Chapter 6  Presence and sources of anthropogenic perfluoro-alkyl acids in high-consumption tap-water based beverages

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Abstract
This study investigates the presence and sources of perfluoroalkyl acids (PFAAs) in tap water and corresponding tap water based beverages such as coffee and cola collected in the city of Amsterdam, The Netherlands. Exposure pathways studies have shown that low concentrations of PFAAs in tap water already may pose a high contribution to daily human exposure.

Tap water samples \((n=4)\) had higher concentrations of PFAAs than the corresponding post-mixed cola \((n=4)\). The lower PFAAs levels in the cola were attributed to the pre-treatment of tap water in the mixing machines and dilution with cola syrup. In coffee samples from a coffee machine perfluorooctanoic acid (PFOA) at 4 ng/L was the dominating analyte \((n=12)\). The concentrations of PFHpA, PFOA and non branched PFOS were found to be significantly higher in manually (self) brewed coffee than in the corresponding tap water \((n=4)\). The contribution from short-chain PFAAs analogues could not be quantified due to low recoveries. Leaching experiments at different temperatures were performed with fluoropolymers-containing tubes to investigate the potential of leaching from tubes used in beverage preparation \((n=16)\). Fluoropolymer tubes showed leaching of PFAAs at high \((\pm80 ^\circ C)\) temperature but its relevance for contamination of beverages in practice is small. The specific contribution from perfluoropolymer tubing inside the beverage preparation machines could not be assessed since no information was available from the manufacturers.

The present study shows that although different beverage preparation processes possibly affect the concentrations of PFAAs encountered in the final consumed product, the water used for preparation remains the most important source of PFAAs. This in turn has implications for areas where drinking water is contaminated. Tap water based beverages will possibly be an additional source of human exposure to PFAAs and need to be considered in exposure modeling.
6.1 Introduction
Perfluoroalkyl acids (PFAAs) are organic compounds with fully fluorinated alkyl chains and a negatively charged acidic head group. These compounds are thermally and biologically stable, which make them interesting for a variety of industrial applications and products. PFAAs were used, as such or as part of a polymer, in the past decades for surface treatment, paper coatings and performance chemicals (Buck et al., 2011).

Important subgroups of PFAAs are perfluoroalkane carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs). Within these classes of compounds perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) are the analytes most frequently studied. They have been found to be persistent in the environment, and in some cases bioaccumulative and toxic (Hekster et al., 2003). Several PFAAs have been found in drinking water (Eschauzier et al., 2012a) and different environmental compartments such as surface water (Eschauzier et al., 2012a), biota and human blood serum (Kannan et al., 2004).

Recently many studies have focused on PFAAs exposure pathways to the human population including food (Fromme et al., 2007), house dust, air and tap water (Vestergren and Cousins, 2009). It was estimated that when assuming a tap water concentration of PFOA of 9 ng.L⁻¹, the intake via water would amount to 55% of the total daily Dutch PFOA intake (Noorlander et al., 2011). However, concentrations of PFAAs in tap water have been shown to exhibit a large variability which depends on contamination sources to the respective regions. For example concentrations of PFOA range between 0.6 and 6.6 ng.L⁻¹ and PFOS between 0.1 and 11 ng.L⁻¹ in background contaminated tap water from different European countries (Skutlarek et al., 2006). In regions nearby point sources like highly industrialized zones or agricultural areas, such as the contaminated Ruhr area in Germany, the values range between 22 and 519 ng.L⁻¹ for PFOA and 3 and 22 ng.L⁻¹ for PFOS (Skutlarek et al., 2006). Tap water produced from surface water will often have a background contamination while tap water produced from ground water is often PFAA free (Eschauzier et al., 2012b).

The presence of PFAAs in tap water (Eschauzier et al., 2012b) and their high contribution to human exposure leads to the question whether tap-water based beverages, do contain PFAAs, and if so what are the sources. In beer, concentrations of PFOA of 0.8–20 ng.L⁻¹ and PFOS of 1.3–39 ng.L⁻¹ (D’Hollander et al., 2009), and in tea a value of 9.5 ng.L⁻¹ PFOA (Haug et al., 2010a) have been reported. Overall the available data is scarce and these studies do not discuss the potential sources. Given the possible high exposure through tap water, more research is required to predict the human exposure to PFAAs through tap-water based beverages.

Tap-water based beverages may also contain additional PFAAs due to sources other than the tap water they contain. Potential sources include the natural ingredients (e.g. coffee beans, tea leaves, barley), industrial beverage processing, beverage contact materials or home preparation (Begley et al., 2005 and 2008; Dolman and Pelzing, 2011). During the preparation process, beverages can be exposed to fluoropolymer materials like tubing in automatic beverage dispensers. PFAAs used as a process aid in the production of these polymers (e.g. polytetrafluoroethylene, PTFE; perfluoro methyl alkoxy, MFA) can potentially leach from the tubing during use. The use of side-chain fluorinated polymers to provide water repellency to paper cups is another potential source of these compounds to tap-water based beverages. One problem in assessing the source of these compounds is that automats are often a “black box” regarding composition of the tu-
bing and the ingredients used for the preparation of the beverages.
The purpose of this study was to investigate the presence and sources of PFAAs in high consumption beverages. Therefore postmixed cola (which is prepared mechanically from syrup and aerated tap water), and brewed coffee obtained from coffee machines were analyzed for the presence of 18 different PFAAs. Additionally hot water from the coffee automat, manually brewed coffee and tap water used to prepare the post-mixed cola was analyzed to determine possible concentration differences. To verify if PFAA residuals can migrate from fluoropolymer materials into beverages, three different tubes approved by the US-Food and Drug Administration were tested for leaching.

6.2 Materials and methods

6.2.1 Sampling locations
Samples were taken for two purposes, viz. to monitor concentrations in tap water, cola and coffee prepared with beverage dispensers, and to track possible sources of the PFAAs in the beverages. Sampling took place between February and April 2011 at various locations (cafés, universities and supermarkets) in Amsterdam, The Netherlands. From two locations brewed coffee \((n = 2)\) and hot water from coffee machines \((n = 2)\) as well as the tap water used \((n = 2)\) for preparation were collected to track the source of the PFAAs to coffee. Furthermore twelve brewed coffee samples \((n = 12)\) from different coffee machines for a general screening were collected from all over the city. Additionally coffee beans from four of these locations were collected to manually brew coffee \((n = 4)\). It was not possible to open the beverage preparation machines to check the tubing used, manufacturers and operators were unwilling to cooperate on this matter. Also post-mixed cola was collected \((n = 4)\) together with corresponding tap water and an additional three cola samples from different parts of town. The post-mixing process consists of purification of tap water through an ion exchanger. Afterwards the water is mixed with concentrated cola syrup \((4/5:1\text{ water:syrup})\). Samples from tap water that had not undergone the purification that was used for the mixing were also collected from the restaurants. All samples were collected into PP bottles. The sample size ranged from 1 L for water to 0.3–0.6 L for cola and coffee. After collection the samples were stored at 5 °C and extracted in duplicate within 2 weeks.

6.2.2 Leaching experiments
Prior to usage each tube was cleaned at 40 °C according to the manufacturer's protocol (http://www.boni-schlauch.de/de/produkte/234) (see SI for protocol). After cleaning the tubes were cut into pieces of approximately two m length. With each kind of tube two experiments with different liquids were conducted: one to mimic cold alcoholic beverages and one to mimic hot non-alcoholic beverages. In the Commission regulation (EU) No 10/2011 (European Commission, 2011) several beverage stimulants are proposed. A mixture of thanol:water 2:8 represents beverage simulant C which is assigned for beverages that have a hydrophilic character, are able to extract hydrophilic substances and have an alcohol content of up to 20%. This includes, e.g., water, clear fruit or vegetables juices, coffee, tea and beer. It was decided to test simulant C at 5 °C to mimic the cold alcoholic beverage since this is the temperature at which soft drinks are provided...
by dispensers. For the non-alcoholic hot beverages rather than simulant C it was decided to use plain water. This was done because the experiment was performed at 80 °C which is the temperature of hot beverages from the coffee and tea machines. Experimental run time was set to 24 h, which represents an unrealistic time scenario since during normal operation the beverages are in contact with the tubes for a few minutes only. However, we aimed at testing a worst case scenario. One L of simulant C was pumped during 24 h through a 2 m tube made of MFA, PTFE or ethylene propylene diene monomer (EPDM) connected end to end via a Norprene tube to the peristaltic pump. This experiment was performed in a cooling room at 5 °C. For the second series of experiments 1 L water was flushed during 24 h through the tube. The water was heated up to 80 °C in a water bath. For every experiment a new piece of tube was used. Each experiment was done in duplicate and the liquid extracted in triplicate. Extraction and analysis procedures were similar to those applied to the other samples. The method blank for each experiment was determined by performing leaching experiments with only the Norprene tube. Both branched and non-branched PFOS were analyzed. In the paper, when referring to PFOS we refer to the non-branched PFOS.

6.3 Results and discussion
The presence of PFAAs in the different beverages analyzed will be discussed first; subsequently potential sources and results of the leaching experiments performed will be discussed for coffee and cola respectively.

6.3.1 Concentrations in beverages
Tap water. The tap water analyzed in this study is the raw water used for the preparation of post-mixed cola and brewed coffee from coffee machines. The levels of PFAAs observed in four tap water samples (a limited number of samples were analyzed since the values obtained confirmed the levels we had analyzed in previous studies) closely resembled each other as demonstrated by the relatively low standard deviation of the mean values, cf. Table 1. This is not surprising, as the samples were collected in Amsterdam, which is served by a single water company using a single production location. The levels of PFAAs correspond fairly well to previously analyzed tap water from the city of Amsterdam (Eschauzier et al., 2012a). The most abundant analyte was PFBA at an average concentration of 15 ng.L⁻¹. The elevated concentrations of PFBA and PFBS in the river Rhine, stem from a known industrial point source (Möller et al., 2010). As river Rhine water is the source water for the Amsterdam drinking water, these polar PFAAs cannot be removed completely during water treatment, are present in the tap water and constitute a comparatively high background (Eschauzier et al., 2012a). The concentrations found are within the range of tap water concentrations reported in other European countries (D’Hollander et al., 2010; Eschauzier et al., 2010, 2012b; Haug et al., 2010).

Cola. The results of the analysis of cola extracts are shown in Table 1. In the post-mixed cola samples (n = 6) seven PFAAs were detected. Again, like in the corresponding tap water, the most abundant compounds were PFBA and perfluorobutanesulfonic acid (PFBS) with mean concentrations of 11±4.0 ng.L⁻¹ and 7.9±5.0 ng.L⁻¹, respectively. Perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), and perfluoroheptanoic acid (PFHpA) were found at lower concentration levels: 2.0±0.55 ng.L⁻¹ (PFPeA),
0.89±0.77 ng.L⁻¹ (PFHxA), and 0.37±0.26 ng.L⁻¹ (PFHpA). PFOS (0.37 ng.L⁻¹) was detected in one cola sample only. Other analytes were present in concentrations close to or below the corresponding LOQs.

Table 1: Average concentrations of PFAAs in tap water, post-mixed cola and brewed coffee from coffee machines (in ng.L⁻¹; standard deviation and range shown).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tap water (Average (n=4))</th>
<th>Post-mixed cola (Average (n=6))</th>
<th>Brewed coffee from coffee machines (Average(n=12))</th>
<th>Ratio tap water/post mixed cola of averages</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>15±3.6 (9.3 - 18)</td>
<td>11 ± 4.0 (2.2 - 14)</td>
<td>- a</td>
<td>1.2</td>
</tr>
<tr>
<td>PFPeA</td>
<td>2.4 ± 0.50 (1.7 - 2.8)</td>
<td>2.0 ± 0.55 (0.52 - 2.2)</td>
<td>- a</td>
<td>1.1</td>
</tr>
<tr>
<td>PFHxA</td>
<td>2.3 ± 0.10 (2.2 - 2.4)</td>
<td>0.89 ± 0.77 (0.16 - 2.0)</td>
<td>- a</td>
<td>2.1</td>
</tr>
<tr>
<td>PFHpA</td>
<td>1.2 ± 0.22 (0.9 - 1.4)</td>
<td>0.37 ± 0.26 (&lt;0.07 - 0.71)</td>
<td>1.4 ± 0.73 (&lt;0.11 - 2.4)</td>
<td>3.9</td>
</tr>
<tr>
<td>PFOA</td>
<td>3.7 ± 0.45 (3.2 - 4.3)</td>
<td>&lt; 3.1 (&lt;3.1 - 8.0)</td>
<td>4.4 ± 3.3 (&lt;3.1 - 8.0)</td>
<td>1.2</td>
</tr>
<tr>
<td>PFNA</td>
<td>0.08 ± 0.06 (&lt;0.04 - 0.2)</td>
<td>&lt;0.07</td>
<td>&lt;0.11</td>
<td>4.0</td>
</tr>
<tr>
<td>PFDA</td>
<td>&lt;0.042 (&lt;0.04 - 0.2)</td>
<td>&lt;0.071 (&lt;0.07 - 0.71)</td>
<td>0.43 ± 0.99 (&lt;0.11 - 2.6)</td>
<td>2.9</td>
</tr>
<tr>
<td>PFBS</td>
<td>16 ± 1.4 (14 - 17)</td>
<td>7.9 ± 5.0 (&lt;0.04 - 12)</td>
<td>2.9 ± 2.9 (&lt;0.06 - 9.8)</td>
<td>2.9</td>
</tr>
<tr>
<td>PFHxsS</td>
<td>0.55 ± 0.10 (0.5 - 0.6)</td>
<td>&lt;0.63</td>
<td>- a</td>
<td>2.9</td>
</tr>
<tr>
<td>PFOS b</td>
<td>&lt; 0.30 (&lt;0.30 - 0.37)</td>
<td>&lt;0.30 (&lt;0.30 - 0.37)</td>
<td>0.64 ± 0.47 (&lt;0.30 - 1.6)</td>
<td>-</td>
</tr>
<tr>
<td>Br-PFOS b</td>
<td>0.32 ± 0.22 (&lt;0.43 - 0.50)</td>
<td>&lt;0.71</td>
<td>&lt;1.1</td>
<td>-</td>
</tr>
<tr>
<td>ΣPFAA</td>
<td>44 ± 4</td>
<td>24 ± 6.6</td>
<td>11 ± 8</td>
<td>2.9</td>
</tr>
</tbody>
</table>

a Analyte peak areas could not be quantified in the coffee samples due to strong matrix effects;
b Non branched perfluorooctanesulfonic acid (PFOS); branched isomers of perfluorooctanesulfonic acid (Br-PFOS);
c LOQ values were counted as zero in the calculation of averages.
Coffee and hot water from coffee machines. The most abundant PFAA in brewed coffee from automatic coffee machines \((n = 12)\) was PFOA with concentrations ranging from \(<3.1\) to \(8.0 \text{ ng.L}^{-1}\). Concentrations of other PFAAs ranged between \(<0.11\) and \(2.4 \text{ ng.L}^{-1}\) for PFHpA, \(<0.11\)–\(2.6 \text{ ng.L}^{-1}\) for perfluorododecanoic acid (PFDA), \(<0.06\)–\(9.8 \text{ ng.L}^{-1}\) for PFBS and \(<0.3\)–\(1.6 \text{ ng.L}^{-1}\) for PFOS. The peak areas of PFBA, PFHxA and perfluorohexanesulfonic acid (PFHxS) could not be quantified in brewed coffee samples due to strong matrix effects. Concentrations of PFAAs in brewed coffee from coffee machines are shown in Table 1. The concentrations of PFAAs detected in hot water were similar to those in the corresponding tap water (see Table 2). Such as observed in Section 6.3.1, concentrations in tap water were similar to those encountered previously in tap water from Amsterdam (Eschauzier et al., 2012a).

### 6.3.2 Sources of PFAAs

Coffee from coffee machines. As shown in the previous section, PFAAs are present in the water-based beverages analyzed. Individual concentrations of PFAAs in the brewed coffee from each single location \((n = 12)\) were individually compared with the average concentrations of tap water used for its preparation \((n = 4)\) with a paired student t-test. This was done so because the tap water for all the coffee machines was from one single source. In coffee from coffee machines concentrations of PFHpA, PFOA and PFOS were significantly higher (Paired student t-test, \(\alpha \leq 0.05\)) than the concentrations of these compounds in the tap water used for their preparation. In this paper we hypothesized and investigated three simultaneously active possible sources to coffee prepared by coffee machines: (i) tap water used, (ii) coffee beans used and (iii) food contact materials in the beverage preparation machine.

(i) Tap water. The PFAAs found in tap water provide a starting contamination of the beverage to be produced. The background or base contamination of a beverage in general will therefore be a result of the tap water concentration which is used to prepare the beverage (see Table 2). As will be explained further, this was observed for the coffee and cola. This has implications for areas where tap water is contaminated and subsequently used as drinking water and for the preparation of tap-water based beverages in automated machines.

(ii) In coffee brewed from beans taken from the coffee machines investigated (i.e. similar beans), PFHpA, PFOA, PFDA, PFBS and PFOS were detected (see Table 2 manually brewed coffee column). The dominating analyte was PFOA at a level of \(9.0\)–\(9.7 \text{ ng.L}^{-1}\). PFBS was found in higher concentration in the blank (Table 2) than in the analyzed water, we have currently no explanation for this finding. In manually brewed coffee significantly higher \((\alpha \leq 0.05\)) concentrations were found of PFOA, PFDA and PFOS compared to tap water used for its preparation. The results show that the coffee beans as a raw material itself provide an additional source of contamination that is not caused by water and filter paper used.

(iii) To test for possible contamination from tubings used in beverage preparation, different tubes were tested for their leaching behavior. The results from the leaching experiments performed are shown in figure 1. For coffee only figure 1A is relevant since these show the leaching experiments at \(80^\circ\text{C}\) which is the water temperature used in coffee machines.
Table 2 Concentrations of PFAA (ng/L) in hot water samples and corresponding tap water and in manually brewed coffee and procedural blanks for brewed coffee.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Tap water A&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Hot water A&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Tap water B&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Hot water B&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Brewed coffee from coffee machines (n=12)</th>
<th>Manually brewed coffee (n=4)</th>
<th>Procedure blank brewed coffee (n=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFBA</td>
<td>10</td>
<td>13</td>
<td>17</td>
<td>18</td>
<td>-&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-&lt;sup&gt;b&lt;/sup&gt;</td>
<td>14±1.1 (13 – 15)</td>
</tr>
<tr>
<td>PFHxA</td>
<td>1.3</td>
<td>1.3</td>
<td>2.3</td>
<td>2.4</td>
<td>-&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.7±0.13 (1.6 – 1.7)</td>
</tr>
<tr>
<td>PFHpA</td>
<td>0.54</td>
<td>0.60</td>
<td>1.7</td>
<td>1.2</td>
<td>1.4±0.73 (&lt;0.11 – 2.4)</td>
<td>1.0±0.22 (0.86 – 1.3)</td>
<td>0.96±0.13 (0.85 – 0.96)</td>
</tr>
<tr>
<td>PFOA</td>
<td>4.5</td>
<td>4.5</td>
<td>3.7</td>
<td>3.6</td>
<td>4.4±3.3 (&lt;3.1 – 8.0)</td>
<td>9.1±0.72 (9.0 – 9.7)</td>
<td>6.2±0.22 (6.0 – 6.1)</td>
</tr>
<tr>
<td>PFNA</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>0.11</td>
<td>0.10</td>
<td>&lt;0.11</td>
<td>&lt;0.11</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>PFDA</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>&lt;0.04</td>
<td>s&lt;0.04</td>
<td>0.43±0.99 (&lt;0.11 – 2.6)</td>
<td>1.4±0.26 (1.2 – 1.4)</td>
<td>0.44±0.02 (0.42 – 0.43)</td>
</tr>
<tr>
<td>PFBS</td>
<td>3.2</td>
<td>3.3</td>
<td>16</td>
<td>19</td>
<td>2.9±2.9 (&lt;0.06 – 9.8)</td>
<td>1.6±0.30 (1.3 – 2.0)</td>
<td>4.3±0.21 (4.0-4.5)</td>
</tr>
<tr>
<td>PFHxS</td>
<td>&lt;0.38</td>
<td>&lt;0.38</td>
<td>0.55</td>
<td>0.74</td>
<td>-&lt;sup&gt;b&lt;/sup&gt;</td>
<td>-&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt;0.38</td>
</tr>
<tr>
<td>PFOS</td>
<td>&lt;0.30</td>
<td>&lt;0.30</td>
<td>&lt;0.30</td>
<td>&lt;0.30</td>
<td>0.64±0.47 (&lt;0.30 – 1.6)</td>
<td>0.53±0.06 (0.49 – 0.57)</td>
<td>&lt;0.30</td>
</tr>
<tr>
<td>Br-PFOS</td>
<td>0.5</td>
<td>&lt;0.43</td>
<td>&lt;0.43</td>
<td>&lt;0.43</td>
<td>&lt;1.1</td>
<td>&lt;1.06</td>
<td>&lt;0.43</td>
</tr>
</tbody>
</table>

<sup>a</sup>Tap water A/hot water A and tap water B/hot water B originated from different drinking water treatment plants.

<sup>b</sup>Analyte peak areas could not be quantified in the coffee samples due to strong matrix effects, see SI for details on recoveries and matrix effects.
Analysis of the extracts from the tube experiments with PTFE and MFA tubing conducted at 80 °C revealed higher concentrations than in the method blank (Norprene tube). For each analyte the leaching rate was calculated by dividing the absolute amount leached from the tubes (i.e. leached amount in 1 L minus amount in blank) by the surface area of the inner tube and the time the experiment was run, giving a leaching rate in pg.min⁻¹.m⁻². The samples obtained from the MFA tube experiment at 80 °C showed leaching rates of: PFPeA (38 pg.min⁻¹.m⁻²), PFHxA (19 pg.min⁻¹.m⁻²), PFHpA (13 pg.min⁻¹.m⁻²), perfluorononanoic acid (PFNA) (6.6 pg.min⁻¹.m⁻²), PFOS (14 pg.min⁻¹.m⁻²) and branched PFOS (7.3 pg.min⁻¹.m⁻²) (see Fig. 1A for the concentrations). The PTFE tubing showed the highest single compound increase (PFOA), and leaching rates of: PFOA (55 pg.min⁻¹.m⁻²) PFHxA (5.2 pg.min⁻¹.m⁻²), and PFHpA (9.5 pg.min⁻¹.m⁻²). The EPDM tube did not show an increase of any analyte, this was expected as the tube was a non-fluoropolymer tube, and therefore no leaching rates were calculated.

As will be shown in the section on cola (below), at temperatures of 5 °C no leaching was observed in any of the tubes tested. Apparently the higher temperatures are important...
for leaching of PFAAs from tubing. This is confirmed by the MFA data in Fig. 1C which show that the MFA tube cleaning step (40°C) leads to high leaching rates of PFAAs: PFPeA (452 pg.min⁻¹.m⁻²), PFHxA (139 pg.min⁻¹.m⁻²), PFHpA (156 pg.min⁻¹.m⁻²), PFOA (72 pg.min⁻¹.m⁻²), and PFNA (98 pg.min⁻¹.m⁻²). One can conclude that the MFA tube leaches at higher temperatures than 5°C. Moreover, since leaching rates are much higher at 40°C than at 80°C, most of the PFAAs are expected to leach out during the initial required cleaning step (see Section 6.2.2) before use of tubing for beverage dispensing. PFOA is known to be used as a process aid during the production of fluoropolymers (Kissa, 2001) and is therefore likely to be a residual in those materials. The amount of PFOA present in a fluoropolymer is largely dictated by its heat-curing history. However, during the PFOA manufacturing other PFAAs are formed as byproducts and these can be present in fluoropolymers as well (Prevedouros et al., 2006). The contribution of fluoropolymer (especially PTFE) to background concentrations of PFAAs in analytical instruments such as LC-MS/MS was observed and described before (Yamashita et al., 2004). The leaching experiments show that the length of the time period the tubes have been in use appears to be important for the leaching rate. After a certain period of time the available PFAAs are expected to have leached out completely from the tube polymers. This issue was not investigated here. Furthermore, a differentiation between pure residuals on the one hand and products resulting from e.g. hydrolysis of ester bonds (e.g. acrylates) by the hot liquid on the other would be an interesting subject of further study.

The setup used for leaching experiments represents a worst case scenario; in practice the coffee is only in contact with a piece of tubing of about 50 cm maximally for about one min maximally. Assuming an amount of coffee of 0.25 L; a 2 m pre cleaned (according to manufacturer standards) PTFE tube with an internal surface area of 0.075 m² (i.e. surface area from our experiments) and a contact time of 1 min this would mean an added absolute amount of 1.1 pg PFOA to one cup of coffee. This simple calculation shows that the theoretical absolute amount of PFAAs leaching from machine- tubes into hot beverages is very low.

A second method to show leaching of PFAAs to beverages was to sample hot (tea) water prepared in a coffee machine. The sampled hot water provides a matrix-free sample that has been in contact with the tubing inside the coffee machine. The analysis and comparison of tap and hot water from the coffee machines did not show any significant difference. This indicates that in the sampled coffee machines the third potential contamination source, viz. the tubing system inside the machine, did not contribute to PFAAs in brewed coffee. The concentrations of PFAAs in tap water (used for the hot water preparation) samples and the corresponding hot water from coffee machines are presented in table 2.

Summarizing the coffee section, the following statements can be made. Three possible sources to the coffee were identified and verified: (i) tap water; (ii) coffee beans or (iii) the tubing present inside the machine (although the composition of the tubing inside the beverage preparation device is unknown). Hot water samples delivered by the coffee machines showed concentrations similar to the corresponding tap water samples, indicating the importance of tap water as a source and the negligible contribution from contact with internal tubing. Although fluoropolymer containing tubes were shown to leach PFAAs when heated to temperatures between 40 and 80°C, analysis of hot water delivered by coffee machines showed that no actual leaching occurred. This is probably due to short contact times, use of non fluoropolymer-containing tubing (which could not be verified) and, possibly, the age of the tubes in case of fluoropolymer containing materials,
where all potential PFAAs may already have leached out. The coffee beans themselves were shown to contribute to the overall concentrations of PFOA, PFOS and PFDA in the brewed coffee.

**Cola from post-mixed cola.** The concentrations of PFAAs found in post-mixed cola, as compared to the corresponding tap water \((n=4)\) that was used to prepare the cola, were significantly \((\alpha \leq 0.05; \text{ paired student } t\text{-test})\) different for PFBA, PFHxA, PFHpA, PFOA, PFHxS and branched PFOS. The concentrations of these compounds were invariably lower in cola than in tap water. Concentrations of PFBS, PFPeA and PFNA were also lower in post-mixed cola compared to the corresponding tap water but not statistically significant \((\alpha \geq 0.05)\). Overall the concentrations of PFAAs in cola were seen to decrease during the post-mixing process when compared to the tap water used for this purpose (see Fig. 1D). The decrease in the finished cola compared to tap water can be attributed to (i) tap water used, (ii) concentrated cola used and (iii) beverage contact materials in the beverage preparation machine: ion exchangers and tubes.

(i) Similar to coffee from coffee machines, the tap water used is an important background to the measured concentration in cola. This can be seen in Fig. 1D where the tap water and cola concentrations do have a similar relative abundance profile.

(ii) The post-mixed cola is prepared from 1 part syrup and 4–5 parts aerated tap water which itself is purified with an ion exchanger prior to mixing. Both processes can lead to a reduction of the concentrations of PFAAs in the end cola. The mixing of cola syrup with water will dilute the concentrations of the PFAA in the final product, whereas the ion exchanger may selectively remove certain PFAAs (see point iii). The concentrations of the analytes in cola were compared to the corresponding concentrations in tap water in Fig. 1D (and Table 1). This showed that concentrations of PFAAs in tap water are about 1.2 times higher than in cola for PFBA, PFPeA and PFOA (Table 1). Other analytes: PFHxA, PFHpA, PFNA, PFBS showed a higher ratio (Table 1) indicating that more than 20% was removed. Possibly both processes play a role simultaneously for these compounds. For PFOS no conclusions can be drawn since its concentration is below the limit of quantitation.

(iii) In the preparation of cola from tap water, two different contact materials are used: ion exchanger and tubing. The ion exchanger possibly removes PFAAs from the tap water which would lead to a lower concentration in the cola. Anion exchangers are able to remove PFAAs from aqueous solutions at medium pH. Examples are the solid phase extraction cartridges like the OASIS-WAX or STRATA-XAW (Bäuerlein et al., 2012). These are weak anion exchangers that are used for example to extract PFAAs from environmental samples prior to analysis. Other examples are the removal of PFOS from wastewater by anion exchange resins (Deng et al., 2010) or from water (Xiao et al., 2012).

Finally, the leaching experiments at \(5^\circ C\) showed no difference between the investigated tubes and method blank (Norprene) (Fig. 1B). Here, the background tap water concentration was the main source of the analytes detected. The present data show that under these conditions no PFAAs are migrating into the liquid passing through the tubes.
6.4 Conclusions
Different PFAAs have been found in post-mixed cola, brewed coffee from coffee machines and tap water at the ng.L⁻¹ level. Sources to the beverages and impact of the preparation of the beverage were investigated.
The most important conclusion from this paper is that coffee collected from coffee machines contained significantly higher concentrations of PFHpA, PFOA and PFOS than the corresponding tap water. Also significantly increased concentrations of PFOA, PFDA and PFOS were found in manually brewed coffee. The increase of concentrations of PFOA and PFOS in the manually and machine brewed coffee compared to the tap water used has been shown to originate from the coffee beans.
PFAAs can leach out of fluoropolymer containing tubes into hot water when contact time is long (24 h in this study). In practice, such tubes may therefore pose an additional exposure source to hot beverages when fluids are left overnight in the tubings or when the tubings are new. However, as calculated above for PFOA and a PTFE tube, the absolute contribution from leaching out of the three polymers tested to the total amount of PFAAs in the drink will be very low.
The cola in post-mixed preparations showed lower concentrations than the tap water used for its preparation. A combination of the dilution step and the purification step inside the cola dispenser are responsible for the observed reduction. The contribution of fluoropolymers from beverage contact materials to the concentrations of PFAAs in cold beverages that come into contact with such materials was shown to be negligible even in a worst case scenario (i.e. 24 h exposure).
The results of this study show that, besides tap water, tap-water based beverages do form a potential additional source of human exposure. Currently tap-water based beverages are not taken into account in human exposure modeling, e.g. (Trudel et al., 2008) who assumed the intake due to water based beverages to be zero. Depending on the quantities consumed, the additional exposure could be important. (Vestergren and Cousins, 2009) showed that low concentrations of PFAAs in drinking water already can contribute to significant human exposure.
As main and final conclusion, this study shows that different beverage preparation processes can increase or decrease the overall concentrations of PFAAs encountered in the final consumer product, but that the source water used for preparing the beverages is the most important source of PFAAs. Consequently, in the assessment of human exposure of PFAAs via the diet it is important to take into account the significant contribution of tap-water based beverages.

Supporting information
Supplementary data to this chapter can be found online at: http://dx.doi.org/10.1016/j.chemosphere.2012.06.070.