A COMPARISON OF ZINC LEVELS IN RUNOFF FROM RUBBERIZED HOT MIX ASPHALT AND CONVENTIONAL PAVEMENT

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ABSTRACT

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High levels of dissolved zinc in water bodies can be toxic to aquatic organisms. There are currently over 40 waterways in California that have on occasion been in exceedance of Clean Water Act minimum toxicity threshold standards for zinc. Recycled tires that contain 1-2% zinc by mass are commonly used in California paving formulations known as Rubberized Hot Mix Asphalt (RHMA). The addition of tires to RHMA increases the zinc content of the pavement in comparison to conventional HMA. This research assesses the zinc content and leaching rate of RHMA in field and laboratory settings to estimate its contribution of zinc to stormwater runoff relative to other significant sources. To compare stormwater runoff zinc concentrations between RHMA and Hot Mix Asphalt (HMA), two laboratory leaching studies and a field paired pavement sampling study were conducted.

The first leaching study assessed zinc leaching from different sizes of passenger and truck tire crumb rubber that is similar to the tire crumb rubber added as an ingredient in RHMA. The results from this study indicate that passenger tire crumb has a higher zinc mass transfer rate than truck tire crumb and that smaller particles increase the zinc leaching rate for both types of tire crumb. After 61 days of leaching in distilled water, the

percentages that were recovered in the leachate were 2 percent and 3 percent of the total zinc contained in the passenger and truck crumb rubber samples, respectively.

The second leaching study observed dissolved zinc leaching from RHMA and HMA pavement cores by submerging duplicate samples of each type in distilled water and determining the zinc concentration in the leachate over time. Both the pavement cores show an initial pulse (40-45 $\mu g/ft^2/day$) of zinc, that declines to near-zero mass transfer after ten days and contributes little or no zinc for the remaining duration of the 61-day (RHMA) and 41-day (HMA) experiments. The percent recovery of zinc within crumb rubber contained in the RHMA was 0.024% after 61 days.

To assess differences in stormwater zinc concentrations between RHMA and HMA pavement, paired pavement runoff samples were collected from both types of pavement in close proximity to each other (at either side of the edge of a change in pavement type). The paired pavement sampling showed 27% higher median dissolved zinc concentrations and 40% higher median total zinc concentrations in stormwater runoff from RHMA compared to HMA across the entire 186 pavement runoff samples. Further analysis suggests that pavement surface characteristics such as age, aggregate gradation and void space can likely impact zinc concentrations in runoff between the two pavement types. This finding suggests that both the material composition and the physical structure of the pavement are important considerations for paired pavement sample comparison.

An application of mass transfer rates found in the leaching studies in addition to literature values for galvanized metal leaching helped demonstrate potential ranges of

environmental loading of zinc from precipitation (wet deposition), RHMA, tire wear, and galvanized metal. Tire wear particle leaching rates were assumed equal to those found in the tire crumb rubber leaching study, though tire wear particles are generally smaller in diameter than crumb rubber. The resulting analysis showed that theoretical environmental mass loading rates along a 1-mile stretch of highway during a 1-year period for 2-lane RHMA, precipitation, tire wear and galvanized metal guard rail are 0.5 lbs, 0.22 lbs, 1 - 9 lbs, and 17 - 87 lbs, respectively. This demonstrated the potential for tire wear and galvanized metal to contribute significantly higher zinc loads to the environment than RHMA. Further assessment of the impact that pavement aging and RHMA aggregate gradation might have on zinc concentrations in stormwater runoff would help refine this analysis.

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ABBREVIATIONS AND ACRONYMS

CalRecycle: California Department of Resources Recycling and Recovery

CRM: crumb rubber modifier

DGAC: dense-graded asphalt concrete

EPA: United States Environmental Protection Agency

HMA: hot mix asphalt

MCL: maximum contaminant level

mg/L: milligram per liter

ND: No Data

OBC: optimum binder content

OGAC: open-graded asphalt concrete

PCC: portland cement concrete

RAC-O: rubberized asphalt concrete open-graded

RAC-G: rubberized asphalt concrete gap-graded

RHMA: rubberized hot mix asphalt

RICE: theoretical maximum density (pavement)

TDA: tire derived aggregate

μg/L: micrograms per liter

INTRODUCTION

In 2018, California disposal and recycling efforts collected an estimated 51.1 million waste tires, 81% of which were effectively diverted from landfills (CalRecycle 2019). Scrap tire reuse has been an effective alternative to historical methods of tire disposal such as illegal stockpiling and dumping in landfills. Discarded unprocessed used tires are commonly referred to as scrap tires. Scrap tires in stockpiles and landfills are a concern to public and environmental health and are impractical due to their large storage footprint. Large voids created by storing scrap tires can trap gases, increase fire risk and harbor rodents and insects that may increase the spread of disease (CalRecycle 2020). As a result, some landfills have now banned scrap tires and efforts to clean up and recycle whole scrap tires are increasing. Crumb rubber is a recycled rubber product derived from scrap tires that is used in civil engineering projects (Figure 1).

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

Crumb rubber production in CA increased by 29 percent in 2018 from 2017, effectively diverting an estimated 8.8 million tires from other disposal methods (CalRecycle 2019). A common usage 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 crumb rubber modified pavements, but will be referred to as RHMA throughout this report.

In 2005, California Legislature passed Assembly Bill number 338 which states, "On and after January 1, 2013, the Department of Transportation shall use, on an annual average, not less than 11.58 pounds of CRM per metric ton of the total amount of asphalt paving materials used (LCD 2005)." This equates to the use of CRM pavements in at least 35% of California Department of Transportation (CalTrans) pavement projects. CalTrans has been refining methods of tire recycling through the use of crumb rubber in paving applications since the 1970's and by 2010, approximately 31 percent of all hot mix asphalt (HMA) annually placed by Caltrans was rubberized, roughly 1.2 million tons of RHMA pavement placed in 2010 (Zhou et al. 2014). A two-inch-thick asphalt resurfacing project that uses CRM pavement 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 the 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 2017;

Zhou et al. 2014). Though there are benefits, concern has been raised about the potential contribution of unwanted constituents in stormwater from RHMA.

Over 40 waterways in California have on occasion been in exceedance of 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 rubberized asphalt mixes in California roadways has called into question whether stormwater runoff from rubberized paving surfaces is a significant contributor to the overall amount of zinc being 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, although Xiao et al. (2017) show that the rate of wear for RHMA is lower than conventional pavement mixes. 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). Although zinc leaches from these materials under various environmental conditions, research into the interaction of CRM 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 various 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 CRM pavements in comparison to conventional non-rubberized asphalt mixtures. Even less literature has been published on comparing the differences in zinc content and leaching rates between CRM and conventional pavements with respect to other point and non-point sources, specifically major ones such as tire wear and galvanized metal.

The objective of this research is to determine whether crumb rubber modifier 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 rate from both the crumb rubber modifier used in RHMA design and from RHMA. 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 stormwater zinc contributions 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

Literature was reviewed to characterize RHMA and its use in roadways. Field and laboratory experiments that study the effects of RHMA on water quality were reviewed as well as studies considering other point and non-point sources of zinc in stormwater such as tire wear particles and galvanized metal. California specific data was collected concerning the amount of RHMA that has been in use as well as some monitoring results of stormwater runoff from those surfaces. Basin-scale mass balance studies that account for zinc coming from different surfaces are described, and taken in context to deposition and distribution patterns of zinc from all point and non-point sources. The following section provides a summary of this information.

Composition of Tires and Crumb Rubber

Tire composition

Detailed physical and chemical characteristics of tires are helpful in determining the composition of crumb rubber that is added as crumb rubber modifier in rubberized asphalt. 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 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 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 the type of vehicle it is designed for. 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) also compiled data from numerous studies to present the mean zinc concentration of passenger and truck tire tread (Table 1). Mean zinc concentrations presented in these data show that common passenger tires contain from 8,470 – 14,800 mg/kg, or approximately 0.85%-1.5% zinc by weight. Truck tires appear to contain a higher concentration of zinc with mean values of 16,000 – 17,000 mg/kg which equate to 1.6 -1.7% zinc by weight.

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

Tire Type	Mean Zinc Concentration (mg/kg)	Source
Car	9,400 (6,100-16,000)	Sweden, 52 tires (Hjortenkrans et al. 2007)
	8,470 (5,650 - 9,640)	New Zealand, 7 tires (Kennedy et al. 2002)
	9500	Netherlands Industry data (Blok 2005)
	14,800 (12,700 - 16,900)	Japan, 2 tires (Ozaki et al. 2004)
	10,250	France (Legret and Pagatto 1999)
	9,600 (320 to 23,000)	EU Rubber Industry survey (Smolders and Degryse 2002)
Truck	17,000	Netherlands Industry Data (Blok 2005)
	16,000 (13,800 - 18,300)	New Zealand, 2 tires (Kennedy et al. 2002)
	17,000 (9,600 to 35,000)	EU Rubber Industry survey (Smolders and Degryse 2002)

Crumb rubber composition

Crumb rubber (CR) is a tire derived product composed of ground scrap tire which usually consists of particle sizes ranging from 0.075mm to 4.75mm and consists only of the rubber components of recycles tires with wire and other parts of tire removed (Heitzman 1992). ASTM D6114 (2019) provides guidelines for CR used in asphalt paving. The requirements specify cleanliness (fiber content<0.5 percent; metal content <0.01 percent), moisture content (<0.75 percent), 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 of different mass ratios of passenger, truck and scrap tires 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, mass content of zinc varied from 1.16 – 2.3 percent (Table 2).

Table 2: Crumb rubber size 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

Water Quality Considerations for using Crumb Rubber

The primary 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 required 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 greater than 40 waterways in California that are considered to be zinc impaired by the aquatic life criteria standards (CASQA 2014). This 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 100mg/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 placed significantly higher at 7,400 µg/l.

On a 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 notably, 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 unable to be 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 increases.

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. It should be noted that the median particle diameters of truck and car rubber used in this experiment were rather fine compared to those used in CRM specification, 65.4 μm and 79.6 μm, respectively. These size ranges are more in-line with tire wear particle sizes, of which the average size has been suggested as 10 – 20 μm (Councell 2004).

The results showed that there was no detectible increase in zinc leaching from the truck tire crumb treated soil columns compared to the control. The passenger tire crumb

treated columns observed a 3-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, the amount of zinc measured in leachate from the passenger tire in acidic soil conditions only equates to approximately 0.66 percent of the total amount of zinc contained within the rubber in the soil. The labile zinc analysis (used to represent all zinc adsorbed in soil and dissolved into pore water) revealed that 10 percent - 40 percent of the total zinc contained within the crumb rubber had leached or adsorbed into the surroundings in the 1-year study period. That is, 10 – 40 percent of the zinc contained within the crumb rubber was lost into the surroundings, but only a small fraction of the total zinc in the crumb rubber (0.66 percent) was found in the leachate. This suggests that the large majority 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. The results suggest that pH may effect 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 tire derived aggregate (TDA) – soil system.

The above studies show that most of the zinc from crumb rubber becomes adsorbed in soil and does not mobilize through soil in pore water or leachate. The direct leaching rate of zinc from crumb rubber submersion in water can be of particular use.

Rhodes et al. (2012) identified a high variability in CR zinc leaching rate from submerged samples. Given the volume of water (500 ml), mass of crumb rubber (25g), and the resulting concentration of zinc in the leachate (0.75 mg/l/day) from this experiment, the mass transfer rate can be calculated as 0.015 mg zinc / gram of rubber / day. This transfer rate was determined to remain relatively constant throughout the 96-hour experiment duration. Assuming a 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 96-hour sample period indicates that approximately 0.33 percent of the total zinc contained within the rubber had leached into the sample. Additionally, they identified: a negative association with CR size (larger particles result in lower concentrations) and a negative association with pH (higher pH results in lower concentration). The change in mass transfer rate with changes in particle size was suggested to be linearly correlated.

Of 15 CR leaching studies reviewed by Rhodes et al. (2012), the longest study occurred over a 1-month period. Finney and Maeda (2016), however, studied leaching rates of various metals from tire derived aggregate and found week 20 to be the earliest time to reach steady state leaching conditions 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/ day in the earliest weeks and reduced to as low as 0.003 mg zinc/ kg of TDA / day around week 65. It should be noted, however, that Finney and Maeda (2016) were studying metals leaching from tire derived aggregate, a tire derived product larger than crumb rubber which also contains metal and textile components. Long-term research

on CR leaching could be beneficial to understanding environmental loading of both CRM pavements and tire debris from roadways.

Crumb Rubber and Rubberized Pavement

Rubberized pavement mixtures are generally used in overlay projects in which a thin layer of RHMA is laid atop a section of conventional Hot Mix Asphalt (HMA) or Portland Cement Concrete (PCC). A chip seal is also a common form of pavement overlay that can use crumb rubber. Chip seal construction begins with laying down asphalt emulsion to seal the existing pavement, then overlaying the seal with crushed rock and finally locking down the crushed rock using a flush coat and sand. HMA 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 mixture impacts the porosity of the resulting pavement. The two main types of HMA used in California are open-graded (target air void content, 5 percent) and gap-graded (target air void content, 15 percent) (Caltrans 2018).

There are two main processes which exist to incorporate CRM into a rubberized asphalt product; the wet process and the dry process. Historically, Caltrans used both wet (CRM mixed into asphalt binder) and dry processes (CRM mixed into aggregate) as well as rubber modified binders containing crumb rubber modifier and polymer modifier. While wet-process mixtures have presented successful field performance and improved pavement properties, dry processes have provided inconsistent results with regards to early raveling and moisture damage (Caltrans 2005). As determined through performance

monitoring of a variety of methods, CalTrans specification now uses a crumb rubber modified binder in the wet-process to generate RHMA (CalTrans 2018).

To construct RHMA using the wet-process, crumb rubber that passes the 2mm 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 content by mass of total CRM (typically truck tires) while the other 75 percent is scrap tire rubber (passenger tires) (CalTrans 2018; Zhou et al. 2014). After the crumb rubber is added to the heated binder in the wet RHMA process, it remains to mix at elevated temperatures of 400 – 425 degrees F for 45 minutes (Van Kirk 2016). Once the asphalt rubber binder is mixed, it is added to the pavement aggregate to meet a 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.

Each of these mixes result in different physical characteristics of the pavement including void space and permeability. Table 3 shows the permeability resulting from field testing of a number of pavement surfaces in California (CalTrans 2008). The tested pavements include RHMA-O and RHMA-G as well as numerous other non-rubberized pavement types that have been used in California.

Table 3: Coefficient of permeability resulting from field testing on 10 different pavement types (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 (64-10)	0.024
Open-Graded Asphalt Concrete (64-16)	0.029
Open-Graded Asphalt Concrete (58-22)	0.026
Open-Graded Asphalt Concrete (64-28)	0.035
Terminal-Blend Modified Binder gap-graded	0.008
Dense-Graded Asphalt Concrete (64-16)	0
Portland Cement Concrete -D	0
Portland Cement Concrete -OG	0.116

Since the crumb rubber percentage of the binder, optimal binder content, and values for crumb rubber zinc content are specified, the percent mass of zinc contained within the pavement from rubber can be calculated. The average crumb rubber zinc content of 1.6 percent from Zanetti et al. (2016) (see Table 2) and the mean CR weight percentage of 20 percent in the asphalt binder were assumed in this calculation. The result indicates that the RHMA-G (gap-graded) design pavement is 1.5 percent crumb rubber by weight and subsequently is approximately 0.024 percent zinc by weight. RHMA-O design (9.5 percent OBC) is approximately 1.9 percent crumb rubber by weight and therefore approximately 0.03 percent zinc. These calculations ignore any zinc contained within the parent material within the pavement aggregate or asphalt binder and are focused solely on the percent zinc due to the inclusion of crumb rubber into the paving process.

Dry processes generally mix the rubber into the aggregate at about 3 percent crumb rubber by weight (Vashisth 1998), and use a lower OBC of approximately 4.5

percent (CalTrans 2005) though this specification is not included or used in current CalTrans design specification and is dependent on gradation targets. Using the same zinc content of 1.6 percent as listed above would indicate a dry-process RHMA sample containing approximately 0.046 percent zinc by weight. Table 4 shows a summary of the CR and zinc content of the various CRM pavement designs. Wet-process calculations assume 1.6 percent zinc content of crumb rubber and 20 percent CR content within the asphalt binder. Dry-process calculations assume 4.5 percent optimal binder content and an aggregate of 3 percent CR by weight.

Table 4: Crumb rubber and zinc content percentages for various crumb rubber modified pavement designs.

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 of zinc contained within a section of pavement. To do so, it is helpful to know the density of the pavement. 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 and when multiplied by the density of water suggests that 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 sometimes referred to as the in-place pavement density is approximately 155.5 lb/ft^3. Once the bulk density is obtained, the amount of zinc contained within the crumb rubber for a given length of road can be calculated. Assuming a stretch of pavement that is 1-mile-long, 24 feet wide (2-lane

highway), and 2 inches thick, the volume of pavement is approximately 21,120 ft^3. Using the bulk density suggests that the weight of one mile of pavement is approximately 3,284,679 lbs. Finally, using the percent zinc by mass of RHMA-G pavement would show that the total amount of zinc contained within 1 mile of 2-lane highway pavement is approximately 788.3 lbs of zinc. Table 5 summarizes the parameters used and results from estimating the mass of zinc contained within 1 mile of RHMA-G 2-lane highway. It is important to note that the majority of this zinc is not bioavailable but instead bound within the pavement, and does not come into contact with surface water or stormwater runoff.

Table 5: Calculation parameters used for estimating the mass of zinc contained within 1 mile of 2-lane highway.

Parameter	Value	Unit
Pavement thickness	2	inches
Pavement width (two lane highway)	24	feet
Pavement volume	21,120	ft^3
RHMA-G RICE value	2.55	
Maximum pavement density	163.7	lb/ ft^3
Bulk pavement density assuming 5 percent air voids (Van Kirk 2016)	155.5	lb/ft^3
Weight of one mile of pavement	3,284,679	lb
Total mass of zinc contained within one mile of RHMA	788.3	lb

Studies on Rubberized Hot Mix Asphalt Zinc Leaching Rates

Vashisth et. al (1998) performed a constituent leaching and simulated rainfall test comparing rubberized and conventional pavement specimens. The RHMA specimens were wet-process RHMA with a CRM content of 1.11 percent of total weight, and dry-

process RHMA with a CRM content of 3 percent total weight. These two pavement types 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 tests were performed, one using neutral pH while the others contained water with pH of 2 (low) and pH of 12 (high). Nitric acid and sodium hydroxide were used to establish the differences in pH. At high and low pH, the dissolved zinc leaching from the RHMA wet and dry-process pavements is higher than the conventional HMA (Table 6). At a neutral pH, however, the dissolved zinc content of the wet-process RHMA was less than the conventional HMA (half as much) while the dry-process showed over double the amount of the conventional HMA.

Table 6: Zinc leachate concentrations from rubberized pavement 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 mixes as before in a simulated environmental conditions test. The pavement specimens 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 7). The result suggests that the wet-process RHMA behaves differently to UV light aging and wear than the other specimens under simulated high-intensity rainfall as compared to its lower leaching rate under the quiescent batch leaching. All of the zinc concentrations in the runoff were similar, considered by the author to be negligible and considerably lower than proposed toxicity limits.

Table 7: Zinc concentrations in runoff from various rubberized pavement specimens under simulated rainfall conditions (Vashisth et. al 1998).

Slab Specimen	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 three specimens of 10 different pavement types (CRM included) under a variety of temperature and age conditions (CalTrans 2008). Pavement specimens tested in the study include RHMA-O, RHMA-G, open-graded asphalt concrete (OGAC), dense-graded asphalt concrete (DGAC), and portland cement concrete (PCC). 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 specimens. Simulated aging was performed on the aged replicates by heating them at 85 degrees Celsius for six days, representative of 15-18 years of in-service pavement life.

The authors initially chose a rainfall event that simulated 0.1 inch of rainfall for a duration of 48 hours as it would be representative of field conditions, however, they

explain the resulting effluent volume would be too small to perform all testing and instead chose a rainfall of nearly double the initial amount. The authors acknowledge this represents an amount of rain that would “flush the specimens 16 times” and that the water flow “would be almost sheet flow.”

Although the resulting metal concentrations are significantly diluted compared to more realistic stormwater runoff volumes, comparisons of constituent concentrations between pavement types and fresh vs. aged pavement specimens are still useful. The result agrees with other findings in that it identified that zinc is more likely to be found in elevated concentrations in runoff from newly paved or sealed surfaces (Mahler et. al 2003). A statistically significant difference in zinc concentration was found between fresh and aged pavement specimens in the cold (4 degree-Celsius) temperature, with fresh specimens presenting higher concentrations of zinc. These findings provide insight to 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 adsorb copper and zinc, suggesting that using concrete in pavement design may effectively reduce zinc loading. Also, with regard to permeable pavement, the authors note that increased surface void space and porosity did little to reduce total copper and zinc loading because low pH

rainwater caused these metals to leach into the water and flow through the sample leading to no significant increase in pollutant retention.

RHMA in California

RHMA paired sampling in California

Due to a high level of variability in point and non-point sources of zinc in urban and transportation associated 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 while still testing 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

Data from paired sampling efforts (CalTrans 2012) are presented initially here and analyzed further in conjunction with additional paired sampling results in the Results and Discussion. Raw data for three CalTrans paired RHMA sampling locations and the resulting figures are shown below and detailed in Appendix A and Appendix J of the CalTrans report. Dissolved and total zinc content in stormwater runoff from HMA and RHMA was determined at Atascadero (Figure 2), Merced (Figure 3) and Visalia (Figure

4). 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. It should be noted that the types of RHMA at each site are different, with RHMA-G in Atascadero, RHMA-G (slurry seal) in Merced and RHMA-O in Atascadero.

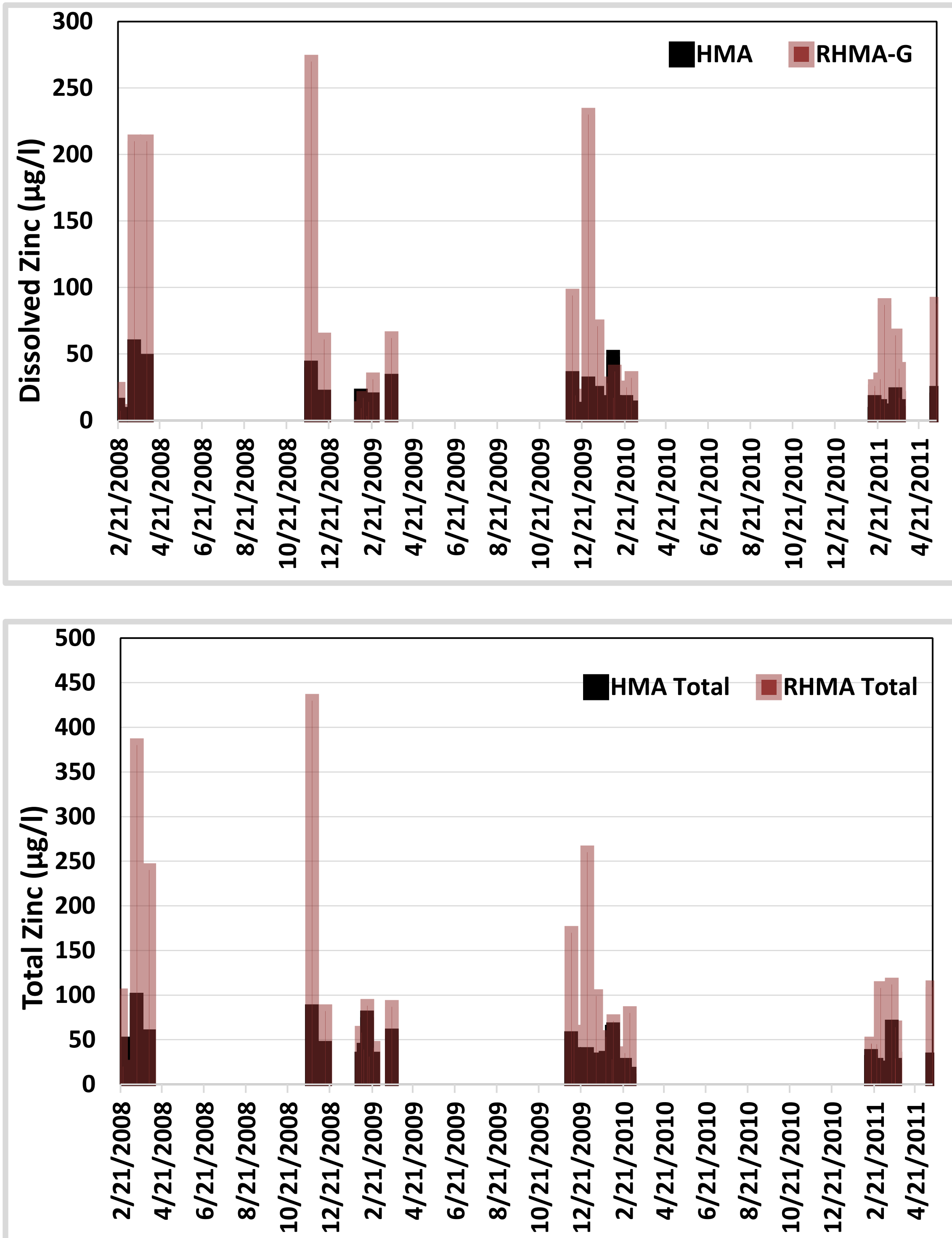
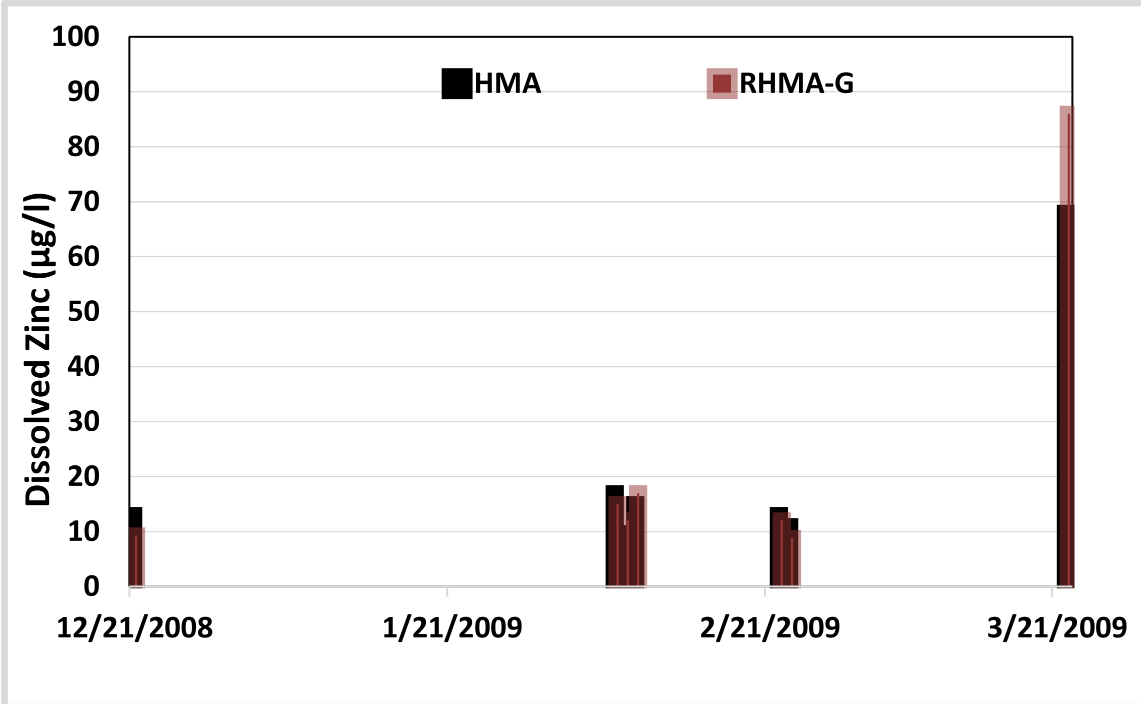


Figure 2: Paired dissolved (top) and total (bottom) zinc HMA and RHMA sampling results from Atascadero, CA (CalTrans 2012).



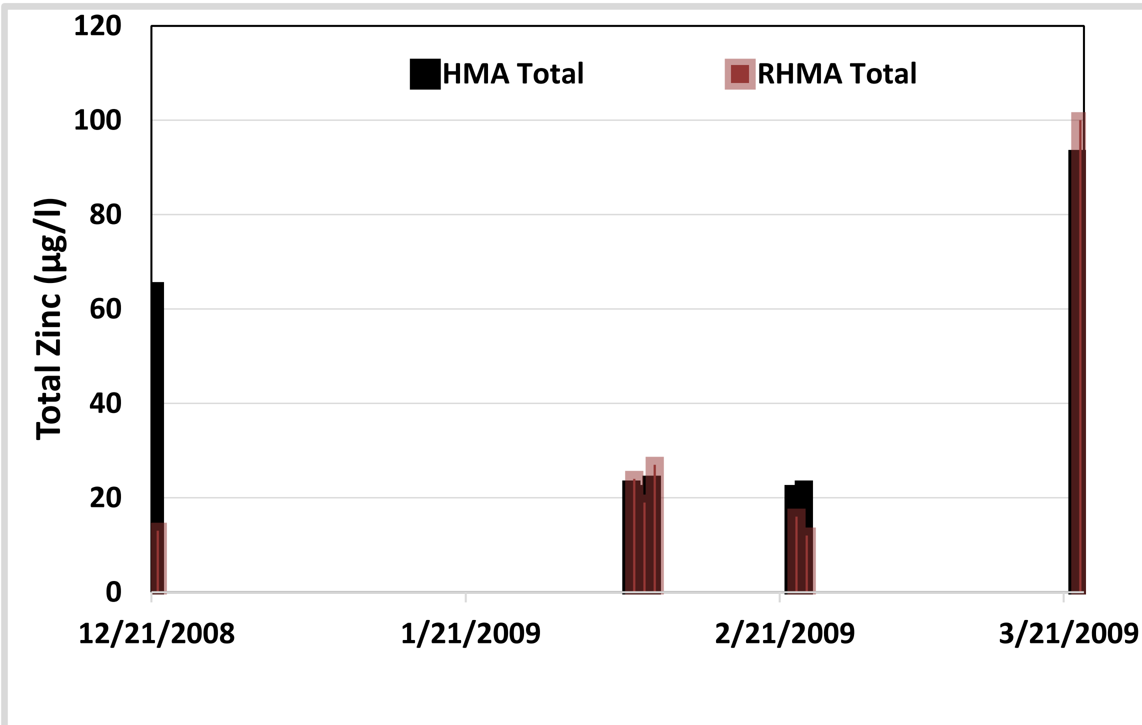
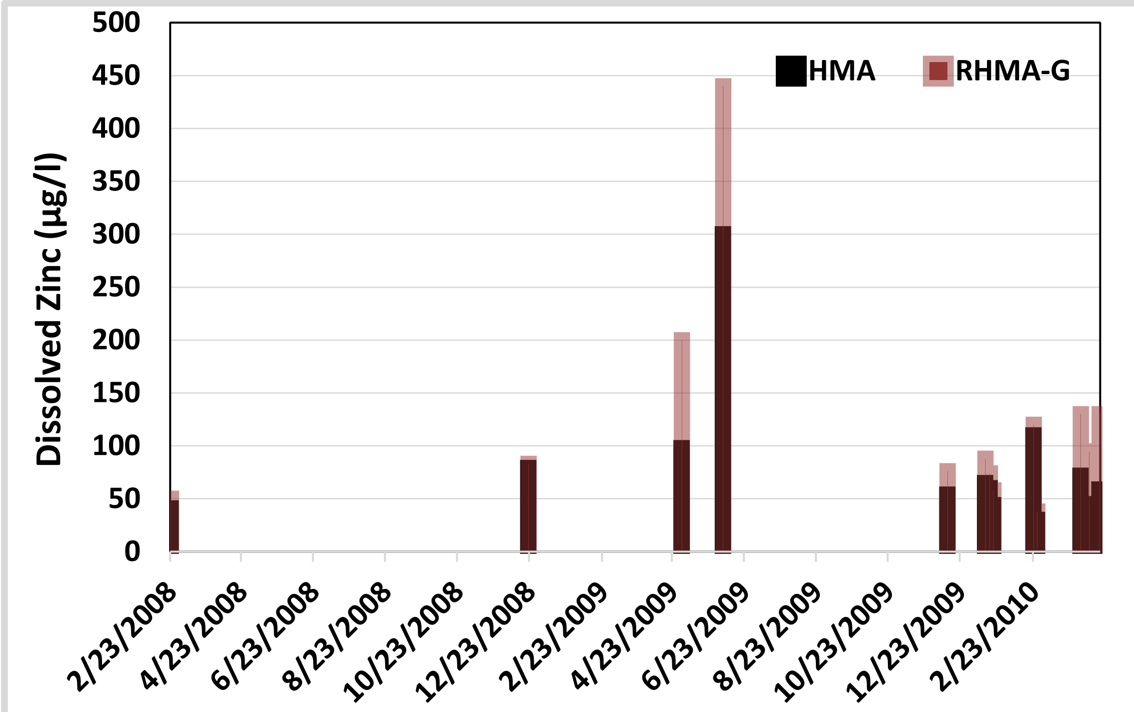


Figure 3: Paired dissolved (top) and total (bottom) zinc HMA and RHMA sampling results from Merced, CA (CalTrans 2012).



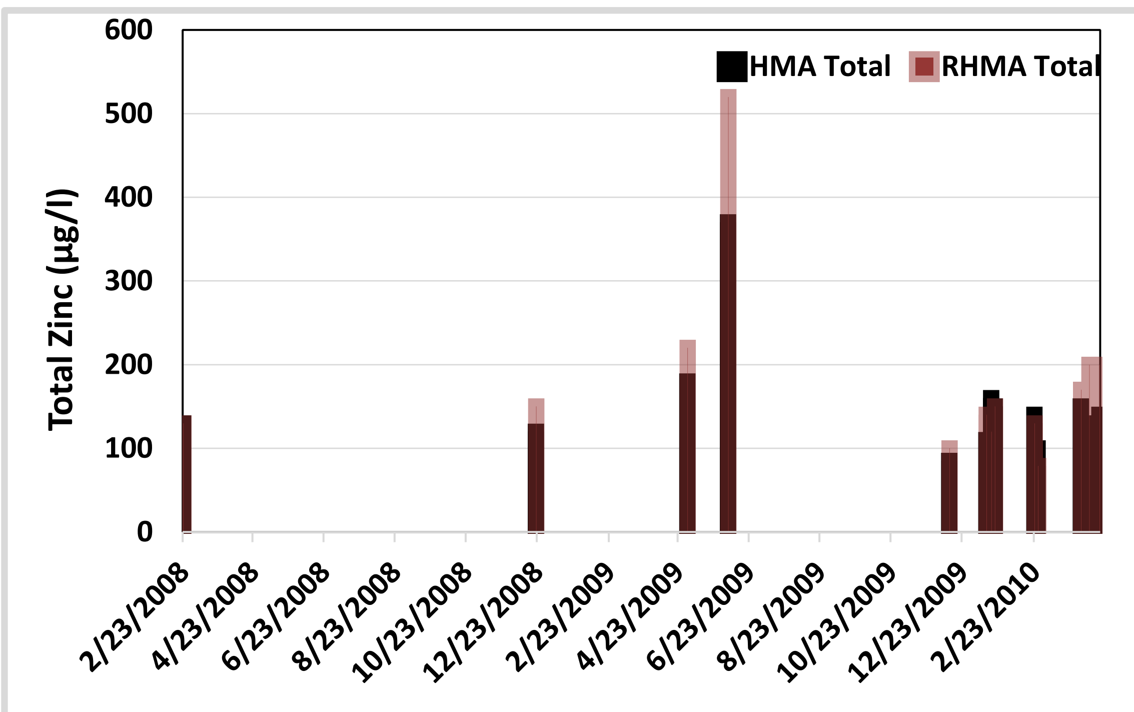


Figure 4: Paired dissolved (top) and total (bottom) zinc HMA and RHMA sampling results from Visalia, CA (CalTrans 2012).

Additional Caltrans pavement monitoring data

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), RHMA-G and RHMA-O (Table 8). RHMA is generally used as an overlay, a prev-entative 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 over seven years. This is compared to newly designed pavement life expectancies of 40 years. These are important factors to consider since both permeability and age of pavement have been suggested to influence the levels of constituents found in stormwater runoff from their surfaces as discussed in the previous section.

Table 8: Permeability of various pavement overlays based on an average of three drainage tests (CalTrans 2012).

Station	Location	Pavement	Overlay Age (years)	Overlay Depth (inches)	Drainage Time (sec)	Drainage Time (sec)	Drainage Time (sec)	Average Drainage Time (sec)	Permea bility (inches/ hour)
208-1T	Willits	OGFC	4.75	2.00	82	69	86	79	107
208-2T	Boonville	OGFC	5	1.67	234	592	310	379	19
208-2C	Boonville	OGFC	9	1.50	291	229	1,156	559	11
208-6T	Atascadero	RHMA-O	4.5	0.97	769	2,062	1,914	1,582	2.6
209-2(T1)	Red Bluff	OGFC	3.3	1.00	43	43	46	44	96
209-2(T2)	Red Bluff	OGFC	3.5	1.00	49	40	48	46	92
209-4T	Marysville	OGFC	2.8	1.50	51	26	24	34	188
209-5T	Davis	OGFC	4.5	1.42	645	696	811	717	8.3
209-5C	Davis	OGFC	16.8	0.75	480	480	480	51,200	0.062
209-6C	Vernalis	RHMA-O	3.8	1.00	434	470	643	516	8.2

CalTrans found that RHMA-O sites, although paved relatively recently, hold the second and third lowest permeabilities of the group tested. The only site with a lower permeability is a 16-year old open-graded friction course.

Characterization of Zinc in Stormwater

The literature reveals that there are a number of significant zinc sources in any urban environment, and that the primary contributions are commonly dependent on

individual characteristics of each location. Aside from metal leaching rates from crumb rubber and rubberized pavement, it is important to consider other significant sources of zinc to stormwater. Point source metals are those that supply pollution from a single location while non-point sources (diffuse sources) are pollutant sources generated over a large location (Chiew et al. 1997).

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. Walker et al. (1999) for example, 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 which also 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 9).

Table 9: Total zinc concentrations in stormwater runoff for four studies as reported by Walker et al. (1998).

Metal	NURP	NWRI	Sault Ste. Marie	Newark
Zinc (μg/l)	92.3-103.7	490	274	180-964

Walker et al. (1999) also reported significant sources of zinc in urban runoff, identified 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 research 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. Transportation related sources were identified including vehicle wear and emissions, tire degradation, and road paint. A list of road and transportation related heavy metal sources is shown in Table 10.

Table 10: Potential sources of copper, lead, and zinc in transportation related materials (Kennedy and Sutherland 2008).

Generic source	Principal source	Zinc source
Vehicles	Tires	Y
Vehicles	Brake pads/linings	Y
Vehicles	Wheel weights	N
Vehicles	Surface treatments/coatings	Y
Vehicles	Emissions	Y
Vehicles	Fluid losses, drips and spills	Y
Vehicles	Air bag initiators	UL
Roads	Road dust	Y
Roads	Road paint	Y
Roads	Road surface (eg bitumen)	UL
Other	Guard Rails	Y
Other	Galvanized Drain Pipes	Y
Other	Light Posts	Y
Other	Sign posts	Y

Note: Y = yes, N = no, P = possible, UL = unlikely.

Deposition and distribution

Identifying heavy metals 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 in which 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 zinc-containing construction materials and tires made up 77-89 percent of zinc 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 length of dry period and potential removal by street sweeping or washoff.

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. Research conducted 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 drifted to a road buffer zone of approximately 10-meters on either side of the pavement.

The concentration of constituent washed away in stormwater varies depending on the constituent form, time elapsed since the last storm (buildup) and runoff volume. Since less energy is required to keep them suspended, peak levels in dissolved pollutants

generally occur before particulate pollutants (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.

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 amount of tires being 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 showed that annual zinc released by tire wear in the U.S is 10,000 - 11,000 metric tons. A comparison with atmospheric deposition suggested that 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 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 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 a range of 16 – 120 million pounds of oil. As cited by CEPA (2006), the New Zealand Ministry of Transport (2002) estimates the rate of oil lost to roadways to be 2.8 ml of oil per 1,000 km. Assuming an oil density of 800 g/l and 0.1% zinc by weight, the amount of zinc polluted by vehicles is 3.58 µg / 1,000 miles.

Heavy metals in 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. McLean et al. (1992) suggest that the background soil zinc concentration will usually vary between 10-300 mg/kg.

Brown and Peake (2005), collected samples of road debris (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 nearby to the roadway sampling locations. The samples were taken over a two-year period including seven storm events. Heavy metal concentrations in the road debris ranged from 241 – 1,325 µg/g for zinc. Drying and measuring the metals 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 metals emission from transportation related sources and found that aside from exhaust particles, 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.

Zinc Urban Stormwater Loading Estimates

Studies on heavy metals and other constituent sources of urban stormwater have been completed. These studies have focused on quantifying the heavy metal concentrations during various storms with sampling stratification of various urban sources such as roadways, rooftops, lawns and parking lots.

Zinc leaching from galvanized, painted, or coated metal surfaces

In 2012 the US produced 3.4 million tons of galvanized steel (AGA 2016). ASTM specification A653 outlines standard specifications for a zinc coated steel sheet by the process of galvanization (zinc coated) or galvannealing (zinc-iron alloy coated) by the hot

dip process. For a common G90 designation (ASTM 2013: Table 2.6) a weight requirement of zinc is specified as 0.90 oz/ft^2, which since this is applied on both sides, then a single side contains zinc at 0.45 oz/ft^2, or 137.2 g/m^2.

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 to be 2.87g 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 following:

- Metal roofing can be a major contributor (up to 75 percent of zinc in an industrial site)
- In a commercial site: roofing 51 percent, tires 20-40 percent
- In a residential site: tires 40 – 80 percent, 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 a three times higher zinc concentration from a roof with galvanized metal compared to a roof without, showing 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 in Christchurch, New Zealand (concrete tile roof, copper roof, galvanized roof, coarse asphalt road). Grab samples and automatic sampling was used to capture samples of the first two liters of runoff (capture of 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 1970 µg/L (over three times the mean zinc concentration found on the coarse asphalt road). This research shows that residential and commercial roofing has a potential to generate high concentrations of zinc in stormwater.

<u>Basin scale zinc contribution assessment</u>

Steuer et al. (1997) sampled heavy metals from 33 sites (eight urban surface source types including high, medium, and low traffic streets, residential driveways, residential rooftops, commercial rooftops and grass area) in an urban catchment basin of Marquette Michigan over the course of 12 storms. Samples were taken concurrently at all 33 sites using automatic street samplers with attention paid to avoidance of capturing first

flush samples. This was done by capturing samples throughout the entire storm thus obtaining event mean concentrations (EMC's) for each storm. Commercial rooftops produced the highest mean concentrations 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 were a major contributor of total zinc (30 percent). A summary of the percent contribution for each location is included in Table 11.

Table 11: Percent contribution of zinc for eight source locations within a catchment basin of Marquette, Michigan (Steuer et al. 1997).

Source	**Percent 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	-

Davis et al. (2001) sampled for a variety of metals in Maryland, USA. Synthetic rainwater was used to collect samples from various outdoor urban surfaces in an attempt to quantify the contribution of each to the total load. The results of zinc loading from common building surfaces is shown in Table 12.

Table 12: Zinc concentration in runoff resulting from spraying synthetic rainwater on outdoor surfaces (Davis et al. 2001).

Material	**Count**	**Mean Zinc Concentration (µg/ m²)**	**Maximum Zinc Concentration (µg/m²)**
Brick	30	2100	23000
Painted wood	13	2800	8400
Concrete	7	1200	1900
Metal	4	690	2500
Unpainted wood	3	330	730

From runoff samples from residential, commercial and institutional roofing, the authors recorded mean zinc concentrations of 100 µg/l, 1100 µg/l, and 1100 µg/l, 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. From sampling of brake materials, the authors estimate that the environmental loading of zinc from brake wear is 89 µg/km/vehicle.

Davis et al. (2001) compile their testing and assumptions to make a basin wide estimate of the percent contribution of each material to 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 13). The authors do however note that their estimates for the loading rate from siding is the equivalent to continuous washing, which is likely not an accurate 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. Still, the relative contributions from this preliminary mass loading balance give useful reference for potential source loading rates.

Table 13: A mass balance estimate for zinc in the urban environment shows that siding and tires are the main contributors (Davis et al. 2001).

Material	Zinc Loading (kg/ha-yr)	Percent of total
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

Literature Summary

While there are many studies addressing the sources of zinc in stormwater runoff, there are challenges, conflicts and gaps in the available information. Findings suggest that significant contributors of zinc to urban stormwater include building siding material (brick and painted wood), atmospheric deposition, tire wear particles and runoff from zinc coated (galvanized) metals (Davis et al. 2001, CASQA 2014; Gunawardena et al. 2013; Kennedy and Sutherland 2008, WSDOE 2008). There is conflicting information as to which of these sources are large contributors, with varying levels of contribution identified from each source in various basin-scale assessments. Though there have been numerous studies that account for and quantify zinc from various sources, less of this research has been focused on transportation related sources and roadways. Little has been done to characterize the differences in zinc leaching rates of RHMA pavement in comparison to conventional HMA.

Studies on zinc leaching from RHMA and HMA pavements are generally either laboratory or field experiments. Results from these studies show little or no difference in leaching rates from RHMA compared to conventional HMA if the testing was performed in the laboratory, while field testing results have shown higher concentrations of zinc in stormwater from RHMA pavement surfaces. 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. This situation supports the need to study these materials in a laboratory controlled environment as well as in-field as an attempt to determine the potential influence of the pavement in a controlled environment as well as when subjected to the many factors involved in actual roadway use.

METHODOLOGY AND APPLICATION

This section provides a description of the experimental methods used in the study. It will first outline details of two laboratory batch leaching experiments, followed by a description of field data collection for assessment of zinc leaching from rubberized 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 200.7 and EPA 200.8 version 4.4 methodology (USEPA 1994).

Materials

Pavement materials used in this analysis were prepared and provided by the California State University, Chico Pavement Preservation Center. Provided materials include: passenger crumb rubber, high natural rubber (truck) crumb rubber, scrap crumb rubber (75 percent passenger, 25 percent high natural rubber), asphalt extender oil, asphalt rubber binder, rubberized asphalt concrete (RHMA) (core compacted and non-compacted forms), and conventional HMA cores. These materials were tested for zinc content (Table 14).

Table 14: Zinc content of various materials used in the laboratory portion of this research.

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

Crumb Rubber Batch Leach Testing

The crumb rubber samples were sieved into three diameter classes for comparison of their relative size classes and distribution (Table 15). Crumb rubber modifier specification requires that 100 percent of the CRM passes the number 10 (2mm) sieve. Since none of the high natural rubber crumb was greater than 2 mm in diameter, two size classes were chosen for analysis as less than 0.5 mm (small) and greater than 0.5 mm (large) for each rubber type. The size classes of 0.5 – 2 mm and > 2 mm were recombined to create a single “large size class for sampling. Figure 5 shows representative material of the two different size classes for passenger tire crumb rubber.

Table 15: Weight and mass percentages for passenger and truck crumb rubber samples as sorted into three size classes.

Size class	Passenger Tire Crumb Mass (g)	Percent of Total Mass (%)	High Natural Rubber Crumb Mass (g)	Percent of Total Mass (%)
<0.5mm	63.7	4	217.4	53
0.5mm-2mm	1451.5	84	193.4	47
>2mm	202.6	12	0	0
Total	1717.8		410.8	

Figure 5: 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).

A crumb rubber leaching study was designed using the passenger and truck crumb rubber. Forty samples were created by taking each size class (small and large) for each of the two types of rubber and creating 10 duplicate samples of each class. This resulted in ten small passenger tire samples (PS), ten large passenger tire samples (PL), ten small truck tire samples (TS), and ten large truck tire samples (TL). Each sample consisted of three grams of tire, submerged in 240 milliliters of distilled water and placed in small bottles (Figures 6 and 7).

Figure 6: The small passenger crumb rubber batch leach test samples.

Figure 7: Forty batch leaching samples, each consisting of three grams of crumb rubber submerged in 240 milliliters of deionized water.

Leachate samples from each of the four categories were filtered using a 1.5-micron glass microfiber filter, preserved in nitric acid and submitted for laboratory testing of dissolved zinc content after various periods of elapsed time. The first two samples were taken after two and four days spent leaching, and these samples were taken in duplicate to assess the consistency in leaching rates across the samples. Each of the

following samples were taken as singular samples in order to maintain enough samples to span an adequately long period of leaching.

RHMA and Conventional Pavement Batch Leach Testing

A pavement core batch leaching test was conducted to assess the rate that dissolved zinc leaches from rubberized pavement, in comparison with conventional pavement. All pavement cores were approximately six-inches in diameter, 2.4 inches tall and weighed between 2308 and 2362 grams (Table 16). A representative RHMA core is shown in Figure 8.

Table 16: Characteristics of two RHMA and two HMA core samples used in leaching experiment.

Parameter	**RHMA Core Characteristics**	**RHMA Core Characteristics**	**HMA Core Characteristics**	**HMA Core Characteristics**
Sample	1	2	1	2
Height (in)	2.4	2.4	2.4	2.4
Diameter (in)	6	6	6	6
Volume (in^3)	67.2	67.2	67.2	67.2
Surface Area (in^2)	101	101	101	101
Weight (g)	2307.7	2341.1	2361.8	2353.7

Figure 8: A representative pavement core used in the pavement core batch leaching test.

Each core was placed into a covered glass jar that contained seven liters of deionized water (Figure 9). Samples were taken after two and four days to assess the initial leaching rate and subsequent samples taken were spaced sufficiently far apart to capture the rate of change of leaching. After the varying time intervals, a 50 ml graduated cylinder was rinsed twice with deionized water and then used to extract 100 ml of water from each pavement bath. The contents of the jars were gently stirred prior to taking a leachate sample to mix any stratification of leached metals. Each sample was preserved in nitric acid and submitted to the laboratory for assessment of dissolved zinc content.

Figure 9: Four pavement cores placed in deionized water to assess the difference in zinc leaching from rubberized pavement in comparison to conventional pavement.

Paired Rubberized Hot Mix Asphalt Stormwater Sampling

Humboldt State University and GHD Consultants began collection of stormwater runoff from paired rubberized and non-rubberized road surfaces for analyzing zinc concentrations on December 20, 2018. This section describes monitoring location characteristics as well as the methodology for sample collection.

To assess differences in stormwater zinc concentrations between RHMA and HMA pavement, runoff samples were collected from both types of pavement in close proximity to each other (at either side of the edge of a change in pavement type). The locations in California where these paired RHMA stormwater runoff samples were collected and the monitoring team responsible for the data collection efforts along with the locations from previous sampling efforts by CalTrans are shown in Figure 10.

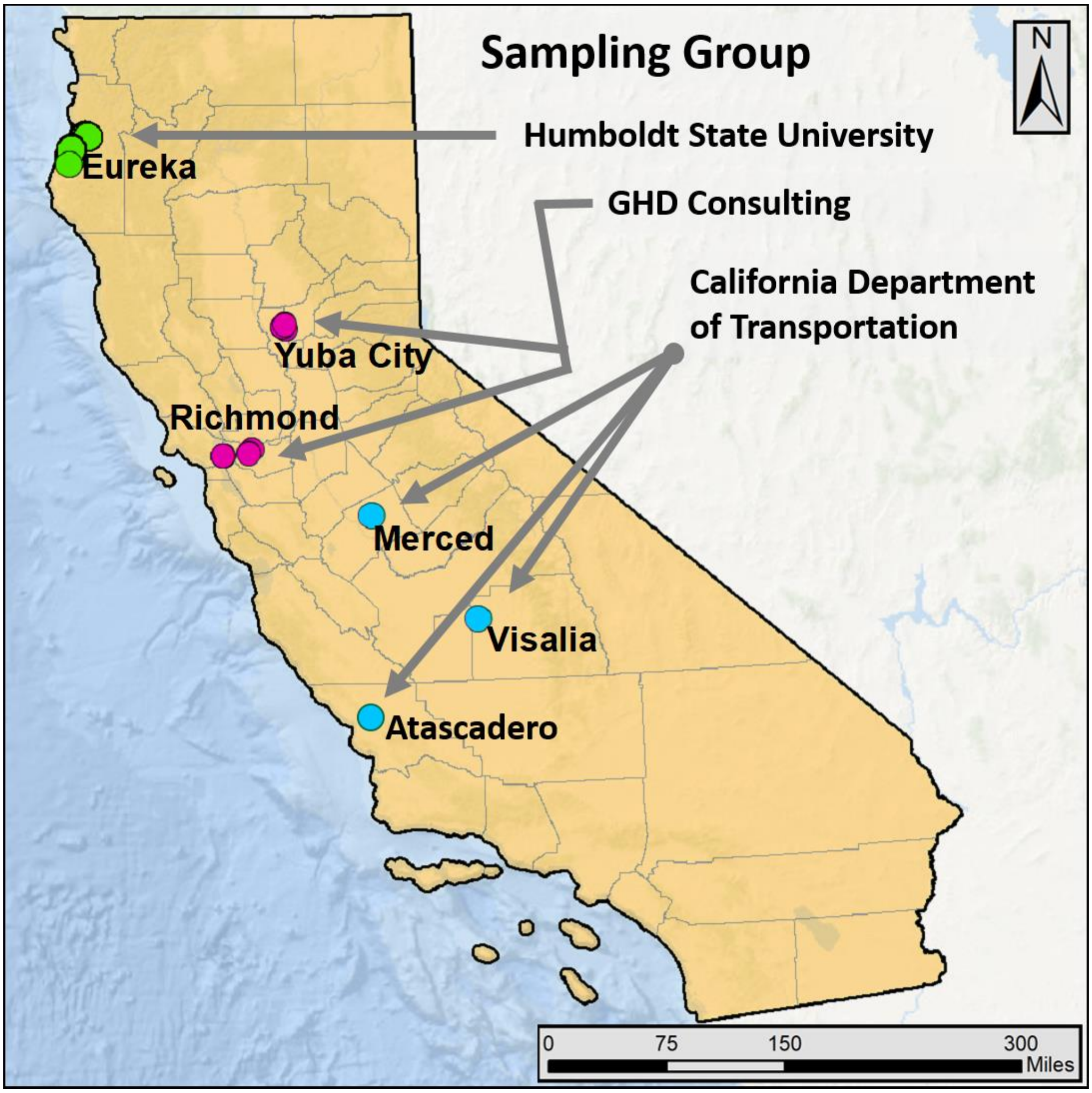


Figure 10: California paired RHMA sampling sites and the associated sampling group.

<u>Description of monitoring locations</u>

Humboldt State University focused on selecting suitable monitoring sites for comparison of stormwater runoff zinc concentrations between conventional pavements and RHMA in Northern California. Eight different roadway monitoring sites were

established, three on conventional pavement and five on RHMA. At each monitoring site, runoff samples were collected from non-RHMA pavement and from RHMA pavement within close spatial proximity (Figure 11). Each of the monitoring sites are located near the start or end of RHMA pavement projects to monitor the difference in zinc concentrations from runoff collected on the conventional and RHMA pavement surfaces while minimizing differences in other potential zinc sources such as traffic, soil type, galvanized metal surfaces, etc. The first monitoring site (299 RAC, 299 non-RAC) is located on Highway 299 near postmile 5.5 and the exit to Blue Lake, CA. The second (101N RAC, 101N Non-RAC) and third (101S RAC, 101S non-RAC) monitoring sites are located at the ends of an RHMA project that extends from the southern end of Eureka near Herrick Avenue on US 101 (postmile 75.1) south to College of the Redwoods (postmile 69.9). The fourth site (101 FSS/FSN RAC) was the southern-most sampling location located on US 101 (postmile 65.4). Both of the monitoring sites in this location tested runoff from RHMA, but were considered sufficiently close to the 101S non-RAC location for paired analysis. A summary of the RHMA projects and the individual monitoring locations is shown in Table 17.

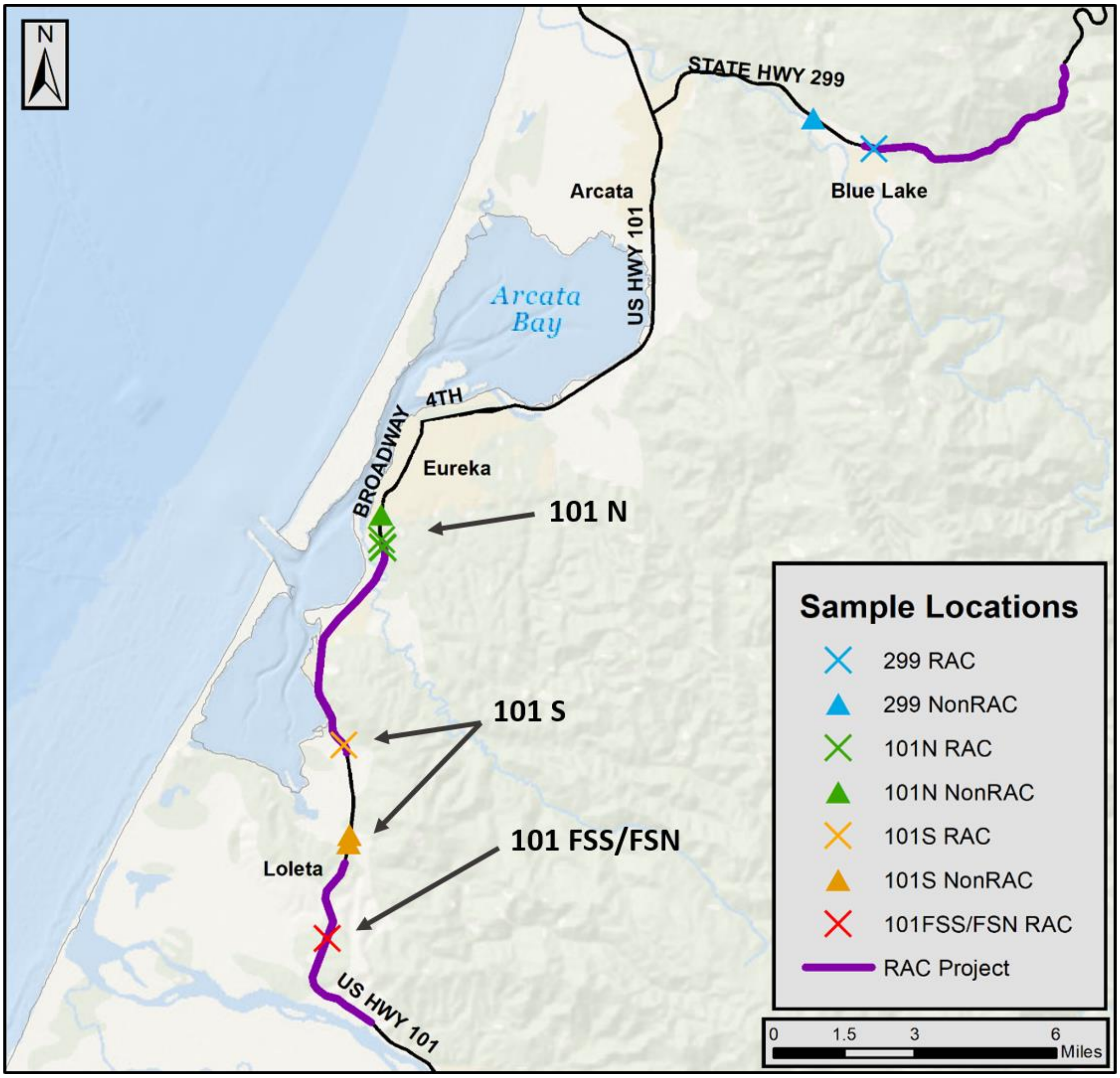


Figure 11: A map showing stormwater runoff monitoring site locations near Eureka, CA and Blue Lake, CA.

To further assess stormwater runoff monitoring site characteristics, shapefiles of annual average daily traffic (AADT) observations and annual average daily truck traffic (AADTT) observations from 2018 (Caltrans 2019) were compared to the selected monitoring site locations (Table 17). Highway 299 AADT estimates are nearly 1/10th of traffic estimates recorded for Highway 101. The Highway 101N monitoring site has the

highest estimated AADT, totaling 33,000 vehicles per day at the 101N non-RAC site and 30,200 vehicles per day near the 101N RAC site. Differences in AADT between RAC and non-RAC sites are relatively small and represent traffic entering or exiting the roadway between sampling locations. Truck traffic accounts for approximately $1/10^{th}$ of the daily traffic at each of the locations. Each of the AADT estimates were located within a quarter mile of each monitoring site, while the AADTT observations were sparser and are coarse approximations. The differences were largest for the Blue Lake site due to the off-ramp for the town being located between the RHMA and NonRHMA sampling sites, and the primary direction of traffic is to and from the town of Blue Lake passing through the Non-RHMA site.

GHD sampling in Yuba City mostly occurred in residential and commercial areas on non-highways. AADT is not readily available in this location, 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 site being within 0.5 miles of each other. The third site was Gray Avenue, a commercial site bordered by parking lots. GHD also sampled in Richmond, on Ohio Ave near the intersections with S 1^{st} Street and S 5^{th} Street. Samples taken on Ohio Ave 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 Ave contains mixed residential and commercial areas, with the commercial areas focused toward the Non-RAC sampling locations.

Table 17: RHMA Paired Sampling Site Characteristics

Location / Sample ID	Roadway	RHMA AADT	Non RHMA AADT	RHMA Project End Date	RHMA Type	Source
Blue Lake - 299	**Highway 299**	5,000	9,800	Aug 2016	Open Graded	RebuildingCA, 2019, Caltrans 2019
Eureka – 101N	**Highway 101**	30,200	33,000	Jan 2015	Gap Graded	RebuildingCA, 2019, Caltrans 2019
Eureka – 101S	**Highway 101**	25,500	22,800	Jan 2015	Gap Graded	RebuildingCA, 2019, Caltrans 2019
Eureka – 101FS	**Highway 101**	23,400	22,800	Fall 2019	N.D.	RebuildingCA, 2019, Caltrans 2019
Merced	**Highway 99**	51,000	51,000	RHMA - Fall 2005 Slurry Seal -Jul 2008	Gap Graded - Slurry Seal	CalTrans 2012
Visalia	**Highway 99**	53,000	53,000	Sept 2005	Gap Graded	CalTrans 2012
Atascadero	**Highway 41**	10,100	10,100	Dec 2005	Open Graded	CalTrans 2012 (Appendix O)

<u>Sample collection</u>

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 metals. Samples were collected from the pavement with a rotary hand pump and bottled on-site (Figure 12).

Figure 12: The rotary hand pump used to collect stormwater samples from pavement.

Generally, the sample collection process would take no more than two hours, after which the 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

The results for this study are presented first as findings of the crumb rubber and pavement leaching studies. The timing of taking samples during the leaching experiments emphasized a few samples early to catch the expected relatively high initial loss rate, and then gradually increasing the time between samples to document the longer term loss rate (Table 18).

Table 18: Elapsed time when each sample was taken for analysis of dissolved zinc content for each of the leaching experiments (days).

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
RHMA	2	4	14	38	61
HMA	2	4	26	49	--
Passenger and Truck Crumb	2	4	21	61	--

After discussing the leaching study results, the paired pavement sampling results and analysis are shown. Third, a comparison of zinc contributions between RHMA, tires and galvanized guardrails is conducted, utilizing some of the leaching rate data that were presented in the preceding sections. Initial discussion of these analyses is included in this section, while additional considerations are introduced in the discussion section that follows.

Crumb Rubber Zinc Leaching

The mass transfer rate of zinc from the crumb rubber was calculated using dissolved zinc concentrations of the leachate compared with the overall zinc mass within each rubber sample. The results for the 61-day period show that the passenger crumb had

a higher average mass transfer rate than truck crumb, and smaller particles have a higher average mass transfer rate than large particles (Figure 13). This result was expected given that passenger crumb rubber contains more zinc and smaller particles have a greater surface area in contact with the water. For the passenger crumb, the mass transfer rate declined throughout the experiment, with the large passenger crumb falling below that of the small truck crumb around day 60. For the truck crumb, the rate declined between two and four days of leaching and was slightly higher for the 21-day and 61-day leaching results (Figure 13). These results suggest that the smaller sized particles expected to be generated from tire wear would have a higher mass transfer rate than the larger sized crumb rubber used in RHMA. Also, it is shown that passenger tires leach zinc at a faster rate in their initial leaching period, and both take at least 60 days to reach a steady leaching rate. Since the crumb rubber used in RHMA contains a high percentage of passenger crumb, this implies that the highest leaching rates of zinc from RHMA will be observed in the first days it is exposed to water.

The pH results show that pH for the passenger and truck crumb ranges from 5.98 to 6.35 (Table 19). Smolders and Degryse (2002) found that the truck crumb rubber has the potential to raise pH of surrounding soil or water. Though a small difference, it has been shown that pH is negatively correlated with zinc leaching rates from crumb rubber (Rhodes et al. 2012).

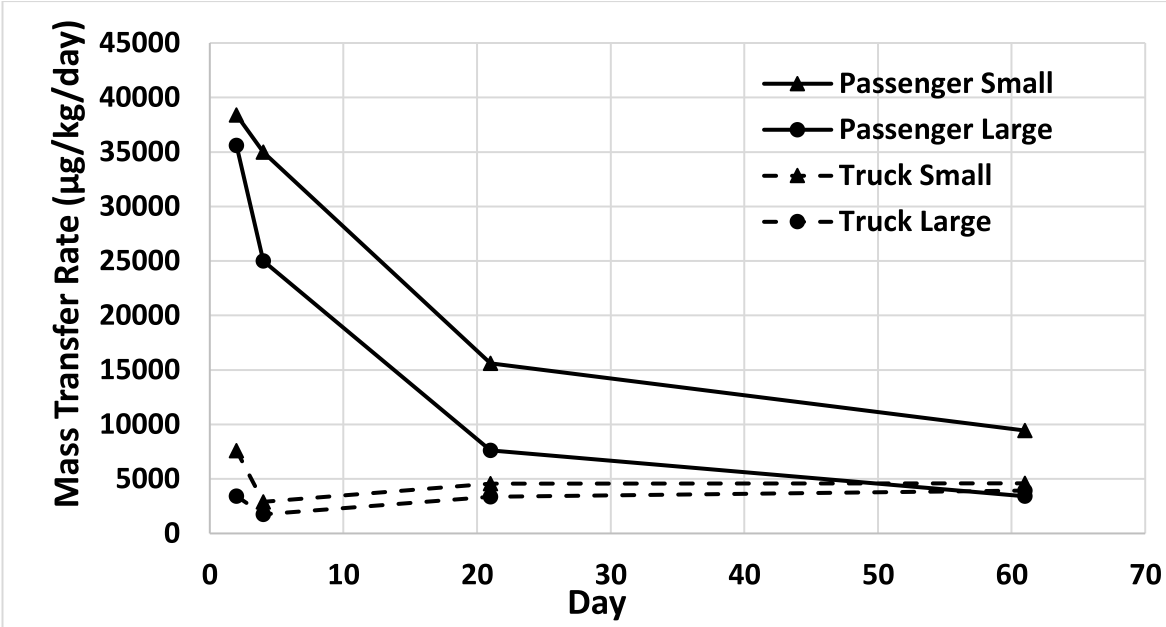


Figure 13: Mass Transfer rates calculated for passenger and truck crumb rubber from the leaching experiment show higher rates from passenger crumb and smaller particle sizes.

Table 19: pH results from four samples tested approximately one hour after initiation of leaching experiment.

Sample	pH
Truck Small	6.35
Truck Large	6.34
Passenger Small	5.98
Passenger Large	6.05

Pavement Zinc Leaching

RHMA and HMA samples were left to leach in distilled water continuously for 61 and 41 days, respectively. These leaching experiments are ongoing. Resulting average sample concentrations show that both of the pavement types gave an initial pulse of zinc into the solution, but the mass transfer rate of each had fallen below 5 µg/ft^2/day within

30 days (Figure 14). The final zinc concentrations of the leachate for each of the RHMA samples were 12 μg/l and 14 μg/l, while both the HMA samples returned non-detect for zinc for their 41-day leaching samples. The mass transfer rates were calculated based on the average leachate zinc concentration from the duplicate core samples. If a sample returned non-detect it was excluded from the average. Non-detect occurred for one HMA sample on days 4 and 26 and for both HMA samples on day 41. Murphy et al. (2015) suggests that pavement samples containing calcium carbonate can adsorb and remove dissolved zinc from a solution. Therefore, it can be speculated that the HMA sample here may have adsorbed zinc, since the first measure showed detectable zinc concentrations in both HMA samples and the reported concentrations decreased until both eventually returned non-detectable levels. 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. It should be noted that although the RHMA samples did not show concentrations consistent with zinc adsorption, the CalTrans specifications for RHMA indicate that calcium carbonate may be added to the crumb rubber at up to three percent of the crumb rubber mass by weight (CalTrans 2018). The potential addition of calcium carbonate to pavement samples may have a significant impact on the concentrations of dissolved zinc coming from their surfaces.

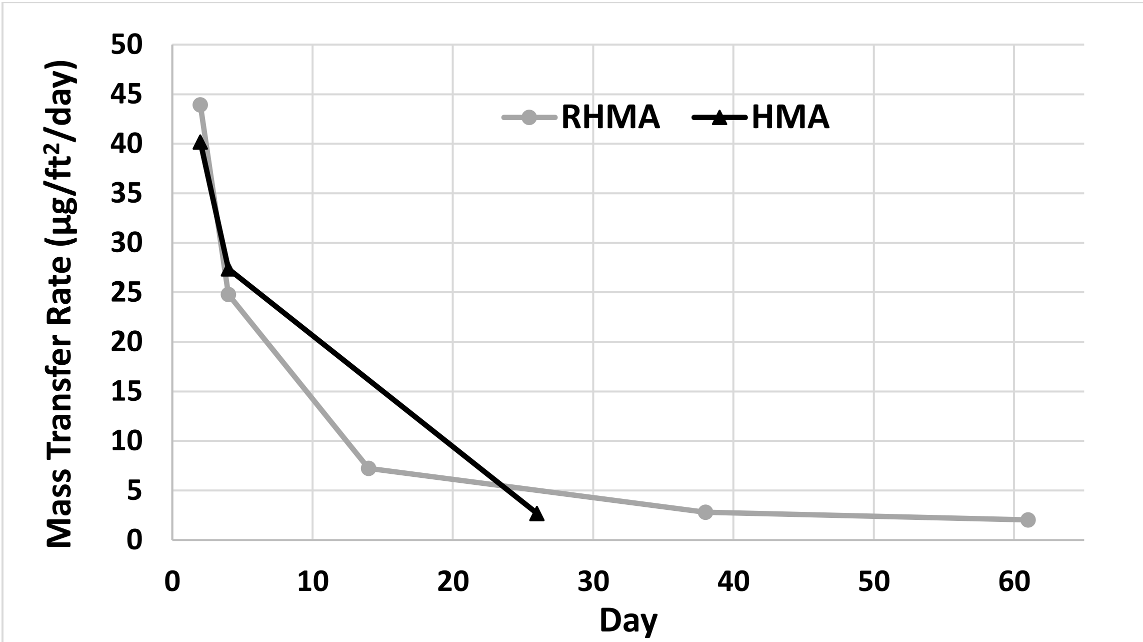


Figure 14: Average RHMA and HMA mass transfer rates show an initial pulse, followed by convergence to nearly zero mass transfer for the remainder of the study.

Combining the results of the leaching studies, at the last sample, the average mass of zinc recovered during the leaching study by passenger tires, truck tires, and RHMA were 1176 µg, 780 µg, and 90 µg, respectively. Assuming that the only zinc contained within the RHMA pavement is within the crumb rubber, then from the leaching results, 0.024 percent of zinc contained within the RHMA pavement was leached out by day 61 (Figure 15). This is in comparison to a crumb rubber zinc recovery (average of small and large sizes) ranging from 2 - 3.1 percent by day 61 (Figure 15). It is important to note that batch leaching does 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, which would likely increase the transfer

rate as wear particles 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 is likely overestimating the transfer rate for RHMA.

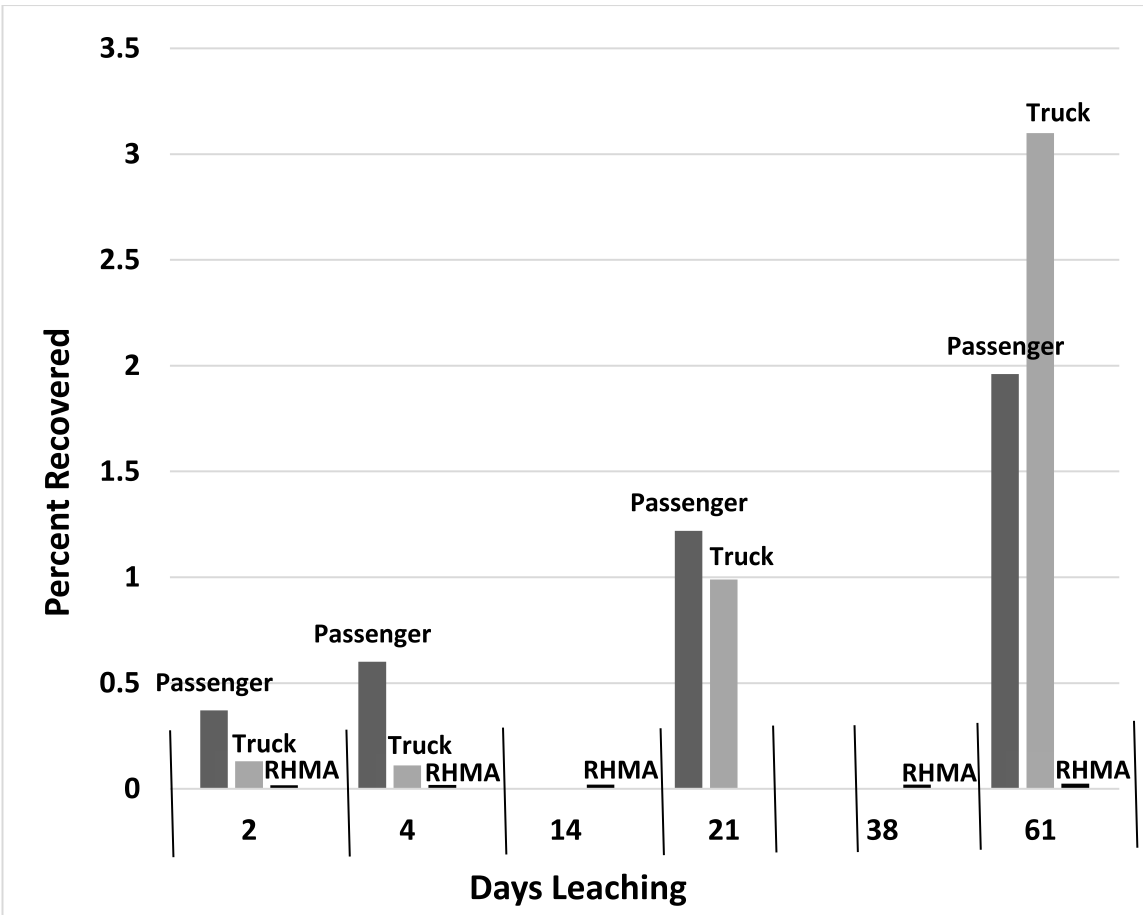


Figure 15: The average zinc recovery comparison between passenger tire, truck tire and rubberized hot mix asphalt shows a higher recovery for the crumb rubber.

There was a notable difference in color between the RHMA and HMA samples after 61 days (RHMA) and 41 days (HMA) of leaching (Figure 16 and Figure 17). While

both types of pavement started off black, by day 41 the HMA sample has a brown color. Brown coloring is likely the result of oxidation, one of the primary causes of pavement wear that leads to a stiffer and brittle pavement. This result highlights the ability of the RHMA to withstand wear and resist degradation compared to the HMA.

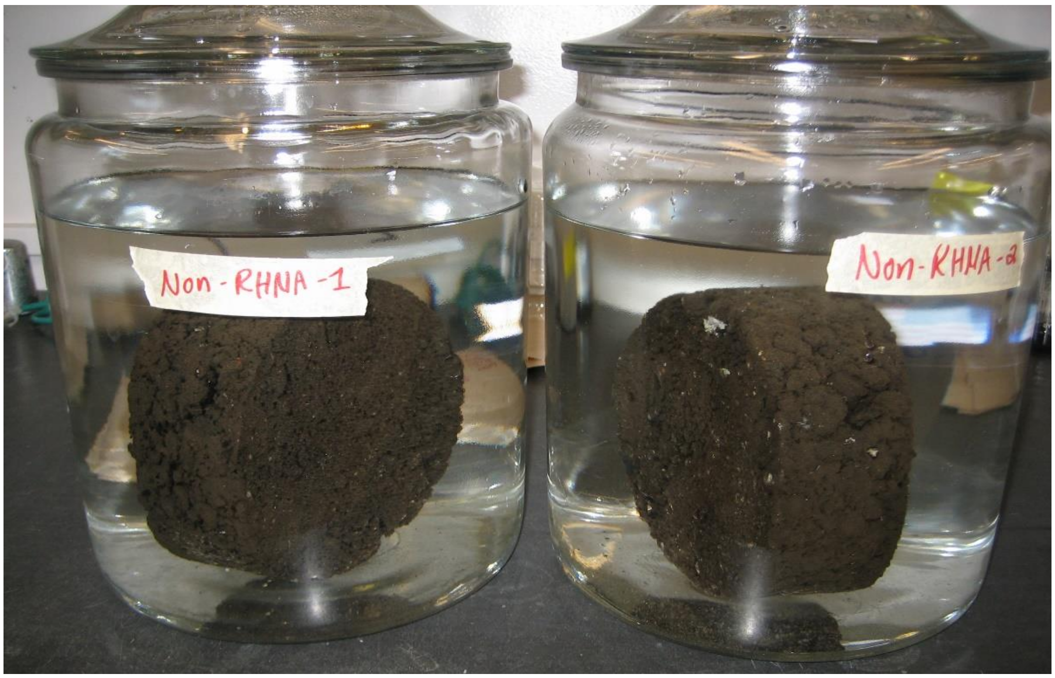


Figure 16: At the end of the leaching study, the HMA samples had turned brown in color, representing oxidation.

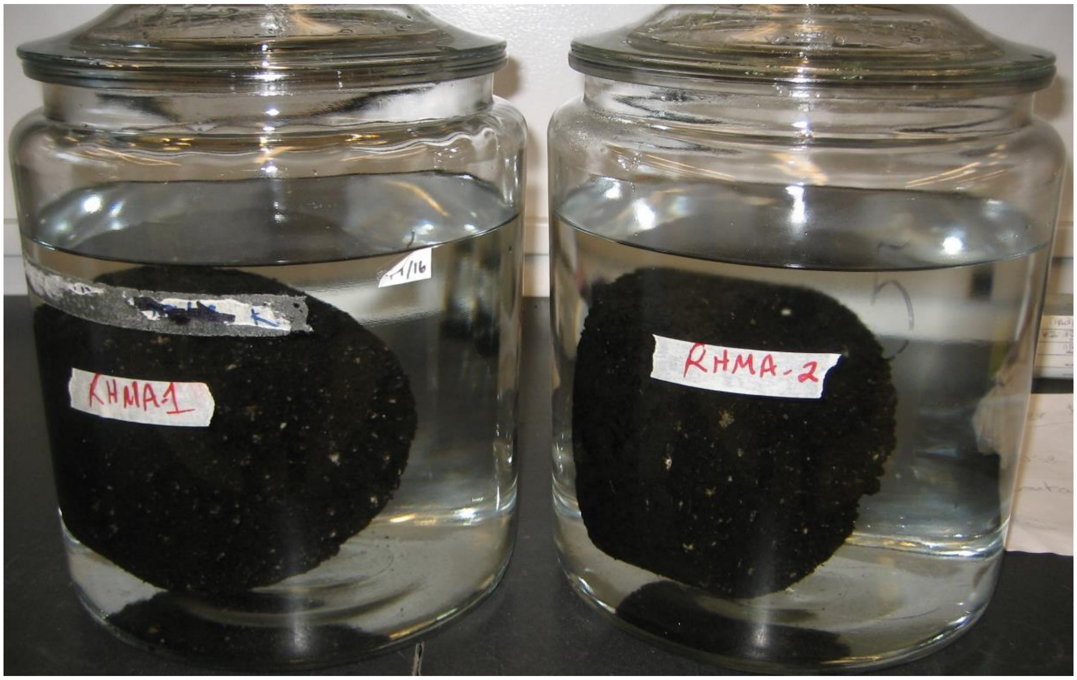


Figure 17: At the end of the leaching study, RHMA had leached 20 days longer than the HMA samples, yet it showed no discoloration or indication of oxidation.

Field Sampling Results

Field sampling results begin with overall descriptive statistics comparing dissolved and total zinc concentrations in runoff from RHMA and HMA surfaces. Sample results are then divided by location, and sites with additional data are further investigated to assess differences in various metal concentrations in stormwater collected from their surfaces. Tables summarizing all data from paired pavement sampling can be found in Appendix A.

All locations

Stormwater zinc concentration statistics were summarized between RHMA and HMA pavements across all locations (Table 20). The median soluble and median total

concentrations of zinc in runoff from RHMA pavements were 50 µg/l and 98 µg/l, respectively. The median soluble and median total zinc concentrations in runoff from HMA were lower at 38 µg/l and 65 µg/l, respectively. This represents a 27 percent lower concentration for soluble zinc and 40 percent lower concentration for total zinc from the HMA surfaces compared to RHMA surfaces.

Table 20: Descriptive statistics comparing RHMA and HMA stormwater zinc concentrations across all sites.

Type	Constituent	Mean	Median	Range
RHMA	Dissolved Zinc (µg/l)	79	50	3-850
	Total Zinc (µg/l)	143	98	12-880
HMA	Dissolved Zinc (µg/l)	46	38	4-300
	Total Zinc (µg/l)	96	65	12-450

Humboldt State University sampling analysis

A total of 65 stormwater runoff samples were collected by Humboldt State University in the Eureka, CA area between December, 2018 and February, 2020. The sampling represents data from eight locations across 16 storm events. Each of the highway runoff samples were analyzed for both soluble and total zinc concentrations. A summary of the samples collected by Humboldt State University is shown in Table 21. In the sample labeling, RAC is used interchangeably with RHMA to represent rubberized pavement. The statistics show a higher concentration of zinc at nearly every RAC site compared to its Non-RAC pair.

Sampling at the Highway 101N RAC location recorded the highest mean total zinc of 225 µg/l. The highest mean soluble zinc concentration of 132 µg/l was recorded at the 299 RAC site. The median at this site, however, was 32 µg/l. The difference in mean

and median values at this site are because the majority of samples recorded were of low concentration, and a single outlier of 850 µg/l skewed the mean.

Table 21: Humboldt State University HWY 101 and HWY 299 paired RAC pavement sampling results representing the zinc concentration in stormwater (µg/l**)**.

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

GHD sampling analysis

The data collected by the GHD Consulting group are presented in Table 22 and Table 23. GHD collected 16 samples over four storms and four locations. The data show high total zinc concentrations from RHMA in Yuba City, however there are only single observations at each location. Four samples collected from the Yuba City locations returned non-detect for both soluble and total zinc concentrations from two RHMA and two HMA sites and are not included in these statistics. The data from the Richmond sites showed considerably higher concentrations from conventional HMA compared to RHMA.

Table 22: Richmond Ohio Ave and Cleveland Ave RHMA paired pavement sampling results representing the zinc concentration in stormwater (µg/l**)**.

	Sample Count	Mean Total	Mean Soluble	Max Total	Max Soluble	Min Total	Min Soluble
HMA	5	196	46	340	68	110	ND
RHMA	5	84	34	96	47	ND	ND

Table 23: Yuba City residential RHMA paired pavement sampling results representing the zinc concentration in stormwater (µg/l**)**.

	Sample Count	Mean Total	Mean Soluble	Max Total	Max Soluble	Min Total	Min Soluble
HMA	3	131	37	170	56	ND	ND
RHMA	3	660	45	670	55	ND	ND

CalTrans sampling analysis

The CalTrans paired sampling data were also divided by location and the descriptive statistics were calculated (Table 24, Table 25, Table 26). The CalTrans data represent 98 samples, capturing 46 storm events across six locations. The CalTrans data also contain information for runoff concentrations of numerous metals in addition to zinc. The first location, Merced, shows little difference between concentrations of zinc in runoff from the two surfaces (Table 24). The RHMA at this location is a gap-graded slurry seal.

Table 24: Merced HWY 99 RHMA paired zinc monitoring does not show a difference in concentrations between the pavement types (µg/l).

	Sample Count	Mean Total	Mean Soluble	Max Total	Max Soluble	Min Total	Min Soluble
HMA	7	38	21	92	68	21	10
RHMA	7	30	23	100	86	12	9

The second site considered is a gap-graded RHMA pavement in Visalia, CA. Zinc concentrations at the Visalia site show an increase in zinc concentration from RHMA when compared with HMA (Table 25). To further investigate this difference, stormwater concentrations of copper were compiled for both pavement types and reviewed. Copper in road runoff is likely associated with brake pad and brake liner wear, and it is not contained in crumb rubber. If high concentrations of copper coincide with high concentrations of zinc, the source of the zinc may be from sources other than the pavement itself.

Table 25: Visalia HWY 99 RHMA paired monitoring results representing the zinc concentration in stormwater (µg/l).

	Sample Count	Mean Total	Mean Soluble	Max Total	Max Soluble	Min Total	Min Soluble
HMA	13	151	81	370	300	85	30
RHMA	13	178	122	520	440	79	38

Figure 18 and Figure 19 show that while zinc levels were elevated for nearly every RHMA sample compared to HMA, this was also the case for copper. The r-squared values demonstrating the correlation of zinc and copper at this site range between 0.82-0.95, indicating a strong correlation for all comparisons of dissolved and total zinc and copper. This result may suggest that higher zinc in RHMA runoff samples compared to HMA samples is due to differences in the physical composition of the pavement rather than leaching of zinc from the rubber in the binder at the RHMA site.

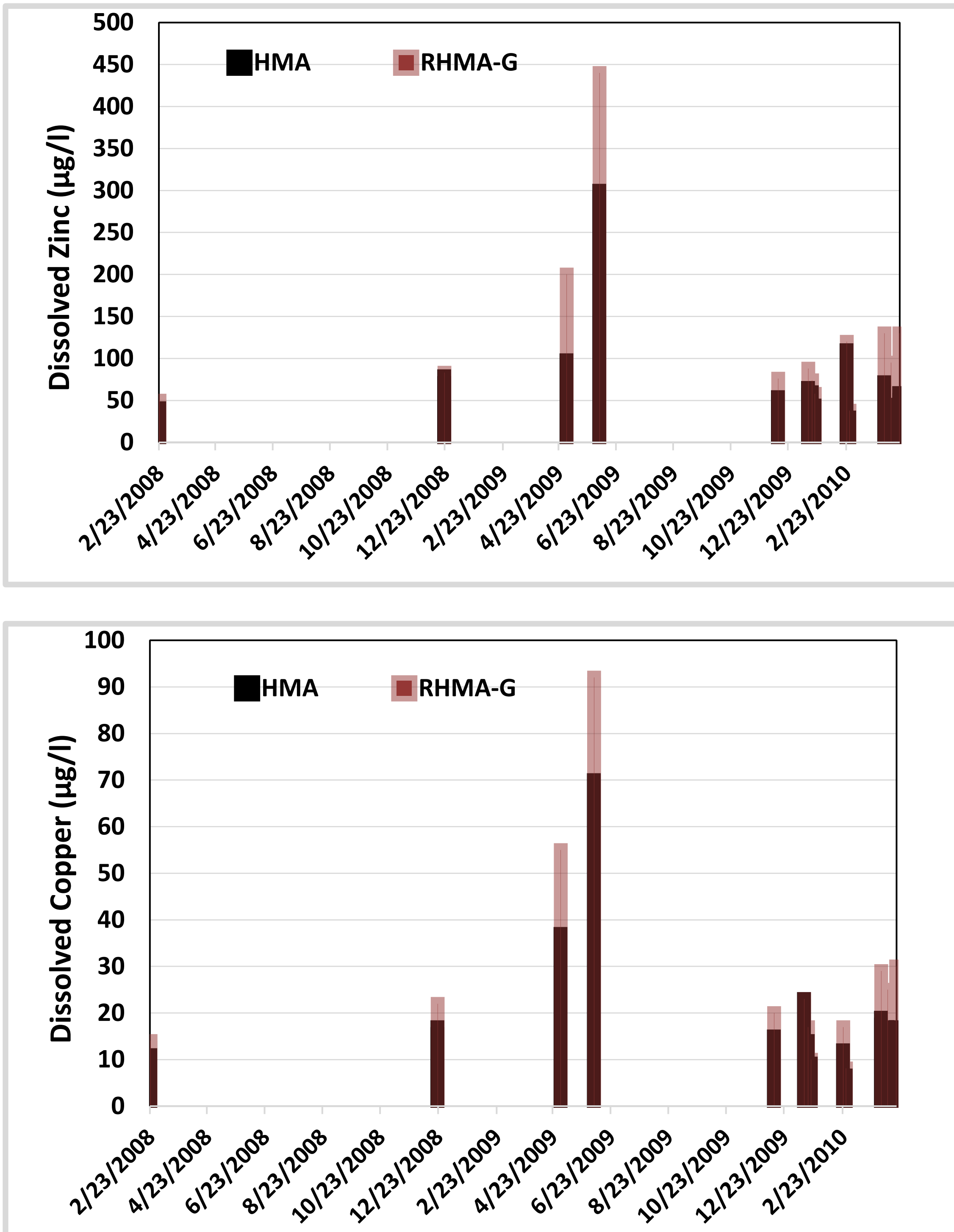
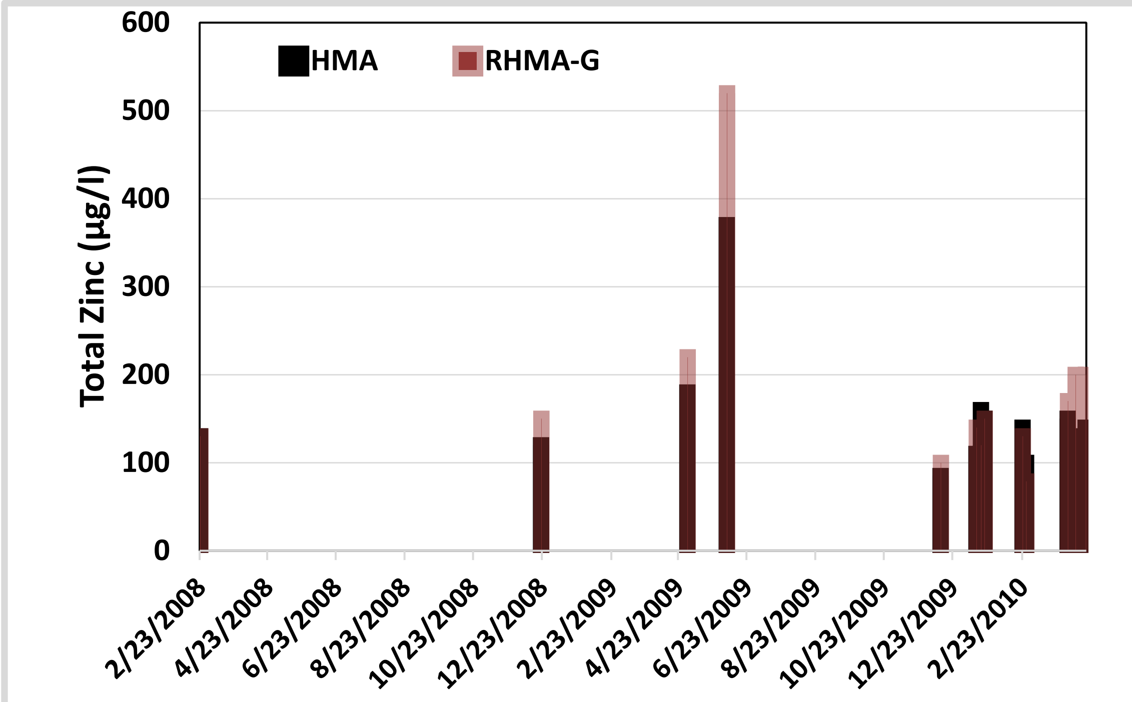


Figure 18: A comparison of dissolved zinc and copper concentration at the Visalia paired sampling location shows a high correlation.



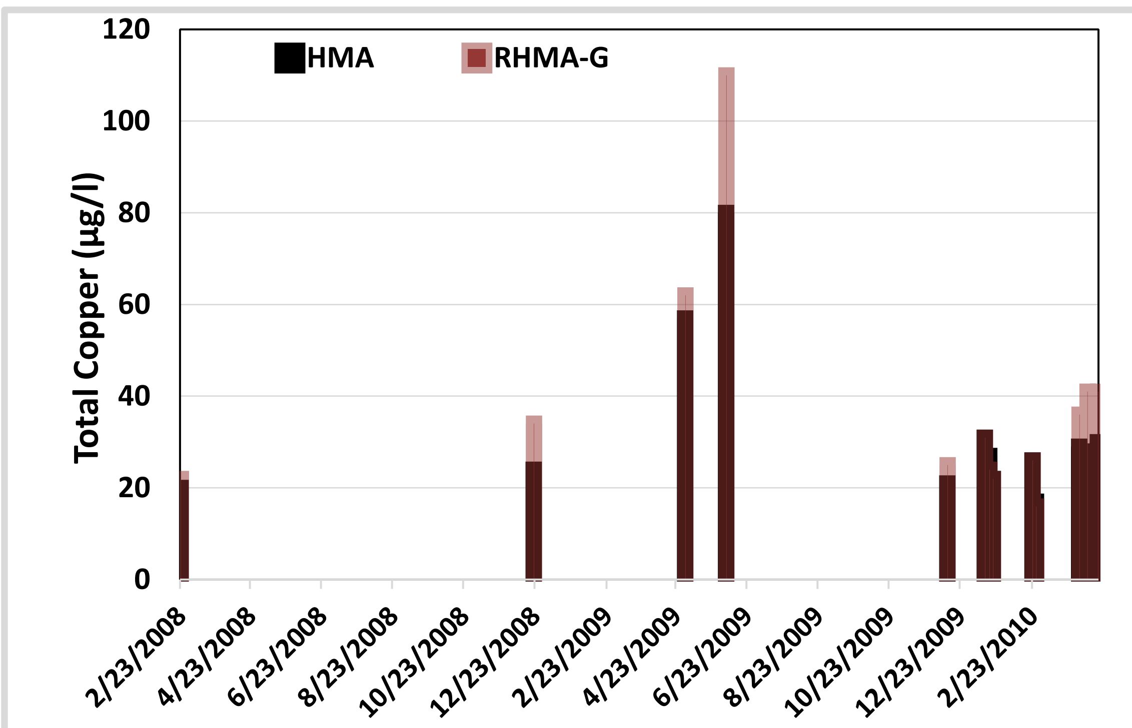


Figure 19: A comparison of total zinc and copper concentration at the Visalia paired sampling location also shows high correlation.

The third CalTrans paired sampling location is Atascadero, CA, an open graded RHMA pavement (RHMA-O). This location demonstrates the greatest difference in zinc concentrations between RHMA and HMA of the three CalTrans sites, with RHMA displaying higher concentrations (Table 26). The same copper assessment as with Visalia was performed at the Atascadero site, shown in Figure 20 and Figure 21. The results show that the correlation between copper and zinc is less prominent, though there appears some correlation between the total metals.

Table 26: Atascadero HWY 41 RHMA paired pavement zinc monitoring results show higher concentrations from RHMA (µg/l).

	Sample Count	Mean Total	Mean Soluble	Max Total	Max Soluble	Min Total	Min Soluble
HMA	28	40	19	95	56	12	4
RHMA	28	104	64	430	270	20	3

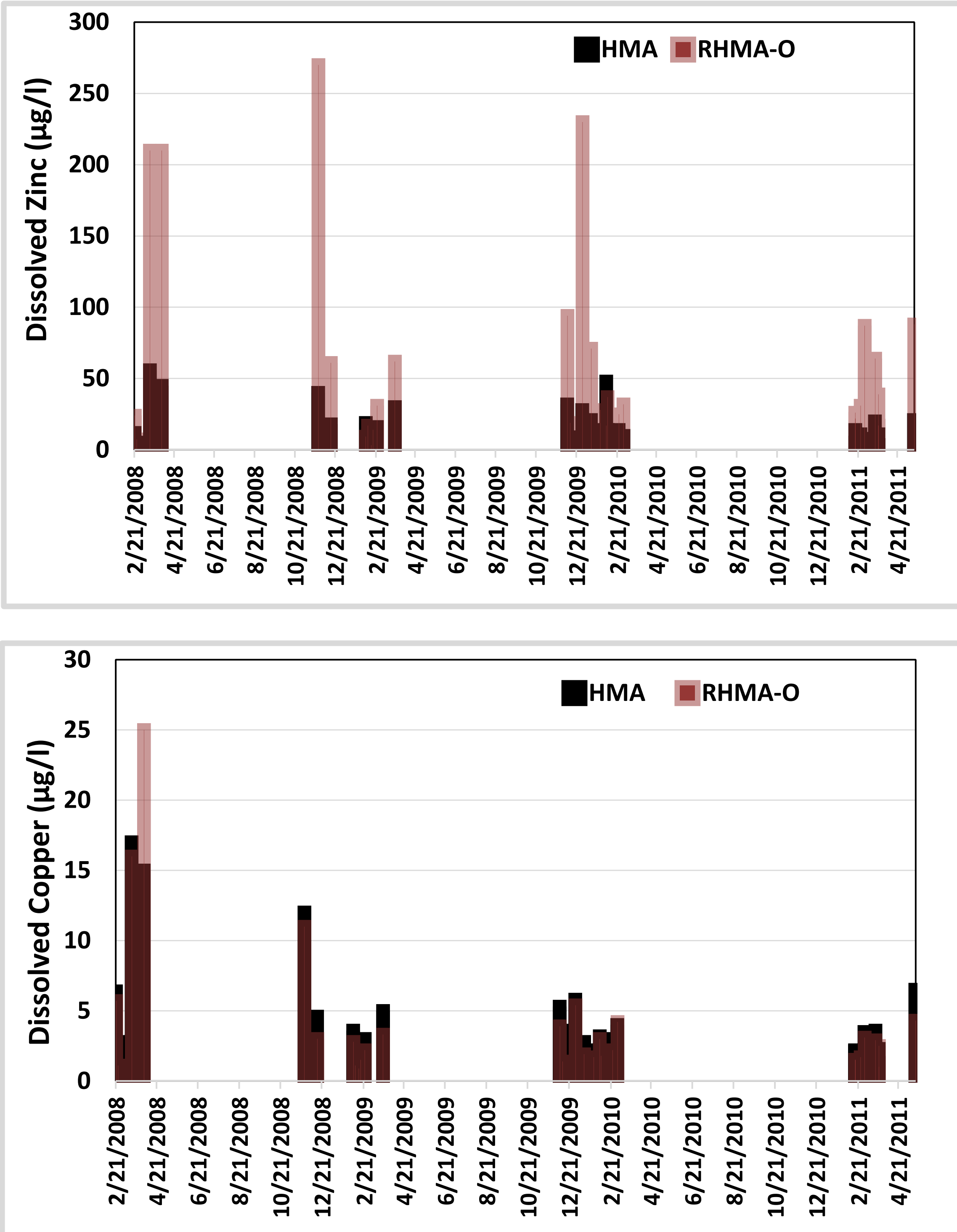


Figure 20: The zinc to copper comparison at the Atascadero site for dissolved metals shows no apparent correlation.

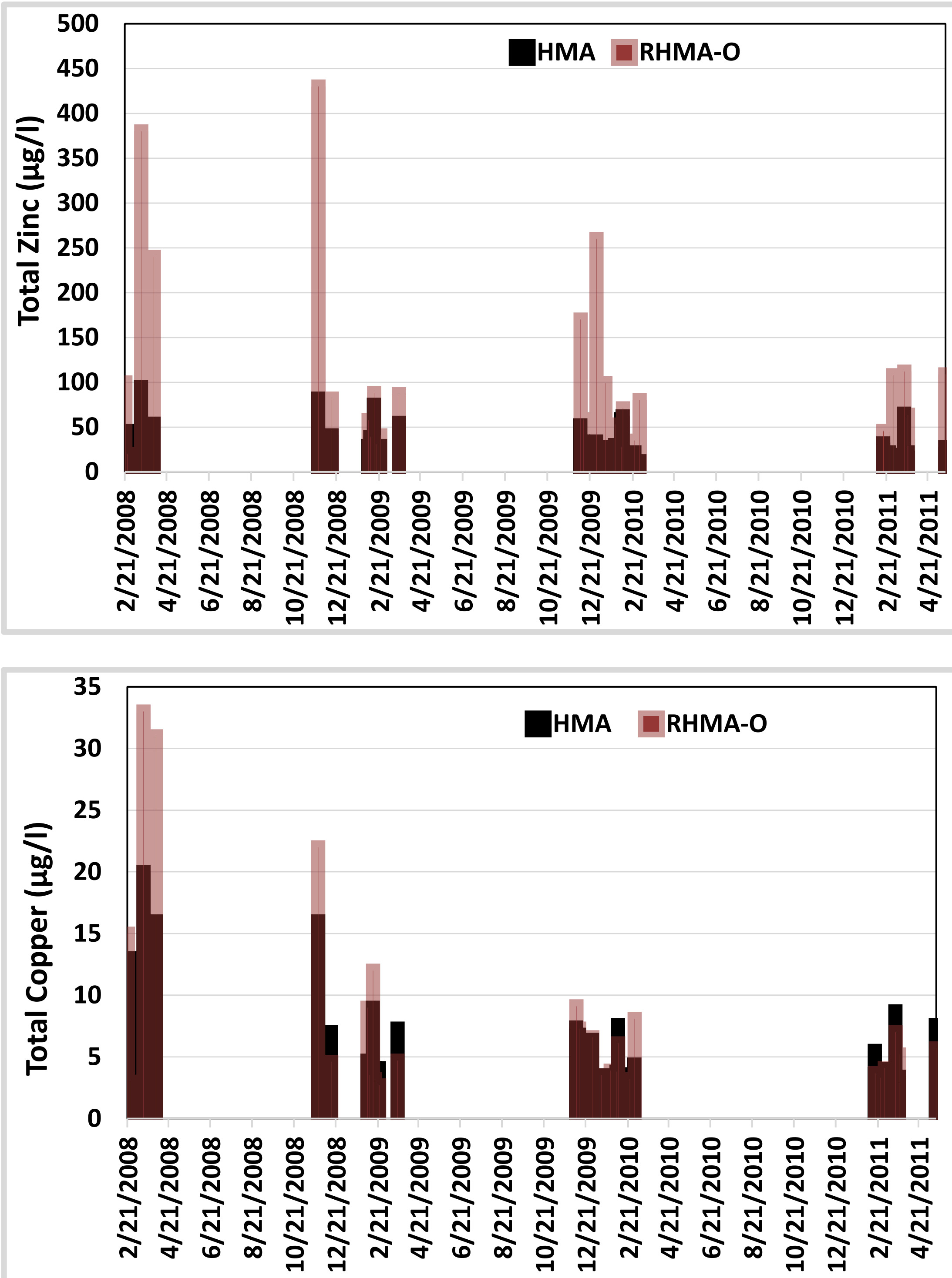


Figure 21: The correlation between total zinc and total copper is weak, with r-squared values ranging from 0.58 – 0.65.

Upon further research into the open graded RHMA in Atascadero, it was discovered that although the permeability of open graded RHMA should be nearly 305 in/hr from laboratory testing of similar pavement, the permeability at the Atascadero site (4.5-year-old pavement at time of testing) showed a permeability of less than 1/10th that rate (2.6 in/hr). This might suggest that the pores of the open graded RHMA at Atascadero have clogged with road dust particles, some of which likely have the ability to leach zinc when saturated. The captured road dust particles may subsequently elevate the levels of zinc through a means other than leaching from the rubberized binder. Additionally, the relatively low concentrations of zinc from the HMA at Atascadero might suggest that it contains calcium carbonate and subsequently adsorbs zinc.

Mass Loading Comparison of Zinc Containing Materials

Four different sources of zinc were quantified and compared relative to eachother on a per mile basis. The four sources that are compared are RHMA, tire wear particles, galvanized guard railing, and precipitation.

RHMA mass loading

Assuming RHMA-G pavement, 1.25 inches thick, 24 feet wide, and 0.016 percent zinc by weight, then the mass of zinc contained within one mile of RHMA is approximately 328 lbs. Results from the leaching study suggest that the percent recovery of zinc from RHMA is 0.024 percent at day 61. This was linearly extrapolated to estimate that the 1-year zinc recovery from RHMA is approximately 0.15 percent. Using the mass

of zinc contained within the pavement and assuming the occasional leaching by stormwater occurs at the same rate as the continuously submerged samples, the stormwater loading rate of zinc from RHMA was estimated at approximately 0.5 lbs/year/mile.

Tire wear particle mass loading

For comparison, a similar calculation can be made regarding leaching of zinc from tire wear particles by stormwater. Assuming the zinc concentration of tire tread is two percent, the estimate of the annual mass loading of the zinc contained in tire wear particles can be calculated given the annual average daily traffic (AADT).

For example, a range of 7 to 76 lb of zinc in the tire particles per year was computed using the lowest, highest and average AADT for the sample sites included in the study (Table 27). Linearly extrapolating the zinc leaching rate for tire crumb (two percent for passenger tires per 61-days, extrapolated to 12 percent annually) and applying that percentage as an adjustment to the loading of zinc from tire wear particles, gives a range of one to nine pounds for annual stormwater zinc loading rates from tire wear particles at these locations (Table 28).

Table 27: Estimated annual zinc loading rates of tire wear particles based on high and low traffic counts from sample sites included in this study.

Location	AADT	Annual Zinc (lb/mile)
Low AADT (Blue Lake)	2500	7
High AADT (Visalia)	26500	76
AVG AADT	13856	40

Table 28: Estimated annual zinc loading rates leached into stormwater from tire wear particles at sample sites included in this study.

Location	Annual Zinc (lb/mile)
Low AADT (Blue Lake)	1
High AADT (Visalia)	9
AVG AADT	5

Galvanized guard rail mass loading

There are many sources of zinc in stormwater runoff from road ways besides tire related products. For example, many roads have galvanized guardrails along at least one side of the pavement and sometimes along the center divider. An estimate of the contribution from loading of zinc from a galvanized guardrail was made for comparison to pavement and tire. Using ASTM standards for a W-Beam design, one mile of galvanized guard rail was found to contain approximately 1,742 lbs of zinc (Table 29). This estimate neglects potential contribution from galvanized posts or mounting hardware.

Table 29: The mass of zinc contained within one mile of guard rail is approximately 1,742 lbs.

Parameter	Value	Unit
Actual height of guard rail (W-Beam)	12.3	inches
Cross-sectional length of guard rail material (one side)	17.6	inches
Area of guard rail in 1 mile	15,488	ft^2
Zinc coating (accounts for both sides)	3.6	oz/ft^2
Mass of zinc in 1 mile of guard rail	1,742	lb

The design life for galvanized metal can be anywhere from 10 – 100 years, usually depending on thickness of the coating (AGA 2010). This estimate is based on the time it takes the railing to display 10 percent corrosion of the underlying steel, which

assumes the zinc coating has dissolved. Assuming a 100-year lifespan, the dissolution of zinc from that surface annually is approximately 17.4 lbs/mile. Since the comparative values (RHMA and tire wear particles) are being analyzed on the basis of quiescent batch leaching, it is more appropriate to treat the galvanized railing as such, which would bring its life expectancy closer to 20 years (100 percent humidity). This results in an environmental loading rate of 87 lbs of zinc per mile per year. If guardrails are on both sides of the roadway, the loading rate of zinc to stormwater would be double these values.

Precipitation monitoring results and mass loading

Precipitation monitoring in Eureka showed a consistently detectable concentration of zinc in rainfall, the average being approximately 8 µg/l (Table 30). GHD Consultants in Santa Rosa recorded one precipitation sample which returned non-detect. The concentration in rainfall is regarded as the atmospheric wet deposition, showing that although it is not a high concentration, wet atmospheric deposition is a large source of zinc on a mass basis in stormwater. This concentration can be assumed relatively homogeneous throughout the region and potentially greater in proximity to traffic due to the contribution of exhaust and tire wear particles to zinc entrainment in the atmosphere.

Table 30: Zinc concentration in rainfall captured near Eureka, CA.

Sample Date	Sample ID	Soluble 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

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), then the wet deposition of zinc on a mile of pavement can be calculated. The volume of water collecting annually on that mile is 12.7 million liters and the resulting mass of zinc is approximately 101 grams/year/mile, or 0.22 lbs/year/mile.

Comparison of significant sources on a per mile basis

When comparing each of the four sources investigated, wet deposition shows the lowest potential annual load of 0.22 lbs of zinc (Table 31). RHMA showed a potential annual contribution of 0.5 lbs of zinc. Tire wear particles had the second highest loading rate, ranging from 1 – 9 lbs and scaling linearly with AADT. The galvanized metal shows a much greater potential to load zinc into the environment estimating 17 – 87 lbs loaded over the course of one year, assuming that the guardrail drains to pavement.

Table 31: A comparison of zinc loading for a 1-mile road on an annual basis for four different sources (lbs/year).

Precipitation (Wet Deposition)	**RHMA**	**Tire Wear**	**Single Galvanized Guard Rail**
0.22 lbs	0.5 lbs	1 - 9 lbs	17 – 87 lbs

DISCUSSION

There are a number of variables and assumptions to be considered when analyzing these results. Though a portion of discussion and comparison to literature values was performed in the results section, this section will expand on the considerations and assumptions associated with this analysis and give a better understanding of interpreting the results. Considerations applied to each of the studies performed will be discussed in the order they were presented.

Crumb Rubber Leaching

Most notable within the crumb rubber leaching study is the influence of particle size on leaching rates (smaller size generating higher leaching and zinc recovery rates). Since the particle sizes analyzed here were specific to the materials used in RHMA, they are not necessarily a good representation of tire wear particle leaching rates, which have been observed to be much smaller particles (10-20 micrometers). The mass transfer rate of zinc from smaller particles is expected to be higher because of greater particle surface area to volume ratio. A portion of the potential overestimate might be accounted for in the fact that the annual mass recovery rate used in the final estimate of zinc loading from tire wear particles was 12 percent, a value extrapolated from the 61-day crumb rubber leaching rate reported here. Since the leaching rates were slowing over time, this linear extrapolation is a conservative estimate that results in an overestimate of the leaching rate, returning a value that is in-line with other studies of fine tire particles such as

Smolders and Degryse (2002). Additionally, the continuous submersion of all tire wear particles is not likely in the field, so this estimate is representative of a worst-case scenario similar to that of tire wear particles transporting to a river bed and leaching continuously.

RHMA and HMA Leaching

For the RHMA leaching study, the RHMA samples studied here are one of a variety of formulations and categorizations of RHMA. For example, a slurry seal RHMA core or an open graded core may present different leaching results compared to the gap-graded RHMA used in this study. Additionally, batch leaching performed here does not replicate cycles of wetting and drying which have been shown to be a primary pavement wearing mechanism. An additional wearing mechanism not captured in this study is UV degradation. The aging/wearing process may expose new binder to stormwater over time and result in a higher effective leaching rate than assumed in this study.

The ratio of water to pavement in the leaching experiments caused both pavement types to operate near the detection limit of 5 µg/l for dissolved zinc testing. The low concentrations are associated with higher uncertainty in lab reported concentrations and may have contributed to variation in leaching rates within all pavement leaching data resulting in an under estimate of the leaching rate.

Paired Pavement Sampling

Although the paired pavement sampling attempts to isolate some environmental factors associated with the buildup and washoff of constituents on the roadway such as weather and road use, there are other factors to consider when analyzing the results. One of the notable differences in the paired sampling data, as was discussed briefly in the results, is the potential for not only the chemical composition of the pavement mix (i.e. crumb rubber or no crumb rubber) but also the physical characteristics of the pavement to impact the build-up and washoff characteristics or leaching of constituents from their surfaces. These physical factors include porosity, air void space, surface area, abrasion potential, surface profile, slope, sinuosity, age, wind profile, aggregate source, and calcium carbonate content. Some of these variables are controlled for by collecting a large sample size over a widespread geographic location, which this study has done. The consistently higher levels of zinc in RHMA suggest that something about that pavement type, the rubberized binder or some combination of the various influential factors increases zinc concentration in stormwater runoff. Another notable consideration is pavement age, for which it has been shown that newer pavement surfaces leach zinc at a higher rate (Murphy et al. 2015). The majority of the RHMA surfaces are more recently constructed than the HMA surface that they are being compared to which might account for some increase in the runoff zinc concentration. Furthermore, every RHMA overlay has been overlain onto some type of pavement, but difficulty in identifying the underlying pavement type and assessing whether it might influence the result is another

source of uncertainty. Further assessment of CalTrans sampling data revealed that as the pavement gradation became more open and porous (RHMA-G Slurry Seal was least permeable and RHMA-O was most permeable), the increase of zinc concentrations in runoff from the RHMA surface became more pronounced.

CONCLUSION

This study assessed the contribution of RHMA to zinc concentrations in road surface stormwater runoff in comparison to conventional HMA. Laboratory testing showed that under batch leaching conditions, the zinc contained within crumb rubber leached into water much more rapidly as individual crumb rubber particles compared to crumb rubber that has been mixed into RHMA pavement. Field testing showed that while stormwater runoff from RHMA pavements contained higher dissolved and total zinc concentrations on average than the paired HMA pavements, differences in the physical characteristics of the pavements were also likely to contribute to the difference in zinc concentrations observed. Physical pavement characteristics that were identified as influential factors to zinc concentration in stormwater runoff include pavement porosity, age, and gradation. Differences in these characteristics are likely to influence the retention or release of zinc from pavement surfaces, effectively hindering comparative analysis of constituent loading between HMA and RHMA surfaces. Dissolved zinc concentrations collected from pavement surfaces in this study occasionally exceeded 120 µg/l, the Criteria Continuous Concentration and the Criteria Maximum Concentration surface water standards. The exceedances occurred on both pavement types and due to the multitude of factors and sources that contribute to the observed concentrations, it is unlikely these exceedances are attributable to the crumb rubber used in RHMA. Using the leaching rates determined in this study as well as ones derived from other studies, tire wear and to a larger extent galvanized metal showed a substantially larger environmental

mass loading rate than RHMA on a typical highway. Though the objectives of this research have been met, there are a number of areas where further research could help improve these estimates and validate these results.

Recommendations for Further Research

More analysis should be directed toward binder wear rates, to gain an understanding of leaching rates from in-field RHMA over time with degradation. Additionally, a leaching study that tests a variety of RHMA pavement types and mix formulas in the laboratory could be conducted to assess leaching rates from more or less porous pavement cores and a variety of RHMA formulations such as ones with and without calcium carbonate. This additional analysis would attempt to verify the findings of Murphy et al. (2015) on the adsorption of zinc by calcium carbonate in the pavement. A long-term leaching study of small sized tire wear particles could also be beneficial to more accurately distinguish leaching rates of tire wear particles and crumb rubber. Since galvanized metal was identified as a potentially large contributor of zinc concentrations in stormwater runoff, analysis of the composition, degradation and zinc transport potential of guard rails and other common galvanized metal features would also be beneficial. Finally, further research addressing the impact of pavement porosity and gradation on the buildup and washoff of constituents over time could be further analyzed to distinguish the influence of the physical composition of pavement on the loading rates of constituents in stormwater runoff from their surfaces.

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APPENDIX

CalTrans Sampling Data

Table 32: Merced paired sampling data for zinc (µg/l).

Date	HMA Dissolved	RHMA Dissolved	HMA Total	RHMA Total
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 33: Visalia paired sampling data for zinc(µg/l).

Date	HMA Dissolved	RHMA Dissolved	HMA Total	RHMA Total
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 34: Atascadero paired sampling data for zinc (µg/l).

Date	HMA Dissolved	RHMA Dissolved	HMA Total	RHMA Total
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 35: Yuba City RHMA paired sample results.

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 36: Richmond RHMA paired sample results.

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 37: Northern California paired sampling results.

Sample Date	Sample ID	Dissolved Zinc (µg/L)	Total Zinc (µg/L)
12/20/2018	299 nonRAC	37	59
12/20/2018	299 RAC	27	40
12/20/2018	101N nonRAC	41	62
12/20/2018	101N RAC	46	76
1/5/2019	299 nonRAC	17	34
1/5/2019	299 RAC	25	49
1/6/2019	101N nonRAC	38	140
1/6/2019	101N RAC	33	290
1/16/2019	299 nonRAC	39	78
1/16/2019	299 RAC	29	34
1/16/2019	101N nonRAC	28	83
1/16/2019	101N RAC	37	190
1/16/2019	101S nonRAC	32	56
1/16/2019	101S RAC	27	51
2/1/2019	101N nonRAC	64	250
2/1/2019	101N RAC	110	260
2/3/2019	299 nonRAC	29	35
2/3/2019	299 RAC	44	41
2/3/2019	101N nonRAC	38	54
2/3/2019	101N RAC	42	91
2/3/2019	101S nonRAC	40	32
2/3/2019	101S RAC	35	45
2/23/2019	299 nonRAC	28	25
2/23/2019	299 RAC	32	25
2/23/2019	101N nonRAC	61	130
2/23/2019	101N RAC	55	110
2/23/2019	101S nonRAC	58	62
2/23/2019	101S RAC	50	170
4/5/2019	299 nonRAC	48	64
4/5/2019	299 RAC	31	39
4/5/2019	101N nonRAC	35	200
4/5/2019	101N RAC	46	150

Table 37: Northern California paired sampling results.

Sample Date	Sample ID	Dissolved Zinc (µg/L)	Total Zinc (µg/L)
4/5/2019	101S nonRAC	57	65
4/5/2019	101S RAC	56	91
5/15/2019	101N nonRAC	100	210
5/15/2019	101N RAC	150	310
5/15/2019	101S nonRAC	80	100
5/15/2019	101S RAC	110	120
9/15/2019	299 RAC	850	880
9/15/2019	299 NonRAC	66	83
9/15/2019	101N RAC	240	360
9/15/2019	101N NonRAC	280	450
9/17/2019	101N nonRAC	81	380
9/17/2019	101N RAC	110	520
9/17/2019	101S nonRAC	77	69
9/17/2019	101S RAC	82	170
9/17/2019	101FSS RAC	210	190
9/17/2019	101FSS RAC	130	140
10/16/2019	299 RAC	74	79
10/16/2019	299 NonRAC	46	75
12/6/2019	299 nonRAC	61	55
12/6/2019	299 RAC	72	50
12/6/2019	101S nonRAC	72	280
12/6/2019	101FSS RAC	63	110
1/21/2020	101N nonRAC	68	150
1/21/2020	101N RAC	40	100
2/16/2020	101S nonRAC	140	140
2/16/2020	101FSN RAC	64	52
2/16/2020	101 FSS RAC	57	50
3/24/2020	101N nonRAC	47	240
3/24/2020	101N RAC	60	240
3/24/2020	101S nonRAC	110	140
3/24/2020	101S RAC	110	240
3/24/2020	101FSS RAC	59	53
3/24/2020	101FSN RAC	91	150