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Snapshot Survey of the Presence of Perfluoroalkyl Substances in Products, Articles, and the Environment in Ecuador

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ABSTRACT

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a legally binding instrument for 186 Parties (status: April 2023). Accordingly, among other responsibilities, countries are obliged to report the production, import, or export of the POPs listed in Annexes A, B, or C; provide information to registers; maintain inventories; and monitor the presence of POPs in the environment. In the broader context of international chemicals and waste management, producer responsibilities, harmonized reporting, and compliance with national and international regulations, Ecuador has addressed the newly listed group of perfluorinated alkyl substances (PFAS) in its national implementation plan and sent selected products from its national market for PFAS analysis. The products analyzed came from the initially listed fields of specific exemptions and acceptable purposes, including: fire-fighting foams; photographic aids; greasers/degreasers; various kinds of paper/packaging; textiles; and leather, coatings, cleaners, metal plating, and pesticides. Our results showed that the three PFAS presently listed in the Stockholm Convention could be quantified in only a few samples; additional PFAS, not yet listed in the Convention also had low detection frequencies. Although the number of samples was limited, the samples covered a large spectrum of sample matrices, making it possible to conclude that—once these products become waste and are regulated under the Basel Convention—they would not constitute a disposal problem. Nevertheless, verification of the presence of PFAS in products on the market is expected to pose an analytical challenge for both, developed and developing countries.

1. Introduction

Through its Ministry of Environment, Water, and Ecological Transition, the Government of Ecuador is implementing a project named the "National program for the environmental sound management and life cycle management of chemical substances," together with the United Nations Development Programme (UNDP) with funds from the Global Environment Facility (GEF)[†]. A baseline assessment undertaken in 2016 concluded that—among other pollutants—one of the newly listed persistent organic pollutants (POPs), perfluorooctane sulfonic acid (PFOS), could be a national priority, since it may be contained in products. PFOS, its salts, and perfluorooctane sulfonyl fluoride (PFOSF) were listed in Annex B of the Stockholm Convention in 2009 [1] and amended in 2019 [2]. The listing of a chemical in Annex B of the Convention implies that there are acceptable purposes for the chemical because no adequate alternatives are available [3–5]. PFOS, which has the structural formula F-$(CF_2)_8$-SO_3H and the CAS number 1763-23-1, is a fully fluorinated (perfluorinated) alkane sulfonic acid (PFSA). It occurs as either a linear (L-PFOS) or branched compound (br-PFOS), depending on the chemical synthesis process. L- and br-PFOS have the same molecular formula, $C_8HF_{17}SO_3$, and are analytically determined as anions (see Ref. [6] for analytical determinations of PFOS and related compounds). The strong C–F bond in the molecule gives it high electronegativity. This property, in

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combination with the small size of the fluorine atoms, gives PFOS and other perfluorinated acids (PFAA)—more specifically, PFSA and perfluorinated carboxylic acids (PFCA)—unique physical–chemical properties such as inertness and exceptional surface-tension-lowering potential. Due to their unique properties, these substances are increasingly being used in various industrial applications [7,8]. In 2019 and 2022, two more PFAA were listed in Annex A of the Stockholm Convention: perfluorooctanoic acid (PFOA), its salts, and PFOA-related compounds [9]; and perfluorohexane sulfonic acid (PFHxS), its salts, and PFHxS-related compounds [10]. PFOS, PFOA, and PFHxS are commonly referred to as perfluorinated or polyfluorinated alkyl substances (PFAS); however, their definitions and the substances included under the term "PFAS," such as non-polymeric and polymeric molecules, vary depending on the authors or authoring institution/organization [8,11–16].

PFOS is persistent and has bioaccumulative and biomagnifying properties. Unlike other POPs, it does not follow the classic pattern of partitioning into fatty tissues; instead, it binds to proteins in the blood and liver. It has the capacity to undergo long-range transport and has been demonstrated to be both ecotoxic and toxic to mammals [17–19]. The International Agency for Research on Cancer (IARC) has not yet classified the carcinogenicity of PFOS or PFHxS to humans (status: March 2023) [20], although PFOA has been classified as being possibly carcinogenic to humans and placed in Group 2B [21].

Subsequent to Ecuador's first assessment of PFOS, the Ecuadorian government and the National Program for the Environmental Sound Management and Life-Cycle Management of Chemical Substances undertook activities to identify imported products and analyze them for PFOS content. The Man Technology Environment (MTM) Research Centre at the School of Science and Technology of Örebro University was contracted to undertake an analysis of the three PFASs listed in the Convention; the spectrum was later extended to a larger number of substances. The MTM Research Centre has already served as an expert laboratory for the analysis of PFAS under a United Nations Environment Programme (UNEP)/GEF project to support Latin American and Caribbean countries in the global monitoring plan (GMP) under the Stockholm Convention [22]; it has detected various PFASs in environmental matrices such as the air [23]; surface water [24]; soil, sediments, and foodstuffs [25]; and human milk [26,27].

The main objective of the Stockholm Convention is to protect human health and the environment from POPs. Therefore, the signatory countries must develop two essential elements: ① A POP national inventory of each of the substances listed in the Convention; and ② maintenance of the actions under the national implementation plan. A POP national inventory is a compilation of information on past and present production of POPs, their imports and exports, and the uses of these substances. As many POPs are used in the manufacture of products or articles that may have a long service life and final disposal, a comprehensive inventory should also estimate the quantity of POPs in the products or articles manufactured or imported in the country across the whole life cycle [28].

Unfortunately, primary data with information on POP substances or products containing them are not always available or are unreliable. Therefore, during the process of revising and obtaining data for the inventory, it is helpful to select and obtain some samples of products to analyze their POP contents, in order to upgrade the inventory based on the available national information. Since there is a strong linkage between multilateral environmental agreements on chemicals and those on waste, all substances listed in the Annexes of the Stockholm Convention on POPs are also subject to management under the Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal [29] when they become waste. Waste consisting of, containing, or contaminated with POPs—including PFOS, PFOA, or PFHxS—above the low POP content must be destroyed or irreversibly transformed. Together, the two conventions cover the whole life cycle of the listed PFAS.

This research analyzing more than 70 samples from Ecuador was triggered by a report published by the Canadian Commission for Environmental Corporation (CEC), which analyzed 137 items of clothing and performance apparel collected in the three North American countries for 31 PFASs [30]. In addition to clothing products, the present study collected and analyzed samples with the aim of quantifying the three PFASs listed in the Stockholm Convention: PFOS [1,2] and its precursor compounds in pesticides; PFOA [9]; and PFHxS, which was listed in 2022 [10], although at the time of this report it was only recommended for listing [31]. We also included more PFAS to obtain a better overview, given that additional PFAS—namely, long-chain PFCA [32]—are under review by the POPs Review Committee.

2. Materials and methods

2.1. Samples

The sampling program was carried out during the first months of 2021 by the team in charge of the POPs inventory, considering general guidance on POPs inventory development [28] and based on a previous inventory on PFOS performed in 2019. Sample selection was determined during the national statistics on imports and production analysis to prepare the PFOA and PFHxS inventories. The criteria considered for selecting the samples to acquire were as follows:

(1) PFAS values contained in the products or brands according to available technical information in the UNEP guidelines;

(2) Occurrence in the literature (e.g., Kotthoff et al. [33], Bečanová et al. [34], Favreau et al. [35], and Herzke et al. [36]);

(3) High import volumes;

(4) Year of manufacture (i.e., imported or manufactured after 2012);

(5) Country of origin (especially countries without PFAS regulations).

Once the samples were obtained, they were sent to the MTM Research Centre, where they were received at the chemical analytical laboratory on March 30, 2021. The samples comprised 39 liquid, five semi-solid, and 30 solid samples (Table 1), including a solid sample that could not be dissolved (sample designated as COP_069). The solid samples were consumer goods; the liquids were water, aqueous film-forming foams (AFFF) (i.e., firefighting), and aviation hydraulic fluids; and, in particular, additives (i.e., additives and aids). Of the pesticides, one was solid and the other semi-solid. A detailed list, including the physical state of the samples, is provided in Table S1 in Appendix A.

2.2. Chemicals analyzed, analytical standards, and reagents

A mixture of native standards of PFAS—including the potassium salt of a technical-grade PFOS containing 78.8% perfluorooctane-1-sulfonate (L-PFOS) and 21.2% of a mixture of branched isomers (br-PFOS), the mass-labeled extraction standard used as an internal standard (IS), and the mass-labeled injection standard used as a recovery standard (RS)—were purchased from Wellington Laboratories (Canada). Details of these standards are described in Ref. [37]. Glacial acetic acid and ammonium acetate (NH_4Ac; > 99.0%) were purchased from Sigma Aldrich (Germany); ammonium hydroxide (25%), acetonitrile (high-performance liquid chromatography (HPLC) grade, > 99.99%), isopropanol (> 99%), and methanol (HPLC grade, > 99.99% and liquid chromatography-mass

Table 1
Overview and number of samples analyzed, including types of samples, classification, and sample names.

Type (number (*N*))	Class	Sample name	*N*
Aviation (10)	AFFF	Ansulite1, Ansulite2, Buckeye, Chemguard, Chemguard AR, Chemguard FP, Mezcla	7
	Aviation hydraulic fluid (HF)	Aviation_HF1, Aviation_HF2, Aviation_HF3	3
MetalPlat (3)	Metal plating	Metal plating, Metal plating Cr, Degreaser MP	3
Pesticide (2)	Pesticide	Antkiller1, Antkiller2	2
Aid (28)	Leather aid	Leather treatment, Leather cleaner	2
	Cleaner	Dishwash, Cleaner_Klinkar, Cleaner interior, Car shampoo	4
	Coolant	Cooland	1
	Degreaser	Degreaser_basic, Degreaser_M, Degreaser prof_H7, Degreaser hands, Degreaser kitchen, Degreaser_Gunk	6
	Greaser add(itive)	Chem oil drilling, Brake fluid, Anticorrosive oil, Motorcycle, Leather greaser1, Leather greaser2, Greaser_EP2 Chevron	7
	Paint	Paint anticorr(osive)	1
	Photo aid	Photofix, Photo developer, Photographic developer_Fotoquim	3
	Polisher	Shoe polish, Wax car1, Wax car2, Wax floor	4
Paper (8)	Paper	Popcorn bag, Carton waxed, Paper waxed1, Paper axed2, Paper baking, Pizza carton, Hamburger box, Carbonless paper	8
Plastic (7)	Plastic	HDPE, polyvinyl chloride (PVC) tube, Plastic fiber, PVC waste, Silicone seat	5
	Wire	E-wire1, E-wire2	2
Textile (11)	Carpet leather	Carpet1, Carpet2, Carpet3, Carpet4, Carpet5, Leather, Leather upholstery	7
	Fabric	Fabric antifluid, Fabric waterproof, Fabric sporting, Fabric umbrella	4
Water (5)	Water	Drinking water, River Teaone, River Guayas, River Guayllamba, River Machángara	5
Grand total			74

spectrometry (LCMS) grade, > 99.9%) were obtained from Fisher Scientific (UK). The water used during the analysis was Milli-Q (18.6 MΩ). SPE-WAX 6-cc cartridges (150 mg, 30 μm) were obtained from Waters (USA).

Samples were analyzed for a set of 29 PFAS, which was a much broader spectrum of PFAS than originally planned. The chemicals included in the targeted analysis were the three substances listed in the Stockholm Convention: PFOS, PFOA, and PFHxS [1,2,9,10]. For PFOS, L-PFOS and br-PFOS were determined separately, and the sum of these two were then added up and reported as ΣPFOS.

The following groups of substances were also analyzed and are separated by a row of grey cells in most results tables: five PFOS precursors, six perfluorosulfonic acids from tetra (perfluorobutane sulfonate (PFBS)) to dodecane (perfluorododecanoic acid (PFDoDS)) (note that PFOS and PFHxS are placed in the first group of Stockholm Convention POPs, referred to as "SC POPs"), 12 perfluorocarboxylic acids from tetra (perfluorobutanoic acid (PFBA)) to octadecanoic (perfluorooctadecanoic acid (PFOcDA)) (note that PFOA is contained in the first group), and up to three fluorotelomer sulfonates (FTSAs). The full list containing the names of the PFAS and their abbreviations is provided in Table S2 in Appendix A. It should be mentioned that the whole list was not applied to all sample types; these cases are shown as "NA" in the table, which means not analyzed.

2.3. Sample preparation and extraction methods

Samples were collected, packaged, and shipped with an express carrier by the Inventory Team in Ecuador. Liquid and semi-liquid samples were placed in high-density polyethylene (HDPE) plastic bottles (250 mL). Solid samples were wrapped in aluminum foil. Upon arrival, samples were stored in a dark room until analysis.

The chemical analytical methods were adjusted to the sample type and then optimized.

2.3.1. Water samples

The analytical method [24] was optimized for a solid-phase extraction (SPE) addressing the extraction of the three PFAS (PFOS, PFOA, and PFHxS) from the samples. Prior to SPE extraction, all samples were sonicated for 10 min in their original HDPE bottle. All samples were then spiked with 5 μL of mass-labeled IS (1.24 ng absolute). The SPE-WAX cartridges were conditioned via the passage of 4 mL of 0.1% ammonium hydroxide in methanol, 4 mL of methanol, and 4 mL of Milli-Q water, in sequence, prior to the loading of 500 mL samples.

After loading the samples, the cartridges were washed with 4 mL of Milli-Q water followed by 4 mL of an ammonium acetate buffer solution (pH 4) and then dried under vacuum for 30 min. The first, neutral fraction to contain perfluorooctane sulfonamide (FOSA) was eluted using 4 mL of methanol. The second, anionic fraction to contain PFCA and PFSA was eluted with 4 mL of 0.1% ammonium hydroxide in methanol. The extracts were evaporated using RapidVap until dryness. 100 μL of methanol was added to fraction one, while 40 μL of methanol and 60 μL of the 300 μL aqueous mobile phase (2 mmol·L^{-1} ammonium acetate in water) was added to fraction two. Both fractions were spiked with 5 μL of RS (1.24 ng absolute), vortex-mixed, and centrifuged for 10 min at 3000 r·min^{-1}. The extracts were transferred to the liquid chromatograph (LC) vials for instrumental analysis.

2.3.2. Paper samples

The steps of the analytical workflow were as follows:

(1) Cut samples with methanol-rinsed scissors and then weigh them to (0.10 ± 0.01) g. Select the area such that that labels or other distinctive features are included. Measure the area because of differences in density (units of concentration: ng·g^{-1} or μg·m^{-2}).

(2) Cut the sample into smaller pieces (6–9 pieces) into a 15 mL polypropylene (PP) tube.

(3) Add about 5000 pg of the IS.

(4) Add 5 mL of methanol.

(5) Shake for 15 min, then sonicate for 15 min.

(6) Centrifuge for 5 min at 3000 r·min^{-1}, then transfer the solvent to a second tube and repeat steps 4–6 once.

(7) Evaporate gently to 0.5 mL.

(8) Add about 2000 pg of the RS.

(9) Store in the freezer overnight or until analysis.

(10) Sonicate and split into two parts (Part A and Part B), before injection.

(11) Extract 100 μL Part A and add 150 μL of Milli-Q water with 2 mmol·L^{-1} NH_4Ac.

(12) Extract 100 μL Part B and add 50 μL of Milli-Q water with 2 mmol·L^{-1} NH_4Ac and 100 μL of methanol.
(13) If cloudy, centrifuge before the injection.
(14) Respectively inject both (11) and (12) to liquid chromatograph-tandem mass spectrometer (LC-MS/MS).

2.3.3. Product samples

Subsamples were provided in separate HDPE bottles without any pretreatment. At the laboratory, the subsamples were gently mixed and then allowed to rest for 10 min before pipetting and diluting with ultrapure water for firefighting foam and pesticide samples or with acetone/isopropanol for greasers, wax, motorcycle or anticorrosive oil, cleaners, paint samples, liquid samples for photographic fixation, and metal plating with a dilution factor of 100. The diluted samples were ultrasonicated for 30 min and left for 12 h. After that, the diluted samples were further diluted 10 fold with methanol. 200 μL of the 1000 fold diluted samples was then transferred to the LC vial with the addition of 2 ng of mass-labeled IS and 300 μL of aqueous mobile phase before instrumental analysis for PFAS.

Four semi-solid or solid samples—namely, COP_077 (Table S19 in Appendix), COP_069 (Table S7 in Appendix), COP_097 (Table S9 in Appendix), and COP_089 (Table S10 in Appendix)—did not undergo an extraction process; rather, they were "only" dissolved, diluted, and injected. For these samples, the limits of quantification (LOQ) were different from those for the other samples of the same type. Sample COP_069, a solid photographic developer, could not be completely dissolved in water, methanol, isopropanol, acetone, or toluene; therefore, the quantity of PFAS in this material may be underestimated. None of the four samples showed any indication of a peak for the PFAS analyzed.

2.3.4. Blank control

Two plastic bottles (HDPE) were used as a blank control to test whether the packaging material had an impact on low-contaminated samples. For each bottle, 5 mL of methanol was placed into the bottle and agitated. The bottle was left still for 1 h. Then, the methanol was removed, evaporated to 1 mL, and injected onto LC–MS/MS. No PFOS, PFOA, or PFHxS was detected at a detection limit of 60 pg per sample.

2.4. Instrumental analysis and quantification

The analysis of the PFAS was done using an ultra-performance liquid chromatography (UPLC) system coupled to a tandem mass spectrometer (Acquity XEVO TQ-S or XEVO TQ-S micro, Waters). Separation was performed on a C_{18} column (1.7 μm, 2.1 mm × 100 mm; Acquity BEH, Waters). The injection volume was 10 μL. The mobile phases used were methanol:water 70:30 (v/v) (Phase A) and methanol (Phase B) with 2 mmol·L^{-1} NH_4Ac in both phases. The flow rate was 0.3 mL·min^{-1}. The LC gradient started with 100% Phase A, held for 0.5 min, increased up to 100% Phase B in 13 min, held until 14 min, and then decreased to 0 Phase B in 14.2 min and equilibrated until 17 min. The mass spectrometer instrumental settings were electrospray ionisation operated in negative mode with a source temperature at 150 °C, desolvation temperature at 400 °C, desolvation gas flow at 800 L·h^{-1}, and cone gas flow at 150 L·h^{-1}. The column temperature was 50 °C.

Each analyte and the branched isomers of PFOS were quantified using a 10 point calibration curve, which was made up of a sequence of concentrations from 6 to 5000 pg·mL^{-1}. The branched isomers of PFOS were reported as the sum of two isomer groups (6-, 2-, and 3-, 4-, 5-PFOS). ΣPFOS is the sum of the L- and br-PFOS. The IS was spiked before extraction to give a recovery-corrected concentration.

2.5. Quality control and quality assurance

SPE manifolds and all equipment used for solvents preparation were cleaned twice with methanol. The Hamilton syringes used for spiking were designated for IS, native, or RS, to avoid cross-contamination. For quality control, two procedural blanks (Milli-Q water) and one spiked Milli-Q water sample (quality control (QC)) were extracted in parallel with seven samples and quantified using mass-labeled standards with a 10 point calibration curve. Procedural blanks were used to check any contamination during the analysis procedure; the spiked QC samples were used to assess the extraction efficiency and repeatability of the method. Precision and accuracy were assessed by spiking 2 ng native PFAS into Milli-Q water (N = 7) [24,38]. The recovery of the three native PFAS in all spiked samples ranged from 98% to 102% (relative standard deviation (RSD) < 10%). The average recoveries of PFOS, PFOA, and PFHxS in the extracted samples ranged from 73% to 110%.

For LC-MS/MS instrumental quality control during sample analysis, methanol was injected after every ten samples to ensure the absence of any contamination from the instrument [38]. The laboratory participated successfully in the fourth round of the UNEP-coordinated interlaboratory assessment for the water test sample and the 14 PFAS determinants, including L-PFOS, br-PFOS, ΣPFOS, PFOA, and PFHxS (satisfactory z-scores; i.e., > -2 and < 2) [25,39–41].

Investigation of contamination during sampling or shipment of the samples was done by analyzing the field blanks; the results showed that none contained any of the three PFAS at quantifiable levels. The limit of detection (LOD) was determined as the average concentration in the procedural blank plus three times the standard deviation. In cases where an analyte was not present in the blanks, the lowest point of the calibration curve was used. The LOQ was determined as the average concentration in triplicate procedural blanks plus ten times the standard deviation. When an analyte was not present in the blanks, the lowest point of the calibration curve was used [24,38]. The LOQs are included in the results tables. For statistical purposes, values below LOQ were set to zero, as the presence of these analytes could not be confirmed analytically.

Standard international (SI) units are used throughout the manuscript; however, since the quantitative results ranged over many orders of magnitude, non-SI units have been used for the grouping of the samples (Table S1), linked to the physical state of the sample as solid, semi-liquid, or solid. The non-SI units are defined as follows [42]: ppm (parts per million, for values of 1×10^{-6} to the SI unit), ppb (parts per billion, 1×10^{-9}), and ppt (parts per trillion, 1×10^{-12}). Subsequently, solid samples are presented at ppb (ng·g^{-1} or μg·kg^{-1}). Liquids are reported at the ppb level (μg·L^{-1}) or, for surface water (river) samples, at the ppt level (ng·L^{-1}).

3. Theory and calculations

The objective of this research was to undertake a chemical analysis of environmental samples and consumer goods found in the markets in Ecuador, quantify the chemical content (in this case, the content of PFAS), and determine the type and scale of PFAS present in the various types of samples. If possible, we also aimed to identify a common pattern within the sample types or to distinguish between them.

All data were maintained in Microsoft Excel for Microsoft 365, Version 2305 (Microsoft Co., Ltd., USA). Visualization and statistical operations were conducted with R (version 4.2.2) using RStudio (version 2022.12.0+353, Posit Software, USA). Bar graphs are used to display data, with height representing the value of each variable. These graphs make it possible to show variations in categories or groups of samples. A single bar chart displays a single value; stacked bars present the summed values.

Box whisker plots are used for the graphical representation of the scale of the measured values. The lower border of the box represents the first quartile (25%), the line inside the box is the median, and the upper border is the third quartile (75%). The whiskers represent the minimum and maximum amounts without outliers. The dots outside the whiskers are outliers, which are defined as all values greater or smaller than the interquartile range multiplied by 1.5. The bar charts and box whisker plots were made using the ggplot2 package.

Heatmaps were used for pattern analysis to show variance across multiple variables by means of different colors; the contribution of up to 18 PFAS were used in the sum of them.

4. Results

A total of 76 samples were analyzed, including two bottle blanks (Table 1 and Table S1). One sample, COP_069, could not be analyzed due to interferences in the chemical analytical laboratory. Each table contains information on the physical state of the sample (i.e., liquid, solid, semi-solid), a classification of the sample regarding type and field of application (e.g., fire-fighting, metal plating, or water), a sample ID, and the analytes.

The analytes are listed in the order used in the listing in the Stockholm Convention, starting with PFOS, including the split into L- and br-PFOS, and followed by ΣPFOS. Next are PFOA and PFHxS, followed by the PFSA. The PFOS precursors were not analyzed (designated as “NA” in most samples) but were taken as target compounds in the pesticides to check for the presence of sulfluramid. Some telomeric PFAS were analyzed; these are included in the tables where analyzed. For a few samples, it was not possible to quantify a specific analyte; these are marked with “NR” (not reported).

4.1. Occurrence of PFAS

Eleven PFAS were not found at quantifiable levels in any of the samples: FOSA, *N*-methylperfluoro-1-octanesulfonamide (NMeFOSA), *N*-methyl perfluorooctane sulfonamidoethanol (NMeFOSE), *N*-ethyl perfluorooctane sulfonamidoethanol (NEtFOSE), perfluoropentane sulfonic acid (PFPeS), perfluoroheptane sulfonic acid (PFHpS), perfluorononane sulfonic acid (PFNS), perfluorodecane sulfonic acid (PFDS), perfluorododecane sulfonic acid

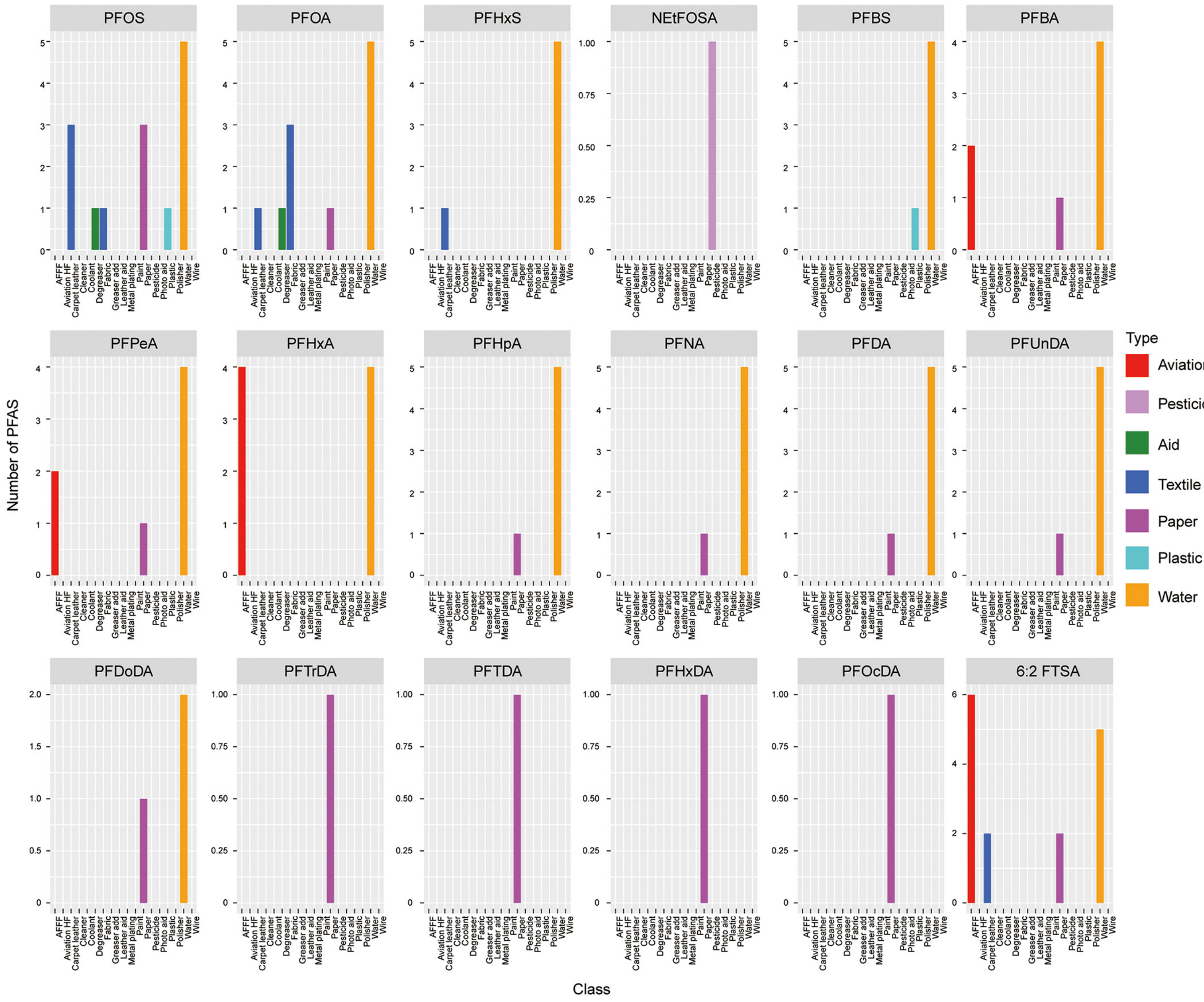

Fig. 1. Stacked bars showing the detection frequency by number of PFAS quantified in the various classes of samples. Colors refer to sample type.

(PFDoDS), 4:2 fluorotelomer sulfonic acid (4:2 FTSA), and 8:2 FTSA. Therefore, these substances are not included in the graphics and are not detailed in the results tables in Appendix A.

Fig. 1 provides a graphic representation of the detection frequency for each of the 18 quantified PFAS, with the sample type listed along the *x*-axis. The highest detection frequency was for 6:2 FTSA, which was quantified in 15 samples; this was followed by PFOS, which was quantified in 14 samples, and then PFOA, which was quantified in 11 samples. PFHxS was found in only six samples.

When grouping was applied according to "type," no PFAS could be quantified in the metal plating group (*N* = 3). A more detailed grouping class identified nine classes with no quantified PFAS. These included aviation hydraulic fluids (*N* = 3), cleaners (*N* = 4), coolants (*N* = 1), greaser additives (*N* = 7), metal plating (*N* = 3), paint (*N* = 1), photo aids (*N* = 2), polishers (*N* = 4), and wire (*N* = 2), for a total of 27 samples. These findings are summarized in Fig. 2.

Fig. 2 also reveals that none of the Stockholm Convention PFAS (SC PFAS) were detected in the AFFF, and that the one PFAS declared as a pesticide contained the PFOS precursor sulfluramid (NEtFOSA) but not PFOS itself.

4.2. Scale of PFAS amounts

The three SC PFAS were analyzed in all samples (*N* = 73); data for the descriptive statistics are shown in Table 2. The large standard deviations of the mean values for all the PFAS shown and for each type of sample indicate that the values were quite scattered. Further,

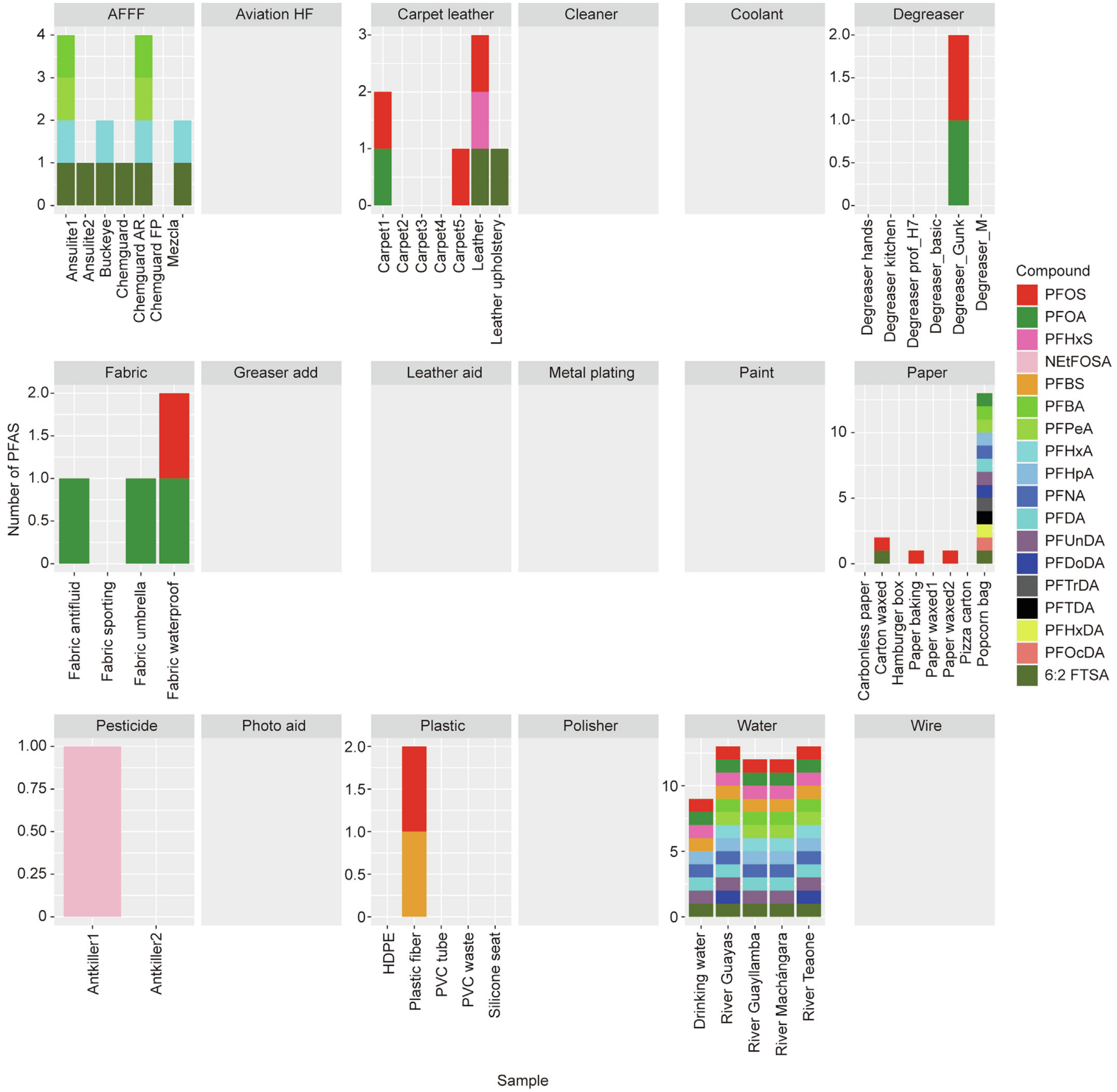

Fig. 2. Stacked bars showing the detection frequency of PFAS in the various classes of samples. Empty boxes indicate that the samples have been analyzed but none of the PFAS could be quantified above the LOQ.

Table 2
Descriptive statistics of the results for three SC PFAS and sulfluramid.

Item	Carpet leather (ng·g^{-1})	Degreaser (ng·g^{-1} or μg·L^{-1})	Fabric (ng·g^{-1})	Paper (ng·g^{-1})	Pesticide (μg·L^{-1})	Plastic (ng·g^{-1})	Water (ng·L^{-1})	Quantified in classes of samples and number of samples
	(N = 7)	(N = 6)	(N = 4)	(N = 8)	(N = 2)	(N = 5)	(N = 5)	
PFOS								
Mean (SD)	0.640 (0.816)	0.188 (0.462)	0.466 (0.932)	0.195 (0.445)	< LOQ	0.404 (0.904)	0.275 (0.213)	6/14
Median (minimum, maximum)	0 (0, 1.79)	0 (0, 1.13)	0 (0, 1.86)	0 (0, 1.29)	< LOQ	0 (0, 2.02)	0.252 (0.0203, 0.608)	
PFOA								
Mean (SD)	0.194 (0.514)	0.279 (0.683)	2.40 (2.55)	5.22 (12.6)	< LOQ	< LOQ	2.37 (2.00)	5/11
Median (min, max)	0 (0, 1.36)	0 (0, 1.67)	1.80 (0, 6.01)	0 (0, 36.1)	< LOQ	< LOQ	1.56 (0.0677, 4.95)	
PFHxS								
Mean (SD)	0.0997 (0.264)	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.116 (0.0690)	2/6
Median (minimum, maximum)	0 (0, 0.698)	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	0.106 (0.0228, 0.192)	
NEtFOSA								
Mean (SD)	NA	< LOQ	NA	NA	75 000 (106 000)	NA	NA	1/1
Median (minimum, maximum)	NA	< LOQ	NA	NA	75 000 (0, 150 000)	NA	NA	
L-PFOS								
Mean (SD)	0.375 (0.507)	0.132 (0.324)	0.274 (0.549)	0.171 (0.380)	< LOQ	0.281 (0.627)	0.191 (0.150)	
Median (minimum, maximum)	0 (0, 1.26)	0 (0, 0.793)	0 (0, 1.10)	0 (0, 1.10)	< LOQ	0 (0, 1.40)	0.163 (0.0103, 0.425)	
br-PFOS								
Mean (SD)	0.265 (0.406)	0.0563 (0.138)	0.192 (0.383)	0.0235 (0.0664)	< LOQ	0.124 (0.277)	0.0844 (0.0635)	
Median (minimum, maximum)	0 (0, 1.04)	0 (0, 0.338)	0 (0, 0.766)	0 (0, 0.188)	< LOQ	0 (0, 0.619)	0.0849 (0.0100, 0.183)	

The quantitative results of the chemical analyses for each sample are provided in Tables S2–S19 in Appendix A. The different units should be noted; these were adjusted to the physical state of the sample and the reference. In general, the units are as follows: ng·L^{-1} for water, μg·L^{-1} for other liquid samples, and ng·g^{-1} for solid samples. For samples that did not undergo an instrumental extraction procedure (i.e., COP_077, COP_089, COP_097, and COP_069), the analysis was done in the μg·g^{-1} range. Since none of the PFAS analytes could be quantified, the values are represented as zero in the following graphics. SD: standard deviation.

it can be seen that the majority of the median values were all zero. The exception was water, which was analyzed at very low trace levels (LOQ = 6.2 pg·L^{-1}, corresponding to ppt levels) and had measurable amounts of the three SC PFAS in all five samples. For PFOS, the remaining median values were all zero; for PFOA, fabrics had a median value of 1.80 μg·kg^{-1}. PFHxS was quantified in only one leather sample, at 0.70 μg·kg^{-1}. An extremely high value of 150 mg·kg^{-1} was found for NEtFOSA in the pesticide sample Antkiller1. The second pesticide sample, Antkiller2, was found to be PFAS-free, and no sulfluramid could be quantified (Fig. 3).

PFOS was quantified to be higher than LOQ in 14 of the 73 samples: namely, four textiles (the Carpets1 and Carpets5, Leather, and Fabric waterproof), one aid (Degreaser_Gunk), one plastic (Plastic fiber), three papers (Carton waxed, Paper waxed, Paper baking), and all five water samples. PFOA was quantified in 11 samples of four types—not including plastic, for which PFOS was higher than LOQ. The highest mean of PFOS was reported in the "carpet leather" group, which included five carpet samples and two leather samples (Table S18 in Appendix A), while the lowest mean was found in the paper carton group, which included eight samples, three of which had concentrations above the LOQ (Table S16 in Appendix A).

The graphical sketch in Fig. 3 shows the sum of the quantified PFAS in each sample as stacked bars, grouped into the eight types of matrices. It can be seen that some types—such as certain textiles (2–6 PFAS quantified), water (9–12 PFAS quantified), and one paper (13 PFAS quantified)—had complex PFAS compositions, whereas the AFFFs were composed of only 1–4 PFAS, and the aid had only two PFAS present. The plastic sample had only PFOS and PFBS present.

The few PFAS that were quantified in the various classes of samples are shown as box whisker plots in Fig. 4. The graphics are dominated by outliers occurring in singular samples, such as 6:2 FTSA in AFFF, PFOA in some paper samples, NEtFOSA in a pesticide, and various PFAS in fabrics and paper.

The greatest number of PFAS was quantified in water (N = 13); however, these were at extremely low levels and the analysis targeted low environmental concentrations, whereas all other sample types were consumer or professional products.

In this study, we were unable to identify a common pattern within the samples from Ecuador. A pattern heatmap is provided in Fig. 5, showing the contribution of each PFAS to the sum of 18 PFAS. In total, there were 25 samples in which at least one PFAS was quantified. In the dendrogram, the distinct location of the sulfluramid pesticide (Antkiller1) can be seen at the lowest line of the heatmap, showing 100% (red color) NEtFOSA content. Similarly, red cells can be assigned to (close to) 100% 6:2 FTSA in AFFF and leather upholstery sample (blue color). PFOS is present at 100% in two samples: Carpet5 and Paper baking. 100% PFOA is evident for Fabric antifluid. Moderate contributions (yellow to orange colors in the heatmap) can be seen for these PFAS in a variety of other sample classes. The remaining PFAS do not make large contributions to the sum of the PFAS we had analyzed (except for one plastic fiber sample that had a 100% contribution from PFBS).

5. Discussion

The analysis of the 74 samples bought in Ecuador and analyzed for up to 29 PFAS showed relatively low detection frequencies for

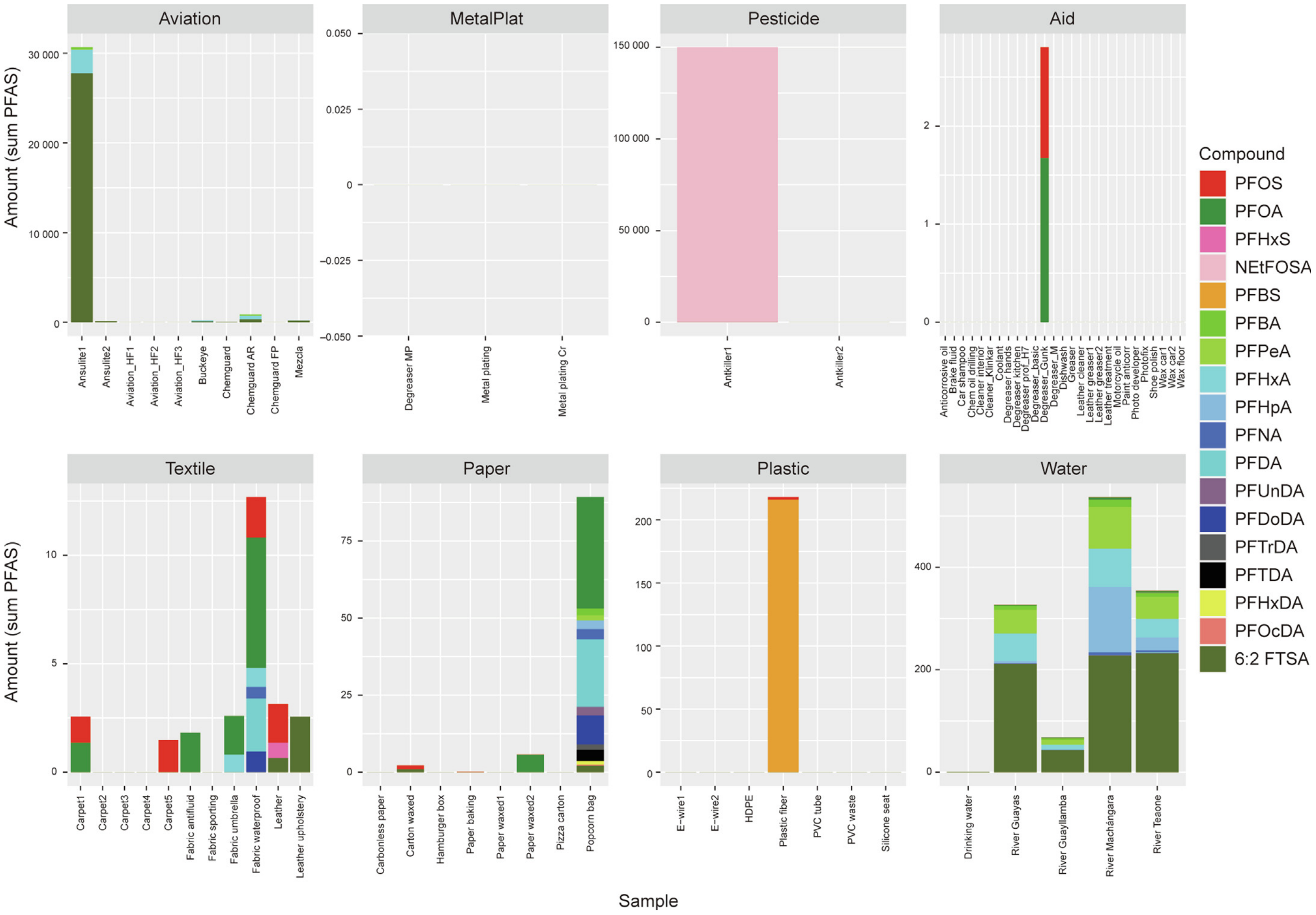

Fig. 3. Stacked bars for all samples analyzed, grouped by type. Units are at the ppb level (ng·g^{-1} or μg·L^{-1}), except for water at ppt level (ng·L^{-1}).

this group of POPs. As expected, a large quantity of NEtFOSA (150 000 μg·L^{-1} or 150 mg·L^{-1}) was quantified in the pesticide sample declared as sulfluramid-containing. In comparison, the pesticide declared to be sulfluramid-free did not contain quantifiable amounts of any PFAS, including NEtFOSA, at an LOQ of 50 μg·L^{-1}. As expected, the fire-fighting foam concentrates contained certain short-chain carboxylic acids and telomers but no sulfonates (PFSA) or longer-chain substances (PFCA).

The five water samples analyzed in this project were collected from four rivers in Ecuador and one drinking water sample. Within the GMP project, eight samples were taken over two years from the Babahoyo River in Guayaquil. These samples had low concentrations: the highest mean value was for PFOS (0.52 ng·L^{-1}; standard deviation (SD): 0.30 ng·L^{-1}), followed by PFOA (0.24 ng·L^{-1}; SD: 0.09 ng·L^{-1}) and PFHxS (0.07 ng·L^{-1}; SD: 0.06 ng·L^{-1}). A summary of the 13 samples analyzed for 11 PFAS is presented in Table S20 in Appendix A. It can be seen that the sum of the 11 PFAS in the four river samples in this study was much higher than those of the previous GMP2 samples. In particular, high values of PFPeA and PFHxA were found—two PFAS that are not under consideration for listing in the Stockholm Convention.

An early study on the presence of PFAS in industrial and consumer products was undertaken in Norway and Sweden by Herzke et al. [36] in 2012. The researchers analyzed samples for 21 PFAS, including fluorotelomer sulfonates and fluorotelomer alcohols (FTOH). They found PFAS in 27 of 30 products, with the highest detection frequency being for FTOH. PFOS were quantified close to the Norwegian limit value: Two pooled leather samples exceeded the regulatory value of 1 g·m^{-2}, and two carpet samples were close to the limit (0.70 μg·m^{-2} and 1.04 μg·m^{-2}).

Dubocq et al. [43] detected the AFFF (including foams) declared to be fluorine-containing and fluorine-free from the European market. In their study, a fluorine mass balance for 24 foams intended for liquid fires was made, and it was confirmed that the foams marketed as fluorine-free did not contain measurable amounts of (17) organofluorine substances at the ppm level. The sum of Σ_{17}PFAS was between 0.4 and 41.2 mg·L^{-1}. PFOS could not be quantified in any of the 24 samples (LOQ < 0.01 mg·L^{-1}, corresponding to 10 μg·L^{-1}); PFOA was quantified in ten samples at concentrations between 0.003 and 0.340 mg·L^{-1}; and PFHxS was quantified in three samples (0.01–0.20 mg·L^{-1}). The most abundant PFAS were 6:2 FTSA, PFBA, PFPeA, PFHxA, PFDA, and PFDoDA, with the maximum concentrations at 25.4, 1.5, 1.1, 10.4, 0.08, and 0.03 mg·L^{-1}, respectively.

An extensive list of PFAS' postulated occurrences was published in 2020 [44]. In the list, the specific functions of individual PFAS—including the ammonium, sodium, lithium, potassium, and silver salts of carboxylic acids and sulfonic acids (as well as tetramethylammonium, tetraethylammonium, triethylammonium, diethanolammonium, tetrabutylphosphonium, and others)—were given, such as making coatings and products to resist water, grease, heat, oil, or stains. PFAS were also found in applications such as mist suppressant in hard chromium plating, photographic materials, the etching and polishing of glass, antistatic in rubber, constituents of AFFF, and flame retardants. It must be stressed that it is analytically impossible to reconstitute a PFAS salt, since the cation and anion are dissociated through the extraction steps. In all chemical analyses using HPLC or

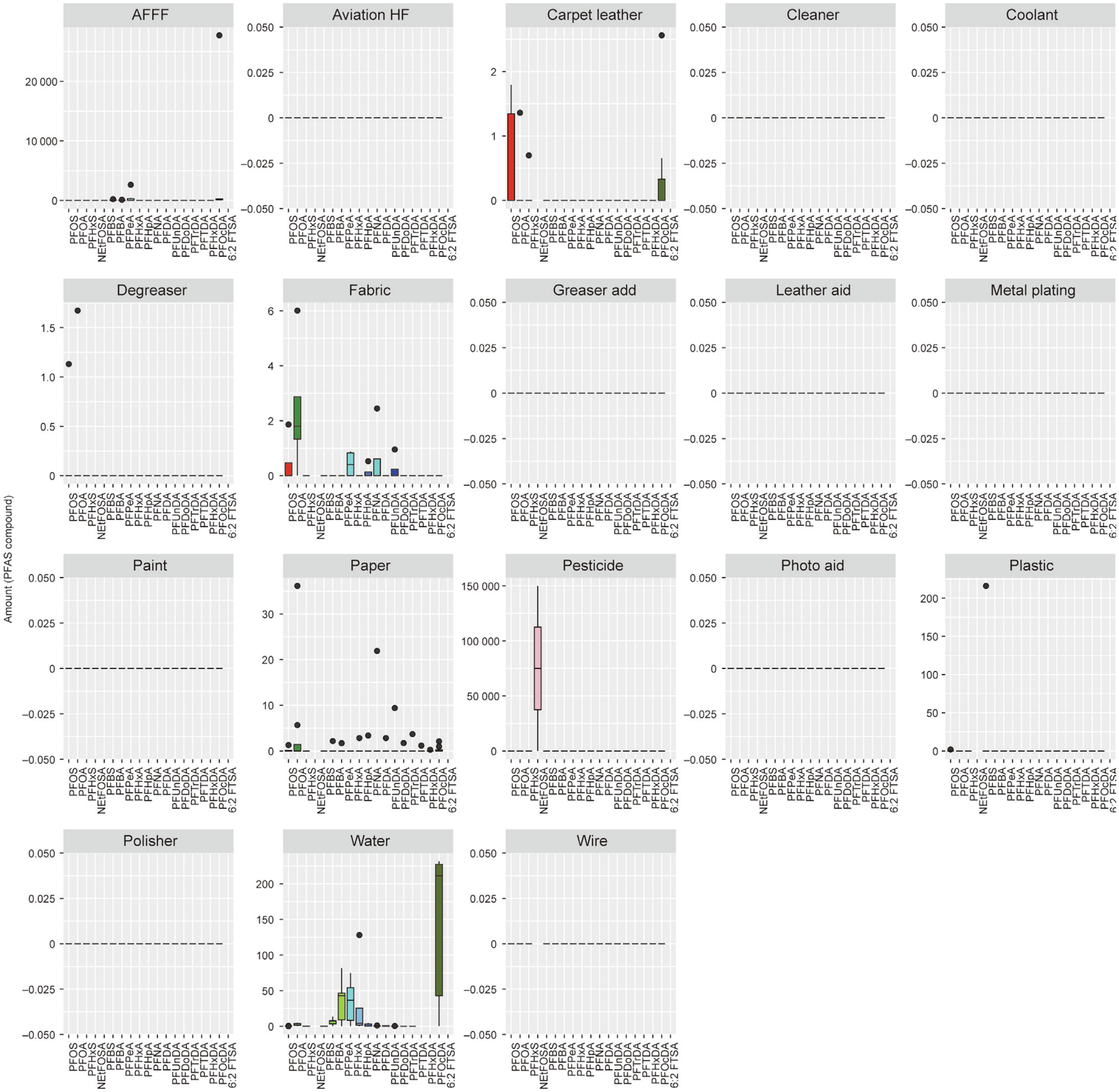

Fig. 4. Box whisker plots for all samples analyzed, grouped by class. Units are at the ppb level (ng·g^{-1} or μg·L^{-1}), except for water (ng·L^{-1}).

UPLC coupled with mass spectrometers, only the anion is determined. Therefore, it is not possible to confirm which PFAS salt was used nor which was present via analyzing the product or environmental samples.

For the SC PFAS, we analytically determined (via tandem mass spectrometry, MS/MS) the compounds with the mass-to-charge ratio (m/z) of the mother ion as follows: m/z 499 for the PFOS anion $C_8F_{17}SO_3^-$ and m/z 299 for the PFHxS anion C_6F_{13}-SO_3^-. Some PFAS that might be perceived as PFOS-, PFOA- or PFHxS-related compounds do not contain the characteristic group shown above. It must also be noted that the PFCA and PFSA with the same number in the name do not have identical structural formulas; for example, perfluorohexanoic acid (PFHxA) has the structural unit $(C_5F_{11})C$, whereas perfluorohexane sulfonic acid (PFHxS) has the structural unit C_6F_{13}. For all these chemicals, the perfluorinated carbon backbone of the molecule is shorter by one CF_2 unit in the PFCA. Examples of PFAS not covered by the definition and our analysis include the chemicals shown in Table 3.

Table 4 provides a comparison of the three SC PFAS (i.e., PFOS, PFOA, and PFHxS) found in this study and Ref. [44]. The functions of the PFAS were listed according to Ref. [44]. The categories of “cleaner,” “coolant,” “degreaser,” “plastic,” “wire,” and “water” were not detected in this study, we only quantified PFAS in degreasers and water PFAS.

Glüge et al. [44] also listed the following functions of PFOS, PFOA, or PFHxS or their presence in processes or applications, which were not addressed by the present study:

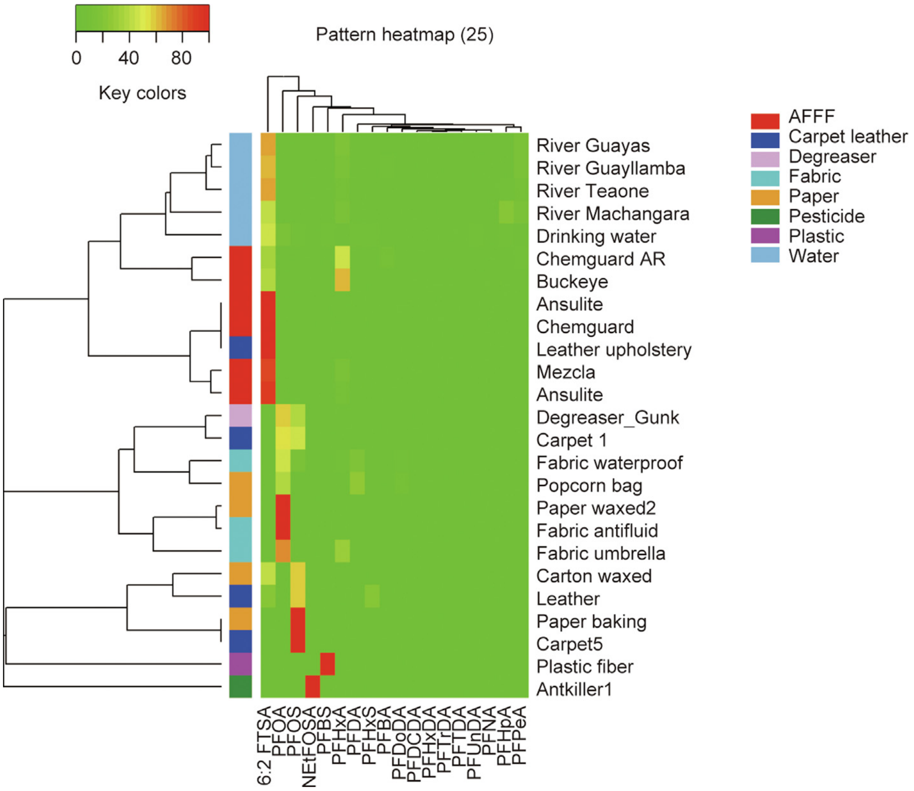

Fig. 5. Heatmap with dendrogram for the pattern of PFAS (*N* = 25).

Table 3
Examples of PFAS that do not contain the characteristic moieties of the SC PFAS.

Chemical name (acid or salt)	Perceived PFAS	Structural formula	Rationale
Perfluorooctane sulfinic acid	PFOS	$C_8F_{17}SO_2H$	1 O missing
Perfluorooctyl phosphonic acid	PFOS	$C_8F_{17}P(=O)(OH)_2$	1 S and 1 O missing
Perfluorohexane sulfinic acid	PFHxS	$C_6F_{13}SO_2H$	1 O missing
Perfluorohexyl phosphonic acid	PFHxS	$C_6F_{13}P(=O)(OH)_2$	1 S and 1 O missing
Potassium perfluorohexanoic acid	PFHxS	$C_5F_{11}COOH$	2 F missing; C in the functional group, not in backbone

PFOS	Used in the etching process of piezoelectric ceramic filters; etching and polishing of glass; etching and polishing of glass; processing aids, specific to petroleum production in plastic material and resin manufacturing Antistatic composition; fat- and water-repellent chamois leather; fluxing agent for plumbing with leaded soldering tin; mold release agent; ore floating; heavy crude oil well polymer blocking remover Detected in circuit boards, detected in intermediate transfer belts of colour copiers and printers; detected in wooden boards; coatings; manufacture of radio, television, and communication equipment
PFOA	Detected in impregnation sprays; renders the surfaces of oil-bearing reservoirs oleophobic; emulsify chlorocarbons; etching of glass; etchant composition for semiconductor devices Used on a mold for processing optical films for liquid crystal displays, mining ore flotation
PFHxS	Photoresist; oil repellent, coating on glass, antistatic rubber Mining (ore flotation)

In a study undertaken for the North America Commission for Environmental Cooperation (CEC), Munoz et al. [30] quantified 30 of the 31 targeted PFAS analytes in at least one sample, with widely different detection frequencies for individual PFAS (range: 0–45%). Long-chain and short-chain PFCAs represented a variable proportion of the sum of targeted PFAS (Σ_{31}PFAS), which ranged from less than the method less than LOD to a maximum of 780 $ng \cdot g^{-1}$, although the median Σ_{31}PFAS was 0.50 $ng \cdot g^{-1}$. PFOS was detected in 16% of the samples at typically low concentrations (< 1 $ng \cdot g^{-1}$ or < 1 $\mu g \cdot m^{-2}$) compliant with the EU Textile Restricted Substance List limit for PFAS residues. In addition, PFOS represented only a minor percentage of the composition profile in most of the contaminated items, while short-chain PFCAs and PFBS were more prevalent. Regardless of the country of purchase or country of manufacture, it was found that the items with the highest PFAS concentrations generally corresponded to materials with specific coatings or membranes. The North American study conducted in 2017 with samples bought in Canada, Mexico, and the United States reported a higher number of PFAS in samples compared to our survey findings. The variation in results could stem from differences in sample origins (e.g., production sources), the timing of sampling, or potentially higher sensitivity in the Canadian study, as indicated by their lower reported LOQs being ten fold lower than those in our study.

Table 4
Comparison of the results from this study for the PFAS analyzed and their postulated uses/presence as determined by Ref. [44] in according to different sample classes.

Application	Ref. [44]	This study
AFFF	PFOS, PFOA, PFHxS PFOA in fluoroprotein	PFOS, PFOA, and PFHxS not detected In addition, 4 PFAS quantified: PFBA, PFPeA, PFHxS, and 6:2 FTSA
Additive in aviation fuel, brake and hydraulic fluids	PFOS	PFOS, PFOA, and PFHxS not detected No other PFAS quantified
Leather, carpets, and their manufacture	PFOS, PFOS, PFHxS	PFOS, PFOA, and PFHxS quantified in addition, 6:2 FTSA quantified
Cleaners	PFOS in cleaning articles after electrolytic or chemical surface treatment	PFOS, PFOA, and PFHxS not detected No other PFAS quantified
Fabric	PFOS, PFOA, PFHxS in membranes for apparel, treated apparel, and esp. sportswear (PFOS), waterproof textiles, or firemen's/pilots'/medical staff textiles (PFOA)	PFOS and PFOA quantified No other PFAS quantified
Metal plating	PFOS and PFOA	PFOS, PFOA, and PFHxS not detected No other PFAS quantified
Paints, prints	PFOS, PFHxS (photoprints and laser prints) PFOA in paints and prints	PFOS, PFOA, and PFHxS not detected No other PFAS quantified
Paper	PFOS in popcorn, cast-coated paper PFOA in sandwich paper, food-packaging materials	PFOS and PFOA detected In addition, 12 PFAS quantified: PFBA, PFPeA, PFNA, PFDA, PFUnDA, PFDoDA, PFTrDA, PFTDA, PFHxDA, PFOcDA, and 6:2 FTSA
Pesticide	Li^{+}PFOS salt and PFOS precursor PFOA in pesticide solutions	PFOS, PFOA, and PFHxS not detected NEtFOSA quantified in sulfluramid pesticide
Photo aid	PFOS, PFOA, PFHxS antistatic, protective for layers	PFOS, PFOA, and PFHxS not detected No other PFAS quantified
Polisher	PFOA in floor polisher PFOS in floor polish	PFOS, PFOA, and PFHxS not detected No other PFAS quantified

6. Conclusions

The PFOS, PFOA, and PFHxS content in chemicals and products (which we found at ng·g^{-1} levels, corresponding to μg·kg^{-1} for paper/packaging and μg·L^{-1} for liquids) can be compared with the definition of low POP content, as adopted by the 16th meeting of the Basel Convention in May 2023 and found in the general technical guidelines of the Basel Convention on POPs waste [45], the "PFOS, PFOA, PFHxS technical guidelines" [46], and the "technical guidelines on pesticides" (for sulfluramid) [47], as shown in Table 2 of Ref. [45]. It must be noted that the Basel Conference of the Parties was unable to agree on low POP content values for all substances, and the numbers in square brackets represent alternatives under discussion. Agreed-upon values without alternatives were only obtained for PFHxS, its salts, and PFHxS-related compounds. The previously adopted value of 50 mg·kg^{-1} will be discussed in the future for PFOS, its salts, and PFOSF. The provisional definitions of the low POP content for the three listed PFAS [45,46] are as follows:

(1) PFOS, its salts, and PFOSF is [5 mg·kg^{-1} or] 50 mg·kg^{-1}.
(2) PFOA, its salts, and PFOA-related compounds is [50 mg·kg^{-1}]. For PFOA and its salts: [1 mg·kg^{-1}] [0.025 mg·kg^{-1}]; and for PFOA-related compounds: [40 mg·kg^{-1}] [10 mg·kg^{-1}].
(3) PFHxS and its salts is 1 mg·kg^{-1} and for PFHxS-related compounds is 40 mg·kg^{-1}.

Based on the definitions given above, the implications for waste management are as follows: Wastes with a content of PFOS, its salts, or PFOSF; a content of PFOA, its salts, or PFOA-related compounds; or a content of PFHxS, its salts, or PFHxS-related compounds at or above the above-listed values must be disposed of in such a way that the POP content is destroyed or irreversibly transformed, in accordance with the methods described in the technical guidelines (Ref. [45], subsection IV.G.2). PFAS wastes with contents of the three PFAS below the values given above should be disposed of in accordance with the methods referred to in the Basel Technical Guidelines (Ref. [45], subsection IV.G.4).

The samples, which were collected in Ecuador in 2021, must be considered as a preliminary orientation; however, we consider them sufficient for drawing initial conclusions. Our measured values and the majority of the values found in the literature for these types of samples were much lower than the low POP content for these matrices once they become waste and are subjected to final disposal. In this regard, many waste streams that are supposed to be contaminated with PFAS would not exceed the low POP content and would not require the application of any of the recommended destruction technologies. The low POP content values currently being discussed under the Basel Convention are 100–1000 times higher than our limit of quantification; therefore, in general, these values can be controlled by qualified laboratories using validated methods. We suggest that recommended analytical methods be provided or the harmonization of sampling characteristics, along with requirements for the instrumentation used in the chemical analysis and reporting of results.

It is important to mention that most of the analyzed products were new products, except for some samples that corresponded to certain industrial wastes, and five water samples. For this reason, they could not meet the definition of low POP content, as defined in the recently approved technical guidelines of the Basel Convention on POP wastes, which establish a threshold of 50 mg·kg^{-1} for PFOS and PFOA, their salts, and their related compounds. However, the obtained results indicate that products entering and being marketed in Ecuador, such as microwave bags and food wrapping papers, may possess certain amounts of PFAS and may contribute to human exposure to PFAS.

The results in this study and in the publication by Herzke et al. [36] indicate a reduction in the content of the POP PFAS in recently manufactured products and thus reveal achievements in reducing and eliminating POPs through Stockholm Convention measures. The implementation of the Stockholm Convention provisions and the newly listed substances that will be regulated in coming years require the international community to coordinate its efforts—in particular, countries with advanced industry should increase their efforts to declare the chemical components contained in their products. The samples obtained in Ecuador and their results indicate the difficulty of tracing products with POPs, considering the myriad of manufactured goods that enter a country year after year. Therefore, basic indications of the chemical identity and content of fluorinated compounds could help to improve waste management approaches and to establish environmental surveillance actions, such as the monitoring of POPs in river water near sanitary landfills.

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Compliance with ethics guidelines

Heidelore Fiedler, Luis Vega-Bustillos, Jenny Arias-Pastrano, Lander Vinicio Pérez-Aldás, and Jose Castro-Díaz declare that they have no conflict of interest or financial conflicts to disclose.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eng.2024.01.013.

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