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The last straw: Characterization of per- and polyfluoroalkyl substances in commercially-available plant-based drinking straws

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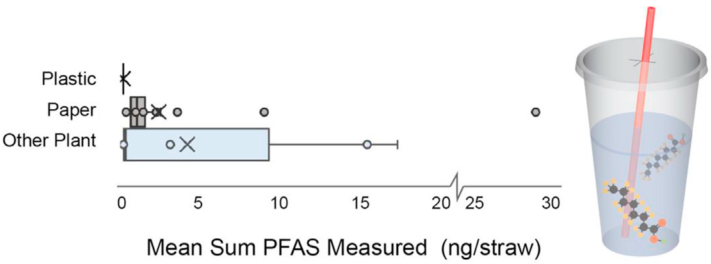
HIGHLIGHTS

- Per- and polyfluoroalkyl substances were found in plant-based drinking straws.
- Both short- and long-chain species were detected.
- PFOS and PFOA were detected repeatedly despite voluntary phase-out in the US.
- Some compounds leached into water at different temperatures.
- Most plant-based straws are not a fully biodegradable alternative to plastic.

GRAPHICAL ABSTRACT



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abstract

Paper and other plant-based drinking straws are replacing plastic straws in commercial settings in response to trending plastic straw bans and the larger global movement for reducing plastic pollution. The water-resistant properties of many plant-based straws, however, may be attributed to the use of per- and polyfluoroalkyl substances (PFAS) during manufacturing. In this study, 43 brands of straws (5 plastic, 29 paper, 9 other plant-based) were analyzed for the presence of 53 semi-volatile PFAS using ultra high-performance liquid chromatography tandem mass spectrometry. While the plastic straws had no measurable PFAS, 21 PFAS were detected in the paper and other plant-based straws, with total mean PFAS concentrations (triplicate analysis) ranging from 0.043 ± 0.004 ng/straw to 29.1 ± 1.66 ng/straw (median = 0.554 ng/straw). Perfluorobutanoic acid (PFBA), perfluorooctanoic acid (PFOA) and perfluorohexanoic acid (PFHxA) were the most frequently detected species. In a follow-up experiment, the brand with the highest PFAS levels and most diversity was tested for leaching in water at initial temperatures of 4 °C, 20 °C, and 90 °C. Approximately 2/3 of the total extractable PFAS leached compared to the initial methanol extraction. Semi-volatile PFAS concentrations measured in this study may be the result of manufacturing impurities or contamination, as PFAS approved for food-contact use are, typically, polymeric species. The presence of PFAS in plant-based drinking straws demonstrates that they are not fully biodegradable, contributing to the direct human ingestion of PFAS and to the cycle of PFAS between waste streams and the environment.

Credit author statement

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a class of anthropogenic chemically- and thermally-stable compounds that are used ubiquitously for their water-, grease- and fire-resistant properties (Buck et al., 2011). These characteristics also make PFAS highly persistent in the environment, and thus, the identification of novel PFAS sources and the corresponding development of strategies for their degradation and environmental remediation is currently a topic of significant interest within environmental and health sciences (Robey et al., 2020; Lu et al., 2020; Meng et al., 2020; Maimaiti et al., 2018). Despite the hazardous and bioaccumulative nature of this class of compounds (Sunderland et al., 2019), they are still widely used in industrial settings and in consumer products worldwide. Long-chain PFAS, such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS), have been studied more extensively, leading to their phase-out and replacement with short-chain and other alternatives (Sheng et al., 2018; Chu et al., 2020; Food and Drug Administ, 2020). The fate, transport, and potential toxic effects of these novel replacement PFAS have yet to be fully assessed.

Single-use compostable food-handling products have flooded the market in recent years as an environmentally-friendly alternative to Styrofoam and plastic. Unfortunately, many of the products marketed as biodegradable, especially those made from paper, have been shown to contain PFAS to make them resistant to rapid deterioration from contact with grease or other fluids (Yuan et al., 2016; Trier et al., 2011; Schaider et al., 2017; Adell, 2020). Whether sent to landfills or processed by commercial composting facilities, the PFAS in these products may not fully degrade for hundreds of years, eventually migrating into the environment via landfill leachate (Robey et al., 2020; Stoiber et al., 2020) or through the land application of compost (Ghisi et al., 2019; Choi et al., 2019), leading to their accumulation in soil, water and living organisms. The paper straw, a popular response to trending plastic straw bans (Schnurr et al., 2018), is one example of a plant-fiber product that advertises 100% biodegradability. However, there is no data available on the PFAS content of these straws, and it is not known if the PFAS potentially present can leach into drinks. Thus, we sought to identify and quantitate PFAS in 43 brands of commercially-available drinking straws (including plastic, paper and other plant-based straws) using a methanol-based extraction and a targeted ultra high-performance liquid chromatography-triple quadrupole tandem mass spectrometry (UHPLC-MS/MS) method. Further, the brand with the highest diversity of PFAS structures and mean total PFAS levels underwent leaching tests with water at different initial temperatures (ice-cold (4 °C), room temperature (20 °C), and boiling (90 °C)), to simulate PFAS leaching into common beverage scenarios, and to preliminarily explore paper straws as an under-studied route of human PFAS exposure.

2. Materials and methods

2.1. Chemicals and samples

Chemicals, standards, and straw samples (five plastic, twenty-nine paper and nine other plant-based; sixteen of which had their individual wrappers tested in addition) were obtained from various sources. Details can be found in the Supplementary Material.

2.2. PFAS extraction and analysis by ultra high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS)

Samples were prepared and extracted using a modified version of the US EPA's NRMRL Solids Extraction Protocol for PFAS Isotope Dilution Analysis (Mills and Impellitteri) using 0.3% methanolic ammonium hydroxide followed by rotation and centrifugation. UHPLC-MS/MS analyses were completed on a Thermo Vanquish UHPLC system (Waltham, MA, USA) coupled to a Thermo Quantis triple quadrupole mass spectrometer (operated in negative selected reaction monitoring mode) with a Phenomenex Gemini C18 column and a gradient elution using water and methanol, both with 5 mM ammonium formate, as described previously (Robey et al., 2020; Da Silva et al., 2020). Further details are given in the Supplementary Material.

2.3. Water leaching experiment

The straw brand with the highest measured total concentration and diversity of PFAS species (#34) was used in a follow-up experiment in which straw pieces were prepared in the same manner as described above and leached in Optima-grade water at three initial temperatures (4 °C, 20 °C, and 90 °C) or 0.3% methanolic ammonium hydroxide (same as total PFAS extraction). Further details are given in the Supplementary Material.

2.4. Data normalization, statistical analyses and quality control

Quantitation for all native PFAS was accomplished using linear regression models from calibration curves built for each analyte. Concentration data were normalized per weight of sample (i.e., ng PFAS per g of straw) as well as per straw (i.e., ng PFAS per 1 straw). Statistically significant differences in PFAS levels were assessed by one-way analysis of variance (ANOVA) with Tukey post-hoc test (significance inferred at $p < 0.05$). Various blanks (extraction, solvent and scissor blanks) were also included. No contamination was observed in any blanks. Further details on quantitation and additional measures that were taken to minimize carryover/contamination are given in the Supplementary Material.

3. Results and discussion

3.1. PFAS profiles in straws and wrappers

The first objective of this study was to identify and quantitate total PFAS in 43 different brands of straws and to compare PFAS species and concentrations among plastic, paper, and other plant-based straws. Out of 53 PFAS that were monitored, 21 were detected and quantified in at least one full set of triplicates in one or more brand of straws. Mean total PFAS concentrations detected in each straw brand are shown in Fig. 1 (in ng/straw; concentrations for each PFAS measured and concentrations per weight of straw (in ng/g) can be found in Supplementary Tables S4 and S5, respectively). PFAS were measured in 36 out of the 38 paper and other plant-based straws included in this study, with total quantified PFAS concentrations ranging from 0.043 ± 0.004 ng/straw (brand #37) to 29.1 ± 1.66 ng/straw (brand #34) (median 0.554 ng/straw). Traditional plastic brands had no quantifiable PFAS. The two most frequently detected PFAS in both the straws and wrappers were perfluorobutanoic acid (PFBA) and PFOA (Figure S1). Interestingly, PFOA and PFOS were detected repeatedly, despite the voluntary phase-out of these legacy PFAS under the PFOA Stewardship

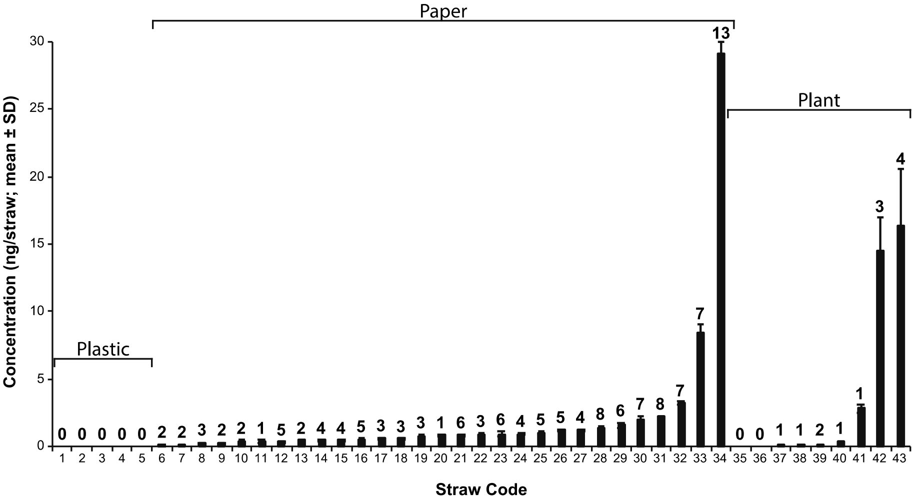

Fig. 1. Total PFAS concentrations (as mean sums ± standard deviation) in ng per individual straws. The numbers above each bar represents the total number of individual PFAS species that were measured in each straw brand.

Program (Environmental Protec, 2010) and their subsequent disallowance in food contact materials by the US Food and Drug Administration (FDA) in 2016 (Food and Drug Administ, 2020). Sixteen out of 18 of the straws claiming FDA approval contained measurable levels of PFOA, and 5 out of 18 contained PFOS. While most straw brands were labeled as manufactured outside of the U.S. (24 out of 43; country of manufacture can be found in Supplementary Table S3), one brand made in the U.S. (brand #15) also had measurable levels of PFOA. Brand #13 claimed to be PFAS-free, however, we detected measurable quantities of PFBA and 6:2 fluorotelomer phosphate diester in that sample. Seventeen of the 21 PFAS found in straws were also found in at least one wrapper sample, but no correlations were observed between the presence and/or magnitude of a certain compound in a straw sample and its corresponding wrapper. Future work should explore the presence of PFAS in wrappers, as well as the relationship between straws and their wrappers. Finally, correlations between the presence of color, country of manufacture or claims of biodegradability and the amount or type of PFAS present in these samples were explored, but none could be established from this relatively small and diverse sample set.

Like in other studies that demonstrated a disparity between the amounts of PFAS species identified via LC/MS and total fluorine measurements (Schaider et al., 2017), the relatively low levels of semi-volatile PFAS measured in these samples are not functional and are not representative of the polymeric species which are FDA-approved for use in food-contact paper and paperboard materials (Schaider et al., 2017; OECD, 2020). PFAS levels measured are also far below the 100-ppm threshold used by independent certifiers of compostability, such as the Biodegradable Products Institute, for determining intentional use (InstituteFluorinat, 2020). Thus, it can be inferred that there may be higher levels of polymeric and volatile species also present in these straws and that, perhaps, the semi-volatile PFAS measured in this study are impurities from manufacturing or recycled materials (OECD, 2020; Peters et al., 2019), and not purposefully added for the function of water-resistance. However, this requires further investigation.

3.2. *Water leaching experiment*

The brand with the highest mean total PFAS concentrations and diversity of PFAS (brand #34, 13 species) was used in a leaching test to evaluate the ability of different compounds to migrate into water at three different initial temperatures. Approximately two-thirds of total extractable PFAS levels (average 1.53 ± 0.122 ng/straw) leached into water at all three temperatures (4 °C, 20 °C, and 90 °C), without a statistically significant difference between them (Fig. 2; concentrations in ng/straw and ng/g of straw can be found in Supplementary Tables S8 and S9, respectively). Shorter-chain PFAS, including PFBA (C4), perfluoropentanoic acid (PFPeA, C5), and PFHxA (C6), appeared to leach nearly completely. Conversely, some long-chain PFAS, such as perfluorotetradecanoic acid (PFTeDA, C14) and perfluorooctadecanoic acid (PFODA, C18), did not leach in this

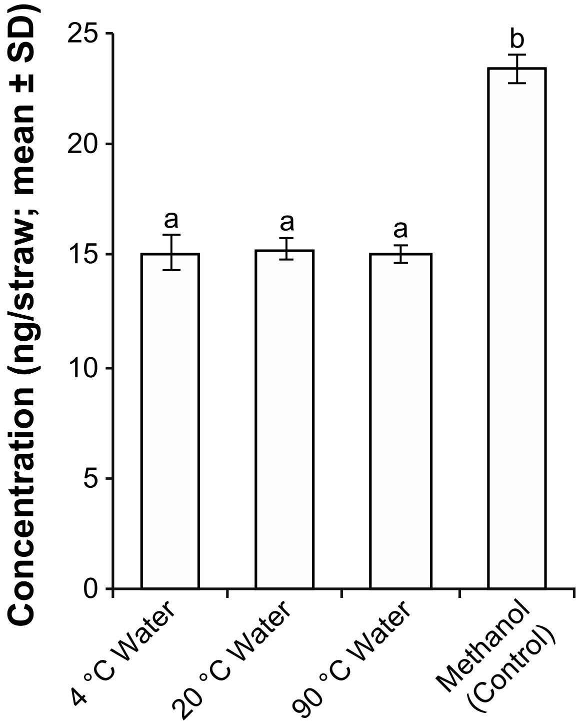

Fig. 2. Total PFAS concentrations (as mean sums ± standard deviation) in ng per individual straws in the water leaching experiment. The letters above each bar represent statistical significance in measured PFAS levels (i.e., '*a*' and '*a*' are not statistically different, but '*a*' and '*b*' are; significance was inferred at $p < 0.05$).

experiment (Supplemental Tables S7 and S8). Leached levels of PFOA (C8) were approximately two-thirds of the solvent-extractable levels in all three water temperatures ($p < 0.001$ for all comparisons against methanol), but differences were not statistically significant between temperatures.

We have demonstrated the presence of short-chain and long-chain PFAS in commercially-available plant-based drinking straws, and the leachability of the shorter-chain species into water at different initial temperatures. PFOA leached from a single straw in this study (average 1.53 ± 0.122 ng/straw) would contribute only 0.1% of the EPA reference dose (20 ng/kg/day) for direct human ingestion of PFOA (Morrissey Donohue et al., 2016). However, nine US states have developed more stringent drinking water guidelines (Post, 2021) and other agencies have proposed stricter daily intake limits for PFOA (Agency for Toxic Substances and Disease Registry, 3 ng/kg/day (Breysse, 2018)) or total PFAS (European Food Safety Authority, 0.63 ng/kg/day (European Food Safety Auth, 2020)). What amount of daily intake is safe, especially considering the accumulation of other sources of regular exposure (Sunderland et al., 2019; Yuan et al., 2016)? Plant-based straws are not a significant proportion of the waste stream. However, this study shows that most paper and other plant-based drinking straws are not fully biodegradable due to the presence of “forever chemicals” and, therefore, are not an environmentally friendly replacement for plastic straws. In the same way that the plastic straw has become the “gateway plastic” at the forefront of the global movement to decrease the use of single-use plastics (Schnurr et al., 2018; Wagner and Toews, 2018), the identification of PFAS in single-use plastic-alternative straws exemplifies the unintended replacement of one ubiquitous, persistent, and bioaccumulative pollutant for another, and suggests that other popular single-use products may also contain considerable amounts of PFAS. Further work remains in screening for PFAS in other food-contact products including volatile and polymeric species, as these could serve as significant contributors to daily PFAS ingestion levels in humans and total PFAS load in the environment (Lohmann et al., 2020), as well as the adoption of nontargeted approaches (Koelmel et al., 2020) for the measurement of new and alternative replacement species that were not included in this targeted study.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.130238.

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