Contribution of Leachate from Rubberized Hot Mix Asphalt to Zinc Loading in Roadway Stormwater Runoff

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Report Title: Contribution of Leachate from Rubberized Hot Mix Asphalt to Zinc Loading in Roadway Stormwater Runoff

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Executive Summary

An estimated 51 million waste tires are generated annually in California. Discarded tires in stockpiles and landfills are a public and environmental health concern and require a large storage volume in landfills. Approximately 82 percent of the scrap tires discarded in 2019 were diverted from landfills through a variety of reuses. For example, tire-derived products have been developed for use as an aggregate fill for civil engineering applications, and as a crumb or ground rubber product for applications such as pavement. Previous research on the use of tire-derived aggregate (TDA) in civil engineering applications where leachate from the TDA was not directly discharged to surface water concluded that the contributions of metals to stormwater runoff were negligible.

This report describes research conducted to determine whether rubberized hot mix asphalt (RHMA), used in a growing number of road pavement projects, is a significant source of zinc to stormwater runoff from roadways. RHMA contains crumb rubber, a recycled rubber product derived from scrap tires. The use of crumb rubber in recycled applications has diverted nearly 20 percent of the total waste tires from other disposal methods over the past several years. The introduction of crumb rubber into paving surfaces not only diverts tires from landfills, but also reduces road noise and increases the longevity of the pavement.

The increasing use of RHMA in California roadways raises the question about the contributions of these surfaces to contaminants in stormwater runoff, with the main contaminant of concern being zinc. While there is reasonable agreement in the literature identifying building siding and roofing materials, atmospheric deposition, tire wear particles, and runoff from zinc-coated (galvanized) metals as potentially significant sources of zinc to urban stormwater, the actual and relative contribution of zinc to stormwater runoff is much less clear due to the complexity of fate and transport processes. Although extensive field and laboratory testing has been carried out to characterize sources of zinc to urban stormwater, little has been done to isolate and characterize the differences in zinc leaching rates of RHMA pavements in comparison to conventional asphalt (HMA) pavements. Even less literature has been published that compares the differences in zinc content and leaching rates of RHMA and HMA pavements compared to other sources such as tire wear and galvanized metal.

To meet the research project objective, laboratory and field data were collected and combined with data from other studies to assess the relative contribution of various sources of zinc in stormwater. Laboratory batch leaching experiments were conducted on both crumb rubber and RHMA pavement cores using pavement materials prepared and provided by the Pavement Preservation Center at California State University, Chico. Zinc leaching rates from both the crumb rubber used in RHMA pavement and from RHMA pavement itself were quantified based on laboratory experiments and

analyses. Field sampling of stormwater runoff from paved RHMA and HMA surfaces was conducted over a 16-month period beginning in December 2018. Sample sites were located near the transition between HMA and RHMA pavement so traffic patterns and atmospheric deposition of particulate matter would be similar for both pavement types. The paired runoff sampling data was used to complement previous sampling efforts by the California Department of Transportation (Caltrans). Humboldt State University (HSU) sampled sites in the North Coast region of California, GHD Inc. sampled sites in the San Francisco and Sacramento area, and Caltrans sampled sites in Central California.

The laboratory leaching experiments conducted on the crumb rubber showed the dissolved zinc mass transfer rate from the crumb rubber continuously submerged in water decreases exponentially from the value found on the first day of sampling, with an order of magnitude reduction after approximately 60 days. Near the end of the 8-month experiment, the zinc mass transfer rates for all crumb rubber samples reached an equilibrium value. As expected, the experiments also showed that the leaching rate of zinc from small diameter (less than 500 µm) crumb rubber particles was much higher than from larger particles due to the larger surface area to volume ratio for smaller particles. The fraction of zinc in tire crumb that leached during the 8-month sample period ranged from 1.5 percent to 7 percent, from larger to smaller crumb sizes respectively.

RHMA and HMA pavement cores made from fresh asphalt that had not been driven on were submerged in distilled water continuously more than eight months. The leachate from the HMA cores had very low zinc concentrations over the first several days, with the remaining samples below the detection limit. The initial detected concentration values were low enough to conclude that the mass transfer rate of any zinc that might be present in the HMA was essentially zero. The resulting calculated cumulative zinc mass transfer rate from the RHMA cores showed a declining trend similar to that observed for the crumb rubber. Leaching rates from the RHMA pavement cores greater than 100 $\mu g/m^2/day$ occurred during the first eight days of continuous submergence, and resulting calculated values indicate that the average zinc mass transfer rate would be less than 10 $\mu g/m^2/day$ for RHMA surfaces that had already experienced at least four days of leaching conditions. The fraction of zinc in the RHMA cores that leached during the sample period was estimated to be less than 0.2 percent of the zinc in the outer 0.1 inch of the RHMA cores.

Artificial aging of RHMA cores during a second leaching experiment did not have a noticeable impact on the zinc leaching rate. Based on these results, aging and dry season interruptions in wetting of the RHMA from stormwater would not be expected to result in an increased zinc leaching rate during subsequent wet periods over the life of the road surface.

The batch leaching experiments do not simulate all factors associated with zinc transfer from the materials under field conditions. The zinc transfer rate might be impacted by factors such as material wear by UV degradation and fatigue from vehicle loading, which would likely increase the transfer rate as wear particles expose new surface areas to leaching. In contrast, the batch leaching test assesses continuously submerged materials, whereas these materials are not generally continuously submerged when in use unless wear particles are transported to water bodies. While not assessing material wear is likely to underestimate the transfer rate, the continuous submersion in the test is likely to overestimate the transfer rate for RHMA.

A total of 81 stormwater runoff samples were collected by HSU in the Eureka area and by GHD in the San Francisco Bay Area and Sacramento between December 2018 and March 2020. The sampling represents data from 12 locations across 20 storm events. Each of the highway runoff samples were analyzed for both dissolved and total zinc concentrations. The mean concentration of total zinc from RHMA pavement was higher than from the HMA pavement at many paired sites; however, there were sites where the opposite was true. Examination of the individual paired observations at each site indicates that the situation is more complex than the mean value would suggest. The results from the HSU and GHD sampling show that pavement type alone cannot be used to predict zinc load from the roadway, and that factors other than pavement type may overwhelm the zinc load from the RHMA. In an effort to gain additional insight into the contribution of RHMA to the zinc load from roadways, additional examination of the HMA-RHMA paired sampling performed by Caltrans was conducted.

The Caltrans highway runoff sampling data used for this project contained 98 runoff samples, capturing 46 storm events across three locations in Central California, each with a HMA and RHMA pavement site. Caltrans determined the concentration of numerous metals in the runoff, including zinc and copper. Including the Caltrans paired sampling data with the HSU and GHD data does not provide more clarity to the question about whether the use of RHMA pavement will result in higher concentrations of zinc in roadway stormwater runoff compared to non-rubberized HMA. As long as zinc is a component of tire rubber, there will be some zinc leached from rubberized pavement. However, the Caltrans data reinforces the conclusion reached with the HSU and GHD paired sampling data that there are other factors besides the addition of rubber to the asphalt binder that determine the resulting concentration of zinc in the runoff.

Using these data as well as data from other studies, the stormwater zinc contributions from RHMA, tire wear particles, wet deposition, and galvanized metal surfaces were quantified and compared. The cumulative mass loading over a typical 10-year life of an RHMA paved surface was estimated for these four sources. Based on the leaching experiments and assuming 240 total days of saturation over the 10-year pavement surface life, the contribution of zinc from the RHMA pavement would be approximately 5 mg/m^2. Using typical tire characteristics, a roadway that is 20 meters wide, annual average daily traffic (AADT) of 5,000 vehicles, and assuming that 10 percent of the zinc contained in tire wear particles ultimately contributes to zinc in roadway stormwater runoff, tire wear particles would account for approximately 263 mg zinc/m^2 over a 10-year period. Based on an average observed precipitation zinc concentration of 8 µg/l and the average annual rainfall in Eureka, the wet deposition of zinc on the pavement due to precipitation would be 86 mg zinc/m^2 over the 10-year pavement life. Finally, using standardized specifications for a Type I galvanized guardrail, the equivalent zinc loading from guardrails along both edges of the roadway would be 1,230 mg/m^2 over a 10-year period (Figure 1).

For the scenarios examined, leaching from the rubber in the binder of RHMA is a comparably minor source of zinc in roadway stormwater runoff, contributing less than 0.3 percent of the total zinc load. In the Eureka area, the load from zinc in precipitation greatly exceeded that of the RHMA leachate and the tire wear particles on a relatively lightly traveled highway. In more arid locations, the contribution from precipitation would be lower (or even zero), but the same would be true of the contribution from the rubberized asphalt. On more lightly traveled roads, the contribution from tire wear particles would be lower, yet an AADT of 500 vehicles per day would result in a contribution five times greater from tire wear compared to leaching from the RHMA surface. Galvanized guardrails, along with other galvanized metal (e.g. signs, light standards) along roads present a potential source of zinc in roadway runoff far in excess of the sources examined in this research.

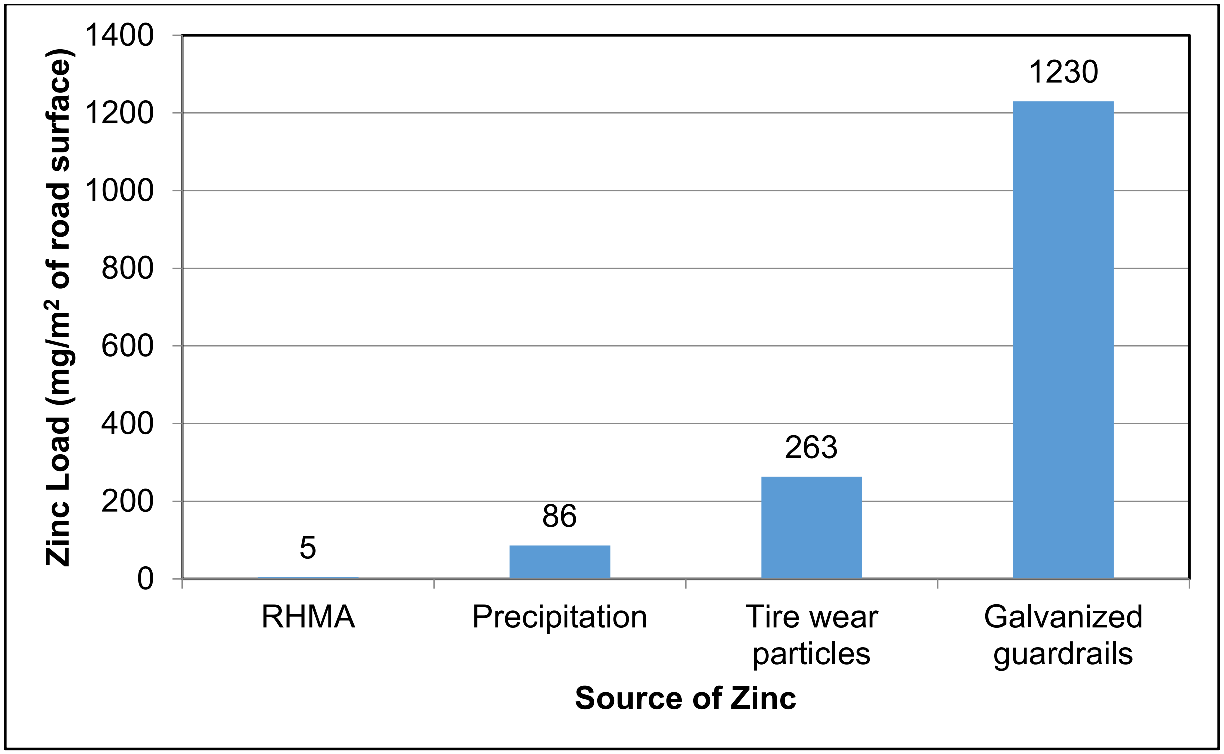

Figure 1: Comparison of zinc load to stormwater runoff off a 20-meter-wide roadway from various sources over a 10-year period. Assumptions for these estimates are based on literature, research analysis, and data collected from Eureka. (Reference Appendix B, Figure 1 Table)

The estimated rates for the contribution of various sources of zinc in roadway runoff shown in Figure 1 are subject to uncertainty due to a number of factors. In addition to the impacts of field conditions that were not replicated in the lab (UV degradation, vehicle impaction etc.), the leaching rate from RHMA is dependent on the degree of previous exposure that the asphalt has had to water and the duration of runoff conditions during the period of interest. In this analysis, the assumption was that there were 240 days of runoff conditions (wet road surface) acting on new RHMA pavement over a 10-year period. At a site with a lower mean annual precipitation rate, the rate of zinc loss per precipitation event would be somewhat higher, but with fewer days of runoff the end result would be a lower total mass of zinc loss from the pavement over the 10-year period.

The contribution of tire wear particles to the zinc load in roadway stormwater runoff is based on an assumed fraction of the particles that remain on the roadway after they are generated by passing vehicles and the fraction of zinc in the particles that would be leached during a relatively short exposure time that the materials would be on the road surface. The assumed values were comparatively conservative, so while parameter uncertainties and site-specific circumstances could change the magnitude of the estimates provided in Figure 1, it is unlikely that the general outcome of the comparison would change. Given a 50-time difference between the relative contribution of leaching from RHMA and tire wear particles under the stated conditions, it is reasonable to conclude that the use of RHMA is not a major factor in the concentration of zinc in roadway stormwater runoff with the possible exception of the first few runoff events on new pavement. A study capturing the first few runoff events from new RHMA pavement would help to fully understand the extent of the initial zinc loading from new RHMA pavement under field conditions.

Based on this research, the use of RHMA pavement plays a minor role in determining the zinc concentration in runoff from road surfaces. Leaching of zinc from tire wear particles generated by vehicles on the roadway and from galvanized materials along the roadway are the largest sources of zinc in the runoff from roads identified in this work, and both deserve additional study. In particular, methods to capture tire wear particles on the road before they can enter a natural waterway would potentially result in a significant reduction of zinc in roadway runoff, and also reduce the net loading of tire-related microplastics to the environment. Methods that reduce the loading of tire wear particles to a natural waterway may also help reduce the loading of other potential stormwater contaminants, such as the recently identified tire rubber-derived compound 6PPD that is reported to be responsible for acute mortality in coho salmon.

Abbreviations and Acronyms

AADT: Annual Average Daily Traffic
AADTT: Annual Average Daily Truck Traffic
AASHTO: American Association of State Highway and Transportation Officials
CalRecycle: California Department of Resources Recycling and Recovery
Caltrans: California Department of Transportation
cm: centimeter
CRM: crumb rubber modifier
DGAC: dense-graded asphalt concrete
Dis. Zinc: dissolved zinc
EPA: United States Environmental Protection Agency
ft: feet
g: grams
ha: hectare
HMA: hot mix asphalt
in: inch
kg: kilogram
lb: pound
m: meter
MCL: maximum contaminant level
mg: milligram
mg/l: milligram per liter
µm: microns
µg/l: micrograms per liter
ND: Non-detect (below the method detection limit)
OBC: optimum binder content
OGAC: open-graded asphalt concrete
PG: performance grade
RHMA: rubberized hot mix asphalt
RHMA-O: rubberized hot mix asphalt concrete open-graded
RHMA-G: rubberized hot mix asphalt concrete gap-graded
RICE: theoretical maximum density (pavement)
TDA: tire-derived aggregate

Introduction

The Department of Resources Recycling and Recovery (CalRecycle) manages the disposal and recycling efforts for an estimated 51 million waste tires generated annually in California (CalRecycle, 2020a). Used tires, commonly referred to as scrap tires, discarded in stockpiles and landfills are a public and environmental health concern and require a large storage volume in landfills. Voids created by scrap tires can trap gases, increase fire risk, and harbor rodents and insects that may increase the spread of disease (CalRecycle 2020b). CalRecycle diverted an estimated 82 percent of the scrap tires discarded in 2019 from landfills through a variety of reuses. Tire-derived products have been developed for use as fuel, as an aggregate fill for civil engineering applications, and as a crumb or ground rubber product for applications such as roofing, playground surfaces, and pavement (CalRecycle 2020a). Extensive studies have concluded the water quality impacts of the use of tire-derived aggregate (TDA) in civil engineering applications is negligible (Humphrey and Katz 2000; Humphrey and Katz 2001; Humphrey and Swett 2006; Finney et al. 2014; Finney and Maeda 2016). This was especially true in in civil engineering applications supported by CalRecycle and where leachate from the TDA was not directly discharged to surface water. Similar research has not been conducted for crumb rubber, a recycled rubber product derived from scrap tires, used in many of the applications (Figure 1).

Figure 1: A representative sample of passenger tire crumb rubber that is less than 2 micrometers in diameter.

Crumb rubber production in California effectively diverted an estimated 8 million to 9 million tires a year from other disposal methods in 2018 and 2019 (CalRecycle

2020a). A common use for crumb rubber is in paving materials known as crumb rubber modified (CRM) pavements. CRM pavement is commonly referred to as rubberized hot mix asphalt (RHMA) and was also referred to as rubberized asphalt concrete (RAC) in California prior to 2014 (Zhou et al. 2014). RAC and RHMA are used interchangeably in the literature to describe CRM pavements but will be referred to as RHMA throughout this report.

Assembly Bill 338 (Levine, Chapter 709, Statutes of 2005) requires the California Department of Transportation (Caltrans) to use a specified amount of CRM in asphalt paving materials that equates to the use of RHMA in at least 35 percent of Caltrans pavement projects (LCD 2005). Caltrans has been refining methods for the use of crumb rubber in paving applications since the 1970s; by 2010, approximately 31 percent of all hot mix asphalt (HMA) annually placed by Caltrans was rubberized, with roughly 1.2 million tons of RHMA pavement placed in 2010 (Zhou et al. 2014). A 2-inch-thick asphalt resurfacing project that uses RHMA is estimated to use about 2,000 scrap tires per lane mile (CalRecycle 2019). The introduction of crumb rubber into paving surfaces not only diverts tires from landfills, but also improves the pavement by reducing road surface sensitivity to cold weather cracking by increased elasticity and resilience, slowing aging and fatigue, and reducing road noise (Caltrans 2005; Shatnawi 2011; Xiao et al. 2017; Zhou et al. 2014).

Though there are benefits for the use of CRM in paving projects, concerns have been raised about the potential contribution of unwanted constituents in stormwater from RHMA, specifically zinc. More than 40 waterways in California have on occasion exceeded zinc standards set forth by the Clean Water Act, reporting levels of dissolved zinc elevated above minimum toxicity thresholds (CASQA 2014). The increasing use of RHMA in California roadways has called into question whether stormwater runoff from these surfaces is a significant contributor to the overall amount of zinc observed in California waterways (Caltrans 2008; CASQA 2014). Traffic and environmental weathering can cause pavement materials to wear down and degrade, potentially creating worn rubber and pavement particles that accumulate in stormwater. Stormwater in contact with worn pavement particles (rubberized and conventional), tire wear particles, and the surface of the pavement itself has been shown to leach metals (specifically zinc), contributing to lower-quality surface waters (Caltrans 2008; Rhodes et al. 2012; Vashisth et al. 1998). Research into the interaction of RHMA pavements and the environment has revealed wide variability in the concentrations of water quality constituents coming from their surfaces (Caltrans 2012; Murphy et al. 2015).

Since zinc has been identified as a constituent of concern in stormwater runoff, many field and laboratory studies have attempted to identify the environmental loading of zinc from a variety of point and non-point sources in urban and transportation-related environments. The literature suggests contributors of zinc to urban stormwater include atmospheric deposition, tire wear particles, and runoff from zinc-coated (galvanized) metals (CASQA 2014; Gunawardena et al. 2013; Kennedy and Sutherland 2008; WSDOE 2008). Although extensive field and laboratory testing has been carried out to characterize sources of zinc to urban stormwater, little has been done to isolate and characterize the differences in zinc leaching rates of RHMA pavements in comparison to HMA pavements. Even less literature has been published on comparing the differences in zinc content and leaching rates of RHMA and HMA pavements compared to other sources such as tire wear and galvanized metal.

The objective of this research is to determine whether CRM within RHMA is a significant source of zinc to stormwater runoff from RHMA pavement. To meet this objective, laboratory and field data were collected and combined with data from other studies to assess the relative contribution of various sources of zinc in stormwater. Laboratory analysis was used to quantify the zinc leaching rates from both the crumb rubber used in RHMA and from RHMA surfaces. Field sampling of stormwater runoff from paved RHMA and HMA surfaces was used to determine whether there is a detectable difference in zinc concentrations between the two pavement types. Using these data as well as data from other studies, the zinc contributions to stormwater runoff from RHMA, tire wear particles, and galvanized metal surfaces were quantified and compared. Review of existing literature was an integral part of this research and revealed numerous sources and factors that can contribute to a large variability of zinc concentrations in stormwater runoff.

Literature Review

This section summarizes a review of the literature that characterizes RHMA, its use in roadways, and the relative contribution of zinc to stormwater runoff when compared to other known sources. The composition and physical properties of RHMA and its components are reported in a number of studies and provide relevant information such as zinc content, particle size, and porosity. A brief overview of regulatory limits for zinc concentrations is presented to put the results from field and laboratory experiments that identify the leaching rates and mobility of zinc from crumb rubber and RHMA into context. The literature reveals that there are many significant zinc sources in urban environments such as transportation-related sources (e.g. tire wear particles) and galvanized surfaces that protect steel and iron building materials. The research reviewed includes analyses focused on one specific source as well as basin-scale assessments that quantified multiple urban sources such as roadways, rooftops, lawns, and parking lots. The combined results of the potential source loading rates reported in the literature allow for comparative analysis of relative contributions to zinc loading. Finally, monitoring results from paired sampling of stormwater runoff from HMA and RHMA surfaces in California are collected and summarized in this section and provide valuable insights for the discussion of the data collected in this sampling effort.

Characteristics of Tires, Crumb Rubber, and Rubberized Asphalt

Tire composition and characteristics

Detailed physical and chemical characteristics of tires provide insight into the composition of crumb rubber that is added to RHMA. An assessment by Dodds et al. (1983) of scrap passenger tires showed mass percentages of typical tire components as: styrene-butadiene copolymer (62.1%) as the tire body, carbon black (31%) for strengthening and abrasion resistance, extender oil (1.9%) as a softening agent to increase workability, zinc oxide (1.9%) and stearic acid (1.2%) to enhance the physical properties of the rubber and increase control in the vulcanization process, sulfur (1.1%) for hardening rubber and preventing deformation, and an accelerator to act as a catalyst in vulcanization. Though construction characteristics are similar, tire composition can vary by vehicle type. For example, the mass percentage of zinc oxide is higher for truck and off-road tires than for passenger tires (Evans and Evans 2006).

The California Stormwater Quality Association (CASQA) compiled data from numerous studies on the mean zinc content of passenger and truck tire tread (Table 1). Mean zinc content presented in these data show that common passenger tires contain from 8,470 to 14,800 mg/kg, or approximately 0.85-1.5 percent zinc by weight. Truck tires typically contain a higher zinc mass fraction, with mean values of 16,000-17,000 mg/kg or 1.6-1.7 percent zinc by weight.

Table 1: A summary of sources for tire tread zinc content (CASQA 2014).

Tire Type	Mean (and Range) Tire Zinc Content (mg/kg)	Literature Source
Car	9,400 (6,100-16,000)	Sweden, 52 tires (Hjortenkrans et al. 2007)
Car	8,470 (5,650-9,640)	New Zealand, 7 tires (Kennedy et al. 2002)
Car	9,500	Netherlands Industry data (Blok 2005)
Car	14,800 (12,700-16,900)	Japan, 2 tires (Ozaki et al. 2004)
Car	10,250	France (Legret and Pagotto 1999)
Car	9,600 (320-23,000)	EU Rubber Industry survey (Smolders and Degryse 2002)
Truck	17,000	Netherlands Industry Data (Blok 2005)
Truck	16,000 (13,800-18,300)	New Zealand, 2 tires (Kennedy et al. 2002)
Truck	17,000 (9,600-35,000)	EU Rubber Industry survey (Smolders and Degryse 2002)

Crumb rubber composition and characteristics

Crumb rubber is made from scrap tires with particle sizes ranging from 0.075 mm to 4.75 mm (Heitzman 1992). ASTM D6114 (2019) provides guidelines for crumb rubber used in asphalt paving. The requirements specify cleanliness (fiber content <0.5%; metal content <0.01%), moisture content (<0.75%), density (equal to 1.15 ± 0.05 g/cm^3), and maximum particle size (2.36 mm) (Bressi et al. 2019). A variety of methods exist to shred existing scrap tires into usable crumb rubber. Most of the processes use mechanical size reduction (shredding and milling) under ambient conditions while some incorporate cryogenic conditions and waterjet technology. Zanetti et al. (2015) characterized the chemical and physical properties of crumb rubber derived from scrap tires from 11 different processing facilities. The authors acknowledge the potential impact that different mass ratios of passenger and truck tires have on the varying levels of zinc content in the samples, but they did not indicate those ratios for the samples listed. Of 16 samples analyzed from the 11 processing facilities, the mass content of zinc varied from 1.16 to 2.3 percent (Table 2).

Table 2: Crumb rubber size, density, and zinc content from 16 different crumb rubber processing facility samples (Zanetti et al. 2015).

Plant	Diameter (mm)	Zinc Content (%)	Density (g/cm^3)
A	0.4–0.7	2.03	1.172
A	0.1–0.3	1.21	1.213
B	0.3–0.7	1.94	1.181
B	0.1–0.4	1.83	1.192
C	0.4–0.7	2.10	1.158
C	0.1–0.4	2.26	1.196
D	0.3–0.7	1.87	1.203
E	0.3–0.6	1.33	1.178
F	0.3–0.7	1.16	1.185
G	0.2–0.6	1.18	1.223
H	0.0–0.7	1.41	1.189
I	0.6–1.5	1.50	1.204
I	0.2–0.7	1.35	1.199
J	0.9–2.2	1.34	1.207
J	0.3–0.6	1.54	1.190
K	0.1–0.5	1.25	1.208

Rubberized pavement composition and characteristics

RHMA is a modified form of HMA, and as such shares much of the physical characteristics and construction practices as HMA. Rubberized pavement mixtures are generally used in overlay projects in which a thin layer of RHMA is laid atop a section of “conventional” HMA or Portland Cement Concrete. A chip seal is also a common form of pavement overlay that can use crumb rubber. Rubber chip seal construction begins with laying down asphalt-rubber emulsion to seal the existing pavement, then overlaying the seal with crushed rock and finally locking down the crushed rock using a flush coat of asphalt emulsion and sand. HMA, and by extension RHMA, is a mixture that combines sand, stone, or gravel together with heated asphalt cement, a product of crude oil.

The gradation and type of aggregate used in an HMA or RHMA mixture impacts the porosity of the resulting pavement. Dense, open, and gap graded aggregate mixtures are commonly used in California. The physical characteristics of the pavement, including void space and permeability, depend on the type of binder used and the grading of the aggregate. In general, open graded pavements are much more permeable compared to gap and dense graded pavements, and pavement with rubberized and conventional binders have comparable permeability with the same aggregate grading (Table 3).

Either the wet process or the dry process is used to incorporate CRM into a rubberized asphalt product. In the wet process, CRM is mixed into the asphalt binder prior to the addition of the aggregate, and in the dry process the CRM is mixed directly with the aggregate. Historically, Caltrans used both wet and dry processes, as well as rubber-modified binders containing CRM and polymer modifier. Caltrans specification now uses a CRM binder in the wet process to generate RHMA based on performance monitoring of a variety of methods (Caltrans 2018a).

To create RHMA using the wet process, crumb rubber that passes the 2 mm number 10 sieve is added at a weight percentage of 20 ± 2 percent to the binder (Van Kirk 2016; Zhou et al. 2014). The CRM must be composed of 25 ±2 percent high natural rubber (typically truck tires) content by mass of total CRM while the other 75 percent is scrap tire rubber (primarily passenger car tires) (Caltrans 2018a; Zhou et al. 2014). After the crumb rubber is added to the heated binder in the wet RHMA process, it is mixed at elevated temperatures of 400-425 degrees F for 45 minutes (Van Kirk 2016). The asphalt rubber binder is then added to the pavement aggregate to meet the minimum optimal binder content (OBC) of 7.5 percent for gap-graded RHMA (RHMA-G) design. The OBC is usually 1-2 percent higher for open-graded RHMA (RHMA-O) pavement design.

Table 3: Coefficient of permeability resulting from field testing on 10 pavement types in common use in California (Caltrans 2008).

Pavement Type	Coefficient of Permeability (cm/s)
Rubberized Asphalt Concrete Open-Graded	0.215
Rubberized Asphalt Concrete Gap-Graded	0.013
Open-Graded Asphalt Concrete (PG 64-10)	0.024
Open-Graded Asphalt Concrete (PG 64-16)	0.029
Open-Graded Asphalt Concrete (PG 58-22)	0.026
Open-Graded Asphalt Concrete (PG 64-28)	0.035
Terminal-Blend Modified Binder – Gap-Graded	0.008
Dense-Graded Asphalt Concrete (PG 64-16)	0.000
Portland Cement Concrete – Dense Graded	0.000
Portland Cement Concrete – Open Graded	0.116

Since the percentage of crumb rubber in the binder (the OBC) and the crumb rubber zinc content are specified, the percent mass of zinc in the pavement from rubber can be calculated. Assuming an average crumb rubber zinc content of 1.6 percent from Zanetti et al. (2015) (Table 2) and a mean crumb rubber weight percentage of 20 percent in the asphalt binder, the RHMA-G (7.5 percent OBC) pavement is 1.5 percent crumb rubber by weight and approximately 0.024 percent zinc by weight (Table 4). Under the same conditions, RHMA-O (9.5 percent OBC) is 1.9 percent crumb rubber by weight and approximately 0.03 percent zinc by weight (Table 4). These calculations ignore any zinc contained within the parent material of the pavement aggregate or asphalt binder and are focused solely on the percent zinc due to the inclusion of crumb rubber into the paving material.

Dry processes generally mix the rubber into the aggregate at about 3 percent crumb rubber by weight (Vashisth et al. 1998) and use a lower OBC of approximately 4.5 percent (Caltrans 2005), although this specification is not included or used in current Caltrans design specifications and is dependent on gradation targets. Using the same zinc content of 1.6 percent as listed above suggests a dry-process RHMA sample contains approximately 0.046 percent zinc by weight (Table 4).

Table 4: Crumb rubber and zinc content of several types of crumb rubber modified pavement.

RHMA Type	Crumb Rubber Content (%)	Zinc Content (%)
RHMA-O Wet Process	1.9	0.030
RHMA-G Wet Process	1.5	0.024
Dry-Process RHMA	2.9	0.046

The percent zinc by weight of the pavement can be used to calculate the overall mass fraction of zinc in pavement if the density of the pavement is known. From the Transportation Research Board (Rao et al. 2013), the RICE (theoretical maximum density) value (based on maximum specific gravity) of RHMA-G pavement is 2.55, so the maximum RHMA-G pavement density is 163.7 lb/ft^3. If a 5 percent air void content is assumed (Van Kirk 2016), then the bulk density or the in-place pavement density is approximately 155.5 lb/ft^3.

Water Quality Considerations for Using Crumb Rubber and Rubberized Hot Mix Asphalt

The tire rubber constituent of concern in this research, zinc, is assessed for its toxicity or impact on aquatic organisms by total and dissolved concentrations under a number of different regulatory frameworks. Relevant frameworks and the resulting criteria thresholds are outlined in this section.

Section 304(a)(1) of the Clean Water Act of 1977 requires the EPA to publish aquatic life criteria standards that reflect the thresholds at which pollutant concentrations impart identifiable effects to organisms. Zinc has been shown to cause behavioral, developmental, reproductive, and toxic responses in many aquatic organisms (Councell et al. 2004). There are more than 40 waterways in California that are considered to be zinc-impaired by aquatic life criteria standards (CASQA 2014). The standard for dissolved zinc in freshwater surface waters is dependent on water hardness and ranges from 108-300 µg/l but is referred to in the 2004 National Recommended Water Quality Criteria update as 120 µg/l (for a water hardness of 100 mg/L) for both the Criteria Continuous Concentration (CCC) and the Criteria Maximum Concentration (CMC) (USEPA 2004). The standard for human consumption of drinking water is significantly higher at 7,400 µg/l.

At the state level, the California Waterboard’s Water Quality Assessment Thresholds table (SRCB 2020) gives a variety of standards for zinc concentration thresholds under different frameworks. Most notable are the California Secondary Maximum Contaminant Limit of 5,000 µg/l and the estuary and ocean water quality criterion of 81 and 90 µg/l for the 4-day and 1-hour averages, respectively.

Crumb rubber leaching rates

Since tires degrade slowly in the natural environment, not all zinc contained within crumb rubber is immediately bioavailable. The rate at which zinc contained within rubber leaches into the surrounding environment (water or soil) is regarded as the mass transfer rate. Zinc within the crumb that is not leached until further degradation is considered particle-bound and will only become bioavailable as the surface area of the particle that is in contact with water or air is exposed.

Smolders and Degryse (2002) assessed the mass transfer rate of zinc from tire particles in soil by placing soil columns augmented with passenger and truck tire particles in an outside setting for one year. The columns allowed free drainage during storm events. Leachate, pore water, and soil within the columns were sampled periodically to determine the percentage of zinc contained within the rubber that leached into surroundings. Isotope dilution was also used at the end of the experiment to determine the amount of labile zinc within the soil.

The results showed that there was no detectible increase in zinc leaching from the truck tire crumb treated soil columns compared to the control (Smolders and Degryse 2002). The passenger tire crumb treated columns observed a three-fold increase compared to the control in leachate concentrations draining from acidic soil conditions (pH 4.9) and no increase in leachate from a silt loam soil of pH 6.1. After one year of exposure, a labile zinc analysis (used to represent all zinc adsorbed in the soil and dissolved into pore water) revealed that 10-40 percent of the total zinc contained within the crumb rubber had leached or adsorbed into the surroundings. The amount of zinc measured in leachate from the passenger tire in acidic soil conditions was approximately 0.66 percent of the total amount of zinc contained within the rubber in the soil. This finding suggests that the large majority of zinc leached from the crumb rubber was adsorbed by the soil.

Another significant finding was that the truck tire mixed soil had a measurable increase in pH over the study period, while the passenger tire soil had no change in pH. These results suggest that pH may affect leachability and mobility of zinc in soil from tire rubber, though the small percentage of total zinc found in leachate after one year of sampling demonstrates the relatively low potential for zinc to migrate into nearby ground or surface water through a soil medium. A similar study by Finney and Maeda (2016) found that zinc is removed from stormwater runoff after having passed through a TDA-soil system.

The median particle diameters of truck and car rubber used by Smolders and Degryse (2002) were fine (65.4 μm and 79.6 μm, respectively) compared to those used in RHMA (0.075mm to 4.75mm). The size range of the particles used in this experiment are more representative of tire wear particle sizes, which have an average size of 10-20 *µ*m (Councell et al. 2004). Thus, it is likely the leaching rates observed in this study are an overestimate of expected leaching rates from crumb rubber.

The above studies indicate that most of the zinc leached from crumb rubber becomes adsorbed in soil and does not mobilize through soil in pore water or leachate. The leaching rate of zinc from crumb rubber directly submersed in water is also relevant. Rhodes et al. (2012) identified a high variability in crumb rubber zinc leaching rate from submerged samples based on published literature data. Rhodes et al. (2012) reported that the zinc mass transfer rate from crumb rubber remained relatively constant throughout their own 96-hour leaching experiment duration. Assuming zinc content of 1.5 percent within the crumb rubber, the 2.5 mg/l of zinc that the authors attained at the end of the experiment indicates that approximately 0.33 percent of the total zinc contained within the rubber had leached into the sample leachate. Additionally, they identified a negative correlation between zinc concentration in the leachate and crumb rubber particle size with larger particles resulting in lower concentrations. They also identified that a higher pH results in lower concentration of zinc in the leachate. The change in mass transfer rate with changes in particle size was suggested to be linearly correlated.

Of 15 crumb rubber leaching studies reviewed by Rhodes et al. (2012), the longest study occurred over a 1-month period. Finney and Maeda (2016) studied leaching rates of various metals from TDA and reported the time to reach steady state leaching conditions was at least 20 weeks, with a longer time needed for samples in continuous submersion. Specific loss rates of zinc in this study started around 0.3 mg zinc/kg of TDA per day in the earliest weeks and reduced to as low as 0.003 mg zinc/kg of TDA per day around week 65. The higher mass transfer rates for zinc observed in the early weeks of the experiment by Finney and Maeda (2016) can be attributed to the use of TDA, a tire-derived product larger than crumb rubber that also contains metal and textile components, including exposed metal wires. The much lower mass transfer rate of zinc observed after week 65 suggests that long-term research on crumb rubber leaching could be beneficial to understanding environmental loading of both CRM pavements and tire debris from roadways over time periods more similar to the lifetime of a road surface.

Rubberized hot mix asphalt zinc leaching rates

Vashisth et al. (1998) performed a constituent leaching and simulated rainfall test comparing RHMA and HMA pavement sample cores. The RHMA samples were wet process RHMA with a CRM content of 1.11 percent total weight, and dry process RHMA with a CRM content of 3 percent total weight. These two pavement cores were compared to a control sample of conventional HMA.

Two laboratory experiments were conducted, the first using quiescent batch leaching with pavement cores while testing the dissolved metals leaching from the cores after 3-hour submersion periods in various pH conditions of deionized water baths. Three different pH conditions were investigated, one using neutral pH while the others contained water with pH of 2 (low, using nitric acid) and pH of 12 (high, using sodium hydroxide). At high and low pH, the dissolved zinc leaching from the RHMA wet- and dry-process pavement cores is higher than from the conventional HMA core (Table 5). At a neutral pH, however, the dissolved zinc content of the leachate from the wet-process RHMA core was less than from the conventional HMA core (half as much) while the dry-process core showed more than double the amount of the conventional HMA core.

Table 5: Concentration of zinc in leachate from conventional and rubberized pavement cores under various pH conditions (Vashisth et al. 1998).

pH	HMA (µg/l)	Wet-Process RHMA (µg/l)	Dry-Process RHMA (µg/l)
2	51	79.5	139
7	5	2.5	11.5
12	14.2	20	147

In a second laboratory experiment, the authors used the same sample cores in a simulated environmental conditions test. The pavement samples were subjected to high-intensity simulated rainfall at pH 7 after subjecting them to simulated wear (UV light simulation, wear exposure). The simulated rainfall runoff from the wet-process RHMA displayed the highest concentration of dissolved zinc at 11.5 µg/l while the conventional HMA and dry-process RHMA resulted in 7.5 and 4.5 µg/l respectively (Table 6). The result suggests that the wet-process RHMA may behave differently to UV light aging and wear than the other samples under simulated high-intensity rainfall as compared to its lower leaching rate under the quiescent batch leaching. However, the authors found their results to be inconclusive as the zinc concentrations from all samples were essentially the same, close to the detection limit of 5 µg/l and considerably lower than proposed toxicity limits (Vashisth et al. 1998).

Table 6: Zinc concentration in runoff from various rubberized pavement samples under simulated rainfall conditions and neutral pH (Vashisth et al. 1998).

Pavement Sample	Zinc (µg/l)
HMA	7.5
Wet-Process RHMA	11.5
Dry-Process RHMA	4.5
Chip Seal HMA	5.5
Chip Seal RHMA (Wet-Process)	7.5

A similar pavement leaching study conducted by Caltrans assessed the toxicity and pollutant discharge from pavement materials generated in runoff from 10 different pavement types (RHMA included) under a variety of temperature and age conditions (Caltrans 2008). Pavement samples examined in the study include RHMA-O, RHMA-G, open-graded asphalt concrete, dense-graded asphalt concrete, and Portland Cement Concrete. Samples were tested at a variety of temperatures, (4, 20, and 45 degrees Celsius), each containing three fresh replicates and three replicates of artificially aged test samples. Simulated aging was performed on the samples by heating them at 85 degrees Celsius for six days, representative of 15 to 18 years of in-service pavement life.

The experimental procedures used resulted in metal concentrations that were significantly diluted compared to more realistic stormwater values; however, comparisons of constituent concentrations between pavement types and fresh vs. aged pavement samples are still useful. The results agree with other findings in that zinc is more likely to be found in elevated concentrations in runoff from newly paved or sealed surfaces (Mahler et al. 2004). A statistically significant difference in zinc concentration was found between fresh and aged pavement samples in the cold (4 degree Celsius) temperature, with fresh samples presenting higher concentrations of zinc. These findings support the possibility of newer pavement projects presenting higher zinc concentrations when compared to older samples, an important finding when considering paired sampling site analysis between pavement types with differing dates of construction.

Murphy et al. (2015) studied the influence of pavement surfaces and types on the attenuation of atmospheric metals. The authors found that carbonates and hydroxides contained within concrete pavement have the potential to absorb copper and zinc, suggesting that the addition of lime in pavement mixtures may effectively reduce zinc loading from the pavement to stormwater runoff.

Additional properties of RHMA that impact water quality

Both permeability and age of pavement have been suggested to influence the levels of constituents found in stormwater runoff from their surfaces. In 2007, Caltrans initiated a four-year stormwater quality monitoring project to assess the performance of permeable pavement at removing stormwater runoff constituents. Caltrans performed a falling head permeability test on a number of different pavement ages and types for this test, including Open Graded Friction Course (OGFC, a type of conventional HMA), RHMA-G, and RHMA-O (Table 7). RHMA is generally used as an overlay, a preventative maintenance that improves an existing paved surface with a non-structural seal or repair. According to the Caltrans Highway Design Manual (Caltrans 2018b), the added service life of the pavement resulting from overlays can vary from a couple of years to more than seven years. This is compared to newly designed pavement life expectancies of 40 years.

Caltrans found that the two RHMA-O sites, although paved relatively recently, hold the second- and third-lowest permeability of the group tested. The only site with a lower permeability is a 16-year-old OGFC. This result is unexpected because open-graded pavements are designed for more rapid drainage and generally have the highest permeability (see Table 3), suggesting that the aggregate grading reported to have been used may not in practice provide the expected permeability.

Table 7: Permeability of various pavement overlays based on an average of three drainage tests (Caltrans 2012).

Location and Station ID	Pavement Type	Overlay Age (years)	Overlay Depth (inches)	Average Drainage Time (sec)	Permeability (inch/hour)
Willits 208-1T	OGFC	4.75	2.00	79	107
Boonville 208-2T	OGFC	5	1.67	379	19
Boonville 208-2C	OGFC	9	1.50	559	11
Atascadero 208-6T	RHMA-O	4.5	0.97	1,582	2.6
Red Bluff 209-2(T1)	OGFC	3.3	1.00	44	96
Red Bluff 209-2(T2)	OGFC	3.5	1.00	46	92
Marysville 209-4T	OGFC	2.8	1.50	34	188
Davis 209-5T	OGFC	4.5	1.42	717	8.3
Davis 209-5C	OGFC	16.8	0.75	51,200	0.062
Vernalis 209-6C	RHMA-O	3.8	1.00	516	8.2

Characterization of Zinc in Stormwater

The literature reveals that there are a number of significant zinc sources in urban environments and that the primary contributions are dependent on the characteristics of each location. Aside from the zinc leaching from crumb rubber and rubberized pavement, it is important to consider other significant sources of zinc to stormwater.

A number of studies have sampled roadway runoff to determine relative contributions of point and nonpoint sources to stormwater constituent concentrations under a variety of different physical and environmental conditions. For example, Walker et al. (1999) reviewed urban stormwater studies and provided a comparison of heavy metal concentrations reported in urban runoff. The comparison includes the results of the National Urban Runoff Program (NURP) as well as three other heavy metal studies that include an average of values taken from data collected by the National Water Research Institute (NWRI). The comparison of results shows the wide variation in zinc across locations and sampling areas (Table 8).

Table 8: Total zinc concentration in stormwater runoff for four studies as reported by Walker et al. (1999).

Location/Study	Zinc Concentration (µg/l)
NURP	92.3 - 103.7
NWRI	490
Sault Ste. Marie, Mich.	274
Newark, N.J.	180 - 964

Walker et al. (1999) also identified significant sources of zinc in urban runoff as atmospheric fallout, corrosion, tires, pavement wear, automobile exhausts, exterior paint, road salt, and terrestrial sources. Such studies are relevant for comparison of field sampling data within this current research project as well as to determine the relative magnitude of contribution from CRM pavements compared to other sources of zinc in the environment, and to formulate an overall zinc loading mass balance.

Transportation-related sources

Kennedy and Sutherland (2008) surveyed urban areas and identified many potential sources of primary heavy metal pollutants to stormwater including zinc (Table 9). Transportation related sources were identified including vehicle and tire wear, motor oil, road debris, and atmospheric emissions.

Table 9: Potential transportation-related souces of zinc in stormwater (Kennedy and Sutherland 2008).

Generic source	Principal source	Zinc source
Vehicles	Tires	Yes
Vehicles	Brake Pads/Linings	Yes
Vehicles	Wheel Weights	No
Vehicles	Surface Treatments/Coatings	Yes
Vehicles	Emissions	Yes
Vehicles	Fluid Losses, Drips, and Spills	Yes
Vehicles	Air Bag Initiators	Unlikely
Pavement	Road Dust	Yes
Pavement	Road Paint	Yes
Pavement	Road Surface (e.g. Bitumen)	Unlikely
Other	Guardrails	Yes
Other	Galvanized Drain Pipes	Yes
Other	Light Posts	Yes
Other	Sign Posts	Yes

Tire wear particles

Tire wear particles have been identified as a significant source of zinc to the environment (Gunawardena et al. 2013; Kennedy and Sutherland 2008). Councell et al. (2004) estimate environmental zinc loading from tires by two methods, one using tire wear rate estimates and vehicle miles driven, and the other using the geometric mean of tire tread contained within a tire and the number of tires used within a year. Sakai (1996), as cited in Councell et al. (2004), estimated tire wear rates for gentle, normal, and hard driving to be 0.023, 0.042, and 0.073 g tread/km per tire and estimated the average tire wear particle to be 10-20 μm in size. The resulting estimate is an annual zinc release by tire wear in the United States of 10,000 to 11,000 metric tons. A comparison with atmospheric deposition suggested the atmospheric deposition rate was 2 μg zinc/cm^2/year, while the tire wear related flux to the environment was 42 μg zinc/cm^2/yr. This estimate considers total zinc contained within tire wear particles and does not investigate the considerably smaller amount that might leach or become bioavailable.

Motor oil

Davis et al. (2001) tested 13 used automobile engine oil samples obtained from automotive service locations in Maryland. The mean concentration of zinc converted from a water oil mixture to metal mass per liter of oil was 125,000 µg/l oil, with higher concentrations recorded in used oil. Zinc is used as an additive in oil to provide wear protection for the engine. WSDOE (2008) identifies motor oil and hydraulic fork oil to be about 0.1 percent zinc by weight (1,000,000 µg/l). The California Environmental Protection Agency (CEPA 2006) estimated the total annual loading of oil to California stormwater statewide as 16-120 million pounds of oil. As cited by CEPA (2006), the New Zealand Ministry of Transport (2004) estimates the rate of oil lost to roadways to be 2.8 ml of oil per 1,000 km driven. Assuming an oil density of 800 g/l and 0.1 percent zinc by weight, the amount of zinc polluted by vehicles from motor oil is 3.58 µg/1,000 vehicle miles.

Road dust

Multiple studies have captured samples of roadway dust and analyzed them for heavy metals. In some cases, the metal concentrations of the roadway samples were compared to concentrations of suspended sediments in nearby stormwater. In this context, it is important to consider the background zinc concentration of soils which may vary between 10-300 mg/kg (McLean et al. 1992).

Brown and Peake (2005) collected samples of road dust (15 combined subsamples from a street sweeper pile) in urban areas of Dunedin, New Zealand, and compared the metal concentrations to that of suspended sediment samples taken from three stormwater drainages near the roadway sampling locations. The samples were taken over a 2-year period, including seven storm events. Heavy metal concentrations in the road dust ranged from 241-1,325 µg/g for zinc. Drying and measuring the metal concentrations of the suspended sediment samples indicated that the concentrations of both the roadway sediment and suspended sediment of the stormwater were similar, suggesting that the roadway material was possibly the source of suspended sediment in the stormwater drainages.

Thorpe and Harrison (2008) reviewed heavy metal emissions from transportation-related sources and found that components of road dust such as exhaust particles and abrasive sources such as brake wear, tire wear, and pavement wear are important sources of heavy metals in the environment. Furthermore, they found that concentrations in these materials can vary widely between manufacturers and lining types. Davis et al. (2001) estimated that the environmental loading of zinc from brake wear alone is 89 µg/km/vehicle.

Atmospheric deposition and distribution

Identifying heavy metal deposition and transport pathways is important to understanding the movement of constituents within a drainage area. Atmospheric deposition, for example, has been identified as a major distribution pathway for non-point source heavy metals in urban stormwater (Gunawardena et al. 2013; Kennedy and Sutherland 2008). Atmospheric deposition occurs as dry deposition when suspended particles settle out of the air or wet deposition when particles are captured by or dissolved in rain. Gunawardena et al. (2013) identified zinc as the most readily dissolved atmospheric heavy metal, claiming it to have the highest atmospheric deposition rate of all heavy metals. Davis et al. (2001) estimate wet and dry deposition of zinc to account for 5 percent of the total annual zinc loading in an urban environment in Maryland. The Auckland Regional Council (Kennedy and Sutherland 2008) identified atmospheric deposition as a major contributor to zinc in urban stormwater, stating that atmospheric deposition along with construction materials and tires made up 77 to 89 percent of zinc found in stormwater runoff. Atmospheric deposition, accumulation of particles from local sources, and redistribution of pollutants from wind and traffic are all factors contributing to pollutant buildup. The level of buildup is also dependent on the rate of deposition, the porosity of the pavement surface, the length of dry periods between runoff events, and potential removal by street sweeping or washoff (Kayhanian and Harvey 2020).

Washoff is the removal of pollutants by precipitation and runoff as stormwater (Chiew et al. 1997). Some studies have attempted to quantify road particle transport mechanisms more specifically. In the Netherlands, Blok (2005) found that approximately 70 percent of tire wear is washed away as runoff, and the remaining 30 percent is entrained into the air and drifts to a buffer zone approximately 10 meters wide on either side of the pavement.

The concentration of a constituent washed away in stormwater varies depending on the constituent form, the time elapsed since the last storm (buildup), and runoff volume. Peak levels in dissolved pollutants generally occur before particulate pollutants, since less energy is required to keep them suspended (Bertrand et al. 1998; Chiew et al. 1997). Bertrand et al. (1998) proposed that a phenomena known as the first flush effect impacts constituent washoff rate, and that 80 percent of the total pollutant mass is washed away in the first 30 percent of pollutant discharge. Though there is speculation on the extent and commonality of this phenomenon, numerous studies have acknowledged its validity (Bertrand et al. 1998; Chiew et al. 1997; Lee and Bang 2000). This is an important concept when considering the timing of stormwater samples being captured at different locations.

Urban infrastructure sources

In urban environments, galvanized surfaces that protect steel and iron materials has been identified as a significant source of zinc to stormwater runoff and have been the focus in a number of studies. Basin-scale assessments on constituent sources of urban stormwater have quantified the heavy metal concentrations during storms with sampling stratification of urban sources such as roadways, rooftops, lawns, and parking lots.

Galvanized, painted, or coated metal surfaces

Zinc is added to paints and coatings for metal surfaces and provides anti-corrosive properties to protect the coated infrastructure. Galvanization is the process of applying a zinc-based protective coating on steel or iron products, and galvanized steel is used in multiple urban applications such as rooftops, guardrails, fencing, walkways, and nuts, bolts, and wires. In 2016, the United States produced 4.4 million tons of galvanized steel (AGA 2018). ASTM specification A653 outlines standard specifications for a zinc-coated steel sheet by galvanization (zinc-coated) or galvannealing (zinc-iron alloy-coated) by the hot dip process. For a common G90 designation (ASTM 2020: Table 2.6) a minimum weight requirement of zinc for a two-sided application is 0.90 oz/ft^2 or 275 g/m^2, where the area is of a single side.

Sullivan and Worsley (2002) investigated the zinc runoff from a number of galvanized and zinc-coated metals over a 16-month study duration and found a total mass of zinc leached from hot-dipped galvanized steel of 2.87 g of zinc/m^2 and 2.36 g/m^2 for galvanneal. Sandberg (N.D.) sampled zinc leachate from galvanized metal estimating the release rate to be 2.6 g of zinc/m^2/y. This research also noted that the time required to reach a steady state of corrosion due to hardening and formation of patina on the surface of the metal can be up to 20 years, and that corrosion was a more significant contributor to metal losses than leaching due to precipitation alone.

A study of zinc in three catchments in Auckland, New Zealand (Kennedy and Sutherland 2008), found that metal roofing was the dominant contributor of zinc for commercial and industrial sites. They indirectly estimated the mix of contributions to the total zinc load from the following urban sites, where the wide range of some values indicates the level of uncertainty of the estimate

- Industrial: metal roofing up to 75 percent
- Commercial: metal roofing 51 percent, tires 20-40 percent
- Residential: tires 40-80 percent, metal roofing 42 percent.

A report by the Washington Department of Ecology (WSDOE 2006) presented similar findings. Reviewing industrial facilities under the Industrial Stormwater General Permit framework, they found that of 28 facilities surveyed, industrial stormwater zinc discharge concentration ranged from 41-629 µg/l. One of the industrial sites monitored over five storm events presented average dissolved zinc levels of 197, 111, 30, and 55 µg/l coming from an asphalt roof with galvanized metal, asphalt roof without galvanized metal, parking lots, and loading docks, respectively. A second facility showed the zinc concentration from a roof with galvanized metal was three times higher when compared to a roof without, with mean dissolved zinc levels of 346 µg/l and 103 µg/l, respectively.

Charters et al. (2016) sampled total suspended solids and heavy metals (copper, lead, zinc) in runoff from 24 rainfall events on four impermeable source locations (concrete tile roof, copper roof, galvanized roof, coarse asphalt road) in Christchurch, New Zealand. Manual and automatic sampling was used to capture samples of the first two liters of runoff (first flush), and another sample was taken once steady state conditions were met. While the highest mean concentration of zinc (397 µg/l) was produced on a coarse asphalt road, under semi-acidic rain conditions, the galvanized roof produced the maximum zinc concentration of 1,970 µg/l, more than three times the mean zinc concentration found on the coarse asphalt road. This research indicates that residential and commercial roofing has a potential to generate high concentrations of zinc in stormwater.

Basin scale zinc contribution assessment

Steuer et al. (1997) sampled heavy metals from 33 sites in an urban catchment basin in Marquette Michigan over the course of 12 storms. The sample sites were from eight urban surface source types including high, medium, and low traffic streets, residential driveways, residential rooftops, commercial rooftops, and grass area. Samples were taken concurrently at all 33 sites using automatic street samplers. Sampling was conducted throughout the entire storm, thus obtaining event mean concentrations (EMCs) for each storm and avoiding first flush samples. Commercial rooftops produced the highest EMCs of dissolved zinc (263 µg/l). In addition, the basin outlet concentrations were monitored to develop a mass budget which compared source area contaminant loads to the outlet concentrations for individual storms. The results indicated that parking lots (30 percent) and roofing (31 percent) were major contributors of total zinc (

Table 10).

Table 10: Contribution of zinc from eight source locations within a catchment basin of Marquette, Michigan (Steuer et al. 1997).

Source	Contribution of Zinc (%)
High-Traffic Street	10 ± 5
Medium-Traffic Street	8 ± 2
Low-Traffic Street	19 ± 7
Residential Roof	15 ± 7
Commercial Roof	16 ± 10
Commercial Parking Lot	30 ± 15
Residential Drive	18 ± 12
Grass area	0

Davis et al. (2001) sampled for a variety of metals in the state of Maryland. Synthetic rainwater was used to collect samples from various outdoor urban surfaces in an attempt to quantify the contribution of each metal to the total load. The results of zinc loading from common building surfaces showed that materials used on the exterior of buildings could be significant contributors of zinc. The mean concentration of zinc in their testing for brick, painted wood, and concrete surfaces exceeded that for metal roofing (Table 11).

Table 11: Zinc concentration in runoff resulting from spraying synthetic rainwater on outdoor surfaces (Davis et al. 2001).

Material	Sample Count	Mean Zinc Concentration (µg/m^2)	Maximum Zinc Concentration (µg/m^2)
Brick	30	2,100	23,000
Painted wood	13	2,800	8,400
Concrete	7	1,200	1,900
Metal	4	690	2,500
Unpainted wood	3	330	730

Davis et al. (2001) examined runoff from roofing surfaces and recorded mean zinc concentrations of 100 µg/l, 1,100 µg/l, and 1,100 µg/l from residential, commercial, and institutional roofing, respectively. The authors also note that the highest concentration observed from roofing material was 7,600 µg/l, which was runoff from a galvanized roofing material.

Davis et al. (2001) used the results from their material testing to compile a basin-wide estimate of the percent contribution of each material to the overall zinc loading. The results suggest that for their specific basin, the two major contributors to zinc in the environment are building siding and tires (Table 12). The authors note that their estimates for the loading rate from siding is the equivalent to continuous washing, which is likely not a reasonable assumption. Additionally, the authors use the leaching rate of tire particles abraded with a steel brush and submerged in water for 24 hours, which is not likely to be representative of the leaching rate that would be sustained over the 1-year analysis duration. The study did not quantify zinc from the road surface material itself as a source. Still, the relative contributions from this preliminary mass loading balance give useful reference for potential source loading rates.

Table 12: Relative contribution of primary soures for zinc in urban stormwater runoff (Davis et al. 2001).

Zinc Source	Zinc Loading (kg/ha-yr)	Relative Contribution of Source (%)
Siding	0.378	58
Roof	0.045	7
Brakes	0.021	3
Tires	0.163	25
Oil Leakage	0.006	1
Wet Deposition	0.013	2
Dry Deposition	0.02	3

Paired sampling in California to assess contributions from RHMA

Due to the high variability of point and non-point sources of zinc in urban and transportation environments, one way to test differences in stormwater constituent attenuation of various pavement types is by paired sampling. This sampling technique identifies the boundaries of two pavement types within a given roadway and samples stormwater runoff from both pavements within close spatial proximity. This strategy attempts to control for various factors such as traffic, background soil levels, and atmospheric deposition and isolate testing for differences in constituents from different pavement types. Caltrans has performed a number of studies involving paired sampling between RHMA and HMA conventional pavement surfaces in California (Caltrans 2012).

Caltrans paired sampling results

Caltrans (2012) conducted paired sampling efforts at three sites in California: Atascadero in San Luis Obispo County, and Merced and Visalia, both in the San Joaquin Valley. The report includes dissolved and total zinc (along with other metals) in stormwater runoff from the paired HMA-RHMA sites collected from 2008 through 2011. The data at these sites show a wide range in the concentrations of zinc found in the runoff between the paired conventional and rubberized surfaces. At the Merced site, the zinc concentrations in the runoff were low, generally less than 25 μg/l total zinc, and the concentration from the HMA and RHMA were nearly the same. Total zinc concentrations at the Visalia and Atascadero sites were higher, often exceeding 100 μg/l, and generally concentrations from the RHMA site were higher than those from the HMA site. Direct comparison between the sites is complicated because of differences in the type of RHMA, the conditions surrounding the roadway, and the road traffic count. The Caltrans report contains limited analysis and interpretation of the data collected; however, these data are analyzed and interpreted in more detail in the results section of this report and provide valuable insights for the data collected in this sampling effort. Raw data for three Caltrans-paired RHMA sampling locations are provided in the Appendix of this report and Appendix J of the Caltrans report.

Literature Summary

While there are many studies addressing the sources of zinc in stormwater runoff, there are challenges, contradictions, and gaps in the available information. Findings suggest that significant contributors of zinc to urban stormwater include runoff from zinc-coated (galvanized) metals and building siding materials (brick and painted wood), atmospheric deposition, and tire wear particles (Davis et al. 2001; CASQA 2014; Gunawardena et al. 2013; Kennedy and Sutherland 2008; WSDOE 2008). While there is reasonable agreement in previous research that identifies the significant potential contributing sources of zinc, the actual contribution of zinc to stormwater runoff is much less clear due to the complexity of fate and transport processes. Although there are numerous studies that account for and quantify zinc from various sources, previous research has not focused on sources directly from roadways. Little has been done to characterize the differences in zinc leaching rates of RHMA pavement in comparison to conventional HMA.

Most studies on zinc leaching from RHMA and HMA pavements are either laboratory or field experiments. Results from these studies are inconclusive in demonstrating that any differences in leaching rates between RHMA and conventional HMA result in a higher concentration of zinc in roadway stormwater runoff. It has been demonstrated that the physical characteristics of the pavement can influence the buildup and washoff patterns of pollutant buildup, but it is unclear whether pavement with high porosity common in newer RHMA surfaces reduces pollutant loading to stormwater. Some research reports no clear indication of pollutant reduction from high-porosity pavement surfaces while others report a significant decrease in pollutant loading. The complexity of zinc deposition and washoff on roadways makes identifying and tracing the contribution of each source difficult in application.

Materials and Methodology

This section provides a description of the materials and experimental methods used in the study. The properties of the materials and procedures used in two laboratory batch leaching experiments are described, followed by a description of field data collection for assessment of zinc leaching from RHMA pavement. The determination of the zinc content of the solids and water samples collected during this project was made by either North Coast Laboratories Ltd. or Alpha Analytical Laboratories Inc., both of which are California state-certified. Determination of zinc in water was made using EPA methods 200.7 and EPA 200.8 version 4.4 (USEPA 1994). The analytical detection limit was 5 µg/l, and zinc concentration levels below this limit were reported as non-detect (ND).

Materials

Pavement materials used in this analysis were prepared and provided by the Pavement Preservation Center at California State University, Chico. Provided materials included: passenger crumb rubber, truck (high natural rubber) crumb rubber, scrap crumb rubber (~75 percent passenger, 25 percent high natural rubber), asphalt extender oil, asphalt rubber binder, RHMA (core compacted and non-compacted forms), and conventional HMA cores. The pavement cores were made from fresh asphalt that had not been driven on. Non-compacted conventional HMA material was not provided for testing. Based on the assumption that the majority of the zinc in asphalt leachate is contributed from the asphalt binder in HMA rather than the aggregate itself (sand, rock) and that the aggregate itself has minimal wear, it was not deemed necessary to obtain and test the HMA aggregate. These materials were tested for zinc content by Alpha Analytical Laboratories (Table 13). While the literature generally reports that truck tire tread contains a higher fraction of zinc than passenger tires, the passenger tire crumb used in this experiment contained 2 percent zinc while the zinc content in the truck tire crumb was 0.8 percent. The laboratory reported zinc content of the uncompacted material used in the RHMA cores of 160 mg/kg (or 0.016 percent) is less than typical literature values of 0.024 to 0.03 percent (Table 4).

Table 13: Zinc content of various materials used in the laboratory portion of this research as determined by California state-certified lab.

Pavement Material	Zinc Content (mg/kg)
Passenger Tire Crumb	20,000
Truck Tire Crumb	8,400
Scrap Tire Crumb	14,000
Asphalt Extender Oil	15
Asphalt Rubber Binder	360
RHMA (Uncompacted)	160

Crumb Rubber Batch Leach Testing

A batch leaching experiment was conducted to investigate the rate of zinc leaching from passenger and truck tire crumb rubber. The scrap tire crumb rubber sample was not included in this experiment as the exact composition of the mixed sample was unknown. The crumb rubber samples were sieved into three diameter classes for comparison of their relative size distribution (Table 14). Since none of the truck tire rubber crumb was greater than 2 mm in diameter, two size classes were chosen for analysis. Crumb particles passing the 0.5 mm sieve were classified as "small," and particles retained on the 0.5 mm sieve) were classified as "large" (Figure 2).

Table 14: Relative mass fraction of passenger and truck crumb rubber samples sorted into three diameter size classes.

Size Class	Passenger Tire Crumb Rubber Mass Fraction (%)	Truck Tire Crumb Rubber Mass Fraction (%)
Less than 0.5 mm	4	53
0.5 mm to 2 mm	84	47
Greater than 2 mm	12	0

Figure 2: Two size classes of passenger tire crumb rubber were selected as greater than 0.5 mm (large, on left) and less than 0.5 mm (small, on right).

Ten samples were created for each size class (small and large) for each of the two types of rubber (passenger and truck). This resulted in 10 small passenger tire samples (PS), 10 large passenger tire samples (PL), 10 small truck tire samples (TS), and 10 large truck tire samples (TL). Each sample consisted of three grams of tire crumb rubber, submerged in 240 milliliters of distilled water and placed in small plastic bottles.

Samples from each of the four categories were filtered using a 1.5-micron glass microfiber filter to remove any crumb rubber particles, preserved in nitric acid, and submitted for laboratory testing of dissolved zinc content after various periods of elapsed leaching time. Replicate samples were collected after two and four days of leaching to assess the consistency in leaching rates across the samples. Results from these first few samples indicated good agreement in the concentration of replicates, so at subsequent leaching periods, replicates were not used.

RHMA and Conventional HMA Pavement Batch Leach Testing

Two pavement core batch leaching experiments were conducted to assess the rate that zinc leaches from RHMA pavement in comparison with conventional HMA pavement. All pavement cores weighed between 2,258 and 2,362 grams (Table 15) and were 6 inches in diameter and 2.4 inches tall (Figure 3).

Table 15: Characteristics of the asphalt pavement core samples used in the two leaching experiments.

Pavement Leaching Experiment	Core	Weight (g)
1	HMA-A	2,361.8
1	HMA-B	2,353.7
1	RHMA-A	2,307.7
1	RHMA-B	2,341.1
2	RHMA-1	2,307.8
2	RHMA-2	2,258.4
2	RHMA-3	2,295.4
2	RHMA-4	2,327.4

Figure 3: A representative core used in the pavement batch leaching experiments.

Each core was placed into a covered glass jar and submerged with a known volume of distilled water. The contents of the jars were gently stirred prior to taking a leachate sample. Samples were preserved in nitric acid and submitted to the laboratory for assessment of total zinc content.

The first pavement core leaching experiment was designed to provide long-term zinc leaching rates for asphalt. Two identical conventional (non-rubberized) HMA cores (HMA-A and HMA-B) and two identical conventional RHMA cores (RHMA-A and RHMA-B) were used in this experiment. Leachate samples were taken beginning on the second day of soaking and continued with an increasing duration between samples until day 240.

Based on previous experiments with TDA, a reduction in the rate of zinc leaching from the asphalt over time was anticipated. The second pavement experiment was designed to determine whether the leaching rate of zinc was dependent on the age of the asphalt, or whether aging might at least temporarily increase the leaching rate. Four identical RHMA cores (RHMA-1, RHMA-2, RHMA-3, and RHMA-4) were allowed to soak for 63 days (Figure 4). Cores RHMA-1 and RHMA-3 were then removed from their jars and subjected to the AASHTO R-30 long term mixture conditioning procedure, which is used to simulate the effect of HMA aging that occurs over the service life of a pavement (AASHTO 2019). The procedure requires that the core samples be placed in an oven at 185 degrees F for 120 hours, followed by a cooling period of 24 hours. After the cores were cool, they were placed back into their soaking jars and leachate samples were collected over the following 29 days and analyzed for total zinc content. This same conditioning procedure was also applied to core RHMA-A from the first experiment that had been soaking for 240 days.

Figure 4: Four identical RHMA pavement cores were each placed in distilled water to determine the zinc leaching rate over time.

Paired HMA – RHMA Pavement Stormwater Runoff Sampling

To assess differences in stormwater zinc concentrations between runoff from RHMA and HMA pavement, samples were collected from a number of paired locations at either side of a change in roadway pavement type. Humboldt State University (HSU) and GHD Consultants collected stormwater runoff from paired rubberized and non-rubberized road surfaces for approximately 16 months beginning in December 2018. The paired runoff sampling data was used to complement the previously described sampling efforts by Caltrans.

HSU sampled sites in the north coast region of California, GHD sampled sites in the San Francisco and Sacramento area, and Caltrans sampled sites Central California (Figure 5). The HSU and Caltrans sites were on state highways while the GHD sites were on commercial and residential streets. Information concerning the paving date and specific type of RHMA used, along with annual average daily traffic (AADT) observations, were available for the highway locations (Table 16) but not the street sampling locations. The AADT estimates are for locations within a quarter mile of each sampling site. Annual average daily truck traffic (AADTT) data was available for some sites, but observations were sparser and are coarse approximations. Monitoring location characteristics as well as the methodology for sample collection are described below.

Description of HMA-RHMA paired sampling sites

HSU focused on selecting suitable sample sites to allow for comparison of the zinc concentration of roadway stormwater runoff from conventional HMA and RHMA pavement in northwest California. Eight different roadway sample sites were established to provide four HMA-RHMA paired samples from three separate RHMA pavement projects (Figure 6). Each of the sampling sites were located near the start or end of a RHMA pavement project to allow comparison of the zinc concentrations in runoff collected on the conventional HMA and RHMA pavement surfaces while minimizing differences in other potential zinc sources such as traffic, soil type, galvanized metal surfaces, etc. Each sample site was selected at a location where runoff was only from the road surface and not from adjacent natural or manmade surfaces. The samples sites listed as NonRHMA were all paved with conventional HMA.

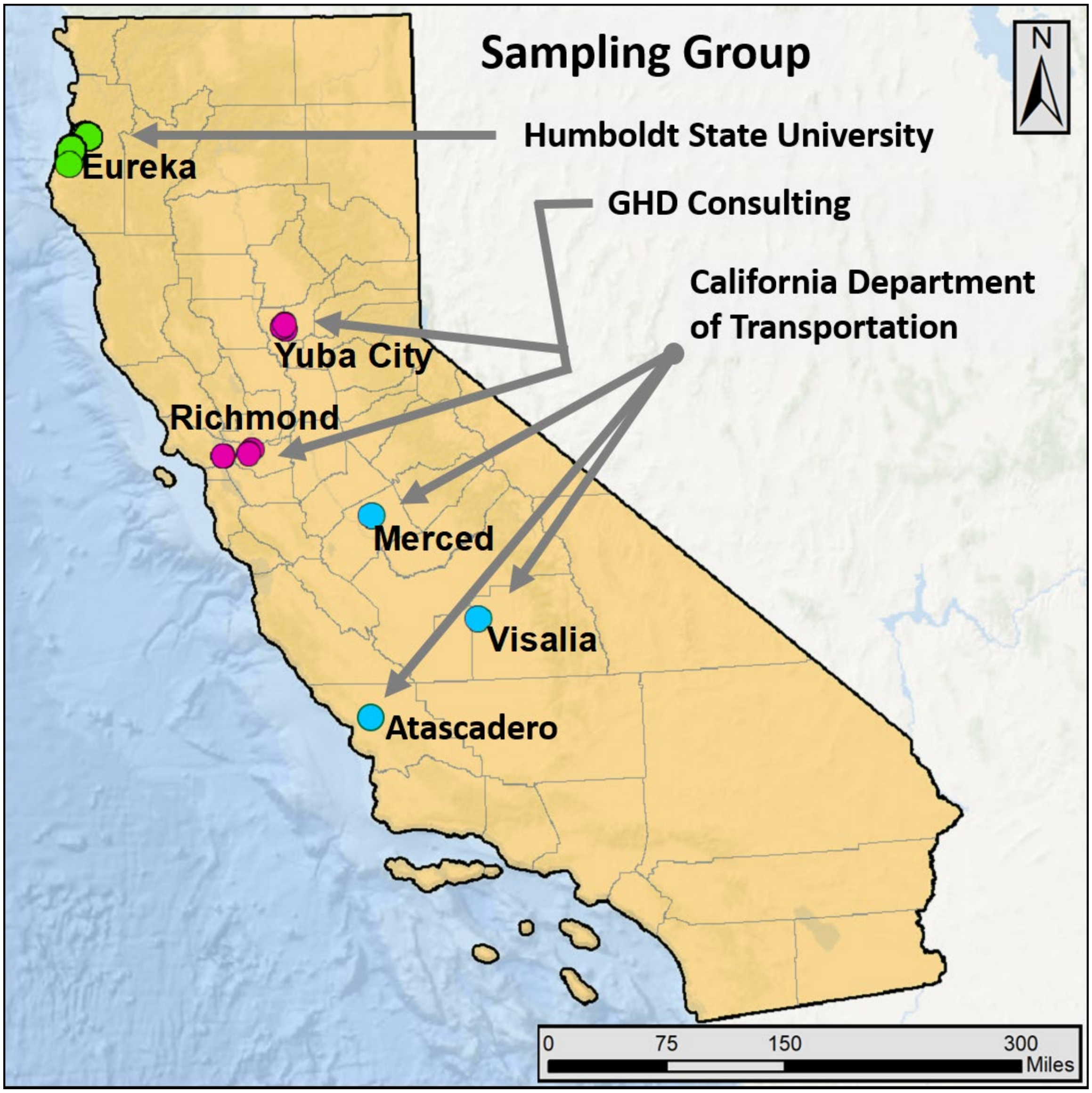

Figure 5: California paired HMA-RHMA pavement sampling sites and the associated sampling group.

Table 16: Traffic counts and RHMA pavement characteristics of state highway paired HMA-RHMA runoff sampling sites.

Location - Sample ID	Roadway Postmile	RHMA AADT	Non RHMA AADT	AADTT to AADT Ratio (%)	RHMA Project End Date	RHMA Type	Source
Blue Lake – 299	Hwy 299 PM 5.5	5,000	9,800	13	Aug 2016	Open Graded	1, 2
Eureka – 101N	Hwy 101 PM 75.1	30,200	33,000	10	Jan 2015	Gap Graded	1, 2
Eureka – 101S	Hwy 101 PM 69.9	25,500	22,800	10	Jan 2015	Gap Graded	1, 2
Eureka – 101FS	Hwy 101 PM 65.4	23,400	22,800	10	Fall 2019	N.D.	1, 2
Merced	Hwy 140 PM 25	3,900	3,900	10	RHMA - 2005 Slurry Seal - 2008	Gap Graded - Slurry Seal	3
Visalia	Hwy 99 PM 47	49,000	49,000	32	Sept 2005	Gap Graded	3
Atascadero	Hwy 41 PM 11	10,100	10,100	15	Dec 2005	Open Graded	4

Sources: [1]Rebuilding CA, 2019; [2]Caltrans, 2019; [3]Caltrans, 2012 (Appx A); [4]Caltrans, 2012 (Appx O)

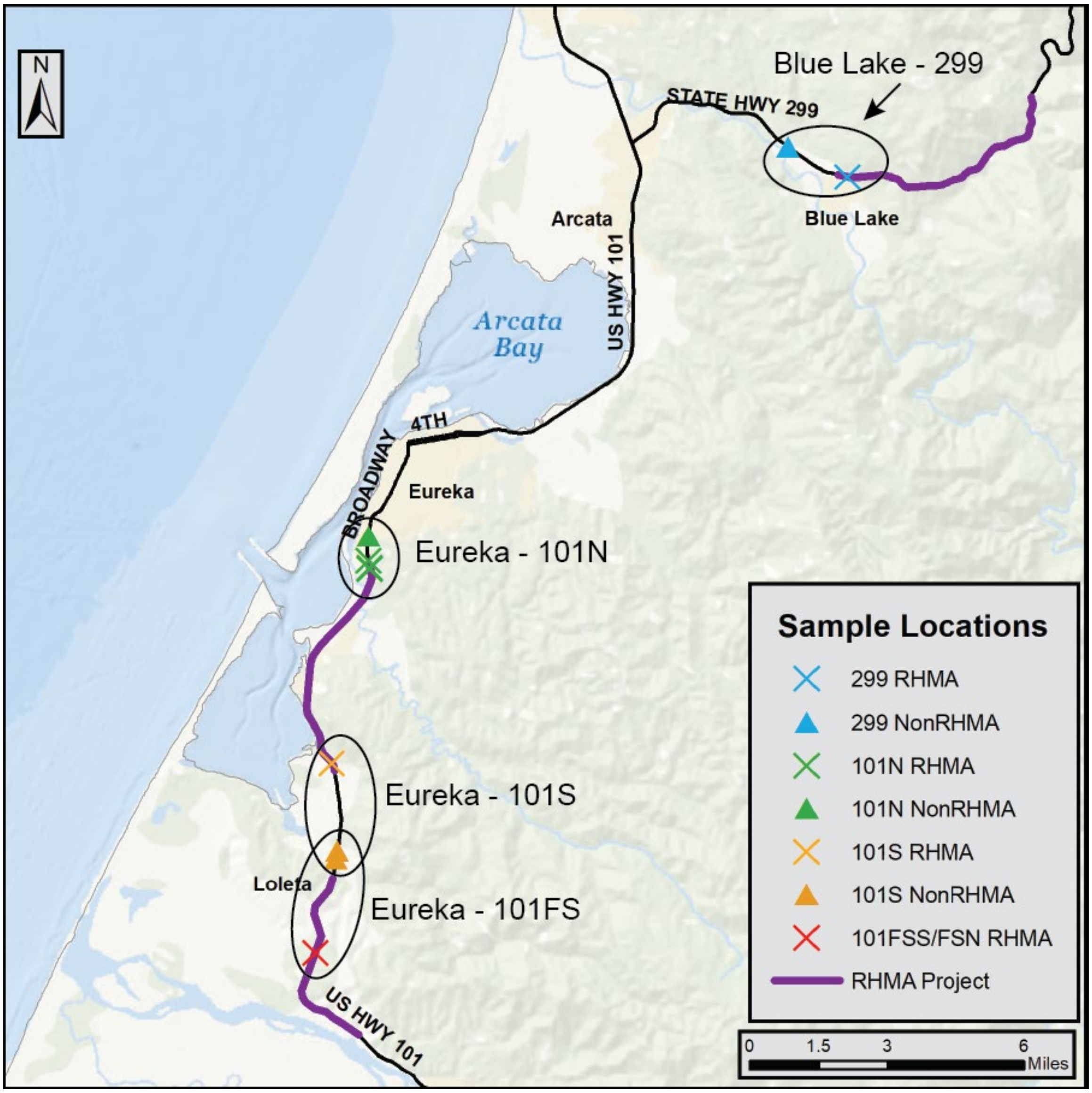

Figure 6: Stormwater runoff monitoring site locations near Eureka and Blue Lake. The locations marked with double symbols indicate a slight change in sample site locations due to accessabiltiy and safety concerns.

The 299 RHMA and 299 NonRHMA sample sites are located along Highway 299 near milepost 5.5 and the exit to the city of Blue Lake. The 101N RHMA, 101N NonRHMA, 101S RHMA, and 101S NonRHMA paired sampling sites are located at the north and south end of an RHMA project that extends from the southern end of the city of Eureka near Herrick Avenue on US 101 (postmile 75.1) south to College of the

Redwoods (postmile 69.9). The 101S NonRHMA site was also paired with the two nearly adjacent RHMA sites, 101 FSS/FSN RHMA, located on US 101 at postmile 65.4. Roadway access issues during the sampling period resulted in having two RHMA sample sites at this location.

Highway 299 is much less traveled compared to Highway 101, with the daily traffic counts at the Highway 299 sites 20 percent of those at the Highway 101 sites. Truck traffic at all sample sites was approximately 10 percent of the AADT. While the AADT for paired HMA and RHMA sites on Highway 101 were nearly the same, the HMA site on Highway 299 had nearly double the traffic count compared to the RHMA site. The differences are due to the off-ramp for the city of Blue Lake being located between the NonRHMA and RHMA sample sites, and the primary direction of traffic is to and from the town passing through the NonRHMA site located west of Blue Lake.

Caltrans collected data from sites in Merced, Visalia, and Atascadero. The Merced and Visalia sampling sites were located along rural regions of Highway 140 and 99 respectively, with irrigated farmland bordering the locations. Highway 140 near Merced was lightly traveled, with the lowest AADT of all the highway sites used in this study. The Visalia location had the highest AADT of any location in the study, nearly twice the next-highest (Eureka 101N). The Caltrans Atascadero sampling site was along a lightly traveled section of Highway 41, with a traffic count similar to the HSU city of Blue Lake site.

GHD sampling in Yuba City mostly occurred in residential and commercial areas on non-highways. AADT was not available in the Yuba City locations, but the residential focus of the GHD samples suggests generally lower traffic areas compared to the highway sampling from HSU and Caltrans. In Yuba City three paired samples were collected, each at a different location. Two were taken on residential roadways (Shanghai Bend Road and Allen Way), with each RHMA and HMA sites being within 0.5 miles of each other. The third site was Gray Avenue, a commercial site bordered by parking lots. GHD also sampled on Ohio Avenue near the intersections with South 1st Street and South 5th Street in Richmond. Samples taken on Ohio Avenue for HMA and RHMA were within 0.2 miles of each other. Three storm events were sampled in this location, and two different paired sampling locations in close proximity were sampled during two of the storms, resulting in five total paired samples. Ohio Avenue contains mixed residential and commercial areas, with the commercial areas focused toward the nonRHMA sampling locations.

Humboldt State University and GHD sample collection

At the selected locations, samples were collected during storms that provided sufficient roadway runoff. The samples were collected on the edge of the pavement, and attention was paid to avoid collection sites in proximity to soils or other sources of metals such as guardrails. Samples were collected from the pavement with a hand-operated rotary pump and bottled on-site (Figure 7).

Figure 7: The rotary hand pump used to collect stormwater runoff samples from pavement.

Generally, the sample collection process would take no more than two hours. Samples to be analyzed for dissolved zinc were filtered using a 1.5-micron glass microfiber filter and preserved using nitric acid, while the total zinc samples were preserved without filtration. Some of the water was used to test the pH of the samples and all samples were submitted to a laboratory for analysis of total and dissolved zinc.

Results and Discussion

The results from the experimental work carried out during this project are presented and discussed in this section. In addition, the results are compared to those from previous researchers to assess the relative contribution of RHMA to the zinc load in stormwater runoff from paved road surfaces. The results from the crumb rubber leaching are presented first, followed by the results from the leaching of HMA and RHMA pavement cores. The results from the HMA-RHMA paired field sampling of stormwater runoff from roadways are then presented. A mass balance analysis of the relative contribution of zinc in roadway stormwater runoff from RHMA compared to tire wear particles is made using the results from the laboratory and field results from this study. The mass balance analysis also includes an estimate of the contribution of galvanized guardrails since this is recognized as potentially a significant source of zinc in runoff from highways.

For all data of zinc concentrations in this project, the analytical method detection limit was 5 μg/l. If an observation was found to have a zinc concentration below the detection limit (i.e. the result reported as ND), the observation was not included in any statistical measure of the results. Many of the figures in this section display results as they were observed over a period of time. Observed data are shown with a symbol, and the observed data in one series are connected with a dashed line. The line is to aid in visually identifying trends, and is not an indication that the relationship between observed points is linear.

Crumb Rubber Batch Leach Testing

The dissolved zinc concentration in the leachate from the tire crumb was determined at eight different leaching times ranging from 2 to 240 days. The time between samples was shorter in the early stages of the experiment to capture the expected high initial leaching rate. The cumulative mass transfer rate of zinc from the crumb rubber was computed as the mass of zinc in the leachate per unit mass of the crumb rubber in the container divided by the elapsed leaching time (μg/kg/day).

As expected, the cumulative zinc mass transfer rate from the crumb rubber was found to rapidly decrease from the value found on the first day of sampling (day 2 of leaching) (Figure 8). This decrease in the cumulative mass transfer rate was particularly rapid for the passenger tire crumb, with an order of magnitude reduction during the first 61 days of leaching for the small-diameter crumb rubber and 21 days for the large-diameter crumb rubber. The initial mass transfer rate of zinc from truck crumb rubber was approximately 20 percent of that from the passenger tire crumb rubber. A lower initial rate was anticipated given the lower zinc content of truck tire crumb rubber compared to passenger tire crumb rubber (see Table 13).

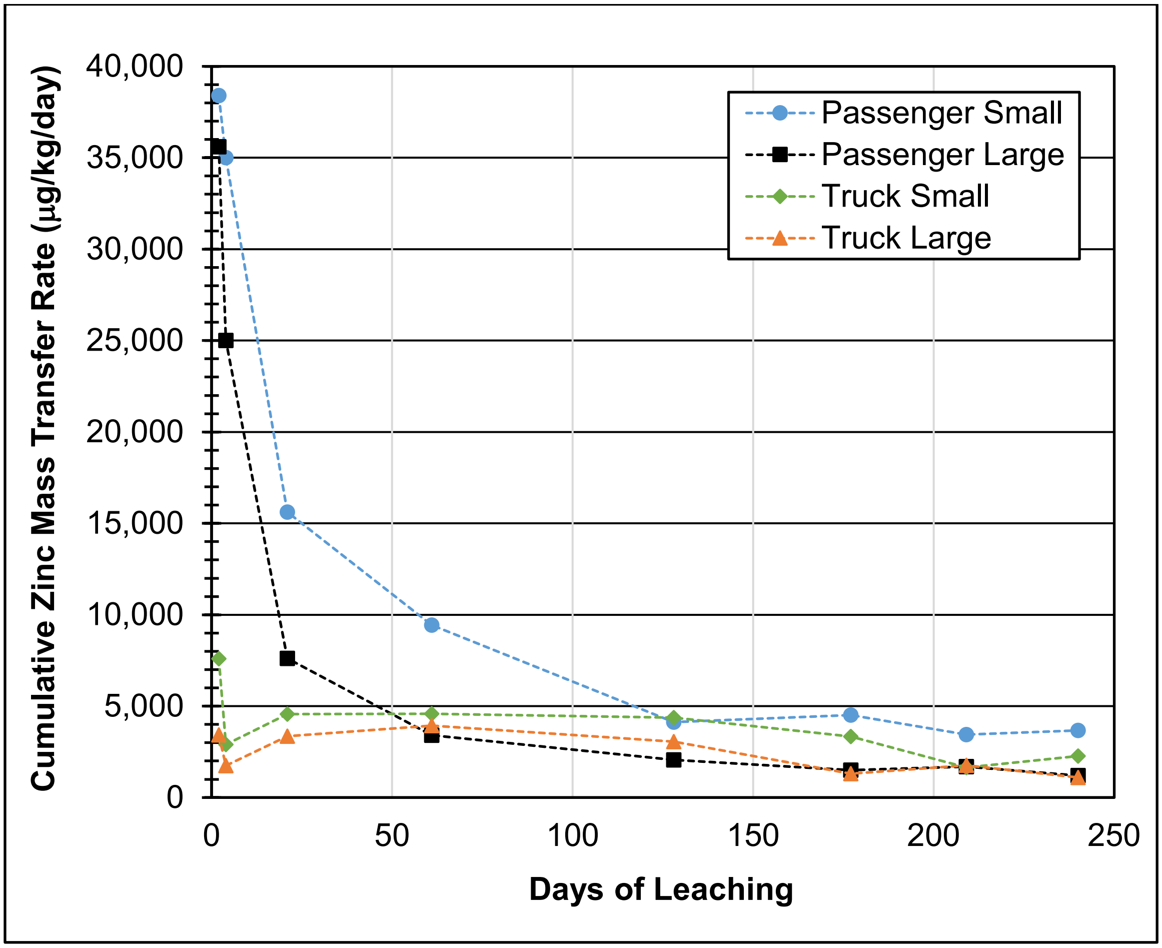

Figure 8: Cumulative zinc mass transfer rate for small- and large-size passenger and truck crumb rubber. (Reference Appendix B, Figure 8 Table)

The cumulative mass transfer rate of zinc from the submerged passenger and truck tire crumb rubber was higher for small diameter samples compared to the large diameter samples (Figure 8). This was especially true of the passenger tire crumb rubber beginning with the day 21 samples compared to the truck tire crumb rubber. The higher mass transfer rate for the smaller-diameter particles is likely due to the greater surface area to volume (and mass) ratio of those particles compared to the larger-diameter particles. Since rubber is not particularly porous, leaching of zinc from the rubber would occur on the surface of the particles. The small-diameter particles would be expected to have a higher zinc loss rate per unit mass of rubber since there is a larger relative surface area for the leaching to occur.

Near the end of the 240-day experiment, the zinc mass transfer rates for both types of crumb rubber and both size categories appear to be reaching an equilibrium value. The zinc mass transfer rate of all but the small-diameter passenger tire crumb rubber changed little after day 61, and the small-diameter passenger tire crumb rubber mass transfer rate changed little after the day 128 observation.

Rhodes et al. (2012) found that the leachate pH is negatively correlated with zinc leaching rates from crumb rubber. Since the pH of the crumb rubber leachate changed little over the course of the experiment (Table 17), it is unlikely that this factor is responsible for the reduction in leaching rate as the leaching time increased. The pH of the passenger tire crumb rubber leachate was 0.1 lower than the pH of the truck crumb rubber leachate. The lower pH might have slightly increased the passenger tire crumb zinc leaching rate compared to the truck tire crumb rubber, but not enough to account for the nearly 50 percent higher rate observed during most of the study period.

Table 17: Crumb rubber leachate pH at the start and end of the experiment.

Sample	Initial Leachate pH	Leachate pH after 240 days
Truck Small	6.4	6.5
Truck Large	6.3	6.4
Passenger Small	6.0	6.2
Passenger Large	6.1	6.1

The lower rate of leaching at the end of the experiment is important in understanding the role that crumb rubber embedded in the surface layer of RHMA pavement has on the zinc load from roadways over the life of the pavement. The long term leaching rate may also be important in determining the contribution tire wear particles transported to a water course have on zinc loading to a watershed, but it is unlikely to be relevant for determining the zinc loading from tire wear particles to pavement stormwater runoff. In most situations, tire wear particles would not accumulate on the pavement surface for years at a time, but instead would be washed off by stormwater or blown off from wind and air currents from passing vehicles. The particles that did lie on the road surface or become embedded in pores of the pavement would be subject to leaching during periods of rain, but those leaching periods would be relatively short. It seems likely that most tire wear particles would have a leaching time less than 61 days over their life on the road surface and would therefore be leaching zinc at the comparatively higher rates observed at the beginning of the experiment.

One situation where rubber particles might be subject to long leaching times on roadways is if these particles become trapped in the pavement. To reduce noise and water ponding on the pavement surface, Caltrans is making frequent use of open-graded conventional and rubberized asphalt mixes. The open-graded mixtures used for the surface pavement course are permeable and have a relatively high void volume compared to more traditional dense-graded mixtures. The porous nature of the surface layer could provide storage volume for tire wear particles that could remain trapped for long periods of time and be subject to leaching zinc during each runoff event over the life of the pavement.

As previously noted for RHMA, the crumb rubber embedded in the surface layer of the asphalt binder can leach zinc since it is exposed to stormwater runoff over the life of the pavement. While determining the size distribution of tire wear particles in actual road conditions is difficult due to interactions with other non-tire road particles, a range of 0.004 to 0.250 mm was reported by Kreider et al. (2010). Caltrans does not specify a particle size distribution of the crumb rubber used in RHMA other than it must pass a 2.36 mm opening sieve (Caltrans 2018a); however, most of the mass in typical crumb rubber would be from particles with an effective diameter greater than 0.1 mm. Therefore, the tire wear particles trapped in the pores of the pavement would be expected to leach zinc at a higher rate than the crumb rubber in the RHMA binder due to the smaller-diameter size of the tire wear particles compared to the binder crumb rubber.

RHMA and Conventional Pavement Batch Leach Testing

Two cores each of HMA and RHMA pavement were submerged in distilled water continuously over eight months. The leachate from both HMA cores had measurable zinc concentrations in the sample taken after two days of leaching (Table 18). For all subsequent samples of HMA-A core leachate, the zinc concentrations were below the detection limit of 5 μg/l. The HMA-B core leachate had a detectable zinc concentration after four days of leaching, but the concentration in the remaining samples was below the detection limit. It is unknown why the initial concentration of zinc in the leachate of both sample cores was initially above the detection limit, and then dropped below. One possible explanation is that some component of the HMA adsorbed leached zinc. HMA specifications allow the addition of calcium carbonate, and Murphy et al. (2015) suggest that pavement samples containing calcium carbonate can adsorb and remove dissolved zinc from a solution. Alternatively, because the concentrations of zinc in the leachate are near the detectable limit, the uncertainty associated with these measurements is large, and the variability in zinc levels may be attributable to the generally low concentrations. In either case, the initial detected concentration values were low enough to conclude that the mass transfer rate of zinc that might be present in the HMA was essentially zero.

Table 18: Total zinc concentration in HMA core leachate.

Days of leaching	HMA-A Leachate Zinc Concentration (μg/l)	HMA-B Leachate Zinc Concentration (μg/l)

2	5.1	11
4	ND	10
26, 49, 116, 263	ND	ND

The concentration of zinc in the leachate from the RHMA cores was above the detection limit for the entire 246-day sampling period. The resulting calculated cumulative zinc mass transfer rate showed a declining trend similar to that observed for crumb rubber (Figure 9). While there were some differences in the cumulative mass transfer rate between the two cores in the first few samples, by day 61 the values for RHMA-A and RHMA-B were nearly identical.

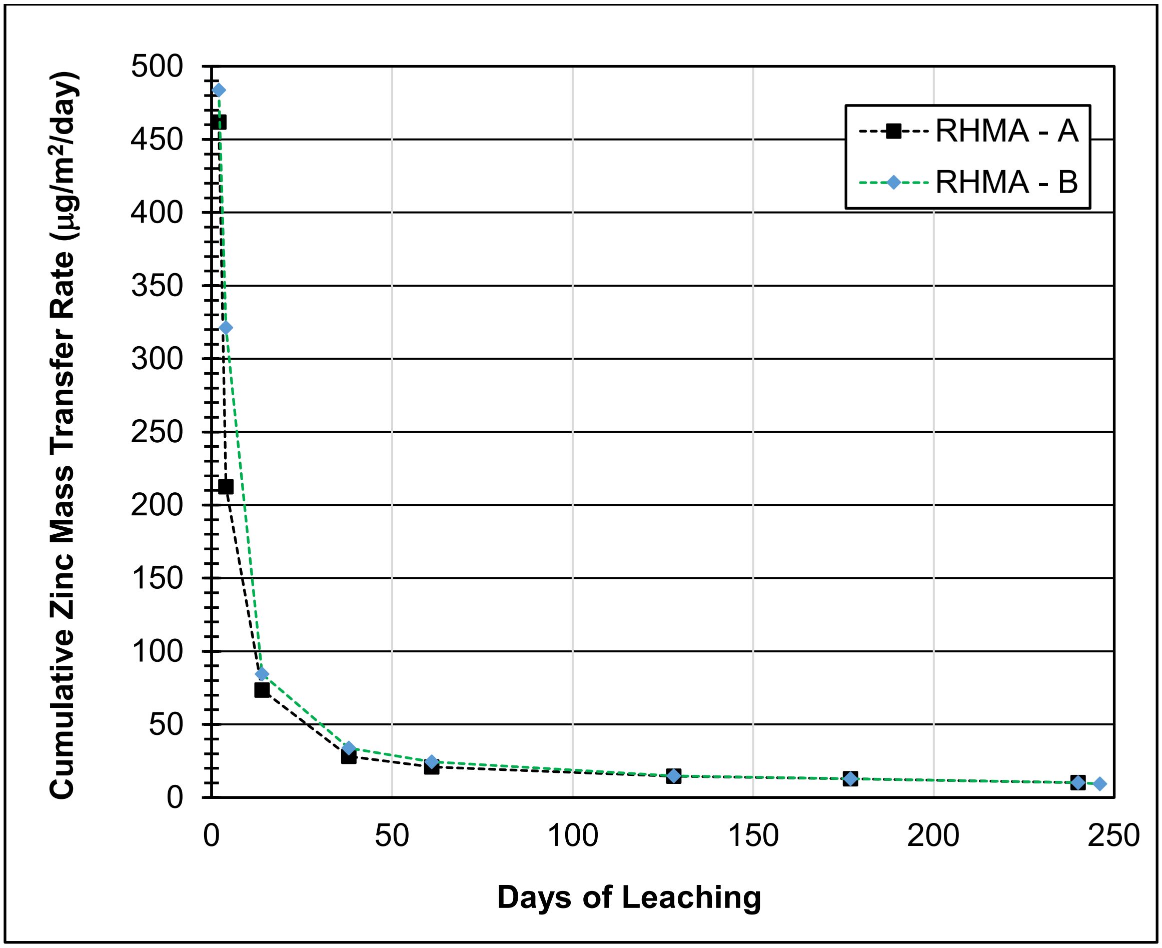

Figure 9: Cumulative zinc mass transfer rates for RHMA cores. (Reference Appendix B, Figure 9 Table)

Since the mass transfer rate is declining over time, and the leaching layer of the RHMA binder is not renewed, the cumulative zinc mass transfer rate is an overestimate of the actual instantaneous rate that would be observed in the field during all but the first few runoff events after the surface was paved. A better estimate of the rate that would be observed at any point in time in the life of the pavement surface can be estimated by dividing the mass of zinc per unit surface area of the RHMA core released during a sample period divided by the length of the sample period. The resulting calculated values indicates that the average zinc mass transfer rate would be less than 10 μg/m^2/day for RHMA surfaces that had already experienced at least four days of leaching conditions (Figure 10).

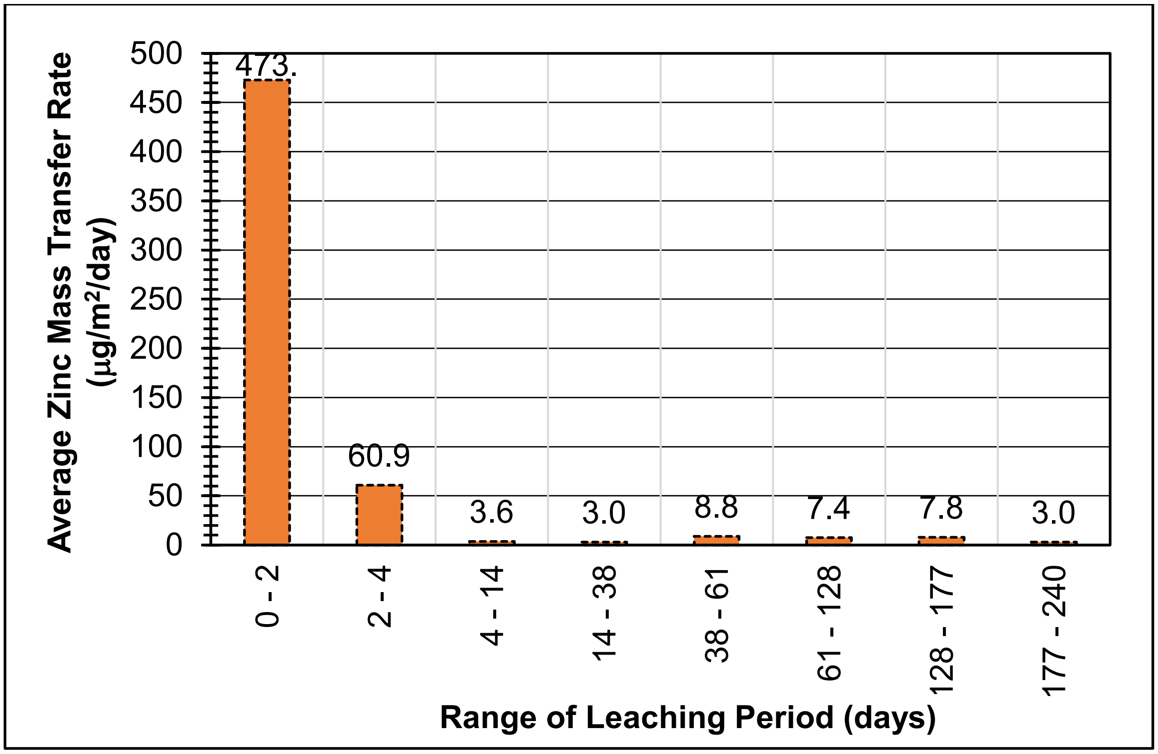

Figure 10: Average zinc mass transfer rate from RHMA cores at different times during the first leaching experiment. (Reference Appendix B, Figure 10 Table)

Photos of the HMA and RHMA cores show an interesting difference in the impact of being submerged in water. At the beginning of the experiment, the four cores all shared the same uniform black color. After 41 days of soaking, the HMA cores had developed a brown tinge while the RHMA cores looked unchanged after 61 days

(Figure 11). While not shown, the RHMA cores did not have any brown coloring even after 246 days of being submerged. The brown coloring may indicate oxidation of the binder in the HMA cores, one of the primary causes of pavement wear that leads to a stiff and brittle pavement. This result would illustrate the ability of RHMA pavement to withstand wear and resist degradation compared to the HMA.

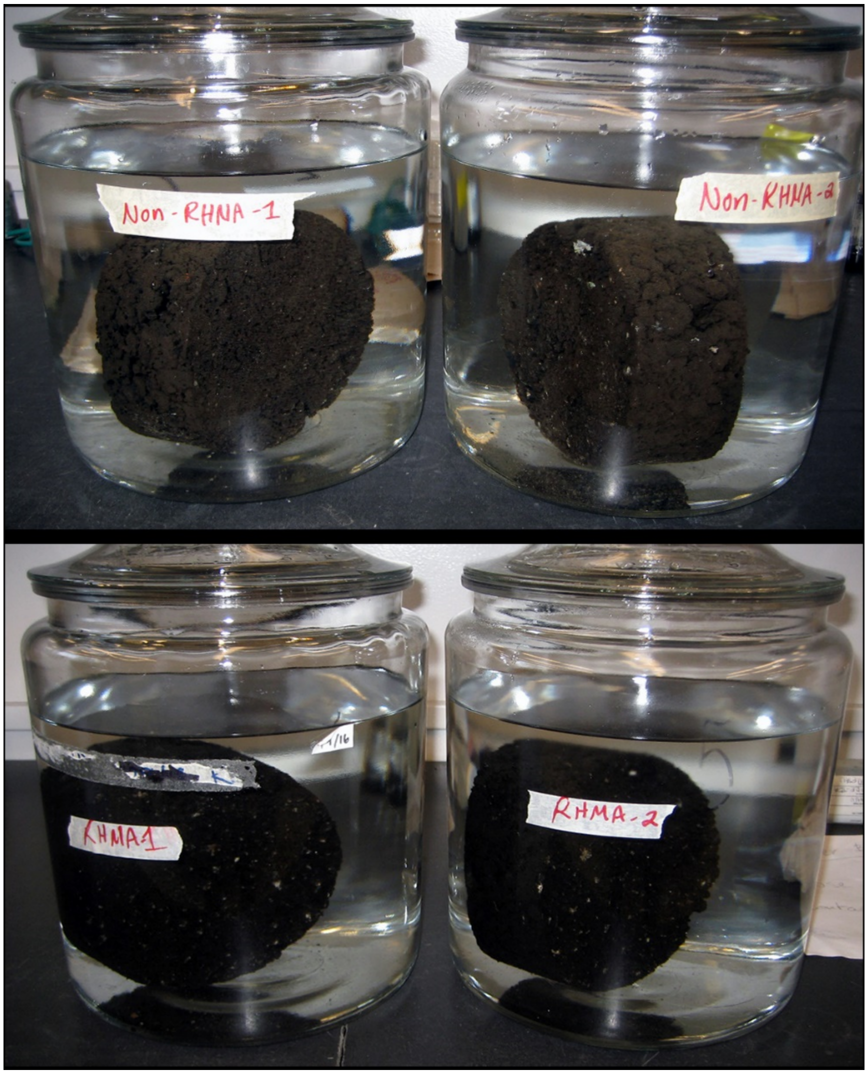

Figure 11: HMA cores (labeled nonRHMA in top photo) developed a brown tint after 41 days while the color of the RHMA cores (bottom photo) was unchanged after 61 days of soaking in distilled water.

To determine whether the leaching of zinc from the RHMA might increase with aging of the pavement, a second leaching experiment was conducted on four RHMA cores. After 63 days of soaking, Core 1 and Core 3 were removed from their jars and artificially aged as described in the Materials and Methodology section. After aging, the samples were placed back in their jars and left to soak for another 31 days. There was considerable variation between the four cores at the first few sample times, but the zinc mass transfer rates were very similar for the later portions of the experiment (Figure 12). While the cumulative zinc mass transfer rate for all four cores was higher in this experiment compared to the first RHMA leaching experiment, the overall trend of a rapid reduction in the rate with time was similar. The average mass transfer rates computed for each of the sample periods for this experiment was also higher than for the first RHMA leaching experiment, with the rate not decreasing to 10 $\mu g/m^2/day$ until after 32 days of leaching time (Figure 13).

The artificial aging of Core 1 and Core 3 does not have any noticeable impact on the zinc leaching rate. No dramatic change in the cumulative zinc mass transfer rate is observed on or after the day 64 sample for those cores (Figure 12), nor is there a notable change in the concentration of the leachate on the first and subsequent samples after the aging (Figure 14). Based on these results, aging and dry season interruptions in wetting of the RHMA from stormwater would not be expected to result in an increased zinc leaching rate during subsequent wet periods over the life of the road surface.

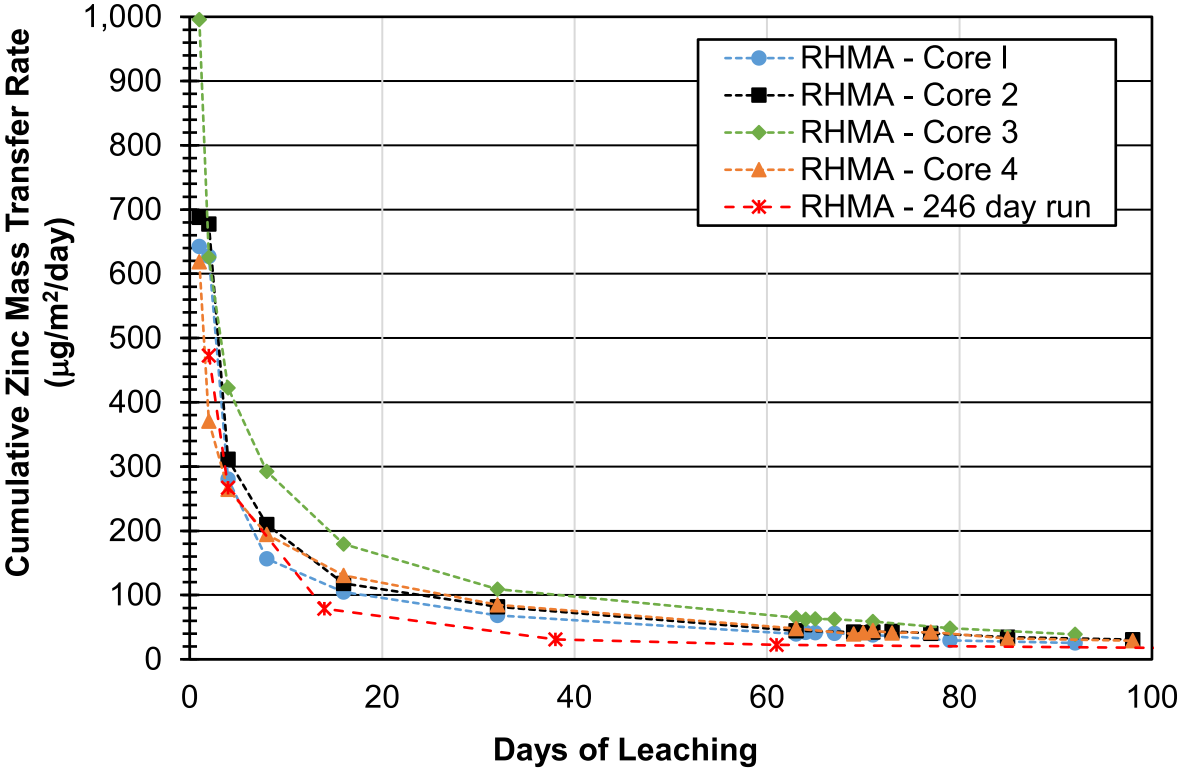

Figure 12: Cumulative zinc mass transfer rates for the four RHMA cores in the second leaching experiment. The results for the average transfer rate from the first experiment are included for comparison. (Reference Appendix B, Figure 12 Table)

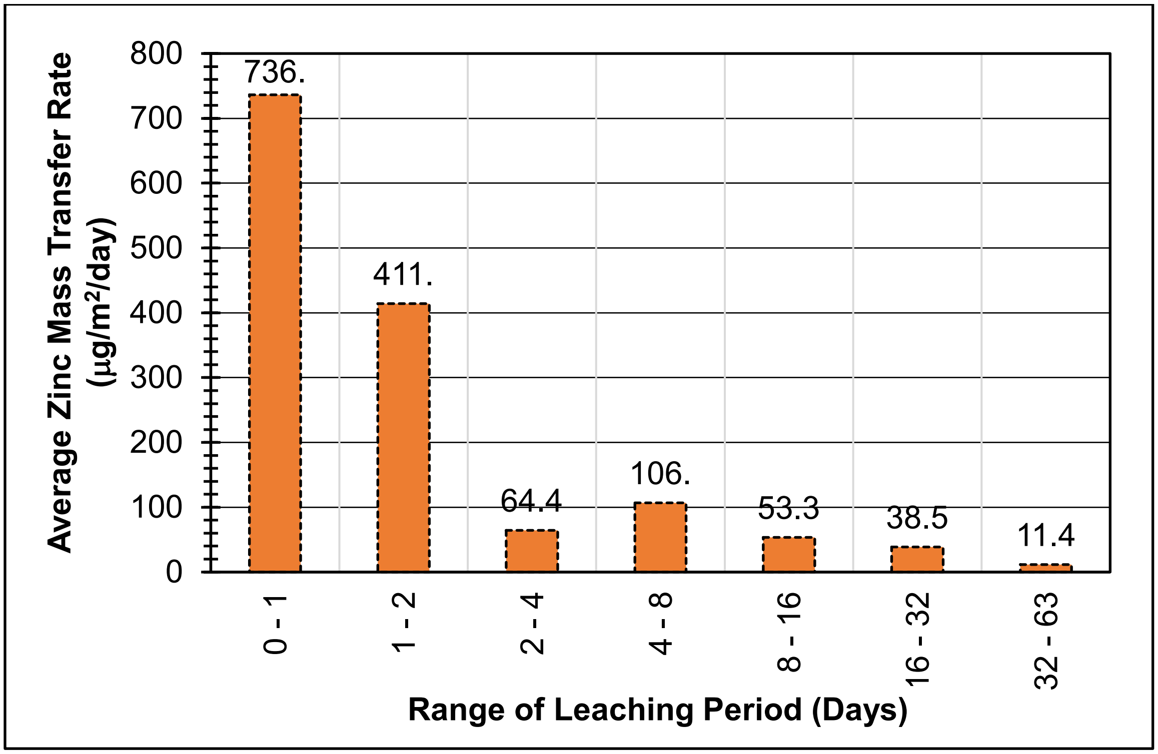

Figure 13: Average zinc mass transfer rate from RHMA cores at different times during the second leaching experiment. (Reference Appendix B, Figure 13 Table)

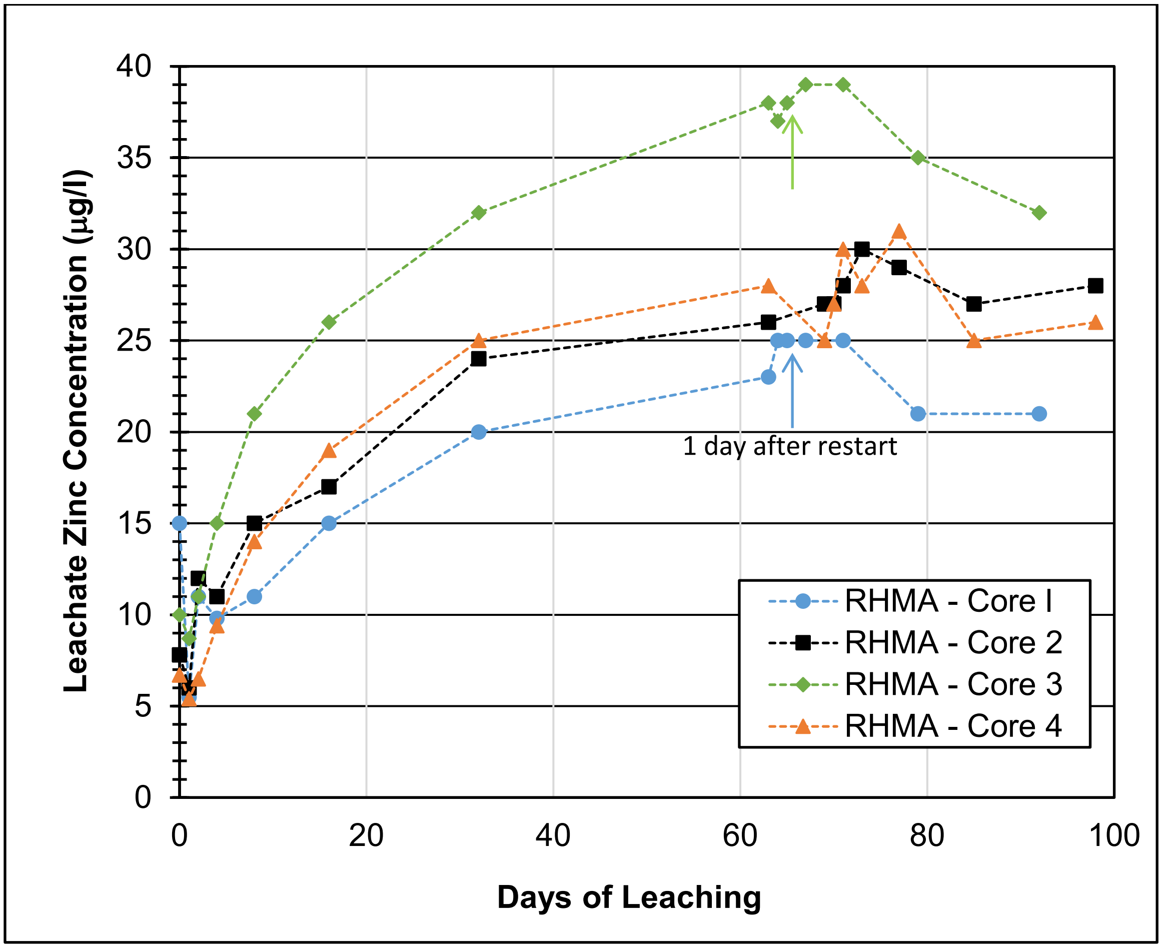

Figure 14: Leachate zinc concentration for all four RHMA cores illustrating little change in leaching behavior in Core 1 and Core 3 after artificial aging. Arrows indicate the sample taken one day after leaching resumed for Core 1 and 3. (Reference Appendix B, Figure 14 Table)

The batch leaching experiments do not simulate all factors associated with zinc transfer from the materials under field conditions. The zinc transfer rate might be impacted by factors such as material wear by UV degradation and fatigue from vehicle loading, which would likely increase the transfer rate as wear particles may expose new surface area to leaching. In contrast, the batch leaching test assesses continuously submerged materials, whereas these materials are not generally continuously submerged when in use unless wear particles are transported to water bodies. Not assessing material wear might underestimate the transfer rate, while the continuous submersion in the test likely overestimates the transfer rate for RHMA.

Knowing the mass fraction of zinc contained in materials that might leach onto roadways during rainfall events doesn’t imply that the zinc “available” (contained within the material) will become mobilized. Even in the smallest tire crumb particles, some fraction of the zinc present is embedded within the material and not subject to mass transfer to the water. The fraction of zinc contained within the crumb rubber and RHMA cores that was measured in the water column was computed from the measured zinc content of the crumb rubber and RHMA material (Table 4) and the leaching sample data (Figure 15).

The fraction of zinc in tire crumb that leached during the sample period of more than 240 days ranged from 1.5 percent to 7 percent, with the large-size crumb being on the low end of the rate. It is unlikely that any tire crumb particle would have a lifespan on the roadway exceeding 250 days, and those particles would only be submerged in water for a small fraction of that time; therefore, most of the zinc contained in tire crumb deposited on the roadway would not contribute to the zinc load in roadway stormwater runoff. While not tested in this study, the same behavior is likely true for tire wear particles, but their smaller size would result in a higher fraction of the zinc contained within the particle leaching out in a given period than observed for the tire crumb.

When computing the fraction of zinc contained within the RHMA cores that was measured in the water column, it was assumed that only the outer 0.1 inch of the core was available for leaching. After nearly 250 days of being submerged, less than 0.2 percent of the zinc in the outer 0.1 inch of the RHMA cores had entered the water column. This suggests that only a very small fraction of the zinc in RHMA pavement would contribute to zinc loading in stormwater runoff from roadways. Using a linear extrapolation from the sample results, even with continuous submergence, less than 3 percent of the zinc present in the top 0.1 inch layer of RHMA would be leached during the typical 10-year life of a pavement section. The estimated fraction of zinc leached is linearly dependent on the assumed depth of material available for leaching. For example, if the leachable depth was 0.05 inch, then the result would be that less than 6 percent of the zinc present in the top 0.05 inch layer of RHMA would be leached during the typical 10-year life of a pavement section.

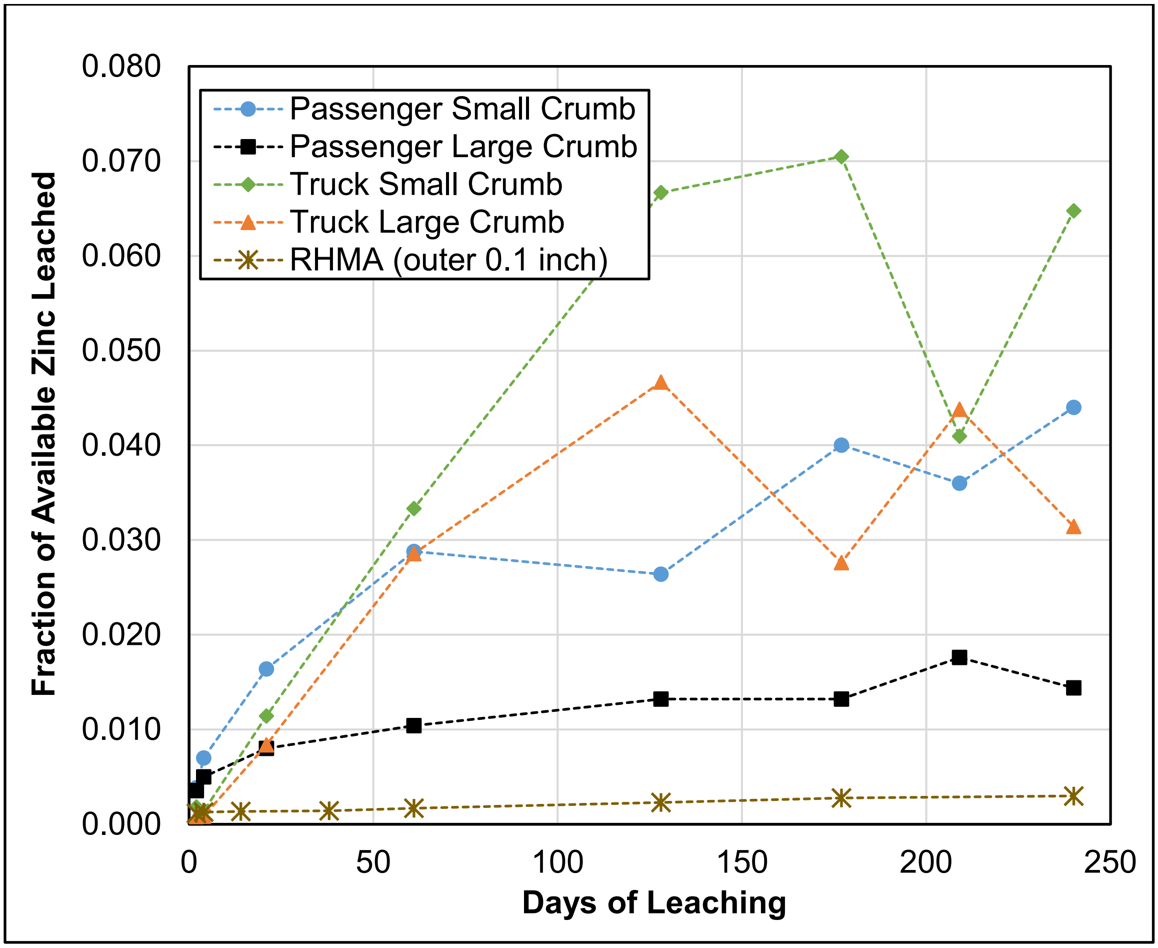

Figure 15: Fraction of zinc contained within crumb rubber and a RHMA core that entered the water column during the leaching experiments. (Reference Appendix B, Figure 15 Table)

Paired HMA-RHMA Pavement Stormwater Runoff Sampling

Results from field sampling of roadway stormwater runoff are presented grouped by data collected by HSU, GHD, and Caltrans. Zinc was the focus of the HSU and GHD sampling, but Caltrans monitored copper in addition to zinc, which is examined to help interpret differences observed in the runoff between the two pavement surfaces. Tables summarizing all data from paired pavement sampling can be found in the Appendix.

Humboldt State University sampling

A total of 65 stormwater runoff samples were collected by Humboldt State University in the Eureka area between December 2018 and March 2020. The sampling represents data from eight locations across 16 storm events. Each sampling event occurred within a few hours of the start of the precipitation, and in many cases, within an hour of sufficient rainfall to result in runoff from the road surface. Each of the highway runoff samples were analyzed for both dissolved and total zinc concentration.

Table 19: Zinc concentration in stormwater runoff from Humboldt State University Hwy 101 and Hwy 299 paired RHMA and pavement sampling.

Sample Location	Sample Count	Mean Total Zinc (µg/l)	Mean Dis. Zinc (µg/l)	Max Total Zinc (µg/l)	Max Dis. Zinc (µg/l)	Min Total Zinc (µg/l)	Min Dis. Zinc (µg/l)
299 RHMA	9	137	132	880	850	25	25
299 HMA	9	56	41	83	66	25	17
101N RHMA	12	225	81	520	240	76	33
101N HMA	12	196	73	450	280	54	28
101S RHMA	7	127	67	240	110	45	27
101S HMA	9	105	74	280	140	32	32
101FS RHMA-N	2	101	78	150	91	52	64
101FS RHMA-S	5	109	104	190	210	50	57
All RHMA[1]	**35**	**159**	**94**	**880**	**850**	**25**	**25**
All HMA[2]	**30**	**127**	**64**	**450**	**280**	**25**	**17**

[1] All samples from RHMA sites treated as a single set. [2] All samples from HMA sites treated as a single set.

The mean concentration of total zinc from RHMA pavement was higher than from the HMA pavement at all but the 101FS paired sites, and for the overall mean from all the sites combined (159 µg/l compared to 127 µg/l (Table 19)). However, examination of the individual paired observations at each site indicates that the situation is more complex than the mean value would suggest. For example, samples were collected during nine rainfall/runoff events at the Blue Lake, Highway 299 site. The total zinc concentration was higher from the HMA pavement for four of the events, approximately the same as from the RHMA pavement for two events, and higher from the RHMA pavement for two events (Figure 16). The mean total zinc concentration at this site was much higher from the RHMA pavement than the HMA pavement (137 µg/l compared to 56 µg/l) due to a single storm event where a total zinc of 880 µg/l from the RHMA pavement was recorded. This extremely high concentration, along with the matching dissolved zinc concentration of 850 µg/l, is almost double that of any other observation from the HSU sites and appears to be a one-off outlier. With the exception of this one event, the concentration from the HMA pavement was higher than from the RHMA pavement when there was a large difference between the zinc concentrations of paired observations.

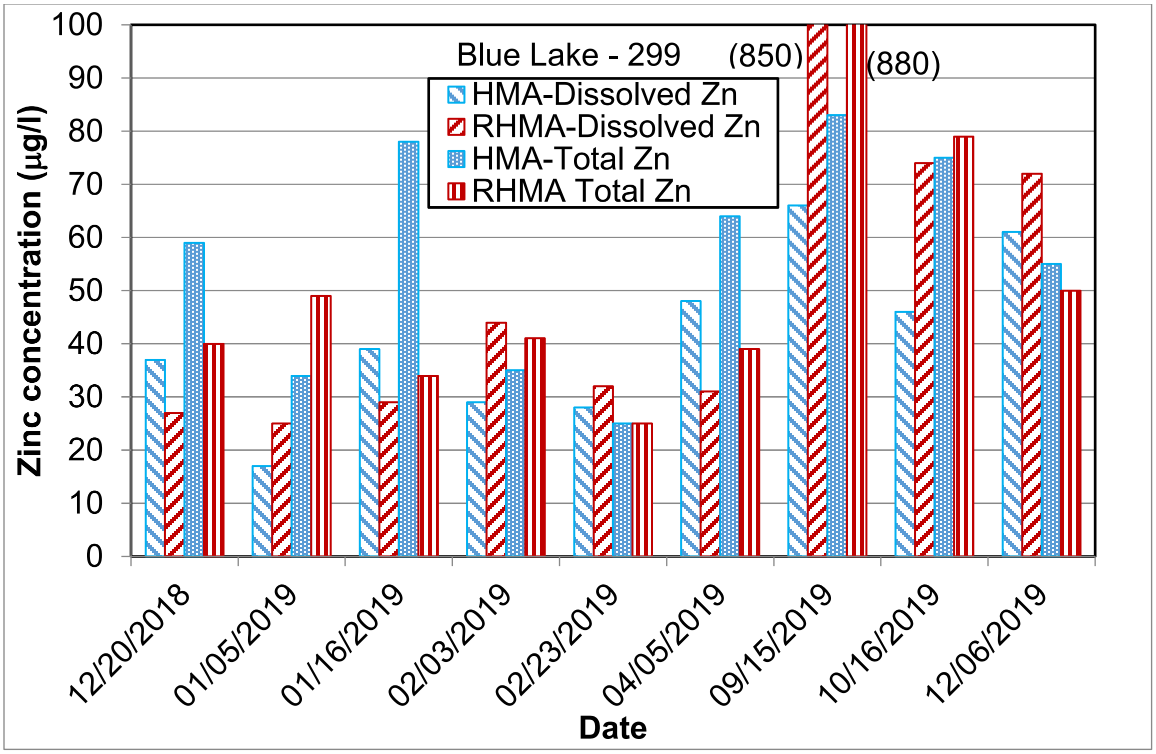

Figure 16: Dissolved and total zinc concentration in stormwater runoff from paired HMA-RHMA pavement at the Blue Lake - 299 location. (Reference Appendix B, Figure 16 Table)

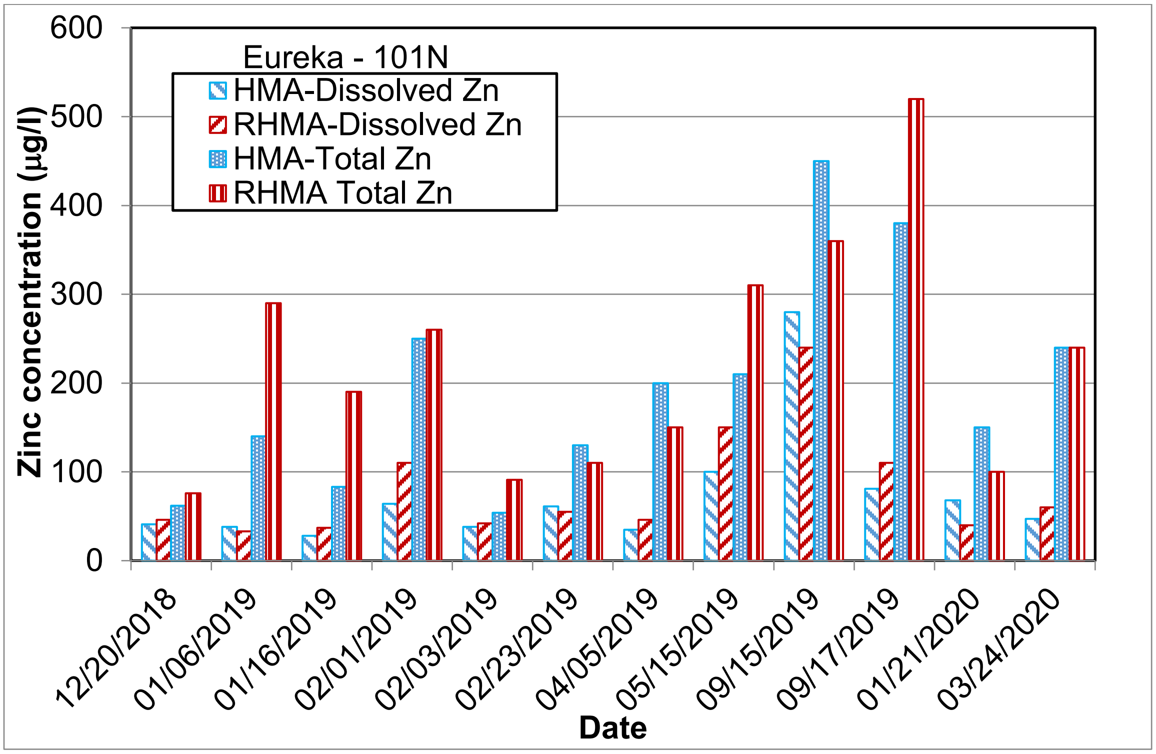

Figure 17: Dissolved and total zinc concentration in stormwater runoff from paired HMA-RHMA pavement at the Eureka - 101N location. (Reference Appendix B, Figure 17 Table)

The difference between the mean total zinc concentrations of the 12 events sampled at the Eureka 101N HMA-RHMA paired sites was smaller than at the Blue Lake 299 site. The mean concentration for total zinc of the RHMA samples was 225 µg/l compared to 196 µg/l for the HMA samples (Table 19). However, the results do not necessarily indicate that runoff from RHMA pavement is generally higher than from HMA pavement. For six of the 12 events sampled, the total zinc concentration was higher in the RHMA sample, for four events it was higher in the HMA sample, and for two events the concentration was approximately the same in the paired HMA-RHMA samples (Figure 17). Perhaps the only trend is that when there is a large difference in the total zinc concentration of runoff between the two pavement types, the RHMA site generally had the higher value. The higher mean for the RHMA samples was due to the three events with differences in total zinc between the RHMA and HMA sample exceeding 100 µg/l.

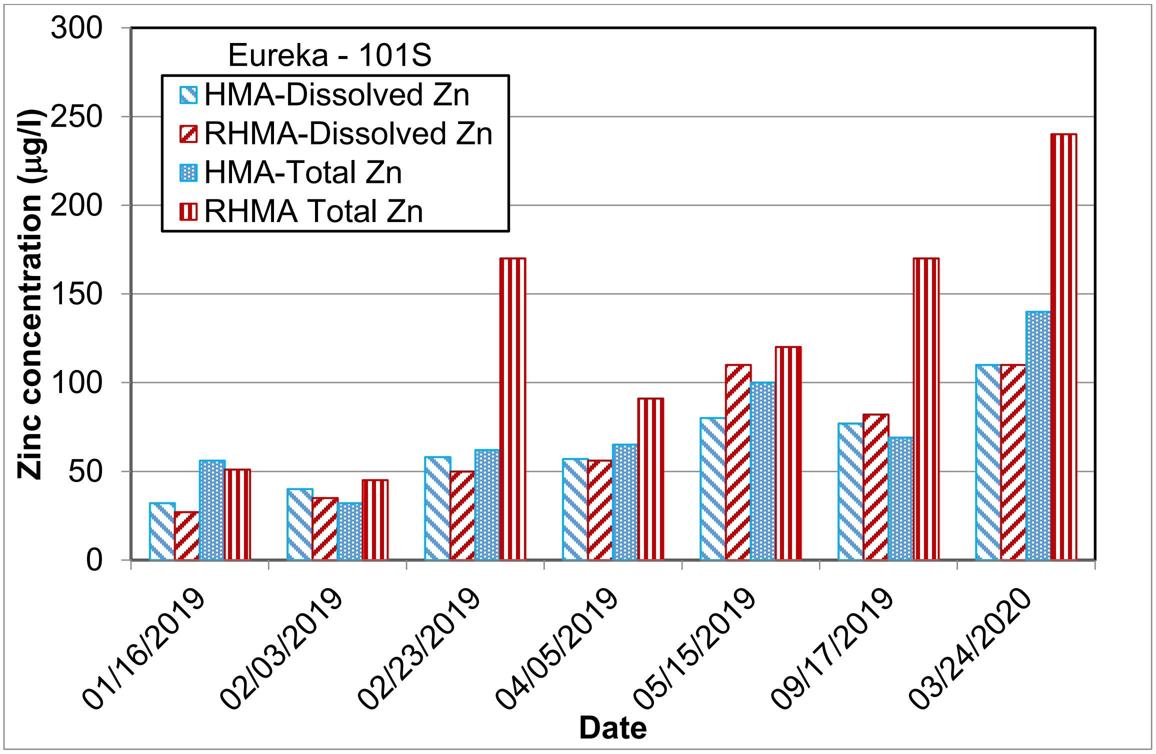

Figure 18: Dissolved and total zinc concentration in stormwater runoff from paired HMA-RHMA pavement at the Eureka – 101S location. (Reference Appendix B, Figure 18 Table)

At the Eureka 101S site, the total zinc concentration in the runoff from the RHMA pavement was nearly always higher than from the paired HMA pavement (Figure 18). The total zinc concentration from the RHMA pavement was higher than the corresponding sample from the HMA for six of the seven total events sampled. The mean concentration of total zinc of the RHMA samples was 127 µg/l compared to 105 µg/l for the HMA samples (Table 19). For three of the seven events, the total zinc concentration from the RHMA site was over 100 µg/l higher than from HMA pavement. However, the same pattern does not hold true for dissolved zinc concentrations where the mean concentration for the HMA samples is higher than the mean concentration for the RHMA samples (74 µg/l compared to 67 µg/l).

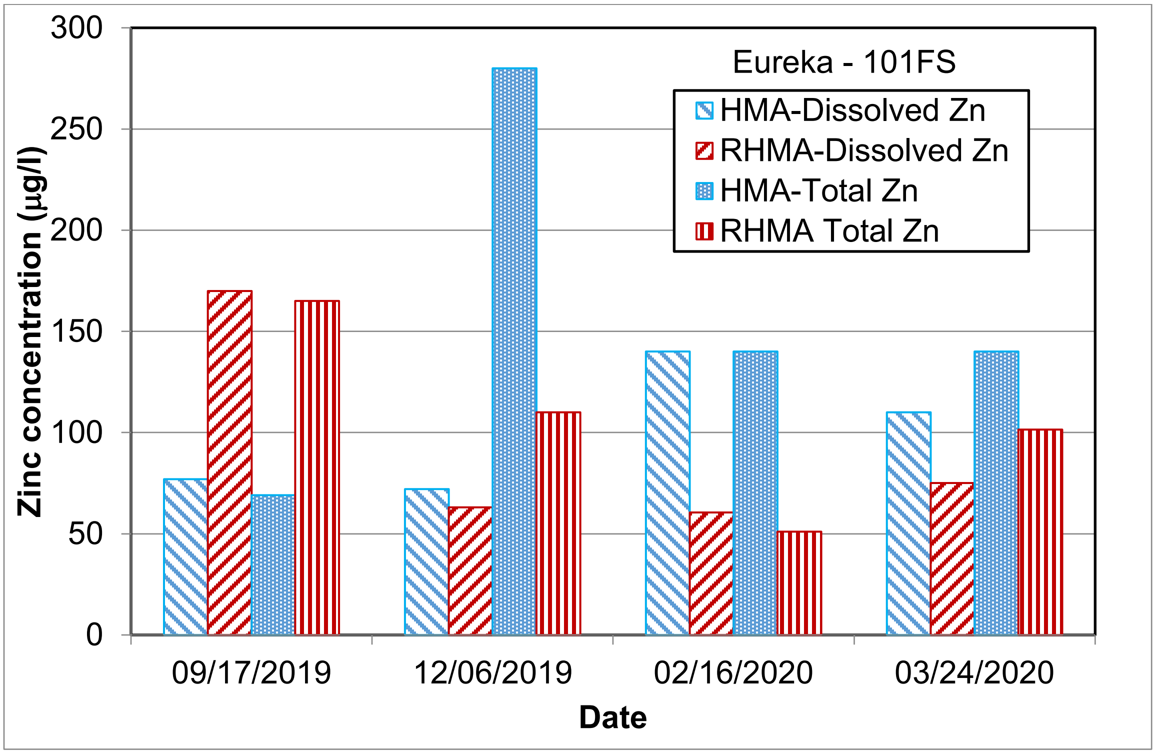

Figure 19: Dissolved and total zinc concentration in stormwater runoff from paired HMA-RHMA pavement at the Eureka – 101FS location. (Reference Appendix B, Figure 19 Table)

The Eureka 101FS site was established to sample from a section of RHMA that had been paved during the summer of 2019. Only four runoff samples were collected from the newly paved RHMA site that could be paired with runoff events from a nearby HMA site. There was some expectation that the zinc concentration from the RHMA samples would be higher than from the HMA site because the laboratory leaching study showed that fresh RHMA does leach zinc. However, this turned out to the true for only the first sampled event, while for the last three events the total zinc concentration was much higher in the runoff from the HMA pavement than from the RHMA pavement (Figure 19). The mean concentration for total zinc of the four RHMA samples was 107 µg/l compared to 157 µg/l for the HMA samples.

GHD sampling analysis

GHD collected 16 samples over four storms and four locations. The data show high total zinc concentrations from RHMA compared to the HMA pavement in Yuba City. The average total zinc concentration of the runoff from the single observation obtained at each of the four locations was 131 µg/l for the HMA pavement and 660 µg/l for the RHMA pavement sites (Table 20). Samples from two RHMA and two HMA sites in Yuba City were non-detect for both dissolved and total zinc concentrations and are not included in these statistics. In contrast to the results from Yuba City, the data from the Richmond sites showed considerably higher concentrations of zinc in the runoff from conventional HMA compared to RHMA pavement (Table 21).

Table 20: Yuba City residential pavement runoff monitoring results from 3 paired samples.

Pavement Type	Mean Total Zinc (µg/l)	Mean Dissolved Zinc (µg/l)	Max Total Zinc (µg/l)	Max Dissolved Zinc (µg/l)	Min Total Zinc (µg/l)	Min Dissolved Zinc (µg/l)
HMA	131	37	170	56	ND	ND
RHMA	660	45	670	55	ND	ND

Table 21: Richmond Ohio Avenue and Cleveland Avenue pavement runoff monitoring results from 5 paired samples.

Pavement Type	Mean Total Zinc (µg/l)	Mean Dissolved Zinc (µg/l)	Max Total Zinc (µg/l)	Max Dissolved Zinc (µg/l)	Min Total Zinc (µg/l)	Min Dissolved Zinc (µg/l)
HMA	196	46	340	68	110	ND
RHMA	84	34	96	47	ND	ND

Summary of HSU and GHD sampling of runoff from paired HMA-RHMA roads

Based on the long-term RHMA leaching experiment, it is certain that some zinc will leach out of RHMA pavement during stormwater runoff events. The field sampling was designed to determine the magnitude of the leaching of zinc from the pavement relative to other sources of zinc that contribute to the final observed concentration in the runoff from the roadway.

At the Blue Lake 299 location, in all but one case, when large differences were observed in the total zinc concentration in stormwater runoff from the HMA site compared to the RHMA site, the HMA site had the higher values. For the Eureka 101N location, the opposite was true, with the events where large differences in the total zinc concentration occurred; the higher values were from the RHMA site compared to the HMA site.

At the other two HSU locations, the situation is different yet. At the Eureka 101S location, the total zinc concentration in the runoff from the RHMA pavement was nearly always higher than from the paired HMA pavement. However, the dissolved zinc concentrations did not follow the same pattern as the total zinc concentrations. At the Eureka 101FS location, the exact opposite was true, with the zinc concentration in the runoff from the HMA pavement nearly always higher than from the paired RHMA pavement. It also appears that with the exception of one storm, the majority of the zinc at this site is in the dissolved form.

The results from the GHD sampling were similar to these of the HSU Eureka 101S and 101FS locations. The zinc concentration in the runoff from RHMA pavement sites was higher than HMA pavement at the Yuba City locations, but higher from the HMA pavement than the RHMA pavement at the Richmond locations.

The results from the HSU and GHD sampling show that pavement type alone cannot be used to predict zinc load from the roadway, and that factors other than pavement type may overwhelm the zinc load from the RHMA. In an effort to gain additional insight into the relative contribution of RHMA to the zinc load from roadways, additional examination of the HMA-RHMA paired sample performed by Caltrans was conducted.

Caltrans sampling analysis

The Caltrans highway runoff data used for this project contained 98 runoff samples, capturing 46 storm events across three locations, each with a HMA and RHMA pavement site. Caltrans determined the concentration of numerous metals in the runoff, including zinc and copper. Samples were obtained from the runoff of seven rainfall events at the Merced Highway 140 location. The RHMA section of this lightly traveled road is gap-graded and was subsequently coated with a Type III (coarse) slurry seal. The zinc concentrations in the runoff were low, generally less than 25 µg/l for both dissolved and total zinc. The average total zinc concentration for the HMA and RHMA pavement samples was of 38 µg/l and 30 µg/l respectively, the lowest average concentrations for any site examined in this project (Table 22). The concentration of zinc in the runoff from the HMA site was five times higher than from the RHMA (64 µg/l compared to 13 µg/l) for the first runoff event. For the remaining six events, the concentration of zinc in the runoff from the HMA and RHMA pavement was approximately the same with no clear evidence that it was generally higher from one type of pavement compared to the other (Figure 20). Because a slurry seal layer had been applied to the RHMA, runoff characteristics may be atypical of most RHMA surfaces, and drawing conclusions on zinc loading from stormwater off RHMA roadways based on the data from the Merced site might be inappropriate.

Table 22: Merced Hwy 140 pavement runoff monitoring results from 7 paired samples.

Pavement Type	Mean Total Zinc (µg/l)	Mean Dissolved Zinc (µg/l)	Max Total Zinc (µg/l)	Max Dissolved Zinc (µg/l)	Min Total Zinc (µg/l)	Min Dissolved Zinc (µg/l)
HMA	38	21	92	68	21	10
RHMA	30	23	100	86	12	9

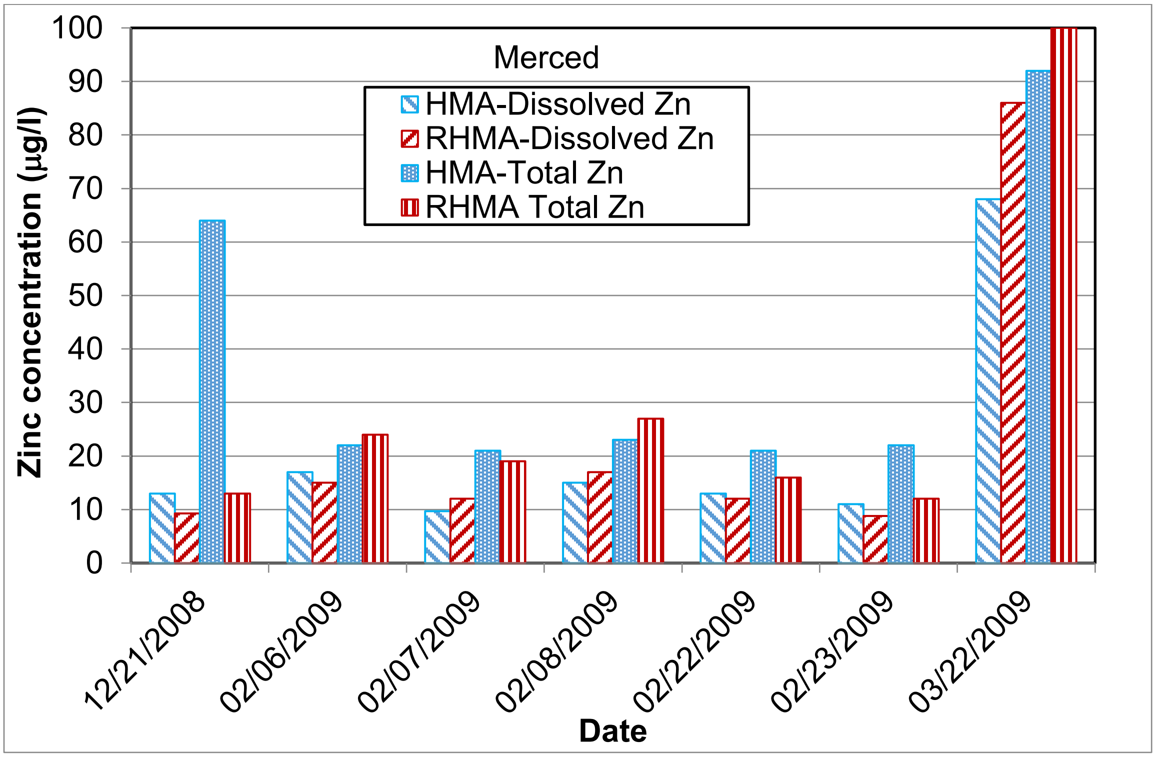

Figure 20: Paired dissolved and total zinc concentrations in runoff from HMA and RHMA pavement in Merced. (Reference Appendix B, Figure 20 Table)

At the Visalia site, the zinc concentrations were much higher than at the Merced site, with total zinc concentrations usually exceeding 100 µg/L (Table 23, Figure 21). While the concentration of zinc from the HMA and gap-graded RHMA were often similar, when there was a difference greater than 50 µg/L between the two pavement types, (2 out of 13 events), the higher concentration was from the RHMA site (Figure 21).

Table 23: Visalia Hwy 41 pavement runoff monitoring results from 13 paired samples.

Pavement Type	Mean Total Zinc (µg/l)	Mean Dissolved Zinc (µg/l)	Max Total Zinc (µg/l)	Max Dissolved Zinc (µg/l)	Min Total Zinc (µg/l)	Min Dissolved Zinc (µg/l)
HMA	151	81	370	300	85	30
RHMA-G	178	122	520	440	79	38

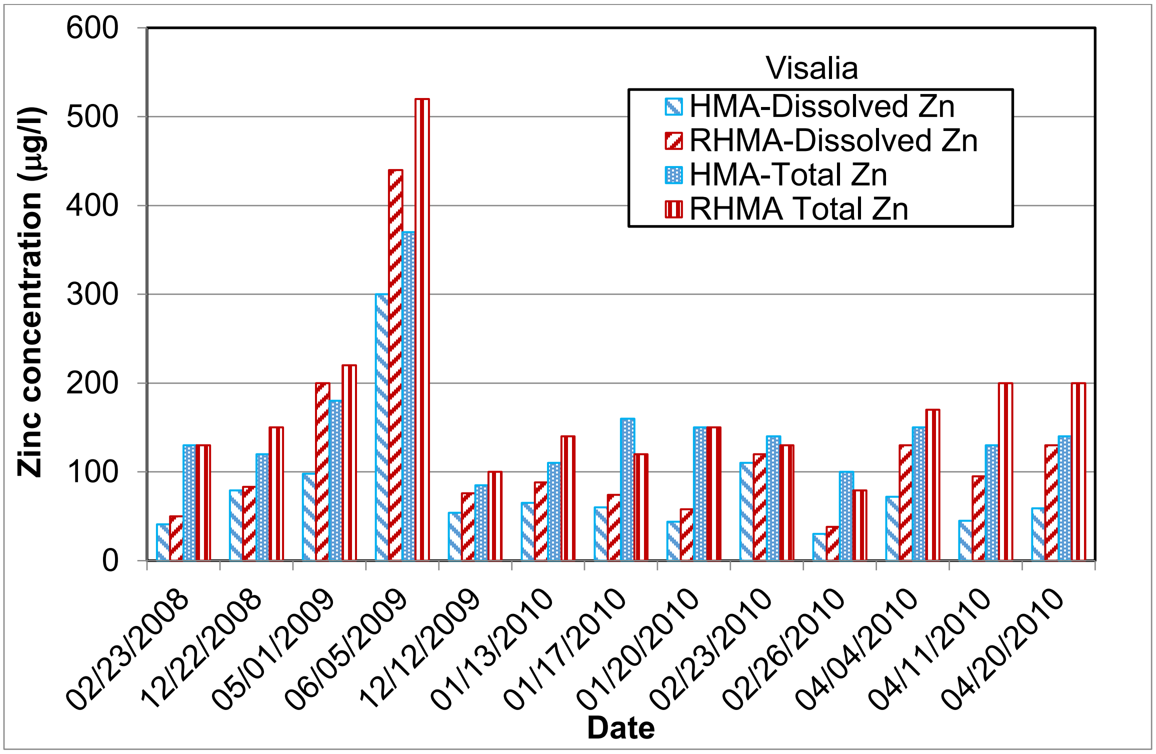

Figure 21: Paired dissolved and total zinc concentrations in runoff from HMA and RHMA pavement in Visalia. (Reference Appendix B, Figure 21 Table)

To investigate whether the higher concentrations of zinc in the runoff from the RHMA pavement compared to the HMA pavement might be due to factors other than the differences in the pavement binder material, the concentration of another metal in the runoff was examined. At Visalia, the correlation between the zinc and copper concentrations in the runoff is remarkable (Figure 22). Note that in Figure 22, the copper concentration has been scaled five times to make the visual comparison with the zinc concentration easier. Copper in road runoff is likely associated with brake pad and brake liner wear, and it is not contained in crumb rubber. Since the events where the concentration of zinc from the RHMA is higher than that from HMA coincide with a higher concentration of copper from the RHMA compared to HMA, it suggests that some factor other than rubber in the RHMA is responsible. Since the RHMA and HMA sample sites are very close together, it is unlikely the concentration differences are due to differences in traffic count, precipitation intensity, or atmospheric deposition. In addition, there are no visible sources of galvanized metal leachate that could enter the roadway in the vicinity of either the HMA or RHMA sample sites. The results suggest that differences in how the two pavement surfaces accumulate, store, and release these metals during rainfall events is likely responsible for the concentration of zinc and copper observed in the runoff at the sites.

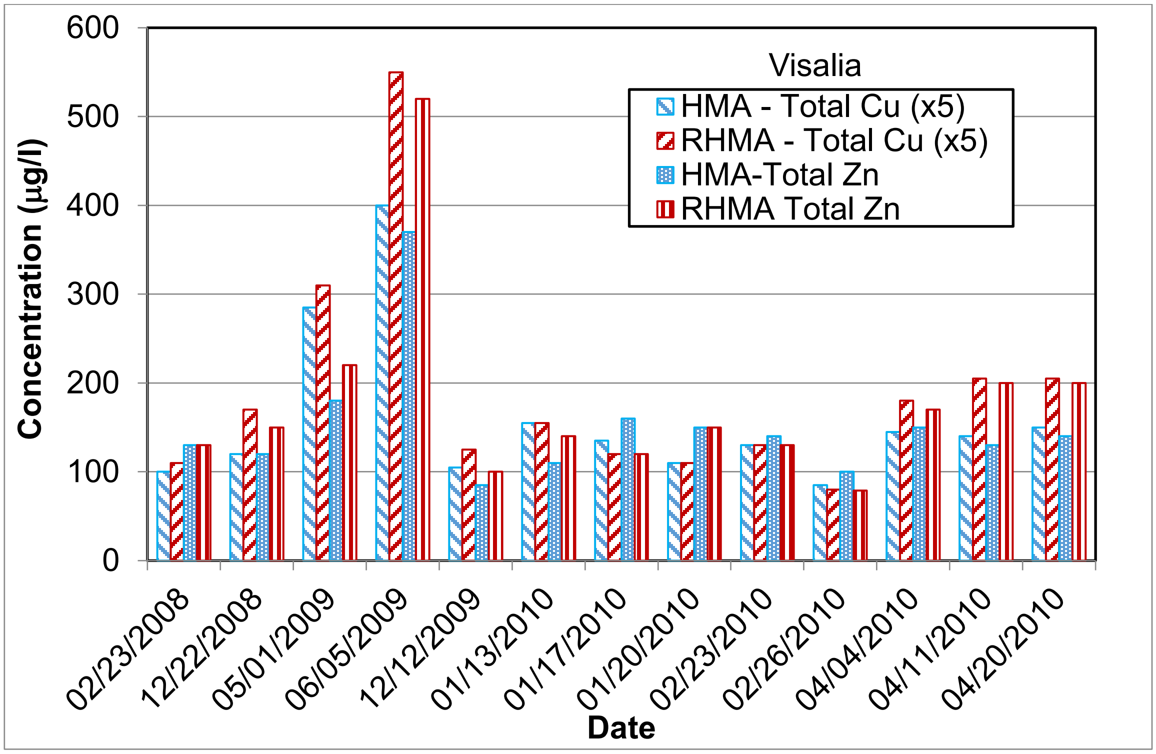

Figure 22: A comparison of total zinc and copper (scaled five times) concentration at the Visalia paired sampling location shows a high correlation (r^2=0.95). (Reference Appendix B, Figure 22 Table)

The differences in zinc concentrations in the runoff between RHMA and HMA pavement were greater at the Atascadero location than at Merced or Visalia. The zinc concentration measured in the open-graded RHMA roadway runoff at the Atascadero location was of comparable magnitude to that at Visalia; however, it was generally much higher (often two to three times higher) than from the HMA pavement (Table 24, Figure 23).

At Atascadero, while the copper concentration is higher in the RHMA runoff compared to the HMA runoff, the correlation between zinc and copper is not as clear as at the Visalia location (Figure 24). The results still suggest that some mechanism or source besides the rubber in the RHMA is at least partially responsible for the elevated zinc concentrations in the runoff compared to the paired HMA location. That source or mechanism is not necessarily responsible for the elevated copper concentration in the RHMA runoff.

Table 24: Atascadero Hwy 41 pavement runoff monitoring results from 28 paired samples.

Pavement Type	Mean Total Zinc (µg/l)	Mean Dissolved Zinc (µg/l)	Max Total Zinc (µg/l)	Max Dissolved Zinc (µg/l)	Min Total Zinc (µg/l)	Min Dissolved Zinc (µg/l)
HMA	40	19	95	56	12	4
RHMA	104	64	430	270	20	3

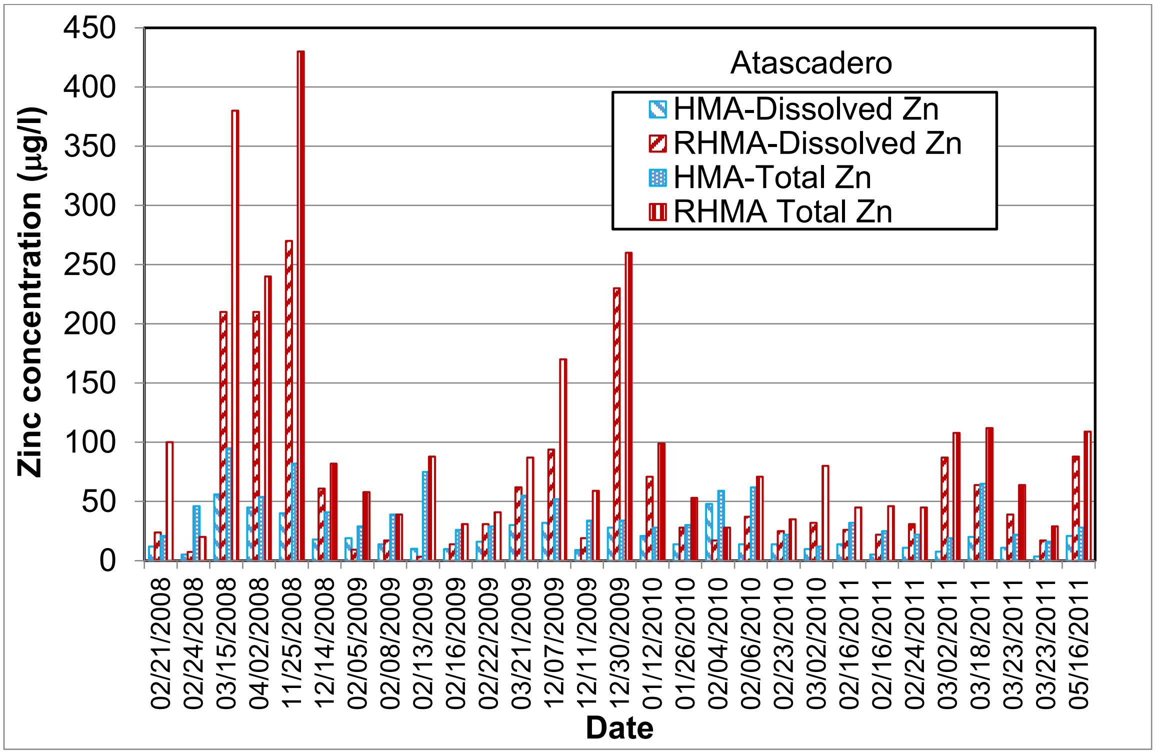

Figure 23: Paired dissolved and total zinc concentrations in runoff from HMA and RHMA pavement in Atascadero. (Reference Appendix B, Figure 23 Table)

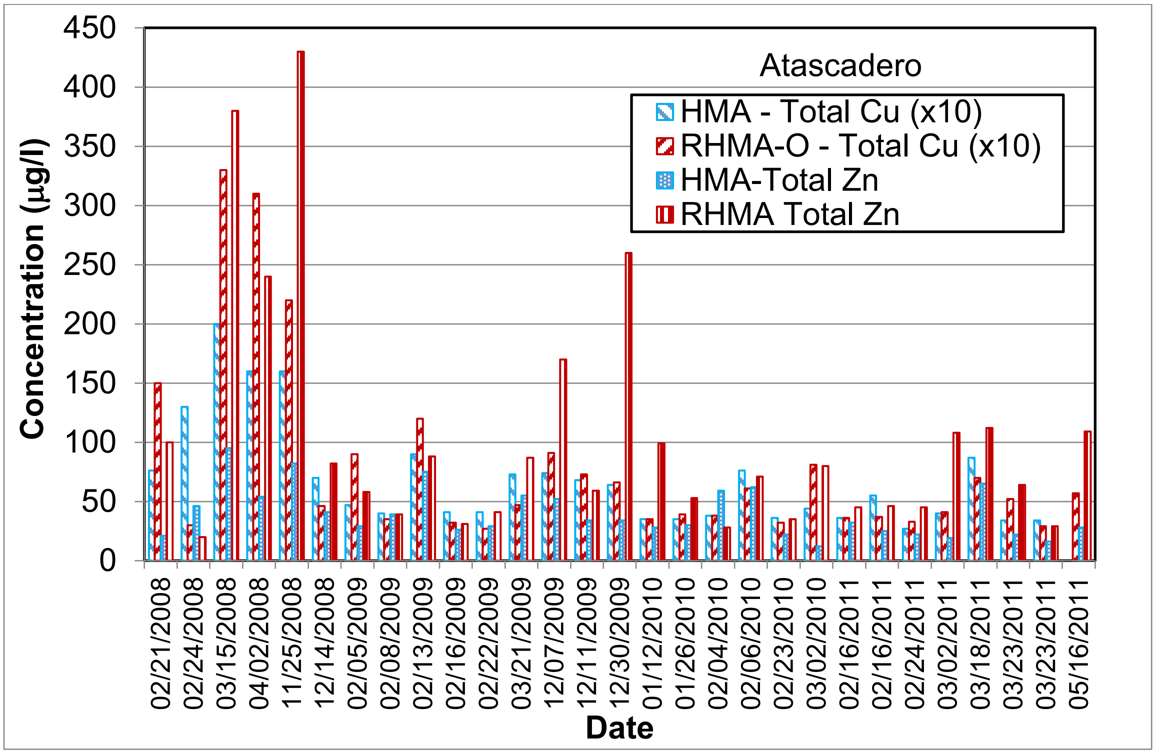

Figure 24: A comparison of total zinc and copper (scaled 10 times) concentration at the Atascadero paired sampling location shows a moderate linear correlation (r^2=0.65). (Reference Appendix B, Figure 24 Table)

Including the Caltrans paired sampling data with the HSU and GHD data does not result in a more definitive answer to the question of whether the use of RHMA pavement will result in higher concentrations of zinc in roadway stormwater runoff than would be expected from non-rubberized HMA. As long as zinc is a component of tire rubber, there will always be some zinc leached from rubberized pavement. However, the Caltrans data reinforces the conclusion reached with the HSU and GHD paired sampling data that there are other factors besides the addition of rubber to the asphalt binder that determine the resulting concentration of zinc in the runoff. In addition, all of the paired sampling data suggest that the fraction of the zinc load from the roadway that is directly attributable to the rubber in the asphalt binder may be very small compared to other potential sources. This issue will be addressed in the next section, where a mass balance analysis is conducted on a prototype roadway with several potential sources of zinc.

Relative Contributions to Zinc Loading from Various Sources

The data collected in the experiments described in the previous section can be used to assess the relative contributions of zinc from a variety of sources. Based on the results of these experiments, the contributions are estimated from three sources: leaching from RHMA pavement, wet deposition from rainfall, and leaching from tire wear particles. Literature data is used to estimate the zinc loading from galvanized guardrails and that loading estimate is compared to the three sources examined in this study.

Contribution to zinc loading from RHMA pavement

The concentration of zinc in roadway runoff can be computed given the runoff rate from a roadway and the zinc loading rate from the roadway surface. For example, if the runoff rate is 1 inch per day and the road surface is delivering zinc at a rate of 10 $\mu g/m^2$ per day, then the resulting concentration of zinc in the runoff would be 0.4 $\mu g/l$ (Figure 25). At a fixed runoff rate, the relationship between zinc loading rate and runoff zinc concentration is linear, so for runoff at 1 inch per day, a zinc loading rate of 60 $\mu g/m^2$ per day and 1000 $\mu g/m^2$ per day results in a zinc runoff concentration of 2.4 and 40 $\mu g/l$ respectively. The relationship is also linear with respect to runoff rate, so for a runoff rate of 2.0 inch per day and a zinc loading rate of 10 $\mu g/m^2$ per day, the zinc runoff concentration would be 0.2 $\mu g/l$.

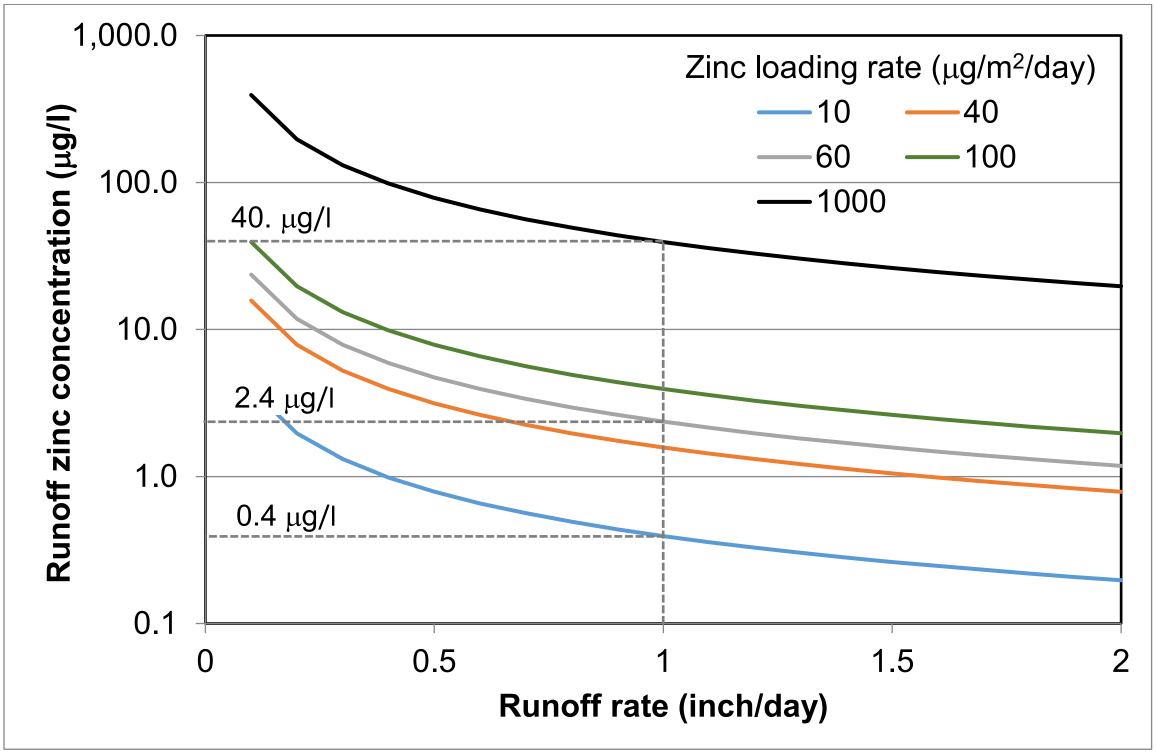

Figure 25: Zinc concentration in runoff from roadways at various zinc loading rates and runoff rates. (Reference Appendix B, Figure 25 Table)

One source of zinc that could contribute to the load in roadway runoff is leaching from the rubberized binder in RHMA. From the RHMA core leaching experiments conducted in this project, the zinc leaching rates varied between 740 and less than 10 µg/m^2 per day (Figure 13). Leaching rates from the RHMA pavement cores greater than 100 µg/m^2 per day only occurred during the first eight days of continuous soaking and were less than 10 µg/m^2/day after 63 days of soaking.

Unless a roadway is in an extremely arid region, the zinc mass transfer rate from RHMA pavement during a runoff event would likely be less than 100 µg/m^2 per day after the first year or two, and at or below 10 µg/m^2 per day for most of the lifetime of the surface. Figure 25 shows that this situation implies that for a runoff rate of 1 inch per day, leaching from the RHMA surface might be responsible for 20 to 30 µg/l of zinc for the first few runoff events, transitioning to less than 4 µg/l for the following runoff events, and less than 1 µg/l for most of the life of the pavement. As the precipitation rate increases, the resulting concentration of zinc in the runoff due to leaching from the RHMA surface decreases. Since the total zinc concentration in the roadway runoff samples collected during this study ranged from 12 to 880 µg/l with a mean value exceeding 100 μg/l, zinc from RHMA leachate would represent a small fraction of the load and other sources must dominate.

The cumulative mass loading over a typical 10-year life of a pavement surface is another measure of the contribution of leaching from RHMA to the total zinc load to the environment from a roadway. In this case, the load from RHMA pavement can be assessed using the cumulative mass transfer rate based on an estimate of the number of days the roadway is saturated with water over 10 years. Assuming the roadway experienced 100 days of accumulated saturated conditions over a 10-year pavement life, the results from the second RHMA leaching experiment suggest a cumulative zinc leaching rate of approximately 30 μg/m^2/day of leaching (Figure 12), or 3 mg/m^2 over a 10-year period. Using the lower mass transfer rates observed in the first leaching experiment (Figure 9) would result in a value of approximately 1.9 mg zinc/m^2 from the RHMA over a 10-year period. Additional cumulative days of leaching would result in more leaching events, but at a lower daily rate. For example, extrapolating from the measured results of the second leaching experiment, after 240 days of saturation the zinc leaching rate would be approximately 19 μg/m^2 per day, or 4.6 mg/m^2 over the 10-year pavement surface life. Using the observed results from the first RHMA leaching experiment, and again assuming 240 total days of saturation over the 10-year pavement surface life, the contribution of zinc from the RHMA pavement would be 2.4 mg/m^2.

Contribution to Zinc Loading from Wet Atmospheric Deposition

Wet atmospheric deposition is another possible source of zinc in roadway runoff during precipitation events. The zinc concentration in samples collected by Humboldt State University during five precipitation events in the Eureka area were all above the detectable level and averaged approximately 8 µg/l (Table 25). The samples were collected more than 30 feet from a very lightly traveled street (AADT < 100) in a residential area. GHD collected one precipitation sample in a residential area of Santa Rosa which had a non-detect zinc concentration. The observed concentrations in the rainwater samples for all five precipitation events are higher than the concentrations estimated from the long-term leaching rates from RHMA pavement (less than 4 µg/l).

Table 25: Zinc concentration in rainfall captured near Eureka.

Sample Date	Sample ID	Dissolved Zinc (µg/l)
3/28/2019	Rain-1	5
3/28/2019	Rain-2	11
5/15/2019	Rain-3	11
5/20/2019	Rain-4	9
10/16/2019	Rain-5	8

While the zinc concentration in wet atmospheric deposition is generally low, it can be a large source of zinc on a mass basis in stormwater runoff. This concentration can be assumed to be relatively homogeneous throughout the region and potentially greater in proximity to traffic due to the contribution of exhaust and tire wear particles entraining zinc in the atmosphere. Using the average observed precipitation zinc concentration of 8 µg/l and the average annual rainfall in Eureka of 42.4 inches (Climate-Data 2020), the wet deposition of zinc on the pavement due to precipitation would be 8.6 mg/m^2/year, or 86 mg zinc/m^2 over the 10-year pavement life. Note that at this location, the contribution of rainfall to the resulting zinc load in roadway runoff is nearly 20 times greater than the contribution from the leaching of zinc from RHMA pavement (2.4 to 4.6 mg zinc/m^2).

Contribution to zinc loading from tire wear particles

Leaching from tire wear particles settled onto the pavement is believed to be a significant source of zinc in roadway stormwater runoff. Using typical tire characteristics (Table 26), a four-wheeled vehicle will generate tire wear particles containing 4,633 µg zinc per vehicle mile driven. For a roadway that is 20 meters wide, an AADT of 1 vehicle would result in 52.54 µg tire wear zinc/m^2 per year, or 0.525 mg tire wear zinc/m^2 over a 10-year period. Since this amount would scale linearly with AADT, for the Blue Lake Highway 299 RHMA site with an AADT of 5,000, tire wear particles would account for 2,625 mg zinc/m^2 over a 10-year period.

The fraction of zinc in the tire wear particles that ultimately contributes to the zinc load in roadway stormwater runoff is situation- and site-specific. Not all of the tire wear particles will remain on the roadway. Tire wear particles are small, with an average diameter estimated to range between 10 and 20 µm (Councell et al. 2004), and are easily transported off the roadway from natural and vehicle-induced air currents. Blok (2005) suggested that 30 percent of the particles become air-entrained and are transported to a buffer zone off the roadway.

Table 26: Assumed tire characteristics used for computing zinc load from tire wear particles.

Tire Characteristic	Assumed Value
Life	40,000 Miles
Tread Wear Depth	0.25 Inch
Tread Width	6 Inch
Diameter	25 Inch
Rubber Specific Gravity	1.2

Zinc Mass Fraction in Rubber	0.02

Depending on the type of roadway surface, some fraction of the particles can be stored in surface voids in the pavement. This would be especially true of porous friction course pavement overlays (open and gap-graded), which is common in RHMA applications. The storage volume is finite, and the number of particles available for leaching and washoff during runoff events would depend on the deposition rate (related to AADT) and the time since the last runoff event.

Not all of the zinc in the particles that are on the roadway will be leached out during runoff events before the particle is washed off the roadway surface. The small size of the particles suggests that the zinc leaching rate will be greater than from crumb rubber particles used in RHMA that were tested in this project. However, experimental work by Smolders and Degryse (2002) suggests that even after a year of exposure to rainfall, tire wear particles still contained between 60 percent and 90 percent of their zinc content. Despite all of the uncertainty, assume that 10 percent of the zinc contained in tire wear particles ultimately contributes to zinc in roadway stormwater runoff. With this conservative estimate and again assuming a 20-meter-wide roadway, tire wear particles would account for approximately 260 mg zinc/m^2 over a 10-year period for the Blue Lake RHMA site, which is nearly three times the contribution from precipitation (86 mg zinc/m^2) and more than 50 times the contribution from leaching of the rubber in the RHMA pavement itself (2.4 to 4.6 mg zinc/m^2).

Contribution to Zinc Loading from Galvanized Guardrails

While not directly studied, and not present at any of the sample sites in this study, the potential contribution of galvanized guardrails to the zinc load from roadway stormwater runoff compared to RHMA leaching, precipitation, and tire wear particles provides context on relative contributions to total zinc loading in stormwater runoff. Many highways have galvanized guardrails along at least one edge of the pavement and sometimes as a center divider. In California, galvanized railing must comply with AASHTO M 180 Class A, Type I W-beam guardrail specifications, except when within 0.5 miles of the coast where Type II railing is required (Caltrans, 2018a). AASHTO M 180 Class A specifications for Type I and Type II guardrails requires a minimum zinc of 1.80 oz/ft^2 and 3.60 oz/ft^2 respectively (AASHTO 2018). Using the AASHTO standard, one mile of a Type I and II galvanized guardrail would contain approximately 871 pounds per mile and 1,742 pounds per mile of zinc respectively (Table 27). This estimate neglects potential contribution from galvanized posts and mounting hardware.

Table 27: Parameters used to compute the mass of zinc contained within one mile of galvanized guardrail.

Parameter	Value	Unit
Actual Height of Guardrail (W-Beam)	12.3	Inches
Cross-Sectional Length of Guardrail Material (One Side)	17.6	Inches
Area of Guardrail in 1 Mile	15,488	ft^2
Zinc Coating (Accounts for Both Sides of Type I Rail)	1.8	oz/ft^2
Mass of Zinc in 1 Mile of Type I Guardrail	871	lb
Zinc Coating (Accounts for Both Sides of Type II Rail)	3.6	oz/ft^2
Mass of Zinc in 1 Mile of Type II Guardrail	1,742	lb

The design life for galvanized metal varies from 10 to 100 years, usually depending on thickness of the coating (AGA 2010). This estimate is based on the time it takes the railing to exhibit 10 percent corrosion of the underlying steel, which assumes all the zinc coating has dissolved. Assuming a 100-year lifespan in which all of the zinc coating has dissolved, the dissolution of zinc from that surface annually is approximately 8.71 lbs/mile and 17.4 lbs/mile for Type I and Type II rail respectively. Assuming there is a Type I guardrail on both edges of a 20-meter-wide roadway, the equivalent zinc loading from the guardrails would be 122.9 mg/m^2/year, or 1,230 mg/m^2 over a 10-year period, more than four times the zinc load from tire wear particles and more than 250 times the load from leaching of the RHMA pavement. If a Type II guardrail were in use, the resulting zinc loading would be 2,460 mg/m^2 over a 10-year period.

Summary of relative contributions to zinc loading

In summary, for the scenarios examined, leaching from the rubber in the binder of RHMA is a comparably minor source of zinc in roadway stormwater runoff (Table 28). In the Eureka area, the load from zinc in precipitation greatly exceeded that of the RHMA leachate, and the tire wear particles on a relatively lightly traveled highway exceeded that of the precipitation. In more arid locations, the contribution from precipitation would be lower (or even zero), but the same would be true of the contribution from the rubberized asphalt. On more lightly traveled roads, the contribution from tire wear particles would be lower, but even an AADT of 500 vehicles per day would result in a contribution five times greater than leaching from the RHMA surface. Galvanized guardrails, along with other galvanized metal (e.g. signs, light standards) along roads present a potential source of zinc in roadway runoff far in excess of the sources examined in this research.

The estimated rates for the contribution of various sources of zinc in roadway runoff shown in Table 28 are subject to uncertainty due to a number of factors. The leaching rate of zinc from RHMA was determined in a laboratory setting and the rate under field conditions might be different. For example, the aging effects of UV radiation and the impact from vehicles might increase the leaching rate. However, the temperature-based aging procedure used on the RHMA cores did not change the leaching rate, and the primary damage to asphalt pavement from vehicle loads is to the impermeable base layer, and not the surface friction coat. The leaching rate from RHMA is also dependent on the degree of previous exposure that the asphalt has had to water and the duration of runoff conditions during the period of interest. In this comparison, the assumption was that there were 240 days of runoff conditions (wet road surface) acting on new RHMA pavement over a 10-year period. If the site of interest had less precipitation, then the leaching rate during any event would be somewhat higher, but with fewer days of runoff the end result would be a lower total mass of zinc loss from the pavement over the 10-year period.

The contribution of tire wear particles to the zinc load in roadway stormwater runoff is based on an assumed fraction of the particles that remain on the roadway after they are generated by passing vehicles and the fraction of zinc in the particles that would be leached during the relatively short exposure time that the materials would be on the road surface. The contribution from tire wear is also dependent on the daily traffic count on the roadway. For this comparison, a comparatively low traffic rate (AADT of 5,000) was used, and a conservative value of 10 percent was used for the net fraction of zinc contained in the tire wear particles that would ultimately be found in the roadway runoff. A lower value of the AADT would reduce the rate of generation of tire wear particles, and a lower value for the fraction of zinc in the tire wear particles that contribute to the load in stormwater runoff is possible, but the value is unlikely change the relative comparison of the zinc load compared to leaching from RHMA.

While parameter uncertainties and site-specific circumstances could change the magnitude of the estimates provided in Table 28, it is unlikely that the general outcome of the comparison would change. Given a 50-times difference between the relative contribution of leaching from RHMA and tire wear particles under the stated conditions, it is reasonable to believe that the use of RHMA pavement is not a major factor in the concentration of zinc of roadway stormwater runoff.

Table 28: Comparison of zinc load to stormwater runoff off a 20-meter-wide roadway from various sources over a 10-year period.

Source	**Assumptions**	**Zinc load to roadway stormwater runoff over a 10-year period (mg/m^2)**
RHMA Rubber Binder	Equivalent of 240 days of leaching conditions at 19 μg/m^2/day	~5
Precipitation	42.4 in/year, 8 μg/l Zn	~90
Tire Wear Particles	10 percent of the zinc contained in the particles is leached into runoff; 5,000 AADT	~260
Galvanized Guardrail	Type I rail along both sides of the road; 100-year life	~1,230

Summary and Conclusions

The objective of this study was to assess the relative contribution of RHMA to zinc in road surface stormwater runoff. The relative contribution of RHMA compared to other sources is of interest since zinc is a component of the crumb rubber used in the RHMA binder and leachate from the pavement surface will always contain some zinc.

Laboratory experiments were used to estimate the leaching rate of zinc from crumb rubber and RHMA pavement cores. These experiments indicated that after any period of submersion in water, a much greater fraction of the zinc contained within the crumb rubber would be leached than from the top surface of an RHMA core. These results indicate that most of the crumb rubber used in the RHMA is not susceptible to leaching because it is covered by the waterproof binder.

As expected, the experiments also showed that the leaching rate of zinc from small diameter (less than 500 μm) crumb rubber particles was much higher than for larger particles due to their larger surface area to volume ratio. This result is relevant when considering the potential contribution of zinc leaching from the even smaller-diameter (average of 10 to 20 μm) tire wear particles that are deposited on the roadway.

Laboratory leaching experiments comparing mass transfer rates from RHMA and HMA pavement cores led to the conclusion that the mass transfer rate of zinc from the HMA was essentially zero. The mass transfer of zinc from the RHMA pavement cores was greater than 100 g/m^2/day, initially declining exponentially over time to an average zinc mass transfer rate of less than 10 g/m^2/day for RHMA surfaces that had already experienced at least four days of leaching conditions. The results from the HSU and GHD sampling show that pavement type alone cannot be used to predict zinc load from the roadway, and that factors other than pavement type may overwhelm the zinc load from the RHMA.

Field samples of runoff from paired HMA and RHMA roadways that otherwise had similar traffic load and precipitation intensities showed that while the mean zinc concentration over all sampled events from the RHMA sites was higher than at the HMA sites, there were many individual runoff events where the opposite was true. In addition to differences in the non-rubber compared to rubberized binder, the paired sites had different aggregate grading resulting in considerable differences in surface porosity and drainage characteristics. Variability in these characteristics may influence the retention or release of zinc from pavement surfaces, and may be responsible for the differences in the zinc loading between HMA and RHMA surfaces.

Leaching of zinc from galvanized guardrails and the direct deposition of zinc by precipitation were also considered as potential contributors to the load in roadway stormwater runoff. The literature suggests that, while not present at the field sites sampled in this study, galvanized metal is a major source of zinc in stormwater runoff in many watersheds. Wet atmospheric deposition was included as a potential source based on measurements of zinc found in precipitation in the project area.

Based on the results from the laboratory and field experiments, the relative contribution of leaching from RHMA pavement to the zinc levels in roadway stormwater runoff was negligible compared to the three other sources examined. On a lightly traveled highway in the study area, over a 10-year period, the estimated contribution of zinc from precipitation would be nearly 20 times greater than from RHMA pavement, and the contribution from tire wear particles would be more than 50 times greater than from RHMA pavement. If present, galvanized guardrails would have contributed more than 250 times the load of zinc in stormwater runoff compared to RHMA pavement.

The results of this research lead to the conclusion that RHMA pavement plays a very minor role in the zinc concentration in stormwater runoff from road surfaces. Laboratory experimental evidence indicates leaching from RHMA during the first few runoff events on new pavement may result in contributions to the concentration of zinc in the runoff comparable to that from tire wear particles, but the contribution is greatly decreased in subsequent events. A study capturing the first few runoff events from new RHMA pavement would help to fully understand the extent of the initial zinc loading under field conditions. Leaching of zinc from tire wear particles generated by vehicles on the roadway and from galvanized materials along the roadway are two of the biggest sources of zinc in runoff from roads; these sources deserve additional study. In particular, methods to capture tire wear particles on the road before they can enter a natural waterway would potentially provide for a significant reduction of zinc in roadway runoff and potentially reduce the net loading of tire-related microplastics to the environment. They may also help reduce the loading of other potential contaminants such as the recently identified tire rubber-derived compound 6PPD that is reported by Tian et al. (2020) to be responsible for acute mortality in coho salmon.

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Appendix A

Caltrans Sampling Data

Table 29: Merced paired sampling data of roadway stormwater runoff.

Date	HMA Dissolved Zinc (µg/l)	RHMA Dissolved Zinc (µg/l)	HMA Total Zinc (µg/l)	RHMA Total Zinc (µg/l)
12/21/2008	13	9.3	64	13
2/6/2009	17	15	22	24
2/7/2009	9.7	12	21	19
2/8/2009	15	17	23	27
2/22/2009	13	12	21	16
2/23/2009	11	8.8	22	12
3/22/2009	68	86	92	100

Table 30: Visalia paired sampling data of roadway stormwater runoff.

Date	HMA Dissolved Zinc (µg/l)	RHMA Dissolved Zinc (µg/l)	HMA Total Zinc (µg/l)	RHMA Total Zinc (µg/l)
2/23/2008	41	50	130	130
12/22/2008	79	83	120	150
5/1/2009	98	200	180	220
6/5/2009	300	440	370	520
12/12/2009	54	76	85	100
1/13/2010	65	88	110	140
1/17/2010	60	74	160	120
1/20/2010	44	58	150	150
2/23/2010	110	120	140	130
2/26/2010	30	38	100	79
4/4/2010	72	130	150	170
4/11/2010	45	95	130	200
4/20/2010	59	130	140	200

Table 31: Atascadero paired sampling data of roadway stormwater runoff.

Date	HMA Dissolved Zinc (µg/l)	RHMA Dissolved Zinc (µg/l)	HMA Total Zinc (µg/l)	RHMA Total Zinc (µg/l)
2/21/2008	12	24	21	100
2/24/2008	5.2	7.4	46	20
3/15/2008	56	210	95	380
4/2/2008	45	210	54	240
11/25/2008	40	270	82	430
12/14/2008	18	61	41	82
2/5/2009	19	9.3	29	58
2/8/2009	14	17	39	39
2/13/2009	10	3.3	75	88
2/16/2009	9.8	14	26	31
2/22/2009	16	31	29	41
3/21/2009	30	62	55	87
12/7/2009	32	94	52	170
12/11/2009	9	19	34	59
12/30/2009	28	230	34	260
1/12/2010	21	71	28	99
1/26/2010	14	28	30	53
2/4/2010	48	17	59	28
2/6/2010	14	37	62	71
2/23/2010	14	25	22	35
3/2/2010	9.9	32	12	80
2/16/2011	14	26	32	45
2/16/2011	5.2	22	25	46
2/24/2011	11	31	22	45
3/2/2011	7.7	87	19	108
3/18/2011	20	64	65	112
3/23/2011	11	39	22	64
3/23/2011	3.5	17	16	29
5/16/2011	21	88	28	109

GHD Paired Sampling Data

Table 32: Yuba City paired HMA (NR) and RHMA (R) sampling data of roadway stormwater runoff.

Sample Date	Sample ID	Dissolved Zinc (µg/l)	Total Zinc (µg/l)
4/5/2019	Yub Shang 0405 R	ND	ND
4/5/2019	Yub Shang 0405 NR	ND	ND
4/5/2019	Yub Allen 0405 R	36	650
4/5/2019	Yub Allen 0405 NR	ND	180
4/5/2019	Yub Gray 0405 R	55	670
4/5/2019	Yub Gray 0405 NR	56	93

Table 33: Richmond paired HMA (NR) and RHMA (R) sampling data of roadway stormwater runoff.

Sample Date	Sample ID	Dissolved Zinc (µg/l)	Total Zinc (µg/l)
3/25/2019	Rich Ohio 2R	25	ND
3/25/2019	Rich Ohio 2EBNR	68	140
3/25/2019	Rich Ohio 2WBNR	43	110
3/25/2019	Ohio Ave 2R	47	96
3/22/2019	Rich Ohio 1R	ND	56
3/22/2019	Rich Ohio 1NR	ND	60
1/16/2020	RichOhio2WBNR	29	340
1/16/2020	RichOhio1EBNR	ND	110
1/16/2020	RichOhio2R	22	73
1/16/2020	RichOhio1R	14	ND

Humboldt State University Paired Sampling Data

Table 34: Northern California paired HMA (NonRHMA) and RHMA sampling data of roadway stormwater runoff.

Sample Date	Sample ID	Dissolved Zinc (µg/l)	Total Zinc (µg/l)
12/20/2018	299 NonRHMA	37	59
12/20/2018	299 RHMA	27	40
12/20/2018	101N NonRHMA	41	62
12/20/2018	101N RHMA	46	76
1/5/2019	299 NonRHMA	17	34
1/5/2019	299 RHMA	25	49
1/6/2019	101N NonRHMA	38	140
1/6/2019	101N RHMA	33	290
1/16/2019	299 NonRHMA	39	78
1/16/2019	299 RHMA	29	34
1/16/2019	101N NonRHMA	28	83
1/16/2019	101N RHMA	37	190
1/16/2019	101S NonRHMA	32	56
1/16/2019	101S RHMA	27	51
2/1/2019	101N NonRHMA	64	250
2/1/2019	101N RHMA	110	260
2/3/2019	299 NonRHMA	29	35
2/3/2019	299 RHMA	44	41
2/3/2019	101N NonRHMA	38	54
2/3/2019	101N RHMA	42	91
2/3/2019	101S NonRHMA	40	32
2/3/2019	101S RHMA	35	45
2/23/2019	299 NonRHMA	28	25
2/23/2019	299 RHMA	32	25
2/23/2019	101N NonRHMA	61	130
2/23/2019	101N RHMA	55	110
2/23/2019	101S NonRHMA	58	62

Sample Date	Sample ID	Dissolved Zinc (µg/l)	Total Zinc (µg/l)
2/23/2019	101S RHMA	50	170
4/5/2019	299 NonRHMA	48	64
4/5/2019	299 RHMA	31	39
4/5/2019	101N NonRHMA	35	200
4/5/2019	101N RHMA	46	150
4/5/2019	101S NonRHMA	57	65
4/5/2019	101S RHMA	56	91
5/15/2019	101N NonRHMA	100	210
5/15/2019	101N RHMA	150	310
5/15/2019	101S NonRHMA	80	100
5/15/2019	101S RHMA	110	120
9/15/2019	299 RHMA	850	880
9/15/2019	299 NonRHMA	66	83
9/15/2019	101N RHMA	240	360
9/15/2019	101N NonRHMA	280	450
9/17/2019	101N NonRHMA	81	380
9/17/2019	101N RHMA	110	520
9/17/2019	101S NonRHMA	77	69
9/17/2019	101S RHMA	82	170
9/17/2019	101FSS RHMA	210	190
9/17/2019	101FSS RHMA	130	140
10/16/2019	299 RHMA	74	79
10/16/2019	299 NonRHMA	46	75
12/6/2019	299 NonRHMA	61	55
12/6/2019	299 RHMA	72	50
12/6/2019	101S NonRHMA	72	280
12/6/2019	101FSS RHMA	63	110
1/21/2020	101N NonRHMA	68	150
1/21/2020	101N RHMA	40	100
2/16/2020	101S NonRHMA	140	140

Sample Date	Sample ID	Dissolved Zinc (µg/l)	Total Zinc (µg/l)
2/16/2020	101FSN RHMA	64	52
2/16/2020	101 FSS RHMA	57	50
3/24/2020	101N NonRHMA	47	240
3/24/2020	101N RHMA	60	240
3/24/2020	101S NonRHMA	110	140
3/24/2020	101S RHMA	110	240
3/24/2020	101FSS RHMA	59	53
3/24/2020	101FSN RHMA	91	150

Appendix B

ADA Tables for Figures

Figure 1 Table: Comparison of zinc load to stormwater runoff off a 20-meter-wide roadway from various sources over a 10-year period. Assumptions for these estimates are based on literature, research analysis, and data collected from Eureka.

Source	Zinc load (mg/m2 on road surface)
RHMA	4.6
Precipitation	86
Tire wear particles	263
Galvanized guardrails	1230

Figure 8 Table: Cumulative zinc mass transfer rate for small- and large-size passenger and truck crumb rubber.

Days Leaching	Mass Transfer Rate Pasenger Small (ug/kg/day)	Mass Transfer Rate Passenger Large (ug/kg/day)	Mass Transfer Rate Truck Small (ug/kg/day)	Mass Transfer Rate Truck Large (ug/kg/day)
2	38400	35600	7600	3420
4	35000	25000	2900	1750
21	15619	7619	4571	3352
61	9443	3410	4590	3934
128	4125	2063	4375	3063
177	4520	1492	3345	1311
209	3445	1684	1646	1761
240	3667	1200	2267	1100

Figure 9 Table: Cumulative zinc mass transfer rates for RHMA cores.

Days Leaching	RHMA-A Mass Transfer Rate (mg/m2/day)	RHMA-B Mass Transfer Rate (mg/m2/day)
2	461.9	483.7
4	212.4	321.3
14	73.4	84.3
38	28.1	33.8
61	20.8	24.4
128	14.6	14.7
177	12.7	12.8
240	10.2	10.2
246		9.3

Figure 10 Table: Average zinc mass transfer rate from RHMA cores at different times during the first leaching experiment.

Range of Leaching Period (days)	Mass Transfer Rate (mg/m2/day)
0 - 2	472.77
2 - 4	60.93
4 - 14	3.65
14 - 38	3.00
38 - 61	8.81
61 - 128	7.45
128 - 177	7.83
177 - 240	3.00

Figure 12 Table: Cumulative zinc mass transfer rates for the four RHMA cores in the second leaching experiment. The results for the average transfer rate from the first experiment are included for comparison.

RHMA - Core 1 Days Leaching	RHMA - Core 1 Mass Transfer Rate total days (ug/m2/day)	RHMA - Core 2 Days Leaching	RHMA - Core 2 Mass Transfer Rate total days (ug/m2/day)	RHMA - Core 3Days Leaching	RHMA - Core 3 Mass Transfer Rate total days (ug/m2/day)	RHMA - Core 4 Days Leaching	RHMA - Core 4 Mass Transfer Rate total days (ug/m2/day)	RHMA - 246 day run Days Leaching	RHMA - 246 day run Mass Transfer Rate total days (ug/m2/day)
1	642.6	1	688.0	1	995.6	1	618.7	2	472.77
2	627.0	2	677.5	2	625.7	2	370.5	4	266.85
4	280.6	4	311.3	4	422.5	4	264.7	14	78.85
8	156.5	8	209.7	8	292.3	8	194.5	38	30.94
16	104.9	16	118.2	16	179.5	16	130.6	61	22.60
32	68.5	32	81.6	32	109.0	32	84.6	128	14.67
63	39.6	63	44.7	63	65.0	63	47.8		
64	42.1	69	42.2	64	62.5	69	39.4		
65	41.4	70	41.6	65	63.0	70	41.5		
67	40.2	71	42.3	67	62.5	71	44.8		
71	37.9	73	43.6	71	59.0	73	41.1		
79	29.6	77	40.2	79	48.5	77	42.4		
92	25.4	85	34.4	92	38.8	85	32.4		
		98	30.7			98	28.9		

Figure 13 Table: Average zinc mass transfer rate from RHMA cores at different times during the second leaching experiment.

Range of Leaching Period (days)	Average Zinc Mass Transfer Rate (mg/m2/day)
0 - 1	736.25
1 - 2	414.09
2 - 4	64.42
4 - 8	106.77
8 - 16	53.30
16 - 32	38.55
32 - 63	11.43

Figure 14 Table: Leachate zinc concentration for all four RHMA cores illustrating little change in leaching behavior in Core 1 and Core 3 after artificial aging. Arrows indicate the sample taken one day after leaching resumed for Core 1 and 3.

RHMA - Core 1 Days Leaching	RHMA - Core 1 Zinc Concentration (ug/l)	RHMA - Core 2 Days Leaching	RHMA - Core 2 Zinc Concentration (ug/l)	RHMA - Core 3Days Leaching	RHMA - Core 3 Zinc Concentration (ug/l)	RHMA - Core 4 Days Leaching	RHMA - Core 4 Zinc Concentration (ug/l)
1	5.5	1	6.0	1	8.7	1	5.4
2	11.0	2	12.0	2	11.0	2	6.5
4	9.8	4	11.0	4	15.0	4	9.4
8	11.0	8	15.0	8	21.0	8	14.0
16	15.0	16	17.0	16	26.0	16	19.0
32	20.0	32	24.0	32	32.0	32	25.0
63	23.0	63	26.0	63	38.0	63	28.0
64	25.0	69	27.0	64	37.0	69	25.0
65	25.0	70	27.0	65	38.0	70	27.0
67	25.0	71	28.0	67	39.0	71	30.0
71	25.0	73	30.0	71	39.0	73	28.0
79	21.0	77	29.0	79	35.0	77	31.0
92	21.0	85	27.0	92	32.0	85	25.0
		98	28.0			98	26.0

Figure 15 Table: Fraction of zinc contained within crumb rubber and a RHMA core that entered the water column during the leaching experiments.

Passenger Small Crumb Days Leaching	Passenger Small Crumb Fraction of Available Zinc Leached	Passenger Large Crumb Days Leaching	Passenger Large Crumb Fraction of Available Zinc Leached	Truck Small Crumb Days Leaching	Truck Small Crumb Fraction of Available Zinc Leached	Truck Large Crumb Days Leaching	Truck Large Crumb Fraction of Available Zinc Leached	RHMA Days Leaching	RHMA (outer 0.1 inch) Fraction of Available Zinc Leached
2	0.003840	2	0.003560	2	0.001810	2	0.000814	2	0.0011529
4	0.007000	4	0.005000	4	0.001381	4	0.000833	4	0.0012999
21	0.016400	21	0.008000	21	0.011429	21	0.008381	14	0.0013455
61	0.028800	61	0.010400	61	0.033333	61	0.028571	38	0.0014331
128	0.026400	128	0.013200	128	0.066667	128	0.046667	61	0.0016801
177	0.040000	177	0.013200	177	0.070476	177	0.027619	128	0.0022892
209	0.036000	209	0.017600	209	0.040952	209	0.043810	177	0.0027572
240	0.044000	240	0.014400	240	0.064762	240	0.031429	240	0.0029874

Figure 16 Table: Dissolved and total zinc concentration in stormwater runoff from paired HMA-RHMA pavement at the Blue Lake - 299 location.

Date	RHMA-Dissolved Zinc (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Dissolved Zinc (ug/l)	HMA-Total Zinc (ug/l)
12/20/2018	27	40	37	59
1/5/2019	25	49	17	34
1/16/2019	29	34	39	78
2/3/2019	44	41	29	35
2/23/2019	32	25	28	25
4/5/2019	31	39	48	64
9/15/2019	850	880	66	83
10/16/2019	74	79	46	75
12/6/2019	72	50	61	55

Figure 17 Table: Dissolved and total zinc concentration in stormwater runoff from paired HMA-RHMA pavement at the Eureka - 101N location.

Date	RHMA-Dissolved Zinc (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Dissolved Zinc (ug/l)	HMA-Total Zinc (ug/l)
12/20/2018	46	76	41	62
1/6/2019	33	290	38	140
1/16/2019	37	190	28	83
2/1/2019	110	260	64	250
2/3/2019	42	91	38	54
2/23/2019	55	110	61	130
4/5/2019	46	150	35	200
5/15/2019	150	310	100	210
9/15/2019	240	360	280	450
9/17/2019	110	520	81	380
1/21/2020	40	100	68	150
3/24/2020	60	240	47	240

Figure 18 Table: Dissolved and total zinc concentration in stormwater runoff from paired HMA-RHMA pavement at the Eureka – 101S location.

Date	RHMA-Dissolved Zinc (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Dissolved Zinc (ug/l)	HMA-Total Zinc (ug/l)
1/16/2019	27	51	32	56
2/3/2019	35	45	40	32
2/23/2019	50	170	58	62
4/5/2019	56	91	57	65
5/15/2019	110	120	80	100
9/17/2019	82	170	77	69
3/24/2020	110	240	110	140
12/6/2019			72	280
2/16/2020			140	140

Figure 19 Table: Dissolved and total zinc concentration in stormwater runoff from paired HMA-RHMA pavement at the Eureka – 101FS location.

Date	RHMA-Dissolved Zinc (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Dissolved Zinc (ug/l)	HMA-Total Zinc (ug/l)
9/17/2019	170	165	77	69
12/6/2019	63	110	72	280
2/16/2020	61	51	140	140
3/24/2020	75	102	110	140

Figure 20 Table: Paired dissolved and total zinc concentrations in runoff from HMA and RHMA pavement in Merced.

Date	RHMA-Dissolved Zinc (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Dissolved Zinc (ug/l)	HMA-Total Zinc (ug/l)
12/21/2008	9.3	13	13	64
2/6/2009	15	24	17	22
2/7/2009	12	19	9.7	21
2/8/2009	17	27	15	23
2/22/2009	12	16	13	21
2/23/2009	8.8	12	11	22
3/22/2009	86	100	68	92

Figure 21 Table : Paired dissolved and total zinc concentrations in runoff from HMA and RHMA pavement in Visalia.

Date	RHMA-Dissolved Zinc (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Dissolved Zinc (ug/l)	HMA-Total Zinc (ug/l)
02/23/2008	50	130	41	130
12/22/2008	83	150	79	120
05/01/2009	200	220	98	180
06/05/2009	440	520	300	370
12/12/2009	76	100	54	85
01/13/2010	88	140	65	110
01/17/2010	74	120	60	160
01/20/2010	58	150	44	150
02/23/2010	120	130	110	140
02/26/2010	38	79	30	100
04/04/2010	130	170	72	150
04/11/2010	95	200	45	130
04/20/2010	130	200	59	140

Figure 22 Table: A comparison of total zinc and copper (scaled five times) concentration at the Visalia paired sampling location shows a high correlation (r^2=0.95).

Date	RHMA-Total Copper (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Total Copper (ug/l)	HMA-Total Zinc (ug/l)
02/23/2008	22	130	20	130
12/22/2008	34	150	24	120
05/01/2009	62	220	57	180
06/05/2009	110	520	80	370
12/12/2009	25	100	21	85
01/13/2010	31	140	31	110
01/17/2010	24	120	27	160
01/20/2010	22	150	22	150
02/23/2010	26	130	26	140
02/26/2010	16	79	17	100
04/04/2010	36	170	29	150
04/11/2010	41	200	28	130
04/20/2010	41	200	30	140

Figure 23 Table: Paired dissolved and total zinc concentrations in runoff from HMA and RHMA pavement in Atascadero

Date	RHMA-Dissolved Zinc (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Dissolved Zinc (ug/l)	HMA-Total Zinc (ug/l)
02/21/2008	24	100	12	21
02/24/2008	7.4	20	5.2	46
03/15/2008	210	380	56	95
04/02/2008	210	240	45	54
11/25/2008	270	430	40	82
12/14/2008	61	82	18	41
02/05/2009	9.3	58	19	29
02/08/2009	17	39	14	39
02/13/2009	3.3	88	10	75
02/16/2009	14	31	9.8	26
02/22/2009	31	41	16	29
03/21/2009	62	87	30	55
12/07/2009	94	170	32	52
12/11/2009	19	59	9	34
12/30/2009	230	260	28	34
01/12/2010	71	99	21	28
01/26/2010	28	53	14	30
02/04/2010	17	28	48	59
02/06/2010	37	71	14	62
02/23/2010	25	35	14	22
03/02/2010	32	80	9.9	12
02/16/2011	26	45	14	32
02/16/2011	22	46	5.2	25
02/24/2011	31	45	11	22
03/02/2011	87	108	7.7	19
03/18/2011	64	112	20	65
03/23/2011	39	64	11	22
03/23/2011	17	29	3.5	16
05/16/2011	88	109	21	28

Figure 24 Table: A comparison of total zinc and copper (scaled 10 times) concentration at the Atascadero paired sampling location shows a moderate linear correlation (r^2=0.65).

Date	RHMA-Total Copper (ug/l)	RHMA-Total Zinc (ug/l)	HMA-Total Copper (ug/l)	HMA-Total Zinc (ug/l)
02/21/2008	15	100	7.6	21
02/24/2008	3	20	13	46
03/15/2008	33	380	20	95
04/02/2008	31	240	16	54
11/25/2008	22	430	16	82
12/14/2008	4.6	82	7	41
02/05/2009	9	58	4.7	29
02/08/2009	3.5	39	4	39
02/13/2009	12	88	9	75
02/16/2009	3.2	31	4.1	26
02/22/2009	2.7	41	4.1	29
03/21/2009	4.7	87	7.3	55
12/07/2009	9.1	170	7.4	52
12/11/2009	7.3	59	6.8	34
12/30/2009	6.6	260	6.4	34
01/12/2010	3.5	99	3.5	28
01/26/2010	3.9	53	3.5	30
02/04/2010	3.8	28	3.8	59
02/06/2010	6.1	71	7.6	62
02/23/2010	3.2	35	3.6	22
03/02/2010	8.1	80	4.4	12
02/16/2011	3.6	45	3.6	32
02/16/2011	3.7	46	5.5	25
02/24/2011	3.3	45	2.7	22
03/02/2011	4.1	108	4	19
03/18/2011	7	112	8.7	65
03/23/2011	5.2	64	3.4	22
03/23/2011	2.9	29	3.4	16
05/16/2011	5.7	109	7.6	28

Figure 25 Table: Zinc concentration in runoff from roadways at various (ug/l)runoff rates by loading rate (ug/m20/day).

Rainfall intensity (inch/day)	10 ug/m2/day	40 ug/m2/day	60 ug/m2/day	100 ug/m2/day	1000 ug/m2/day
0.1	3.937	15.748	23.622	39.370	393.701
0.2	1.969	7.874	11.811	19.685	196.850
0.3	1.312	5.249	7.874	13.123	131.234
0.4	0.984	3.937	5.906	9.843	98.425
0.5	0.787	3.150	4.724	7.874	78.740
0.6	0.656	2.625	3.937	6.562	65.617
0.7	0.562	2.250	3.375	5.624	56.243
0.8	0.492	1.969	2.953	4.921	49.213
0.9	0.437	1.750	2.625	4.374	43.745
1	0.394	1.575	2.362	3.937	39.370
1.1	0.358	1.432	2.147	3.579	35.791
1.2	0.328	1.312	1.969	3.281	32.808
1.3	0.303	1.211	1.817	3.028	30.285
1.4	0.281	1.125	1.687	2.812	28.121
1.5	0.262	1.050	1.575	2.625	26.247
1.6	0.246	0.984	1.476	2.461	24.606
1.7	0.232	0.926	1.390	2.316	23.159
1.8	0.219	0.875	1.312	2.187	21.872
1.9	0.207	0.829	1.243	2.072	20.721
2	0.197	0.787	1.181	1.969	19.685