EPA/EGLE Fume Suppressant Study

July 9, 2020

EGLE Water Resources Division (WRD), Emerging Pollutants Section
The United States Environmental Protection Agency (EPA) Region V
EPA Office of Research and Development (ORD)

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Agenda

- What are PFAS and Why are they Important?
- Chrome Platers & the PFAS Story
- EPA R5 Fume Suppressant/Effluent Study
- The Fume Suppressant & Surface Water Connection
- EPA/EGLE Fume Suppressant Study Design
- Results
- Q & A

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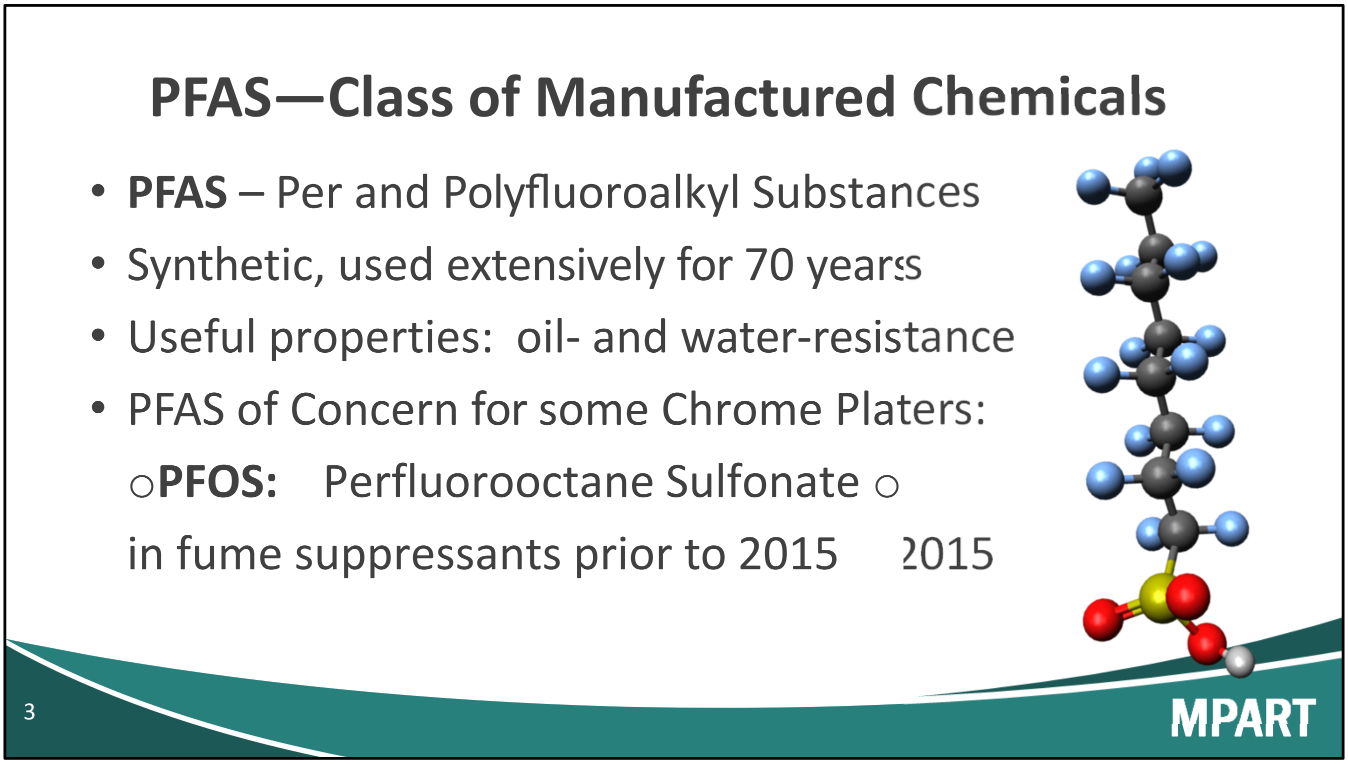


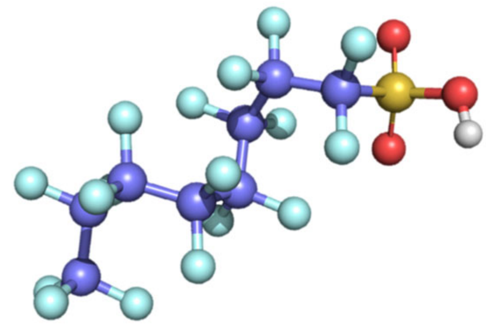
- Most of you are likely familiar with what PFAS are and why they are important, but we have a broad audience, so just to make sure that we're all on the same page,
- PFAS are a class of synthetic chemicals—not naturally occurring.
- We have used them extensively over the past 70 years
- Some have special properties—like being resistant to water and oil—that have made them very useful in manufacturing commercial products.
- They are **Emerging** pollutants: science about impacts and nature of chemicals is still being developed. There is a lot that we don't know yet.

PFAS of Concern in Michigan for surface waters:

- PFOS: Perfluorooctane Sulfonate &
- PFOA: Perfluorooctanoic acid

Why the Concern?

- Widespread
- Do not break down easily - hard to get rid of
- Bioaccumulative – build up in our bodies
- Some PFAS may affect health
- Lack of information
- Lack of standards



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We are concerned about PFAS for a number of reasons.
PFAS are widespread in the environment and don't break down easily. They bioaccumulate and

May build up in our body tissues and tissues of fish and other organisms

Studies, primarily with PFOA and PFOS, show health effects from ingestion such as

- Lower birth weight
- Immune system effects
- Liver and thyroid damage
- Kidney and Testicular cancer

Chrome Platers & the PFAS Story

- EPA lists hexavalent chromium as a known human carcinogen (inhalation pathway)
- National Emission Standards for Hazardous Air Pollutants (NESHAP) for Chromium Electroplating
  - **Fume** suppressants are effective at controlling hexavalent chromium emissions
  - Widespread use due to simplicity, cost and effectiveness
- PFAS concerns were raised to EPA subsequent to the NESHAP

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Kim Harris and Erin Newman, EPA Region 5 in Chicago, which covers six states including Michigan, have jointly worked on PFAS releases from chrome plating facilities since 2005. They will now discuss why fume suppressants are used in this sector, their 2009 study on fume suppressant use, and their work to phase out the use of PFOS in fume suppressants in 2012.

Many Current and Past Partners

- State of Minnesota
- Industry Representatives
- The National Association for Surface Finishing
- EPA's Office of Air Quality, Planning and Standards
- EPA's Office of Chemical Safety and Pollution Prevention
- EPA's Office of Water

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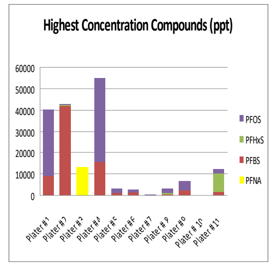
EPA R5 Fume Suppressant/Effluent Study

- In 2009, EPA conducted a chromium electroplating study to examine PFOS releases from effluent waters
- 11 plating facilities in Chicago and Cleveland were sampled for PFAS compounds
- PFAS was found to be released in the effluent of virtually all of the facilities sampled
- The study supported revision to chromium MACT standard phasing out **PFOS**-containing fume suppressants by 2015



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Kim Harris: EPA has been working on this issue for over a decade. In 2007, the state of Minnesota discovered high PFOS levels at a WWTP that was traced back to a chromium electroplater. The state questioned whether releases from chromium electroplating facilities could be a widespread source of PFOS in the environment or if this was just a localized event. So, we conducted a small study to examine whether PFOS may be getting into the effluent waters and discharging to wastewater treatment plants (WWTPs). We sampled 4 Chicago and 7 Cleveland platers for 13 PFAS analytes and found that yes, PFOS was routinely being released as well as analytes in the effluent of virtually all of the facilities tested.

Our study influenced OAQPS to revise the chromium MACT standard, essentially phasing-out PFOS-containing mist suppressants as an allowable treatment technology for chromium electroplaters. The phase-out was completed in Sept 2015.

EPA R5 Fume Suppressant/Effluent Study

EPA worked with EGLE to study PFAS releases from chrome platers/chromic acid etchers

- Subset inadvertently releasing PFOS into environment despite ban/phase-out
- PFOS-containing fume suppressants phased out in 2015
- New fume suppressants generally contain PFAS

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Kim Harris: So, fast forward to today – Region 5 is continuing to work on the plater issue. We thought we found a solution through the phase out but a subset of chromium electroplaters (chromic acid etch platers -
as known as the plating on plastics) are still releasing PFOS into the environment despite the phase-out.

As mentioned before, PFOS-containing mist suppressants phased-out completely by 2015; however, the newer products, while they are PFOS free, they are not PFAS-free and have a shorter-chained formulations

EGLE Water Quality Criteria for PFAS

- Michigan developed Rule 57 Human Noncancer Values (HNV) for PFOA (2011) and PFOS (2014) in surface waters

PFAS	HNV (nondrinking)	HNV (drinking)	FCV, ppt	FAV, ppt	AMV, ppt
PFOS	12	11	140,000	1,600,000	780,000
PFOA	12,000	420	880,000	15,000,000	7,700,000

Human Noncancer Values (HNVs); Aquatic Life Final Chronic Value (FCV), Final Acute Value (FAV), and Aquatic Maximum Value (AMV)

- PFOS builds up in fish tissue to a higher degree than PFOA

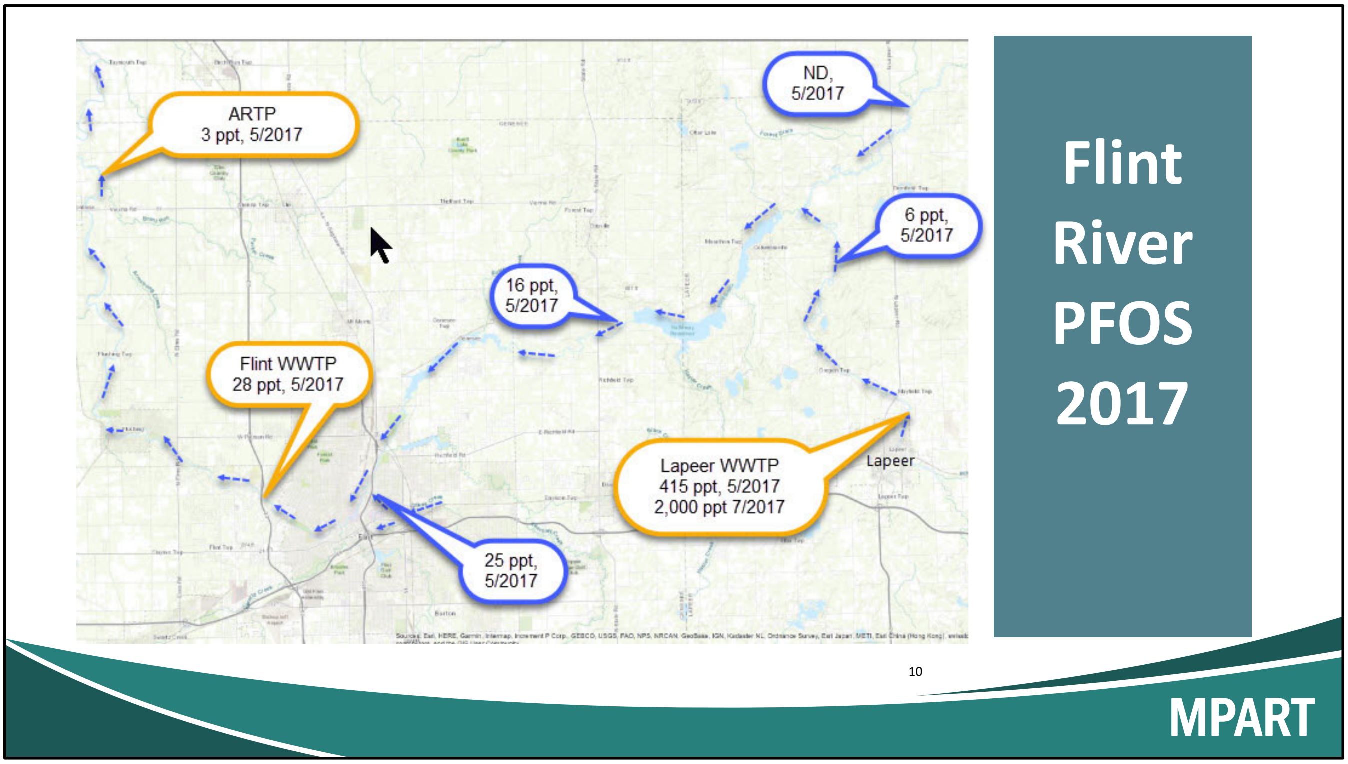
(Presentation Returns to Carla Davidson)

Michigan became involved in the PFAS story because we have water quality criteria for 2 PFAS--PFOS and PFOA-- (these are state standards developed in 2014 and 2011) which is why we focused on these pollutants.

This table shows various criteria that we use to develop our WQS. The criteria on the right are protective of aquatic life; those on the left are protective of humans eating the fish.

As you can see, criteria protecting humans are much more stringent that those protecting fish.

Surface water criteria are so low due to bio-accumulative nature of PFOS in fish.



In order to make sure that Michigan's surface waters were meeting the WQS, Michigan has studied PFAS in lakes and streams for a number of years.

- EGLE conducted surface water monitoring in May of 2017 to locate the source(s) of PFOS to the Flint River found in earlier statewide and targeted area sampling.
- Orange balloons here are WWTP effluent; blue balloons are surface water samples
- We sampled Lapeer WWTP's effluent along with Flint WWTP and the ARTP WWTP in May 2017
- Results of the 2017 monitoring identified elevated levels of PFOS in the effluent from the Lapeer WWTP

Source Identified

- Chrome plating facility using PFOS-free fume suppressants
- Discontinued use of PFOS-based fume suppressants in 2013

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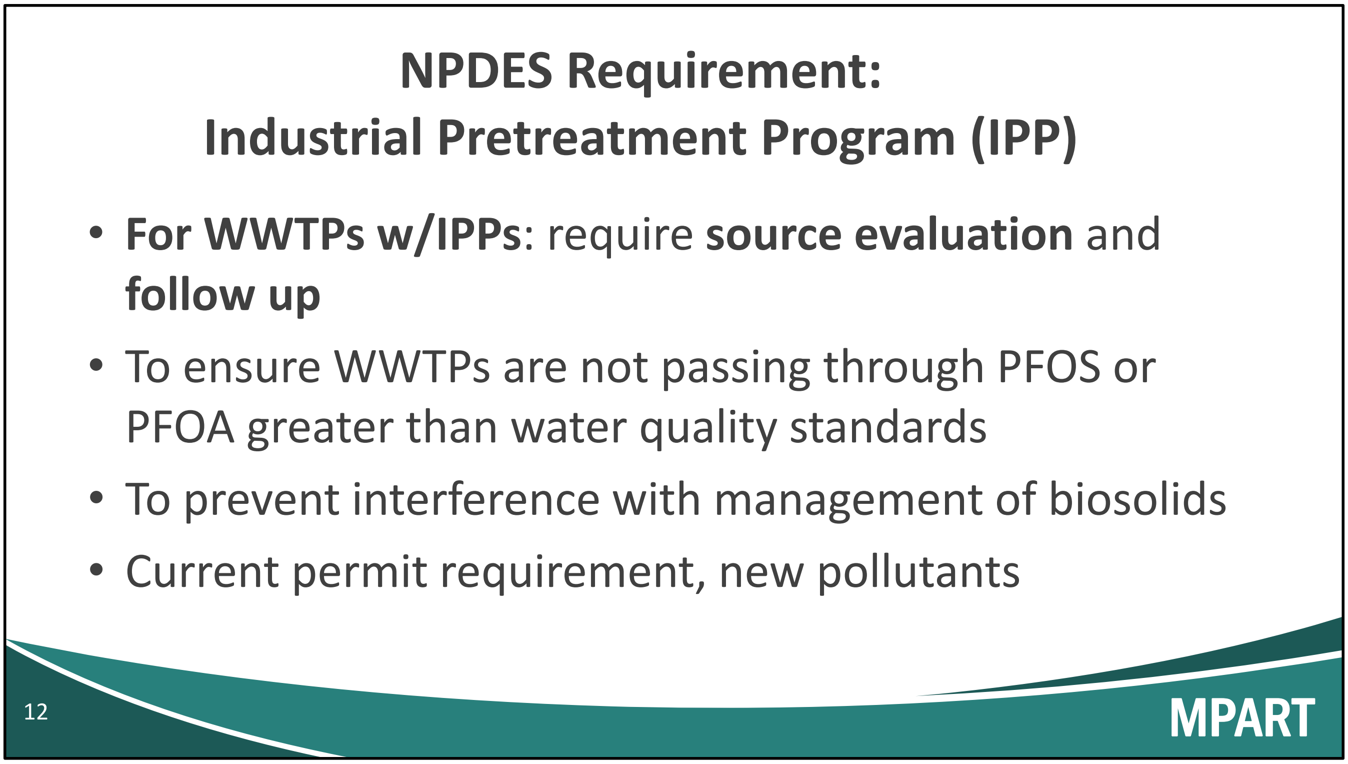
- July follow up Sampling data showed that the source to the WWTP was a metal finisher, a chrome plater
- Fume Suppressants were used by the plater to meet NESHAP air regulations and protect workers from hexavalent chromium fumes.
- This plater had discontinued use of PFOS-containing fume suppressants in 2013, 4 years prior to EGLE sampling and 2 years before they were required to under the air regulations.
- We were surprised to find that PFOS concentrations in the effluent were still so high. There was a question as to whether PFOS free demisters may change in the harsh environment of etch and plating tanks or if PFOS was still present in the PFOS-free products.
- We knew that there were many other metal finishers, including chrome platers, in Michigan and were concerned about other potential discharges of PFOS from these industries



Because of our concerns about other WWTPs potentially discharging PFOS, EGLE started the IPP PFAS Initiative in Michigan, using an existing regulatory program—the National Pollutant Discharge Elimination System or NPDES-- to address these new pollutants

- For WWTPs w/IPPs, we required source evaluation and follow up
- To ensure WWTPs do not **pass through** PFOS or PFOA greater than water quality standards to surface water
- Or accept PFOS or PFOA in quantities that interfere with the **management of biosolids**
- This is a current NPDES permit requirement, but for new pollutants

Sources of PFOS to WWTPs in Michigan

Industry/Category/Type	Total Number Evaluated *	Number (%) Sources of PFOS by Type**	Range Effluent PFOS exceeding screening level of 12 ppt
Solid Waste Landfills* **	57	**49** (86%)	20-5,000
Metal Finishing	320	**47**(15%)	20 to 240,000
• Chrome Plating	50	33 (66%)	24-240,000
• Chromate Conversion Coating	24	12 (50%)	16-9,950
Contaminated sites	40	**20** (50%)	14-34,000
Centralized Waste Treaters (CWTs)	17	**11** (65%)	13-8400
Paper manufacturing, packaging	14	**9** (64%)	16-410
Industrial laundry facilities	7	**5** (71%)	24-69
Chemical manufacturers	17	**4** (24%)	18-4,600,00
AFFF-contaminated sewers	2	**2** (100%)	240-45,000

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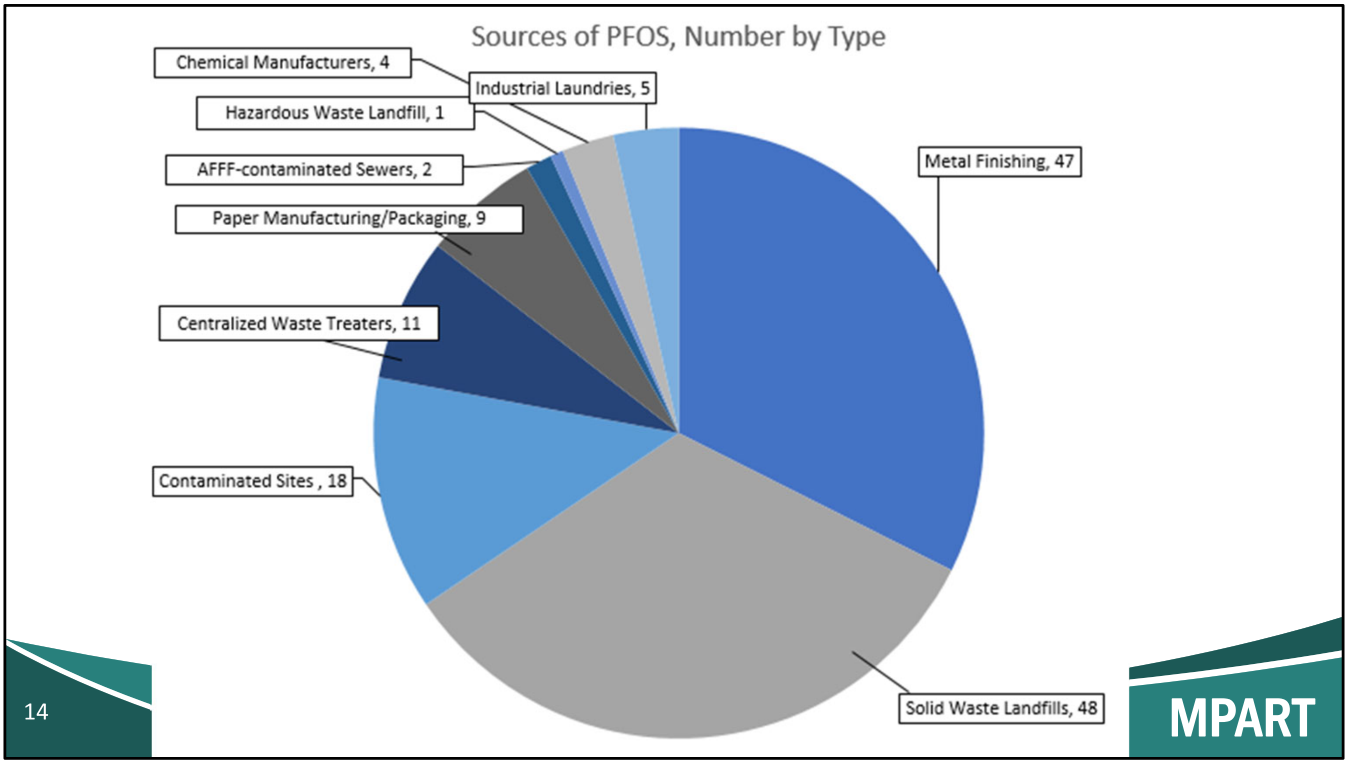
This Table shows our findings so far about sources of PFOS in Michigan—I want to let you know that through the IPP PFAS Initiative, we've found a number of sources of PFOS to WWTPs. We define sources as those having greater than 12 ppt PFOS in their effluent. You can see here that solid waste landfills, metal finishing, and contaminated sites were the most prevalent sources of PFOS found.

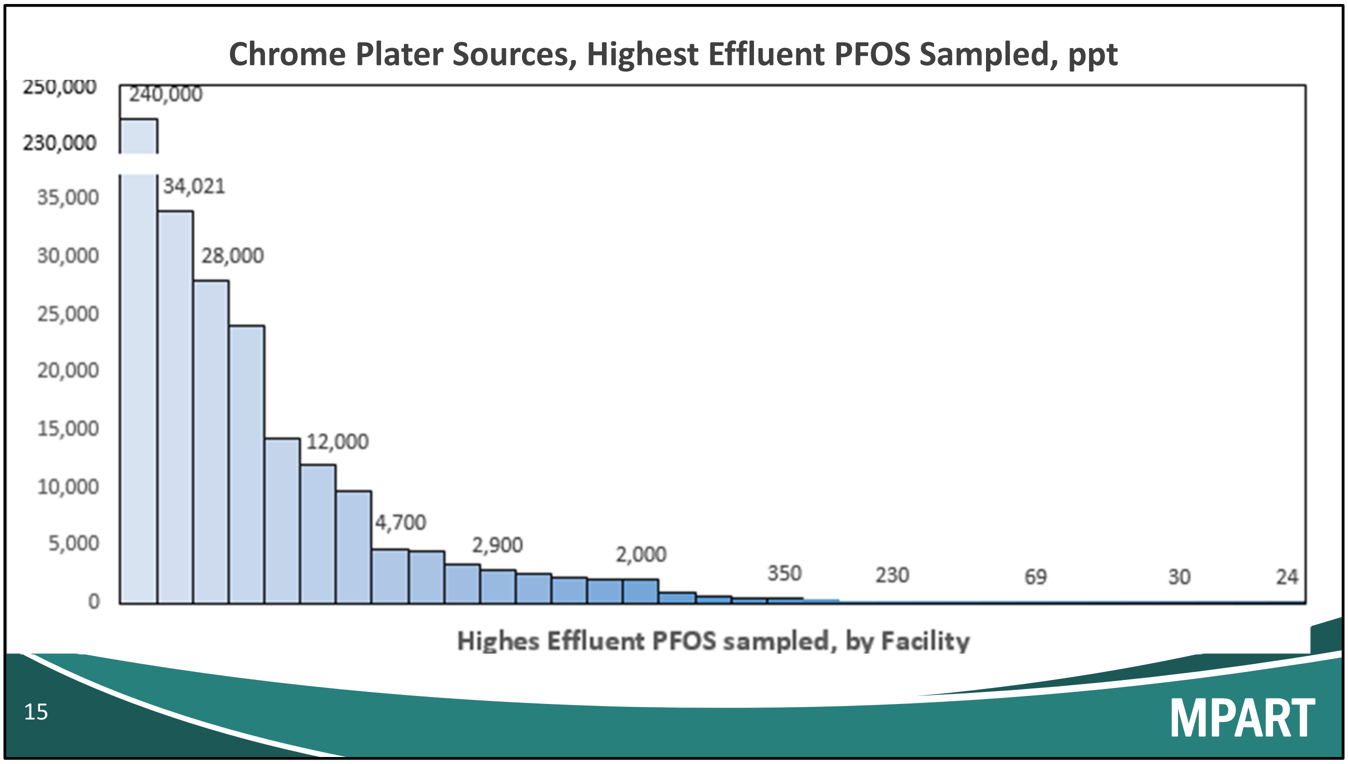
You can see from the column on the right that there was often a wide range of PFOS found in the effluent within these categories.

You can also see that only 15% of the metal finishers in Michigan were found to have PFOS above screening levels in their effluent.. with, 66% of Chrome Platers and 50% of facilities with a chromate conversion coating step that had levels of PFOS above screening levels.

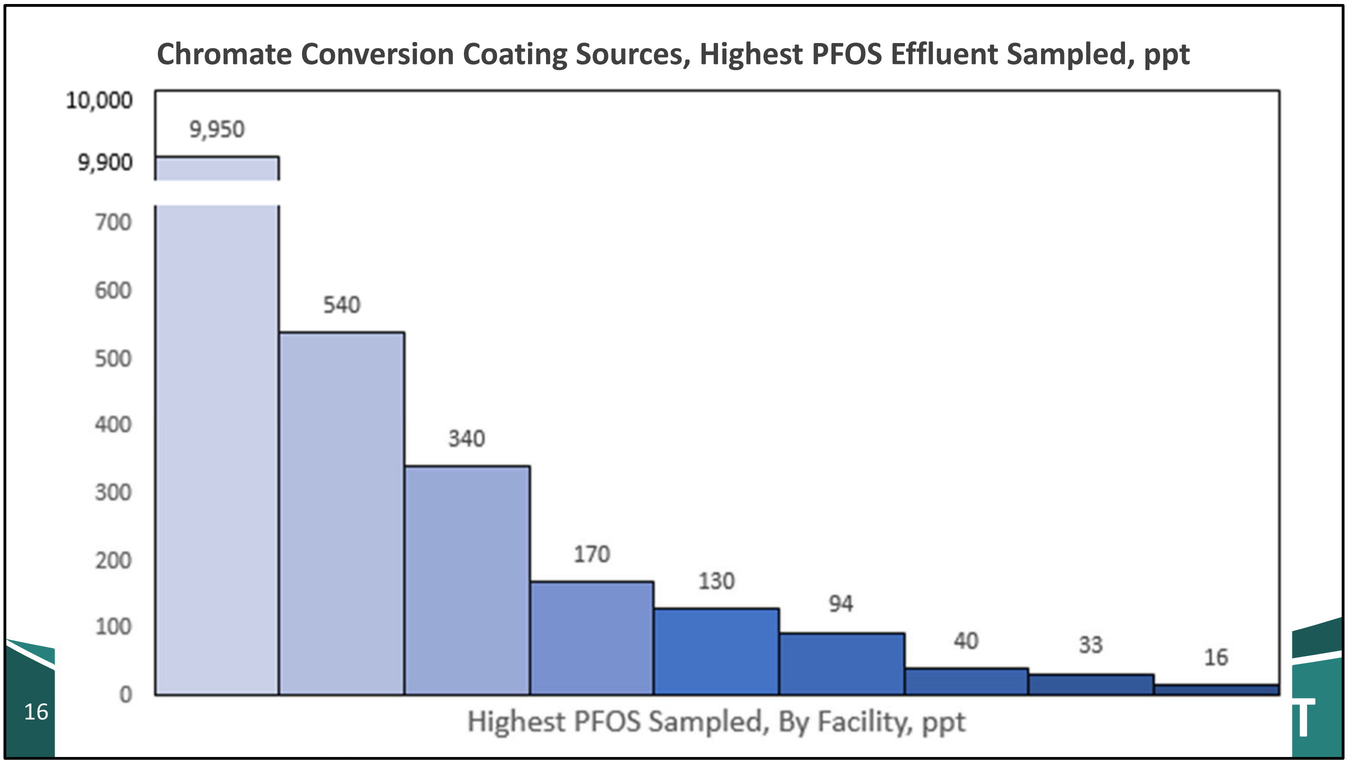
I should note that the number of facilities here are ***estimates*** based on a variety of information (surveys, interviews, reports) of industries that were evaluated and found to be sources of PFOS in Michigan, and the numbers are approximate. The numbers also apply only to Michigan, which of course does not have industries of every type.



This is another way of looking at the same data. Note that this chart looks only at number of sources of PFOS, but not concentrations of PFOS in effluent, loadings to WWTPs, or impacts on WWTPs or surface waters. As you can see, Metal finishers were some of the most prevalent sources of PFOS to WWTPs in Michigan.



Looking at the ranges of PFOS in chrome plater effluent for the platers exceeding screening levels, there is a large range of effluent concentrations. Not included here are those chrome platers (17 of 33) that had PFOS less than screening levels. Note these are the highest concentrations, prior to any pretreatment for PFAS.



To a lesser extent, some facilities that use a chromate conversion coating step were found to have PFOS, and they also had a large range of PFOS, although most were less than 1,000 ppt. This is again the highest effluent sampled, prior to any pretreatment for PFAS. Half of the chromate conversion coaters sampled (12 of 24) did not have PFOS greater than screening levels.

Purpose of Study

Is PFOS in chrome plater effluent linked to currently-used products?

- Analyze Fume Suppressants for PFAS
  - ➢Is PFOS present?
  - ➢Are precursors to PFOS present?
- Analyze Chrome Plater Effluent for PFAS (prior to any pretreatment for PFAS)
  - ➢Compare to Currently-Used Products

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The fume suppressant study was done to answer the question of whether PFOS in chrome plater effluent is linked to currently-used products

For the study, we Analyzed Fume Suppressants for PFAS

- To determine if PFOS was present or if
- precursors to PFOS were present—longer chains PFAS that could break down to PFOS
- EPA ORD also Analyze Chrome Plater Effluent for PFAS prior to any pretreatment for PFAS—over half had pretreatment already installed at the time of the sampling (July 2019)
- And compare PFAS found in currently-used products

Fume Suppressant Study Design

- Sample 11 chrome platers (some with chrome etching):
  - 11 effluent samples
  - 12 fume suppressant samples (9 different products, 3 replicates)
  - Includes a sister plant (newer) that never used PFOS-containing fume suppressant (but does use PFAS-containing product)
- Analyze with Targeted and Non-Targeted Analysis

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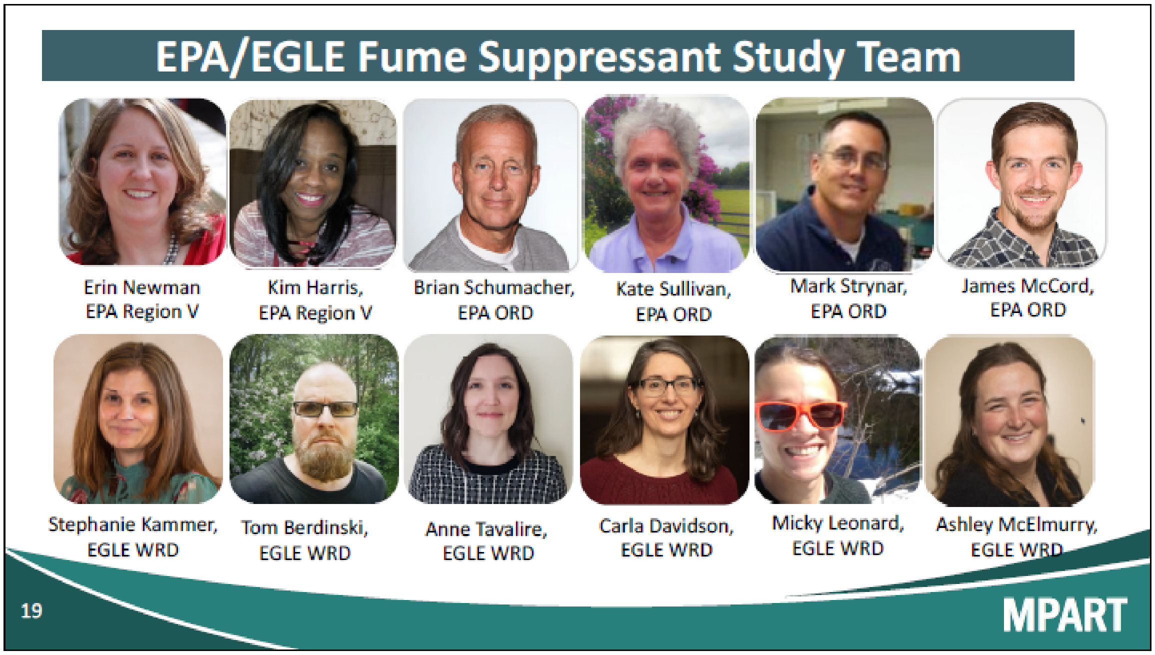
We reviewed data from the IPP PFAS initiative and developed a list of chrome platers that had been found to discharge PFOS in their wastewater and also currently used fume suppressants.

- We got approval from 11 chrome platers (voluntary study) to take sample of their effluent and fume suppressants. A couple of platers had FS that they had used previously, and we took samples of those FS as well.
- We ended up with 12 fume suppressant samples (9 different products, 3 replicates)
- Samples also included effluent from One sister plant (newer) and had never used PFOS-containing fume suppressant (but does use PFAS-containing product)
- Analyzed products and effluent with Targeted and Non-Targeted Analysis



The Study team:
Erin Newman, is a scientist with the EPA's Air Division. Kim Harris is a scientist with the Water Division and the Region 5 PFAS Coordinator. . The remainder of the EPA team work for the Office of Research and Development's Center for Environmental Measurement and Modeling. James McCord and Mark Strynar are chemists and are the principal investigators for this project. Kate Sullivan is the project coordinator. Brian Schumacher is the Director of the Ecosystems Processes Division.

EPA Region V requested technical assistance from EPA's Office of Research a & Development (ORD) to develop a plan and conduct the study for EGLE.
EGLE agreed to find plater effluent and fume suppressants to sample, take the samples (Micky Leonard and Ashley McElmurry with assists from Tom Berdinski, Anne Tavalire, and me) and ship the samples to ORD for analysis.
EPA ORD provided a technical report with interpretation of the data and communication of the findings left to EGLE.
EGLE recently posted a study report online that includes a summary of the findings along with the anonymized data reports from EPA

Types of Analysis

- **Targeted Analysis:** Reports exact quantities of specific "targeted" chemicals (24 MPART Minimum Analytes + GenX)

- **Non-Targeted Analysis:** more qualitative but can detect unanticipated chemicals and show relative abundance of various compounds

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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.

Non-targeted 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.

Approaches to Chemical Measurements

	Targeted	Screening	Discovery
Chemical Targets	Few, selected chemicals	100s – 100,000s per library	Any chemical
Method of Analysis	Focused method	Non-Targeted Method	Non-Targeted Method
Chemical Structure	Known	Known in library	Unknown
Reference Data	Available	Some, maybe simulated	Some, maybe simulated
Standards	Available	For common compounds	Unlikely

Complex, More Time-Consuming Analysis

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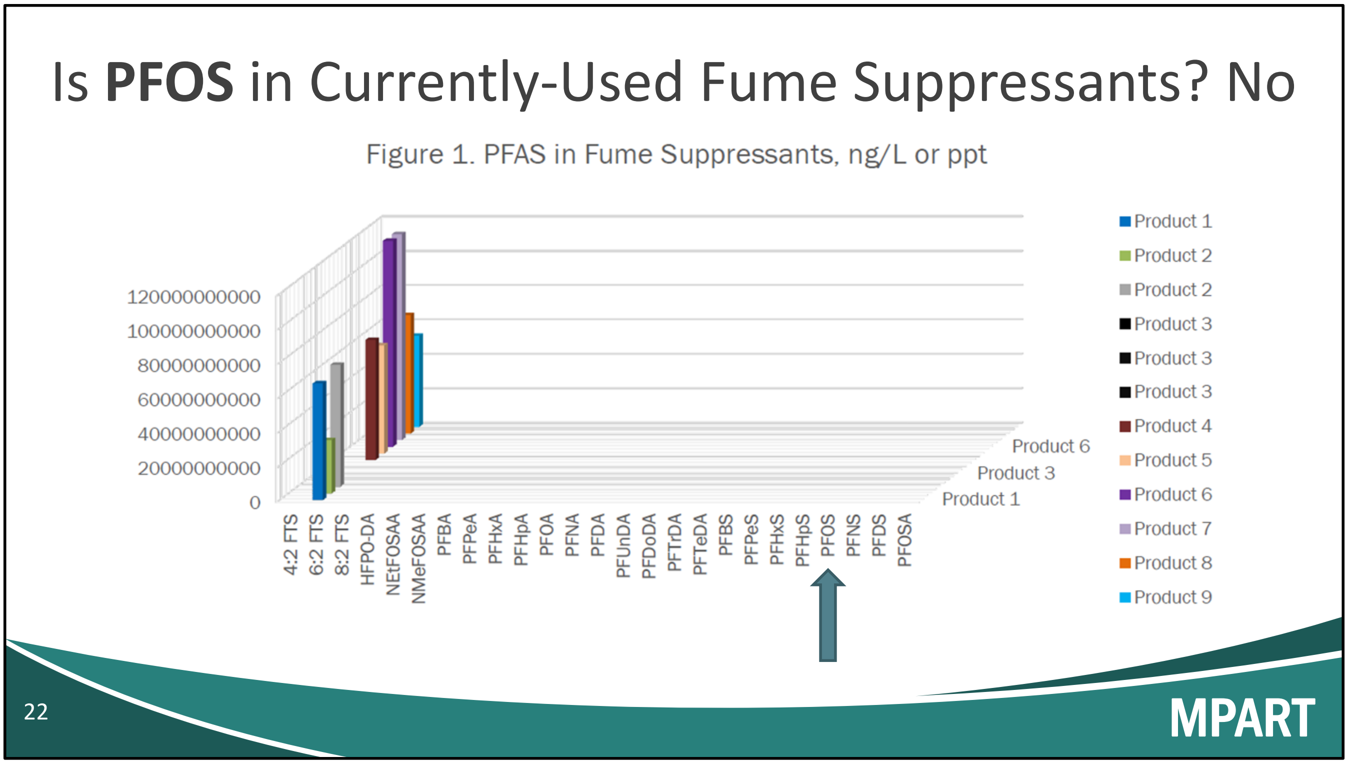


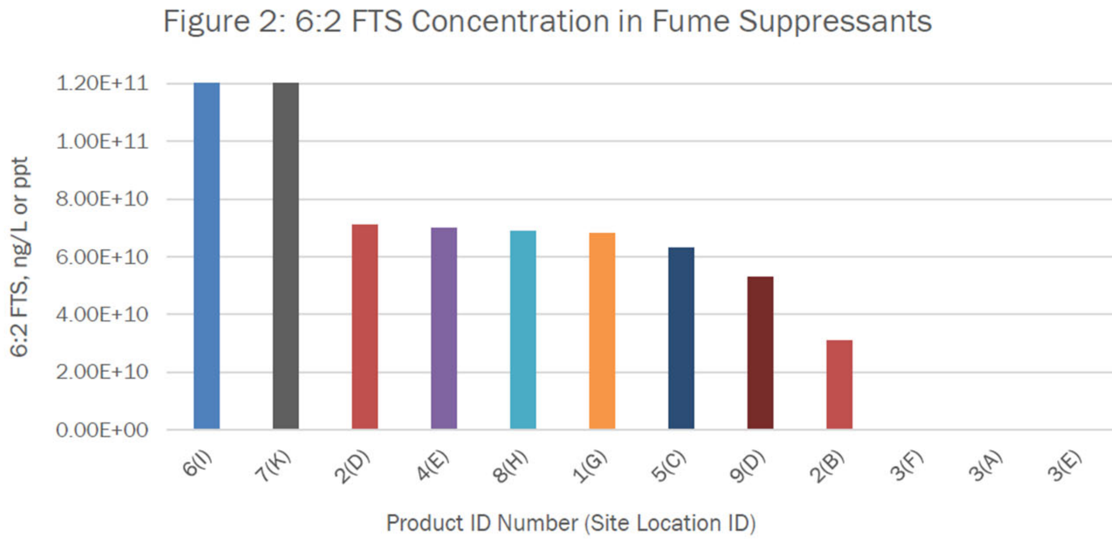
Results of targeted and NTA showed that No products contained PFOS.

8 of the 9 products included 6:2 FTS in the targeted analysis, which is shown here.

You can see here there is a lot of blank space, including column for PFOS, which is marked with an arrow.

One product contained no PFAS.

What PFAS are in Fume Suppressants? 6:2 FTS



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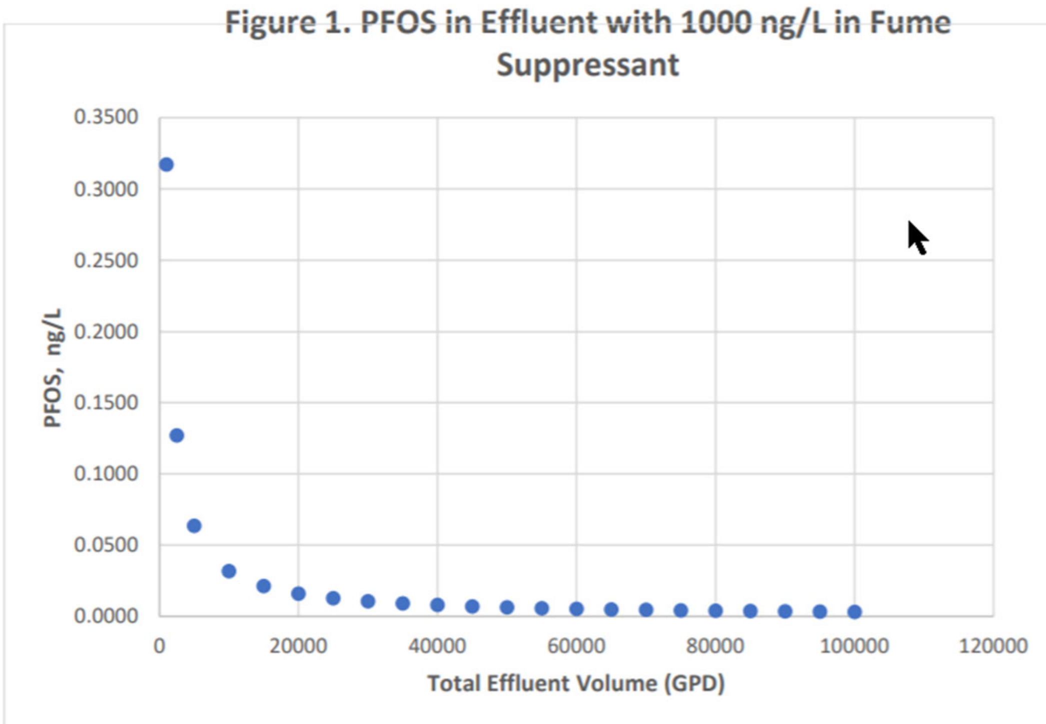
This chart shows the same data in a different way—this shows only the 6:2 FTS results.

It shows targeted analysis of 9 different products (same colors for each product-2 red for product 2; no bars for product 3)) with results for each sample location (plater).
One product used by 3 facilities has no 6:2 FTS so there are no bars.

6:4 FTS was also identified in the NTA, but in much lower abundance.

Product Analysis Reporting Limits



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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 500-10,000 times (see USEPA, ORD, Report #1, Table 3), the quantification level for analytes not detected, including PFOS, is less than 1,000 nanograms per liter (ng/L) or ppt

Given that 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.

Here, concentrations of PFOS in effluent are shown , theoretically, if 1000 ppt of PFOS were present in all current fume suppressant used by a facility and all FS were discharged along with the effluent/

You can see that <1 ng/l (ND) would be present in effluent even with effluent flow as low as 1000 GPD, which would be a very small discharge for a plater and wouldn't provide much dilution

We asked some participants how much FS they used in a day to develop this example.

Is 6:2 FTS (or 6:4 FTS) a PFOS precursor?

- Neither 6:2 FTS (or 6:4 FTS) are precursors to PFOS.
- Both are shorter-chain PFAS that cannot break down to the longer-chain PFOS.

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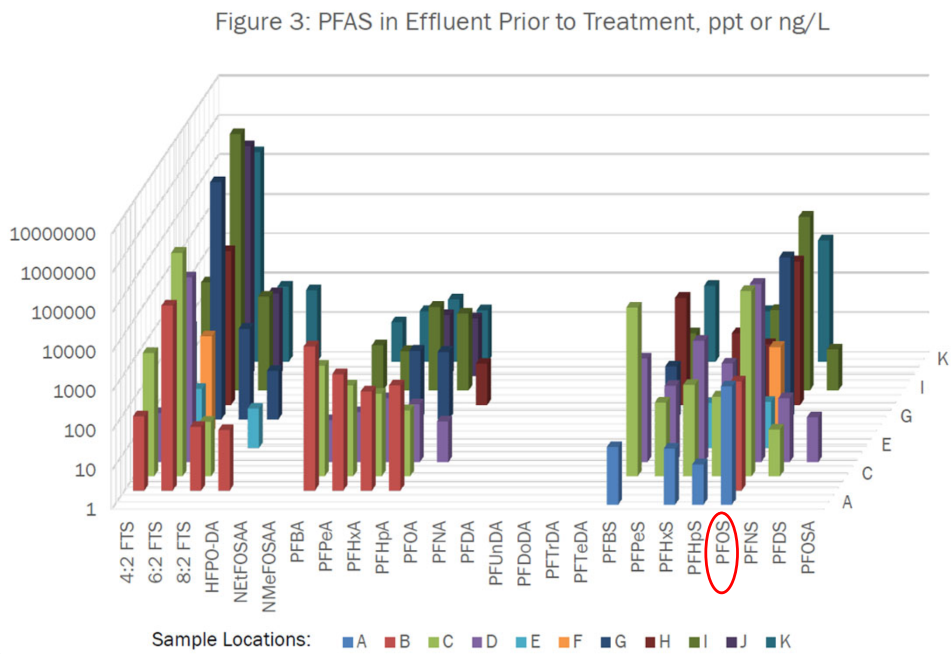
Neither 6:2 FTS (or 6:4 FTS) found in the currently-used fume suppressants are precursors to PFOS.

Both are shorter-chain PFAS that cannot break down to the longer-chain PFOS.

Which PFAS are in Chrome Plater Effluent?



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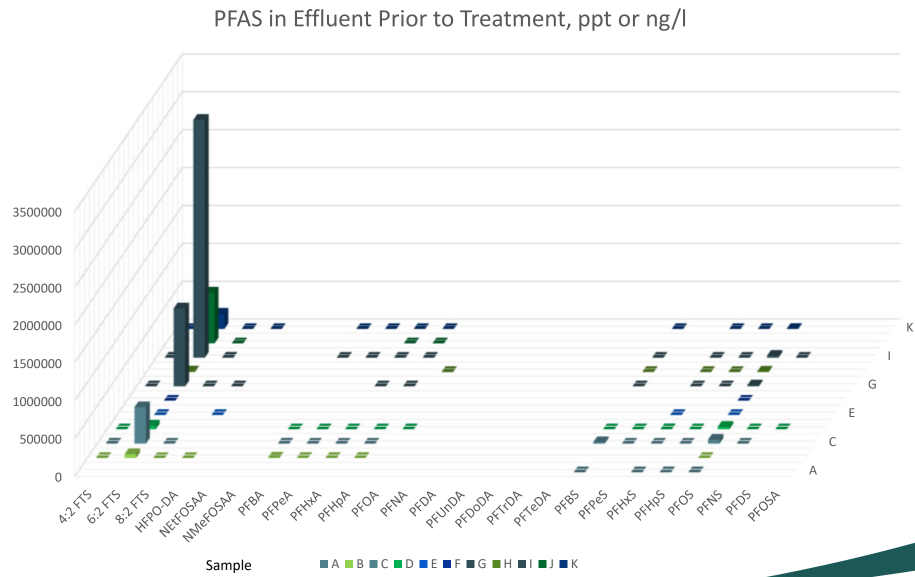
This chart shows PFAS found in chrome plater effluent prior to any PFAS pretreatment.

You can see here that the PFAS found in effluent are much more complex than those found in the products. Note—log scale; otherwise you'd primarily see 6:2 FTS;

PFOS (circled in red) was present in the effluent although it was not found in currently-used fume suppressants

Which PFAS are in Chrome Plater Effluent?



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These are the same effluent results in straight scale—6:2 FTS is the most abundant compound for most of the platers sampled, which makes sense since that is the chemical currently used by most of the platers. Note that 3 platers were not using a current product that contained 6:2 FTS or PFAS and had much lower concentrations of PFAS in their effluent. All of the plater effluent samples (taken prior to pretreatment for PFAS) contained PFAS.

PFAS in Effluent

- Most PFAS is 6:2 FTS, likely from current products (except at platers using Product 3)
- Are other PFAS in effluent breakdown products from **6:2 FTS**?
  - Beyond scope of this study
  - Terminal breakdown products are PFPeA, PFHxA, and 5:3 FTCA
  - Intermediates? Unclear

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- Most PFAS in effluent is 6:2 FTS, likely from current products (except at platers using Product 3)
- It is beyond the scope of this study whether other PFAS in effluent are breakdown products from 6:2 FTS.
- The Terminal breakdown products for 6:2 FTS are listed here (PFPeA, PFHxA, and 5:3 FTCA)
- Intermediates breakdown products are more complicated and also unclear since there are different breakdown pathways

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

Simplified Effluent Data

(prior to any PFAS pretreatment)

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-This slide is another look at the effluent data but simplified—you can see how much of the currently-used PFAS chemical, 6:2 FTS, is present in comparison with the PFOS residuals and other PFAS (grouped together).

-You can see the plant here (J) that never used PFOS-containing fume suppressants with ND PFOS in their effluent. (I should note that RLs for effluent are <10 ppt for NDs)

-We learned that there is nothing unexpected going on with the products—they are PFOS free (good news) and the hard work that the platers are doing to pretreat their effluent and clean/replace equipment and surfaces is worthwhile and what needs to be done. Some were fearing that their efforts were not working as expected because the replacement products had PFOS, but that doesn't appear to be the case—it's just very difficult to get rid of PFOS residuals at a facility.

-The bad news is that the only way out is through—simple product substitution *WAS* not and *IS* not enough to eliminate PFOS for chrome platers that used PFOS-containing chemicals. In many cases, cleaning will not be effective because of the large concentrations of PFOS formerly used—even if most of the product is cleaned from surfaces, there will still be enough residue left for plater effluent to exceed target levels.

-The other bad news is that 6:2 FTS is very similar to PFOS in structure and uses up carbon sites in treatment media. We don't know a lot about the non-PFAS product except that it contains complex hydrocarbons and fatty acids, which may be coconut oil. We don't know much yet about its impacts on product quality, carbon treatment media or air handling equipment.

Substantial Reductions in PFOS Concentrations at WWTPs

Municipal WWTP	PFOS, Effluent (ppt, most recent**)	PFOS Reduction in Effluent (highest to most recent)	Actions Taken to Reduce PFOS
Lapeer	8.4	99%	Treatment (GAC) at source (1)
Wixom	18*	99%	Treatment (GAC) at source (1)
Ionia	<7.5	99%	Treatment (GAC) at source (1)
Port Huron	13*	99%	Source control/reduction at source
Howell	4.3	97%	Treatment (GAC/resin) at source (1)
Bronson	6.9	95%	Treatment (GAC) at source (1)
Kalamazoo	3.1	92%	Treatment (GAC) at sources (2), change water supply
K I Sawyer	13*	95%	Eliminate leak AFFF, some cleaning
GLWA (Detroit)	30*	23%	Treatment (GAC) at sources (9)
Belding	7.2	49%	Restricted landfill leachate quantity accepted

*Greater than Water Quality Standards **Data received/processed as of April 30, 2020

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The IPP PFAS Initiative has been a success with significant reductions in PFOS discharged from WWTPs— a number of WWTPs have had significant reductions in their effluent—8 WWTPs with over 90% reduction, primarily due to the installation of pretreatment at sources.

6 of the top 7 WWTPs on this list had a single source (all chrome platers) and when PFOS pretreatment was installed, the PFOS in their effluent was reduced substantially. The efforts of the plating industry have made a difference in water quality in Michigan and that we appreciate their cooperation.

Summary

- No currently-used fume suppressants contained PFOS or PFOS precursors
- PFOS found in untreated effluent is likely due to historical use and the nature of "forever chemicals"
- Currently-used fume suppressants may contain other PFAS compounds, primarily 6:2 FTS

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To summarize

- No currently-used fume suppressants contained PFOS
- No currently-used fume suppressants contained PFOS precursors
- PFOS found in untreated effluent is likely due to historical use and the nature of "forever chemicals"
- Currently-used fume suppressants may contain other PFAS compounds, primarily 6:2 FTS—8 of the 9 products sampled in the study used 6:2 FTS

PFAS Reports & Information

- EPA/EGLE Fume Suppressant Study Report
- Summary Report, Municipal Wastewater and Biosolids/Sludge & PFAS
- MPART Wastewater Treatment Plants/Industrial Pretreatment
- Industrial Pretreatment Program PFAS Initiative

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- EPA/EGLE Fume Suppressant Study Report
- Summary Report, Municipal Wastewater and Biosolids/Sludge & PFAS
- MPART Wastewater Treatment Plants/Industrial Pretreatment
- Industrial Pretreatment Program PFAS Initiative

EPA/EGLE Fume Suppressant Study Panelists


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