PER- AND POLYFLUORINATED ALKYL SUBSTANCES (PFAS) CYCLING WITHIN MICHIGAN: CONNECTIONS BETWEEN CONTAMINATED SITES, LANDFILLS, AND WASTEWATER TREATMENT PLANTS

by

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The disposal and treatment of Per- and Polyfluorinated Alkyl Substances (PFAS) contaminated solid and liquid wastes, and associated cycling within the natural and engineered environment is a complex topic. PFAS data on contaminated sites, landfill leachates, the influent, effluent, and biosolids from wastewater treatment plants (WWTPs) within Michigan were compiled from publicly available and private sources. Most of the datasets are based on a 28-analyte suite generated using a modified form of the US EPA 537 analytical method, with a subset of data from the 18-analyte ASTM D7979-19 method. Approximately 70% of the 171 contaminated sites in Michigan have maximum groundwater concentrations less than 2000 ppt. Analysis of these sites by source release indicate that four dominant PFAS sources – landfills, aqueous film forming foams (AFFF), metal platers, and automotive/metal stamping – account for 75% of the contamination. Diverse chemical signatures were observed for leachates collected from 19 landfills (mostly type II municipal) with the dominant PFAS being PFOA and PFOS, as well as shorter-chained compounds (e.g., PFHxA, PFBA, and PFBS). Analysis of PFAS carbon chain length as a function of landfill age shows the transition of C8s in leachate from older landfills to C4s and C6s in younger landfills, consistent with the voluntary phasing out and

replacement of C8s. PFAS mass flux in leachate for the landfills studied range between 5 – 2,000 g/yr and were highest for active landfills which generate greater leachate volumes and contain fresh PFAS wastes. Detailed study of 10 WWTPs with industrial pretreatment programs indicate numerous chemical transformations across the plants that yield PFAS effluent concentrations that are significantly (up to 19 times) greater than influent concentrations. These ‘apparent’ increases in total PFAS are attributed to transformations of undetected polyfluorinated precursors in the influent to stable perfluorinated compounds detected in the effluent. Perfluorinated compounds – PFOA, PFHxA, PFPeA, PFBA, and PFBS – show the greatest across the plant changes with increases ranging from 20% to nearly 2,000%. PFOS concentrations decreased across 6 WWTPs, consistent with the strong tendency to accumulate in biosolids. Estimated mass flux rates from the WWTPs to receiving water bodies of generally unregulated PFAS range from 40 g/yr to 128 kg/yr.

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1. Introduction

Per- and polyfluoroalkyl substances (PFAS) consist of a group of over 5,000 manmade aliphatic compounds that contain at least one carbon-fluorine (C-F) bond (Buck et al., 2011; Hamid et al., 2018; ITRC, 2020). The C-F bond is one of the strongest bonds in nature (O'Hagan, 2008) and is responsible for the high resistance of PFAS (particularly the perfluorinated compounds where carbon atoms are fully fluorinated) to all natural forms of degradation, (i.e., biological, chemical, and physical) (3M 2000; USEPA 2008; Hamid et al., 2018; Schulz et al., 2003). This environmental recalcitrance has led the PFAS family to be referred to as "forever chemicals" (Miner et al., 2021; Prevedouros et al., 2006). PFAS are known to cause adverse health impacts at parts per trillion concentrations and accumulate in humans and animals primarily through ingestion (Chou et al. 2019; Kennedy et al., 2004; Shin et al., 2011; Sunderland et al., 2019; Trudel et al., 2008). Once released into the natural environment, PFAS bioaccumulate in ecosystems and the food web (Conder et al., 2008; Furdui et al., 2007; Martin et al., 2004).

PFAS is a broad term that encompasses many individual compounds that can be further categorized into several groups based on molecular structure (Buck et al., 2011). The first division is typically polymers and nonpolymers. Polymers include fluoropolymers, perfluoropolyethers, and side chain fluorinated polymers (Buck et al., 2011). Nonpolymers are comprised of perfluoroalkyl substances, which are fully fluorinated and stable, and polyfluoralkyl substances, which have a hydrogen or oxygen atom attached to at least one carbon in the compound making it partially fluorinated, increasing the chances to transform into more terminal perfluoroalkyl acids (Buck et al., 2011). Perfluoroalkyl substances include perfluoroalkyl acids (PFAAs), most notably perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). Perfluorocarboxylates are known to be produced as biodegradation products of fluorotelomer alcohols (FTOHs) in the activated sludge process (Wang et al., 2017). Polyfluoroalkyl substances include fluorotelomer sulfonic acids (FTSAs), fluorotelomer carboxylic acids (FTCAs), (FTOHs), perfluoroalkane sulfonamido ethanols (FASEs), perfluoroalkane sulfonamide (FASA), and perfluoroalkane sulfonamido acetic acids (FASAAs) (De Silva et al., 2021). While PFAAs have received the greatest amount of attention and are overrepresented in analytical suites used to quantify PFAS concentrations in biosolids, biota, drinking water, and wastewater, polyfluorinated compounds make up a majority of PFAS in the world today (Wang et al., 2017).

Functionally, PFAS are surfactants, with a water-soluble (hydrophilic) head and water repellant (hydrophobic) tail, giving them water, grease, and stain-resistant properties making them widely utilized in manufacturing (Beecher, 2019; Hekster et al., 2003; KEMI, 2015; Schultz et al., 2003). Many consumer products contain PFAS including cosmetics, fast food wrappers, herbicides, nonstick cookware, personal hygiene products, pesticides, stain-resistant carpet, waterproof clothing, waxes, and wetting agents (Chou et al., 2019; Houtz et al., 2013; Kissa 2001; Kotthoff et al., 2015; Whitehead et al., 2021). PFAS also have a high resistance to thermal degradation, making them ideal for aqueous film forming foams (AFFF) used to suppress petroleum-based fires at public and private airports and military installations worldwide (Dean et al., 2020).

PFAS have been produced since the 1940s (Dean et al., 2020), and have been detected worldwide, including remote areas such as Antarctica and the Arctic (Butt et al., 2011; Miner et al., 2021). PFAS are released to the environment via disposal of liquid and solid wastes, leaching from landfills, wastewater treatment plants (WWTPs), use of AFFFs at public and private airports, military bases, refineries, tank farms fire stations, and direct release from manufacturing and industrial processes. Production and use of long chain (≥ 8 carbons) PFAS was voluntarily halted in the mid-2000s in North America, Europe, and Australia due to environmental concerns and replaced with shorter chain compounds (Dean et al., 2020). For example, PFBS (C4) is a short chain replacement for PFOS (C8) (USEPA, 2020). Recent studies indicate that short chain PFAS replacements are also persistent and have adverse human and environmental effects (Cousins et al., 2016; Kotlarz et al., 2020; Scheringer et al., 2014). Buck et al. (2011) states that “replacement” perfluoroalkyl carboxylic acids contain less than seven carbons and “replacement: perfluoroalkyl sulfonic acids contain less than six carbons. For the purpose of this study, PFAS with eight or more compounds are considered long chain and PFAS with less than eight are considered short chain. Although equally recalcitrant, short chained PFAS are less sorptive, more mobile, and less bioaccumulative in the environment than legacy C8 compounds (Buck et al., 2011; Chow et al., 2021).

The recalcitrance of PFAS leads to complex cycling within the atmosphere, biosphere, geosphere, and hydrosphere. Figure 1 depicts the life cycle and shows the movement of PFAS in natural and engineered systems, and proper management of PFAS requires that mass fluxes of PFAS between these systems be quantified.

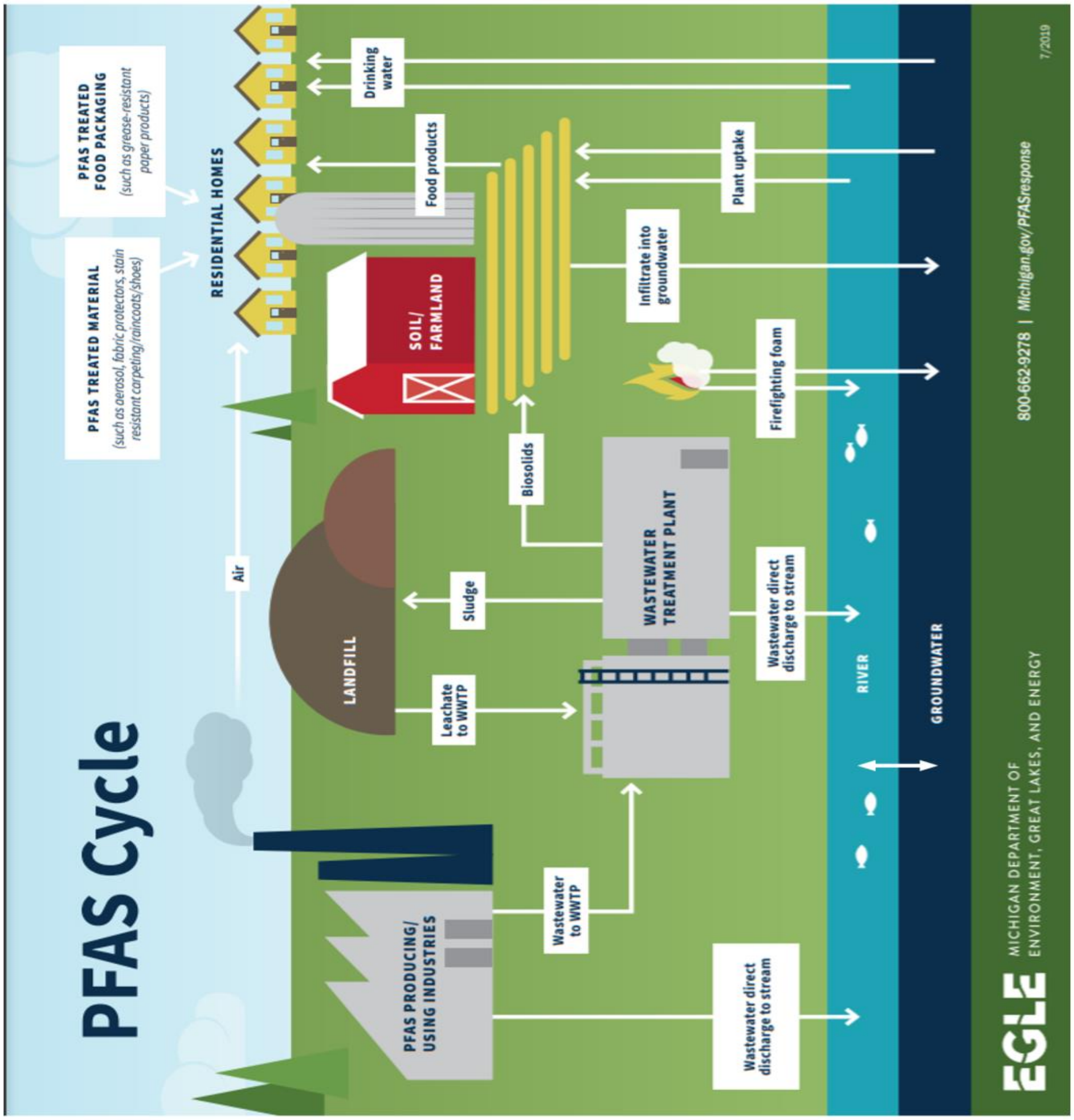

Figure 1. PFAS life cycle diagram developed by the Michigan Department of Environment, Great Lakes, and Energy (EGLE, 2021b)

Monitoring concentrations and composition of PFAS in engineered systems (e.g., landfills, WWTPs) is powerful tool for identifying sources of PFAS release to the environment. Releases of PFAS from different industries and fire training/suppression activities can be identified, even distinguished, by monitoring PFAS concentrations and compositions in WWTPs and landfills receiving these waste streams or downgradient from these sources. Currently no treatment of drinking water, wastewater, leachate, and other waste streams effectively removes all PFAS (e.g., granular activated carbon (GAC), reverse osmosis, ion exchange). These treatments concentrate rather than destroy PFAS and residuals must be disposed of in landfills or other natural or engineered systems that will increasingly become PFAS repositories. As a result, the mass fluxes of PFAS between some compartments in Figure 1 are likely to increase and require monitoring to properly manage PFAS contamination. All landfills receive solid waste containing PFAS from a variety of sources, including consumer products wastes from contaminated sites (e.g., soils, sludges, wastewaters) and residuals from treatment of PFAS-contaminated waste streams (e.g., spent activated carbon, spent ion exchange resins, reverse osmosis reject), industrial wastes, and biosolids and activated sludge from wastewater treatment. Many household products (e.g., clothing, fast food wrappers, furniture, microwave popcorn packaging, non-stick cookware, and waterproof and stainproof carpet, and other textiles) contain PFAS (Gallen et al., 2018; Mahinroosta et al., 2020; Ross et al., 2018). As solids in landfills decompose, PFAS and other contaminants become available to partition to the aqueous phase as leachate. In older landfills and legacy dump sites that are unlined, leachate enters groundwater and contaminates nearby household and public wells and/or is discharged to surface water (Hepburn et al., 2019). Modern landfills are designed to capture leachate using impermeable liners and leachate collection systems to reduce groundwater contamination (Hamid et al., 2018; Lema et al., 1998; Renou et al., 2008). Leachate is either treated onsite or discharged to a WWTP under a National Pollution Discharge Elimination System (NPDES) permit (Renou et al., 2008), using either sewers or tanker trucks.

Landfills serve as a repository for PFAS and as such will be a long-term secondary source of PFAS to the environment for decades to come (Allred et al., 2015; Hamid et al., 2018; Robey et al., 2020). Since C8s (PFOA and PFOS) began to be replaced with shorter chain PFAS, such as C6s (e.g., PFHxA, PFHxS) and C4s (e.g., PFBA, PFBS) (Benskin et al., 2012) these shorter chain PFAAs have become more abundant in landfill leachate. Shorter chain PFAAs are also more water soluble than long chain PFAAs and have a lower tendency to partition to solid phase due to their higher solubility (Benskin et al., 2012). Despite the shift towards shorter chained compounds, PFOA and PFOS are still abundant in recent landfill leachate samples, particularly in older landfills. Leachate volumes and PFAS concentrations depend on climate, leachate management, waste composition, and age (Hamid et al., 2018). Wet climates can lead to higher PFAS concentration in leachate than semi-arid and arid climates as precipitation is a driving factor in leaching (Lang et al., 2017).

WWTPs accept and treat liquid waste from a variety of contributors including domestic, commercial, and industrial sources. While wastewater streams from commercial and industrial sources can be more concentrated with PFAS, domestic wastewater streams also commonly contain PFAS due to its prevalence in household products (Gallen et al., 2018) Landfill leachate often represents a concentrated wastewater stream of PFAS; however, these concentrations often become diluted at WWTPs due to overall influent volumes (MWRA, 2019). Dilution may be favorable for environmental regulations, which are concentration based, but does not affect overall mass balance of PFAS through a WWTP. WWTPs are not equipped to treat PFAS and instead rely on source reduction, which can include industrial pretreatment. PFAS typically pass through a WWTP untreated and are then discharged with the effluent to surface water, or in some cases, to a rapid infiltration basin. As a result, WWTPs are a major contributor of PFAS to surface water (Ahrens et al., 2009; Sinclair and Kannan, 2006). Groundwater recharged by rapid infiltration basins has shown levels of PFAS exceeding MCLs (EGLE, 2021c). Similar contamination may occur via septic systems in more rural settings.

Recent sampling indicates that WWTPs can have lower concentrations of PFAS in the influent than effluent due to transformation of polyfluorinated precursors into more stable terminal PFAA during the wastewater treatment process (Hamid, 2018; Houtz et al., 2013). PFAA concentrations have been shown to increase during aerobic and anaerobic digestion (Guerra et al., 2014). WWTPs produce a byproduct sludge called activated sludge or biosolids, which consist of microorganisms that grow on and treat biodegradable compounds in wastewater. These solids must be separated from the liquid effluent before being discharged, and are typically treated by incineration, landfilling, or land application as fertilizer and soil amendment (MWRA, 2019). In Michigan, the term biosolids refers specifically to activated sludge that has been treated (usually with lime or similar products) to kill pathogenic bacteria to ensure its safety for land application (EGLE, 2021a). Because PFAS have a natural tendency to partition onto microorganisms, WWTPs also generate a solid PFAS-contaminated waste stream. When PFAS-contaminated biosolids or active sludge are landfilled, PFAS leach out of the biosolids, and the leachate either discharges to a WWTP or contaminates groundwater and/or surface water, thus perpetuating the PFAS cycle shown in Figure 1. The PFAS cycle is also perpetuated if PFAS-contaminated biosolids are land applied, as the PFAS then leach into groundwater.

Biosolids from WWTPs are often land applied to fields to provide plant-available nutrients, (e.g., nitrogen and phosphorus) and also serve as an organic amendment to improve soil fertility (Beecher, 2019). Spreading PFAS-contaminated biosolids can contaminate soil, crops, surface water, and groundwater (Lindstrom et al., 2011; Sepulvado et al., 2011). The Michigan Department of Environment, Great Lakes, and Energy (EGLE) considers 20 µg/kg to be typical for non-industrially impacted biosolids and 150 µg/kg to be the threshold for industrially impacted WWTP biosolids (EGLE, 2021a). Biosolids between 20 and 150 µg/kg may still be land applied in Michigan at a reduced rate of 1.5 dry tons/acre-year as long as a source reduction plan is developed (EGLE, 2021a). If the PFOS concentration is greater than 150 µg/kg biosolids must be disposed of using a method other than land application (incineration or landfilling). Incineration of sludge can greatly decline (2 to 10 fold) the PFAS concentration in solid waste (Loganathan et al., 2007). Polyfluoroalkyl substances from biosolids, which degrade much more readily than perfluorinated substances, have been shown to biodegrade and result in plant uptake (Hamid, 2016; Zhang et al., 2021). In the U.S., around 60% of biosolids are applied to soils (Beecher, 2019). In Michigan, the majority of land applied biosolids are injected into the soil which drives soils to serve as a long term source of PFAS (Shin et al., 2011; Weber et al., 2017). At Stoneridge Farm in Maine, cow milk was found to contain PFAS. The farm received paper mill residuals as well as land applied municipal biosolids as fertilizers from the early 1980s to 2004. In 2016 and 2017, Stoneridge Farm sampled its surface water, milk, feed, and manure. The milk had a concentration of 1,420 ppt PFOS which was well above Maine's Department of Agriculture action level for milk of 210 ppt and well above the current EPA health advisory level for drinking water of 70 ppt for combined [PFOA]+[PFOS]. PFOS contaminated hay grown on the farm that was fed to cows resulting in elevated PFOS levels in milk (Beecher, 2019). A soil sample taken from the farm had a PFOS concentration of 878 ppb. Beecher (2019) estimated that PFOS concentrations in the land-applied biosolids would have been 67,000 ppb.

Aqueous Film Forming Foams (AFFF) have been used for fire suppression of high temperature hydrocarbon fuel fires at airports and military bases since the 1960s (ITRC, 2018). The foam is also used at oil refineries, fire departments, and chemical plants that contain flammable materials. PFAS released to the environment from AFFF occurs during periodic training, actual fires, and from spills or leaks. AFFF has an aqueous layer that suffocates the fire and remains after it is sprayed to protect against reignition (ITRC, 2018). PFAS is used in the foam to lower the surface tension at the air foam interface (Moody and Field, 2000) and their resistance to thermal degradation make PFAS the ideal surfactants for use in AFFF. Three distinct types of AFFF have been manufactured over the years. The first-generation AFFF contains mostly PFOS and PFHxS and some PFOA. This foam was used until the early 1970s although it is still commonly stored and used in many locations. The second-generation AFFF was used from the 1970s until the mid 2010s. It is comprised of precursors created during the

ECF production process (Backe et al., 2013). The most recent, third-generation AFFF contains no PFOS or precursors that can break down into PFOS and is comprised mostly of 6:2 and 4:2 FTS compounds (Wang et al., 2013). The degradation product of 6:2 FTS is PFHxA (Weiner et al., 2013) which is even more mobile in the environment than PFOS due to its higher solubility and lower tendency to adsorb to solids (Vierke et al., 2013), although PFHxA has been found to be less toxic than PFOS and PFOA (Klaunig et al., 2015). Although the first- and second-generation foams have been discontinued, they are still in use and/or being stored at some facilities. When AFFF is sprayed, PFAS infiltrate to contaminate groundwater and can also contaminate nearby surface water via runoff although in some cases runoff is captured and discharged to WWTPs.

Groundwater contamination from PFAS may result from a variety of sources including leachate from legacy landfills and dump sites, releases from industrial sites, septic systems, leaking sewer lines, biosolids and WWTP effluent where groundwater-surface water connections are present. PFAS plumes can migrate through the subsurface and contaminate sources of private and municipal drinking water. Contaminated groundwater may also discharge into surface water in gaining streams or lakes where the groundwater is infiltrating through the subsurface into the water body. Due to their hydrophobic and hydrophilic properties, some PFAS, such as PFOS and PFOA, have the tendency to accumulate along air-water interfaces (Brusseau, 2018). In some areas in Michigan, turbulent flows within a river current or wind currents across a lake can promote the formation of surface water foams that can contain extremely high levels of PFAS (EGLE, 2020c). There are currently seven surface water bodies in Michigan with observations of foam (EGLE, 2020c).

EPA (2021) reports that PFAS can be transported through air and precipitation. PFAS has been detected in habited and uninhabited environments around the world such as the Arctic and Antarctic (Bengtson et al., 2010; Butt et al., 2011; Kwok et al., 2010). A study conducted in Ohio, Indiana, and Wyoming, sampled for 10 PFAS and had detections in all 54 rainwater samples collected (Pike et al., 2021). PFOA and PFOS concentrations were similar to previous studies whereas PFBA and GenX had higher concentrations than previous studies. Rainwater has higher detections of short chain compounds due to their higher solubility in water than long chain compounds (Pike et al., 2021).

Biota, including plants and animals, can become contaminated with PFAS from contaminated groundwater and surface water. Some PFAS, such as PFOS, tend bioaccumulate and biomagnify within ecosystems (Conder et al., 2008). Fish tissue sampled from Clark's Marsh and Huron River in Michigan commonly had PFOS concentrations in hundreds to thousands of parts per billion, approximately 2-4 orders of magnitude higher than measured surface water concentrations. A Michigan Department of Health and Human Services (MDHHS) study sampled a deer from Clarks Marsh with a PFOS concentration of 547 ppb which exceeded the 300 ppb recommended action level for human consumption (MDHHS, 2018).

The objective of this study is to focus on the cycling of PFAS within the engineered and natural environment through intensive study of contaminated sites, landfill leachate, wastewater treatment plant influent, effluent, and biosolids. Due to proactive, state-wide regulatory standards, Michigan has developed one of the best PFAS datasets in the world for this purpose. Several studies in the literature have provided in-depth reviews of PFAS for a subset of WWTPs and landfills (Benskin et al., 2012; Hamid et al., 2018; Lang et al., 2017; Liu et al., 2021; Robey et a., 2020). However, this is the first study that seeks to integrate PFAS cycling within contaminated sites, landfills, and WWTPs from a state-wide perspective. Characteristics such as carbon chain length trends, mass loading, percent composition trends, and percent difference between influent and effluent concentrations are defined and quantified using a 28-analyte PFAS suite. Two industrially impacted WWTPs with multiple sampling dates are used to study chemical transformations within the wastewater treatment process. Details on the collection of datasets from public and private sources are provided in Section 2, followed by detailed analysis of contaminated sites, landfill leachate, and WWTP influent, effluent, and biosolids in Section 3, and study conclusions in Section 4.

2. Methods

PFAS data on landfill leachate, WWTP influent, effluent, and biosolids within Michigan were compiled from publicly available and private sources. Only datasets containing the 28-analyte suite generated using a modified form of the US EPA 537 or ASTM D7979 analytical methods were used in our study. A data sharing agreement was formed between Western Michigan University and EGLE. The MIWaters database, which contains public records from all WWTPs within Michigan, was also used to obtain data. For several landfills and WWTPs, data was obtained directly from the operators. Landfill leachate volumes were derived from the

Michigan Waste and Recycling Association (MWRA) report (MWRA, 2019), and correspondence with EGLE personal. Leachate volumes are not reported for three of the studied landfills: State Disposal Landfill, RJL Landfill, or North Kent Landfill.

For this study, 10 industrially impacted WWTPs and 19 landfills within Michigan were investigated. Due to PFAS being an emerging contaminant, only recent (2018-2020) sampling dates were available. A majority of the landfills are Type II Municipal Solid Waste Landfills with two exceptions: (1) Georgia Pacific Charleston Landfill located in Climax, Michigan is an inactive, legacy Type I landfill that accepted paper waste from nearby paper mills, and (2) Allen Park Clay Mine Landfill originated as a clay mine for brick and cement applications until Ford Motor Company converted it to a Type I landfill for disposal of automotive waste. The site has since been redeveloped into a 1 million square foot retail center.

All WWTPs analyzed were industrially impacted and known to have elevated concentrations of PFAS that accept and treat wastewater generated by small communities up to 2.8 million customers. The Kalamazoo Water Reclamation Plant (KWRP) is the only WWTP facility in Michigan that actively treats for PFAS using powder activated carbon (PAC). The KWRP has actively used PAC to treat for pharmaceutical chemicals discharged directly to the WWTP for many years prior to the emergence of PFAS as a contaminant. Publicly accessible biosolids data were difficult to obtain as only a small subset of WWTPs reported sampling on MIWaters, while many others did not report any biosolids data.

All sampling was conducted in compliance with the state issued “General PFAS Sampling Guidance” document that provides detailed procedures to collect and handle PFAS samples, improve sampling quality and consistency, and prevent cross contamination (MDEQ, 2018). Items such as low-density polyethylene (LDPE) bottles, Teflon tubing, and fluorinated ethylene propylene (FEP) labware, and clothing items with resistance to water, oil, stains, insect, or UV light were prohibited during collection and/or analysis of PFAS samples (MDEQ, 2018). Field and equipment blanks were used to both demonstrate either the lack of or to identify cross contamination.

Currently, the USEPA has not developed a method that utilizing Liquid Chromatography tandem Mass Spectrometry (LC/MS-MS) and isotope dilution to analyze PFAS in matrices other than drinking water (MDEQ, 2018). US EPA Method 537 Rev 1.1 analyzes 14 compounds in drinking water only. This method uses solid phase extraction liquid chromatography/tandem mass spectrometry to test per- and polyfluorinated alkyl substances in drinking water (Shoemaker, 2018). In 2020, Method 537.1 was created to add testing capabilities resulting in a total of 18 compounds in drinking water. At the time of this study, Michigan requires 28 compounds to be tested (Table 1) which is not possible with USEPA Method 537 Rev 1.1 or USEPA Method 537.1. To analyze for 28 compounds, laboratories use what is referred to as 537 Modified, which uses isotope dilution and includes additional standards to expand the analysis suite (MDEQ, 2018). This modified 537 method is not an approved method for drinking water analysis by the US EPA. Each participating analytical laboratory determines the quality control parameters and all other modifications which may result in some laboratory to laboratory variation. The 537 Modified method has been used statewide to analyze PFAS in various non drinking water matrices, including biota, landfill leachate, wastewater treatment plant influent, effluent, and biosolids.

A subset of PFAS data associated with leachate from landfills discharging into the GLWA WWTP utilized ASTM D7979-19. This method excludes 9 PFAS that are included in the 537 modified method: 4:2 FTS, 6:2 FTS, 8:2 FTS, PFPrOPrA, NaDONA, NEtFOSAA, NMeFOSAA, PFODA, and PFTA. These PFAS are denoted with an asterisk in Table 1.

Table 1. The 28 PFAS analyte suite required for testing in Michigan along with recently promulgated maximum contaminant levels (MCLs) in drinking water.

Chemical Name	Acronym	Chemical Formula	Chain Length	MCL[1]
Sodium dodecafluoro-3H-4, 8-dioxanonanoate	NaDONA*	C7H5F12NO4	GenX	N/A
Perfluoro-2-propoxypropanoic acid, Hexafluoropropylene oxide dimer acid	PFPrOPrA*	C6HF11O3	GenX	370
4:2 Fluorotelomer sulfonic acid	4:2 FTS*	C4F9CH2CH2SO3	C4	N/A
Perfluorobutanesulfonic acid	PFBS	C4F9SO3H	C4	420
Perfluorobutanoic acid	PFBA	C3F7COOH	C4	N/A
Perfluoropentanesulfonic acid	PFPeS	C5F11SO3H	C5	N/A
Perfluoropentanoic acid	PFPeA	$C_5HF_9O_2$	C5	N/A
6:2 Fluorotelomer sulfonic acid	6:2 FTS*	C6F13CH2CH2SO3	C6	N/A
Perfluorohexanesulfonic acid	PFHxS	C6F13SO3H	C6	51
Perfluorohexanoic acid	PFHxA	C5F11COOH	C6	400000
Perfluoroheptanesulfonic acid	PFHpS	C7F15SO3H	C7	N/A
Perfluoroheptanoic acid	PFHpA	C6F13COOH	C7	N/A
N-ethyl perfluorooctanesulfonamidoacetic acid	NEtFOSAA*	C8F17SO2N(C2H5)CH2COOH	C8	N/A
N-methyl perfluorooctanesulfonamidoacetic acid	NMeFOSAA*	C8F17SO2N(CH3)CHCOOH	C8	N/A
Perfluorooctanesulfonamide	FOSA	C8F17SO2NH2	C8	N/A
8:2 Fluorotelomer sulfonic acid	8:2 FTS*	C8F17CH2CH2SO3	C8	N/A
Perfluorooctanesulfonic acid	PFOS	C8F17SO3H	C8	16
Perfluorooctanoic acid	PFOA	C7F15COOH	C8	8
Perfluorononanesulfonic acid	PFNS	C9F19SO3H	C9	N/A
Perfluorononanoic acid	PFNA	C8F17COOH	C9	6
Perfluorodecanesulfonic acid	PFDS	C10F21SO3H	C10	N/A
Perfluorodecanoic acid	PFDA	C9F19COOH	C10	N/A
Perfluoroundecanoic acid	PFUnA/PFUdA	C10F21COOH	C11	N/A
Perfluorododecanoic acid	PFDoA	C11F23COOH	C12	N/A
Perfluorotridecanoic acid	PFTeDA	C12F25COOH	C13	N/A
Perfluorotetradecanoic acid	PFTA*	C13F27COOH	C14	N/A
Perfluorohexadecanoic acid	PFHxDA	C16HF31O2	C16	N/A
Perfluorooctadecanoic acid	PFODA*	C18HF35O2	C18	N/A

[1] Michigan MCLs accepted on 08/03/2020

*indicates compounds not included in ASTM D7979 used for analysis of GLWA associated landfills

3. Results and Discussion

In this study, PFAS contaminated sites in Michigan are used to analyze trends in PFAS sources as well as concentration levels. Landfill data is used to examine trends in leachate volume, composition, mass flux, and carbon chain length. WWTP influent, effluent, and biosolids data is used for analysis of PFAS composition, effluent volume, mass loading, as well as total PFAS trends. In this analysis, the total PFAS refers to the sum of the 28 compounds in ppt required for testing in Michigan. The compositional trends use PFAS in order of decreasing chain length as described in Table 1.

3.1 Contaminated Sites

Michigan is one of the leading states in the nation in testing public and private water sources to reduce human exposure PFAS. In 2016, the USEPA issued a drinking water health advisory limit for PFOS and PFOA at 70 ppt (Hamid et al., 2018). This is the limit that Michigan used until August of 2020, when new maximum contaminant levels (MCLs) for drinking water were published for seven compounds: PFBS 420 ppt, PFHxS 51 ppt, PFHxA 400,000 ppt, PFOS 16 ppt, PFOA 8 ppt, PFNA 6 ppt, HFPO-DA 370 ppt (Table 1) (EGLE, 2020b). Any site can be considered contaminated in Michigan if any of these MCLs are exceeded. The decrease from 70 ppt combined PFOA/PFOS to 8 ppt PFOA and 16 ppt PFOS has resulted in multiple PFAS contaminated sites in the state qualifying as contaminated. MPART has currently declared a total of 171 sites within Michigan to be contaminated with PFAS. Figure 2 represents Michigan's 171 PFAS contaminated sites listed on the MPART website as of 07/07/2021 characterized according to source.

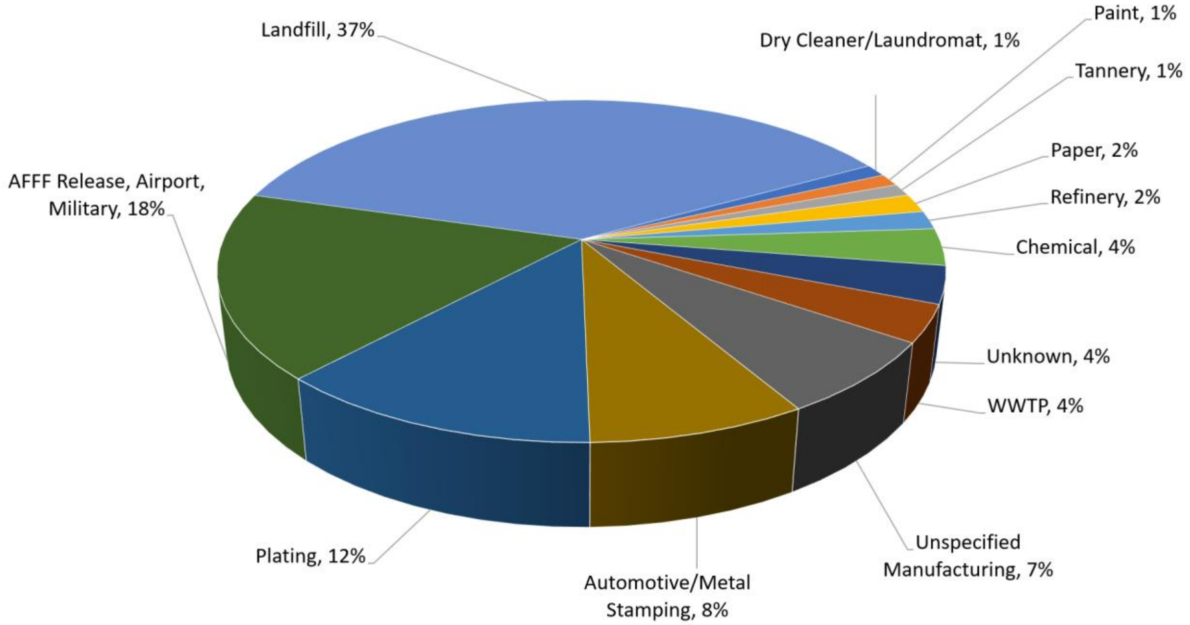

Figure 2 Pie chart displaying 171 MPART PFAS contaminated sites grouped by source type.

Upon analysis, four major sources account for 75% of the contaminated sites: legacy landfills (37%); AFFF, which encompasses uses of AFFF for fire suppression at military bases and airports (18%); metal platers, which utilized PFAS from mist suppressants using compounds such as Cl-PFESAs, also known as F-53B, and PFOS (Liu et al., 2019) (12%); and automotive/metal stamping (8%). The remaining sources include unspecified manufacturing, which includes sites with activities other than chemical manufacturing (7%); manufacturing chemicals and products such as hydraulic fluid, lubricants, underbody coatings, and other specialty chemicals (4%); unknown sources that lack a responsible party (4%); WWTPs (4%); oil refineries (2%); paper producing industries, which used PFAS as a stain and oil proofing agent on the paper (EGLE, 2021b) (2%); paint manufacturing (1%); tanneries using PFAS as a waterproofing agent in the leather treatment process (1%); and dry cleaners and laundromats (<1%).

The total source mass of PFAS is largely unknown for these contaminated sites. Instead, we use the maximum reported concentration of PFOA+PFOS to better understand the relative magnitudes of contamination for each of the 171 sites and group the sites into 7 arbitrary bins: <70, 70-100, 100-500, 500-2000, 2000 - 10,000, 10,000-100,000, and greater than 100,000 ppt (Figure 3). Maximum concentration data could not be obtained from 22 sites, and these sites are depicted in the “unknown” category and excluded from the analysis. Approximately 80% of PFAS contaminated sites in Michigan have maximum concentrations under 2000 ppt. The largest group of 43 sites (25%) have maximum concentrations less than 70 ppt and were added in response to Michigan promulgating 8 ppt PFOA and 16 ppt PFOS MCLs. A total of 11 sites (6%) narrowly exceed the previous health advisory limit in the 70-100 ppt. The 100-500 ppt and 500-2000 groups contain 30 sites (18%) and 33 sites (19%), respectively. The 2000-10,000 ppt and 10,000-100,000 ppt groups contain 12 sites (7%) and 15 sites (9%), respectively. Only 5 sites (~3%) have maximum concentrations exceeding 100,000 ppt.

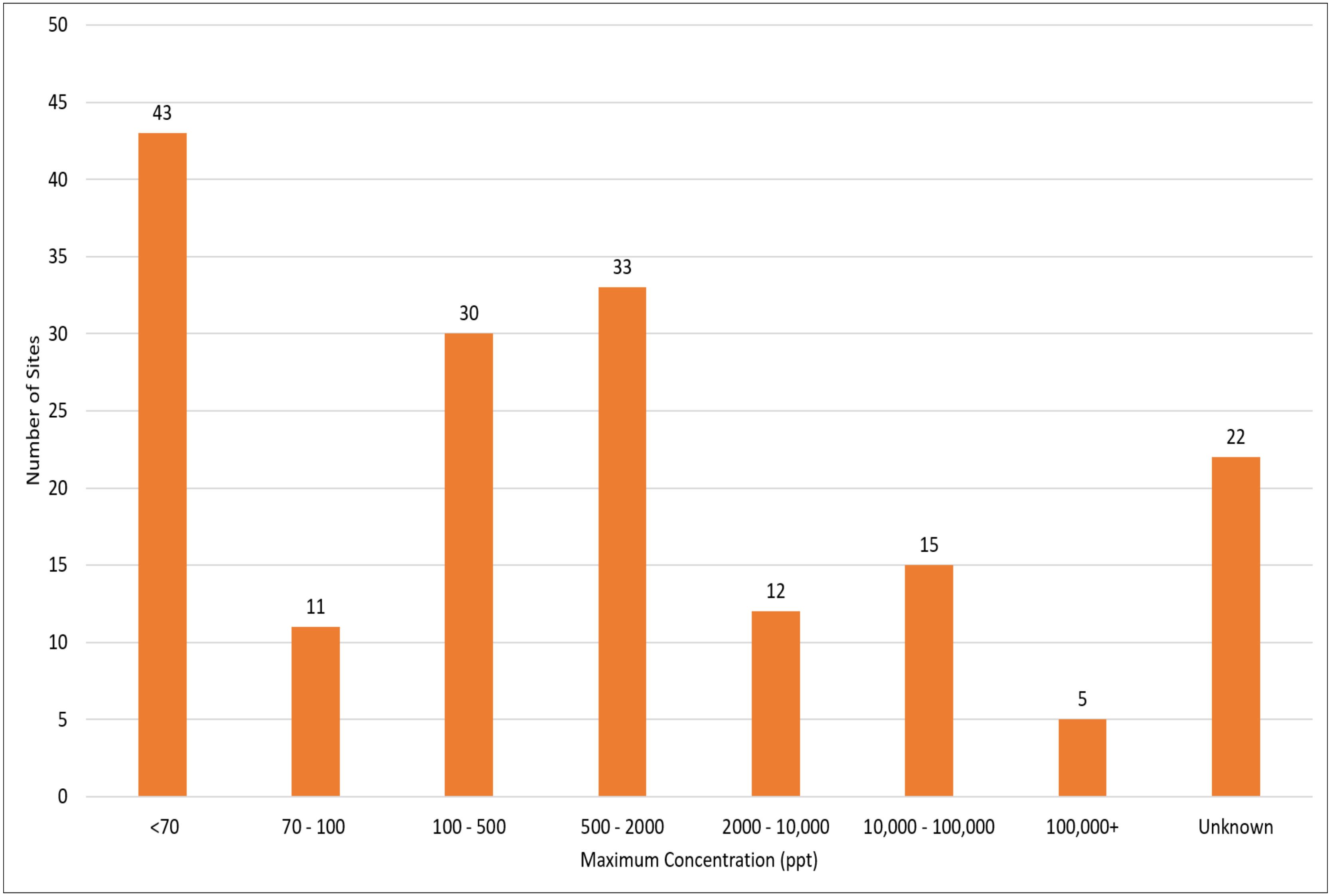

Figure 3. Michigan's PFAS contaminated sites categorized by concentration range.

3.2 Landfills

A total of 19 landfills are analyzed in this study. Selection of these sites primarily revolved around the availability of data on the 28-PFAS analyte suite. A total of 11 of the sites are Type II municipal landfills, the remaining either Type I construction waste landfills, or unknown classification. Ten landfills in this study are inactive and nine are currently active. Details on each landfill including dates of operation, location, status, total PFAS concentration are provided in Table 2.

Leachate volumes vary from 8 m^3/d at the Georgia Pacific Landfill to 368 m^3/d at the City of Pontiac Landfill (Table 2). A clear distinction in leachate volume is observed from the operational status of the landfills (active vs. inactive). Total PFAS annual mass fluxes are calculated as a product of leachate volume and concentration (Table 2, Figure 4). PFAS mass fluxes for active landfills (86 to 1998 g/yr) are generally 1-2 orders of magnitude higher than inactive landfills (5 to 41 g/yr). This is generally attributed to the addition of clay caps upon landfill closure to reduce the infiltration of precipitation, and resultant leachate volume (Lang et al., 2017).

Percent PFAS composition of landfill leachate chemistry for a representative sample of each landfill is used to characterize the presence and dominance of individual PFAS compounds (Figure 5). Total PFAS leachate concentration is displayed at the top of each bar and ranges from 208 – 23,458 ppt.

Table 2. Michigan landfills (n=18) analyzed in this study.

Name	Dates of Operation	City	Status	Landfill Type	Analysis Method	WWTP	Total PFAS (ppt)[5]	Average Leachate Volume (m^3/d)	Annual Mass Flux (g/yr)
Eagle Valley Recycle & Disposal Facility	1985-2021	Orion	Open	Type II	ASTMD7979	GLWA	6028	112	246
Woodland Meadows North Landfill	1974-1992	Wayne	Closed	Type II	ASTMD7979	GLWA	1995	57	41
Woodland Meadows RDF Van Buren	1994-2021	Wayne	Open	Type II	ASTMD7979	GLWA	28650	137	1429
Southeastern Oakland County	1980-2000[1]	Rochester Hills	Closed	Type II	ASTMD7979	GLWA	323	142	17
South Macomb Disposal Authority	1968-1975	Macomb	Closed	N/A	ASTMD7979	GLWA	150	265	15
Allen Park Clay Mine Landfill	1950-2003	Allen Park	Closed	Type III	ASTMD7979	GLWA	233	133	11
City of Pontiac	1984-2006	Pontiac	Open	Type II	ASTMD7979	GLWA	643	368	86
Waterford Hills Landfill	1981-1991	Waterford	Closed	N/A	ASTMD7979	GLWA	3200	8	9
Pine Tree Acres, Inc.	1987-2021	Lenox	Open	Type II	ASTMD7979	GLWA	19500	280	1998
Oakland Heights Development, Inc.	1980-2021	Auburn Hills	Open	Type II	ASTMD7979	GLWA	3711	114	155
Cork Street Landfill	1925-1992	Kalamazoo	Closed	Type III	537 Modified	KWRP	539, 336[2]	60, 336	12, 41
Northern Oaks	1992-2021	Harrison	Open	Type II	537 Modified	KWRP	5647	65	133
Georgia Pacific Charleston Landfill	1997-2010[3]	Climax	Closed	Paper Waste	537 Modified	KWRP	1167	11	5
Pitsch Landfill	1973-2021[4]	Belding	Open	Type II, III	537 Modified	Belding WRRF	9664	57	201
St. Clair County Landfill	1967-2021	Port Huron	Open	Type II	537 Modified	Port Huron WWTP	11117	125	506
Menominee Landfill	1981-2021	Menominee	Open	Type II	537 Modified	Menominee WWTP	13000	50	236
North Kent Landfill	1977-1986	Rockford	Closed	Type II	537 Modified	North Kent SA	5676		
State Disposal Landfill	1966-1976	Plainfield Township	Closed	N/A	537 Modified	North Kent SA	717		
RJL Landfill		Auburn Hills	Closed	N/A	ASTMD7979	GLWA			

Footnotes

[1] EGLE estimate.

[2] Two separate outfalls, MDS listed first & MDS2 listed second

[3] EGLE estimate of mid to late 1990s to 2010s

[4] EGLE estimate of early to mid 1970s

[5] Average Total PFAS

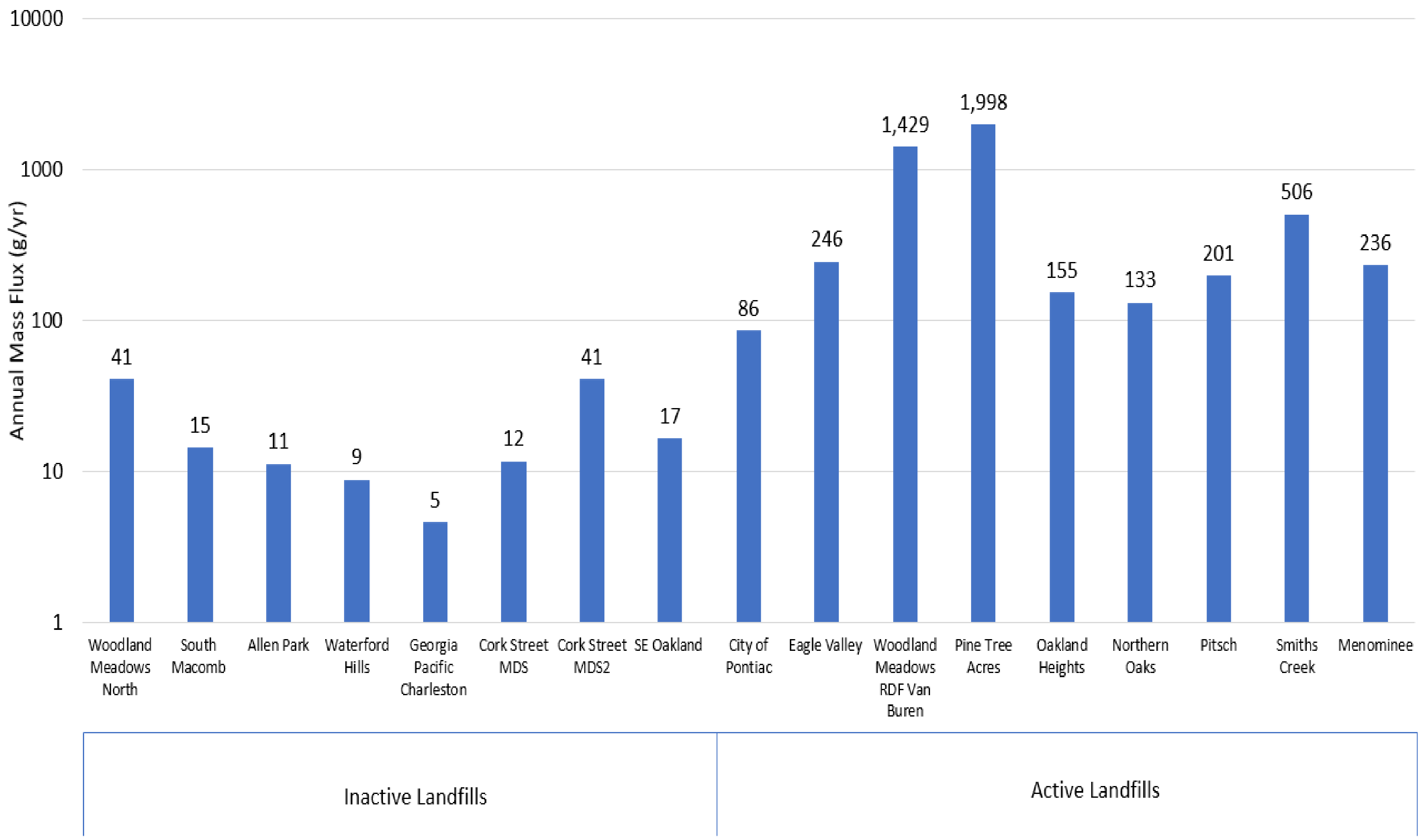

Figure 4. Mass flux (g/yr) of total PFAS (n=28) for inactive and active landfills studied.

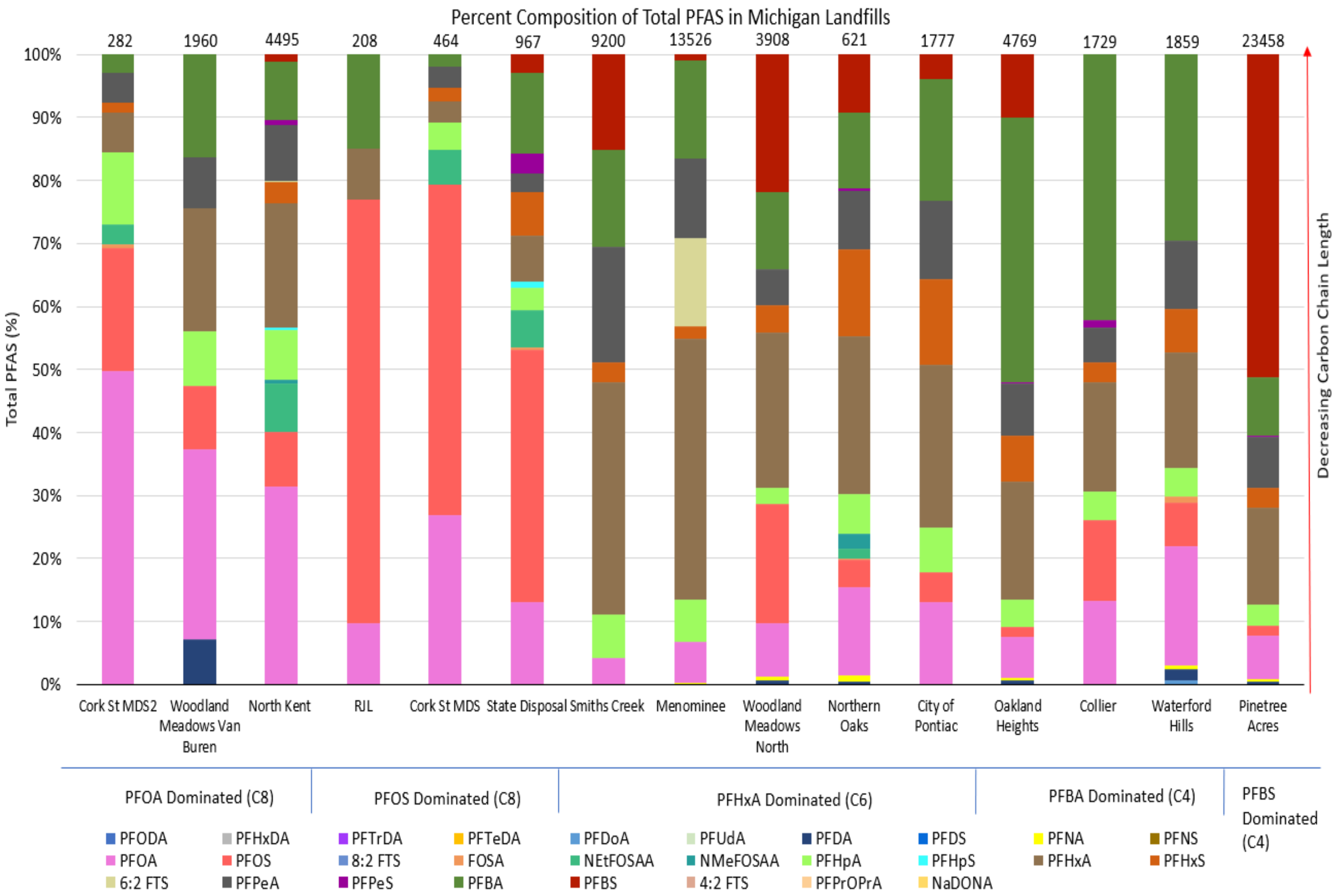

Figure 5. Percent composition of total PFAS in Michigan landfill leachate arranged in order of decreasing chain length and organized according to dominant compounds. Total PFAS concentration in ppt is located at the top of each column.

Landfills are located on the x-axis according to the dominant PFAS compound with decreasing carbon chain length from the left to right. To simplify the display of the full 28 analyte suite, the vertical placement of PFAS is ordered in decreasing chain length from bottom to top as shown in Table 1. While it is nearly impossible to avoid using similar colors for some compounds, the color scheme used avoids the assignment of similar colors for PFAS with similar carbon chain lengths. This is intended to facilitate more rapid comparisons between different leachates and the dominance of different chain-length PFAS.

Only five landfills are C8 dominated (PFOS or PFOA, Figure 5). This is particularly interesting as Michigan landfill operators only need to regulate these two PFAS, and the vast majority of PFAS regulation and medical studies focus on only these two compounds. Cork Street MDS and MDS2 are two different outfalls connected to two different cells in the same closed landfill. Cork Street MDS2, Woodland Meadows Van Buren, and North Kent landfills are PFOA dominated, and RJL, Cork Street MDS, and State Disposal landfill are PFOS dominated. Both RJL and Cork Street MDS are comprised of over 50% PFOS (C8). Five landfills: Smiths Creek, Woodland Meadows North, Northern Oaks, and City of Pontiac are PFHxA (C6) dominated. Oakland Heights, Collier, and Waterford Hills are PFBA (C4) dominated, and Pinetree Acres is PFBS (C4) dominated.

The leachate PFAS compositions, as total C8, C6, and C4 normalized by total PFAS, are also analyzed by carbon chain length as a function of operational start date (Figure 6).

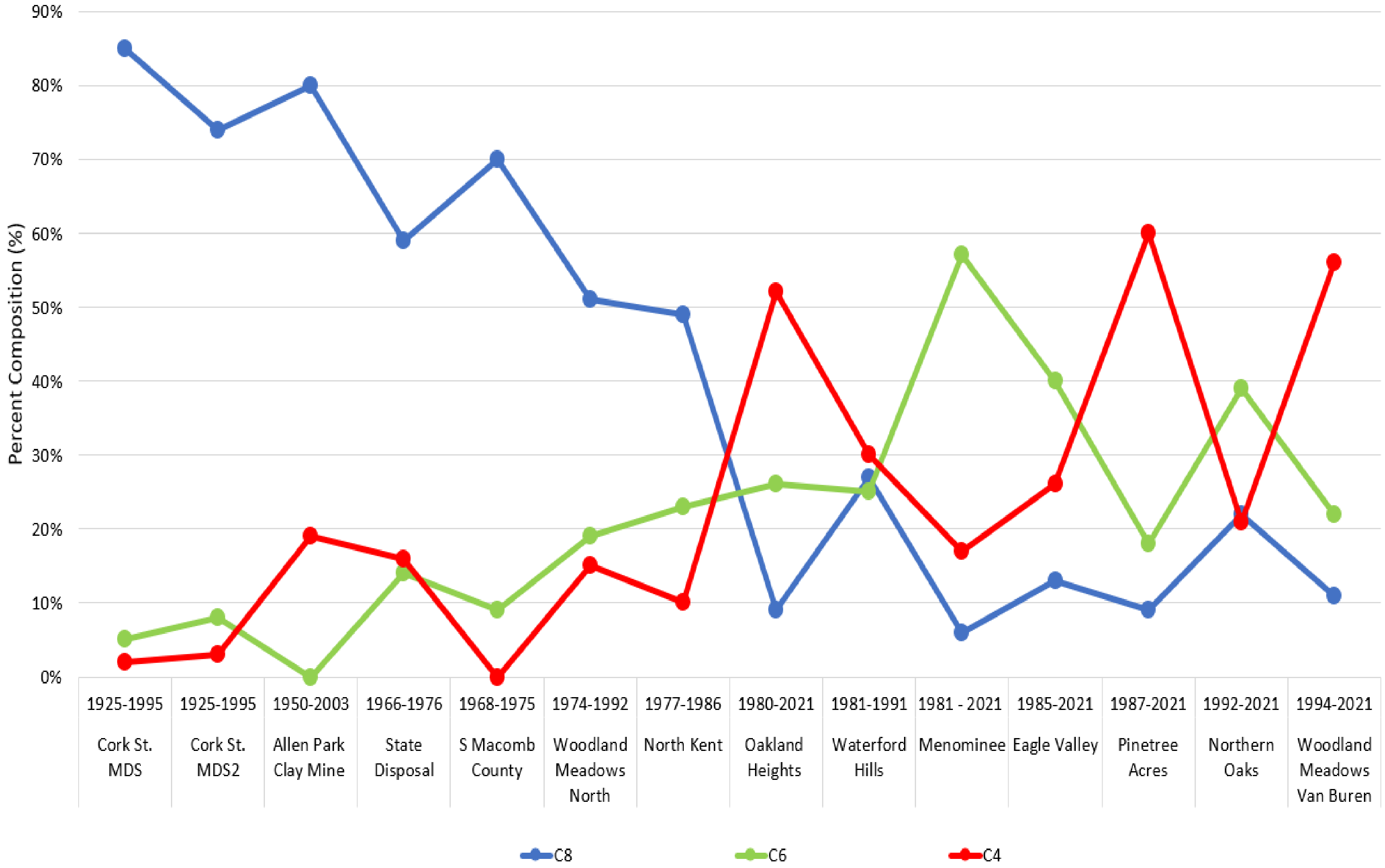

Figure 6. C8, C6, and C4 carbon chain length trends of municipal waste landfills in Michigan as a function of landfill operation start date.

The trends denote a shift from long chain to short chain compounds where C8s decrease with operational age to shorter chained C4 and C6 compounds. The older landfills such as Cork Street, Allen Park, State Disposal, and South Macomb County have C8 compositions ranging from 59% to 85%. The C4 and C6 compositions for these landfills are minimal ranging from 0% to 19%. Starting in the 1970s with North Kent Landfill and Oakland Heights Landfill, a large decline in C8 composition occurs. The landfills created after 1980 have fluctuating chain length compositions, yet in all cases, the compositions of C4 and C6 increase.

An unnamed (per operator request) midsize municipal landfill in Michigan provided PFAS data sampled from 2018-2020 for 9 individual cells with waste composition ranging from as early as the 1980s (or possibly before) to current that allow for more in-depth analysis of carbon chain length as a function of age of the waste (Figure 7). Several dates of operation were approximated by the landfill operator as the exact dates were unknown. The compositions of C8, C6, and C4 PFAS are based on calculated averages from sampling dates from 2018-2020. Overall, the plot shows similar trends to Figure 6 with the older cells having higher compositions of long chain C8 compounds, and lower compositions of short chained compounds. The newer cells generally exhibit increases in C4 and C6 replacements and decreases in C8 compounds.

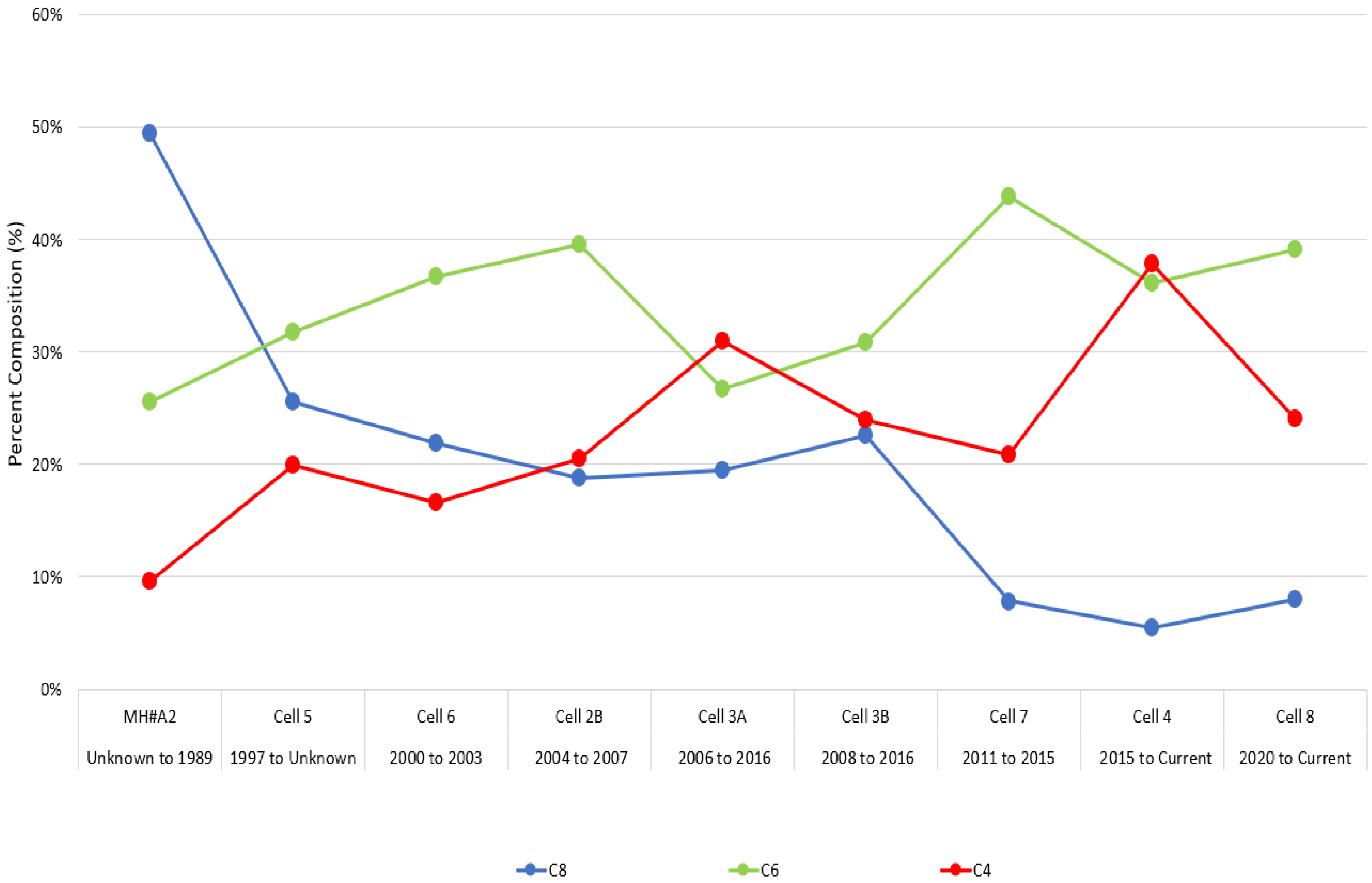

Figure 7. Carbon chain length trends for multiple cells of different age within an unnamed midsized municipal landfill in Michigan

MH #A2 is one of two outfalls for Cell A, which is the oldest cell that for which adequate data could be obtained. The start date of the cell is not known but it was closed in 1989. The compositions are 49%, 26% and 10%, for C8, C6 and C4, respectively. Cells 5, 6, 2B, 3A, and 3B have operational dates ranging from 1997 to 2016 and have relatively similar C8 compositions to each other with C8 compositions ranging from 19%-25%, C6 compositions ranging from 27%-39%, and C4 compositions ranging from 17%-31%. Cell 7, which operated from 2011 to 2015, shows a significant decrease in C8 and increase in C6 compositions compared to Cell 3B. Cells 4 and 8 have operational dates from 2016 and 2020, respectively, and have PFAS compositions similar to Cell 7: C8 is less than 10%, C6 ranges from 36%-44%, and C4 ranges from 21%-38%. Both Figures 6 and 7 show an inverse relationship between C4 and C6 composition, where higher C6 compositions are accompanied by lower C4 compositions, and vice versa.

Limited field studies have been conducted on PFAS in the environment, with most studies focusing on laboratory tests performed at the bench-scale (Allred et al., 2015; Lang et al., 2016). The increase of shorter chain compounds in leachate can be attributed to the industry shift towards short chain alternatives, as well as the ability for short chain PFAS to move through the subsurface (Benskin et al., 2012; Higgins and Luthy, 2006). Long chain compounds are more likely to sorb to soil whereas short chain PFAS have a lower binding capacity and higher mobility (Gagliano et al. 2020). This could explain why long chain compounds are still being leached out of landfills although production and usage have stopped. Vermont (2018) found active landfills to have around 25,000 ppt total PFAS (using a 29-analyte suite) which is comparable to the active landfills in this study (1777-23,458 ppt). The landfills in which C4 and C6 are the dominant PFAS tend to have higher total PFAS concentrations (621-23,458 ppt) than long chain dominant landfills (208-4495 ppt). These concentration differences could in part be attributed to lower performance of short chain compounds in consumer goods resulting in higher amounts of chemicals being used (Scheringer et al., 2014).

Landfills do not typically treat PFAS on-site but instead discharge leachate to various WWTPs, either piped or via tanker trucks. In fact, most of the landfill leachate data used in this study were obtained from WWTP operator data collected from influent wastewater streams. Michigan landfills contribute less than 10% of total PFOA and PFOS mass loadings to WWTP (MWRA, 2019). However, PFOS and PFOA represent only a subset of PFAS in leachate received by WWTPs. The 28-PFAS analytical suite currently used in Michigan disregards thousands of potential compounds that may be present in leachate. Even with limited analyte suites, mass loadings of the total PFAS in leachate can be significant. Lang et al. (2017) estimated that in 2013, the total mass loading from landfills in the U.S. ranged from 563-628 kg/yr using a 70 PFAS suite. One study conducted in Florida analyzed PFAS concentrations in waste vehicle leachate and landfill leachate (Liu et al., 2021) and determined that precursors transformed to more terminal PFAAs while in the landfill. Waste vehicle leachate tended to contain more PFAA precursor compounds and landfill leachate contained more terminal short chain PFAS.

3.3 WWTP

Ten industrially-impacted WWTPs were investigated (Table 3). In 2018, Michigan started the Industrial Pretreatment Program (IPP) PFAS initiative that requires all industrial contributors to municipal WWTPs with IPPs (n=95) to be identified and screened for PFAS (EGLE, 2020a). If wastewater streams have PFAS above the 70 ppt PFOS+PFOA MCL, source reduction efforts were then conducted, which include replacing PFOA+PFOS with shorter chained PFAS alternatives, installation of pretreatment systems, and/or waste removal from contaminated sites. To date, these regulatory efforts have been solely focused on PFOS and PFOA and disregard all other PFAS. In addition to industrial wastewater streams, 27 WWTPs in Michigan accept leachate from at least one landfill (MWRA, 2019). For example, GLWA, a very large WWTP in Detroit, accepts leachate from nine different landfills.

Table 3. Industrially impacted WWTPs (n=10) in Michigan analyzed in this study.

Name	City	Surface Water Body Discharge	Analysis Method	Average Daily Flow (m^3/day)	Influent Total PFAS Average (ppt)	Effluent Total PFAS Average (ppt)	Annual Mass Flux (kg/yr)
GLWA WRRF	Detroit	Rouge River	537 Modified	2443299	122	143	128
Port Huron WWTP	Port Huron	St. Clair River	537 Modified	37066	301	294	4
Grand Rapids WRRF	Grand Rapids	Grand River	537 Modified	154518	859	1114	63
North Kent SA WWTP	Grand Rapids	Grand River	537 Modified	14023	118	617	3
3 Rivers WWTP	3 Rivers	St. Joseph River	537 Modified	5458	489	475	0.95
KI Sawyer WWTP	Gwinn	Silver Lead Creek	537 Modified	796	44	143	0.04
Kalamazoo WRRF	Kalamazoo	Kalamazoo River	537 Modified	109721	42	79	3
Bronson WWTP	Bronson	Swan Creek	537 Modified	2312	131	50	0.04
Downriver WTF	Wyandotte	Trenton Channel / Detroit River	537 Modified	223231	67	95	8
Lapeer WWTP	Lapeer	South Branch Flint River	537 Modified	5912	127	170	0.37

3.3.1 WWTP Influent and Effluent

Due to chemical and biochemical transformations that are part of domestic wastewater treatment, influent and effluent are characterized separately in WWTPs. The format and organization of the PFAS composition plots for WWTP influent and effluent are the same as those used for landfill leachate, including the colors assigned to individual compounds. Figure 8 shows the influent percent composition of the ten WWTP analyzed in this study. Total PFAS concentrations of the 28-analyte suite are listed at the top of each column and range from 17 – 314 ppt. Five (50%) of the WWTPs: Bronson, Downriver, North Kent, Lapeer, and KI Sawyer are dominated by PFOS in the influent wastewater stream, while none of the WWTPs are PFOA dominated. Kalamazoo and Port Huron WWTPs (20%) are PFHxA (C6) dominated. GLWA and Grand Rapids WWTP (20%) have significant concentrations of 6:2 FTS (C6) in the influent, dissimilar to the other WWTPs which have minor concentrations of this fluorinated precursor. Approximately 80% of Grand Rapids WWTP influent is made up of 6:2 FTS. Three Rivers WWTP (10%) influent is dominated by PFBS (C4), but also has approximately 25% PFHxA (C6).

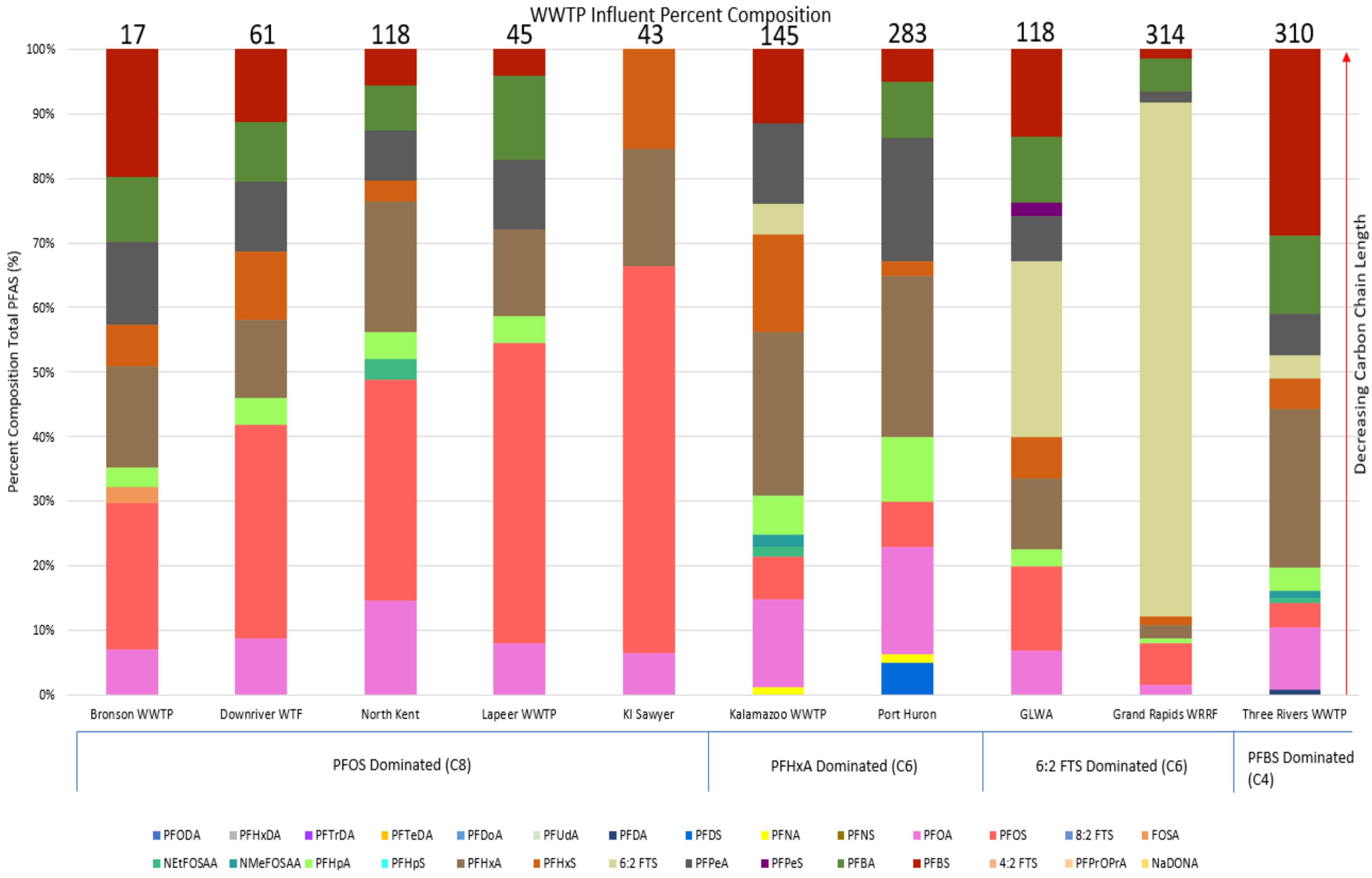

Figure 8. Percent composition of total PFAS in WWTP influent arranged in order of decreasing chain length. The WWTPs are organized according to dominant compounds. Total PFAS concentration in ppt is located at the top of each column.

Representative effluent compositions for these same WWTPs are provided in Figure 9. Total PFAS concentrations for the 28-analyte suite are significantly higher in the effluent than in the influent for all the WWTPs studied, and range from 81 to 1357 ppt. Grand Rapids had the largest increase (a factor of 4.3) from an influent concentration of 314 ppt total PFAS to an effluent concentration of 1357 ppt total PFAS. Effluent concentrations of three WWTPs (Bronson, Downriver, KI Sawyer) are PFOS dominant (30%), compared to the five WWTPs (Bronson, Downriver, KI Sawyer, Lapeer, North Kent) (50%) with PFOS dominant influent. GLWA and Grand Rapids WWTP (20%) effluent compositions remain 6:2 FTS dominant. At GLWA and Grand Rapids WWTP, concentrations of 6:2 FTS increased across the plant from 32-43 ppt and 250-1200 ppt, respectively (Figure 8 and 9). Port Huron WWTP (10%) effluent is PFHxS dominant. Three (30%) WWTPs (Kalamazoo, Lapeer, North Kent) have effluent that is PFPeA (C5) dominant, though the influent of none of these WWTPs contained PFPeA greater than 13%. Consistent with the influent composition, effluent composition of the Three Rivers WWTP (10%) remains PFBS dominant. Observations of higher average daily effluent concentrations is consistent with previous work showing precursor transformation to PFAAs during activated sludge treatment (Sinclair and Kannan, 2006; Nguyen et al., 2019).

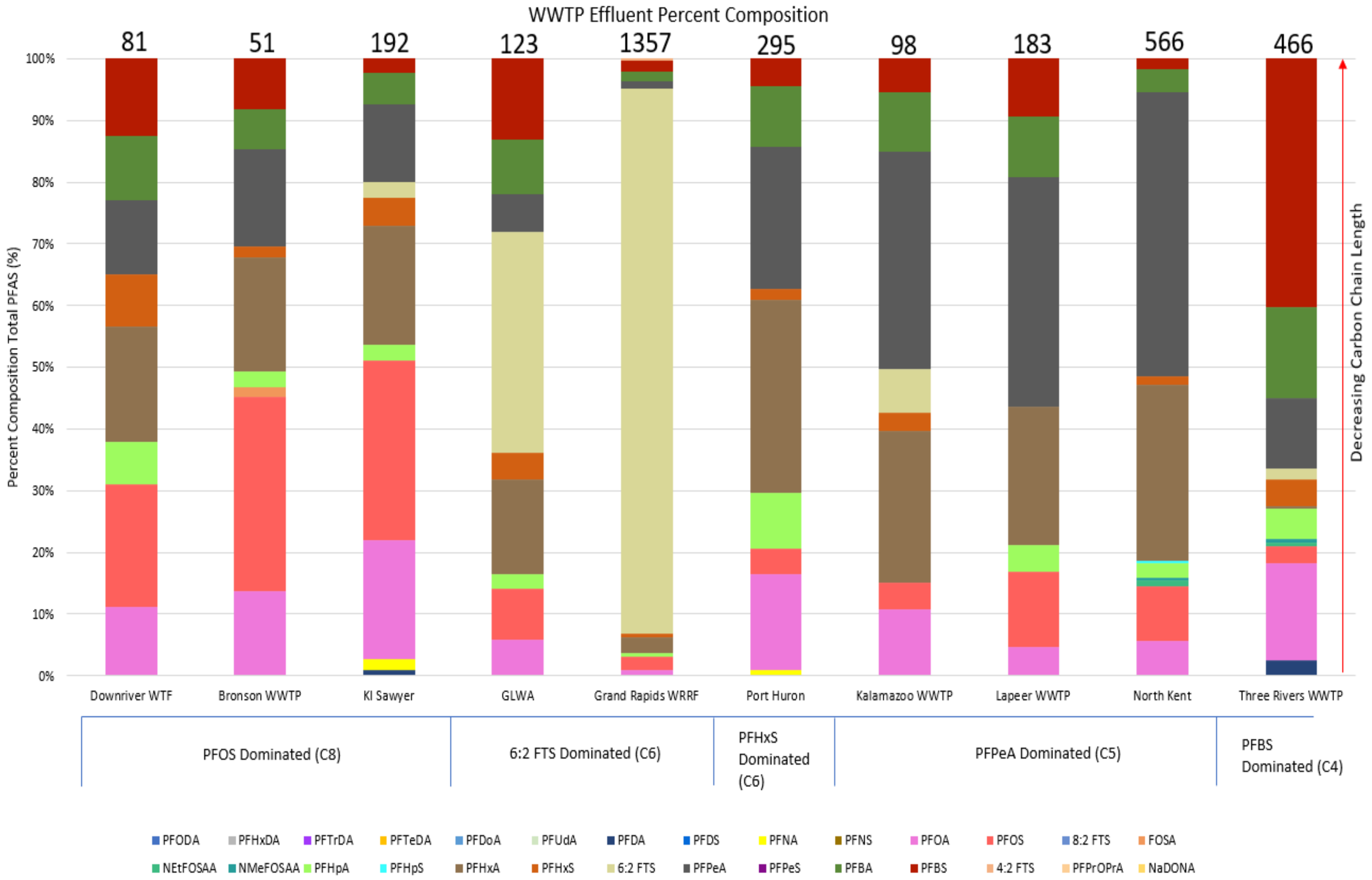

Figure 9. Percent composition of total PFAS in WWTP effluent arranged in order of decreasing chain length and organized according to dominant compounds. Total PFAS concentration in ng/l is located at the top of each column.

Out of the ten WWTPs studied, GLWA and Kalamazoo were selected for more in-depth analysis of the chemical transformations that occur in the wastewater treatment process. GLWA is the state's largest WWTP serving over 2.8 million wastewater users on the southeast side of Michigan. Kalamazoo Water Reclamation Plant (KWRP) serves 150,000 customers and is the only WWTP in Michigan that uses Powder Activated Carbon (PAC) in its treatment process. Although PAC adsorbs PFAS, it was added to the KWRP treatment system prior to the emergence of PFAS for the purpose of adsorbing and removing from the water pharmaceuticals and precursors discharged to the plant by a local pharmaceutical manufacturer without pretreatment.

Total PFAS for the 28-analyte suite for influent and effluent for KRWP and GLWA are compared in Figure 10. The influent concentrations are represented by the blue bar and effluent concentrations are represented by the orange bar. Multiple samples from the same month were averaged to compute daily concentration values for each month. The only sampling date for KRWP where the average daily influent is greater than the effluent is September of 2018 with daily influent and effluent concentrations of 87 and 74 ppt, respectively (Figure 10a). All other effluent average daily concentrations for KRWP are greater than the influent concentrations by a factor of 1.2 to 12. For GLWA, total PFAS in the influent is less than the effluent and ranges from 78-174 ppt total PFAS, with effluent ranging from 107-219 ppt (Figure 10b). Effluent concentrations are greater than influent by a factor of 1.1 to 1.6, save 10/15/2020 and 11/12/2020 where influent concentrations are greater than effluent.

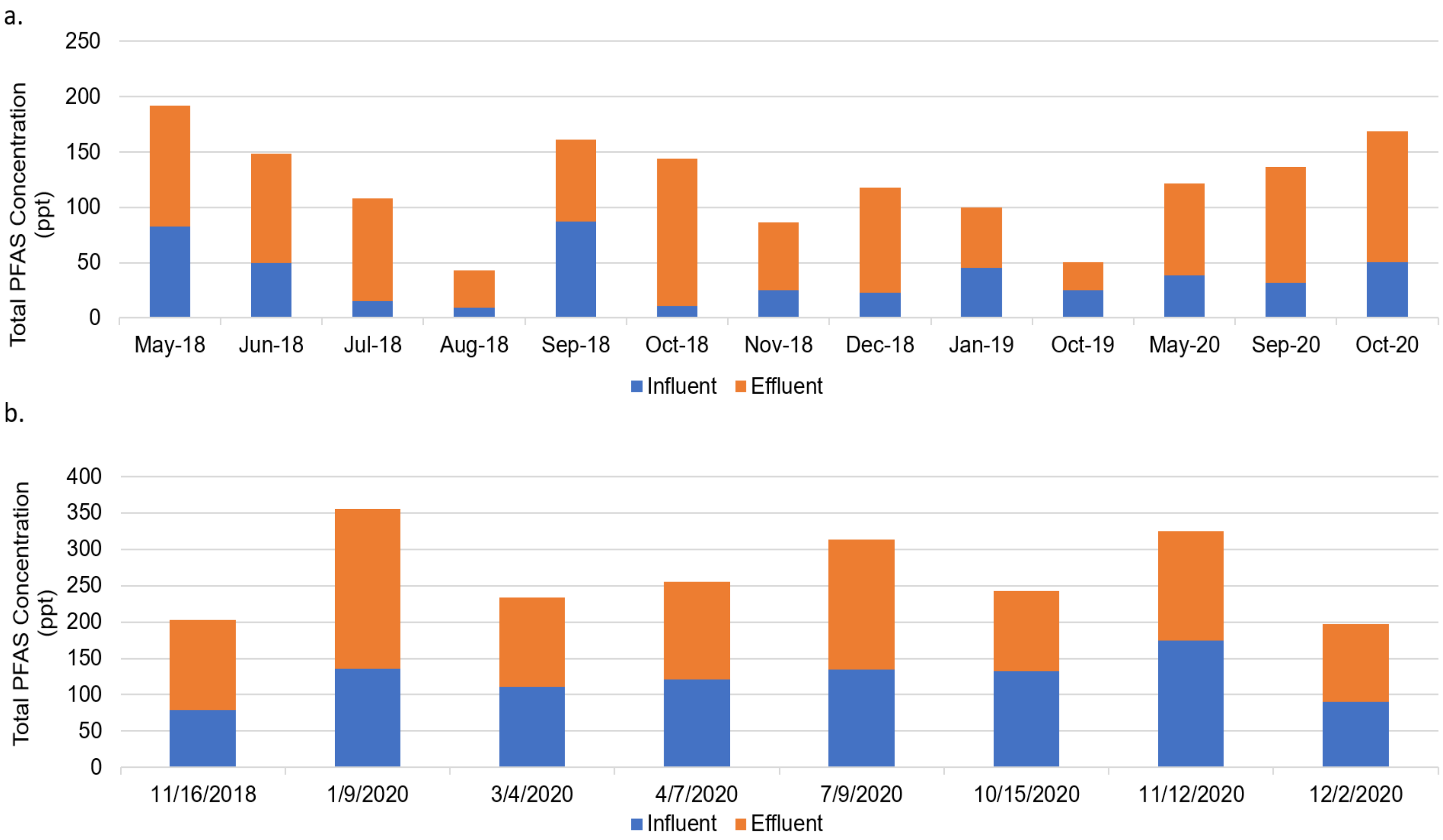

Figure 10a. Daily averages for influent vs effluent concentrations at Kalamazoo Water Reclamation Plant (KWRP). The blue column represents influent concentration, and the orange column represents effluent concentration. Figure 10b represents daily averages for influent vs effluent concentrations at Great Lakes Water Authority (GLWA).

Transformations between the influent and effluent waste streams are analyzed for each of the 28 analytes using percent difference plots. The calculations are performed such that higher concentrations in the effluent are positive (net gain). Conversely, negative percent differences indicate higher concentrations in the influent than effluent (net loss). The percent difference plots are restricted to the PFAS that show the largest changes, resulting in 6 PFAS for KWRP (PFOA, PFOS, PFHxA, PFPeA, PFBA and PFBS) and 7 PFAS (PFOA, PFOS, PFHxA, 6:2 FTS, PFPeA, PFBA and PFBS) for GLWA. All of these PFAS are PFAAs, except for 6:2 FTS which is a polyfluorinated precursor. Several PFAS in the 28-compound suite are not included on the graph due to lack of appreciable change from influent to effluent. One of these is PFNA, which was also found not to change significantly in a previous study analyzing seven PFAS in six Danish WWTPs (Bossi et al., 2008).

Figure 11 shows the percent difference graph for KWRP. PFOA (C8) shows increasing influent to effluent trends, having only one sample date with a decrease in concentration across the plant. Trends for PFOS (C8) are less clear with multiple positive and negative (and frequently near zero) percent differences. PFHpA (C7) tended to show net losses in the effluent (not shown). PFHxA (C6) exhibited large increases in concentration through the treatment system for nearly every single sampling date.

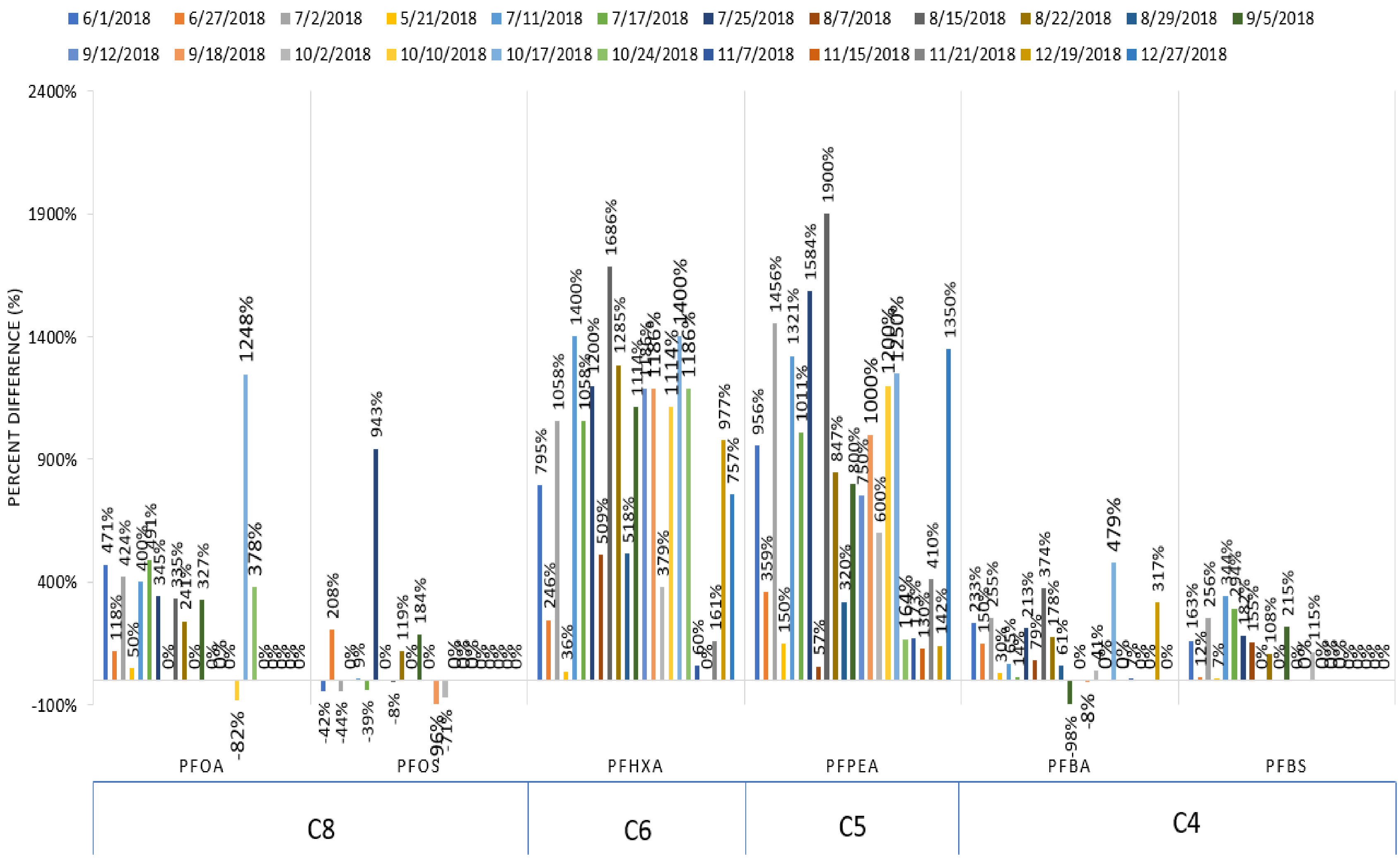

Figure 11. Percent difference between influent and effluent WWTP concentrations for the Kalamazoo Water Reclamation Plant (KWRP). Positive values represent increases in PFAS concentration from influent to effluent.

The highest percent difference for PFHxA (C6) is a remarkable 1686% increase in the effluent. PFPeA (C5) also exhibited increases in every sampling date, with percent differences ranging from 57% to 1900% increases in the effluent. PFBA (C4) and PFBS (C4) both primarily increased through the treatment system, but at much lower increases than PFHxA (C6) and PFPeA (C5). Percent differences for PFBA and PFBS (both C4s) range from 0% to 344% and 98% to 479%, respectively. Figure 12 contains the percent difference graph for GLWA. PFOA and PFOS both show several negative and positive percent differences, with PFOS trends generally an overall net loss across the plant. Effluent concentrations for PFHxA are greater than influent with increases ranging from 48% to167%. Concentrations of PFHxS decrease from influent to effluent for every sample date, except on 4/7/2020, with percent differences of -5% to -29%. Polyfluorinated 6:2 FTS exhibited multiple positive and negative percent differences ranging from 37% to 408% and -14% to -60%, respectively. Concentrations of PFBA and PFBS both generally increase in the effluent. PFBA ranged from 5% to 64% with two samples being -9% and -25%. PFBS ranged from 0% to 115% from influent to effluent as well as one sampling date being -36%.

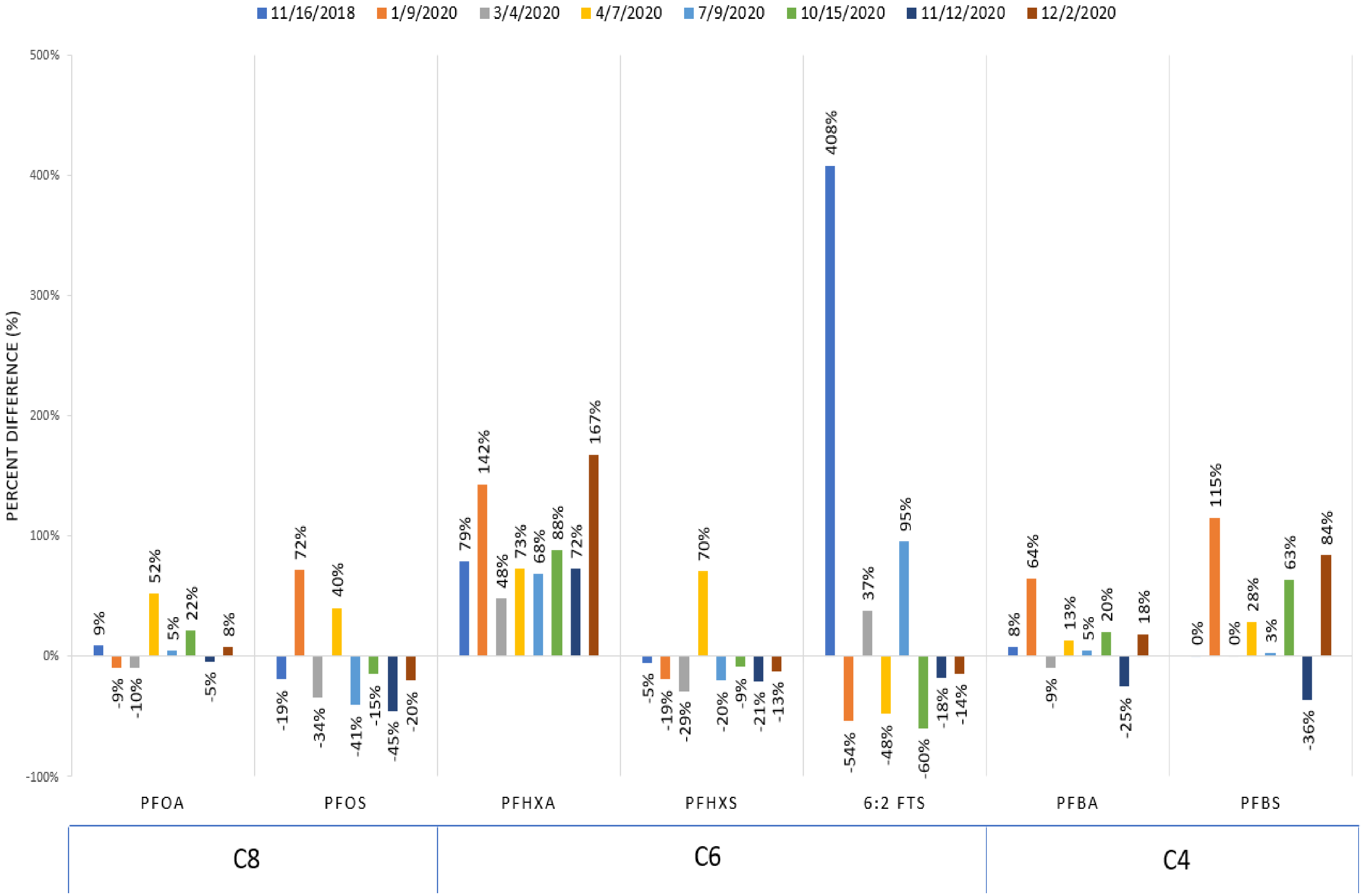

Figure 12. Percent difference between influent and effluent WWTP concentrations of Great Lakes Water Authority (GLWA). Positive values represent increases in PFAS concentration from influent to effluent.

Annual total PFAS mass loading rates for the 10 WWTP are estimated from concentration data of the 28-analyte suite and WWTP discharge data from MIWaters (Figure 13). KI Sawyer and Bronson WWTPs have the lowest mass loading rates to receiving water bodies, both are approximately 0.04 kg/yr. Grand Rapids and GLWA WWTPs have the greatest total PFAS mass loading rates to receiving water bodies at approximately 63 kg/yr and 128 kg/yr, respectively. Bossi et al. (2008) found mass flows of industrial WWTPs to be 10 g/yr to 147 g/yr with an average of 96 g/yr using a seven PFAS suite. This estimate is comparable to the mass flows of 40 g/yr from both KI Sawyer and Bronson WWTPs while being 3 orders of magnitude less than the average mass flow of 21 kg/yr in the current study (Figure 13). All estimated WWTP loading rates are very large considering that toxicity limits for all regulated PFAS in drinking water are in the parts per trillion range. Additionally, 21 of the 28 (75%) PFAS are terminal PFAAs and certainly more undetected PFAS are being discharged into receiving water bodies.

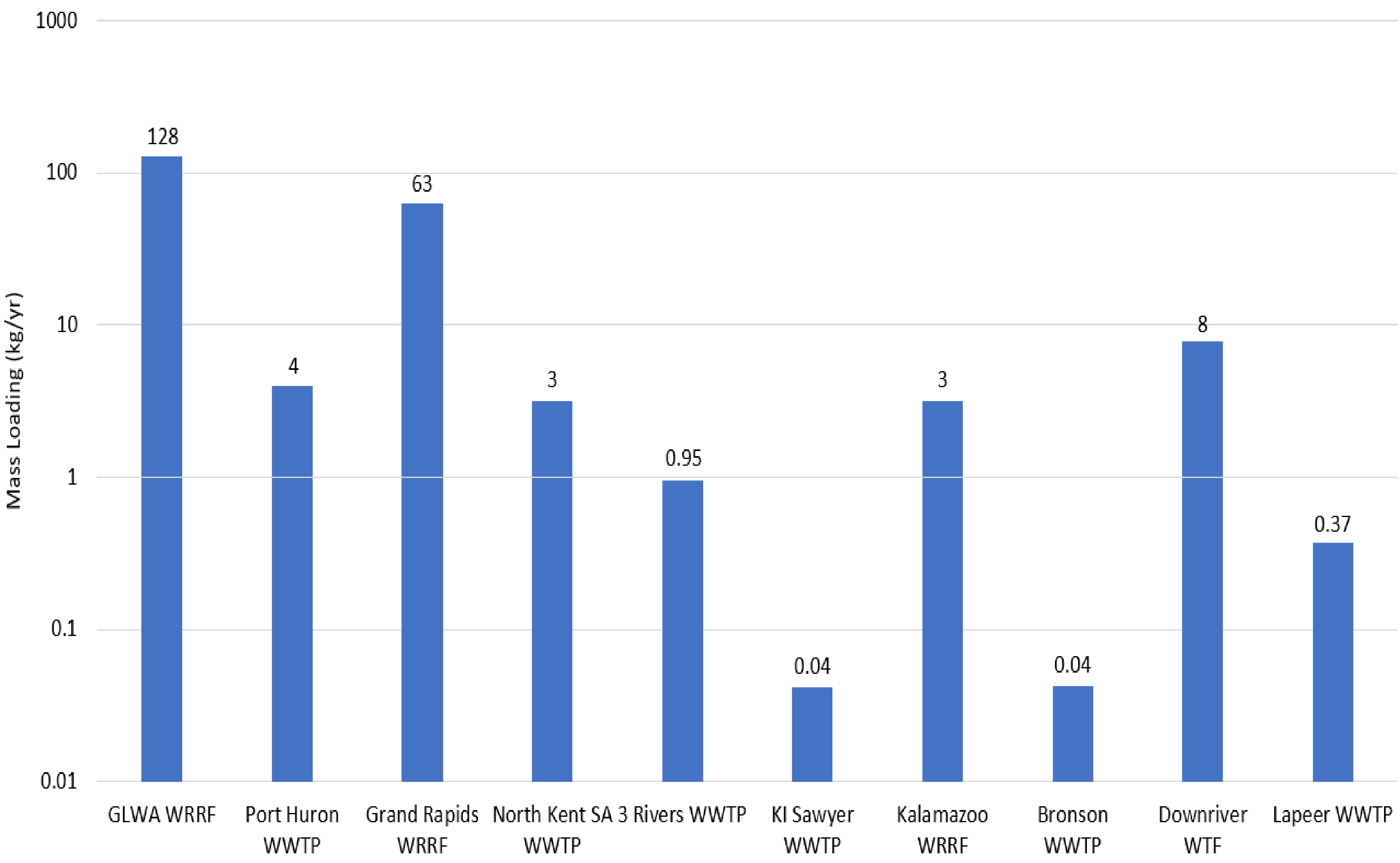

Figure 13. Mass flux (kg/yr) of total PFAS (n=28) for WWTPs studied.

3.3.2 WWTP Biosolids

Activated sludge and biosolids generated at WWTPs also contain PFAS, because PFAS tend to adsorb to organics, including the biomolecules in bacteria. Significantly less sampling of PFAS in biosolids has been conducted in Michigan than WWTP influent and effluent. Few WWTPs have available data on PFAS concentrations in their biosolids, let alone results from more than one sampling period. Similar to data from landfill and WWTPs, PFAS composition plots were developed for 11 samples of biosolids from six WWTPs: Bronson, Downriver, GLWA, KI Sawyer, Menominee, and Three Rivers (Figure 14). With the exception of Menominee all these WWTPs were also part of influent-and-effluent study. Concentrations of total PFAS are located at the top of each column and range from 18 ppb to 7017 ppb. Biosolids from Bronson WWTP (n=4) and KI Sawyer (n=3) show high variability (greater than two orders of magnitude) with total PFAS concentration ranging from 56 ppb to 7017 ppb and 93 ppb to 4530 ppb, respectively, for the 28-analyte suite. Downriver, GLWA, and Three Rivers each have one biosolid dataset with total PFAS of 46 ppb, 18 ppb, and 626 ppb, respectively.

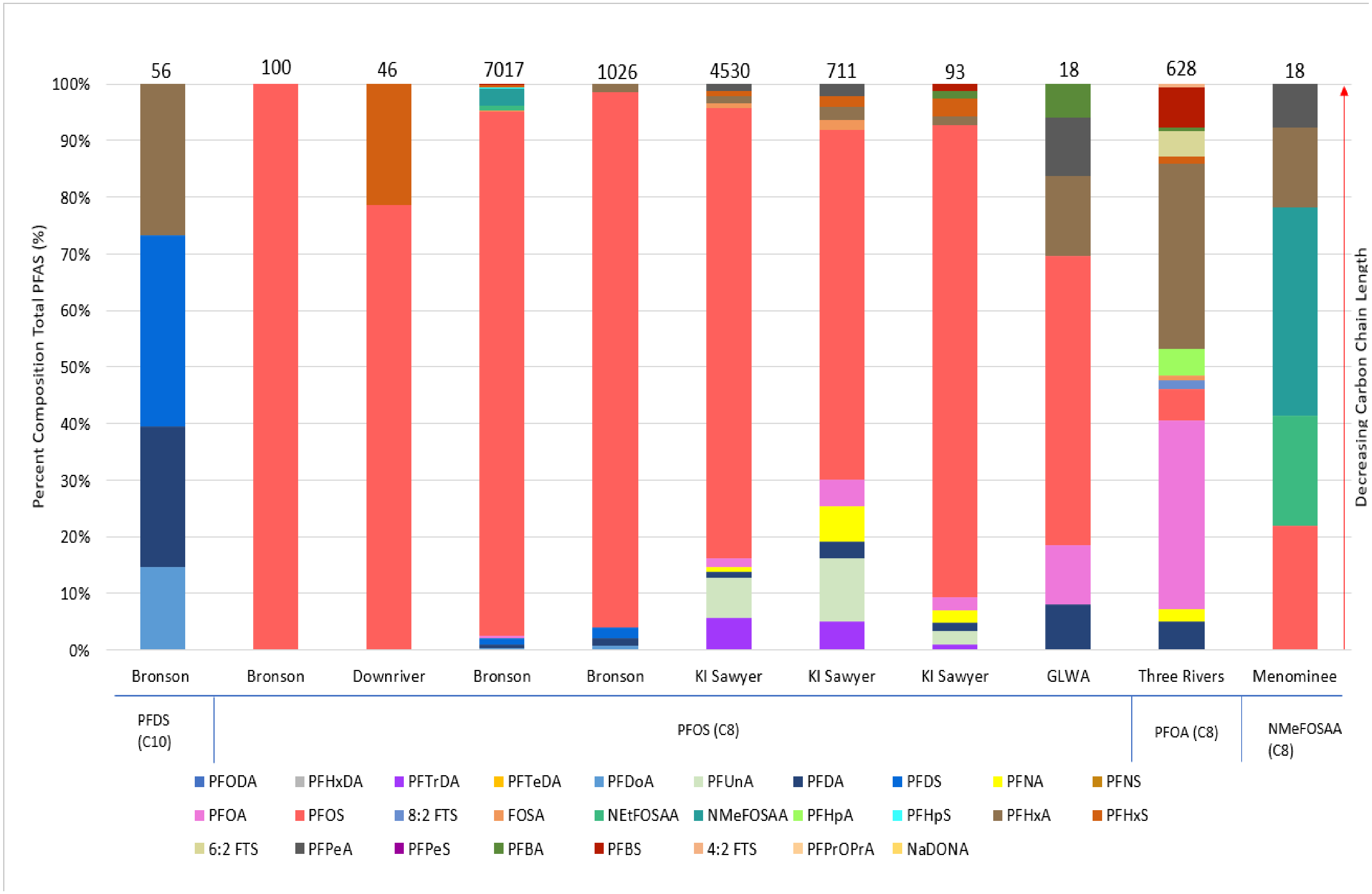

Figure 14. Percent composition of biosolid samples from 6 Michigan WWTPs. Total PFAS concentration in µg/kg (ppb) is located at the top of each column.

The composition of PFAS on these biosolid samples skew heavily towards long chain PFAS, with the dominant PFAS in the biosolids being C8 or larger and only very minor components of short chained PFAS. PFOS is the dominant compound in 8 of the 11 (73%) samples, with the other three samples being PFDS (C10), PFOA (C8), and NMeFOSSAA (C8) dominant. The Bronson WWTP generated a total of four biosolid samples, three of which are PFOS dominant and contained very little PFDS, and one PFDS dominant sample that did not contain any PFOS or PFOA. A single biosolid sample from the Three Rivers WWTP is only slightly PFOA dominant (33%) with 32% PFHxA (C6). One biosolid sample from the Menominee WWTP was dominant in NMEFOSAA which was only detected in one other biosolid sample (Bronson). Insufficient biosolids data precluded: (1) estimation of annual PFAS mass loading of biosolids as either untreated sewage sludge to landfills or treated biosolids that are land applied, and (2) mass balance computations between WWTP influent and effluent to determine if net losses of some compounds in the wastewater stream, particularly PFOS, can be attributed to biosolid sorption.

Michigan biosolids are comprised primarily of long chain PFAS, which supports the hypothesis that shorter chain PFAS in landfills originate from sources other than biosolids Consistent with our data, Bossi et al. (2008) found that PFCAs with an even number of carbon atoms were more abundant in biosolids PFCAs having an even number of carbon atoms, which is consistent with even-carbon-numbered PFAS (C8 and C10) present in Michigan biosolid samples. In our study, WWTP biosolid and effluent PFOS concentrations ranged from 4 ng/g-6500 ng/g and 1 ng/l – 210 ng/l, respectively. Loganathan (2007) also found that samples of biosolids had higher concentrations of PFOS (43-993 ng/g) than wastewater samples (8.1-47 ng/l). Biosolids act as a sorbent for long chain PFAS such as PFOS which explains the observation that PFOS concentrations consistently decreased across WWTPs while shorter chain PFAS increased.

4. Conclusions

PFAS move through different natural and engineered systems in the environment, and the largest group of PFAS-contaminated sites in Michigan is landfills. Landfills reflect the replacement of C8 PFAS (e.g., PFOA and PFOS) with C6 and C4 PFAS. Landfills that discharge to WWTPs also contribute a significant fraction of total PFAS entering WWTPs. WWTPs only comprise 4% of Michigan's PFAS-contaminated sites but are responsible for discharging large amounts (measured in kg) of PFAS directly to surface waters. Current technology (GAC) is effective at removing long-chain PFAS from wastewater but are less effective at removing short-chain PFAS. Most WWTP lack PFAS removal which leads effluent concentrations to commonly increase across the plant up to 19 times the original influent concentration. Most WWTPs do not remove PFAS from the water. This, combined with release of PFAAs that accompanies the breakdown polyfluorinated precursors during treatment results in concentrations of some PFAAs increasing across the plants as much as 19 times. While total PFAS concentrations across WWTPs often increase, concentrations of PFOS tend to decrease due to a high tendency to adsorb to biosolids. The PFAS that accumulate most in biosolids tend to be long chain (C8) (e.g., PFOA and PFOS) and should be closely monitored to ensure safe land application.

5. Data Gaps and Future Research

During this study, it was observed that some Michigan landfills only had sampling data available for PFOS and PFOA which does not fully characterize the amount of PFAS in the leachate. Recent findings prove that PFOS and PFOA are only a small fraction of the total PFAS in the world (USEPA, 2021).

The number of compounds analyzed in wastewater should be increased. The EPA needs to publish a universal method for PFAS in nondrinking water sources so all labs can follow identical procedures. This will help clear up discrepancies from lab to lab. More toxicology data needs to be collected to develop MCLs for additional compounds. Currently only seven PFAS compounds out of potentially thousands are being regulated in Michigan. In order to regulate more compounds, treatment plants must have the technology to achieve the concentrations the MCLs. New sustainable treatment methods need to be developed to treat for shorter chain compounds. GAC is effective at capturing long chain PFAS such as PFOS and PFOA but the short chain PFAS are not captured.

Biosolids are an area of growing concern in Michigan. Ongoing research is being conducted in Michigan into what concentrations of biosolids can be safely land applied and what can be done with those that are too contaminated. Landfilling should not be an option for biosolids that are contaminated as it just continues the PFAS cycle.

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