Stormwater Contaminants of Concern and Best Sampling Practices

A Review of Current Literature

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April 22, 2025

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1. Purpose

This literature review summarizes current scientific literature and published analytical methods to provide guidance on sampling stormwater for various contaminants of emerging concern (CECs) for the 2024 Stormwater Action Monitoring (SAM) funded study entitled: Monitoring for Stormwater Contaminants of Emerging Concern in Western Washington. Several CECs are receiving increasing scientific and regulatory attention due to their impacts on ecological and/or human health. This review focuses on a subset of CECs with growing recognition of their toxicity and ubiquity in environmental pathways such as roadway runoff: 6PPD-quinone (6PPDQ) and related compounds; per- and polyfluorinated alkyl substances (PFAS); and microplastics, including tire rubber-derived components of environmental microplastics (MP). For this subset of CECs, there exist several data gaps around the chemical characteristics, environmental occurrence, fate outcomes, or analytical methods needed to fully understand and mitigate their environmental risks.[1–4] While global research and agency efforts are helping to fill in these data gaps, standardized methods for sampling and processing of these contaminants in stormwater have yet to be fully validated or optimized. This literature review aims to communicate outcomes and implications of some key studies and data sources for appropriate sampling practices for 6PPDQ, PFAS, and MP. In addition, this review briefly addresses the environmental relevance and sampling methods for other important CECs including: polyaromatic hydrocarbons (PAHs), pharmaceuticals and personal care products (PPCPs), polybrominated diphenyl ethers (PBDEs), and other roadway-derived organic chemicals such as Hexa(methoxymethyl)melamine (HMMM). This literature review focuses on stormwater management efforts in the Pacific Northwest, especially with respect to understanding potential contaminant sources and dynamics relevant to western Washington State.

While optimal sampling methods will evolve with time as new and critical CECs arise, consistent methods grounded in best practice can generate high-quality and reliable data to define roadway runoff pollution. With respect to the stormwater studies occurring in Washington State, challenges arise from the different target analytes that require different materials, collection methods, and analytical techniques. The disparate chemical characteristics and conflicting requirements of these new classes of CECs means that standardized, one-size-fits-all sampling protocols are not practical. Here, the goal is to communicate some key attributes of the above-mentioned CEC classes to better enable their sampling and analysis in roadway runoff-impacted environmental systems. This review provides a summary of published studies conducted on key CECs in stormwater samples (particularly from roadways), surveys appropriate and recommended sampling approaches and analysis concerns for these key CECs, and addresses additional contaminants for potential prioritization in aquatic habitats affected by roadway runoff.

2. Literature Review

2.1. Introduction

Below is a summary of past research, current research focus, and data gaps where additional research needs to be conducted.

2.1.1. Previous Research

Stormwater, defined as runoff during and following precipitation and snowmelt events, including surface runoff, drainage, and interflow[5], is recognized as a source of anthropogenic contaminants to receiving waters.[1,2] In some locations and periods, snow melt can generate contaminant export during dry weather conditions that are not directly associated with an ongoing storm event. However, at most locations in the western Pacific Northwest, the vast majority of stormwater impacts to receiving water quality occur during wet season precipitation events of fall, winter, and spring, typically with the strongest and largest storms of the year occurring October to December, and continuing through the winter until tapering off in May to June.[6] During the summer, the Mediterranean climate of the Pacific Northwest typically results in very few storms that generate runoff, and thus there are more limited risks of water quality degradation during the summer. However, the dry summers also represent a long period for roadway-derived and other anthropogenic contaminants to accumulate on roads and urban surfaces, potentially raising risks of disproportionate water quality impact during the first significant storms of the fall wet period.

This review will primarily focus on organic CECs associated with roadway runoff, while noting that many organic contaminants present in runoff arise from multiple sources.[1,3] Some toxic and harmful contaminants present in runoff includes contaminants from roadways and highways with active traffic, and to a lesser degree, from parking lots.[7,8] Roadway runoff is most impacted by vehicles and is disproportionately rich in vehicle-derived contaminants, including chemicals used in vehicle fluids (e.g., antifreeze, windshield washer fluid, brake fluid, motor oil, lubricants, power steering fluid), as well as chemicals leaching out of exhaust particles, tire rubber, vehicle care products, and automotive plastics.[2,9] In addition to the vehicle-derived contaminants, runoff from roadways also include herbicides, antioxidants used on roadways (e.g., road striping paint cleaner, bridge paint antioxidants), as well as other contaminants that are present due to human contact or human presence (e.g., caffeine, ibuprofen, DEET, cotinine).[4] Sources of organic chemicals in runoff from non-roadway developed areas include roofing and building materials, paints and coatings, residential and commercial pesticides and herbicides, and other specialized industrial, commercial, and residential activities.

For decades, management of sources of metals, such as copper and zinc, which can be found in in brake pads, tires, galvanized metal fences, roofs, and building materials, has been a focus for stormwater management.[10–12] In addition to metals, regulatory management of stormwater has also focused on petroleum hydrocarbons, oils and grease, PAHs, salts (in winter-affected regions), nutrients, and indicator bacteria. These pollutant classes are well characterized in stormwater studies and regulatory toxicity endpoint and exposure risk evaluations[13]. Strategies to sample, measure, manage, and treat these constituents became highly developed and reliable in industrial effluents and municipal wastewater discharges. Regulatory management strategies encourage passive and natural treatment systems (i.e., "green stormwater infrastructure") that are lower cost and spatially match the widely distributed and diffuse nature of roadway runoff discharges. While these approaches are generally effective and popular with the public, most of the urban stormwater volume remains under- or untreated because of technical and economic limitations of widespread implementation of stormwater treatment at scale.

2.1.2. Current Research

While decades of research has characterized the contribution of roadway runoff to toxic loading in our receiving waters[14,15], roadway runoff has recently been identified as a major source of toxic tire-derived chemicals, as well as tire road wear particles (TRWP) and microplastics (MP), which are shown to be harmful or toxic to aquatic organisms.[1,2,16,17] While the chemical complexity of stormwater has been documented in research worldwide, biological observations of stormwater linking mortality in coho salmon and other impacts to salmon (e.g., effects of copper exposure on olfaction) in the Pacific Northwest were important motivating factors that led to the development of advanced chemical characterization and biological assessment of roadway runoff composition.[2,6,11,18–20] For example, the regional focus on understanding the water quality of stormwater-linked coho salmon mortality events, called urban runoff mortality syndrome (URMS), led to the application of advanced environmental mass spectrometry techniques to urban stormwater.[4,9,21] These studies identified tire rubbers as a primary source of multiple, abundant chemical contaminants with toxic properties, eventually leading to the discovery of 6PPD-quinone (6PPDQ) as a ubiquitous and highly toxic pollutant of roadway runoff. Data from the Pacific Northwest and around the globe suggest that 6PPDQ is often present at concentrations exceeding biological thresholds for acute mortality effects for 6PPDQ-sensitive aquatic organisms.[7,8,22–25] The potential for tire rubber to act as a source of multiple classes of contaminants, often at high concentrations, has now been well established in the scientific literature.[1,2,20,26–28] These studies have also highlighted the importance of transformation products of industrial chemicals within roadway runoff as drivers of environmental hazard, including the widespread presence of many poorly characterized compounds that had toxic and bioactive attributes. [7,20,29–32] For example, given the environmental instability of both parent PPD antioxidants and primary products like 6PPDQ, characterizing their relative chemical composition, along with co-occurring stable terminal products across various sample types and treatment systems, remains a critical need for effective management of tire rubber-derived chemicals[33,34]

In parallel with the recent research efforts around 6PPDQ and tire rubber-derived CECs, the potential risks of environmental MP have grown recently and led to efforts to understand the sources and fate of MP, including the portion of microplastics derived from tire rubber (i.e., tire wear particles (TWP), or tire and road wear particles (TRWP)).[3,16,35,36] While methods for quantifying MP are relatively advanced in some contexts, such as ocean sediments and open waters, the lack of standardized methods for quantifying microplastics in stormwater in roadway environments reflects a current data gap in the scientific literature.[3] With the growing recognition that tire rubber-derived contaminants are an important source of water quality impairment, there exists a clear need to understand the occurrence, fate, and chemical characteristics of TWP and TRWP that can act as a mobile and legacy source of toxic contaminants.[36–38] To a large degree, this particular set of topics remains in its infancy, despite the obvious implications of TWP and TRWP as a source of toxic chemicals such as 6PPDQ and the clear need for management of these constituents in roadway environments.[3]

2.1.3. Research Needs

With the discovery of new CECs, especially those with structural characteristics unlike prior classes of environmental pollutants, there exist multiple uncertainties regarding optimal methods for sampling and analysis in stormwater. For instance, very little insight into highly hydrophobic and persistent PFAS compounds, which are characterized by exceedingly stable carbon-fluorine bonds, can be derived from understanding other types of legacy organic pollutants. PFAS have become a particularly important class of CECs over time due to their environmental persistence, ubiquity, chemical complexity, and growing recognition of their toxic attributes, particularly with respect to human health. While they have been a focus of research attention for over 20 years, it was not until recent reports of their occurrence in stormwater discharges that they were recognized for their ubiquity, persistence, and formation of products with adverse health consequences for humans from multiple precursor compounds in stormwater.[32] Similarly, quinone transformation products like 6PPDQ, along with the entire class of aromatic amines typical of multiple classes of industrial chemicals used in tires (like diphenylguanidines, dicyclohexylurea, 6PPD, and HMMM, among others), represent relatively novel and understudied classes of environmental contaminants where substantial uncertainty exists with respect to monitoring methods and assessment strategies.

One of the most challenging aspects of runoff sampling is related to the highly dynamic and time-sensitive nature of contaminant transport and observed concentrations across various sample types during storm events.[1,9,32,39] These dynamic location and time-dependent characteristics present substantial technical and management challenges for the detection, characterization, and treatment of trace organic pollutants in roadway runoff, including novel CECs.[9,39] Concentrations of organic contaminants in runoff are highly variable because of the diversity of contaminant sources across the developed landscape. Storm events that mobilize and transport these contaminants are dynamic and variable with time. The degree of dilution, as well as the attenuation process in pipe systems and the receiving waters, can be considerable.[40–42] A growing body of evidence suggests that high traffic areas contain enough rubber-derived mass such that the environmental occurrence of these CECs is a transport-limited process rather than a mass-limited one, leading to dilution-independent export to receiving waters.[39,42] Understanding these factors will be critical to sampling storm events effectively and eventually implementing management strategies.

2.2. Constituents of Concern

Below is a summary of the main CECs of focus in this literature review: 6PPDQ, PFAS, and MP, and TRWP.

2.2.1. 6PPD-Quinone, or “6PPDQ”

6PPDQ is a recently discovered, yet highly toxic, transformation product of the common tire rubber anti-ozonant 6PPD. In late 2020, Tian et al. first reported 6PPDQ as the “primary causal toxicant” for decades of previously unexplained observations of mortality in coho salmon after rain events.[7,8] The parent compound 6PPD is a *para*-phenylenediamine (PPD) antioxidant that is the most common antioxidant compound added to tires, with at least 270,000 tons of 6PPD produced annually across the globe.[23] 6PPD protects tire rubber by scavenging atmospheric ozone to form 6PPDQ as an oxidation product; yields of this reaction tend to be around only ~1 percent of 6PPD mass. Current research shows that this 6PPDQ formation reaction only occurs in air and not in water, implying that 6PPDQ formation potential will depend on whether tires, TWP, and TRWP are subject to atmospheric contact or not.[30,33] 6PPDQ formation can occur both on the surface of tires or on TWP/TRWP mass dispersed throughout the environment, whether on roadway surfaces or throughout roadway-impacted environments. Once 6PPDQ is formed, it can be transported into the surrounding environment by leaching processes from tire rubber from any of these sources via rainwater, as well as possible airborne and particle transport pathways.[34,37,43]

Additionally, there is a legacy mass of tire rubber dispersed in waste tire materials, recycled tire products, tire dumps, and tire reefs.[17] 6PPD has been the primary rubber antioxidant used for at least the last 50 years, though there is at present a data gap on whether old tires and recycled tire products present a significant source of leached 6PPDQ in our receiving waters.

Driven by its longstanding and abundant use in tire rubber (~1 percent of tire rubber mass is 6PPD in all tires globally) and ubiquitous presence in roadway runoff (concentrations of hundreds to thousands of nanograms per liter (ng/L) for busy roads), 6PPDQ is likely to occur in all roadway runoff and most receiving waters downstream of higher trafficked roadways receiving roadway runoff, likely at concentrations lethal to the most sensitive species of fish.[8,23,41] Notably, while 6PPDQ is not toxic to all species of fish, for the group of salmonids that are sensitive to its presence 6PPDQ is highly toxic and now regarded to be one of the two most toxic chemicals for which the EPA has published aquatic life screening criteria with respect to acute toxicity.[8,22,24,25] One primary management need for regional 6PPDQ data collection is a better understanding of landscape and storm conditions that drive the creation of hot spots and hot moments for its environmental occurrence, including basic attributes of fate and transport in roadway-impacted environments of western Washington.

2.2.2. Per- and Poly-Fluoroalkyl Substances, or "PFAS"

Per and polyfluoroalkyl substances (PFAS) are a group of "forever chemicals", so called because of their ability to persist in the environment, even over time scales of centuries to millennia[44]. They have been in production for at least 70 years and are characterized by the presence of strong fluorine-carbon bonds. One key attribute of PFAS is their high resistance to thermal and oxidative degradation[44]. This attribute, combined with their typically amphiphilic characteristics with polar head groups and non-polar hydrophobic tails, provides a relatively unique set of characteristics for an industrial chemical class. The chemical industry has exploited these characteristics to such a degree that as a class, PFAS now encompass thousands of different individual chemicals found in a wide variety of disparate products and applications. However, the most toxicologically significant PFAS species detected in the environment are often considered to be perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS)[45]. These chemicals have been used industrially since the 1940s because of their ability to repel water and grease, resist thermal breakdown, and act as a flame retardant. The amphiphilic and hydrophobic structures of PFAS, combined with their typically low concentrations (often below 5 ng/L), makes them especially difficult to sample because they can irreversibly sorb onto many sample container materials and bias the sample, plus it is easy to contaminate samples during sampling. PFAS are widely present in foods, food packaging, drinking water, various consumer products, and household dusts; such sources are especially concerning for potential human exposure because PFAS have been shown to disrupt thyroid function, decrease immune responses, and may be carcinogenic in humans[45].

2.2.3. Microplastics (“MP”) and Tire and Road Wear Particles (“TRWP”)

Microplastics (MP) are synthetic polymer particles that are smaller than ~5 mm in diameter and can vary greatly in their size, shape, and composition depending on how they were formed and where they occur[46]. They can either be formed as primary MP (e.g., fibers and microbeads), which are manufactured as MP directly, or as secondary MP, which are formed when larger plastic materials are degraded and fragmented during use and environmental disposal or transport (e.g., plastic trash fragmenting into microplastics)[47]. Degradation of plastic materials can occur with exposure to light, mechanical damage, oxidation, or biological consumption.[48] Despite these processes, plastics are considered to be persistent in the environment with half-lives ranging into centuries-long time scales. In general, exposure to MP via inhalation or ingestion pathways can cause health effects on humans or other organisms[49]. This may be due to physical risks of microplastics uptake, harmful bacteria or chemicals adsorbed to the MP surface, or toxic chemicals like plasticizers and additives present within the MP themselves.[50–52]

One important type of MP is TWP and TRWP, comprised of elastomeric polymeric materials, especially those derived from tire rubber[53]. These are a particularly complicated and chemically complex form of MP because rubber tends to be denser than other plastic polymers, plus at least 10-fold more mass of additive chemicals are typically used within elastomeres, including many compounds with well-known toxic attributes. TWP and TRWP are discrete particles of rubber that are shed from tires, where TRWP particles represent the fraction of tire derived particles that include aggregates of minerals and roadway materials as part of the particle. The size of TWP and TRWP are dependent on a wide range of factors such as car type, driving speed, weather conditions, and more[54]. This size variability makes it difficult to estimate generation rates, although estimations range anywhere from 0.5 to 2.5 kilograms per capita per year[55]. Once generated, TWP and TRWP can become aerosolized, transport away from the roadway, or remain on the roadway surface.

TWP can form complexes with other roadway materials and become TRWP, which further complicates their fate and transport as the composition and densities and characteristics of these particles are non-uniform and not well understood[54]. Interactions with roadway surfaces can incorporate mineral and asphalt content to the rubber material, altering the typical shape and size attributes and changing the density and transport properties of TRWP[56]. These disparate chemical and physical attributes make it difficult to standardize sampling and extraction methods for both MP and TWP/TRWP because techniques that work for one constituent might not necessarily work for the other[50]. For example, dense TRWP may transport in benthic sediments, via siltation, while lighter MP may remain within surface water[57]. TWP and TRWP are of particular concern for runoff because they can act as a primary source of toxic chemicals that leach out of them over time, such as 6PPDQ and many other co-present rubber chemical additives and anti-degradants.

2.3. Sampling Methods

For environmental monitoring purposes, 6PPDQ and PFAS now have documented sampling methods published by the EPA (draft method 1634 and method 1633, respectively). Absent any specialized site or analytical data to promote alternative options, these methods should be currently considered as the definitive sources of sampling and analytical methodologies for stormwater samples. Sampling methods for MP and TWP/TRWP are not standardized and many aspects of their collection and analysis reflect syntheses or best practices based on expert knowledge and various published research and monitoring strategies.

2.3.1. 6PPDQ

Sampling methods for 6PPDQ in environmental samples are largely based on EPA Standard Method 1634, while noting that the basic procedures for sampling trace organic CECs are largely derived from EPA method 1694 (the method for personal care products), which is now well developed and deeply validated across at least 20 years of monitoring effort. Some reported 6PPDQ methods use analytical approaches that include broad spectrum analysis of PPDs, PPD transformation products, tire rubber chemicals, and roadway contaminants, forming a set of roadway-derived analytes that will likely eventually result in some version of an adapted 1694 method adapted to roadway CECs.[58,59] At the current time, 6PPDQ should be collected in amber glass bottles with polytetrafluoroethylene (PTFE) lined caps, if possible. Sample sizes depend on instrument performance, but are typically 125 mL, 250 mL, or 1 liter and have minimal to no headspace. Based on Method 1634, samples can be stored up to 14 days prior to extraction and then up to 28 days after, although it is not anticipated that there will be any particular challenges around much longer storage of SPE extracts if kept cold. 6PPDQ samples can be collected using a variety of methods, such as stainless steel or glass dippers for grab sampling in water bodies. Additionally, to address dynamic concentration and to understand mass loads, the EPA recommends that ISCO automated samplers with glass or fluoropolymer tubing be used to collect samples remotely. If using peristaltic pumps, a minimal amount of silicone tubing should be used onsite to fill sample containers, as 6PPDQ is prone to sorb irreversibly to silicone.[60] It is also important to note that the stability and attributes of 6PPDQ are not yet fully defined; researchers have observed 6PPDQ instability in the presence of air, and potentially co-interferences within roadway runoff and environmental samples can result in rapid partial loss of 6PPDQ. As a redox-active quinone, multiple poorly understood oxidative and reactive pathways are potentially applicable to 6PPDQ sampling, storage, processing, and analysis steps. It is regarded by most researchers as a difficult analyte to work with and sometimes exhibits surprising behaviors. Recommended sampling materials and storage methods for 6PPDQ in water can be found in Table 1.

2.3.2. PFAS

When sampling for PFAS, EPA Standard Method 1633[61] recommends using high density polyethylene (HDPE) bottles with polypropylene or linerless HDPE caps. Sample sizes should be 125, 250, or 500 mL, and bottles should be filled to the shoulder. Samples can be stored for up to 28 days if held at less than 6°C, or for 90 days if held at -20°C, although the persistent nature of most PFAS reflects relatively limited risks of sample instability during storage. PFAS can be sampled using stainless steel devices or peristaltic pumps with HDPE tubing. Due to their ubiquity in consumer goods, cross contamination of PFAS during sample collection is a major concern and steps should be taken to avoid contamination during sampling.[62] Previous protocols have identified extensive lists of materials to avoid when sampling, which include PTFE (e.g., jar lids, tubing), waterproof coatings (e.g., Goretex), and pipe threads and tape.[62] It is also recommended to increase the frequency of field and laboratory blanks from that of other stormwater constituents to help identify sampling contamination issues. With respect to a mixed-analyte sampling strategy, it is important to note that PFAS has its own sampling protocol that tends to be distinct from many other trace organic CECs. For example, unlike almost all other organic analytes, PFAS should not be collected or stored in glass containers. Recommended sampling materials and storage methods for PFAS sampling in water matrices can be found in Table 1.

Table 1. Recommended Sampling Materials and Storage Procedures for PFAS and 6PPDQ Samples.

Constituent	Bottle and Cap Material	Bottle/ Sample Size	Headspace	Holding times	Holding Temperature
6PPDQ *(EPA Method 1634 and Lane et al.)*[46,47]	Amber glass with PTFE lined caps	125 mL, 250 mL, or 1 L	Minimal to none	14 days prior to extraction and 28 days of storage after	<6°C
PFAS *(EPA Method 1633)* [44]	HDPE with Polypropylene or linerless HDPE cap	125, 250, or 500 mL	Fill to Shoulder	28 days (or 90 days if held at -20°C)	<6°C

2.3.3. TWPs/TRWP and MP

There are no current standardized methods for sampling of TWP/TRWP or MP. Sample collection should integrate the entire flow field as much as possible so as not to miss any MP or TWP particles of interest[56]. However, best practices for storing and containing samples are similar for both. The TWP and MP table in Appendix A summarizes the sampling methods and materials of documented studies of MP or TWP in stormwater.

Plastic containers and sampling materials are not recommended for MP samples as there is a large potential for cross contamination from preexisting MP within the containers. Both plastics and rubber materials should be avoided as much as possible. The studies in Table 2 demonstrate that glass and metal containers are the standard container type for MP sampling. To analyze MP, two approaches can be used—either pumping large quantities of water through filters on-site or collecting a discrete sample and then filtering for particles in the lab. Both strategies must integrate the flow field as much as possible. As a result, container sizes can vary greatly, but in general, 10 liters to as much as 1,000 liters are typically needed and recommended to ensure statistically significant detection of both MP and TWP whenever their environmental concentrations are low[63]. Additionally, as the studies in Table 2 show, storage temperatures of 4°C are preferred (although may not be necessary from a stability perspective), which is largely consistent with the EPA methods for PFAS and 6PPDQ. Whether or not headspace is present should have little impact on TWP samples, as this will not impact the concentration of particles in the solution. Samples should be kept in the dark to reduce photodegradation. As with PFAS, MP are ubiquitous in consumer goods and present a high potential for cross contamination of samples during sampling and sample processing. Previous protocols have identified possible sources of MP that should be avoided during sample collection, including synthetic clothing that contains MP fibers (e.g., synthetic fiber materials like Nylon and Spandex)[64]. Further, lab grade water used in sample container cleaning should be verified as MP free, and all wash and sampling equipment and tubing should be plastic-free[64].

2.3.4. Summary of Sampling Complications

Another complication with sampling 6PPDQ, PFAS, and MP in tandem is the potential for sample contamination, specifically PFAS and MP, due to their ubiquitous nature in the environment. For 6PPDQ, sample contamination possibilities are more limited because the primary source of 6PPDQ is currently believed to be tire rubber, and this type of rubber is not commonly found built into stormwater sampling equipment. 6PPDQ has been found to be present in some common products used during field sample collection and in laboratories, such as some rubber shoe soles, laboratory stoppers, and rubber gaskets, the use of which should be avoided when collecting and analyzing samples where trace 6PPDQ detections are expected. [17,65] PFAS, on the other hand, is in thousands of different products with higher potential to contaminate samples. Rodowa et al. detected 83 ug/m^2 PFOA in marker ink and 0.77 ug/m^2 PFBS in duct tape, indicating high concentrations of PFAS in materials commonly used in sampling[66]. The study on the whole indicated that samples are unlikely to come in direct contact with many PFAS containing materials; however, care needs to be taken to ensure that cross contamination by the person sampling does not occur.

MP have similar source complexities as PFAS in that they are also found widely in the environment and in many sampling materials. MP have been found to shed from synthetic clothing and lab coats and cause sample contamination issues.[67] Additionally, using old lab supplies or materials can cause degradation of the plastic and therefore lead to MP contamination[64]. Prior to sampling, field and laboratory equipment should be inspected and assessed to reduce MP contamination effects. Even with proper lab protocols, over 30 percent of detected MP can be attributed to contamination and without any protocol over 70 percent can be due to contamination.[51] For this reason, field and lab blanks are an inherent part of MP sampling plans.

2.4. Review of Measured CEC Concentrations in Roadway Runoff and Receiving Waters

2.4.1. 6PPDQ in Roadway Runoff and Receiving Waters

Since its discovery in 2021, many studies have been conducted to measure 6PPDQ concentrations in urban and roadway runoff and in receiving waters. The 6PPDQ table in Appendix A summarizes 6PPDQ concentrations for a few of the most relevant studies.

6PPDQ is currently believed to be transported into and through aquatic habitats via three main pathways—dissolved in water, associated with suspended particulates, and as tire particles. The dissolved pathway reflects situations where the 6PPDQ mass becomes fully dissolved into water upon wetting, as when vehicle tires on the road get wet during rainstorms and 6PPDQ washes off the tire, or off of wetted

TWP and TRWP. Because "dissolved" is an operational definition, the "dissolved" fraction of 6PPDQ likely contains 6PPDQ attached to small pieces of the molecular film of 6PPD oxidation products that wash off tire surfaces, as well as 6PPDQ contained on tiny pieces of tire rubber that are sub-micron sized and reflect high surface area TWP that are effectively dissolved in their transport characteristics.[35]

Many site-, storm-, time-, and traffic-dependent factors are known to affect the concentration of 6PPDQ in roadway runoff, resulting in very dynamic and variable concentrations on roadways and in the environment.[23,41] Runoff concentrations depend on tire wear accumulation, traffic patterns, storm size, and 6PPDQ leaching potential, along with other fate and transport variables. Most of these factors remain poorly understood and are the subject of active research. Understanding these factors will greatly improve the understanding of 6PPDQ fate and transport and help to optimize management strategies for this contaminant.

Notably, researchers report near 100 percent detection frequency for 6PPDQ in roadway runoff, especially for roads that are more highly trafficked (e.g., exceeding 2,000 to 5,000 average annual daily traffic rates).[20,38] Many researchers have now reported roadway runoff concentrations in the hundreds of ng/L for roadway runoff prior to its entry into receiving waters, reflecting the strong possibility that almost all trafficked roads will have 6PPDQ concentrations above EPA Aquatic Life Screening values (currently 11 ng/L) in roadway runoff for most storms, and usually also above LC_{50} values (e.g., 41 ng/L per Lo et al.) for coho salmon.[68] On multilane highways, 6PPDQ concentrations can sometimes attain the 1,000 to 3,000 ng/L range, often 10 to 30+ times higher than LC_{50} values for coho salmon and sometimes 100-fold or more higher than EPA Aquatic Life Screening values.[8,31,38,42,69–72] For the busiest roads, 6PPDQ concentrations are likely to range from 100 to 1,000+ ng/L in runoff, with hundreds of ng/L being common for many storms and conditions. For less trafficked roads, 6PPDQ concentrations may typically be only near or below 100 ng/L in runoff, and likely even in the tens of ng/L ranges for lower trafficked roads that lack much tire wear accumulation or vehicle traffic. Some efforts have been made to develop a quantitative relationship between traffic volumes and 6PPDQ concentrations but, due to seasonal variations in both rainfall and vehicle travel, a definitive quantitative relationship has yet to be developed[73].

Watershed scale sampling studies are limited, making predictions on fate and time of concentration difficult. For example, the University of Washington has now developed an extensive data set for Miller Creek (Burien, WA), a small coho bearing watershed where annual rates of URMS in adult coho salmon are typically 60 to 70 percent.[8,9,39] By now, detailed water quality data exist from at least 25 storms in Miller Creek over the past 5 years. Before storms, 6PPDQ averaged ~1 ng/L in baseflow. Once it rained, 6PPDQ was present in 100 percent of creek samples after the storms affected baseflow. About half of the sampled storms had maximum 6PPDQ concentrations in the range of 20 to 100 ng/L, and about half the storms have 6PPDQ concentrations exceeding 100 ng/L, rising as high as 150 to 200 ng/L. The peak concentrations typically only persist for a few hours, although potentially higher concentrations may exist for even shorter periods in small watersheds that lack much dilution capacity. These observations are generally consistent with observations in other small watersheds.[39,41,42]

Observations in Miller Creek and other western Washington watersheds are consistent with reports from coho-bearing and near-road watersheds on Vancouver Island (British Columbia, Canada), which now has the world's most extensive dataset for 6PPDQ in aquatic habitats. Jaeger et al. reported similar 6PPDQ dynamics and maximum concentrations of 132 ng/L for three small watersheds that are similar to Miller Creek.[41] Monaghan et al. reported concentrations up to 180 ng/L in several creeks on Vancouver Island.[72] An extensive data dashboard called "tireweartoxins.com" now lists results for over 3,600 6PPDQ measurements across Vancouver Island collected between the years of 2023 and 2025. During storms, samples from various types of "point sources" reflecting roadway runoff (before discharge to the environment) had 6PPDQ concentrations of 100 to 1200 ng/L across Vancouver Island, consistent with other estimates of roadway runoff concentrations.

In aquatic habitats and receiving waters near roads, many sampled locations had no 6PPDQ detected or had low concentrations of less than 5 ng/L, indicating that 6PPDQ can sometimes be absent from locations near roads, or that roadway runoff pathways to receiving waters did not exist, at least at the time samples were collected. However, dozens of watersheds on Vancouver Island now have reported 6PPDQ concentrations over 10 ng/L (concentrations where at least some coho mortality would occur in the most sensitive individual fish) for some samples during storm events, and 6PPDQ has been reported in some coho bearing watersheds at concentrations as high as 400 ng/L. These are the highest concentrations of 6PPDQ yet reported for aquatic habitats that contain salmonids, and they indicate a dire threat to 6PPDQ-sensitive species that may be present in those locations.

Notably, some of the highest reported 6PPDQ concentrations were reported at locations within medium sized communities on Vancouver Island, and often those that simply have a busy road over a small sized creek. Such situations are common across many locations outside of highly urbanized areas. Highly trafficked roads with a direct entry pathway for roadway runoff to small streams or receiving waters, with limited dilution potential in the receiving water, may best explain the highest reported concentrations.

The data in Washington State and the extensive data from British Columbia also align with various global reports for 6PPDQ concentrations in smaller receiving waters (large rivers tend to have lower concentrations and more evidence of dilution and peak lag), indicating that 6PPDQ concentrations in receiving waters share many similarities regardless of study location. Samples collected across the United States from stormwater-impacted systems detected 6PPDQ in 45 percent of the samples at concentrations up to 150 ng/L.[59] In the Great lakes region, 6PPDQ was present in 80 percent of the samples at concentrations up to 88 ng/L.[70] In Michigan, concentrations reached 37 ng/L in stormwater-affected watersheds. In Australia, Rauert et al. reported 100 percent 6PPDQ detection frequency in a small runoff-impacted watershed and concentrations up to 88 ng/L during storms.[36] Combined with the more extensive Washington State and Vancouver Island data, a clear pattern is evident with the dynamic concentrations present in small watersheds after storms, high 6PPDQ detection frequencies, and concentrations commonly in the tens of ng/L, reaching the low hundreds of ng/L for more impacted and roadway runoff affected aquatic habitats.

Treatment data are still somewhat scarce, albeit underway, for 6PPDQ. A 2024 study by Poggioli et al. focused on the effectiveness of green stormwater infrastructure on treating stormwater[74]. Bioretention cells were found to be the most efficient treatment type, the monitoring results of which were in agreement with prior observations from the Puget Sound region, demonstrating the capability of reducing 6PPDQ loads by up to 80 percent. This suggests that there is potential for treatment of 6PPDQ using known stormwater treatment measures, although 80 percent removal efficacy would be insufficient for many of the more highly trafficked locations where concentrations can attain several hundreds of ng/L in direct roadway runoff. Bioretention facilities, however, have demonstrated acute mortality reduction for coho salmon[75]. More research needs to be conducted in this area to conclude effective treatment and management strategies for 6PPDQ.

2.4.2. PFAS in Stormwater

The PFAS table in Appendix A is a summary of relevant studies evaluating PFAS concentrations in stormwater, noting that data are somewhat scarce and are generally inconsistent with respect to PFAS composition. This emphasizes a data gap, as there are limited recent data published on PFAS in stormwater, especially for some of the newer and novel PFAS classes recently found in other sample types. It is difficult to make solid conclusions from the data available for western Washington; however, there are some observable trends. For one, the highest concentration of total PFAS in stormwater is from Murakami et al. (2009), at 390 ng/L[76]. That sample was collected near highways with higher traffic density than any of the other studies included in this review, although the source of the PFAS was somewhat unclear. In addition to the many sources for PFAS in urban areas, there are also multiple car components made with PFAS, although diffuse urban sources of PFAS and transport pathways are not yet fully understood and may be a significant factor to overall PFAS pollution. Additionally, it is important to note that different studies often report different individual PFAS chemicals, meaning comparison of results is difficult if the same parameters are not being reported. Overall, there are limited data on PFAS concentrations in stormwater , indicating that additional data collection should be conducted.

2.4.3. TWP and MP Concentrations in Stormwater

The table in Appendix A is a summary of studies analyzing TWP and MP concentration ranges in both sediment and stormwater in relation to land use. This research has been limited in scope and there are few studies solely focusing on TWP and stormwater. With rising focus on 6PPDQ and other roadway contaminants, the number of studies will increase but as of now there are limited data on TWP concentrations in stormwater. Additionally, with no standardized methods for evaluating TWP concentrations, comparing studies is difficult. While there are many studies on MP in stormwater, few of them specify whether the MP found include rubber particles or TWP, so there are potentially more data that could be used if polymers were specified in previous work.

From the studies included in Appendix A, the highest sediment concentration of TWP was observed in a sedimentation basin next to a highway with values as high as 480 mg/g[77].. Lange et al. reported the highest concentration of TWP in stormwater with up to 740 particles per liter[78], while Parker-Jurd et al. found concentrations of 3.5 mg/L[79]. This highlights another complication when analyzing TWP concentrations—without standardized methods and reporting strategies, it is difficult to compare results. Ultimately, TWP concentrations are likely to vary greatly depending on land use and location; however, this cannot currently be supported by the literature as not enough standardized data exist.

A review of MP concentrations in stormwater is in the TWP and MP table in Appendix A. The results from these studies have very wide ranges of concentrations of MP, with surprisingly low concentrations of less than 1 particles per liter in New Jersey[80], and high values of 18,966 particles per liter in Venice, Italy[81], although some reviews have found concentrations can vary anywhere from less than 1 particle per cubic meter all the way to 10^8 particles per cubic meter[82]. There does not seem to be any correlation between land use and MP concentration in the studies collected, with some urban areas having relatively low concentrations. Other studies, however, have been able to link land use to MP concentration with urban areas having much higher concentrations than rural areas[82]. Ultimately, MP generation, fate, and transport in stormwater are not well understood, and to better characterize this MP sources, fate, and transport, standardized sampling methods are going to be imperative.

2.5. Storm Timing of Sample Collection

Similar to TWP, there is no standardized method for timing the collection of grab samples during storms or determining when water quality is most impacted by storm and location conditions for 6PPDQ and PFAS sampling. For these parameters, researchers at the University of Washington and various reports in the scientific literature generally recommend collecting samples in the early to mid-storm stage, along the rising and peaking limbs of the hydrograph, when pollutant concentrations are at their highest[39,83]. If sample capacity permits, it is also valuable to sample throughout storm periods, including well after rain has tapered off, to determine mass dynamics and loadings during storm events. The timing of stormwater grab samples in recent studies are summarized below in Table 2.

Table 2. Summary of Studies Sampling Stormwater and their Sample Timing.

Study	Location	Analyte	Sample Timing
Johannessen 2022[24]	Toronto, Canada	6PPDQ	Precipitation events greater than 20 mm
Werbowski 2021[12]	San Francisco, CA	6PPDQ	Storms with greater than 1.3 cm
Jaeger 2024[30]	Nanimo, BC	6PPDQ	2 dry days since last rainfall and greater than 5 mm
Peter 2020[43]	Burien, WA	Tire particle derivatives	At least 48-hour long storm event
Boni 2022[17]	New Jersey, USA	MP	Storms totaling between 1.5 and 4.5 cm of cumulative rainfall
Ziajahromi 2021[18]	Gold Coast, Australia	6PPDQ	During heavy rain events (greater than 34 mm per day)
Johannessen 2021[28]	Toronto, Canada	HMMM	During major rain events (greater than 10 mm)
Zhang 2023[31]	Guangzhou, China	6PPDQ	Initial 30 minutes of rainfall
Lange 2021[20]	Sundsvall, Sweden	TWP	Rain events greater than 5 mm
Nguyen 2011[36]	Singapore River, Singapore	PFAS	10 minutes after the onset of rain event
Zushi 2009[37]	Yokohama City, Japan	PFAS	Rainfall events ranging from 1 to 3 mm and within 10 minutes of storm starting
Houtz 2011[38]	San Francisco Bay Area, CA	PFAS	Samples collected during rise, peak, and fall of storm hydrograph
Xiao 2012[40]	Minneapolis, USA	PFAS	Rain events greater than 8 mm per hour

These studies indicate that there are a variety of approaches to determining sample timing. Most sampling strategies are based on waiting for a certain amount of precipitation to occur prior to sampling, along with criteria for antecedent dry period. Of the studies compiled here, the average amount of precipitation that occurred before sampling is 13.7 mm, although it is noteworthy that the University of Washington has observed drastic degradation of water quality in Miller creek after storms of only 3 to 5 mm. Using this method raises some issues as the values chosen are very site dependent—a storm with 1 cm of precipitation might be small in a frequent rainfall city such as Seattle but unlikely somewhere like the gold coast of Australia, making this method difficult to standardize.

Another preferred sampling strategy is capturing the "first flush," which is the concept that 40 to 80 percent of pollutants are within the first 20 to 30 percent of runoff.[84] This method can be seen in the Nguyen et al. (2011) and Zushi et al. (2009), studies which both collected samples within the first 10 minutes of the storm starting[85,86]. Recently, however, Peter et al. (2020)[39] measured tire derived chemicals in stormwater and found that while peak concentrations of pollutants are sometimes reached during the first flush, peak values in some cases corresponded with peak stormflow and stayed at high levels for longer than previously anticipated, indicating middle and end flush dynamics that can exist during storms. This is important because it suggests that the precise timing of a storm might have less impact on results than previously suggested. Such results may also reflect characteristics of transport-limited contaminant dynamics, an area of active investigation and data collection across several research groups globally.

2.6. Review of other CECs

Across the wide array of potential CECs to characterize in stormwater, PFAS, 6PPDQ, and TWP/TRWP have gained widespread attention due to the existence of toxicological data that suggests harm at very low concentrations. While the focus on their toxic attributes is well placed, there exist many other CECs present in runoff that also have toxic attributes that should be considered in further research on stormwater hazard. Additionally, there exist many abundant CECs in roadway runoff with concentrations even reaching 1,000 to 20,000 ng/L, but with little to no toxicological data currently available, despite structural evidence of bioactivity or chemical functional groups which are likely associated with toxic effects. In addition to MP, PFAS and 6PPDQ, the EPA has designated polycyclic aromatic hydrocarbons (PAHs), and pharmaceuticals and personal care products (PPCPs) as pollutants of concern meriting management attention in stormwater.[87] The national oceanic and atmospheric administration (NOAA) lists all of these, as well as PBDEs, as constituents of potential concern.[88] In addition, research efforts are highlighting the presence of a wide array of PPDs, PPDQs, related transformation products, and other abundant roadway contaminants, some of which have well described toxic attributes. As possible, helping to define the co-occurrence, sources, fate, and transport of these contaminants would be valuable in understanding the extent of rainfall-induced water quality degradation.

2.6.1. PAHs

PAHs are a group of compounds made up of multiple aromatic rings. They are formed when there is incomplete burning of organic matter such as in gasoline or coal. In the environment, PAHs can bind to soil particles, dissolve in water, or enter the atmosphere, depending on the specific PAH congener[89]. Because PAHs are a byproduct of incomplete gasoline combustion, they have high concentrations near major roadways and can therefore make their way into stormwater. Multiple PAHs have been found to be carcinogenic to humans and animals[89] and immunotoxic to certain fish[90]. Due to toxicity both to humans and fish, PAHs should be included in future stormwater assays.

The EPA has developed Method 610[91] as guidance for PAH sampling. For grab sampling, either 1-liter or 1-quart amber glass bottles should be used with a Teflon lined screw cap. Amber glass bottles are essential to ensure no photodegradation of samples occurs. If using a peristaltic pump to collect samples, a minimal amount of compressible silicone tubing should be used. Samples should be stored at 4°C and the amount of headspace or length of time a sample can be held are not specified.

2.6.2. PPCPs

Pharmaceuticals and personal care products encompass a large number of different chemicals. The most concerning of these are antibiotics, prescription and non-prescription drugs, hormones, and fragrances[92]. These chemicals are widely used across human populations and their environmental occurrence generally tracks with human contact and use, generating frequent detection for receiving waters proximate to human settlement. Somewhat surprisingly, many PPCPs are commonly detected in roadway runoff and stormwater samples, although they are not common analytes of interest for stormwater researchers.[39] PPCP impacts on aquatic organisms are quite varied. Estrogenic compounds has been shown to have negative impacts on fish reproductive systems and neuroactive antidepressants have been found concentrated in fish brains and other organisms[92].

In regards to sampling, the EPA has developed Method 1694[93] for PPCPs. For grab sampling, samples should be collected in 1-liter amber glass bottles with screw caps. Samples should be kept below 6°C and extracted within 7 days of collection but preferably within 48 hours. After extraction occurs, samples can be stored for 40 days before analysis.

2.6.3. PBDEs

Polybrominated diphenyl ethers (PBDEs) are a class of chemicals that have been added to consumer goods to act as fire retardants. PBDEs have been found to bioaccumulate in aquatic organisms, especially bivalves, and some of them are categorized as human carcinogens[94]. No standardized methods exist for sampling PBDEs and there has been limited research on PBDEs in stormwater, so this is an area that needs to be explored more.

2.6.4. Tire Additives and Roadway-Derived CECs

While 6PPDQ has been identified as a highly toxic contaminant, many other co-present tire additives are detected in stormwater, including many that are at much higher concentrations than 6PPDQ, and some with known toxic properties. PPDs encompass many other tire additives and lead to many transformation products, including PPDQs. The toxicities of many of these other tire additives and their transformation products are not well understood, although aromatic amines are generally a chemical class that can be toxic. Notably, their concentrations in stormwater can be quite high, often much higher than 6PPDQ. HMMM and diphenylguanidine (DPG) are tire-derived chemicals that have been found in stormwater alongside 6PPDQ, although their impacts on aquatic species are still largely unknown. Their concentrations can exceed 10,000 ng/L, and DPG has been reported in roadway runoff at concentrations over 50,000 ng/L by several studies. Sampling methods for all of these chemicals are similar to that for 6PPDQ and should follow EPA Method 1634, or 1694 more broadly.[58] It is also important to understand the environmental occurrence and fate of PPDs in general, because various PPD derivatives are currently being suggested as replacements for 6PPD in tire rubber while their environmental impacts are poorly defined. It should be noted that whatever replaces 6PPD in tire rubber will immediately become one of the most ubiquitous and abundant new global CECs of roadway runoff, with significant exposure potential for both humans and ecosystems.

3. Conclusion

With increasing attention being given to stormwater contaminants, it is of paramount importance that proper and consistent sampling is performed. For many of the CECs, there are already well-defined sampling methods by the EPA but work still needs to be done to establish sampling methods and standard reporting procedures for other CECs, including TWP and MP. While some work has been accomplished in identifying stormwater contaminants and their concentrations, many data gaps persist that are recommended to be filled with further data collection and sample analysis.

4. References

(1) Mutzner, L.; Furrer, V.; Castebrunet, H.; Dittmer, U.; Fuchs, S.; Gernjak, W.; Gromaire, M.-C.; Matzinger, A.; Mikkelsen, P. S.; Selbig, W. R.; Vezzaro, L. A Decade of Monitoring Micropollutants in Urban Wet-Weather Flows: What Did We Learn? *Water Res.* **2022**, *223*, 118968. https://doi.org/10.1016/j.watres.2022.118968.

(2) Zhang, K.; Zheng, Z.; Mutzner, L.; Shi, B.; McCarthy, D.; Le-Clech, P.; Khan, S.; Fletcher, T. D.; Hancock, M.; Deletic, A. Review of Trace Organic Chemicals in Urban Stormwater: Concentrations, Distributions, Risks, and Drivers. *Water Res.* **2024**, *258*, 121782. https://doi.org/10.1016/j.watres.2024.121782.

(3) Mayer, P. M.; Moran, K. D.; Miller, E. L.; Brander, S. M.; Harper, S.; Garcia-Jaramillo, M.; Carrasco-Navarro, V.; Ho, K. T.; Burgess, R. M.; Thornton Hampton, L. M.; Granek, E. F.; McCauley, M.; McIntyre, J. K.; Kolodziej, E. P.; Hu, X.; Williams, A. J.; Beckingham, B. A.; Jackson, M. E.; Sanders-Smith, R. D.; Fender, C. L.; King, G. A.; Bollman, M.; Kaushal, S. S.; Cunningham, B. E.; Hutton, S. J.; Lang, J.; Goss, H. V.; Siddiqui, S.; Sutton, R.; Lin, D.; Mendez, M. Where the Rubber Meets the Road: Emerging Environmental Impacts of Tire Wear Particles and Their Chemical Cocktails. *Sci. Total Environ.* **2024**, *927*, 171153. https://doi.org/10.1016/j.scitotenv.2024.171153.

(4) Du, B.; Lofton, J. M.; Peter, K. T.; Gipe, A. D.; James, C. A.; McIntyre, J. K.; Scholz, N. L.; Baker, J. E.; Kolodziej, E. P. Development of Suspect and Non-Target Screening Methods for Detection of Organic Contaminants in Highway Runoff and Fish Tissue with High-Resolution Time-of-Flight Mass Spectrometry. *Environ. Sci. Process. Impacts* **2017**, *19* (9), 1185–1196. https://doi.org/10.1039/C7EM00243B.

(5) Phase 1 Municipal Stormwater Permit, 2024. https://fortress.wa.gov/ecy/ezshare/wq/permits/MS4_2024_Phase%20I_FinalPermit.pdf.

(6) Scholz, N. L.; Myers, M. S.; McCarthy, S. G.; Labenia, J. S.; McIntyre, J. K.; Ylitalo, G. M.; Rhodes, L. D.; Laetz, C. A.; Stehr, C. M.; French, B. L.; McMillan, B.; Wilson, D.; Reed, L.; Lynch, K. D.; Damm, S.; Davis, J. W.; Collier, T. K. Recurrent Die-Offs of Adult Coho Salmon Returning to Spawn in Puget Sound Lowland Urban Streams. *PLoS ONE* **2011**, *6* (12), e28013. https://doi.org/10.1371/journal.pone.0028013.

(7) Tian, Z.; Zhao, H.; Peter, K. T.; Gonzalez, M.; Wetzel, J.; Wu, C.; Hu, X.; Prat, J.; Mudrock, E.; Hettinger, R.; Cortina, A. E.; Biswas, R. G.; Kock, F. V. C.; Soong, R.; Jenne, A.; Du, B.; Hou, F.; He, H.; Lundeen, R.; Gilbreath, A.; Sutton, R.; Scholz, N. L.; Davis, J. W.; Dodd, M. C.; Simpson, A.; McIntyre, J. K.; Kolodziej, E. P. A Ubiquitous Tire Rubber–Derived Chemical Induces Acute Mortality in Coho Salmon. *Science* **2021**, *371* (6525), 185–189. https://doi.org/10.1126/science.abd6951.

(8) Tian, Z.; Gonzalez, M.; Rideout, C. A.; Zhao, H. N.; Hu, X.; Wetzel, J.; Mudrock, E.; James, C. A.; McIntyre, J. K.; Kolodziej, E. P. 6PPD-Quinone: Revised Toxicity Assessment and Quantification with a Commercial Standard. *Environ. Sci. Technol. Lett.* **2022**, *9* (2), 140–146. https://doi.org/10.1021/acs.estlett.1c00910.

(9) Peter, K. T.; Tian, Z.; Wu, C.; Lin, P.; White, S.; Du, B.; McIntyre, J. K.; Scholz, N. L.; Kolodziej, E. P. Using High-Resolution Mass Spectrometry to Identify Organic Contaminants Linked to Urban Stormwater Mortality Syndrome in Coho Salmon. *Environ. Sci. Technol.* **2018**, *52* (18), 10317–10327. https://doi.org/10.1021/acs.est.8b03287.

(10) O'Sullivan, A.; Wicke, D.; Cochrane, T. Heavy Metal Contamination in an Urban Stream Fed by Contaminated Air-Conditioning and Stormwater Discharges. *Environ. Sci. Pollut. Res.* **2012**, *19* (3), 903–911. https://doi.org/10.1007/s11356-011-0639-5.

(11) McIntyre, J. K.; Baldwin, D. H.; Meador, J. P.; Scholz, N. L. Chemosensory Deprivation in Juvenile Coho Salmon Exposed to Dissolved Copper under Varying Water Chemistry Conditions. *Environ. Sci. Technol.* **2008**, *42* (4), 1352–1358. https://doi.org/10.1021/es071603e.

(12) McIntyre, J. K.; Davis, J. W.; Hinman, C.; Macneale, K. H.; Anulacion, B. F.; Scholz, N. L.; Stark, J. D. Soil Bioretention Protects Juvenile Salmon and Their Prey from the Toxic Impacts of Urban Stormwater Runoff. *Chemosphere* **2015**, *132*, 213–219. https://doi.org/10.1016/j.chemosphere.2014.12.052.

(13) Hobbs, W.; Lubliner, B.; Kale, N.; Newell, E. Western Washington NPDES Phase 1 Stormwater Permit: Final Data Chracterization 2009-2013, 2015.

(14) Control of Toxic Chemicals in Puget Sound: Phase 3 Data and Load Estimates, 2011.

(15) Marsalek, J.; Rochfort, Q.; Brownlee, B.; Mayer, T.; Servos, M. An Exploratory Study of Urban Runoff Toxicity. *Water Sci. Technol.* **1999**, *39* (12), 33–39. https://doi.org/10.1016/S0273-1223(99)00315-7.

(16) Wagner, S.; Hüffer, T.; Klöckner, P.; Wehrhahn, M.; Hofmann, T.; Reemtsma, T. Tire Wear Particles in the Aquatic Environment - A Review on Generation, Analysis, Occurrence, Fate and Effects. *Water Res.* **2018**, *139*, 83–100. https://doi.org/10.1016/j.watres.2018.03.051.

(17) *6PPD & 6PPD-quinone*. https://6ppd.itrcweb.org/ (accessed 2025-01-29).

(18) Feist, B. E.; Buhle, E. R.; Arnold, P.; Davis, J. W.; Scholz, N. L. Landscape Ecotoxicology of Coho Salmon Spawner Mortality in Urban Streams. *PloS One* **2011**, *6* (8), e23424. https://doi.org/10.1371/journal.pone.0023424.

(19) Seiwert, B.; Nihemaiti, M.; Troussier, M.; Weyrauch, S.; Reemtsma, T. Abiotic Oxidative Transformation of 6-PPD and 6-PPD Quinone from Tires and Occurrence of Their Products in Snow from Urban Roads and in Municipal Wastewater. *Water Res.* **2022**, *212*, 118122. https://doi.org/10.1016/j.watres.2022.118122.

(20) Alhelou, R.; Seiwert, B.; Reemtsma, T. Hexamethoxymethylmelamine – A Precursor of Persistent and Mobile Contaminants in Municipal Wastewater and the Water Cycle. *Water Res.* **2019**, *165*, 114973. https://doi.org/10.1016/j.watres.2019.114973.

(21) Peter, K. T.; Herzog, S.; Tian, Z.; Wu, C.; McCray, J. E.; Lynch, K.; Kolodziej, E. P. Evaluating Emerging Organic Contaminant Removal in an Engineered Hyporheic Zone Using High Resolution Mass Spectrometry. *Water Res.* **2019**, *150*, 140–152. https://doi.org/10.1016/j.watres.2018.11.050.

(22) Brinkmann, M.; Montgomery, D.; Selinger, S.; Miller, J. G. P.; Stock, E.; Alcaraz, A. J.; Challis, J. K.; Weber, L.; Janz, D.; Hecker, M.; Wiseman, S. Acute Toxicity of the Tire Rubber-Derived Chemical 6PPD-Quinone to Four Fishes of Commercial, Cultural, and Ecological Importance. *Environ. Sci. Technol. Lett.* **2022**, *9* (4), 333–338. https://doi.org/10.1021/acs.estlett.2c00050.

(23) Zoroufchi Benis, K.; Behnami, A.; Minaei, S.; Brinkmann, M.; McPhedran, K. N.; Soltan, J. Environmental Occurrence and Toxicity of 6PPD Quinone, an Emerging Tire Rubber-Derived Chemical: A Review. *Environ. Sci. Technol. Lett.* **2023**, *10* (10), 815–823. https://doi.org/10.1021/acs.estlett.3c00521.

(24) Roberts, C.; Lin, J.; Kohlman, E.; Jain, N.; Amekor, M.; Alcaraz, A. J.; Hogan, N.; Hecker, M.; Brinkmann, M. Acute and Subchronic Toxicity of 6PPD-Quinone to Early Life Stage Lake Trout

(Salvelinus Namaycush). *Environ. Sci. Technol.* **2025**, *59* (1), 791–797. https://doi.org/10.1021/acs.est.4c09090.

(25) Hiki, K.; Yamamoto, H. The Tire-Derived Chemical 6PPD-Quinone Is Lethally Toxic to the White-Spotted Char Salvelinus Leucomaenis Pluvius but Not to Two Other Salmonid Species. *Environ. Sci. Technol. Lett.* **2022**, *9* (12), 1050–1055. https://doi.org/10.1021/acs.estlett.2c00683.

(26) Klöckner, P.; Seiwert, B.; Wagner, S.; Reemtsma, T. Organic Markers of Tire and Road Wear Particles in Sediments and Soils: Transformation Products of Major Antiozonants as Promising Candidates. *Environ. Sci. Technol.* **2021**, *55* (17), 11723–11732. https://doi.org/10.1021/acs.est.1c02723.

(27) Seiwert, B.; Klöckner, P.; Wagner, S.; Reemtsma, T. Source-Related Smart Suspect Screening in the Aqueous Environment: Search for Tire-Derived Persistent and Mobile Trace Organic Contaminants in Surface Waters. *Anal. Bioanal. Chem.* **2020**, *412* (20), 4909–4919. https://doi.org/10.1007/s00216-020-02653-1.

(28) Overdahl, K. E.; Sutton, R.; Sun, J.; DeStefano, N. J.; Getzinger, G. J.; Ferguson, P. L. Assessment of Emerging Polar Organic Pollutants Linked to Contaminant Pathways within an Urban Estuary Using Non-Targeted Analysis. *Environ. Sci. Process. Impacts* **2021**, *23* (3), 429–445. https://doi.org/10.1039/D0EM00463D.

(29) Zhao, H. N.; Hu, X.; Gonzalez, M.; Rideout, C. A.; Hobby, G. C.; Fisher, M. F.; McCormick, C. J.; Dodd, M. C.; Kim, K. E.; Tian, Z.; Kolodziej, E. P. Screening P-Phenylenediamine Antioxidants, Their Transformation Products, and Industrial Chemical Additives in Crumb Rubber and Elastomeric Consumer Products. *Environ. Sci. Technol.* **2023**, *57* (7), 2779–2791. https://doi.org/10.1021/acs.est.2c07014.

(30) Hu, X.; Zhao, H. N.; Tian, Z.; Peter, K. T.; Dodd, M. C.; Kolodziej, E. P. Transformation Product Formation upon Heterogeneous Ozonation of the Tire Rubber Antioxidant 6PPD (N-(1,3-Dimethylbutyl)-N′-Phenyl-p-Phenylenediamine). *Environ. Sci. Technol. Lett.* **2022**, *9* (5), 413–419. https://doi.org/10.1021/acs.estlett.2c00187.

(31) Cao, G.; Wang, W.; Zhang, J.; Wu, P.; Zhao, X.; Yang, Z.; Hu, D.; Cai, Z. New Evidence of Rubber-Derived Quinones in Water, Air, and Soil. *Environ. Sci. Technol.* **2022**, *56* (7), 4142–4150. https://doi.org/10.1021/acs.est.1c07376.

(32) Peter, K. T.; Gilbreath, A.; Gonzalez, M.; Tian, Z.; Wong, A.; Yee, D.; Miller, E. L.; Avellaneda, P. M.; Chen, D.; Patterson, A.; Fitzgerald, N.; Higgins, C. P.; Kolodziej, E. P.; Sutton, R. Storms Mobilize Organophosphate Esters, Bisphenols, PFASs, and Vehicle-Derived Contaminants to San Francisco Bay Watersheds. *Environ. Sci. Process. Impacts* **2024**, *26* (10), 1760–1779. https://doi.org/10.1039/D4EM00117F.

(33) Zhao, H. N.; Hu, X.; Tian, Z.; Gonzalez, M.; Rideout, C. A.; Peter, K. T.; Dodd, M. C.; Kolodziej, E. P. Transformation Products of Tire Rubber Antioxidant 6PPD in Heterogeneous Gas-Phase Ozonation: Identification and Environmental Occurrence. *Environ. Sci. Technol.* **2023**, *57* (14), 5621–5632. https://doi.org/10.1021/acs.est.2c08690.

(34) Fohet, L.; Andanson, J.-M.; Charbouillot, T.; Malosse, L.; Leremboure, M.; Delor-Jestin, F.; Verney, V. Time-Concentration Profiles of Tire Particle Additives and Transformation Products under Natural and Artificial Aging. *Sci. Total Environ.* **2023**, *859*, 160150. https://doi.org/10.1016/j.scitotenv.2022.160150.

(35) Klöckner, P.; Seiwert, B.; Weyrauch, S.; Escher, B. I.; Reemtsma, T.; Wagner, S. Comprehensive Characterization of Tire and Road Wear Particles in Highway Tunnel Road Dust by Use of Size

and Density Fractionation. *Chemosphere* **2021**, *279*, 130530. https://doi.org/10.1016/j.chemosphere.2021.130530.

(36) Rauert, C.; Charlton, N.; Okoffo, E. D.; Stanton, R. S.; Agua, A. R.; Pirrung, M. C.; Thomas, K. V. Concentrations of Tire Additive Chemicals and Tire Road Wear Particles in an Australian Urban Tributary. *Environ. Sci. Technol.* **2022**, *56* (4), 2421–2431. https://doi.org/10.1021/acs.est.1c07451.

(37) Hu, X.; Zhao, H. (Nina); Tian, Z.; Peter, K. T.; Dodd, M. C.; Kolodziej, E. P. Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber-Derived Toxicant 6PPD-Quinone. *Environ. Sci. Process. Impacts* **2023**, *25* (5), 901–911. https://doi.org/10.1039/D3EM00047H.

(38) Chen, X.; He, T.; Yang, X.; Gan, Y.; Qing, X.; Wang, J.; Huang, Y. Analysis, Environmental Occurrence, Fate and Potential Toxicity of Tire Wear Compounds 6PPD and 6PPD-Quinone. *J. Hazard. Mater.* **2023**, *452*, 131245. https://doi.org/10.1016/j.jhazmat.2023.131245.

(39) Peter, K. T.; Hou, F.; Tian, Z.; Wu, C.; Goehring, M.; Liu, F.; Kolodziej, E. P. More Than a First Flush: Urban Creek Storm Hydrographs Demonstrate Broad Contaminant Pollutographs. *Environ. Sci. Technol.* **2020**, *54* (10), 6152–6165. https://doi.org/10.1021/acs.est.0c00872.

(40) Carpenter, C. M. G.; Wong, L. Y. J.; Gutema, D. L.; Helbling, D. E. Fall Creek Monitoring Station: Using Environmental Covariates To Predict Micropollutant Dynamics and Peak Events in Surface Water Systems. *Environ. Sci. Technol.* **2019**, *53* (15), 8599–8610. https://doi.org/10.1021/acs.est.9b02665.

(41) Jaeger, A.; Monaghan, J.; Tomlin, H.; Atkinson, J.; Gill, C. G.; Krogh, E. T. Intensive Spatiotemporal Characterization of the Tire Wear Toxin 6PPD Quinone in Urban Waters. *ACS EST Water* **2024**, *4* (12), 5566–5574. https://doi.org/10.1021/acsestwater.4c00614.

(42) Liu, Y.-H.; Mei, Y.-X.; Liang, X.-N.; Ge, Z.-Y.; Huang, Z.; Zhang, H.-Y.; Zhao, J.-L.; Liu, A.; Shi, C.; Ying, G.-G. Small-Intensity Rainfall Triggers Greater Contamination of Rubber-Derived Chemicals in Road Stormwater Runoff from Various Functional Areas in Megalopolis Cities. *Environ. Sci. Technol.* **2024**, *58* (29), 13056–13064. https://doi.org/10.1021/acs.est.3c10737.

(43) Foscari, A.; Seiwert, B.; Zahn, D.; Schmidt, M.; Reemtsma, T. Leaching of Tire Particles and Simultaneous Biodegradation of Leachables. *Water Res.* **2024**, *253*, 121322. https://doi.org/10.1016/j.watres.2024.121322.

(44) Brunn, H.; Arnold, G.; Körner, W.; Rippen, G.; Steinhäuser, K. G.; Valentin, I. PFAS: Forever Chemicals—Persistent, Bioaccumulative and Mobile. Reviewing the Status and the Need for Their Phase out and Remediation of Contaminated Sites. *Environ. Sci. Eur.* **2023**, *35* (1), 20. https://doi.org/10.1186/s12302-023-00721-8.

(45) *1 Introduction – PFAS — Per- and Polyfluoroalkyl Substances*. https://pfas-1.itrcweb.org/1-introduction/ (accessed 2025-01-29).

(46) Hartmann, N. B.; Hüffer, T.; Thompson, R. C.; Hassellöv, M.; Verschoor, A.; Daugaard, A. E.; Rist, S.; Karlsson, T.; Brennholt, N.; Cole, M.; Herrling, M. P.; Hess, M. C.; Ivleva, N. P.; Lusher, A. L.; Wagner, M. Are We Speaking the Same Language? Recommendations for a Definition and Categorization Framework for Plastic Debris. *Environ. Sci. Technol.* **2019**, *53* (3), 1039–1047. https://doi.org/10.1021/acs.est.8b05297.

(47) Athey, S. N.; Erdle, L. M. Are We Underestimating Anthropogenic Microfiber Pollution? A Critical Review of Occurrence, Methods, and Reporting. *Environ. Toxicol. Chem.* **2022**, *41* (4), 822–837. https://doi.org/10.1002/etc.5173.

(48) Chamas, A.; Moon, H.; Zheng, J.; Qiu, Y.; Tabassum, T.; Jang, J. H.; Abu-Omar, M.; Scott, S. L.; Suh, S. Degradation Rates of Plastics in the Environment. *ACS Sustain. Chem. Eng.* **2020**, *8* (9), 3494–3511. https://doi.org/10.1021/acssuschemeng.9b06635.

(49) Bai, C.-L.; Wang, D.; Luan, Y.-L.; Huang, S.-N.; Liu, L.-Y.; Guo, Y. A Review on Micro- and Nanoplastics in Humans: Implication for Their Translocation of Barriers and Potential Health Effects. *Chemosphere* **2024**, *361*, 142424. https://doi.org/10.1016/j.chemosphere.2024.142424.

(50) *Microplastics*. https://mp-1.itrcweb.org/ (accessed 2025-01-29).

(51) Charlton-Howard, H. S.; Bond, A. L.; Rivers-Auty, J.; Lavers, J. L. 'Plasticosis': Characterising Macro- and Microplastic-Associated Fibrosis in Seabird Tissues. *J. Hazard. Mater.* **2023**, *450*, 131090. https://doi.org/10.1016/j.jhazmat.2023.131090.

(52) Zimmermann, L.; Bartosova, Z.; Braun, K.; Oehlmann, J.; Völker, C.; Wagner, M. Plastic Products Leach Chemicals That Induce In Vitro Toxicity under Realistic Use Conditions. *Environ. Sci. Technol.* **2021**, *55* (17), 11814–11823. https://doi.org/10.1021/acs.est.1c01103.

(53) Leads, R. R.; Weinstein, J. E. Occurrence of Tire Wear Particles and Other Microplastics within the Tributaries of the Charleston Harbor Estuary, South Carolina, USA. *Mar. Pollut. Bull.* **2019**, *145*, 569–582. https://doi.org/10.1016/j.marpolbul.2019.06.061.

(54) Chae, E.; Jung, U.; Choi, S.-S. Types and Concentrations of Tire Wear Particles (TWPs) in Road Dust Generated in Slow Lanes. *Environ. Pollut.* **2024**, *346*, 123670. https://doi.org/10.1016/j.envpol.2024.123670.

(55) Mennekes, D.; Nowack, B. Tire Wear Particle Emissions: Measurement Data Where Are You? *Sci. Total Environ.* **2022**, *830*, 154655. https://doi.org/10.1016/j.scitotenv.2022.154655.

(56) Cowger, W.; Gray, A. B.; Guilinger, J. J.; Fong, B.; Waldschläger, K. Concentration Depth Profiles of Microplastic Particles in River Flow and Implications for Surface Sampling. *Environ. Sci. Technol.* **2021**, *55* (9), 6032–6041. https://doi.org/10.1021/acs.est.1c01768.

(57) Murphy-Hagan, C.; Gray, A. B.; Singh, S.; Hapich, H.; Cowger, W.; Seeley, M. E.; Waldschläger, K. Microplastic Characterization and Transport Mode —A Flow-Integrated Approach to Sampling Urban Waterways. *Environ. Res.* **2025**, *269*, 120908. https://doi.org/10.1016/j.envres.2025.120908.

(58) Draft Method 1634 Determination of 6PPD-Quinone in Aqueous Matrices Using Liquid Chromatography with Tandem Mass Spectrometry (LC/MS/MS).

(59) Lane, R. F.; Smalling, K. L.; Bradley, P. M.; Greer, J. B.; Gordon, S. E.; Hansen, J. D.; Kolpin, D. W.; Spanjer, A. R.; Masoner, J. R. Tire-Derived Contaminants 6PPD and 6PPD-Q: Analysis, Sample Handling, and Reconnaissance of United States Stream Exposures. *Chemosphere* **2024**, *363*, 142830. https://doi.org/10.1016/j.chemosphere.2024.142830.

(60) Hu, X.; Zhao, H. (Nina); Tian, Z.; Peter, K. T.; Dodd, M. C.; Kolodziej, E. P. Chemical Characteristics, Leaching, and Stability of the Ubiquitous Tire Rubber-Derived Toxicant 6PPD-Quinone. *Environ. Sci. Process. Impacts* **2023**, *25* (5), 901–911. https://doi.org/10.1039/D3EM00047H.

(61) Method 1633 Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous, Solid, Biosolids, and Tissue Samples by LC-MS/MS.

(62) *11 Sampling and Analytical Methods – PFAS — Per- and Polyfluoroalkyl Substances*. https://pfas-1.itrcweb.org/11-sampling-and-analytical-methods/ (accessed 2025-02-11).

(63) Cross, R. K.; Roberts, S. L.; Jürgens, M. D.; Johnson, A. C.; Davis, C. W.; Gouin, T. Ensuring Representative Sample Volume Predictions in Microplastic Monitoring. *Microplastics Nanoplastics* **2025**, *5* (1), 5. https://doi.org/10.1186/s43591-024-00109-2.

(64) Frond, H. D.; Wong, D. C.; Coffin, D. S. Standard Operating Procedures for Extraction and Measurement by Infrared Spectroscopy of Microplastic Particles in Drinking Water.

(65) Zhao, H. N.; Hu, X.; Gonzalez, M.; Rideout, C. A.; Hobby, G. C.; Fisher, M. F.; McCormick, C. J.; Dodd, M. C.; Kim, K. E.; Tian, Z.; Kolodziej, E. P. Screening P-Phenylenediamine Antioxidants, Their Transformation Products, and Industrial Chemical Additives in Crumb Rubber and Elastomeric Consumer Products. *Environ. Sci. Technol.* **2023**, *57* (7), 2779–2791. https://doi.org/10.1021/acs.est.2c07014.

(66) Rodowa, A. E.; Christie, E.; Sedlak, J.; Peaslee, G. F.; Bogdan, D.; DiGuiseppi, B.; Field, J. A. Field Sampling Materials Unlikely Source of Contamination for Perfluoroalkyl and Polyfluoroalkyl Substances in Field Samples. *Environ. Sci. Technol. Lett.* **2020**, *7* (3), 156–163. https://doi.org/10.1021/acs.estlett.0c00036.

(67) Scopetani, C.; Esterhuizen-Londt, M.; Chelazzi, D.; Cincinelli, A.; Setälä, H.; Pflugmacher, S. Self-Contamination from Clothing in Microplastics Research. *Ecotoxicol. Environ. Saf.* **2020**, *189*, 110036. https://doi.org/10.1016/j.ecoenv.2019.110036.

(68) Lo, B. P.; Marlatt, V. L.; Liao, X.; Reger, S.; Gallilee, C.; Ross, A. R. S.; Brown, T. M. Acute Toxicity of 6PPD-Quinone to Early Life Stage Juvenile Chinook (Oncorhynchus Tshawytscha) and Coho (Oncorhynchus Kisutch) Salmon. *Environ. Toxicol. Chem.* **2023**, *42* (4), 815–822. https://doi.org/10.1002/etc.5568.

(69) Challis, J. K.; Popick, H.; Prajapati, S.; Harder, P.; Giesy, J. P.; McPhedran, K.; Brinkmann, M. Occurrences of Tire Rubber-Derived Contaminants in Cold-Climate Urban Runoff. *Environ. Sci. Technol. Lett.* **2021**, *8* (11), 961–967. https://doi.org/10.1021/acs.estlett.1c00682.

(70) Helm, P. A.; Raby, M.; Kleywegt, S.; Sorichetti, R. J.; Arabian, G.; Smith, D.; Howell, E. T.; Thibeau, J. Assessment of Tire-Additive Transformation Product 6PPD-Quinone in Urban-Impacted Watersheds. *ACS EST Water* **2024**, *4* (4), 1422–1432. https://doi.org/10.1021/acsestwater.3c00589.

(71) Jiang, Y.; Wang, C.; Ma, L.; Gao, T.; Wāng, Y. Environmental Profiles, Hazard Identification, and Toxicological Hallmarks of Emerging Tire Rubber-Related Contaminants 6PPD and 6PPD-Quinone. *Environ. Int.* **2024**, *187*, 108677. https://doi.org/10.1016/j.envint.2024.108677.

(72) Monaghan, J.; Jaeger, A.; Jai, J. K.; Tomlin, H.; Atkinson, J.; Brown, T. M.; Gill, C. G.; Krogh, E. T. Automated, High-Throughput Analysis of Tire-Derived p-Phenylenediamine Quinones (PPDQs) in Water by Online Membrane Sampling Coupled to MS/MS. *ACS EST Water* **2023**, *3* (10), 3293–3304. https://doi.org/10.1021/acsestwater.3c00275.

(73) Somepalli, K.; Andaluri, G. Spatiotemporal Distribution and Environmental Risk Assessment of 6PPDQ in the Schuylkill River. *Emerg. Contam.* **2025**, *11* (2), 100501. https://doi.org/10.1016/j.emcon.2025.100501.

(74) Poggioli, M.; Cavadini, G. B.; Zheng, Z.; Rodriguez, M.; Mutzner, L. The Impact of Blue-Green Infrastructure on Trace Contaminants: A Catchment-Wide Assessment. *Water Res. X* **2024**, *25*, 100261. https://doi.org/10.1016/j.wroa.2024.100261.

(75) McIntyre, J. K.; Spromberg, J.; Cameron, J.; Incardona, J. P.; Davis, J. W.; Scholz, N. L. Bioretention Filtration Prevents Acute Mortality and Reduces Chronic Toxicity for Early Life Stage Coho Salmon (*Oncorhynchus Kisutch*) Episodically Exposed to Urban Stormwater Runoff. *Sci. Total Environ.* **2023**, *902*, 165759. https://doi.org/10.1016/j.scitotenv.2023.165759.

(76) Murakami, M.; Shinohara, H.; Takada, H. Evaluation of Wastewater and Street Runoff as Sources of Perfluorinated Surfactants (PFSs). *Chemosphere* **2009**, *74* (4), 487–493. https://doi.org/10.1016/j.chemosphere.2008.10.018.

(77) Klöckner, P.; Seiwert, B.; Eisentraut, P.; Braun, U.; Reemtsma, T.; Wagner, S. Characterization of Tire and Road Wear Particles from Road Runoff Indicates Highly Dynamic Particle Properties. *Water Res.* **2020**, *185*, 116262. https://doi.org/10.1016/j.watres.2020.116262.
(78) Lange, K.; Magnusson, K.; Viklander, M.; Blecken, G.-T. Removal of Rubber, Bitumen and Other Microplastic Particles from Stormwater by a Gross Pollutant Trap - Bioretention Treatment Train. *Water Res.* **2021**, *202*, 117457. https://doi.org/10.1016/j.watres.2021.117457.
(79) Parker-Jurd, F. N. F.; Napper, I. E.; Abbott, G. D.; Hann, S.; Thompson, R. C. Quantifying the Release of Tyre Wear Particles to the Marine Environment via Multiple Pathways. *Mar. Pollut. Bull.* **2021**, *172*, 112897. https://doi.org/10.1016/j.marpolbul.2021.112897.
(80) Boni, W.; Arbuckle-Keil, G.; Fahrenfeld, N. L. Inter-Storm Variation in Microplastic Concentration and Polymer Type at Stormwater Outfalls and a Bioretention Basin. *Sci. Total Environ.* **2022**, *809*, 151104. https://doi.org/10.1016/j.scitotenv.2021.151104.
(81) Rosso, B.; Corami, F.; Vezzaro, L.; Biondi, S.; Bravo, B.; Barbante, C.; Gambaro, A. Quantification and Characterization of Additives, Plasticizers, and Small Microplastics (5–100 Mm) in Highway Stormwater Runoff. *J. Environ. Manage.* **2022**, *324*, 116348. https://doi.org/10.1016/j.jenvman.2022.116348.
(82) Koelmans, A. A.; Mohamed Nor, N. H.; Hermsen, E.; Kooi, M.; Mintenig, S. M.; De France, J. Microplastics in Freshwaters and Drinking Water: Critical Review and Assessment of Data Quality. *Water Res.* **2019**, *155*, 410–422. https://doi.org/10.1016/j.watres.2019.02.054.
(83) Cowger, W.; Gray, A.; Brownlee, S.; Hapich, H.; Deshpande, A.; Waldschläger, K. Estimating Floating Macroplastic Flux in the Santa Ana River, California. *J. Hydrol. Reg. Stud.* **2022**, *44*, 101264. https://doi.org/10.1016/j.ejrh.2022.101264.
(84) Gao, Z.; Zhang, Q.; Li, J.; Wang, Y.; Dzakpasu, M.; Wang, X. C. First Flush Stormwater Pollution in Urban Catchments: A Review of Its Characterization and Quantification towards Optimization of Control Measures. *J. Environ. Manage.* **2023**, *340*, 117976. https://doi.org/10.1016/j.jenvman.2023.117976.
(85) Nguyen, V. T.; Reinhard, M.; Karina, G. Y.-H. Occurrence and Source Characterization of Perfluorochemicals in an Urban Watershed. *Chemosphere* **2011**, *82* (9), 1277–1285. https://doi.org/10.1016/j.chemosphere.2010.12.030.
(86) Zushi, Y.; Masunaga, S. First-Flush Loads of Perfluorinated Compounds in Stormwater Runoff from Hayabuchi River Basin, Japan Served by Separated Sewerage System. *Chemosphere* **2009**, *76* (6), 833–840. https://doi.org/10.1016/j.chemosphere.2009.04.004.
(87) *Stormwater Pollutants of Emerging Concern | US EPA*. https://www.epa.gov/npdes/stormwater-pollutants-emerging-concern (accessed 2025-01-29).
(88) *Contaminants of Emerging Concern - NCCOS - National Centers for Coastal Ocean Science*. https://coastalscience.noaa.gov/science-areas/pollution/modern-use-chemicals/ (accessed 2025-01-29).
(89) *Polycyclic Aromatic Hydrocarbons (PAHs) | Public Health Statement | ATSDR*. https://wwwn.cdc.gov/TSP/PHS/PHS.aspx?phsid=120&toxid=25 (accessed 2025-01-30).
(90) Collier, T. K.; Anulacion, B. F.; Arkoosh, M. R.; Dietrich, J. P.; Incardona, J. P.; Johnson, L. L.; Ylitalo, G. M.; Myers, M. S. Effects on Fish of Polycyclic Aromatic HydrocarbonS (PAHS) and Naphthenic Acid Exposures. In *Fish Physiology*; Elsevier, 2013; Vol. 33, pp 195–255. https://doi.org/10.1016/B978-0-12-398254-4.00004-2.
(91) Method 610: Polynuclear Aromatic Hydrocarbons.

(92) *Toxicological Issues Associated With PPCPs | Department of Toxic Substances Control*. https://dtsc.ca.gov/pharmaceutical-waste/toxicological-issues-associated-with-ppcps/ (accessed 2025-01-30).
(93) Method 1694: Pharmaceuticals and Personal Care Products in Water, Soil, Sediment, and Biosolids by HPLC/MS/MS. **2007**.
(94) *What are PBDEs?* https://oceanservice.noaa.gov/facts/pbde.html (accessed 2025-01-30).

Appendix A

CEC Literature Review Summary Table

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Science + Planning + Design

Table A-1. Relevant Studies of 6PPDQ Concentrations in Roadway Runoff and Related Receiving Waters.

Analyte/s [6PPDQ, PFAS, Microplastics/ TWP]	Study	Location	Stormwater / Dust/ Sediment (W/D/S)	Analytical Method	Sampling Method	Sample Timing	Holding times	Holding Temp	Bottle and Cap Material	Bottle/ Sample Size	Headspace	Land Use	Low Concentration	High Concentration
6PPDQ	*EPA Method 1634-6PPDQ*	N/A, conducted in lab	W	LC-MS	N/A, conducted in lab	N/A, conducted in lab	14 days to extract sample, 28 days to store	<6°C	Amber galss with PTFE cap	250 mL	None	N/A methods study	N/A methods study	N/A methods study
6PPDQ	*Jaeger et al 2024* 6PPDQ Spatial-temporal	Nanaimo BC, Canada	W	LC-MS	Grab sample directly into amber glass bottles	Needed to have 2 dry days since rainfall and >5 mm	Needs to Arrive at lab within 24 hours	4°C	Amber glass with PTFE cap	250 mL	Less than 5% headspace	Urban	6 ng/L	164 ng/L
6PPDQ	*Lane et al 2024*, sampling methods	N/A, conducted in lab	W	LC-MS	N/A, conducted in lab	N/A, conducted in lab	75 days	5°C	Glass w/PTFE-lined caps	1 L or 125 mL	Minimal	residential and parking lot	N/A methods study	N/A methods study
6PPDQ	*Poggioli 2024*, BGI	Fehraltorf, Switzerland	W	HPLC/HRMS	Automated sampler	When CSO had >6 cm of water	N/A	-20°C	Glass	Unspecified	Unspecified	Urban Catchment 46% impervious	.05 ug/L	0.31 ug/L
HMMM													.65 ug/L	3.99 ug/L
DPG													2.51 ug/L	9.06 ug/L
6PPDQ	*Zhang 2023*, 23 additives and TPs	Guangzhou, China	W	UHPLC-HRMS	Grab samples of surface runoff, WWTP influents and effluents, river surface water samples, and drinking water samples	Initial 30 minutes of rainfall event	48 hours to extract	4°C	Amber glass bottle	1 L	Unspecified	Unclear	0.53 ng/L (farmland)	1,562 ng/L (courtyard)
DPG													18.9 ng/L (farmland)	58780 ng/L (Road)
6PPD													Non detectable (farmland)	7.52 ng/L (Road)
6PPD	*Zeng 2023*, Quinones in Sediments, river estuaries coasts	Pearl River Delta, China	S	LC-MS	"Van Veen" Grab samples of sediments at various depths	Not Applicable, retroactive study	Unspecified	-20°C	Unspecified	Unspecified	Unspecified	Not applicable	Undetectable (deep sea)	468 ng/g dry weight (urban rivers)
6PPDQ													Undetectable	18.2 ng/g dry weight (urban rivers)
PPDs	*Cao 2022*, Quinones Water Air Soil	Hong Kong, China	W	UHPLC-HRMS	Teflon tubes	Unclear	Unspecified	"on ice"	Teflon tubes	200 mL	Unspecified	Urban	0.74 ug/L PPDs 0.21 ug/L 6PPDQ	3.87 ug/L PPDs 2.43 ug/L 6PPDQ
			S		Stainless steel shovel	Non-rainy days	Unspecified	Unspecified	Unspecified	Unspecified	Unspecified	Roadside for high and parking lot for low concentration	41.8 ng/g 6PPDQ	234 ng/g 6PPDQ
6PPDQ	*Deng 2022*, Urban Road dust	Guangzhou, China	D	UHPLC-HRMS	Vacuum with 25 um pore size nylon bag	Unclear	Unspecified	Sieve held at -20°C until analysis	Unspecified	Unspecified	Unspecified	Urban Road and parking lot dust	10.5 ng/g	509 ng/g

Table A-1 (continued). Relevant Studies of 6PPDQ Concentrations in Roadway Runoff and Related Receiving Waters.

Analyte/s [6PPDQ, PFAS, Microplastics/ TWP]	Study	Location	Stormwater/ Dust/ Sediment (W/D/S)	Analytical Method	Sampling Method	Sample Timing	Holding times	Holding Temp	Bottle and Cap Material	Bottle/ Sample Size	Headspace	Land Use	Low Concentration	High Concentration
6PPDQ	*Rauert 2022*, TWP and chems Urban Tributary	Brisbane, Australia	W	LC-MS	Grab sample	Collected during major storm events	Unspecified	-20°C	Polypropylene Jar	600 mL	Unspecified	Low Density Residential, environment conservation area	0.38 ng/L	88 ng/L
DPG													13 ng/L	1,079 ng/L
HMMM													0.5 ng/L	5.3 ng/L
Benzotriazoles/ benzothiazoles													2 ng/L	450 ng/L
6PPDQ	*Challis 2021*, Rubber contaminants in cold climate	Saskatoon, Canada	W	UHPLC-HRMS	Grab sample with 5L plastic pail lowered via rope	Wet weather events	Unspecified	Unspecified	Nalgene	4 L and 1 L	Unspecified	Residential, industrial, and retail	86 ng/L	1400 ng/L
DPG													4 ug/L	364 ug/L
6PPDQ	*Johannessen 2021*, TW compounds in urban waters	Toronto, Canada	W	UHPLC-HRMS	Stainless-steel bucket grab sample/ automated sampler	Wet samples during precip events >20 mm and >25 mm, dry sample	Unspecified	-18°C	PET	300–1000 mL	Unspecified	Major Urban traffic and WWTP effluent	0.21 ug/L	0.72 ug/L
DPG													0.03 ug/L	0.76 ug/L
HMMM													-	11 ug/L (D200)
6PPDQ	*Johannessen 2021*, 6PPDQ DPQ Urban	Toronto, Canada	W	UHPLC-HRMS	Automated sampler	Automated sampler was triggered when water levels began to rise >10 mm	Unspecified	-18°C	PET	300 mL	Unspecified	Urban, near major highways	0.25 ug/L	2.3 ug/L
DPG													Unspecified	0.22 ug/L
HMMM	*Johannessen 2021*, HMMM urban	Toronto, Canada	W	UHPLC-HRMS	Automated sampler collecting 3-hour composite samples over 42-hour period	Major rain events (>10 mm)	Unspecified	-18°C	Sampled in polyethylene bottles then subsampled to PET	900 mL per composite	Unspecified	Unspecified	Unclear	2.08 ug/L
6PPDQ	*Monaghan 2021*, 6PPDQ MS Nanaimo	Nanaimo BC, Canada	W	MS	Unspecified	Unclear	1 week	4°C	Amber glass with PTFE cap	40–1000 mL	Unspecified	Unspecified	Methods Test	

Table A-2. Relevant Studies of PFAS in Roadway Runoff and Related Receiving Waters.

Analyte/s [6PPDQ, PFAS, Microplastics/ TWP]	Study	Location	Stormwater/ Dust/ Sediment (W/D/S)	Analytical Method	Sampling Method	Sample Timing	Holding times	Holding Temp	Bottle and Cap Material	Bottle/ Sample Size	Headspace	Land Use	Low Concentration	High Concentration
PFAS	*EPA Method 1633-PFAS*	N/A, conducted in lab	W	LC-MS	Grab sample w/ sample container attached to pole	N/A, conducted in lab	28 days (Or 90 days)	<6°C (@-20C)	HDPE with Polypropylene or linerless HDPE cap	500, 250, 125 mL	To shoulder	N/A methods study	N/A methods study	N/A methods study
			S	LC-MS	Stainless steel scoops or spoons	N/A, conducted in lab	90 days	<6°C	HDPE with Polypropylene or linerless HDPE cap	500 mL	3/4 Full			
PFAS	*Codling 2020,* PFAS Canada	Saskatoon, Canada	W	LC-MS	By hand where possible or food grade bucket grab sample	Runoff events during spring melt, rainstorms in late spring, and summer	Unspecified	Unspecified	High-density polyethylene	2 L	Unspecified	Urban	6.5 ng/L	14.0 ng/L
PFAS	*Procopio 2017,* PFAAs New Jersey	New Jersey, USA	W	HPLC-MS	Unclear	Unclear	Unspecified	Unspecified	Unspecified	Unspecified	Unspecified	54% forest, wetlands, water and 43% Developed	PFOA 79 ng/L, PFHxA 11 ng/L, PFOS 21 ng/L, PFBA 17 ng/L, PFPA 32 ng/L	
PFAS	*Xiao 2012,* PFA in urban SW runoff	Minneapolis, USA	W	HPLC-MS	Lowering containers into stormwater flow from street level down into drain holes	Rain events larger than 8 mm/hour	Unspecified	4°C	Polyethylene	4 L	Unspecified	Commercial and heavily trafficked areas	14.3 ng/L PFAAs	96 ng/L PFAAs
PFAS	*Houtz 2011,* Oxidated Conversion PFAS	San Francisco Bay area	W	HPLC-MS	Sampled in center of runoff channel with a stainless steel bailer then decanted into precleaned 1L HDPE	Samples collected during rise, peak, and fall of storm hydrograph	3 months	4°C	HDPE	1 L	Unspecified	Urban	PFOS 2.6 ng/L PFOA 2.1 ng/L PFHxA 0.9 ng/L	PFOS 26 ng/L PFOA 16 ng/L PFHxA 9.7 ng/L
PFAS	*Nguyen 2011,* PGAS urban watershed	Singapore River, Singapore	W	LC-MS	Automated samplers for river collection and unclear for rainwater on filed but likely grab sample	10 minutes after the onset of the rain event	Unspecified	4°C	Polypropylene	Unspecified	Unspecified	Urban marina	57 ng/L dry weather	138 ng/L wet weather
PFAS	*Murakami 2009,* WW and runoff PFSs	Kanto region, Japan	W	LC-MS	Composite samples collected directly from drain pipes	During first and second flushes	Unspecified	5°C	Unspecified	Unspecified	Unspecified	Highways with 30,000 to 88,000 ADT	LOD	~390 ng/L total PFAS
PFAS	*Zushi 2009,* First Flush PFAS	Yokohama City, Japan	W	HPLC-MS	Automated sampler collecting 1L every hour	Rainfall events ranging from 1–3 mm within 10 minutes	10 days	2°C	Polypropylene	1 L	Unspecified	Dense Urban	River concentrations of PFDA and PFUnA increased by factors of 3.4 and 2.0 during rain events respectively	

Table A-3. Relevant Studies of TWPs in Roadway Runoff and Related Receiving Waters.

Analyte/s [6PPDQ, PFAS, Microplastics/ TWP]	Study	Location	Stormwater/ Dust/ Sediment (W/D/S)	Analytical Method	Sampling Method	Sample Timing	Holding times	Holding Temp	Bottle and Cap Material	Bottle/ Sample Size	Headspace	Land Use	Low Concentration	High Concentration
TWPs	*Molazadeh 2023,* TWP urban lake	Brabrand Lake, Denmark	S	uFTIR and Py-GC/MS	Van Veen grab sampling of 2–3 kg of sediment	Dry period, no rain at least 2 days prior	Unspecified	5°C	Glass Jar	2–3 kg bulk sediment	Unspecified	Urban CSOs, stormwater, and WWTP	19 mg/kg TWP	
TWPs	*Lange 2021,* Rubber removal Bioretention	Sundsvall, Sweden	W	Stereo Microscopy	Automatic composite samples	Rain events greater than 5mm	Unspecified	Unspecified	HDPE	1.8 to 20 L	Unspecified	Total impervious area of 4.7 ha	<0.31 particles/L (100-300 um)	740 particles/L (100-300 um)
TWP	*Werbowski 2021,* Anthro particles	San Francisco Bay area	W	FTIR	100L pumped through 2 stainless steal sieves sized 125 and 255 um	Storms with >1.3 cm of rainfall within 6h or 1.9 cm within 12h	Unspecified	Not specified just placed in cooler	Glass	Unspecified	Unspecified	Large Variety	1.1 particles/L	24.6 particles/L
TWPs	*Parker-Jurd 2021,* quantifying TWPs in mult pathways	Plymouth and Bristol, UK	W	Py-GC-MS	Grab samples	Wet weather events	Unspecified	Unspecified	Glass Duran Jars	5 L and 10 L x 2 replicates	Unspecified	Residential urban	2.5 mg +/- 1 mg/L	
TRWPs	*Klockner 2020,* TRWP dynamic properties	Leipzig, Germany	S and D	UPLC-MS	Road Dust samples taken from street sweeping vehicles in plastic bucket, Sediment samples from sedimentation basin using beaker on telescoping rod, and sediment from settling ponds	Not Applicable, retroactive study	Unspecified	Unspecified	Unspecified	Unspecified	Unspecified	Urban and Highway	0.17 mg/g	480 mg/g
TWPs	*Ziajahromi 2020,* TPs treated wetland	Gold Coast, Australia	S and W	FTIR	Top 5 cm of sediment were collected with a stainless steel shovel and transferred to glass jars as well as water samples taken in the middle of water body and passed through sieves	Water samples collected during heavy rain event (>34 mm/d)	Unspecified	Unspecified	Glass	1 L	Unspecified	Constructed wetland	0.9 particles/L	4 particles/L
TWPs	*Li et al 2005,* size dist. HW runoff	Los Angeles, USA	W	Particle sizing system	Grab Sample with polypropylene container from a free waterfall at drainage pipe	Collection began after runoff started and continued every hour thereafter	Unspecified	Unspecified	Amber Bottle	4 L	Unspecified	Dense Urban with heavy traffic	Smallest particle size: 2 um	Largest particle size: 1,000 um

Table A-4. Relevant Studies of MPs in Roadway Runoff and Related Receiving Waters.

Analyte/s [6PPDQ, PFAS, Microplastics/ TWP]	Study	Location	Stormwater/ Dust/ Sediment (W/D/S)	Analytical Method	Sampling Method	Sample Timing	Holding times	Holding Temp	Bottle and Cap Material	Bottle/ Sample Size	Headspace	Land Use	Low Concentration	High Concentration
MPs	*Cho 2023*, MP Intra-event variability	Gumi, South Korea	W	FTIR	Automated sampler collecting composite sample over 6 hours collecting 6 L total which is filtered through 20-um stainless steel sieve	During storm events	Unspecified	Unspecified	Glass	6 L sample collected on site	Unspecified	Industrial and Residential	1 ng/L	1,080 ng/L
MPs	*Boni 2022*, MP at stormwater outfalls	New Jersey, USA	W	ATR-FTIR	Sampling jars attached to sampling poles lowered by researchers into flow stream to collect samples. Sieved at lab 500–2000 um and 250–500 um	During storm events totaling between 1.5 and 4.5 cm of cumulative rainfall	Up to 2 days before extraction in the dark	4°C	Glass	1 L composites to total 5 L	Unspecified	Urban landscape with heavily trafficked highways	0.3 particles/L	0.8 particles/L
MPs	*Rosso 2022*, MPs 5–100 um HW SW runoff	Venice, Italy	W	uFTIR	Glass flask affixed to Stormwater Drain	Set up to collect rainfall events >5 mm	Unspecified	Unspecified	Glass	1 L	Unspecified	Highway 71,000 ADT	11,932 particles/L	18,966 particles/L
MPs	*Smyth 2021*, Bioretention MPs	Toronto, Canada	W	FTIR	Automated sampler collected when >4 cm runoff in flume	>4 cm in sampling device	Unspecified	Unspecified	LDPE and HDPE	2 L	Unspecified	Parking Lot	4 microparticles/L	186 microparticles/L
MPs	*Wang 2021*, MP seasonal variation	Manas River, China	W	SEM/ uFTIR	Grab sample using stainless steel sampler	Unclear	Unspecified	4°C	Glass Bottle	1 L replicates x 3	Unspecified	Urban industrial and agricultural	10 particles/L	22 particles/L
MPs	*Chen 2020, MPs Shanghai*	Shanghai, China	W and S	uFTIR-ATR	Stainless Steel 80 um mesh net immersed into channel, grab samples at same location, and automated sampler	During rain events	Unspecified	4°C	Glass	3 L and 5 L	Unspecified	Varied by sample mix of urban and agriculture	14.4 particles/L in creek	8,505.5 particles/kg sediment at pump outlets
MPs	*Grbic 2020, Ontario MPs*	Toronto, Canada	W	Raman spectroscopy	Automated sampler collected 4-L 24-hour composites at WWTPs. Grab samples with stainless steel 4-L bucket	Unclear	Unspecified	Unspecified	Amber Bottle	4 L	Unspecified	WWTP effluent and urban creeks and rivers	0.8 particles/L	15.4 particles/L
MPs	*Pinon-Colin 2020, MPs Tijuana*	Tijuana, Mexico	W (and some incidental S)	FTIR-ATR	Grab sample using small iron bucket	During rain events	Unspecified	Unspecified	Glass	1 L	Unspecified	Residential/ industrial/ commercial with low traffic densities	66 particles/L	191 particles/L
MPs	*Leads 2019, TWPs and MPs SC estuary*	Charleston Harbor, US	S	Visual ID	Sediment collected with steel trowel and placed in stainless steel bucket, separation using NaCl mixture and sieving	Not Applicable, retroactive study	Unspecified	Unspecified	Amber glass Jar	250 mL	Unspecified	"Forested land and urban land"	0 particles/m^2	652 microplastics/m^2