (Eq. 1), with R² values ranging from 0.99
345 (PFOS) to 0.97 (PFUnA). Equation (1) supports either a classical two-compartment
346 partition model (Higgins et al., 2007; Landrum, 1989) or a more sophisticated
347 adsorption-like accumulation model (Liu et al., 2011). Model parameter *a* is related to
348 the exposure concentration ($C_{\text{sed-oc}}$) and uptake and depuration rates (k_u and k_e
349 respectively).

350 Model parameter *b* is related to the elimination rate (k_e). As chironomids grow during
351 the experiment, the elimination rate (k_e) should be corrected according to Eq. (3)
352 (Spacie and Hamelink, 1985),

353
$$k_e' = k_e + g \quad \text{Eq. (3)}$$

354 The complete two-compartment model includes a λ term in order to account for
355 the chemical concentration decline in sediment. This term is set to 1, as in eq. 1, when
356 sediment concentrations do not vary significantly during the experiment (that is, if the

357 flux from sediment to organisms is much lower than the overall compound mass in
358 sediment). This was the case in the current experiment (Table S5). In this case, equation
359 (1) can be solved easily, with b being the apparent elimination rate (k_e' in h^{-1}), and

360
$$a = (k_u/k_e) * C_{sed-oc} \quad \text{eq. (4)}$$

361 with k_u the uptake rate ($\text{g}_{oc} \cdot \text{g}_{ww} \cdot \text{h}^{-1}$) and C_{sed-oc} the concentration in sediment normalized
362 to the organic carbon content ($\text{ng} \cdot \text{g}_{oc}^{-1}$).

363 Applying this approach, yields (k_u , k_e , and k_e') were obtained for PFTrDA, PFUnA,
364 PFOS, and FOSA) (Table 3). These data are only informative because no depuration
365 data were available.

366 The adsorption-like model (Liu et al., 2011) was developed initially for an uptake
367 experiment from water. We assumed that it could also apply to accumulation from
368 sediment and food as in our study. Nevertheless, it cannot be solved without depuration
369 data because three variables are included in the terms a and b instead of two as in the
370 two-compartment model:

371
$$a = (n * k_u * C_{sed}) / (k_u * C_{sed} + k_e) \quad \text{Eq. (5)}$$

372
$$b = k_u * C_{sed} + k_e \quad \text{Eq. (6)}$$

373 where n is the number of adsorption sites.

374 4.4 Contamination routes

375 All compounds accumulated by the chironomids were detected in sediment. PFUnA,
376 PFOS, and 6:2 FTSA were also quantified in both pore and overlying water and
377 PFTrDA was detected in overlying water. In addition, some compounds, such as
378 PFUnA, PFOS, and FOSA, were found in food added (Tetramin[®]) to chironomids,
379 which did not affect accumulation in chironomids (i.e., the balance between

380 accumulation and depuration) because these compounds were not detected in control
381 chironomids (PFAS concentrations <LDs).

382 These results therefore suggest that there are two contamination routes for the
383 PFASs, which differ according to the compounds. The contamination routes for
384 substances found in both pore water and sediment (particles) were via food and
385 tegument. For other compounds, found only in sediment, the contamination route was
386 only trophic.

387 These observations are supported by the growth data: larvae grew more in test
388 sediments than in the control setting, although they received the same quantity of
389 Tetramin[®]. These results indicate that larvae fed on organic carbon from the sediment
390 and thus may have absorbed the PFAS associated with particles. On the other hand, the
391 chironomid $\delta^{13}\text{C}$ values were almost identical in test and control organisms, suggesting
392 that the proportion of C obtained by the larvae from the sediment was limited. This is
393 consistent with the findings reported by Goedkoop et al. (2006), which showed that
394 about 90% of the carbon intake was from added food. However, both $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$
395 values for Tetramin[®] were mean values because Tetramin[®] is a mixture of animal (fish,
396 crustaceans, mollusks) and plant (cereals) ingredients, each having its own isotopic
397 composition. Chironomids may feed selectively on certain components of the added
398 food (Goedkoop et al., 2006). Therefore, the observed chironomid $\delta^{13}\text{C}$ signature may
399 be influenced by sediment organic carbon.

400 **5. Conclusion**

401 Results from this study indicate that *C. riparius* accumulated four long-chain
402 perfluoroalkyl carboxylates (PFUnA, PFDoA, PFTrDA, and PFTeDA), a perfluoroalkyl
403 sulfonate (PFOS), a precursor (FOSA), and a fluorotelomer (6:2 FTSA) from sediment.

404 No short-chain PFAS, detected mostly in water, were accumulated by chironomids. No
405 trends were observed for BSAFs, in contrast to studies by Higgins et al. (2007) and
406 Lasier et al. (2011). The contamination pathways appeared to be trophic (sediment
407 particles) and tegumentary (pore water) for PFUnA, PFOS, and 6:2 FTSA and only via
408 the trophic pathway for the other compounds. Growth data support the trophic
409 contamination route but isotopic data are difficult to interpret because of food added
410 during the experiments. PFUnA, PFTrDA, and PFOS data fit an exponential rise model;
411 apparent uptake and elimination constants can thus be proposed on the basis of the
412 classical partition model (Landrum, 1989; Spacie and Hamelink, 1985). Elimination
413 experiments should be conducted to determine the elimination kinetics experimentally
414 in this species.

415 **Acknowledgments**

416 This study was funded by the Rhone-Mediterranean and Corsica Water Agency and the
417 Rhone-Alpes Region within the Rhone ecological restoration plan. We thank Bernard
418 Motte (IRSTEA), Raphael Barlon, and the Centre d'Observation de l'Ile du Beurre team
419 (Condrieu, France) for their assistance during the sampling campaigns and chemical
420 laboratory analysis (UR MALY, IRSTEA Lyon-Villeurbanne) for monitoring the
421 physicochemical characterization of sediment, and Linda Northrup for copyediting the
422 text as well as two anonymous reviewers for their constructive remarks.

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- 567
- 568

569
570 Table 1: PFAS concentrations in chironomids at the end of E1 and E2 exposures ($\text{ng}\cdot\text{g}^{-1}$
571 ww). E1 with standard deviation ($n = 3$) and E2 with analytical error calculation relative
572 to spiked samples (Table S3). PFTeDA “trace” means that concentrations were between
573 LD and LQ.

574
575 Table 2: BSAF_{ww} ($\text{g}_{\text{oc}}\cdot\text{g}_{\text{ww}}^{-1}$) for chironomids and for *Lumbriculus variegatus* (Higgins
576 et al., 2007; Lasier et al., 2011); n.d, not detected, *PFTeDA, as guidelines only
577 (because $\text{LD} < \text{PFTeDA concentrations in chironomids} < \text{LQ}$).

578
579 Table 3: Model parameters with (k_e') and without growth correction (k_u, k_e)
580

581
582 Figure 1: Study site of the Rhône River, France. BER = Beurre Island, Plant = PFAS
583 production plant. The river runs from north to south.

584
585 Figure 2: Kinetics of PFASs accumulation in fourth instar larvae of *C. riparius*, in the
586 E2 experiment. Left, PFSAs; right, PFCAs (PFTeDA concentrations were between LD
587 and LQ). Error bars represent the analytical error estimated from the relative standard
588 deviation of triplicate recovery rate tests performed on spiked samples (Table S3).

589
590 Figure 3: PFCA accumulation in E1 (left, $\text{LD} < \text{PFTeDA concentrations} < \text{LQ}$) and E2
591 (right) experiments. Error bars represent the analytical error estimated from the relative
592 standard deviation of triplicate recovery rate tests performed on spiked samples (Table
593 S3); on the right graph they represent the standard deviation between three replicates (n
594 = 3).

595

596 Figure 4: Partitioning between different compartments: green represents PFASs in food
597 or from a food source, and brown, in the same manner, for sediment. For chironomids,
598 the blue frames represent both sediment (brown) and pore water (blue) sources for
599 PFASs.

600
601
602

Table 1 : PFAS concentrations in chironomids at the end of E1 and E2 exposures

Compounds	PFASs in chironomids at the end of E1 (ng.g ⁻¹ ww)	PFASs in chironomids at the end of E2 (ng.g ⁻¹ ww)
PFUnA	0.79 ± 0.10	0.80 ± 0.08
PFDoA	0.11 ± 0.01	0.14 ± 0.01
PFTTrDA	1.71 ± 0.42	2.42 ± 0.17
PFTeDA trace	0.05 ± 0.001	0.08 ± 0.02
PFOS	0.16 ± 0.02	0.13 ± 0.02
FOSA	0.05 ± 0.01	0.05 ± 0.02
6:2 FTSA	0.07 ± 0.03	0.08 ± 0.005

Table 2: BSAF_{ww} (g_{oc}·g_{ww}⁻¹)

Compounds	Fluorinated carbon number	BSAF _{ww} chironomid	BSAF _{ww} Higgins et al., 2007	BSAF _{ww} Lasier et al., 2011
PFUnA	10	0.020	0.44 ± 0.11	0.29, CV= 40
PFDoA	11	0.004	0.45 ± 0.08	0.34, CV=40
PFTTrDA	12	0.042	n.d	0.62, CV=44
PFTeDA*	13	0.004	n.d	0.63, CV=47
PFOS	8	0.023	0.83 ± 0.20	0.49, CV=50
6:2 FTSA	6	0.018	n.d	n.d
FOSA	8	0.098	n.d	n.d

Table 3: Model parameters

Compounds	a	ku	ke' (b)	ke
PFUnA	0.83 ± 0.03	0,0009	0.04 ± 0.01	0,03
PFTTrDA	2.56 ± 0.11	0,0015	0.03 ± 0.01	0,02
PFOS	0.14 ± 0.008	0,0009	0.04 ± 0.01	0,03
FOSA	0.06 ± 0.01	0,0022	0.02 ± 0.01	0,01

Figure 1 : Study site

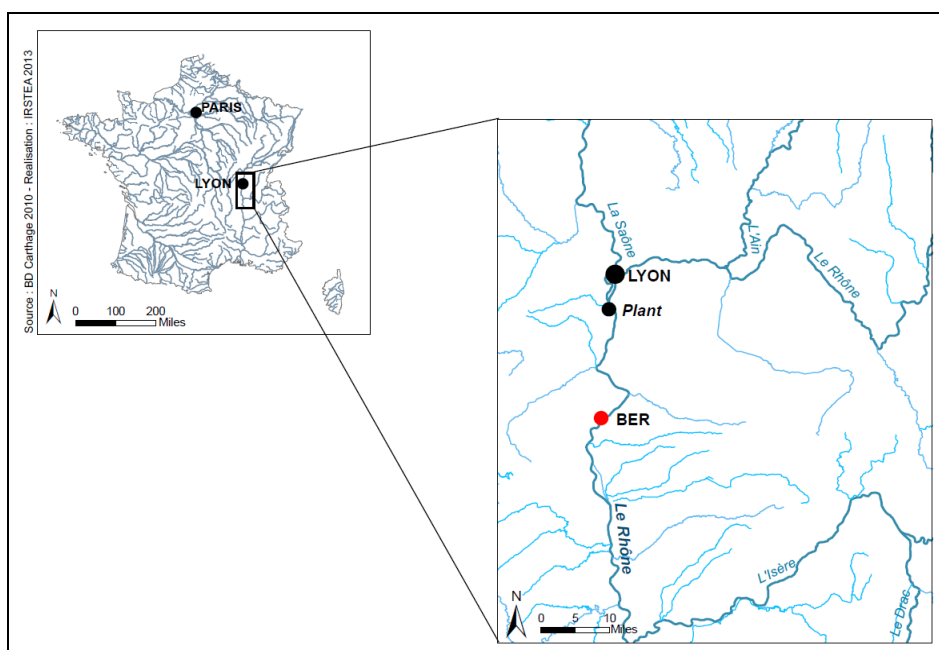


Figure 2: Kinetics of PFAS accumulation in fourth instar larvae of *Chironomus riparius*.

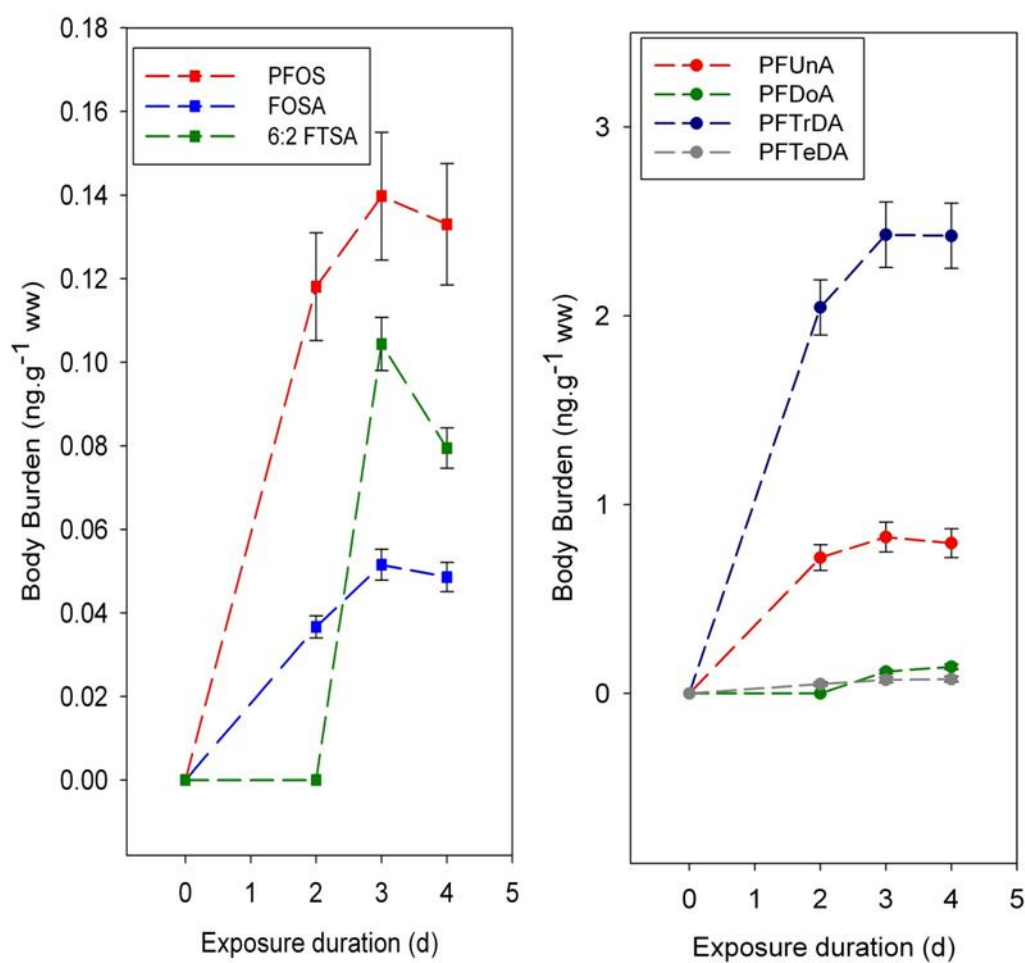


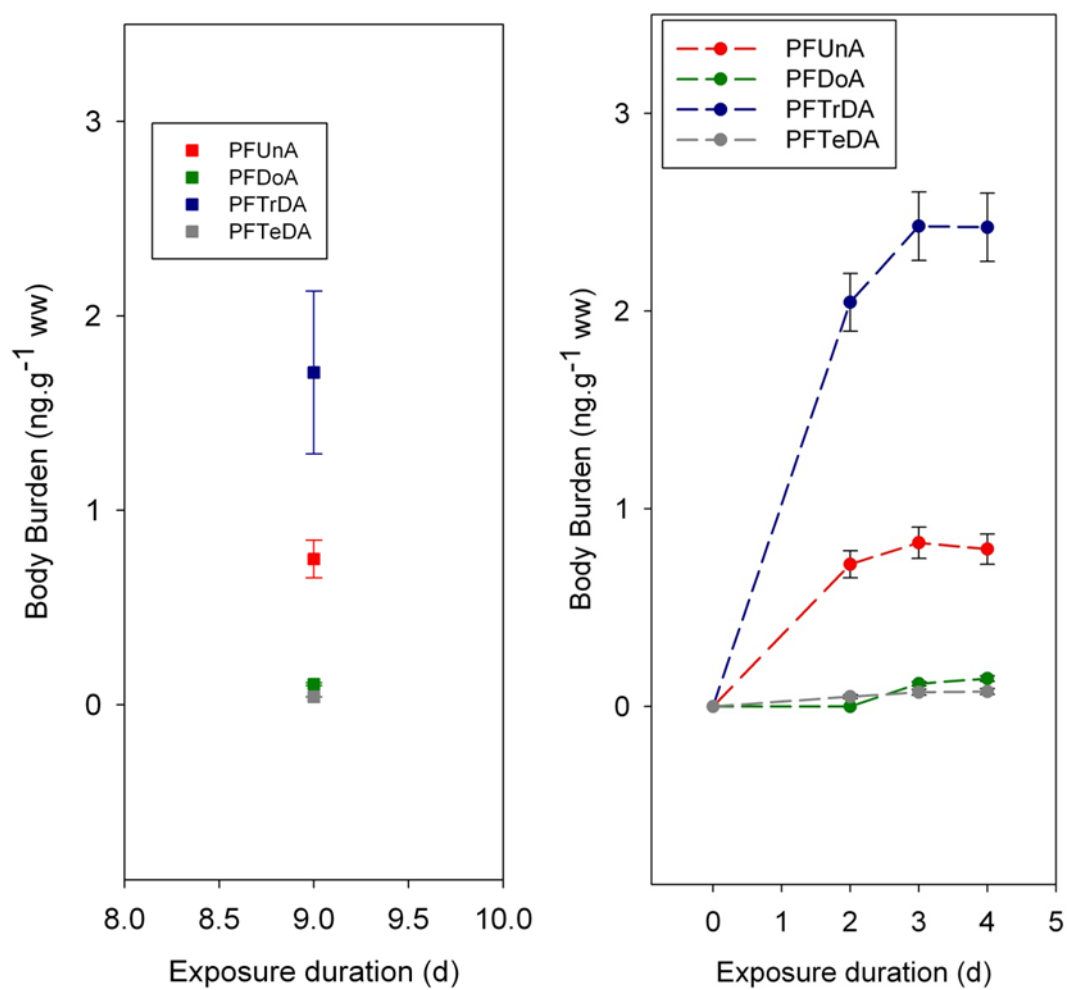
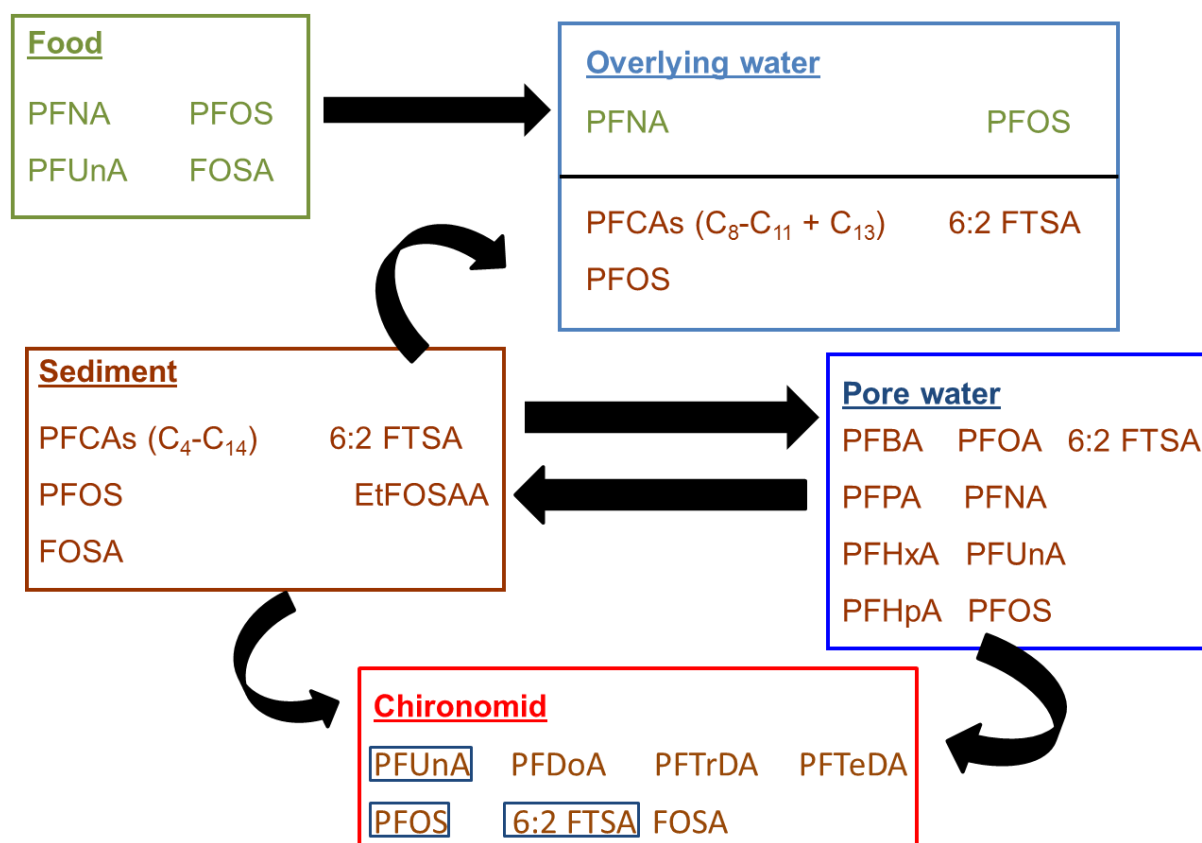
Figure 3: PFCA accumulation in E1 (left) and E2 (right) experiments.

Figure 4: Partition between different compartments

Supplementary Material

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Author-produced version of the article published in Environmental Pollution (2014), vol. 189, 27-34
The original publication is available at <http://www.sciencedirect.com/>
doi : 10.1016/j.envpol.2014.02.018