MICHIGAN DEPARTMENT OF
ENVIRONMENT, GREAT LAKES, AND ENERGY

STUDY RESULTS:

Targeted and Nontargeted Analysis of PFAS in Fume Suppressant Products at Chrome Plating Facilities

June 2020

EGLE, WATER RESOURCES DIVISION
800-662-9278 | Michigan.gov/EGLE

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MICHIGAN DEPARTMENT OF
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INTRODUCTION

Beginning in 2017 the Michigan Department of Environment, Great Lakes, and Energy (EGLE) found unexpectedly high levels of perfluorooctane sulfonic acid (PFOS) in chrome plating wastewater (i.e., effluent), which is generally routed to wastewater treatment plants (WWTP) for treatment along with municipal sanitary wastewater before discharge to lakes and streams. In 2018 EGLE asked the U.S. Environmental Protection Agency's (USEPA) Office of Research and Development (ORD) to conduct a study to answer the question of whether the "PFOS-free" fume suppressants (also called mist suppressants or surfactants) are really PFOS-free and/or if PFOS concentrations were being generated within the harsh environment of the plating process from the breakdown of long-chain precursors in the replacement products.

EGLE and the USEPA conducted the study to assist in compliance efforts undertaken by the chrome plating industry in Michigan, where many platers have had to invest significant resources to install pretreatment systems to remove PFOS from their process wastewater even though they complied with federal requirements to discontinue use of the PFOS-based fume suppressants years prior. Samples of 9 different fume suppressants and effluent from 11 platers were collected in July 2019. Final reports of the analysis were received from the USEPA late February 2020.

BACKGROUND AND PURPOSE

Fume suppressants are commonly used by electroplating facilities for controlling air emissions and reducing worker exposure to hexavalent chromium, a known human carcinogen and inhalation hazard. The USEPA required chrome platers to stop using PFOS-containing fume suppressants in chrome plating tanks in September 2015 due to concerns about human health and environmental impacts.

Through a statewide initiative, EGLE's Water Resources Division found that some electroplaters who stopped using PFOS-containing fume suppressants years ago were still discharging PFOS to sanitary sewers in concentrations that resulted in municipal WWTPs exceeding state water quality standards. These exceedances continued even after extensive cleaning and disposal efforts.

Concurrently, EGLE's Air Quality Division conducted inspections at several chrome platers in Michigan and found that PFOS-based fume suppressants were no longer in use at these facilities and they had switched to "PFOS-free" replacement products. Federal regulations define "PFOS-free" fume suppressants as containing less than one percent PFOS by weight. EGLE was concerned that PFOS may still be present in the replacement products at levels that met the federal definition but would still exceed the very low screening concentrations, which are measured in ppt.

In addition, many of these PFOS-free replacement products are still based on PFAS compounds, and EGLE questioned whether potential long-chain precursors in the replacement products could be converting to PFOS within the harsh environment of the plating process. To answer these questions, EGLE asked the USEPA's ORD to conduct a study to investigate whether the "PFOS-free" fume suppressants are really PFOS-free and/or if PFOS is being generated within the harsh environment of the plating process from the breakdown of long-chain precursors in the replacement products.

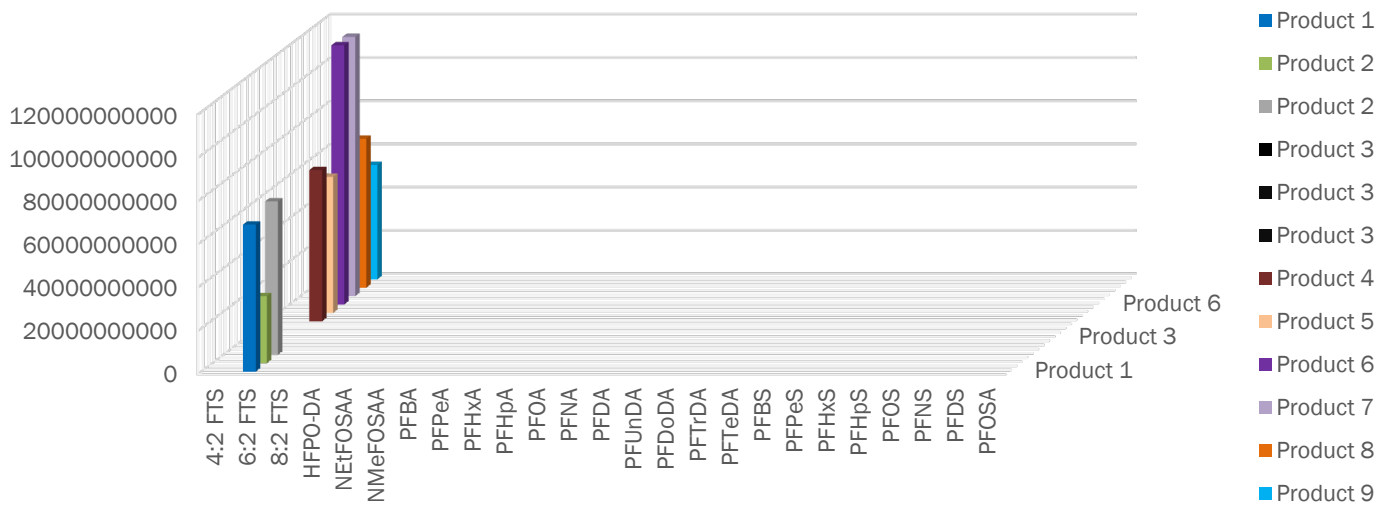
EGLE and the USEPA conducted this study to assist in compliance efforts undertaken by the chrome plating industry. A number of platers in Michigan have had to invest significant resources to install pretreatment systems to remove PFOS from their process wastewater, conduct cleaning, and replace equipment. For the study, EGLE worked with 11 chrome platers across the state to sample fume suppressant products and process wastewater (after pretreatment for metals and pH but prior to any pretreatment for PFOS and before discharge to the municipal sanitary sewer). These chrome platers agreed to participate in the study on a voluntary basis to provide valuable information to the plating industry. The USEPA provided its analytical expertise to identify and quantify PFAS, both legacy and novel, in fume suppressants and effluent.

FINDINGS

FUME SUPPRESSANT SAMPLING

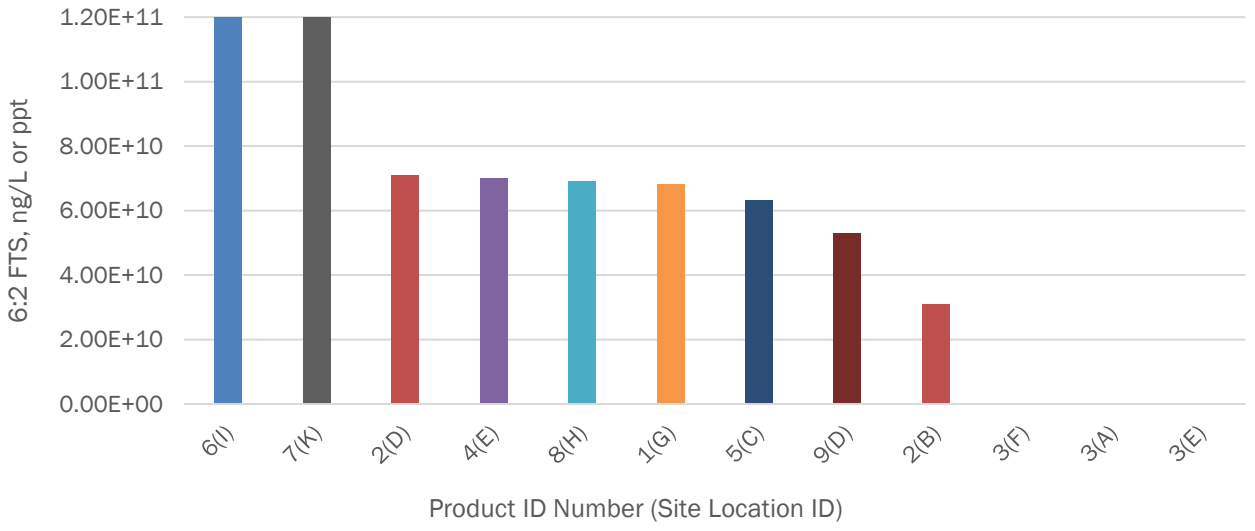
None of the currently used fume suppressants were found to contain detectable amounts of PFOS. In addition, none of these replacement products were found to contain PFOS precursors, which are specific longer-chain per- and polyfluoroalkyl substances (PFAS) that could break down into PFOS. In the targeted analysis, only one PFAS compound, 6:2 fluorotelomer sulfonates (FTS), was found in the currently used fume suppressants (Figure 1). Current discharges of PFOS are, therefore, assumed to be associated with historical use of PFOS-containing products.

Figure 1. PFAS in Fume Suppressants, ng/L or ppt



Of the nine different products sampled, eight contained 6:2 FTS as the primary PFAS chemical used to replace PFOS when analyzed using targeted analysis. There are no federal or state restrictions on the use of 6:2 FTS in replacement products; 6:2 FTS is not a precursor for PFOS. Fume suppressant concentrations of 6:2 FTS are shown in Figure 2.

Figure 2: 6:2 FTS Concentration in Fume Suppressants

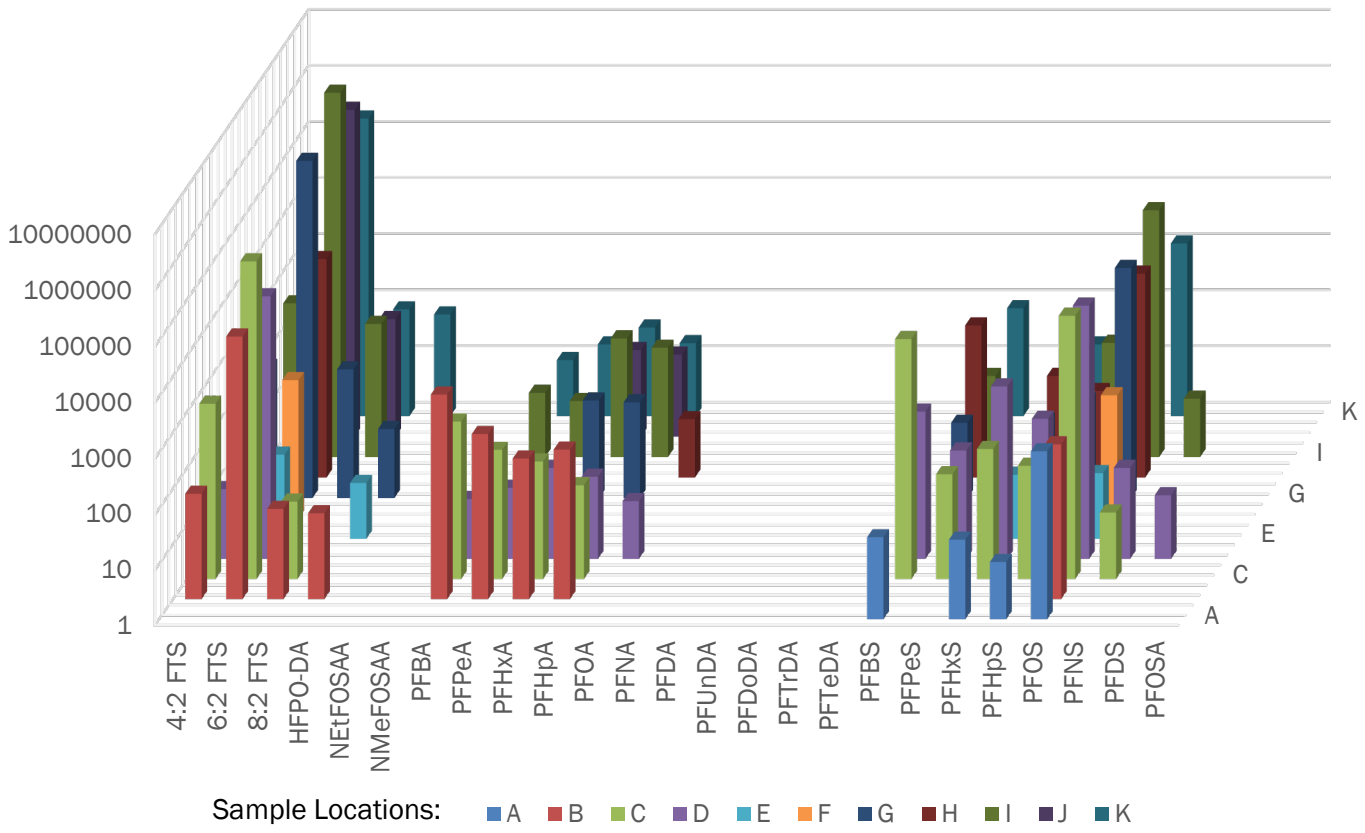


Nontargeted analysis also showed one other PFAS compound, 6:4 FTS, for those same eight products but in much lower abundance. This analyte is not listed in Figure 2 since it was not one of the analytes targeted for analysis. One product contained no PFAS compounds and instead used a different type of chemistry.

EFFLUENT SAMPLING

PFOS found in effluent samples, which were collected prior to any pretreatment for PFOS, ranged from 15 parts per trillion (ppt) to 51,700 ppt (see Figure 3; note: log scale). Since fume suppressant analysis found no PFOS or long-chain precursors in currently used fume suppressants, it can be concluded that the PFOS detected in the effluent from these facilities is from historical use of PFOS-based fume suppressants prior to the ban in September 2015. As you can see in Figure 3, PFAS found in the effluent was much more complex than in the products (Figure 1). Effluent contained significant concentrations of 6:2 FTS, PFOS, and other PFAS compounds. Effluent results are shown by sample location in Attachment 1.

Figure 3: PFAS in Effluent Prior to Treatment, ppt or ng/L



More than half of the platers had pretreatment for PFOS installed at the time of the study. To obtain appropriate data for the study, effluent samples were collected before any pretreatment at the plating facilities and prior to mixing with other wastewaters to maximize the amount of PFAS captured and researchers' ability to trace PFAS to its source. PFAS levels in these effluent samples were therefore much greater than the concentrations that were discharged into WWTPs and subsequently into surface waters and are not reflective of concentrations to which people would be exposed. See Attachment 1 for effluent results by sample location.

The Industrial Pretreatment Program PFAS Initiative requires WWTPs to implement controls to reduce PFOS sources to their system. Beginning in October 2021 National Pollutant Discharge Elimination System (NPDES) permits for WWTPs with the potential to exceed water quality standards will include limits for PFOS and perfluorooctanoic acid (PFOA). Until that time, NPDES permits will include monitoring and pollutant reduction requirements.

There is more to be gleaned from this report and scientists will continue to review the results.

NOTES ON DETAILED ANALYTICAL RESULTS

Detailed analytical results are included as Attachment 2, *Laboratory Data Report #1: Targeted Analysis of PFAS in Fume Suppressant Products and Effluent Samples* (USEPA, ORD, Report #1), and Attachment 3, *Laboratory Data Report #2: Nontargeted Analysis of PFAS in Fume Suppressant Products and Effluent Samples* (USEPA, ORD, Report #2). The USEPA's ORD analyzed the samples using targeted and nontargeted analysis. The targeted analysis is the type typically done by commercial laboratories and reports exact quantities of specific "targeted" chemicals. Nontargeted analysis is more qualitative but can detect unanticipated chemicals and show relative abundance of various compounds. By its nature, nontargeted analysis is more variable and uncertain, but allows a broad-brush view of the composition of the products and effluents.

When reading the laboratory data reports, please keep the following items in mind:

USEPA, ORD, Report #1: Targeted Analysis

- Twenty-five PFAS chemicals were identified for targeted analysis (see USEPA, ORD, Report #1, Table 2), including the list of 24 analytes published by the Michigan PFAS Action Response Team (MPART) in July 2019 and a Gen X compound.
- With targeted analysis, researchers first select chemicals to look for and conduct tests using an authentic chemical standard obtained from commercial sources or from chemical standards developed by the USEPA through ongoing research.
- Since most fume suppressants contained high concentrations of 6:2 FTS, samples had to be diluted to avoid contaminating analytical equipment. Dilution factors ranged from 500 to 10,000 times (see USEPA, ORD, Report #1, Table 3), the quantification level for analytes not detected is less than 1,000 nanograms per liter (ng/L). Given the amount of product used is highly diluted, however, we can still draw the conclusion that PFOS present in effluent is not attributable to current fume suppressant use. See Attachment 4 for example calculations.

USEPA, ORD, Report #2: Nontargeted Analysis

- Seven additional PFAS compounds (which were not one of the 25 targeted analytes) were tentatively identified in the effluent samples.
- One additional PFAS analyte, 6:4 FTS, was identified in the eight products that contained 6:2 FTS, but in a much lower abundance.
- Nontargeted analysis can detect a broad range of PFAS without having a preconceived list of chemicals that are present. The chemicals are identified by a combination of high-resolution accurate mass, molecular fragmentation, and comparison to reference compound databases. Identifications of chemical compounds are tentative and there is greater uncertainty associated with concentration estimates due to the lack of authentic chemical standards for comparison. PFAS compounds that are shown as abundant are more certain. Table 2 discusses the relative confidence the scientists have with the data and the basis for the identification.

- Nontargeted analysis is useful when considering targeted methods are geared toward a relatively small number of the PFAS, representing a small fraction of chemicals that make up this class of chemicals.
- Note that all data in the USEPA, ORD, Report #2 is reported in "peak area counts" and not concentrations. These counts are a record of the number of molecules detected and show relative abundance rather than specific amounts.
- The colors in Table 4 highlight relative abundance, with red cells being the most abundant and green cells showing the absence or likely absence of a PFAS compound.

EGLE will reach out to metal finishers in Michigan, as well as state and national stakeholder groups, to provide detailed results of the study and answer any questions. Results will be available through the MPART Web site, Michigan.gov/PFASResponse.

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ATTACHMENT 1: Effluent Results (Simplified) by Sample Location

Data are arranged from greatest total PFAS concentration to least.

Location Sample ID	Total (ppt)	6:2 FTS (ppt)	PFOS (ppt)	23 Other PFAS Analytes (ppt)
I	3,166,509	3,140,000	25,300	1,209
G	1,043,339	1,030,000	12,700	639
J	672,399	672,000	**ND**	399
C	556,393	482,000	51,700	22,693
K	204,615	203,000	1,200	415
D	85,455	49,500	33,700	2,255
B	58,239	51,000	610	6,629
H	12,837	7,880	4,330	627
A	1,130	**ND**	1,060	70
F	452	294	158	**ND**
E	71	32	15	24

In the following charts, 6:2 FTS is shown in green, PFOS is shown in blue, and the other 23 analytes, if detected, are combined and shown in yellow.

Location Sample ID	Total (ppt)	6:2 FTS (ppt)	PFOS (ppt)	23 Other PFAS Analytes (ppt)
I	3,166,509	3,140,000	25,300	1,209
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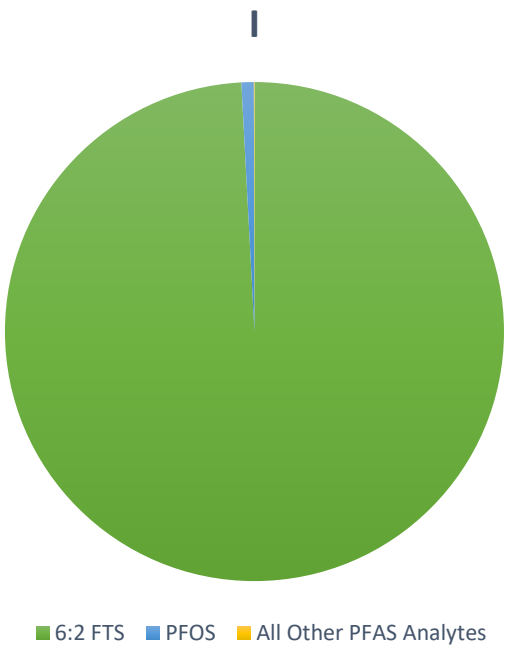

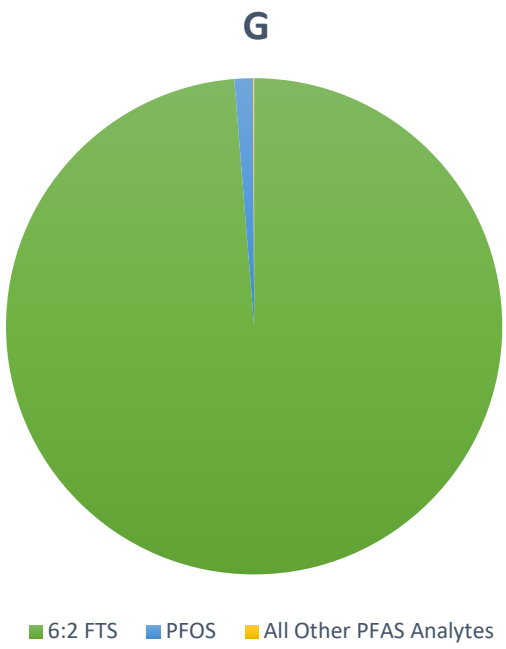

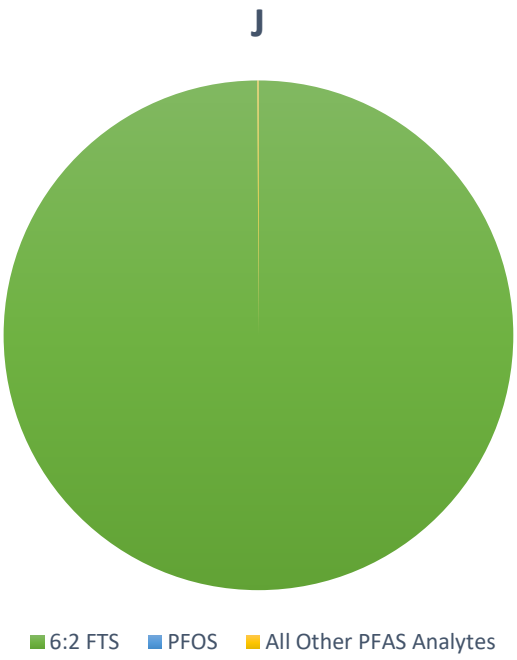

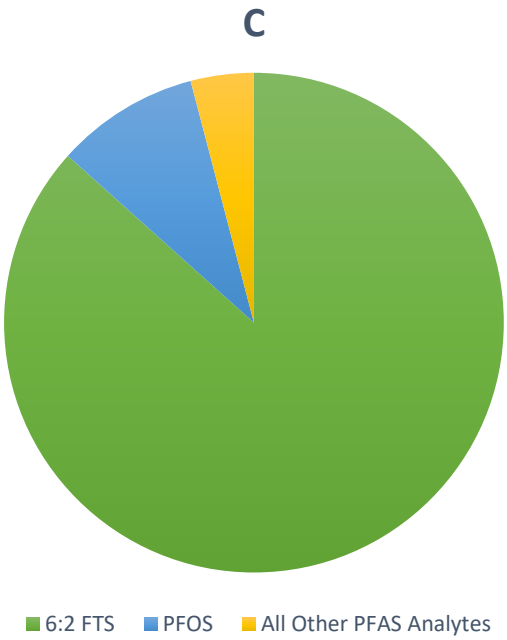

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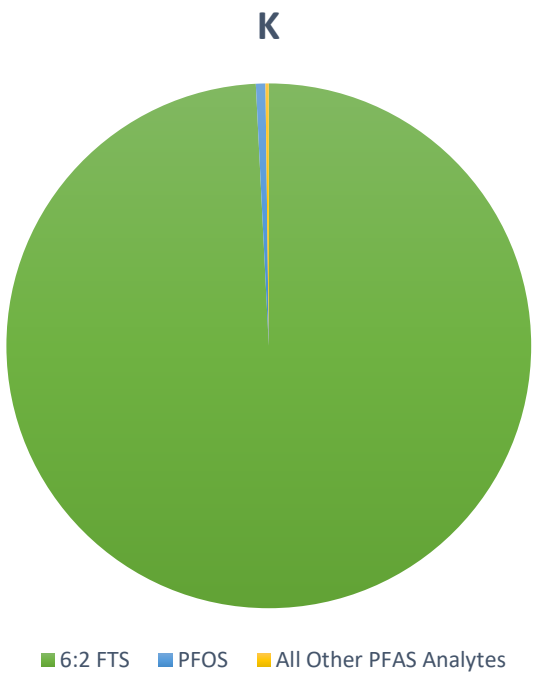

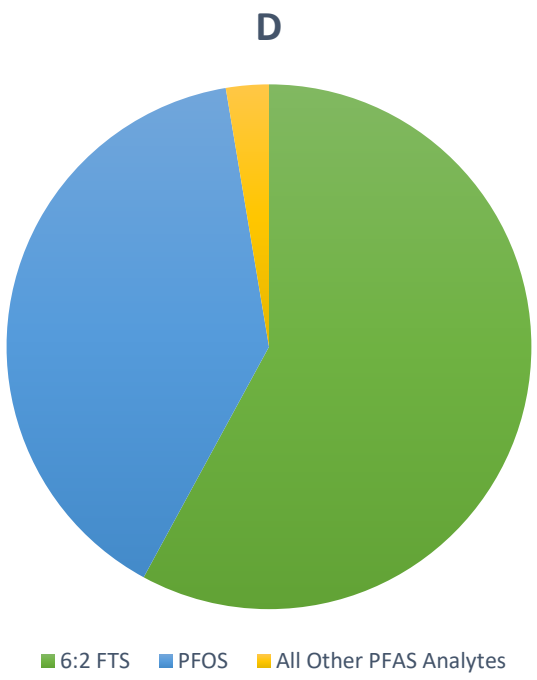

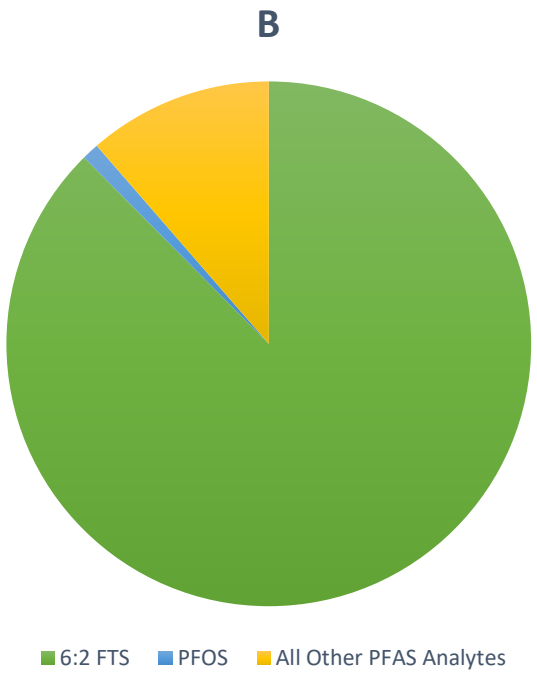

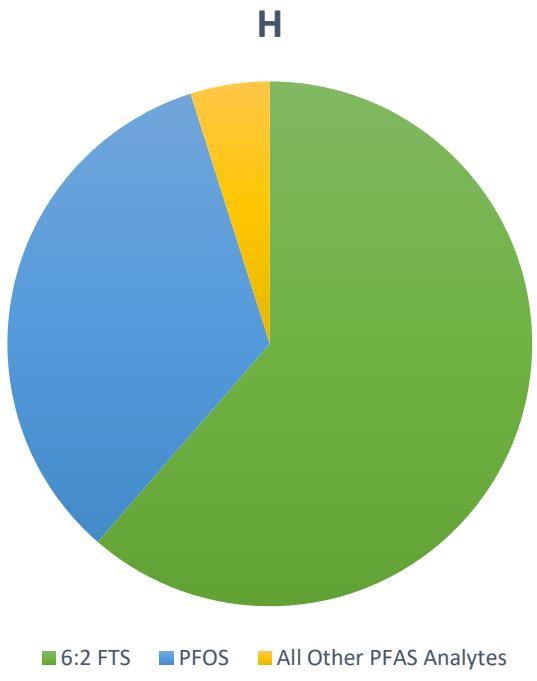

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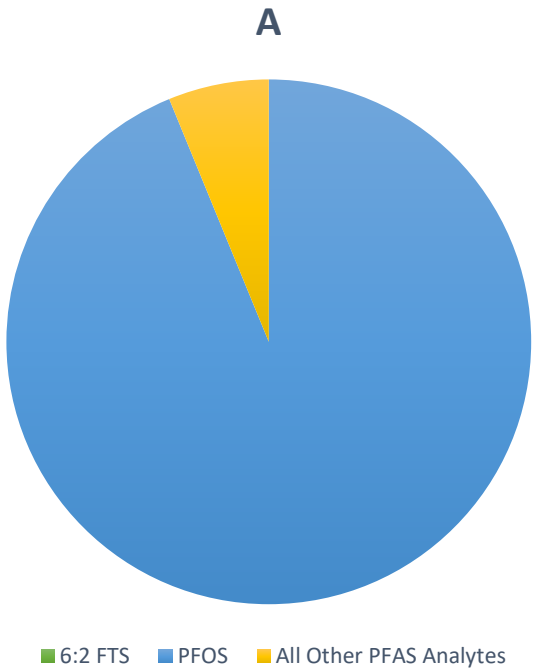

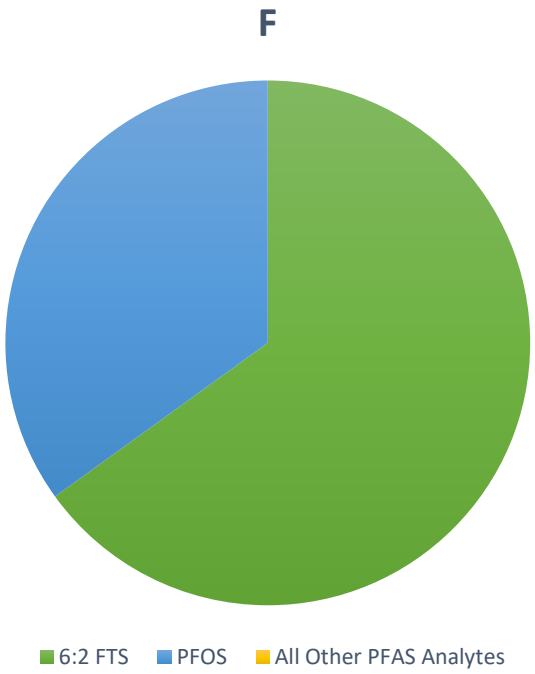

ATTACHMENT 2: USEPA Laboratory Report #1

Targeted Analysis of PFAS in Fume Suppressant Products and Effluent Samples

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CENTER FOR ENVIRONMENTAL MEASUREMENT AND MODELING
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
RESEARCH AND DEVELOPMENT

February 19, 2020

Kurt A. Thiede
Regional Administrator
U.S. EPA Region 5
77 W Jackson Blvd
Chicago, IL 60604

Dear Kurt:

I am pleased to provide the enclosed first report from our ongoing collaborative technical support to EPA Region 5 and the Michigan Department of Environment, Great Lakes and Energy (EGLE) assisting with concerns about environmental contamination associated with use of fume suppressants containing per- and polyfluoroalkyl substances (PFAS) at chrome plating facilities. This report is in response to a March 2018 request from the EPA Region 5 Deputy Regional Administrator asking for laboratory assistance analyzing PFAS in use within Michigan. The enclosed Report #1 provides targeted analysis laboratory results that quantify various PFAS found in fume suppressant products and facility pre-treatment effluent samples at multiple chrome plating facilities.

It is our understanding that this information was requested to help in ongoing investigations into the presence of PFAS in the environment near chrome plating facilities of interest. This request relates to our research capabilities and interests applying targeted and non-targeted analysis methods for discovery of the nature and extent of PFAS environmental occurrence that may be potentially associated with industrial releases. EPA continues to develop analytical methods for many PFAS compounds in various media including some of those included in this report. We are providing the results of our analysis as they become available.

In this report, we provide PFAS identification and quantitative analytical results for 25 PFAS in 13 fume suppressant product samples and 12 pre-treatment effluent samples. We do not interpret exposure or risk from these values. EPA does not currently have final health-based standards, toxicity factors, or associated risk levels for PFAS, other than perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorobutanesulfonic acid (PFBS). While the data provided in the attached report indicate the presence (or lack) of PFAS in the samples, we do not have sufficient information to offer interpretations related to human or environmental exposure and risk.

Thank you for inviting us to be part of this effort that helps to further both EPA's and Michigan's understanding of an important issue in the state. This is just one of many Agency efforts that demonstrates EPA's commitment to cooperative federalism.

If you have any questions or concerns, do not hesitate to contact me at (919) 541-2107 or via email at watkins.tim@epa.gov or Brian Schumacher at (702) 798-2242 or via email at schumacher.brian@epa.gov. I look forward to our continued work together.

Sincerely,

Timothy H Watkins

Timothy H. Watkins
Director

Enclosure

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PFAS Associated with Chrome Plating Facilities in Michigan

Laboratory Data Report #1: Targeted Analysis of PFAS in Fume Suppressant Products and Effluent Samples

Background. The Michigan Department of Environment, Great Lakes, and Energy (EGLE), in coordination with EPA Region 5, requested the Office of Research and Development's (ORD's) technical support in analyzing per- and polyfluoroalkyl substances (PFAS) in products used as fume suppressants and that may potentially be found in effluent from chrome plating facilities. EGLE assumed responsibility for the collection of the fume suppressant products and effluent samples from chrome plating facilities in Michigan and their shipment to the ORD laboratory[1]. ORD was responsible for sample extraction and analysis. ORD's analysis and report team members that contributed to this effort are listed in Table 1.

Table 1. EPA Office of Research and Development Lab Analysis and Report Team.

Responsibility	Personnel
ORD Principal Investigators	James McCord, Mark Strynar
Laboratory chemistry	James McCord
Quality Assurance Review	Margie Vazquez, Sania Tong-Argao
Management coordination and review	Myriam Medina-Vera, Brian Schumacher, Tim Buckley, Kate Sullivan
Report preparation	Kate Sullivan

This 1st report includes targeted analysis results for 25 samples collected from fume suppressant products and effluents at 11 chrome plating facilities in Michigan. Effluent at all the sampled facilities is combined with other wastewater streams and sent for treatment at municipal wastewater treatment plants. More than half of the sampled facilities also have onsite PFAS pretreatment systems. For purposes of the study, all effluent samples were collected prior to any treatment.

EGLE collected samples on July 22 and 23, 2019 in containers provided by ORD. We also report results for 10 field quality assurance samples including 2 field blanks (FB), 2 trip blanks (TB), 2 equipment blanks (EB), and 4 blanks spiked with known concentrations of analytes. Samples were sent to and analyzed under the direction of Dr. James McCord at ORD's laboratories in Research Triangle Park, N.C., following targeted analysis procedures. Samples were received on July 25, 2019.

The current data report provides a simple representation and summary of targeted analysis results. Therefore, the description of methods and quality assurance are brief and high-level. Additional reports and/or publications may be developed that will include a more detailed

[1] U.S. EPA National Exposure Research Laboratory, Project Study Plan: Identification of PFAS in Fume Suppressants in Chromium Electroplating Facilities, D-IO-0032097-QP-1-0, 12Jul2019.

description of methods, quality assurance procedures and interpretation of data. As study partners/collaborators, we anticipate that EGLE and Region 5 will assist in these reports and publications.

Methods in Brief. Effluent and fume suppressant samples were analyzed by ultra-performance liquid chromatography mass spectrometry (UPLC-MS) using targeted workflow methods described within our laboratory Quality Assurance Project Plan[2] and McCord *et al*. 2019[3]. In brief, water samples (500 mL) were filtered and then extracted using a WAX solid phase extraction cartridge. PFAS was removed from the cartridge in methanol and the volume reduced to 1 mL under a gentle stream of dry nitrogen. An aliquot of the 1 mL concentrated sample was injected into a Waters Acquity ultra performance liquid chromatograph (UPLC) coupled to a Waters Xevo TQ-S micro triple quadrupole mass spectrometer.

ORD analyzed samples for PFAS compounds listed in Table 2. This list is consistent with the PFAS minimum laboratory analyte list provided by EGLE and includes Perfluorooctanoic Acid (PFOA) and Perfluorooctane Sulfonate (PFOS). Table 2 provides the formula, monoisotopic mass, CAS registry number (CASRN) and the CompTox DSSTox substance identifier (DTXSID) for each compound. Additional information about these compounds can be obtained from EPA's Chemistry dashboard (https://comptox.epa.gov/dashboard) (U.S. EPA CompTox, 2019)[4].

PFAS concentrations for 25 PFAS compounds listed in Table 2 were determined with calibration curves derived from authentic standards using a traditional targeted UPLC-MS/MS approach. For each of the analytes, a matched stable isotope labeled internal standard (when available) or a closely eluting labeled standard (when an exact match was not available), was used. There is a wide range in compound concentrations across fume suppressant products and effluent samples that required adaptation during analysis including dilution and calibration with internal or external standards that varied between samples and analytes. Fume suppressant product samples required significant dilution (500 to 10,000 times) and were quantified with calibration using external standards. The majority of the analytes in the effluent samples required no dilution and were quantified with a stable isotope internal standard corrected calibration curve within a range from 10 to 150 ng/L. Concentrations of PFOS and 6:2 FTS were very high in many samples and exceeded the ability to perform stable isotope labeled quantitation. PFOS and 6:2 FTS were reanalyzed after preparation in dilutions ranging from 5 to 500 times and concentrations were determined from external standard calibration curves.

Samples with no identifiable peak are labeled Non-Detect ("ND") in the tables and samples with concentrations less than 10 ng/L (i.e. Limit of Quantitation, LOQ) are flagged "U". Effluent samples that exceed the upper calibration range are flagged "JC1". Table 4 provides the dilution

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[2] National Exposure Research Laboratory Quality Assurance Project Plan: Targeted analyses of Per- and Polyfluoroalkyl Substances (PFAS) in Liquid Samples. J-WECD-0031917-QP-1-0. May 2019.

[3] McCord, J., Strynar, M. Identifying Per- and Polyfluorinated Chemical Species with a Combined Targeted and Non-Targeted-Screening High-Resolution Mass Spectrometry Workflow. *J. Vis. Exp.* (146), e59142, doi:10.3791/59142 (2019). https://www.jove.com/video/59142/identifying-per-polyfluorinated-chemical-species-with-combined

[4] U.S. EPA CompTox Chemicals Dashboard https://comptox.epa.gov/dashboard

factors used to process effluent samples (flagged "Dx"). The calibration range determined for undiluted samples was adjusted by the dilution factor when applying the "U" and "JC1" flags. Results that may not fully account for matrix effects due to loss of signal from the internal standards in highly diluted samples are flagged "JIS1" and are considered estimates.

Fume Suppressant Product Samples. Table 3 provides concentrations of PFAS in the fume suppressant products used at the chrome plating facilities in ng/L. A total of 9 different products were analyzed. Several products are used at multiple facilities and are grouped accordingly in Table 3. Product 6 is used at both facilities I and J but was only sampled at the I facility. Two additional products that are not in current use (products 4 and 9) were also provided by the facilities.

Due to the high concentrations of chemical additives in the fume suppressant products, samples were diluted from 500 -10,000 times as indicated in Table 3 to avoid contaminating the analytical instruments with 6:2 Fluorotelomer sulfonic acid (6:2 FTS) and other, non-fluorinated, components. Due to the large dilution factor, all fume suppressant PFAS concentrations are considered estimates and PFAS compounds which may be present in concentrations < 1,000 ng/L may not have been detected in samples diluted as much as 10,000 times.

The only PFAS compound observed in the fume suppressant products with targeted analysis was 6:2 FTS, which was present in very high concentrations in all products except product 3 where it was not detected.

Pre-treatment Effluent Samples. Table 4 provides concentrations for effluent samples. Concentrations of most of the 25 PFAS compounds were not detected or were below LOQ in most of the effluent samples. However, 6:2 FTS concentrations in effluent samples were significant at facilities where the fume suppressant product also had high concentrations of 6:2 FTS. No 6:2 FTS was found in fume suppressant product 3 and associated effluent concentrations were relatively low or not detected where this product was used (F, A, and E). Although PFOS was not detected in any product samples, PFOS was observed at high concentrations in most of the effluent samples, with the exception of samples E and J. Similarly, other PFAS were identified and quantified in some effluent samples even though they were not found in the fume suppressant products currently in use at the facility. Because effluent samples were collected prior to treatment, PFAS levels in the effluent samples may be much greater than the concentrations that are discharged into surface waters, and sample results should not be considered reflective of levels to which people may be exposed.

Sample QA/QC Summary. Table 5 provides concentrations of PFAS in the trip, field, and equipment blanks and in spiked samples. Trip and field blanks were generally free of PFAS although HFPO-DA and 6:2 FTS were each observed in concentrations >LOQ in one trip blank and one field blank, respectively. Equipment blanks used to obtain an effluent sample at one site (K) had some contamination of 6:2 FTS and PFOS greater than the LOQ. Samples potentially affected by this contamination are flagged as "B2" in Table 4.

Spiked samples were prepared from spiked reagent water at 30 and 100 ng/L in the laboratory and were delivered to the field and mock sampled. These spikes are intended to control for the effects of shipping, such as bottle adhesion and recovery, sample stability, and effects related to the sampling procedure. They do not exhibit matrix effects. Each spiked sample analysis was replicated in the laboratory. Individual analytes exceeding the QC goal of ±20% the known spike

* Facility IDs on this page were anonymized by EGLE.

concentration are flagged as "JR5" in Table 5. Spike recovery was generally biased low, averaging 23% below the known spike concentrations. Spike recoveries tended to decrease as the carbon chain length increased. Thus, actual concentrations may be somewhat higher than reported.

Precision criteria for field duplicates with concentrations exceeding the LOQ, presented as the relative percent difference (RPD), averaged 15% and no sample/analyte comparison exceeded the project goal of <30% RPD. Laboratory precision, indicated by the RPD between the spiked blank laboratory replicates, averaged 12%.

Table 2. PFAS Analyzed in Fume Suppressants and Facility Effluent by UPLC-MS.

Short Name	Chemical Name	Formula	Monoisotopic Mass (g/mol)	CAS Registry Number	DTXSID
4:2 FTS	Fluorotelomer sulphonic acid 4:2	$C_4F_9CH_2\ CH_2SO_3$	327.9816	757124-72-4	DTXSID30891564
6:2 FTS	Fluorotelomer sulphonic acid 6:2	$C_6F_{13}CH_2\ CH_2SO_3$	427.9752	27619-97-2	DTXSID6067331
8:2 FTS	Fluorotelomer sulphonic acid 8:2	$C_8F_{17}CH_2\ CH_2SO_3$	527.9698	39108-34-4	DTXSID00192353
HFPO-DA (GenX)	Perfluoro(2-methyl-3-oxahexanoic) acid	$C_6HF_{11}O_3$	329.9750	13252-13-6	DTXSID70880215
N-EtFOSAA	2-(N-Ethylperfluorooctanesulfonamido) acetic acid	$C_8F_{17}SO_2N(C_2H_5)CH_2COOH$	584.9903	2991-50-6	DTXSID5062760
N-MeFOSAA	2-(N-Methyllperfluorooctanesulfonamido) acetic acid	$C_8F_{17}SO_2N(CH_3)CHCOOH$	570.9746	2355-31-9	DTXSID10624392
PFBA	Perfluorobutanoic Acid	$C_4HF_7O_2$	213.9865	375-22-4	DTXSID4059916
PFPeA	Perfluoropentanoic Acid	$C_5HF_9O_2$	263.9833	2706-90-3	DTXSID6062599
PFHxA	Perfluorohexanoic Acid	$C_6HF_{11}O_2$	313.9801	307-24-4	DTXSID3031862
PFHpA	Perfluoroheptanoic Acid	$C_7HF_{13}O_2$	363.9769	375-85-9	DTXSID1037303
PFOA	Perfluorooctanoic Acid	$C_8HF_{15}O_2$	413.9737	335-67-1	DTXSID8031865
PFNA	Perfluorononanoic Acid	$C_9HF_{17}O_2$	463.9705	375-95-1	DTXSID8031863
PFDA	Perfluorodecanoic Acid	$C_{10}HF_{19}O_2$	513.9673	335-76-2	DTXSID3031860
PFUnDA	Perfluoroundecanoic acid	$C_{11}HF_{21}O_2$	563.9641	2058-94-8	DTXSID8047553
PFDoDA	Perfluorododecanoic	$C_{12}HF_{23}O_2$	613.9609	307-55-1	DTXSID8031861
PFTrDA	Perfluorotridecanoic acid	$C_{13}HF_{25}O_2$	663.9577	72629-94-8	DTXSID90868151
PFTeDA	Perfluorotetradecanoic acid	$C_{14}HF_{27}O_2$	713.9545	376-06-7	DTXSID3059921
PFBS	Perfluorobutane Sulfonate	$C_4HF_9SO_3$	299.9503	375-73-5	DTXSID5030030
PFPeS	Perfluoropentanesulfonic acid	$C_5HF_{11}SO_3$	349.9471	2706-91-4	DTXSID8062600
PFHxS	Perfluorohexane Sulfonate	$C_6HF_{13}SO_3$	399.9439	355-46-4	DTXSID7040150
PFHpS	Perfluoroheptanesulfonic acid	$C_7HF_{15}SO_3$	449.9407	375-92-8	DTXSID8059920
PFOS	Perfluorooctane Sulfonate	$C_8HF_{17}SO_3$	499.9375	1763-23-1	DTXSID3031864
PFNS	Perfluorononanesulfonic acid	$C_9HF_{19}SO_3$	549.9343	68259-12-1	DTXSID8071356
PFDS	Perfluorodecanesulfonic acid	$C_{10}HF_{21}SO_3$	599.9311	335-77-3	DTXSID3040148
PFOSA	Perfluorooctanesulfonamide	$C_8F_{17}SO_2NH_2$	498.9535	754-91-6	DTXSID3038939

Table 3. PFAS Concentrations in Fume Suppressant Products Used at Chromium Plating Facilities Determined with Targeted Analysis.

	Product 1		Product 2		Product 3			Product 4	Product 5	Product 6	Product 7	Product 8	Product 9
Sample ID	**G FS**	**G FS DUP**	**B FS**	**D FS1**	**F FS**	**A FS**	**E FS**	**E FSxtra**	**C FS**	**I FS**	**K FS**	**H FS**	**D FS2**
Dilution Factor	*10,000*	*10,000*	*10,000*	*10,000*	*500*	*500*	*500*	*10,000*	*10,000*	*10,000*	*10,000*	*10,000*	*10,000*
Units / Analyte	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
4:2 FTS	-	-	-	-	-	-	-	-	-	-	-	-	-
6:2 FTS	6.8E+10 JC1, JIS1	7.9E+10 JC1, JIS1	3.1E+10 JC1, JIS1	7.1E+10 JC1, JIS1	-	-	-	7.0E+10 JC1, JIS1	6.3E+10 JC1, JIS1	1.2E+11 JC1, JIS1	1.2E+11 JC1, JIS1	6.9E+10 JC1, JIS1	5.3E+10 JC1, JIS1
8:2 FTS	-	-	-	-	-	-	-	-	-	-	-	-	-
HFPO-DA	-	-	-	-	-	-	-	-	-	-	-	-	-
NEtFOSAA	-	-	-	-	-	-	-	-	-	-	-	-	-
NMeFOSAA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFBA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFPeA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFHxA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFHpA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFOA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFNA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFDA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFUnDA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFDoDA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFTrDA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFTeDA	-	-	-	-	-	-	-	-	-	-	-	-	-
PFBS	-	-	-	-	-	-	-	-	-	-	-	-	-
PFPeS	-	-	-	-	-	-	-	-	-	-	-	-	-
PFHxS	-	-	-	-	-	-	-	-	-	-	-	-	-
PFHpS	-	-	-	-	-	-	-	-	-	-	-	-	-
PFOS	-	-	-	-	-	-	-	-	-	-	-	-	-
PFNS	-	-	-	-	-	-	-	-	-	-	-	-	-
PFDS	-	-	-	-	-	-	-	-	-	-	-	-	-
PFOSA	-	-	-	-	-	-	-	-	-	-	-	-	-

(Dash): Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.
JCI: Sample result exceeds the upper calibration range.
JIS1: Internal standard diluted out due to high analyte concentration; matrix interferences may not be accounted for.

*Sample IDs in this table were anonymized by EGLE.

Table 4. PFAS Concentrations in Effluent Determined with Targeted Analysis.

	Facility Effluent Samples											
Sample ID	**A EFF**	**B EFF**	**C EFF**	**D EFF**	**E EFF**	**F EFF**	**G EFF**	**H EFF**	**I EFF**	**J EFF**	**J DUP**	**K EFF**
Analyte	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L	ng/L
4:2 FTS	U	80	1,390 D2	18	U	U	218 JC1	U	552 JC1	210 JC1	183 JC1	68
6:2 FTS	U	51,000 D3, JC1, JIS1	482,000 D4, JC1, JIS1	49,500 D3, JC1, JIS1	32 B2	294 JC1, B2	1,030,000 D2, JC1, JIS1	7,880 D1, JC1, JIS1	3,140,000 D6, JC1, JIS1	672,000 D2, JC1, JIS1	1,100,000 D5, JC1, JIS1	203,000 D4, JC1, JIS1
8:2 FTS	ND	43	25	ND	ND	ND	197 JC1	ND	237 JC1	125	103	80
HFPO-DA	ND	36 B2	ND	ND	10 B2	ND	17 B2	ND	ND	ND	16 B2	65 B2
NEtFOSAA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
NMeFOSAA	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
PFBA	U	4,710 D2, JC1	670 D2	12	U	U	U	U	14	U	U	10
PFPeA	ND	930 D2	210 D2	19	U	U	U	U	10	U	U	19
PFHxA	U	340 D2	130	43	U	U	55	U	131	35	37	38
PFHpA	ND	490 D2	49	30	U	ND	51	U	89	29	24	20
PFOA	U	U	U	11	U	U	U	11	U	U	U	U
PFNA	U	U	U	ND	U	U	U	U	U	U	U	U
PFDA	U	ND	U	U	ND	ND	U	U	U	U	U	U
PFUnDA	U	ND	ND	U	ND	U	ND	ND	U	ND	ND	ND
PFDoDA	ND	U	U	ND	ND	U	U	U	U	U	U	ND
PFTrDA	ND	ND	ND	ND	ND	ND	U	ND	ND	ND	ND	ND
PFTeDA	ND	ND	ND	ND	ND	ND	ND	U	ND	ND	ND	ND
PFBS	31	U	19,800 D2, JC1	434 JC1	U	`	22	516 JC1	28	U	U	84
PFPeS	U	U	77	88	U	ND	U	U	ND	U	U	U
PFHxS	28	U	217 JC1	1,220 JC1	14	U	24	65	28	U	U	19
PFHpS	11	U	109	323 JC1	ND	U	55	35	109	U	U	12
PFOS	1,060 JC1	610 D2	51,700 D4, JC1, JIS1	33,700 D2, JC1, JIS1	15	158 JC1	12,700 D2, JC1, JIS1	4,330 D1, JC1, JIS1	25,300 D6, JIS1	U D2	U D5	1,200 D4, JIS1
PFNS	U	U	16	43	U	ND	U	U	11	U	U	U
PFDS	U	U	U	14	ND	U	U	ND	U	U	U	U
PFOSA	ND	U	U	U	U	ND	U	ND	U	U	U	U

ND	Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.
U	LOQ: Peak area detected but concentration less than the concentration of the lowest standard calibration curve.
Dx	Sample is diluted by a factor: D1=5X, D2=10X, D3=20X, D4=50X, D5=100X, D6=500X.
JC1	Sample result exceeds the upper calibration range.
JIS1	Internal standard diluted out due to high analyte concentration; matrix interferences may not be accounted for.
B2	Analyte found in associated trip or field blank > LOQ and sample concentration is within 10X level of blank contamination; reported sample concentration may be elevated.

*Sample IDs in this table were anonymized by EGLE.

Table 5. PFAS Concentrations in QC samples in ng/L. Samples were not diluted.

	Trip Blanks		Equipment Blanks		Field Blanks		Spiked Samples --30 ng/L				Spiked Samples -- 100 ng/L			
Sample ID	**TB-A**	**TB-B**	**KEBAM**	**BEBAM**	**DFBAM**	**FB**	**QC1A Rep 1**	**QC1A Rep 2**	**QC1B Rep 1**	**QC1B Rep 2**	**QC2A Rep 1**	**QC2A Rep 2**	**QC2B Rep 1**	**QC2B Rep 2**
Units / Analyte	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**	**ng/L**
4:2 FTS	U	U	U	U	U	ND	24	28	31	29	85	85	74 JR5	96
6:2 FTS	U	U	350 JC1	15	U	33	27	26	29	27	91	85	86	87
8:2 FTS	ND	ND	ND	U	ND	ND	43 JR5	17 JR5	35	15 JR5	60 JR5	68 JR5	97	86
HFPO-DA	20	ND	ND	U	U	ND	23 JR5	24	25	27	89	88	88	79 JR5
NEtFOSAA	U	ND	ND	ND	ND	ND	16 JR5	U JR5	15 JR5	21 JR5	68 JR5	54 JR5	75 JR5	73 JR5
NMeFOSAA	ND	ND	ND	ND	ND	ND	34	ND JR5	14 JR5	10 JR5	58 JR5	62 JR5	85	168 JC1, JR2
PFBA	U	U	U	U	U	ND	26	25	27	27	80	80	83	82
PFPeA	U	ND	U	ND	U	ND	22 JR5	23 JR5	24	23 JR5	83	77 JR5	77 JR5	78 JR5
PFHxA	U	ND	U	U	U	ND	25	27	27	28	87	82	91	84
PFHpA	U	U	U	ND	U	ND	28	26	29	30	86	83	90	92
PFOA	U	U	U	U	U	U	22 JR5	21 JR5	25	25	82	73 JR5	76 JR5	76 JR5
PFNA	U	U	U	U	U	U	23 JR5	22 JR5	24	24	69 JR5	72 JR5	79 JR5	73 JR5
PFDA	U	U	U	ND	ND	U	23 JR5	23 JR5	25	23 JR5	77 JR5	71 JR5	69 JR5	72 JR5
PFUnDA	U	U	ND	ND	ND	ND	19 JR5	19 JR5	21 JR5	20 JR5	69 JR5	62 JR5	72 JR5	71 JR5
PFDoDA	ND	U	ND	U	U	U	ND JR5	14 JR5	18 JR5	16 JR5	37 JR5	37 JR5	ND JR5	65 JR5
PFTrDA	U	U	ND	ND	ND	ND	19 JR5	18 JR5	20 JR5	19 JR5	22 JR5	24 JR5	45 JR5	43 JR5
PFTeDA	U	U	ND	U	ND	ND	12 JR5	17 JR5	12 JR5	17 JR5	10 JR5	13 JR5	41 JR5	49 JR5
PFBS	U	U	U	ND	U	ND	29	25	31	25	84	75 JR5	93	83
PFPeS	ND	U	ND	ND	ND	ND	30	27	31	32	104	95	108	99
PFHxS	U	U	U	U	U	U	23 JR5	26	28	25	80	80	85	83
PFHpS	ND	ND	ND	ND	ND	ND	22 JR5	22 JR5	25	24	72 JR5	75 JR5	81	85
PFOS	U	U	15	47	U	U	22 JR5	21	25 JR5	25 JR5	82	73 JR5	76 JR5	76 JR5
PFNS	U	U	U	U	ND	U	14 JR5	13 JR5	12 JR5	14 JR5	50 JR5	44 JR5	48 JR5	45 JR5
PFDS	U	U	U	ND	U	U	11 JR5	13 JR5	11 JR5	10 JR5	35 JR5	32 JR5	49 JR5	43 JR5
PFOSA	ND	U	U	U	U	U	15 JR5	24	18 JR5	31	74 JR5	58 JR5	81	81

ND	Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.
U	LOQ: Sample value > Limit of Detection but less than lowest standard concentration of the calibration curve.
JC1	Sample result exceeds the upper calibration range.
JR5	Spiked field sample result does not meet QC acceptance criteria for recovery (±20%).

*Sample IDs in this table were anonymized by EGLE.

ATTACHMENT 3: USEPA Laboratory Report #2

Non-targeted Analysis of PFAS in Fume Suppressant Products and Effluent Samples

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CENTER FOR ENVIRONMENTAL MEASUREMENT AND MODELING
RESEARCH TRIANGLE PARK, NC 27711

OFFICE OF
RESEARCH AND DEVELOPMENT

February 19, 2020

Kurt A. Thiede
Regional Administrator
U.S. EPA Region 5
77 W Jackson Blvd
Chicago, IL 60604

Dear Kurt:

I am pleased to provide the enclosed second report from our ongoing collaborative technical support to EPA Region 5 and the Michigan Department of Environment, Great Lakes and Energy (EGLE) assisting with concerns about environmental contamination associated with use of fume suppressants containing per- and polyfluoroalkyl substances (PFAS) at chrome plating facilities. This report is in response to a March 2018 request from the EPA Region 5 Deputy Administrator asking for laboratory assistance analyzing PFAS in use within Michigan. The enclosed Report #2 provides non-targeted analysis laboratory results that identify various PFAS found in fume suppressant products and pre-treatment effluent samples collected at multiple chrome plating facilities.

It is our understanding that this information was requested to help in ongoing investigation into the presence of PFAS in the environment near chrome plating facilities of interest. This request relates to our research capabilities and interests applying targeted and non-targeted analysis methods for discovery of the nature and extent of PFAS environmental occurrence that may be potentially associated with industrial releases. EPA continues to develop analytical methods for many PFAS compounds in various media including some of those included in this report. We are providing the results of our analysis as they become available.

In this report, we provide PFAS identification and semi-quantitative analytical results. We do not interpret exposure or risk from these values. EPA does not currently have final health-based standards, toxicity factors, or associated risk levels for PFAS, other than perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorobutanesulfonic acid (PFBS). While the data provided in the attached report indicates the presence (or lack) of PFAS in the samples, we do not have sufficient information to offer interpretations related to human or environmental exposure and risk.

Thank you for inviting us to be part of this effort that helps to further both EPA's and Michigan's understanding of an important issue in the state. This is just one of many Agency efforts that demonstrates EPA's commitment to cooperative federalism.

If you have any questions or concerns, do not hesitate to contact me at (919) 541-2107 or via email at watkins.tim@epa.gov or Brian Schumacher at (702) 798-2242 or via email at schumacher.brian@epa.gov. I look forward to our continued work together.

Sincerely,

Timothy H Watkins

Timothy H. Watkins
Director

Enclosure

CC:
Erin Newman, USEPA, Region 5
Kimberly Harris, USEPA, Region 5
Charlotte Bertrand, USEPA OW
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PFAS Associated with Chrome Plating Facilities in Michigan

Laboratory Data Report #2: Non-targeted Analysis of PFAS in Fume Suppressant Products and Effluent Samples

Background. The Michigan Department of Environment, Great Lakes, and Energy (EGLE), in coordination with EPA Region 5, requested the Office of Research and Development's (ORD's) technical support in analyzing per- and polyfluoroalkyl substances (PFAS) used as fume suppressants and that may potentially be found in effluent from chrome plating facilities. EGLE assumed responsibility for the collection of the fume suppressant products and effluent samples from chrome plating facilities in Michigan and their shipment to the ORD laboratory[1]. ORD was responsible for sample extraction and analysis. ORD's analysis and report team members that contributed to this effort are listed in Table 1.

Table 1. EPA Office of Research and Development Lab Analysis and Report Team.

Responsibility	Personnel
ORD Principal Investigators	James McCord and Mark Strynar
Laboratory chemistry	James McCord
Quality Assurance Review	Margie Vazquez, Sania Tong-Argao
Management coordination and review	Myriam Medina-Vera, Brian Schumacher, Kate Sullivan
Report preparation	Kate Sullivan

This 2nd report includes non-targeted analysis results for 25 samples collected from fume suppressant products and effluents at 11 chrome plating facilities in Michigan. Effluent at all the sampled facilities is combined with other wastewater streams and sent for treatment at municipal wastewater treatment plants. More than half of the sampled facilities also have onsite PFAS pretreatment systems. For purposes of the study, all effluent samples were collected prior to any treatment.

EGLE collected samples on July 22 and 23, 2019 in containers provided by ORD. We also report results for 6 field quality assurance samples including 2 field blanks (FB), 2 trip blanks (TB), and 2 equipment blanks (EB). Samples were sent to and analyzed under the direction of Dr. James McCord at ORD's laboratories in Research Triangle Park, NC, following non-targeted analysis procedures. Samples were received on July 25, 2019.

The current data report provides a simple representation and summary of non-targeted analysis results. Therefore, the description of methods and quality assurance are brief and high-level. Additional reports and/or publications may be developed that will include a more detailed description of methods, quality assurance procedures, and statistical interpretation of the data. As study partners/collaborators, we anticipate that EGLE and Region 5 will assist in these reports and publications.

[1] U.S. EPA National Exposure Research Laboratory, Project Study Plan: Identification of PFAS in Fume Suppressants in Chromium Electroplating Facilities, D-IO-0032097-QP-1-0, 12Jul2019.

Methods in Brief. Effluent and fume suppressant samples were analyzed by ultra-performance liquid chromatography mass spectrometry (UPLC-MS) using methods described within our Laboratory Quality Assurance Project Plan[2] for non-targeted analysis and McCord *et al*. 2019[3]. In brief, water samples (500 mL) were filtered and then extracted using a WAX solid phase extraction cartridge. PFAS was removed from the cartridge in methanol and the volume reduced to 1 mL under a gentle stream of dry nitrogen. An aliquot of the 1 mL concentrated sample was injected into a Thermo Vanquish ultra performance liquid chromatograph coupled to a Thermo Orbitrap Fusion mass spectrometer. Product samples with high concentrations of chemical additives in the products were diluted from 500 - 10,000 times to avoid contaminating the analytical instruments. Specifically, 6:2 FTS was found to be in high abundance in many of the fume suppressant products and effluent samples. High abundances of other, non-fluorinated, product components were also present in the fume suppressant products and effluent samples.

Non-targeted analysis (NTA) provides two important measurements. The first is a tentative identification of PFAS compounds detected in the sample. PFAS are tentatively identified based on a combination of mass spectral data along with patterns of fragmentation compared to on-line and in-house mass-spectral libraries. Analytes in each sample and process blank were identified to various levels of confidence depending on how much combined evidence from manual examination of MS/MS fragmentation spectra and/or comparison with mass spectral libraries.

The second measurement is an indication of the relative abundance of the PFAS present in the sample. The mass spectrometer detector provides integrated peak areas for the chromatogram of the compound mass (+/- 5ppm) at the specified retention time. The peak area counts are proportional to the mass of PFAS in the sample. Since the sample and injection volume are held constant, the peak area counts are also proportional to concentration, although the relationship varies based on compound.

It is important to understand how results of non-targeted analysis differ from those produced during routine laboratory analysis. Without a standard curve to calibrate the relationship between peak area and a mass or concentration value, the peak area counts alone should be considered a semi-quantitative indicator of relative abundance. Analyte peak areas can be compared between samples in a sample set to obtain relative concentrations but cannot be directly compared between analytes. Our experience indicates that measured abundances for PFAS are four to six orders of magnitude higher than the ppt concentration (e.g. 1e7 ~ 100 ppt) not accounting for dilutions during sample preparation. Peak area counts are expected to have much greater inherent sampling and analytical variability, which may become evident in reproducibility assessments. For example, it is possible for field duplicates to differ by two or three-fold or more, and laboratory replicates to have greater variability than typically observed in routine laboratory analysis. Any application of NTA results should consider this inherently greater uncertainty.

---

[2] National Exposure Research Laboratory, Quality Assurance Project Plan: Non-targeted Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Liquid Samples. J-WECD-0031918-QP-1-0. Aug 30, 2019.

[3]

https://www.jove.com/video/59142/identifying-per-polyfluorinated-chemical-species-with-combined

The non-targeted analytical data generated by LC/MS were considered as a "detect" when acceptable chromatographic peaks and spectra were evident. Samples without a detectable peak are reported as "ND". Samples with detected analytes were further screened to determine the reporting limit (RL) that accounts for contamination that may have occurred during sampling and analysis including field, laboratory, and instrument blanks. The RL was established for each compound by statistical analysis of the combined laboratory and field blanks, where RL =AVE [blanks] + 3x STD [blanks]. Sample values less than this statistically defined threshold are reported as "<RL".

Summary of Results

Compound Identification. Across all the fume suppressant products and effluent samples, the 23 PFAS compounds listed in Table 2 were detected with NTA and tentatively identified by chemical formula, name, monoisotopic mass and retention time, CAS registry number (CASRN), and CompTox Identification Number (DTXSID), when available. PFAS compounds with a CASRN are registered in EPA's Chemistry dashboard where additional information can be found (U.S. EPA CompTox, 2019)[4]. Note that there are only 16 unique PFAS compounds identified in Table 2. Several of the primary compounds have 1 or more isomers which have the same intrinsic properties but are distinguished by analytical retention time. The analyst's confidence in PFAS compound identification is also provided as defined in the Table 2 footnote. Compounds that did not have sufficient PFAS characteristics (rating #4) or were not identified to the chemical formula level (rating #5) are not reported.

All 23 of the PFAS compounds identified by NTA (Table 2) were observed in the pre-treatment effluent samples but only two were observed in the fume suppressant product samples. Nine of the 16 unique compounds (isomers combined) were quantified by targeted analysis in MI EGLE Report #1. NTA analysis identified 7 additional PFAS compounds (isomers combined) in the effluent samples, the most abundant of which were tentatively identified as cyclic perfluorinated sulfonates (Chem Ref # 15-19).

The automated library search identified additional compounds in the product samples to the formula level. None of these additional compounds were polyfluorinated or had other characteristic PFAS features and are not reported. The additional compounds in the fume suppressant products were primarily very long-chained organic compounds (98% C14 to C64) that included mostly linear hydrocarbon sulfonates, phosphates, carboxylic acids and ethoxylates.

Abundance of Compounds. Semi-quantitative results are given as peak area counts in Tables 3, 4, and 5. Peak area counts have been adjusted for the level of dilution by a constant multiplier applied to each sample. Fume suppressant product samples were diluted by a factor of 500 or 10,000. Some effluent samples were diluted by factors ranging from 5 to 500, depending on the sample and analytes present.

Fume Suppressant Products. Table 3 provides the peak area of PFAS in the fume suppressant products used at the chrome plating facilities. A total of 9 different products were analyzed. Several products are used at multiple facilities and are grouped accordingly. The same product is

[4] U.S. EPA CompTox Chemicals Dashboard https://comptox.epa.gov/dashboard

used at both facilities I and J but was only sampled at the I facility. Two additional products that are not in current use (products 4 and 9) were also provided by the facilities.

Only two PFAS compounds were identified in the fume suppressant products with NTA. The primary compound was 6:2 FTS with lesser amounts of 6:4 FTS. These compounds were found in high abundance in all of the products except product 3 where neither was detected. NTA results for 6:2 FTS in fume suppressant products are consistent with those from targeted analysis that were provided in MI EGLE Report #1[5].

Pre-treatment Effluent Samples. Table 4 provides NTA results for the effluent samples. The peak areas are superimposed on a heat map where gradations in color reflect seven classifications of peak area from low (non-detect and less than reporting limit, RL) to high (>1,000,000). The heat map is useful in showing where PFAS "light-up" in terms of detection and high peak areas. Heatmap values >100,000 (yellow, orange and red tones) have the highest confidence that a compound is present in relatively higher abundance.

The NTA results for effluent samples are generally consistent with those reported with targeted analysis in MI EGLE Report #1. Among the 9 compounds quantified in both targeted analysis and NTA, there was 81% agreement on the presence or absence of measurable amounts of the compounds among samples. The general pattern of abundance by analyte and sample were also relatively consistent between targeted and NTA results, but the NTA results vary more widely. Targeted analysis results should be considered more reliable when both are available.

There is a high abundance of 6:2 FTS and 6:4 FTS in the pre-treatment effluents from facilities where there is also a high abundance in the fume suppressant product used at that location. We observed other PFAS in the effluents but not in the contemporary fume suppressant products. NTA analysis detected the presence of the cyclic perfluorinated sulfonate compounds (Chem Ref #'s 15-19) in many of the effluent samples and their relative abundances were roughly equal to PFOS abundances in some of the samples. Because effluent samples were collected prior to treatment, PFAS levels in the effluent samples may be much greater than those that discharged into surface waters, and sample results should not be considered reflective of levels to which people may be exposed.

Quality Assurance Samples. Table 5 provides results for field, trip, and equipment blanks. No PFAS compounds were detected at levels greater than the reporting limit in the blanks. As a measure of reproducibility in the effluent samples, the relative percent difference (RPD) of a laboratory replicate (G Rep, Table 4) averaged 24% for all valid analyte comparisons. The RPD of the effluent sample field duplicate pair (J/J DUP) averaged 72% while the fume suppressant product duplicate (G/G DUP) averaged 12%.

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[5] EPA Region 5/EGLE Report #1. PFAS Associated with Chrome Plating Facilities in Michigan. Laboratory Data Report #1: Targeted Analysis of PFAS in Fume Suppressant Products and Water Samples. U.S. EPA/ORD, February 2020.

* Facility IDs on this page were anonymized by EGLE.

Table 2. PFAS Tentatively Identified in Fume Suppressants and Effluent at Chrome Plating Facilities by UPLC-MS.

Chem. Ref. #	Tentatively Identified Compound Name	CASRN	Formula	DTXCID	Monoisotopic Mass (g/mol)	RT	Confidence
1	6:2 Fluorotelomer sulfonic acid (6:2 FTS)	27619-97-2	C8 H5 F13 O3 S	DTXCID7037711	427.9758	6.54	1
2	6:4 Fluorotelomer Sulfonic Acid (6:4 FTS)		C10 H9 F13 O3 S		456.0071	7.08	2b
3	4:2 Fluorotelomer sulfonic acid (4:2 FTS)	757124-72-4	C6 H5 F9 O3 S	DTXSID30891564	327.9814	4.14	1
4	8:2 Fluorotelomer sulfonic acid (8:2 FTS)	39108-34-4	C10 H5 F17 O3 S	DTXCID10114844	527.9697	7.73	1
5	Perfluorobutane sulfonic acid (PFBS)	375-73-5	C4 H F9 O3 S	DTXCID3010030	299.9502	2.83	1
6	Perfluorohexanesulfonic acid (PFHxS) - Linear	355-46-4	C6 H F13 O3 S	DTXCID2011859	399.9444	6.01	1
7	Perfluorohexanesulfonic acid (PFHxS) - Branched Isomer	355-46-4	C6 H F13 O3 S	DTXCID2011859	399.9444	5.81	1
8	Perfluoroheptanesulfonic acid (PFHpS)	375-92-8	C7 H F15 O3 S	DTXCID1039347	449.9406	6.74	1
9	Perfluorooctane sulfonic acid (PFOS) - Linear	1763-23-1	C8 H F17 O3 S	DTXCID1011864	499.9386	7.30	1
10	Perfluorooctane sulfonic acid (PFOS) - Branched Isomer	1763-23-1	C8 H F17 O3 S	DTXCID1011864	499.9387	6.90	1
11	Perfluorooctane sulfonic acid (PFOS) - Branched Isomer	1763-23-1	C8 H F17 O3 S	DTXCID1011864	499.9387	7.10	1
12	Perfluorooctane sulfonic acid (PFOS) - Branched Isomer	1763-23-1	C8 H F17 O3 S	DTXCID1011864	499.9386	7.15	1
13	Perfluoropentanoic acid (PFPeA)	2706-90-3	C5 H F9 O2	DTXCID9037612	263.9834	2.15	1
14	Perfluoropentanesulfonic acid (PFPeS)	2706-91-4	C5 H F11 O3 S	DTXCID4037613	349.9470	4.89	1
15	Perfluorocyclohexyl sulfonic acid	2106-55-0	C6 H F11 O3 S	DTXCID10197556	361.9471	4.87	3
16	Perfluoro-4-(perfluoroethyl)cyclohexylsulfonic acid	646-83-3	C8 H F15 O3 S	DTXCID70227328	461.9412	6.60	3
17	Perfluoro-4-(perfluoroethyl)cyclohexylsulfonic acid	646-83-3	C8 H F15 O3 S	DTXCID70227328	461.9412	6.39	3
18	Perfluoro-4-(perfluoroethyl)cyclohexylsulfonic acid	646-83-3	C8 H F15 O3 S	DTXCID70227328	461.9412	6.49	3
19	Perfluoro-4-(perfluoroethyl)cyclohexylsulfonic acid	646-83-3	C8 H F15 O3 S	DTXCID70227328	461.9412	6.72	3
20	1,2,2,3,3,4,5,5,6,6-Decafluoro-4-(trifluoromethyl)cyclohexanesulfonic acid	742-73-4	C7 H F13 O3 S	DTXCID20815698	411.9442	5.87	3
21	6:2 Fluorotelomer phosphate monoester	57678-01-0	C8 H6 F13 O4 P	DTXCID00200745	443.9800	6.38	2a
22	Chlorinated 6:2 Fluorotelomer sulfonic acid		C8 H4 Cl F13 O3 S		461.9367	6.96	2b
23	1,1,2,2,3,3,4,4-Octafluorobutane-1-sulphonic acid	70259-86-8	C4 H2 F8 O3 S	DTXCID801022285	281.9598	1.02	3

Confidence:

1= Confirmed by comparison with reference chemical

2a= Likely structure based on computerized spectrum match

2b= Likely structure based on manual interpretation of MS/MS spectrum

3= Tentative candidate or MS data insufficient for unequivocal identification beyond class (i.e. PFAS chemical)

4 = Formula level identification only (MS/MS unavailable)

5= Exact mass level identification only (no predicted formula)

Table 3. PFAS Peak Area Counts in Fume Suppressant Products Used at Chromium Plating Facilities Determined by Non-targeted Analysis.

	Product 1		Product 2		Product 3			Product 4	Product 5	Product 6	Product 7	Product 8	Product 9
	G FS	**G FS DUP**	**B FS**	**D FS1**	**F FS**	**A FS**	**E FS**	**E FS-xtra**	**C FS**	**I FS**	**K FS**	**H FS**	**D FS2**
Dilution Factor	*10,000*	*10,000*	*10,000*	*10,000*	*500*	*500*	*500*	*10,000*	*10,000*	*10,000*	*10,000*	*10,000*	*10,000*
Units / **Chem. Ref. #**	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count
1	1.3.E+07	1.5.E+07	6.0.E+06	1.3.E+07	-	-	-	1.4.E+07	1.2.E+07	2.1.E+07	2.2.E+07	1.5.E+07	1.0.E+07
2	7.1.E+04	8.0.E+04	2.5.E+04	5.1.E+04	-	-	-	7.8.E+04	2.7.E+04	1.2.E+05	1.6.E+05	1.5.E+04	4.2.E+04
3	-	-	-	-	-	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-	-	-	-	-	-
6	-	-	-	-	-	-	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-	-	-	-	-	-	-
8	-	-	-	-	-	-	-	-	-	-	-	-	-
9	-	-	-	-	-	-	-	-	-	-	-	-	-
10	-	-	-	-	-	-	-	-	-	-	-	-	-
11	-	-	-	-	-	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-	-	-	-	-	-
13	-	-	-	-	-	-	-	-	-	-	-	-	-
14	-	-	-	-	-	-	-	-	-	-	-	-	-
15	-	-	-	-	-	-	-	-	-	-	-	-	-
16	-	-	-	-	-	-	-	-	-	-	-	-	-
17	-	-	-	-	-	-	-	-	-	-	-	-	-
18	-	-	-	-	-	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-	-	-	-	-	-
21	-	-	-	-	-	-	-	-	-	-	-	-	-
22	-	-	-	-	-	-	-	-	-	-	-	-	-
23	-	-	-	-	-	-	-	-	-	-	-	-	-

- (Dash): Non-detect based on criteria of signal-to-noise contrast and temporal continuity of signal.

* Sample IDs in this table were anonymized by EGLE.

Table 4. PFAS Peak Area Count in Effluent Samples from Chromium Plating Facilities Determined by Non-targeted Analysis.

	A EFF	B EFF	C EFF	D EFF	E EFF	F EFF	G EFF	G Rep	H EFF	I EFF	J EFF	J DUP	K EFF
Dilution Factor	*1*	*20*	*50*	*20*	*1*	*1*	*100*	*100*	*5*	*500*	*100*	*100*	*1*
Units / Chem. Ref. #	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count
1	<RL	53,200,000	449,000,000	102,000,000	<RL	<RL	952,000,000	894,000,000	<RL	4,520,000,000	2,190,000,000	973,000,000	341,000,000
2	<RL	464,000	1,570,000	284,000	<RL	<RL	1,950,000	1,890,000	<RL	23,800,000	3,850,000	8,370,000	1,110,000
3	<RL	529,000	2,830,000	208,000	87,700	121,000	931,000	1,160,000	157,000	3,620,000	2,200,000	1,070,000	651,000
4	155,000	<RL	<RL	172,000	<RL	<RL	352,000	329,000	<RL	315,000	464,000	204,000	352,000
5	<RL	<RL	196,000,000	4,880,000	<RL	<RL	274,000	267,000	5,490,000	926,000	<RL	282,000	1,180,000
6	425,000	102,000	2,820,000	74,600,000	65,700	<RL	340,000	368,000	879,000	1,650,000	288,000	<RL	550,000
7	67,500	10,200	361,000	7,740,000	6,780	<RL	30,400	39,300	120,000	161,000	27,800	17,200	64,400
8	338,000	<RL	1,640,000	4,650,000	<RL	29,000	533,000	538,000	602,000	1,490,000	<RL	<RL	332,000
9	5,740,000	885,000	106,000,000	265,000,000	<RL	<RL	36,500,000	65,100,000	9,450,000	128,000,000	<RL	<RL	9,710,000
10	107,000	131,000	14,000,000	4,100,000	<RL	28,600	386,000	1,010,000	749,000	2,600,000	143,000	272,000	482,000
11	<RL	<RL	72,900,000	41,800,000	<RL	<RL	8,390,000	10,400,000	6,250,000	29,200,000	<RL	<RL	3,880,000
12	1,120,000	<RL	30,300,000	54,400,000	<RL	<RL	9,290,000	11,900,000	3,770,000	35,400,000	<RL	<RL	2,560,000
13	<RL	18,400,000	10,500,000	4,770,000	<RL	<RL	1,490,000	1,850,000	<RL	8,260,000	1,040,000	834,000	2,080,000
14	25,500	<RL	578,000	3,520,000	<RL	<RL	9,670	19,700	40,900	25,800	<RL	10,900	26,700
15	3,090	9,140	15,600,000	337,000	935	776	28,000	17,300	830,000	25,300	1,370	12,400	33,100
16	<RL	74,300	197,000,000	14,900,000	10,300	37,700	2,110,000	3,560,000	1,060,000	308,000	41,200	119,000	979,000
17	<RL	14,600	94,200,000	4,080,000	<RL	7,700	1,190,000	1,130,000	326,000	108,000	6,820	40,000	193,000
18	<RL	<RL	44,600,000	1,460,000	<RL	<RL	611,000	435,000	117,000	182,000	62,700	44,300	144,000
19	<RL	6,920	25,900,000	1,300,000	<RL	<RL	479,000	476,000	65,600	84,200	6,840	33,800	261,000
20	<RL	<RL	47,700,000	895,000	<RL	<RL	161,000	129,000	201,000	<RL	<RL	<RL	<RL
21	17,900	7,630	10,000	5,350	<RL	<RL	435,000	443,000	<RL	878,000	916,000	428,000	12,500
22	<RL	26,000	756,000	175,000	<RL	<RL	1,480,000	1,600,000	<RL	10,600,000	5,560,000	2,230,000	864,000
23	<RL	4,830	2,450,000	82,200	<RL	<RL	<RL	8,700	18,200	17,600	<RL	8,990	82,500

<RL Sample value less than reporting limit.

* Sample IDs in this table were anonymized by EGLE.

LEGEND	
Color	**Peak Area Category**
U	Less than the Reporting Limit (RL)
	>RL - 50,000
	50,000 - 100,000
	100,000 - 200,000
	200,000 - 500,000
	500,000 - 1,000,000
	>1,000,000

Table 5. PFAS Peak Area Counts in Blanks Determined in Non-targeted Analysis.

	FB	DFBAM	TB (A)	TB (B)	BEBAM	KEBAM
Dilution Factor	*1*	*1*	*1*	*1*	*1*	*1*
Units / Chem. Ref. #	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count	Peak Area Count
1	<RL	<RL	<RL	<RL	<RL	<RL
2	<RL	<RL	<RL	<RL	<RL	<RL
3	<RL	<RL	<RL	<RL	<RL	<RL
4	<RL	<RL	<RL	<RL	<RL	<RL
5	<RL	<RL	<RL	<RL	<RL	<RL
6	<RL	<RL	<RL	<RL	<RL	<RL
7	<RL	<RL	<RL	<RL	<RL	<RL
8	<RL	<RL	<RL	<RL	<RL	<RL
9	<RL	<RL	<RL	<RL	<RL	<RL
10	<RL	<RL	<RL	<RL	<RL	<RL
11	<RL	<RL	<RL	<RL	<RL	<RL
12	<RL	<RL	<RL	<RL	<RL	<RL
13	<RL	<RL	<RL	<RL	<RL	<RL
14	<RL	<RL	<RL	<RL	<RL	<RL
15	<RL	<RL	<RL	<RL	<RL	<RL
16	<RL	<RL	<RL	<RL	<RL	<RL
17	<RL	<RL	<RL	<RL	<RL	<RL
18	<RL	<RL	<RL	<RL	<RL	<RL
19	<RL	<RL	<RL	<RL	<RL	<RL
20	<RL	<RL	<RL	<RL	<RL	<RL
21	<RL	<RL	<RL	<RL	<RL	<RL
22	<RL	<RL	<RL	<RL	<RL	<RL
23	<RL	<RL	<RL	<RL	<RL	<RL
<RL	Sample value is less than reporting limit.					

* Sample IDs in this table were anonymized by EGLE.

LEGEND	
Color	**Peak Area Category**
U	Less than the Reporting Limit (RL)
	>RL - 50,000
	50,000 - 100,000
	100,000 - 200,000
	200,000 - 500,000
	500,000 - 1,000,000
	>1,000,000

ATTACHMENT 4: Effect of 1,000 ppt (ng/L) PFOS in Fume Suppressant

Example of a Medium-Size Plater Using Chrome Etch Tanks and Chrome Plating Tanks

Given the addition of a total of 1,200 milliliters (mL) of fume suppressant (per day) with an overall 75,000 gallons per day (GPD) of wastewater and assuming a worst-case scenario of 1,000 ng/L PFOS in the product, the calculation below shows that concentration of PFOS in the effluent (without treatment) would be 0.0042 ppt.

$$1200\ mL * \frac{1\ \mu g}{L} * \frac{1\ L}{1000\ mL} * \frac{1}{75{,}000\ GPD} * \frac{1\ gal}{3.785\ L} * \frac{1000\ ng}{1\ \mu g} = 0.0042 \frac{ng}{L}$$

$$= 0.0042\ ppt\ PFOS\ in\ effluent$$

As an alternative scenario, if the entire contents of a chromium plating tank (containing 900 mL of product and 1,256 gallons of wastewater) were discharged without dilution as a slug, the effluent would be 0.19 ppt PFOS. For this example, the chrome plating tank has the highest concentration of PFOS in the facility. This calculation is shown below.

$$900\ mL * \frac{1\ \mu g}{L} * \frac{1\ L}{1000\ mL} * \frac{1}{1{,}256\ GPD} * \frac{1\ gal}{3.785\ L} * \frac{1000\ ng}{1\ \mu g} = 0.19 \frac{ng}{L}$$

$$= 0.19\ ppt\ PFOS\ in\ chrome\ tank$$

If one 1,500-gallon etch tank with 100 mL of fume suppressant were discharged, the maximum concentration of PFOS would be less than that in the chrome tank at just 0.018 ng/L. This calculation is shown below.

$$100\ mL * \frac{1\ \mu g}{L} * \frac{1\ L}{1000\ mL} * \frac{1}{1{,}500\ GPD} * \frac{1\ gal}{3.785\ L} * \frac{1000\ ng}{1\ \mu g} = 0.018 \frac{ng}{L}$$

$$= 0.018\ ppt\ PFOS\ in\ etch\ tank$$

Based on the above calculation, this quantification level is sufficient to draw conclusions about the origin of the PFOS present in effluent because even if a product with nondetectable PFOS had a concentration of 1,000 ng/L (ppt) PFOS (the maximum that would not be detected), PFOS would still not be detectable in the chrome tanks, etch baths, and effluent. Quantification or detection levels ranged from 2 to 10 ng/L (ppt) for PFOS in effluent.

The above example is from a medium-sized plater. Platers in Michigan discharge from hundreds to 400,000 GPD of wastewater. The following figure shows calculations of what 1,200 mL of fume suppressant containing 1,000 ng/L PFOS would yield across different total effluent volumes (from 1,000 to 100,000 GPD). This example assumes all fume suppressant added in a day is discharged in the effluent and 1,200 mL of fume suppressant per day is used for platers of all sizes.

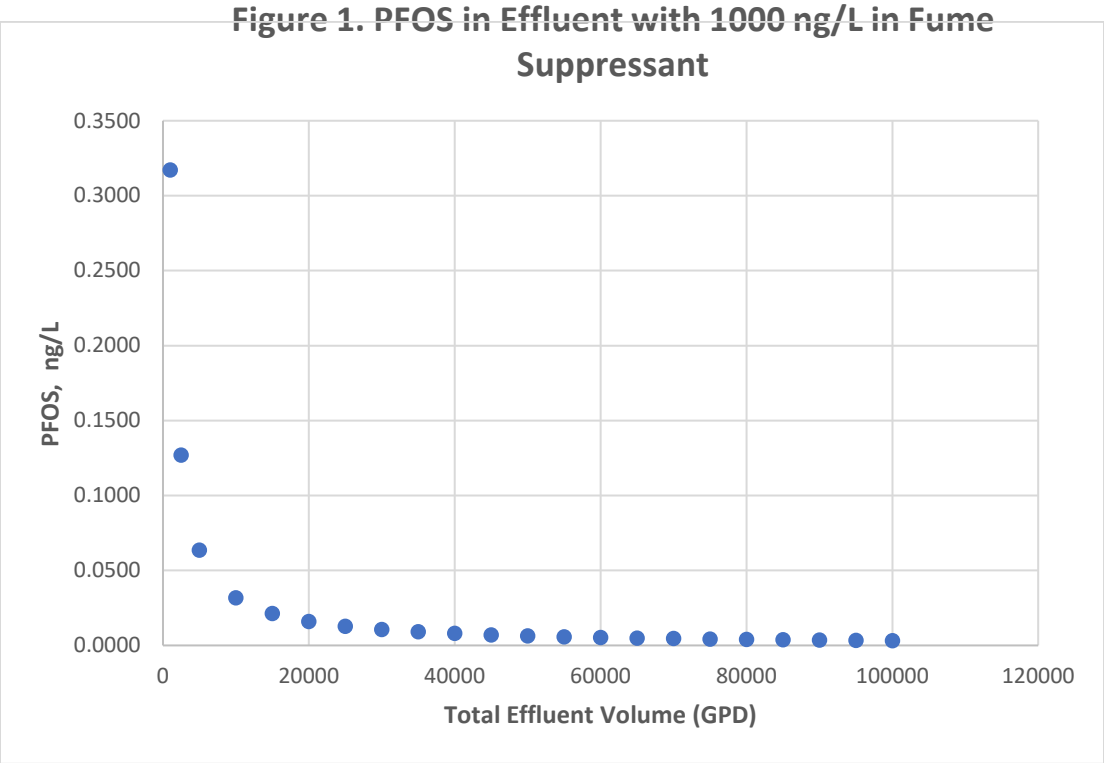
Figure 1. PFOS in Effluent with 1000 ng/L in Fume Suppressant
PFOS, ng/L
0.3500
0.3000
0.2500
0.2000
0.1500
0.1000
0.0500
0.0000
0
20000
40000
60000
80000
100000
120000
Total Effluent Volume (GPD)