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1   Do concentrations of perfluoroalkylated acids (PFAAs) in isopods reflect

2   concentrations in soil and songbirds? A study using a distance gradient from a

3   fluorochemical plant

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Abstract

Perfluoroalkylated acids (PFAAs) are persistent chemicals that have been detected globally in the environment and in wildlife. Although it is known that PFAAs sorb to solid matrices, little is known on PFAA concentrations in soils. PFAA pollution has often been studied in aquatic invertebrates. However, this has rarely been done on terrestrial species. In the present study, we examined whether the concentrations of 15 PFAAs in isopods (Oniscidae), collected at a fluorochemical plant and in four other areas, representing a gradient in distance from the pollution source (1 km to 11 km), were related to those in the soil and in eggs of a songbird, the great tit (*Parus major*), collected in the same areas. Additionally, we examined the effect of physicochemical properties such as total organic carbon (TOC) and clay content on the relationship between the concentrations in soil and isopods. Finally, we examined the composition profile in the soil and isopods.

Mean PFOS and PFOA concentrations of 1700 ng/g dw and 24 ng/g dw were detected in the soil at the plant. PFOS and PFPeA were the dominant PFAAs in isopods and were detected at mean concentrations of 253 and 108 ng/g ww, respectively. The great tit eggs showed elevated mean PFOS concentrations of 55970 ng/g ww. In most cases, PFAA concentrations decreased with increasing distance from the plant.

As PFAA concentrations in isopods were correlated with concentrations in the soils, isopods could serve as a bioindicator for PFAA concentrations in soils. Additionally, there were indications that isopods could also serve as a bioindicator for PFAA concentrations in eggs of great tits. However, these indications were only the case at two locations, showing the need to further monitor the possibilities of using isopods as a bioindicator for PFAA concentrations in song bird eggs.

Keywords: Soil; Isopods; Perfluoroalkylated acids; Songbirds; Bioindicator

Capsule

37   Elevated PFAA concentrations in isopods reflected concentrations in songbird eggs and in soil, indicating

38   that trophic transfer of PFAAs from soil, via isopods, to songbirds might play a role in the PFAA exposure

39   of terrestrial songbirds.

Introduction

The global distribution of perfluoroalkylated acids (PFAAs) over the past decades has led to a growing scientific attention and public concern towards these chemicals. The strong carbon-fluorine bonds and their hydrophobic and lipophobic character result in outspoken physicochemical properties, which make them suitable for numerous applications such as soil repellents, food-contact paper and fire-fighting foams (Buck et al., 2011; Kissa, 2001). These applications may cause PFAAs to end up in the environment either through direct pollution or via environmental degradation of precursor compounds (Buck et al., 2011; Prevedouros et al., 2006). Additionally, gas- and particle-phase atmospheric long-range transport may also result in the distribution of PFAAs in the environment (Barber et al., 2007; Ellis et al., 2003; Schenker et al., 2008). PFAAs have been reported globally in the environment, wildlife and humans (Butt et al., 2010; D'Hollander et al., 2010; Giesy & Kannan, 2001, 2002; Groffen et al., 2017, 2018; Houde et al., 2006; Miller et al., 2015), which shows their bioaccumulative potential.

Due to their high bioaccumulative potential and toxicity (Conder et al., 2008), there has been a growing scientific concern towards long-chain perfluoroalkyl sulfonic acids (PFSAs) and perfluoroalkyl carboxylic acids (PFCAs) over the past decades (Conder et al., 2008). In 2002, the major manufacturer of PFAAs, 3M, phased-out the production of perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3H$), perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$) and related compounds, based on their persistence in the environment, widespread distribution and potential health effects. Additionally, PFOS was included in the Stockholm Convention on Persistent Organic Pollutants in 2009, which allows limited on-going use of PFOS. Although these measures appear to have reduced environmental PFOS concentrations, concentrations of other PFAAs are sometimes still rising (Ahrens et al., 2011a; FIlipovic et al., 2015a; Groffen et al., 2017, 2019; Miller et al., 2015). Furthermore, short-chain PFAAs, which are widely used as alternatives to long-chain PFAAs, are known to have extremely persistent final degradation products resulting in a permanent exposure of

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63   organisms to these compounds (Brendel et al., 2018). Therefore, it is still necessary to further monitor

64   PFAAs in the environment.

65   Soils are important sinks for many persistent organic pollutants (POPs), such as polybrominated diphenyl

66   ethers (PBDEs), polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and

67   dibenzofurans (PCDD/Fs) (Cetin et al., 2017; Maqsood & Murugan, 2017; Mueller et al., 2006; Rankin et

68   al., 2016; Xiao et al., 2016). Although it is known that PFAAs sorb to solid matrices (Ahrens et al., 2011b;

69   Li et al., 2018; Miao et al., 2017; Qian et al., 2017; Rankin et al., 2016; Wei et al., 2017), there is limited

70   knowledge on the possible role of soils as sinks for PFAAs.

71   Invertebrates have been used in numerous field studies that monitor PFAA concentrations. However,

72   most of these studies target aquatic invertebrates (e.g. Babut et al., 2017; Groffen et al., 2018; Lescord et

73   al., 2015; Loi et al., 2011), whereas field data on terrestrial invertebrates remain scarce. Only one field

74   study has been performed on isopods in Belgium (D'Hollander et al., 2014), one on adult Odonata in South

75   Africa (Lesch et al., 2017) and one on earthworms in the USA (Zhu and Kannan, 2019). Other studies on

76   terrestrial invertebrates, were often performed on earth worms under laboratory conditions (e.g. Das et

77   al., 2015; Zhao et al., 2013; Zhao et al., 2017). Furthermore, the relationships between PFAA

78   concentrations in the soil and invertebrates, and the effects of physicochemical properties on these

79   relationships, have rarely been studied (Das et al., 2015). Finally, information on trophic transfer in the

80   terrestrial food chain, from soil to invertebrates and eventually vertebrates, is scarce (D'Hollander et al.,

81   2014).

82   In the present study we measured the concentrations of multiple PFAAs in the soil and isopods along a

83   distance gradient from a fluorochemical plant, and investigated whether the concentrations in the isopods

84   were correlated to the PFAA concentrations in the soil and in the eggs of great tits (*Parus major*), which

85   were collected at the same time and locations by Groffen et al. (2019). Additionally, we examined the role

86 of physicochemical properties of the soil such as total organic carbon (TOC) and clay content on the

87 relationship between PFAA concentrations in the soil and isopods. Finally, the composition profiles in the

88 soil and isopods were determined.

89 **Materials and method**

90 *Sample collection*

91 Soil and invertebrate samples were collected in June 2016. Five sampling sites (Figure 1), representing a

92 gradient from the 3M fluorochemical plant in Antwerp, Belgium, were selected based on prior

93 biomonitoring studies in the vicinity of this plant (Dauwe et al., 2007; D'Hollander et al., 2014; Groffen et

94 al., 2017; Hoff et al., 2005; Lopez-Antia et al., 2017): 3M, Vlietbos (1 km SE from 3M), Rot-Middenvijver

95 (hereafter Rot; 2.3 km ESE from 3M), Burchtse Weel (3 km SE from 3M) and Fort 4 (11 km SE from 3M).

96 At each location approximately 10 soil samples were collected, within a 3 m radius of nest boxes that were

97 used in multiple biomonitoring studies (e.g. Groffen et al., 2019), by using a stainless steel shovel. Samples

98 were sieved through an ASTM E 11-81 Test Sieve (1.7 mm) and stored in 50 mL polypropylene (PP) tubes

99 until further analysis. At the same sites where the soil samples were collected, isopods (Oniscidae) were

100 collected by picking them off the ground, trunks of trees and rotting wood, and pooled (N ≥ 10) into 50

101 mL PP tubes. As variation in PFOS concentrations within a clutch has been demonstrated for Audouin's

102 gulls (*Larus audouinii,* Vicente et al., 2015), we expected that sampling a fixed egg of each nest would

103 reduce the variation among nests at a site compared to random sampling (Groffen et al., 2019). Therefore,

104 we collected the third egg of great tit nests, before incubation had started during the breeding season of

105 2016.

106 The PFAA concentrations in bird eggs in the present study are a part of a larger dataset, reported by

107 Groffen et al. (2019). All samples were stored at -20°C prior to further analyses.

108 *Sample extraction*

109   Prior to the analysis, soil samples were air-dried and eggs were homogenized by repeatedly sonicating

110   and vortexing. To each sample, 10000 pg (80 μL, 125 pg/μL) of the ISTD mixture was added. After mixing,

111   10 mL of ACN was added and samples were sonicated (3 x 10 min, Branson 2510) and left overnight on a

112   shaking plate (135 rpm, room temperature, GFL 3020, VWR International, Leuven, Belgium). After

113   centrifugation (4°C, 2400 rpm, 10 min, Eppendorf centrifuge 5804R, rotor A-4-44), the supernatant was

114   transferred to a 14 mL PP tube. Chromabond HR-XAW Solid Phase Extraction (SPE) cartridges (Application

115   No. 305200, SPE department, Macherey-Nagel, Germany, 2009) were conditioned with 5 mL of ACN. After

116   equilibration with 5 mL of MQ, the samples were loaded onto the cartridges. The cartridges were washed

117   with 5 mL of 25 mM ammonium acetate in MQ and 2 mL of ACN and eluted with 2 x 1 mL of 2% ammonium

118   hydroxide in ACN. The eluent was dried completely using a rotational-vacuum-concentrator (Eppendorf

119   concentrator 5301, Hamburg, Germany) and reconstituted with 200 μL of 2% ammonium hydroxide in

120   ACN. Samples were vortex-mixed for at least one minute and filtrated through an Ion Chromatography

121   Acrodisc 13 mm Syringe Filter with 0.2 μm Supor (PES) Membrane (VWR International, Leuven, Belgium)

122   attached to a PP auto-injector vial.

123   The extraction procedure for the isopods was based on a method described by Powley et al. (2005) with

124   minor modifications. The isopods were homogenized using a TissueLyser LT (Qiagen GmbH, Germany)

125   with stainless steel beads (5 mm; Qiagen GmbH, Germany). The protocol follows the same steps as

126   described previously for the method in soil and eggs until the samples were centrifuged (4°C, 2400 rpm,

127   10 min, Eppendorf centrifuge 5804R, rotor A-4-44). Hereafter, the supernatant was transferred to a 15

128   mL PP tube and dried to approximately 0.5 mL in the rotational-vacuum-concentrator. To eliminate

129   pigments, the concentrated extract was transferred to a PP Eppendorf tube containing 50 mg of

130   graphitized carbon powder (Supelclean ENVI-Carb, Sigma-Aldrich, Belgium) and 50 μL of glacial acetic acid.

131   In addition, 2 x 250 μL of ACN, used to rinse the 15 mL tubes, was added to the Eppendorf tubes. These

132   tubes were vortexed and centrifuged (4°C, 10000 rpm, 10 min, Eppendorf centrifuge 5415R; Rotor F 45-

133 24-11) and the supernatant was treated equal as the eluent from the method described for soil and egg

134 samples.

135 *Chemical analysis*

136 All used abbreviations are according to Buck et al. (2011). Fifteen target analytes were selected, including

137 4 PFSAs and 11 PFCAs. All target analytes and the isotopically mass-labelled internal standards (ISTDs;

138 Wellington Laboratories, Guelph, Canada) used in the quantification of these analytes are illustrated in

139 Table 1. In addition, HPLC grade Acetonitrile (ACN; LiChrosolv, Merck Chemicals, Belgium), ammonium

140 acetate (VWR International, Belgium), ammonium hydroxide (Filter Service N.V., Belgium) and Milli-Q

141 (MQ; 18.2 mΩ; TOC: 2.0 ppb; Merck Millipore, Belgium) were used.

142 *UPLC-TQD analysis and quantification*

143 To analyze the PFAAs, we used ultra-performance liquid chromatography-tandem mass spectrometry

144 (UPLC-MS/MS, ACQUITY, TQD, Waters, Milford, Ma, USA). Target analytes were separated using an

145 ACQUITY BEH C18 column (2.1 x 50 mm; 1.7 μm, Waters, USA) and an ACQUITY BEH C18 pre-column (2.1

146 x 30 mm; 1.7 μm, Waters, USA) was inserted between the solvent mixer and the injector to retain any

147 PFAAs contamination originating from the system. The mobile phase solvents were A) 0.1% formic acid in

148 water and B) 0.1% formic acid in ACN. The flow rate was set at 450 μL/min with an injection volume of 10

149 μL. The gradient started at 65% A, decreased in 3.4 min to 0% A and returned to 65% A at 4.7 min. Multiple

150 reaction monitoring (MRM) of two diagnostic transitions per target analyte was used to identify and

151 quantify the PFAAs. The diagnostic transitions are displayed in Table 1.

152 *Physicochemical properties of the soil*

153 To determine the organic carbon content (TOC) of the soil, the loss on ignition method, as described by

154 Heiri et al. (2001), was used. Approximately 1 g of the soil was oven-dried at 60°C. Empty aluminum-foil

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155   bags were dried at 105°C for at least 2 hours, cooled to room temperature in a desiccator and weighed.

156   Hereafter, the bags were filled with the dried soil, weighed and oven-dried at 105°C for at least one day.

157   After cooling down, the samples were weighed again and incinerated in a muffle furnace at 550°C for at

158   least 5 hours. Finally, after cooling down in a desiccator, weight loss was determined and TOC was

159   calculated using Formulas 1 and 2.

160    $LOI_{550}(\%) = \frac{(DW_{105} - DW_{550})}{DW_{105}} * 100$ Formula 1.

161    $TOC\ (\%) = \ LOI_{550}/1.742$ Formula 2.

162   With LOI, the loss on ignition after 550°C and DW the dry weight of the sample after drying at 105°C or

163   550°C.

164   The clay content (particles with a size < 4 μm) of the soil was assessed by using a Malvern Mastersizer

165   2000 and Hydro 2000G. Prior to the analysis the samples were pretreated with 40 mL 33% hydrogen

166   peroxide (VWR Chemicals, Leuven, Belgium) and 9 mL 30% hydrochloric acid (VWR Chemicals, Leuven,

167   Belgium) to destruct organic material and iron conglomerates in the soil. In addition, the samples were

168   boiled to speed up the destruction process, and sieved over a 2.0 mm test sieve prior to the analysis.

169   *Quality assurance*

170   Per 10 samples, one procedural blank was analyzed as quality control. Concentrations in the blanks were

171   all <LOQ. Method recoveries for the target analytes varied between 4% and 50% in the isopod samples

172   and between 16% and 100% in soil samples. Individual limits of quantification (LOQs) were determined

173   based on a signal-to-noise (S/N) ratio of 10 and are displayed in Table 2 for soil, Table 3 for isopods and

174   Table 4 for great tit eggs.

175   *Statistical analyses*

176   Statistical analyses were performed using R Studio and Graphpad Prism 7.04. To obtain a normal

177   distribution, PFAA concentrations and TOC values were log-transformed. Compounds with a detection

178   frequency below 50% at a location were excluded from further analysis.

179   A reverse Kaplan-Meier (KM) analysis and a Mantel-Cox pairwise comparison test were used to evaluate

180   differences between locations in PFAA concentrations in soil and in isopods. As this test is nonparametric,

181   untransformed data was used to perform the analysis. The reverse KM test is commonly used in the

182   survival analysis of left censored data (Gillespie et al., 2010) and is a useful tool to cope with

183   concentrations below the LOQ (Groffen et al., 2017; Jaspers et al., 2013). In all other analyses,

184   concentrations <LOQ were substituted with a value of LOQ/2 (Bervoets et al., 2004; Custer et al., 2000).

185   Relationships between PFAA concentrations in the soil and in isopods and the role of the physicochemical

186   properties on these relationships were tested using multiple linear regressions. Spearman correlation

187   tests were used to test for associations between PFAA concentrations in the soil and physicochemical

188   characteristics of the soil and for associations between TOC and clay content. Similarly, concentrations in

189   the soil and isopods were correlated (spearman correlation test) with concentrations in third egg of great

190   tits (*Parus major*) collected from the nest boxes. Differences between locations in TOC and clay content

191   were assessed using a One-way ANOVA.

192   **Results**

193   *PFAA concentrations in soil, isopods and songbird eggs*

194   Table 2 shows an overview of the median and mean concentrations, ranges and detection frequencies of

195   PFAAs in the soil. Figure 2 shows the concentrations of PFBA, PFOA, PFDoDA, PFBS and PFOS in the soil in

196   function of the distance from the pollution source. The center of the fluorochemical plant was considered

197   as the pollution source (0 m). Only PFBA, PFOA, PFDoDA, PFBS and PFOS were detected at >50% of the

198   sites. Therefore, only these PFAAs have been used in further statistical analysis. PFBA concentrations did

199   not differ among study sites (all p > 0.05). PFOA concentrations at the plant site were significantly higher

200   than those at all other locations (all p < 0.001). PFOA concentrations at Rot were also significantly higher

201   than those at Burchtse Weel (p = 0.025) and Fort 4 (p = 0.05). Similarly, PFDoDA concentrations were

202   significantly higher at the plant site compared to Vlietbos and Fort 4 (both p < 0.001). Concentrations of

203   PFBS were significantly higher at the plant site compared to Vlietbos (p = 0.031) and finally, PFOS

204   concentrations at the plant site were significantly higher compared to all other locations (all p < 0.001).

205   At Vlietbos, the PFOS concentrations were significantly higher than all locations further away (all p <

206   0.001), whereas the PFOS concentrations at Rot were significantly lower than those further away at

207   Burchtse Weel and Fort 4 (both p < 0.005).

208   An overview of median and mean concentrations, ranges and detection frequencies of PFAAs in isopods

209   is given in Table 3. PFOS was the only PFAA with detection frequencies > 50% at all of the sites. Therefore,

210   only PFOS was included in further statistical analysis. Figure 3 shows the PFOS concentrations in isopods

211   in function of the distance from the pollution source. PFOS concentrations were significantly higher at 3M

212   compared to all other locations (all p < 0.001). In addition, the PFOS concentrations at Vlietbos and

213   Burchtse Weel were both significantly higher than those at Rot (p = 0.003 and 0.001, respectively).

214   Finally, an overview of median and mean concentrations, ranges and detection frequencies in great tit

215   eggs is given in Table 4. The results in Table 4 are a part of a larger dataset reported by Groffen et al.,

216   2019. The concentrations in bird eggs in function of the distance from the pollution source are displayed

217   in Figure 4. PFOS concentrations were significantly higher at 3M compared to all other locations (all p <

218   0.001). Furthermore, PFOS concentrations at Rot were significantly higher than those at Vlietbos (p =

219   0.019) and Fort 4 (p < 0.001). Similarly, concentrations of PFNA were also significantly higher at 3M

220   compared to the other locations (all p < 0.001). Songbird eggs at 3M also contained significantly higher

221   concentrations of PFOA (p = 0.030), PFDA (p < 0.001), PFDoDA (p < 0.001) and PFTrDA (p = 0.002), PFTeDA

222   (p = 0.028) than at Fort 4. Concentrations of PFDA and PFDoDA were significantly higher at 3M compared

223   to Rot (both p < 0.001). Finally, PFDoDA and PFTrDA concentrations were significantly higher at 3M

224   compared to Burchtse Weel (both p < 0.001) and PFTrDA concentrations at 3M were also higher compared

225   to Vlietbos (p = 0.003).

226   *Correlations between PFAA concentrations in isopods, soil and songbird eggs*

227   The PFOS concentrations in the isopods were related to those in the soil when all locations were combined

228   (Fig 5. Solid line; p < 0.001, R^2 = 0.75). Although, not significant (both p = 0.06), there was an indication

229   that both TOC and clay content of the soil had a positive effect on this association. Further analysis on the

230   individual sites revealed that only at 3M the PFOS concentrations in isopods were associated with only

231   the PFOS concentrations in the soil (Fig 5. Dashed line; p = 0.005, R^2 = 0.64) and clay content and TOC

232   played no role in this. Furthermore, at 3M, the PFOA concentrations in isopods were not related to those

233   in the soil. The PFDoDA concentrations in the isopods, on the other hand, were related to those in the soil

234   (p = 0.017; R^2 = 0.75) and to the clay content (p = 0.035). Similarly, PFTrDA concentrations in isopods were

235   positively related to those in the soil (p = 0.007; R^2 = 0.83) and clay content (p = 0.015). PFTeDA

236   concentrations were also positively related between isopods and soil (p < 0.001; R^2 = 0.94). PFBS

237   concentrations were not related in the isopods and soil. Finally, PFDS concentrations in isopods were

238   positively related to those in the soil (p = 0.01; R^2 = 0.63).

239   As mentioned before, soil and invertebrate samples were collected in the immediate vicinity of nest boxes

240   that were used in previous biomonitoring studies. We found no significant correlations between PFAA

241   concentrations in the soil and those in the third egg of great tits (all p > 0.05). However, there were

242   significant positive correlations between PFDoDA (p = 0.010, ρ = 0.711), PFTrDA (p = 0.040, ρ = 0.608),

243   PFOS (p = 0.009, ρ = 0.734) and PFDS (p = 0.008, ρ = 0.720) concentrations in isopods and the third egg at

244   3M. In addition, PFOA (p = 0.071, ρ = 0.546) and PFTeDA (p = 0.067, ρ = 0.545) concentrations in the eggs

245 and isopods showed a trend at 3M. Finally, PFOS concentrations in the eggs and isopods were also

246 positively correlated at Rot (p = 0.028, ρ = 0.761).

247 *Associations with physicochemical properties of the soil*

248 The organic carbon content (TOC) and clay content of the soil at each location are reported in Table 5.

249 TOC differed significantly among locations (p < 0.001), caused by a significantly lower TOC at Rot

250 compared to all other locations (all p < 0.003). The clay content was significantly different among locations

251 (p < 0.001), which was the result of a significantly higher clay content at Burchtse Weel and Fort 4

252 compared to 3M (both p < 0.004) and Rot (both p < 0.001). Furthermore, the clay content was significantly

253 higher at Fort 4 compared to Vlietbos (p = 0.007). When all locations were combined, there was a

254 significant positive correlation between TOC and clay content of the soil (p < 0.001, ρ = 0.773). When

255 looking at the individual locations, similar correlations were observed at 3M (p < 0.001, ρ = 0.853),

256 Burchtse Weel (p = 0.021, ρ = 0.733) and Fort 4 (p = 0.006, ρ = 0.731).

257 A significant positive correlation between PFBA concentrations in the soil and TOC content was only

258 observed at 3M (p = 0.034, ρ = 0.613) and Burchtse Weel (p = 0.01, ρ = 0.767) and a marginally significant

259 correlation was observed at Vlietbos (p = 0.071, ρ = 0.627). PFNA concentrations at 3M were also

260 positively correlated with TOC content (p = 0.001, ρ = 0.822). PFBS concentrations at 3M were significantly

261 correlated with TOC (p = 0.005, ρ = 0.776) and at Vlietbos these concentrations showed a trend with TOC

262 content (p = 0.070, ρ = 0.627). PFOS concentrations were strongly correlated with TOC content at 3M (p

263 < 0.001, ρ = 0.909) and Burchtse Weel (p < 0.001, ρ = 0.818), but not at the other locations. PFHxA, PFOA,

264 PFUnDA, PFDoDA, PFTrDA, PFTeDA and PFDS concentrations in the soil were not correlated with TOC

265 content at sites where these compounds had a detection frequency >50%. At 3M, positive correlations

266 were observed between the clay content and the soil concentrations of PFNA (p = 0.029, ρ = 0.626), PFBS

267 (p = 0.004, ρ = 0.790) and PFOS (p = 0.019, ρ = 0.678). PFOS concentrations in the soil at Burchtse Weel

268 were also correlated to the clay content of the soil (p = 0.027, ρ = 0.709).

269 **Discussion**

270 *PFAA concentrations*

271 For most PFAAs, detected in more than 50% of the samples, concentrations decreased with increasing

272 distance from the fluorochemical plant in both isopods and soil samples. However, PFOS concentrations

273 at Rot were lower than those detected further away at Burchtse Weel and Fort 4. This latter result is likely

274 the outcome of differences in physicochemical properties of the soil between locations, which will be

275 discussed later. Previous studies conducted near the same fluorochemical plant also revealed that PFAA

276 concentrations decreased with increasing distance from the plant in wildlife such as invertebrates

277 (D'Hollander et al., 2014) birds (Dauwe et al., 2007; Groffen et al., 2017, 2019; Hoff et al., 2005; Lopez-

278 Antia et al., 2017) and mammals (D'Hollander et al., 2014).

279 To be able to compare the PFAA concentrations in the soil with literature, some examples of PFAA

280 concentrations reported in soils are shown in Table 6. The mean PFOS concentration in the soil at 3M in

281 the present study (1700 ng/g dw) was much higher than those detected at Blokkersdijk (69 ng/g ww;

282 D'Hollander et al., 2014), which is approximately 0.5 – 1.5 km east from the 3M fluorochemical plant in

283 Antwerp. Compared to the PFOS concentrations in the soil at Vlietbos (1 km SE from the plant; 22 ng/g

284 dw), the concentrations at Blokkersdijk in 2006 were higher. This is likely the result of the voluntary phase-

285 out by 3M of PFOS, PFOA and related products in 2002, which appear to have reduced environmental

286 PFOS concentrations, whereas concentrations of other PFAAs are still rising (Ahrens et al., 2011a; Filipovic

287 et al., 2015a; Groffen et al., 2017, 2019; Miller et al., 2015). In addition, the wind in Belgium is mainly

288 coming from the south-west (Royal Meteorological Institute Belgium (KMI), 2018), which would indicate

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289   that aerial deposition of PFAAs should mainly affect areas north to east from the fluorochemical plant,

290   which include Blokkersdijk.

291   Soil PFOA and PFOS concentrations at the plant site were similar to those at a firefighting training facility

292   in Sweden (6.98 – 287 ng/g for PFOA and 118 – 8520 ng/g for PFOS), where PFAA-contaminated aqueous

293   film fighting foams were used (Filipovic et al., 2015b). Rankin et al. (2016) reviewed the continental PFAA

294   concentration ranges in soils. Geometric means of the ΣPFCAs and ΣPFSAs in Europe were 1000 pg/g dw

295   and 808 pg/g dw, respectively. PFCA and PFSA concentrations in the present study were much higher than

296   the European mean. The ΣPFSA concentrations were higher than the ΣPFCA concentrations in Europe

297   (Rankin et al., 2016), which is in agreement with our results, as PFOS concentrations were much higher

298   than those of any other analyte. The PFOA concentrations in the soil (62.5 ng/g) collected from a

299   fluorochemical industrial park in China (Lu et al., 2018) were higher than those at 3M in Antwerp.

300   However, concentrations of other PFCAs were much lower in China than in the present study. PFOA, PFHxS

301   and PFOS concentrations at 3M were much lower than those measured in the soil near an active

302   fluorochemical manufacturing facility in Wuhan, China (Wang et al., 2010), where concentrations of 50.1,

303   35.3 and 2583 ng/g PFOA, PFHxS and PFOS, respectively, were detected. However, compared to an

304   inactive plant in the same area in China (0.79, 0.11 and 7.06 ng/g for PFOA, PFHxS and PFOS; Wang et al.,

305   2010), the concentrations at 3M in the present study were much higher. PFOA and PFOS concentrations

306   at Fort 4, approximately 11 km from the fluorochemical plant, were similar to those near the inactive plant

307   in China. PFOA and PFOS concentrations (2.2 and 0.82 ng/g respectively) in the soil along the estuaries

308   and coastal areas along the South Korean west coast, an area which is highly industrialized and urbanized

309   (Naile et al., 2013), were also much lower than those reported at 3M. PFOA concentrations were,

310   however, similar to those at the other sampling sites. Wang et al. (2013) reported PFOA, PFDA, PFUnDA,

311   PFTrDA and PFOS concentrations in soils from Liaodong Bay, China, which is an area with concentrated

312   fluorine industry parks, that were all much lower than those detected in most of the sites in the present

313   study. Although PFOS concentrations in the soils of a U.S. metropolitan area, near Cottage Grove, where

314   a former PFAA manufacturer is located, were much lower than those at 3M, the range of PFOA

315   concentrations observed in the US was similar to the one observed at 3M in Belgium. PFOS concentrations

316   in the US were very similar to those detected at Vlietbos, approximately 1 km away from the

317   fluorochemical plant (Xiao et al., 2015). Finally, Zhu and Kannan (2019) determined PFCA concentrations

318   in the soil of the Little Hocking well field in Washington County, Ohio, USA. With exception of PFUnDA,

319   the concentrations in Washington County were all higher than those reported at 3M in the present study.

320   When we compare the PFOS concentrations in isopods during the present study with a previous study

321   near the Antwerp hot-spot by D'Hollander et al. (2014), median PFOS concentrations in isopods collected

322   at Blokkersdijk (497 ng/g ww) and Galgenweel (3 km SE; 269 ng/g ww) were higher than the median PFOS

323   concentration is isopods collected at the plant site in the present study (185 ng/g ww). Again, this could

324   possibly be explained by the voluntary phase-out of PFOS in 2002. The study performed by D'Hollander

325   et al. (2014) was the only study that examined PFAA concentrations in isopods. Only two other field

326   studies were performed on terrestrial invertebrates. Lesch et al. (2017) detected PFAAs in adult Odonata

327   from South Africa. Median PFOS (highest median of 16 ng/g ww) and PFOA (highest median of 0.89 ng/g

328   ww) concentrations in the Odonata were much lower than those detected at the plant site in the present

329   study (185 ng/g ww and 7.56 ng/g ww for PFOS and PFOA, respectively), but were higher than the

330   concentrations in the adjacent sites. Zhu and Kannan (2019) reported concentrations of multiple PFCAs in

331   earthworms, collected at the Little Hocking well field, Ohio, USA. Similarly to the study area in the present

332   study, this site is historically contaminated by a nearby fluorochemical manufacturing facility. Although

333   the mean PFPeA concentrations detected in earthworms (1.2 ng/g dw) were much lower than those

334   reported at the plant site in the present study (108 ng/g ww), concentrations of PFOA (270 ng/g dw), PFNA

335   (13 ng/g dw), PFDA (26 ng/g dw), PFUnDA (110 ng/g dw) and PFDoDA (200 ng/g dw) in the earthworms

336   were much higher (Zhu and Kannan, 2019).

16

337   As was mentioned before, the concentrations determined in great tit eggs were part of a larger dataset.

338   A comparison of these concentrations with literature has already been done by Groffen et al., 2019.

339   *Correlations between PFAA concentrations in isopods, soil and songbird eggs*

340   We observed a positive relationship between PFOS concentrations in isopods and soil when all locations

341   were combined, and at 3M individually. Furthermore, we found evidence that PFDoDA, PFTrDA, PFTeDA

342   and PFDS concentrations in isopods reflect the concentrations of these compounds in the soil. For PFDoDA

343   and PFTrDA the concentrations in the isopods were not only positively related to the concentrations in

344   the soil, but also to the clay content of the soil. These results were expected as isopods are exposed to

345   soils and therefore, soils are most likely an important pathway of PFAA exposure to these invertebrates.

346   We also correlated PFAA concentrations in isopods and soil with those in the eggs of great tit, to determine

347   the possibility of trophic transfer as a pathway of the PFAA concentrations in the songbirds and eventually

348   in their eggs. In general, PFAA concentrations in the soil were not correlated with those in the eggs of

349   great tit, indicating that soil concentrations were not representative of the concentration in the eggs. This

350   was expected, as great tits are insectivorous songbirds that mainly feed on invertebrates (mainly

351   caterpillars), berries and seeds, depending on the season (del Hoyo et al., 2007). This might also explain

352   the positive correlations between concentrations in the eggs and those in isopods at 3M and Rot. Although

353   these correlations were not observed at the other locations, there is an indication that PFAA

354   concentrations in the isopods are a potential source of PFAAs in the birds.

355   *Associations with physiochemical properties of the soil*

356   Our results, that PFOS soil concentrations at Rot were significantly lower than those at Burchtse Weel and

357   Fort 4, both further away from the fluorochemical plant, could be explained by a lower TOC content at

358   Rot. The maximum sorption capacity of the soil is to a large extent influenced by soil organic carbon

359   content (Miao et al., 2017). Soil organic carbon content has shown to be positively correlated with the

360 sorption capacity of soils (Milinovic et al., 2015; Wei et al., 2017). This indicates that more PFAAs will

361 adsorb to the soil when the TOC is higher. Soils with smaller particles, such as clay, will have more

362 functional groups like hydroxyl and carboxyl groups than bigger particles, which results in more binding

363 sites to facilitate the sorption of the contaminants (Qi et al., 2014). Therefore, it was expected that PFAA

364 concentrations in the soil would be higher in areas where the clay content is higher. The positive

365 correlations between clay content and soil concentrations of PFNA, PFBS and PFOS at 3M and Burchtse

366 Weel were therefore expected.

367 *PFAA profile*

368 Figure 6 shows the PFAA profiles in soil, invertebrates and songbird eggs at all the sampling sites. Similarly

369 to previous analyses, only analytes with a detection frequency of at least 50% were taken into account.

370 Consequently, locations with no analyte detected in more than 50% of the samples, or only one PFSA

371 and/or PFCA detected in frequencies higher than 50% (e.g. PFOA and PFOS in soil collected from Rot) were

372 not included in the figures, as their profile would result in 100% contribution of these compounds.

373 PFOS was the major contributor to the PFSA concentrations in the soil (Fig. 6b) at the plant site (97 ± 1%)

374 and at Vlietbos (89 ± 2%), in isopods (88 ± 4% at 3M; Fig. 6c) and in bird eggs at all locations (100% with

375 exception of 3M: 99.5%). Furthermore, due to the high PFOS concentrations in both matrices, PFOS can

376 be considered to be the dominant contributor to the total PFAA concentrations in the soil, eggs and

377 isopods. With regard to the PFCA profile, PFOA was the dominant contributor in soil (Fig. 6a), whereas

378 PFPeA became more dominant in isopods. In bird eggs, the PFCA profile at 3M was dominated by PFOA,

379 whereas PFTrDA had a higher contribution at the other sites (Fig. 6d).

380 These patterns are generally in agreement with other studies on PFSAs in soil and invertebrates and PFCAs

381 in soil. Rankin et al. (2016) performed a global survey on the distribution patterns and mode of occurrence

382 of PFSAs and PFCAs and they reported that, in general, PFOA and PFOS were the most abundant analytes

383   in the soil. The dominance of PFOS in the soil was also reported by Naile et al. (2013) as the PFOS

384   concentrations in soil samples, collected along the west coast of Korea, were also higher than those of the

385   other PFSAs. The dominance of PFOA in soils was similar to a study by Filipovic et al. (2015b) in which the

386   relative contribution of PFOA in the soil, polluted due to historical usage of aqueous film forming foam,

387   was higher than the one of PFHxA. PFOA was also the dominant PFCA in soils, collected near a

388   fluorochemical industrial park in eastern China (Lu et al., 2018).

389   No studies have been performed on the pollution of multiple PFAAs in isopods. Although D'Hollander et

390   al. (2014) reported PFOS concentrations in isopods, they did not study other PFAAs and were therefore

391   unable to determine PFAA profiles. Similar to our results, Zhao et al. (2013) observed that PFOS

392   concentrations were higher in earthworms, exposed for 30 days to a soil contaminated with a 200 ng/g

393   PFAAs mixture, than those of other PFSAs. PFOS was also the dominant PFSA in earthworms exposed in

394   biosolid amended soils (Navarro et al., 2016). PFCA profiles in isopods were different from those in

395   earthworms, exposed to mixtures of PFAAs. Zhao et al. (2013) observed that PFDoDA was the dominant

396   contributor to the ΣPFCAs, whereas PFPeA had the second lowest concentrations. Similar results were

397   obtained by Zhao et al. (2016), where biota accumulation factors (BAFs) increased with the increase in

398   carbon chain length in earthworms exposed to spiked soils. These results suggest different exposure

399   pathways for earthworms and isopods, which is possibly the result from differences in diet and feeding

400   behavior.

401   The dominance of PFOS in the PFAA profile of the bird eggs was in agreement with literature (e.g. Ahrens

402   et al., 2011a; Custer et al., 2012; Groffen et al., 2017). Similarly, Groffen et al. (2017) already mentioned

403   that the dominance of PFOA to the ΣPFCAs at the plant site and the dominance of PFTrDA at sites further

404   away could possibly be explained by the direct deposition of PFOA close to the plant, whereas further

405   away atmospheric and biological degradation of volatile polyfluorinated precursor compounds might

406   explain the dominance of PFTrDA.

407   Surprisingly, the contribution of PFBA increased with increasing distance from the fluorochemical plant,

408   which is likely the result of different ways of pollution or a different pollution source. The PFCA profile

409   close to the plant site could be explained by the influence of a direct pollution source, where PFOA is the

410   main product (Prevedouros et al., 2006), whereas further away from the plant atmospheric degradation

411   of volatile precursor compounds such as fluorotelomer alcohols (FTOHs) could play a role.

412   **Conclusions**

413   The PFOS concentrations in soil in the present study were often much higher than those reported in

414   literature, with exception of those measured in soils at an active fluorochemical manufacturing facility in

415   China. Compared to the European geometric means, the concentrations of PFOS and PFOA in soils were

416   much higher in the present study. In isopods, the concentrations have decreased compared to a previous

417   study conducted in the same area, which might be the result of the voluntary phase-out by 3M in 2002.

418   PFOS and PFOA concentrations in all matrices were elevated at the plant site and decreased with

419   increasing distance from the fluorochemical plant. However, there were some deviations in this pattern,

420   which were likely the result of differences in physicochemical properties of the soil.

421   Our results show that PFAA concentrations in the soil were not suitable indicators of the PFAA

422   concentrations in eggs of great tit. However, we observed positive correlations between the

423   concentrations in isopods and those in great tit eggs, which indicates that PFAA concentrations in isopods

424   can be used to estimate concentrations in great tit eggs. However, these correlations were only observed

425   at 3M and Rot and therefore, more research is necessary to further investigate the use of isopods as

426   indicators of PFAA-pollution in great tit eggs.

427   **Acknowledgements**

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Figures and Tables

Figures

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Figure 1. Overview of the study area in Antwerp, Belgium. Sampling locations are indicated as letters: A. Fluorochemical plant 3M, B. Vlietbos, C. Middenvijver-Rot, D. Burchtse Weel, E. Fort 4. Figure adopted from Groffen et al. (2019).

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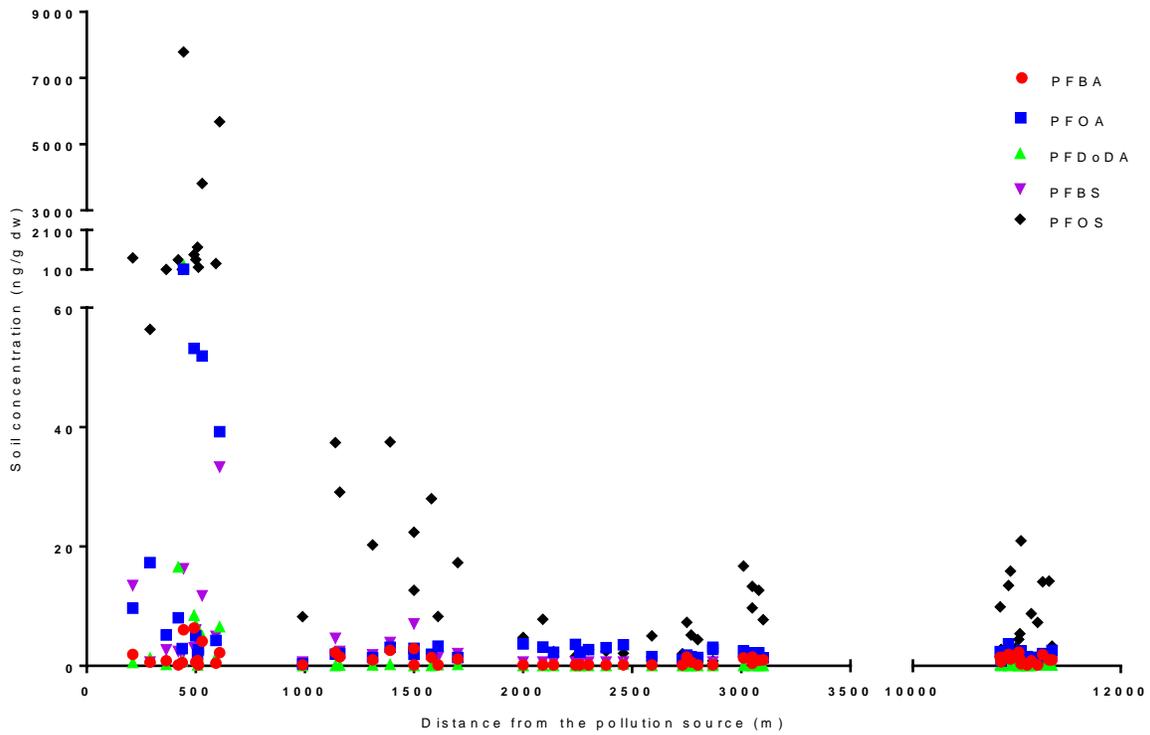
Figure 2. PFAA concentrations (ng/g dw) in soil collected along the distance gradient from the pollution source. The center of the
fluorochemical plant is selected as the start of the gradient (0 m).

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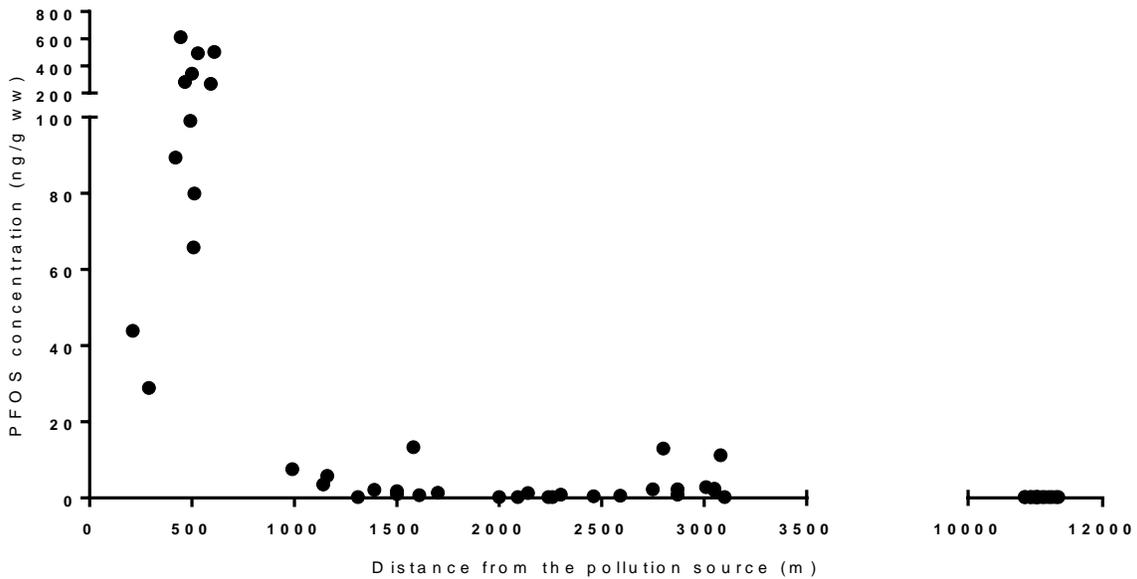
Figure 3. PFOS concentrations (ng/g ww) in isopods, collected along the distance gradient from the pollution source. The center
of the fluorochemical plant is selected as the start of the gradient (0 m).

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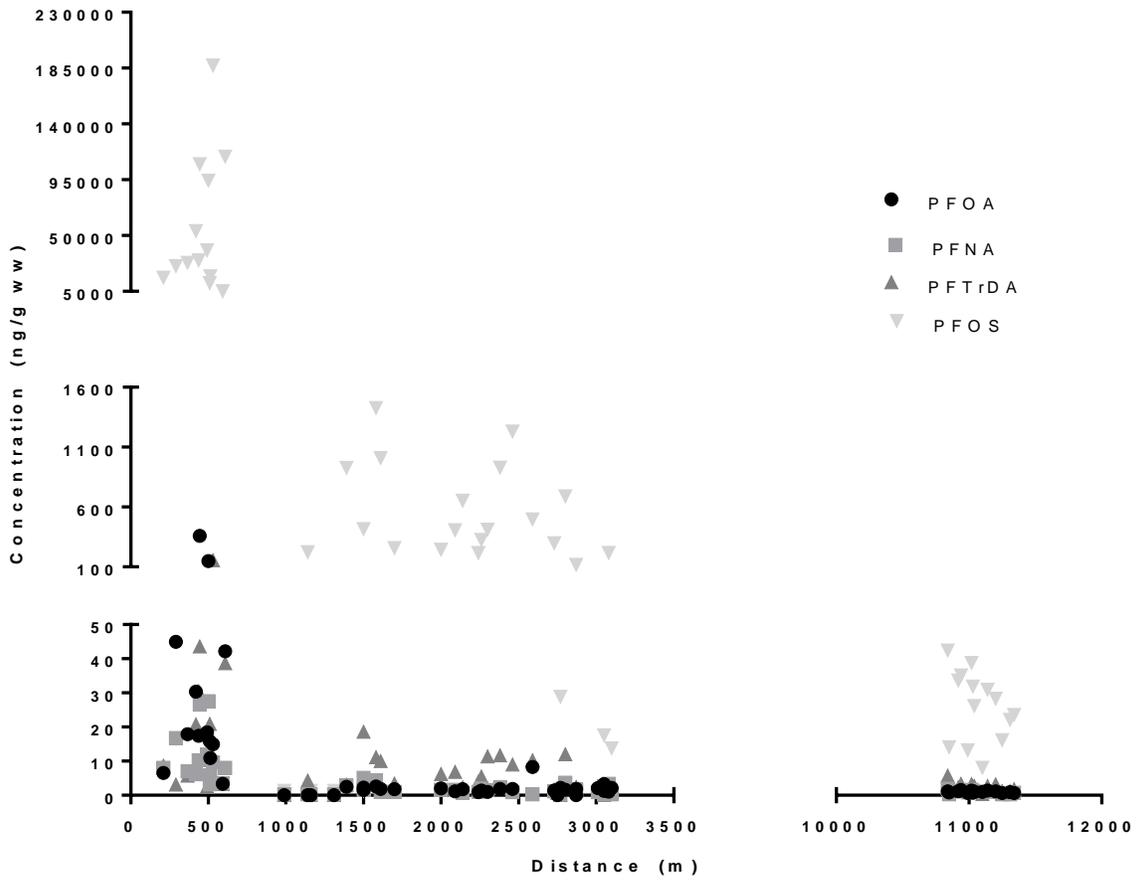
Figure 4. PFAA concentrations (ng/g ww) in great tit eggs collected along the distance gradient from the pollution source. The center of the fluorochemical plant is selected as the start of the gradient (0 m). The presented data is part of a larger dataset, reported by Groffen et al. (2019).

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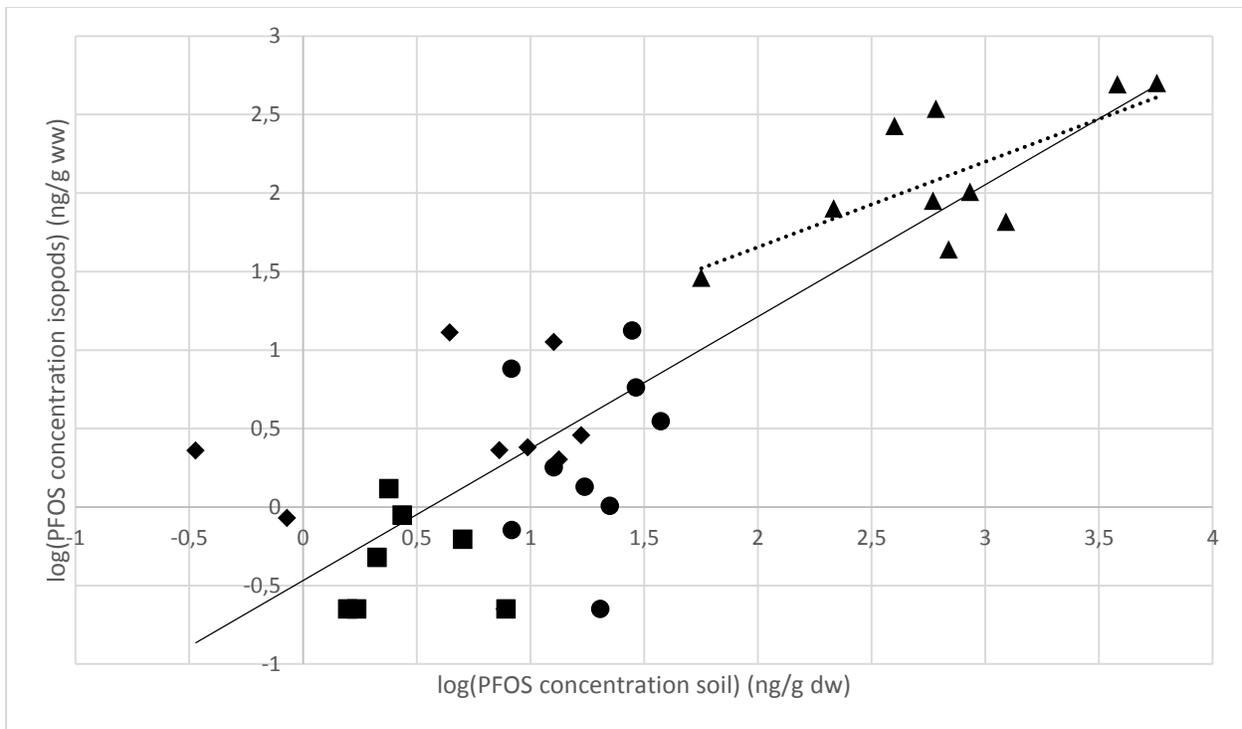
Figure 5. Associations between PFOS concentrations in isopods and PFOS concentrations in the soil. Different symbols resemble different sampling locations: triangles = 3M, dots = Vlietbos, squares = Rot and diamonds = Burchtse Weel. The solid line is the regression curve of the entire dataset (p < 0.001, R^2 = 0.75), the dashed line is the regression curve for 3M (p = 0.005, R^2 = 0.64).

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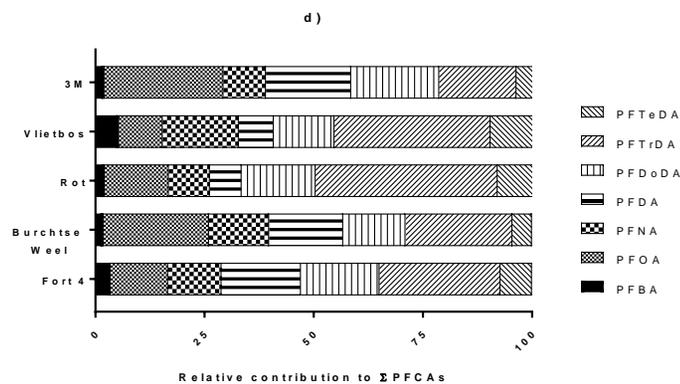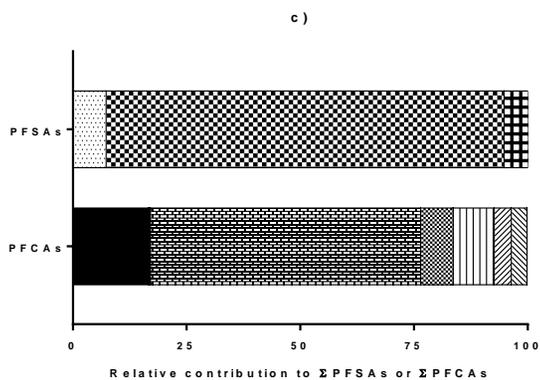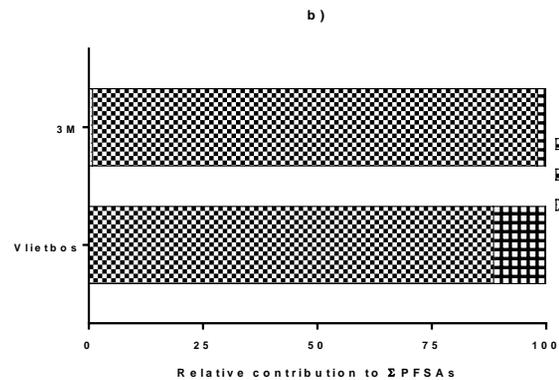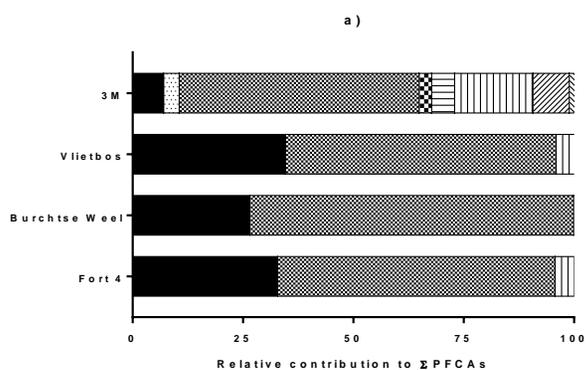
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619 *Figure 6. Composition profile of PFAAs in soil and isopods. A) PFCA composition profile in soil samples. B) PFSA composition profile in soil samples. C) Composition profile of PFSAs*
620 *and PFCAs in isopods, collected at the 3M fluorochemical plant. D) Composition profile of PFCAs in song bird eggs.*

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622 *Tables*

623 *Table 1. Target analytes, isotopically mass-labelled internal standards (ISTDs) used for quantification and MRM transitions.*

Compound	Internal standard (ISTD) used for quantification	Precursor ion (m/z)	Product ion (m/z)	
			Diagnostic product ion 1	Diagnostic product ion 2
PFBS	$^{18}O_2$-PFHxS	299	80	99
PFHxS	$^{18}O_2$-PFHxS	399	80	99
PFOS	[1,2,3,4-$^{13}C_4$]PFOS	499	80	99
PFDS	[1,2,3,4-$^{13}C_4$]PFOS	599	80	99
PFBA	$^{13}C_4$-PFBA	213	169	169
PFPeA	$^{13}C_4$-PFBA	263	219	219
PFHxA	[1,2-$^{13}C_2$]PFHxA	313	269	119
PFHpA	[1,2-$^{13}C_2$]PFHxA	363	319	169
PFOA	[1,2,3,4-$^{13}C_4$]PFOA	413	369	169
PFNA	[1,2,3,4,5-$^{13}C_5$]PFNA	463	419	169
PFDA	[1,2-$^{13}C_2$]PFDA	513	469	219
PFUnDA	[1,2-$^{13}C_2$]PFUnDA	563	519	169
PFDoDA	[1,2-$^{13}C_2$]PFDoDA	613	569	319
PFTrDA	[1,2-$^{13}C_2$]PFDoDA	663	619	319
PFTeDA	[1,2-$^{13}C_2$]PFDoDA	713	669	169

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626 *Table 2. Individual limits of quantification (LOQs; ng/g dw, determined as 10x the S/N ratio), median and mean concentrations (ng/g dw), range (ng/g dw) and detection frequencies*
627 *(Freq) of PFAAs in soil collected at the five sampling sites: a perfluorochemical plant and at four sites with increasing distance from the plant site (i.e. 1 km Vlietbos, 2.3 km Rot, 3*
628 *km Burchtse Weel and 11 km Fort 4). Different letters indicate significant differences (p ≤ 0.05) between sampling sites in PFAA concentrations with a detection frequency > 50%.*

		PFCAs											PFSAs			
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS
LOQ		0.30	0.97	0.31	1.67	0.73	0.26	0.33	0.27	0.08	0.04	0.04	1.31	4.91	0.67	3.26
Plant (n = 13)	Median	0.85 A	<LOQ	0.42	<LOQ	8.07 A	0.34	<LOQ	0.43	1.39 A	0.59	0.06	4.01 A	<LOQ	606 A	3.34
	Mean	1.92	5.54	2.11	1.43	24	0.83	1.05	8.89	28	12	1.18	7.84	6.88	1700	33
	Range	<LOQ – 6.33	<LOQ – 26	<LOQ – 11	<LOQ – 4.75	1.97 – 114	<LOQ – 2.53	<LOQ – 7.28	<LOQ – 105	0.16 – 316	0.05 – 126	<LOQ – 12	<LOQ – 33	<LOQ – 32	56 – 7800	<LOQ - 282
	Freq	85	46	62	23	100	69	46	77	100	100	54	92	31	100	54
Vlietbos (n = 10)	Median	1.28 A	<LOQ	<LOQ	<LOQ	1.94 BC	<LOQ	<LOQ	<LOQ	0.09 B	<LOQ	<LOQ	2.13 B	<LOQ	21 B	<LOQ
	Mean	1.33	<LOQ	<LOQ	<LOQ	2.05	<LOQ	<LOQ	<LOQ	0.12	<LOQ	<LOQ	2.79	<LOQ	22	<LOQ
	Range	<LOQ – 2.92	<LOQ – 1.03	<LOQ – 0.37	<LOQ	<LOQ – 3.30	<LOQ – 0.44	<LOQ – 0.48	<LOQ – 0.47	<LOQ – 0.24	<LOQ – 0.09	<LOQ	<LOQ – 7.04	<LOQ	8.24 – 37	<LOQ
	Freq	70	10	10	0	90	30	10	30	50	0	0	90	0	100	0
Rot (n = 10)	Median	<LOQ	<LOQ	<LOQ	<LOQ	2.89 C	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.41 C	<LOQ
	Mean	<LOQ	<LOQ	<LOQ	<LOQ	2.71	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.26	<LOQ
	Range	<LOQ	<LOQ	<LOQ	<LOQ	1.12 – 3.69	<LOQ	<LOQ	<LOQ	<LOQ – 0.36	<LOQ	<LOQ	<LOQ	<LOQ	1.57 – 7.81	<LOQ
	Freq	0	0	0	0	100	0	0	0	10	0	0	0	0	100	0
Burchtse Weel (n = 10)	Median	0.78 A	<LOQ	<LOQ	<LOQ	1.98 B	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	7.51 D	<LOQ
	Mean	0.77	<LOQ	<LOQ	<LOQ	2.03	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	7.82	<LOQ

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	Range	<LOQ – 1.48	<LOQ	<LOQ	<LOQ	1.37 – 3.12	<LOQ – 0.38	<LOQ	<LOQ – 0.54	<LOQ – 0.28	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ – 17	<LOQ
	Freq	70	0	0	0	100	10	0	20	10	0	0	0	0	90	0
Fort 4 (n = 14)	Median	1.08 A	<LOQ	<LOQ	<LOQ	1.83 B	<LOQ	<LOQ	<LOQ	0.13 B	<LOQ	<LOQ	<LOQ	<LOQ	8.03 D	<LOQ
	Mean	1.12	<LOQ	<LOQ	<LOQ	1.95	<LOQ	<LOQ	<LOQ	0.12	0.06	<LOQ	<LOQ	<LOQ	8.84	<LOQ
	Range	<LOQ – 2.27	<LOQ – 1.65	<LOQ	<LOQ	0.82 – 3.66	<LOQ – 0.53	<LOQ – 0.47	<LOQ – 0.41	<LOQ – 0.29	<LOQ – 0.19	<LOQ	<LOQ	<LOQ	<LOQ – 21	<LOQ
	Freq	86	21	0	0	100	29	14	14	57	36	0	0	0	93	0

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		PFCAs											PFSAs			
		PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFDoDA	PFTrDA	PFTeDA	PFBS	PFHxS	PFOS	PFDS
LOQ		1.34	1.84	4.80	6.92	0.74	0.31	0.98	1.20	0.96	0.30	1.40	2.66	6.74	0.45	0.99
Plant (n = 12)	Median	12	87	<LOQ	<LOQ	7.56	<LOQ	<LOQ	<LOQ	2.17	1.41	3.23	6.52	<LOQ	185 A	<LOQ
	Mean	12	108	<LOQ	32	18	<LOQ	<LOQ	6.25	68	20	8.8	8.31	9.33	253	39
	Range	2.51 – 30	<LOQ – 292	<LOQ	<LOQ – 313	1.58 – 121	<LOQ – 1.18	<LOQ – 1.74	<LOQ – 66	<LOQ – 729	<LOQ – 193	<LOQ – 62	<LOQ – 26	<LOQ – 26	29 – 611	<LOQ – 388
	Freq	100	92	0	17	100	17	33	25	83	92	67	67	42	100	50
Vlietbos (n = 10)	Median	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.98 B	<LOQ
	Mean	1.79	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.46	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.75	<LOQ
	Range	<LOQ – 6.95	<LOQ	<LOQ	<LOQ	<LOQ – 1.72	<LOQ	<LOQ – 1.25	<LOQ – 5.26	<LOQ	<LOQ – 0.32	<LOQ	<LOQ – 5.96	<LOQ	<LOQ – 13	<LOQ
	Freq	40	0	0	0	10	0	10	40	0	10	0	30	0	90	0
Rot (n = 8)	Median	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ C	<LOQ
	Mean	1.79	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.22	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.53	<LOQ
	Range	<LOQ – 8.21	<LOQ	<LOQ	<LOQ	<LOQ – 1.02	<LOQ	<LOQ – 0.99	<LOQ – 3.28	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ – 1.31	<LOQ
	Freq	25	0	0	0	13	0	13	25	0	0	0	0	0	50	0
Burchtse Weel (n = 10)	Median	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.31 B	<LOQ
	Mean	<LOQ	<LOQ	<LOQ	<LOQ	0.86	<LOQ	1.11	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4.13	<LOQ

	Range	<LOQ – 5.04	<LOQ	<LOQ	<LOQ	<LOQ – 3.28	<LOQ	<LOQ – 3.13	<LOQ – 3.08	<LOQ – 1.26	<LOQ – 0.77	<LOQ	<LOQ – 2.97	<LOQ	<LOQ – 13	<LOQ
	Freq	30	0	0	0	40	0	30	20	10	10	0	10	0	90	0
Fort 4 (n = 14)	Median	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Mean	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Range	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ – 0.75	<LOQ	<LOQ – 1.56	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Freq	0	0	0	0	7	0	7	0	0	0	0	0	0	0	0

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Table 4. Individual limits of quantification (LOQs; ng/g dw, determined as 10x the S/N ratio), median and mean concentrations (ng/g dw), range (ng/g dw) and detection frequencies (Freq) of PFAAs in eggs of great tit collected at the five sampling sites: a perfluorochemical plant and at four sites with increasing distance from the plant site (i.e. 1 km Vlietbos, 2.3 km Rot, 3 km Burchtse Weel and 11 km Fort 4). Different letters indicate significant differences (p ≤ 0.05) between sampling sites in PFAA concentrations with a detection frequency > 50%. The presented data are a part of a larger dataset reported by Groffen et al., 2019.

		PFCAs							PFSAs	
		PFBA	PFOA	PFNA	PFDA	PFDoDA	PFTrDA	PFTeDA	PFOS	PFDS
LOQ		0.261	0.045	0.586	0.425	0.444	0.256	0.355	2.55	5.92
Plant (n = 13)	Median	<LOQ	18A	8.09A	13A	18A	21A	3.13A	29958A	73
	Mean	1.61	56	11	23	35	32	4.97	55970	415
	Range	<LOQ − 11	3.36 − 359	3.25 − 28	3.46 − 102	2.21 − 133	2.53 − 155	<LOQ − 22	5111 − 187032	9.44 − 1489
	Freq	31	100	100	100	100	100	69	100	100
Vlietbos (n = 10)	Median	<LOQ	1.65AB	1.07B	<LOQ	<LOQ	3.33B	<LOQ	241B	<LOQ
	Mean	0.31	1.26	1.72	0.54	1.95	5.44	1.14	426	<LOQ
	Range	<LOQ − 1.42	<LOQ − 2.61	<LOQ − 5.12	<LOQ − 2.08	<LOQ − 6.37	<LOQ − 19	<LOQ − 3.93	<LOQ − 1427	<LOQ
	Freq	20	60	60	20	40	70	40	60	0
Rot (n = 10)	Median	<LOQ	1.56AB	1.33B	1.17B	2.40B	6.58AB	1.40AB	409C	<LOQ
	Mean	0.32	2.16	1.31	1.22	2.56	6.90	1.26	521	<LOQ
	Range	<LOQ − 1.03	0.90 − 8.33	<LOQ − 2.26	<LOQ − 2.72	<LOQ − 5.05	1.71 − 12	<LOQ − 2.26	217 − 1230	<LOQ
	Freq	30	100	90	70	90	100	80	100	0
Burchtse Weel (n = 10)	Median	<LOQ	1.75AB	0.81B	<LOQ	0.69B	2.12B	<LOQ	79BC	<LOQ
	Mean	<LOQ	1.57	1.30	1.36	1.71	2.73	0.6	140	<LOQ
	Range	<LOQ	<LOQ − 3.26	<LOQ − 3.66	<LOQ − 5.49	<LOQ − 6.94	<LOQ − 12	<LOQ − 3.58	14 - 690	<LOQ
	Freq	0	80	60	30	50	80	20	100	0
Fort 4 (n = 14)	Median	<LOQ	1.01B	1.0B	1.54B	1.51B	2.39B	0.66B	27B	<LOQ
	Mean	0.31	1.01	1.0	1.59	1.54	2.39	0.58	26	<LOQ

	Range	<LOQ − 0.86	0.65 − 1.53	<LOQ − 1.91	<LOQ − 4.90	<LOQ − 3.14	0.38 − 5.74	<LOQ − 0.96	8.08 − 42	<LOQ
	Freq	50	100	79	79	93	100	71	100	0

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642   *Table 5. Physicochemical properties of the soil at each location; mean total organic carbon (TOC) content in % ± st. dev. and clay content (% ± st. dev.)*

	3M	Vlietbos	Rot	Burchtse Weel	Fort 4
TOC (%)	3.4 ± 3.0	5.8 ± 2.2	0.7 ± 0.2	4.2 ± 2.8	6.2 ± 3.6
Clay content (%)	1.1 ± 0.9	1.5 ± 0.6	0.4 ± 0.3	2.8 ± 1.1	3.1 ± 1.7

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Table 6. PFAA concentrations (ng/g) in soils published in literature. *Mean concentrations; $^\$$Active fluorochemical plant; ranges are illustrated by '-'; ND = not detected; Blanks = analyte was not included in the study.

Location	Year	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	PFTrDA	PFBS	PFHxS	PFOS	Publication
Blokkersdijk, Belgium*	2006												69	D'Hollander et al., 2014
Galgenweel, Belgium*	2006												<LOD (2.4)	D'Hollander et al., 2014
Main firefighting training facility, Air force base F18, Tullinge Riksten, Sweden[a]	2011					6.98 – 287							118 – 8520	Filipovic et al. 2015b
Daikin Co, Lit, Fluorochemical Industrial Park, China*	2015	0.6	0.3	0.9	<0.5	62.5	0.2	<0.5	0.2	<0.2	<0.5	<0.5	64.6	Lu et al., 2018
Estuarine and coastal areas along the west coast, South Korea.*	2009		ND	ND	ND	2.2	ND	ND	ND		ND	ND	0.82	Naile et al., 2013
Fluorochemical manufacturing facility in Wuhan, China$^{\$,}$*	2009					50.1						35.3	2583	Wang et al., 2010
Fluorochemical manufacturing facility, Hubei Province, China*	2009					0.79						0.11	7.06	Wang et al., 2010
Hubei Province, China*	2009					<LOD						0.01	0.65	Wang et al., 2010

Location	Year													Reference
Liaodong Bay, China	2008					<LOD – 0.32		<LOD – 0.06	<LOD – 0.30	<LOD – 0.46			<LOD – 0.42	Wang et al., 2013
Highway 10, Cottage Grove to Big Lake, USA	2012					5.5 – 125.7							0.2 – 28.2	Xiao et al., 2015
Little Hocking well field, Washington County, Ohio, USA*	2009				2.0	130	2.7	4.3	7.6					Zhu and Kannan 2019
3M fluorochemical plant, Belgium*	2016	1.92 (<LOQ – 6.33)	5.54 (<LOQ – 26)	2.11 (<LOQ – 11)	1.43 (<LOQ – 4.75)	24.0 (1.97 – 114)	0.83 (<LOQ – 2.53)	1.05 (<LOQ – 7.28)	8.89 (<LOQ – 105)	12.0 (0.05 – 126)	7.84 (<LOQ – 33)	6.88 (<LOQ – 32)	1700 (56 – 7800)	The present study

[a]Concentrations were the result of aqueous firefighting foams rather than those of an industrial source.