Zinc Sources in California Urban Runoff

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CALIFORNIA STORMWATER QUALITY ASSOCIATION

PREFACE

This report was prepared for the California Stormwater Quality Association (CASQA) under the supervision of CASQA's Watershed Management & Impaired Waters Subcommittee. It is a component of CASQA's Source Control Initiative which seeks to address stormwater and urban runoff pollutants at their sources. The study was commissioned to develop scientific information to inform decision-making by CASQA and stormwater permittees for the reduction of zinc as a water pollutant and to identify major and minor sources of zinc in order to assist agencies focus control measures in a cost-effective manner.

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ZINC SOURCES IN CALIFORNIA URBAN RUNOFF

TABLE OF CONTENTS

Tables

Figures

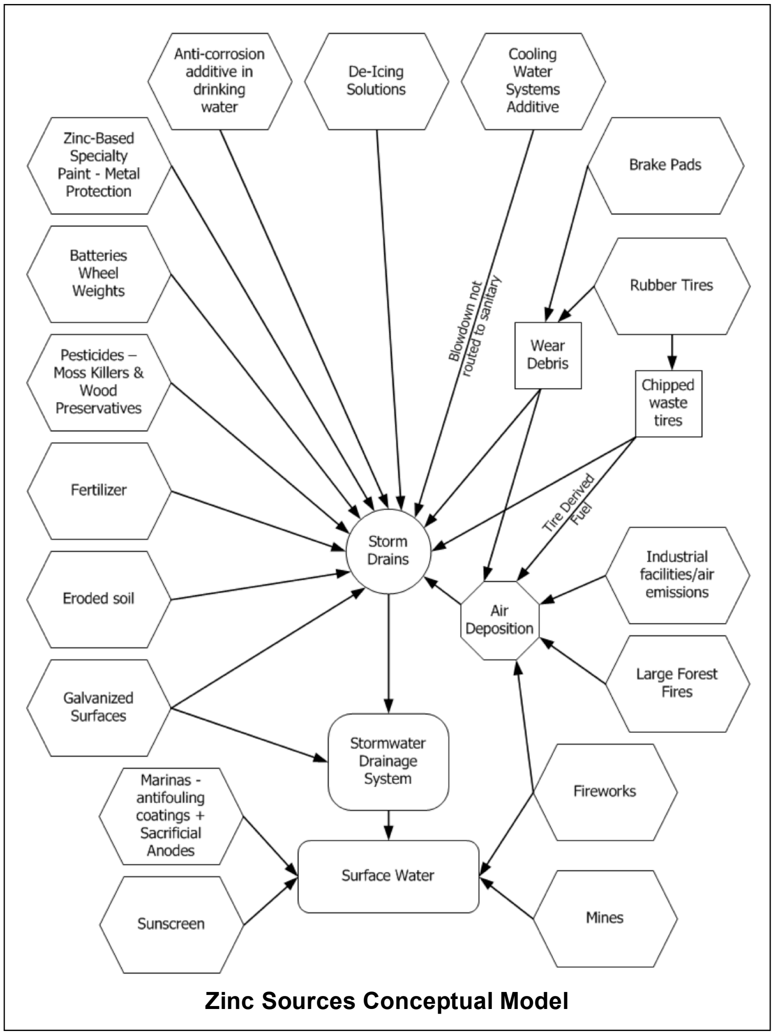
ZINC SOURCES IN CALIFORNIA URBAN RUNOFF

EXECUTIVE SUMMARY

Elevated zinc concentrations in urban runoff must be addressed for Clean Water Act compliance in many California urban areas, particularly in the Los Angeles and San Diego regions, which have multiple Total Maximum Daily Loads (TMDLs) for zinc. Treating urban runoff to achieve compliance, while theoretically feasible, could cost billions of dollars statewide. Controlling zinc at its source is a promising alternative. The purpose of this report is to use existing scientific literature to determine the major sources of zinc in California urban runoff, to identify promising source control strategies for the major sources, and to recommend next steps toward implementing zinc source control. This report presents the first thorough review of true urban runoff zinc sources and estimation of their relative contributions to urban runoff zinc loads in the United States.

The goal of this report is to identify "true sources" of zinc—the zinc-containing materials that first release zinc into the urban environment. Flows that convey zinc to a water body, such as runoff from types of land uses, air deposition, and discharges from human activities are not true sources. Data characterizing these "conveyances" are used to trace the path back to true zinc sources.

To facilitate the examination of each potential zinc source—and to clarify the distinction between true sources and conveyances, a conceptual model illustrating the pathways by which zinc washes from true sources into urban runoff was developed. The literature review clarified the link between zinc air deposition, which is often named a major zinc "source," and vehicle tires. A separate tire-specific conceptual model clarifies the pathways by which zinc from tires reaches urban runoff. Although tire-wear debris is well dispersed in urban environments, about half of this debris remains on or immediately adjacent to the road, where it makes its largest contribution to urban runoff zinc loads.



Zinc Sources Conceptual Model

Using Los Angeles County as an example, available information was carefully assessed to identify the major and minor true sources of zinc in California urban runoff. The information in this report was assembled from available data sources. No sampling or chemical analysis was conducted for this report. All prioritization was done on the basis of gross estimates of the potential annual urban runoff zinc load from the source. This report does not provide detailed quantitative estimates, which must be based on watershed-specific information. The environmental fate and bioavailability of zinc from its various sources and zinc chemistry in California watersheds are beyond the scope of this report.

The major sources of zinc in urban runoff are outdoor zinc surfaces (especially galvanized surfaces) and tire wear debris. Some watersheds contain local zinc sources that could contribute significant quantities of zinc to urban runoff. These potential major local zinc sources cannot be prioritized generically. Examples include sources like zinc-containing paint, tire shred and crumb products, industrial air emissions, zinc-rich soils, and mining. Many minor zinc sources that do not contribute significant quantities of zinc to urban runoff exist. Examples include vehicle brake pads, wheel weights, vehicle exhaust, zinc-preserved wood, and non-zinc roofing and siding.

Many zinc source characterization information gaps were identified, but only a few of these gaps are likely to significantly affect decisions about prioritizing zinc sources for urban runoff management actions. Additional information to characterize zinc sources that would be most useful for zinc runoff management decisions is:

- Measurement of zinc releases in runoff from rubberized asphalt pavement.
- Data on the market presence of zinc-containing paints, particularly paints with antimicrobial zinc additives, and the zinc concentrations in runoff from new and aged outdoor paints with antimicrobial zinc additives.

If California agencies require more accurate estimates of zinc emissions from major zinc sources to support zinc reduction actions, the data that would most reduce uncertainties is:

- Zinc content and wear rates of California tires
- California-specific zinc emissions factors from outdoor zinc surfaces, which can be based on runoff from test panel systems located in California.

Promising source control strategies exist for zinc in urban runoff. Using available information, potential source control strategy options for major zinc sources were reviewed, focusing on those that may be feasible, practical, and cost-effective. The report summarizes information from the literature, but does not provide a detailed assessment of source control options and quantitative reduction estimates. For outdoor zinc surfaces, both source control and on-site treatment of concentrated runoff appear to be technically feasible. Reducing zinc from tires will pose a greater challenge, as low-zinc and zinc-free products have little market presence and tire wear debris is widely dispersed across urban environments, making it very difficult to collect.

California state and local governments and industries seeking to reduce zinc concentrations in urban runoff should integrate source control into their zinc management programs. The report recommends the following general steps:

1. Develop a watershed-specific zinc source inventory based on local watershed information.
2. Integrate source control into zinc load reduction programs. The promising strategies reviewed in this report are intended to be a starting point for developing source-specific programs appropriate for local watersheds.

3. Employ source control to reduce zinc in runoff from industrial facilities. Source control can be implemented alone or in combination with low-cost runoff treatment systems.
4. Consider collaborating with other California governments and industries to implement statewide zinc source control actions. Potential statewide actions include:
   - Developing a menu of zinc source control strategies for municipalities.
   - Petitioning the California Department of Toxic Substances Control to require evaluation of zinc in tires under its Safer Consumer Products Regulations.
   - Seeking integration of water quality considerations into California Department of Resources Recycling and Recovery's waste tire market development programs.
   - Seeking integration of water quality considerations into U.S. EPA's review of zinc biocides.

1.0 INTRODUCTION

1.1 Purpose and Scope of This Report

Zinc levels are commonly elevated in urban runoff (EPA 1983; EPA 1993; Center for Watershed Protection 1996; Kennedy and Sutherland 2008). California's list of water bodies designated as impaired under the Federal Clean Water Act (the "303(d) List") includes more than 40 waters with zinc impairments, about half of which receive urban runoff. Adopted Total Maximum Daily Loads (TMDLs) in the Los Angeles and San Diego regions pose compliance challenges for municipalities.

Treating urban runoff to achieve compliance, while theoretically feasible, could cost billions of dollars statewide. Source control is a promising alternative; however, information is needed to provide the scientific basis for selection of source control actions. Although information characterizing sources of zinc in urban runoff exists, prior to the initiation of this study, a thorough review of true zinc sources and estimation of their relative contributions to zinc loads in urban runoff in the United States was not available in the scientific literature.

The purpose of this report is to use existing scientific literature to determine the major sources of zinc in California urban runoff, to identify promising source control strategies for the major sources, and to recommend next steps toward implementing zinc source control.

This report does not address discharges into or effluent from industrial or municipal wastewater treatment plants, nor does it address non-urban zinc sources, like sediment erosion from open space and mine drainage. Examination of zinc fate, transport (other than transfer into urban runoff), bioavailability, and toxicity are not part of the scope of this report.

The information in this report was assembled from available data sources. Only existing information was used. Sampling and chemical analysis were not conducted.

1.2 Report Organization

This report is organized as follows:

- *Section 1* (this section) provides the background and scope of the report.
- *Section 2* describes the methods used to identify major zinc sources in urban runoff.
- *Section 3* describes the approach to the literature review and summarizes previous zinc source identification studies.
- *Section 4* reviews zinc uses, identifies a preliminary list of potential sources of zinc in urban runoff. .
- *Section 5* provides the conceptual model that guided the assessment of potential zinc sources.
- *Section 6* details the assessment of zinc sources, identifying major zinc sources, local zinc sources of potential importance in some California urban watersheds, and minor zinc sources.
- *Section 7* reviews control measure options for major zinc sources, focusing on promising opportunities for zinc source control.

- *Section 8* provides conclusions and recommendations.
- *Section 9* lists the references cited in the body of the report.

2.0 METHODOLOGY

This source identification study involved the following five steps.

(1) Literature review (Section 3). A literature and zinc-containing product review was conducted to identify known and potential sources of zinc in urban runoff. The focus of the review was to identify:

- Information about zinc's presence and usage in outdoor products and in products that may be discharged into storm drain systems,
- Data on the concentration or quantity of zinc in products and their emissions, runoff, or discharges,
- Metrics appropriate for estimating zinc source quantities in urban runoff (e.g., sales data, vehicle kilometers traveled), and
- Potential source control measures.

(2) Initial analysis of available information (Sections 4 and 5). The uses of zinc were reviewed to identify common California zinc uses with potential pathways for release to the storm drain system. A key step in the analysis was the separation of true sources (i.e., zinc-containing products like tires, building materials, and biocides) from conveyances (i.e., air deposition, building runoff), based on a simple conceptual model linking zinc sources to urban waterways.

(3) Identification of major zinc sources (Section 6). On a generic basis, using Los Angeles County as an example, available information was carefully assessed to identify the major true sources of zinc in California urban runoff. Additional zinc sources that may be locally important in some geographic areas were identified, but not prioritized because prioritization would require specific information about local watersheds. All prioritization was done on the basis of gross estimates of the potential annual urban runoff zinc load from the source. This report does not provide detailed quantitative estimates, which must be based on watershed-specific information.

(4) Preliminary identification of potential control strategies (Section 7). Using available information, potential source control strategy options for major zinc sources were reviewed, focusing on those that may be feasible, practical, and cost-effective. A table in Section 6 briefly lists potential control strategies for additional zinc sources that do not appear in all geographic areas, but that may be locally important in some areas.

(5) Prioritization of information gaps (Sections 6 and 8). The quality and quantity of information available to characterize each major or potentially major zinc source was evaluated. The report identifies information gaps that are most likely to affect management decisions.

3.0 LITERATURE REVIEW

3.1 Approach

This report is based on a review of existing information available from reliable sources. The review was thorough, but not comprehensive. Resources were identified through scientific literature indexing services, Internet searches, and citations in related studies.[1]

The primary types of information sources were:

- Published scientific literature (e.g., peer-reviewed and other journals).
- Technical reports and data summaries prepared by or for U.S. local, state, Federal, and international government agencies and zinc industry organizations.
- Industry publications describing zinc uses and maintenance practices.

The literature review identified more than 200 relevant scientific papers and government agency and industry reports.

Although available resources were insufficient to allow for a full peer review of every publication, the general quality of each information source was assessed by examining the methodology of the study, and its level of rigor, use of quality controls, and consistency with information from other sources. The report does not rely on resources that were judged to be of poor quality. Information assembled in the review was interpreted in its entirety, which entailed some reinterpretation of previously published conclusions in light of the context of the full set of information resources (e.g., see Section 5).

Literature reviewed is cited throughout the report and listed in Section 9, References. Citations in the text use standard abbreviated scientific citation format, e.g. "(Author year)." The full reference can be found in Section 9 under the author's name.

3.2 Previous Zinc Source Identification Studies

The first step in the literature review was to identify and review prior reports examining zinc sources in urban runoff. Four detailed zinc source inventories (from New Zealand, the Netherlands, Washington State, and San Diego) and several other studies were identified. These previous studies are discussed below.

Auckland, New Zealand

In 2008, the Auckland Regional Council completed a zinc source inventory for urban runoff in three watersheds (Kennedy and Sutherland 2008). The study reviewed the following potential sources of zinc in urban runoff: vehicle tires; brake pads; exhaust; oil, grease and lubricants; soils; road surfaces; building roofs, walls, treated wood, and other building materials; galvanized non-building structures (e.g., light poles); household products and soil amended with these products (including pesticides and fertilizers); litter; road accidents; fireworks; potable water; industrial air emissions; and air deposition (which is a pathway, not a source, as explained in Section 4.2).

The Auckland Regional Council found that tires, zinc-containing construction materials, and air deposition were major sources of zinc. Together, these three sources accounted for 77-89% of zinc runoff in the three watersheds. All other sources were estimated to be

[1] The author wishes to acknowledge the City of San Diego, Weston Solutions, California State University Sacramento Office of Water Programs, and the Brake Pad Partnership for generously sharing their related literature searches.

relatively minor (fertilizers <8%, all other sources <5%). The estimation method did not account for cross-media transfer, such as the contribution of tires to zinc air deposition measurements, nor did it correct for the potential presence of zinc in the wet air deposition sampling data (which was based on roof runoff data).

The Auckland Regional Council report recommended refining the tire and construction materials runoff estimates and examining the potential contributions from zinc-based paints (Kennedy and Sutherland 2008).

Netherlands

Monitoring data indicate that concentrations of zinc in surface waters in the Netherlands exceed environmental quality standards in some locations (Vos and Janssen 2008). Consequently, the Netherlands National Institute for Public Health and the Environment conducted relatively extensive zinc source identification studies to support development of control measures (Vos and Janssen 2008, Verschoor and Brand 2008; Verschoor 2008; Ten Broeke 2008; Netherlands 2008a, 2008b, 2008c, 2008d, 2008e). The Netherlands studies, which considered all pathways for zinc transport to surface waters, addressed urban runoff as a pathway for zinc to reach municipal wastewater treatment plants, since the Netherlands' urban areas are served by combined sewer systems.

The primary urban runoff zinc sources examined in the Netherlands inventory were tires, outdoor zinc-containing construction materials, fertilizer, industrial facilities, and atmospheric deposition (which is a pathway, not a source). The inventory also considered special sources like sacrificial anodes on boats and zinc-containing greases.

The Netherlands studies found that diffuse sources, like tires and construction materials, are the primary sources of zinc washed into surface water. Sources estimated to be relatively small include brake pads, pesticides, zinc greases, vehicle oil and grease, and pavement wear. Of the urban runoff zinc sources, tires and zinc-containing construction materials were the largest identified sources (Vos and Janssen 2008).

Puget Sound, Washington

The Washington Department of Ecology identified the primary sources of several chemicals of concern, including zinc, in the Puget Sound basin (Washington Ecology 2011, Washington Ecology and King County 2011; Whiley 2011). Washington's zinc source identification and control measures reports estimated annual releases, pathways and loadings of zinc, and established priorities for possible actions to reduce pollutant levels. The study reviewed the following potential sources of zinc in urban runoff: roofing materials, tires, motor oil, vehicle brake pads, and industrial air emissions.

Although the study found that roofing materials were the largest zinc source in the watershed, its roof runoff estimates were inflated. The study used literature data for runoff from non-zinc roofing materials that did not accurately represent these materials, due to the presence of other zinc sources on the tested roofs.[2] Estimates of total zinc runoff load from zinc-containing roof materials were on the same order of magnitude as estimated zinc releases from tires, and more than an order of magnitude greater than other urban runoff zinc source estimates (Washington Ecology 2011). The Washington study did not estimate zinc releases from non-roof zinc building materials, such as fencing and guardrails (Washington Ecology and King County 2011).

[2] Test systems used to generate these inaccurate data had galvanized steel in roof construction (e.g., flashing), galvanized gutters and downspouts, or air deposition from upwind zinc-emitting industry and/or nearby roads (Chang and Crowley 2003; Chang et al. 2004; Davis et al. 2001). Subsequent investigations by Washington Ecology confirmed that non-zinc containing roofing materials are not a significant zinc source (Washington Ecology 2014c).

Chollas Creek, San Diego, California

On the basis of a literature review and site-specific data, Weston Solutions estimated the major sources of zinc in San Diego's Chollas Creek watershed (Weston Solutions 2011). Weston Solutions prioritized transportation and building materials zinc sources based on the literature review, finding that tires and outdoor galvanized materials were likely to be the major zinc sources in the watershed. Surveys of the watershed showed that although asphalt shingle is the most common roof type in the watershed, galvanized materials like roofing and gutters occur frequently, particularly in the industrial portions of the watershed. Modeling suggested that both tire wear (which distributes zinc throughout the watershed via air deposition) and galvanized materials are likely major zinc sources within the watershed (Weston Solutions 2011).

Other Studies

Davis et al. (2001) completed a preliminary exploration of sources of zinc in urban runoff. The data included not only true sources, but also conveyances of zinc from other sources (e.g., zinc flashing), and surfaces subject to zinc air deposition from near or distant sources (roofs, building walls). Similarly, many inventories, such as those by Pitt et al. (1995) and Steuer et al (1997) examine runoff from various surfaces receiving zinc deposition and/or land use categories rather than true sources. These data collection methods provide correlations and information for subsequent source identification work, but do not identify the true sources of measured zinc.

4.0 INITIAL ANALYSIS OF AVAILABLE INFORMATION

4.1 Zinc Uses

Among all metals, zinc ranks fourth (after iron, aluminum, and copper) in annual worldwide consumption (Bradl 2005). According to the International Zinc Association, worldwide zinc production exceeds 11 million tons annually. Most of this production becomes products containing metallic zinc or zinc alloys. Less than 10% of zinc is turned into zinc compounds such as zinc oxide and zinc borate (IZA 2011).

Recycling of zinc scrap and used zinc products is growing rapidly. Recycling currently generates about 40% of the world's zinc supply. Mining of zinc-rich ores provides the remaining zinc (IZA 2011).

About half of all zinc is used as a coating, called "galvanizing," to protect steel from rusting. Common methods for applying the zinc coating are "hot dip galvanizing," where small or large steel pieces parts are dipped into a plating tank, and "continuous galvanizing," where sheet steel is passed through a plating bath. Galvanized metals are widely used in construction and manufacturing, such as in roofing, piping, nails and bolts, flashing, gutters, structural framing and supports, vehicle body and structural parts, and culverts (IZA 2011).

Hot-Dipped Galvanized Nails

About one-third of all zinc is mixed into alloys with other metals, including brass and alloys to create "die cast" parts, which form the structural underpinnings of many diverse consumer products such as door locks, cell phones, staplers, and coffee makers. A relatively small fraction (about 6%) of zinc is formed into sheets used in building exterior components and as the core for the U.S. one-cent coin (IZA 2011). Other miscellaneous zinc uses include battery electrodes and sacrificial anodes for boats.

The most used zinc compound is zinc oxide, which is an ingredient in many products—most importantly rubber. Rubber comprises 60% of the U.S. zinc oxide market (IZA 2006a). The diversity of zinc oxide-containing products includes ceramics, paints, light-emitting diodes, fireworks, dietary supplements, and photocopiers. Other zinc compounds are used in paints, fabric products, pesticides (moss killers, fungicides, wood preservatives, antimicrobials), fertilizers, and plastics (IZA 2011).

Throughout the world, zinc occurs naturally in soil (Bradl 2005). In California, soil zinc concentrations average about 150 parts per million (ppm), with a few soil types exceeding 200 ppm (Bradford 1996). Living organisms contain small quantities of zinc, which is an essential trace element (Bradl 2005). For example, human body tissue zinc concentrations are in the range of 100 to 300 ppm (McBean 1972).

4.2 Identifying True Sources of Zinc in Urban Runoff

The goal of this report is to identify "true sources" of zinc—the zinc-containing material that first releases zinc into the urban environment. This entails reviewing zinc's many uses in urban environments, the exposure of each zinc use to urban runoff, and data characterizing the environmental releases and flows of zinc in runoff from each use. This report examines all applications of zinc—including zinc metal, zinc compounds, and zinc alloys.

In theory, there are thousands of potential sources for zinc to be released into urban runoff. Since the purpose of this report is to identify major sources, it does not include a comprehensive review of every theoretically possible zinc source.

Zinc sources in urban runoff must be located, used or emitted outdoors. Many zinc-containing products remain indoors or beneath facades; these have limited potential to release zinc to surface waters.

Many scientific studies identified in the literature review purport to identify pollutant sources, but actually examine flows that convey zinc to a water body. For example, a common design to examine pollutant sources into a large water body is to obtain data about the water in rivers and creeks flowing into the water body, the wastewater treatment plants discharging to it, and the material deposited by air onto the water body's surface. In urban runoff studies, the following flows are sometimes called "sources" of zinc in urban runoff:

- Runoff from residential, commercial, industrial, and institutional land uses
- Discharges from vehicle washing
- Runoff from streets and parking lots
- Air deposition

None of these are actual sources of the pollutant—they are discharges that convey the pollutant from its primary source, e.g., a product containing the chemical or an emission from a facility that uses the chemical, into the water body. Although data from conveyances can be used to trace back toward true sources, these data are otherwise not used in this report.

The following are zinc sources, but are not part of this analysis because these discharges are not ordinarily part of urban runoff:

- Wastewater treatment plants and all discharge sources to the sewer system
- Local reservoir releases
- Non-urban soil erosion
- Agricultural runoff
- Landfill leachate

4.3 Preliminary List of True Sources of Zinc in Urban Runoff

The literature review identified the following potential categories of sources of zinc in urban runoff:

- Unprotected outdoor zinc surfaces such as galvanized roofing, gutters, fencing, piping, guard rails, light poles, and mechanical equipment; galvalume roofing and siding; zinc metal sheet roofing and siding; brass sculpture and ornamentation; and zinc-containing paints

- Rubber, including tires, reuse of waste tires (such as fill for artificial turf fields, chips for playground surfaces, and tire-derived fuel), and non-tire uses of virgin rubber like channel-lining material

- Other vehicle-related items: brake pads, wheel weights, exhaust, grease additive, motor oil/lubricating oils additive, asphalt

- Boat-related zinc uses: sacrificial anodes, marine antifouling paint, grease additives
- Zinc pesticides: zinc-preserved wood, zinc-based moss control products, swimming pool biocides, zinc phosphide rat killer, zinc granule-impregnated asphalt roofing shingles
- Anti-corrosion additives for drinking water and for water-containing equipment
- Air emissions: fireworks, forest fires, volcanoes, re-suspension of zinc from historic emissions sources
- Industrial facilities: air emissions, runoff,
- Miscellaneous uses of zinc metal and alloys: die cast zinc products, coins, candle wicks, batteries
- Miscellaneous uses of zinc compounds: cosmetics and personal care products, glow-in-the-dark products like toys, fluorescent tubes, waterproofing agent, glass and ceramics, plastics, sealants, mastics additive / preservative; waxes and polishes, zinc phosphate cleaners, de-icing products
- Soils, including zinc fertilizers

5.0 CONCEPTUAL MODEL

To facilitate the examination of each potential zinc source, a conceptual model illustrating the pathways by which zinc washes from true sources into urban runoff was developed (see Figure 1). The model is based on prior work modeling pollutants in urban runoff as well as the zinc-specific information obtained through the literature review.

The model includes major and potentially major zinc sources, but excludes most minor sources. Because the focus is on sources that may occur in urban runoff, it excludes wastewater (sewage) and non-urban zinc sources.

The conceptual model focuses on connections between zinc sources—specifically outdoor zinc sources—and surface waters. It identifies both direct and indirect pathways linking each zinc source with surface waters. The conceptual model clarifies the separation of true zinc sources (e.g., tires) from conveyances (e.g., air deposition of tire wear debris).

Several scientific papers have suggested that air deposition is a major source of zinc in urban runoff (e.g., Sabin et al. 2005; Sabin et al. 2006a; Lim et al 2006; Van Metre 2003; Rocher et al. 2004). The literature review clarified the link between zinc air deposition and one specific urban zinc source—vehicle tires. To facilitate understanding of this linkage, a separate conceptual model for zinc in tires was developed (Figure 2).

Tires consist of multiple layers of rubber. The outer rubber layer—the tire tread—contacts the road surface. Whenever a vehicle is driven, the rubber tire tread slowly wears off as the tires roll across the pavement. Abrasion creates small rubber particles known as “tire wear debris.” Tire wear debris particles are very small. Their diameters generally range between about 5 micrometers (μm) and 220 μm, with an average of about 75 μm (Kreider et al. 2010).

Once deposited on the road, the action of vehicle tires grinds up tire wear debris and mixes it with other materials, like pavement debris and soil. This grinding process reduces particle size, producing particles with an average diameter of about 50 μm (Adachi and Tainosho 2004; Kreider et al. 2010).

Eventually tire wear particles are ground into the pavement, lifted into the air and carried away from the road surface, or washed off into roadside soils or storm drains. About half of tire wear debris is estimated to remain on or immediately adjacent to the road. An estimated 70% of tire wear debris remaining on roads may be washed off by rain (Blok 2005). This is the primary pathway for zinc from tires to be washed into urban runoff.

Most of the half of tire wear debris that does not land on the road is re-suspended into the air. Tire wear particles are in a size range that typically falls out of the air relatively quickly, i.e. within a few meters (Blok 2005). The tire particles distribute primarily in the near roadside area, within a few meters of the pavement edge. Consistent with this distribution, zinc deposition and zinc concentrations in roadside soils are highest within about 6 meters of the pavement edge (Wik and Dave 2009; Blok 2005; Cadle and Williams 1978). Continuing lower levels of measurable deposition occur to about 30 meters from the road edge (Wik and Dave 2009).

Zinc concentrations in small roadside particles (between 2 and 63 μm) are 8-10 times higher than zinc concentrations in large roadside particles (>500 μm) (Deletic and Orr

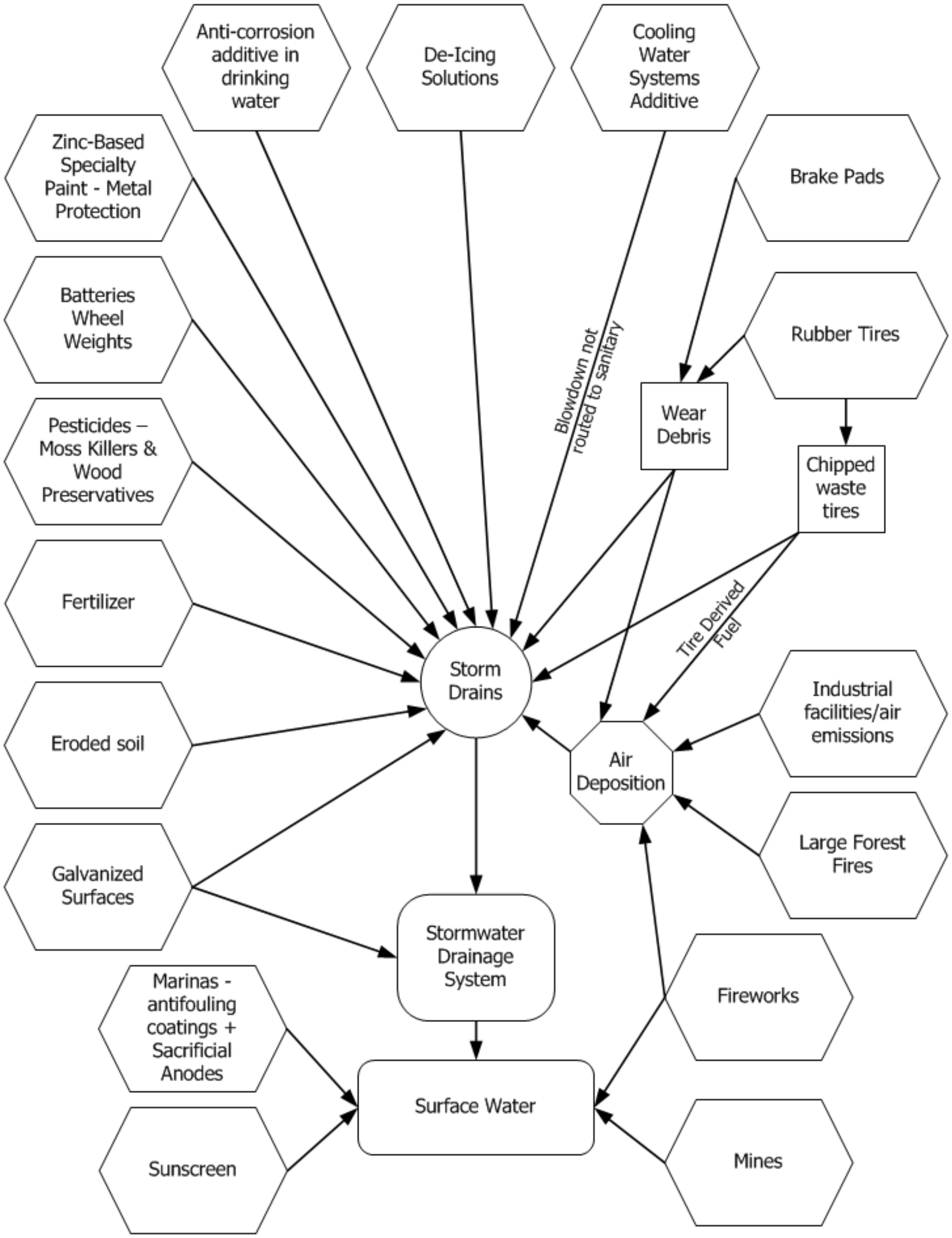


Figure 1. Zinc Sources Conceptual Model

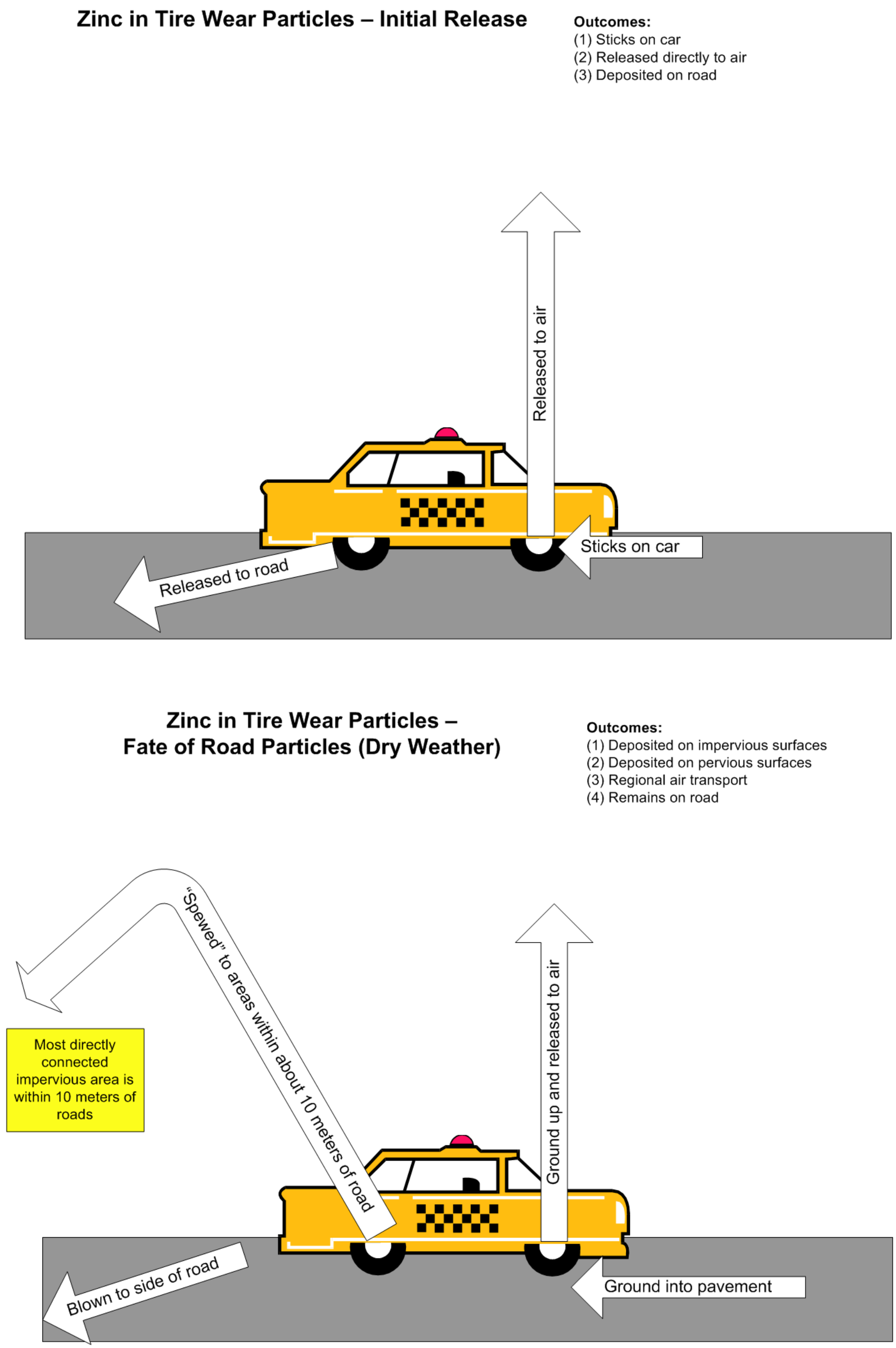


Figure 2. Tire Wear Debris and Air Deposition Conceptual Model

2005). Most of the mass of zinc in roadside particles is in particles smaller than 500 µm (Sansalone and Tribouillard 1999). These findings reinforce the conceptual model of zinc distribution from tire wear debris.

Tire wear debris includes a small fraction of very small particles with aerodynamic diameter less than 1 µm (Cadle and Williams 1978; Sadiktsis et al. 2012; Gustafsson et al. 2007; Kreider 2010). These very small particles, which comprise only a small fraction of tire zinc emissions, disperse throughout the urban environment.

Ultimately, between its air and water transport pathways, tire wear debris is well dispersed in urban environments. It has been found in air, water, soils, sediments, and biota (Wik and Dave 2009).

At first glance, this conceptual model appears inconsistent with some air deposition data. There are two major reasons for apparent inconsistency:

- Sampling methods. Because sample collection methods often exclude particles larger than air quality regulatory cutoffs of 10 µm diameter ("PM_{10}") and 45 µm diameter (total suspended particulate or "TSP"), typical air particulate sampling methods collect less than half of zinc emissions from tires (Lim et al. 2006).
- Sampling locations. Some studies overestimate regional zinc deposition because samples were collected in locations within the primary deposition zone for tire wear debris (e.g., Van Metre 2003) or near to local zinc air emissions sources like port facilities using zinc painted marine shipping containers (Sabin and Schiff 2007). Other studies have used elevated sampling locations and avoided all roads, thus avoiding measuring most zinc deposition from tires.

Only one identified study specifically examined the deposition of larger sized particles near a highway (Sabin et al 2006b). In this Los Angeles County study, the spatial pattern of zinc deposition was consistent with the literature described above and this conceptual model.

6.0 URBAN RUNOFF ZINC SOURCE ASSESSMENT

6.1 Prioritization of Zinc Sources

On the basis of the literature review and the conceptual model, zinc sources in urban runoff were divided into the following groups:

(1) Major sources – zinc-containing outdoor materials (e.g., galvanized steel) and rubber from tires

(2) Potentially major local sources – sources that occur only in limited locations, but that could be major sources in those locations

(3) Minor zinc sources

The prioritization exercise was informed by the sources cited in the detailed discussion below and by previous zinc source identification studies, three of which included detailed zinc source inventories for specific urban watersheds.

6.2 Major Zinc Sources

6.2.1 Outdoor Zinc Surfaces

Both galvanized steel and zinc sheet have many outdoor uses that put zinc in contact with urban runoff. Galvanized steel has long served as cost-effective roofing, gutters, flashing, drainage pipe, and fencing in urban communities, particularly in industrial areas. In addition to traditional galvanized steel and zinc sheet, zinc-containing outdoor building materials include Anthra Zinc, Galvan, Galvalume, and spray-on zinc coatings. (Zinc paints are also used outdoors; these are discussed in Section 6.3.1 below).

In California residential areas, galvanized gutters and fencing are common, but galvanized roofing is uncommon. Although zinc sheet has not historically been a common California building material, in recent years, zinc sheet has drawn interest in the design community for its appearance and longevity when used as building roofing and siding for commercial and institutional buildings.

Not all outdoor zinc materials have exposed zinc surfaces. Zinc, galvanized, and galvalume sheet materials are often pre-painted prior to installation to provide the desired color and to minimize maintenance. Some materials are commonly painted after installation (e.g., building flashing and gutter exteriors). When first sold, galvanized products—particularly sheet roofing—sometimes have a thin, temporary passivation coating that may be of a polymer (called "TOC") or chromate,[3] which prevents unsightly streaking prior to installation.

Galvanized roofs are common on low-cost structures
(Photo: Achim Hering)

Since the late 1980s, a series of publications has revealed relatively high concentrations of zinc in runoff from outdoor zinc surfaces (Yaziz et

[3] Decreasing in popularity due to its content of highly toxic chromium(VI).

al. 1989; Good 1993; Rocher et al. 2004; Mendez et al. 2010; Heijerick et al 2002; Lindstrom and Odnevall Wallinder 2011; Bertling et al. 2006; Robert-Sainte et al. 2009; Schriewer et al. 2008). For example, Clark et al. (2008) report measuring 5,000-30,000 micrograms per liter (µg/L) zinc in runoff from a galvanized roof panel. Tobiason and Logan (2004) reported zinc concentrations as high as 20,000 µg/L in initial runoff from galvanized highway guardrails. Schriewer et al. (2008) measured concentrations up to 30,000 µg/L in first flush flows from a zinc sheet roof, decreasing to about 5,000 µg/L later in storm events. Runoff from a 10-year old Galvalume roof reportedly contained up to 400 µg/L zinc (Tobiason and Logan 2004). Heijerick et al. (2002) measured zinc concentrations from 2,300 to 8,400 µg/L in runoff from uncoated zinc, galvanized, Anthra Zinc, Galvan, Galvalume, and sprayed-on zinc surfaces.

Consistent with the frequent occurrence of zinc materials like galvanized roofing in California industrial areas, urban runoff zinc concentrations are usually highest from industrial land uses (e.g., Tiefenthaler et al. 2008; Center for Watershed Protection 1996).

Once exposed to the outdoor environment, zinc surfaces develop a patina, which is actually a layer of oxidation products formed by zinc's interaction with the air (Zaso 2009; Lindstrom and Odnevall Wallinder 2011). The rate of patina formation and its specific chemical composition depend on local air quality, particularly the levels of sulfur dioxide and chloride (and to a lesser extent, ozone levels) (IZA 2000; Reiss et al. 2004; Bertling et al. 2006). When water flows over outdoor zinc surfaces, oxides in the patina slowly wash away. Because the chemical composition of the patina affects washoff, local air quality conditions strongly affect zinc runoff concentrations (Leuenberger-Minger et al. 2002; Zaso 2009; Reiss et al. 2004; Lindstrom and Odnevall Wallinder 2011).

Zinc runoff loads from outdoor zinc surfaces. The amount of zinc washed off outdoor zinc surfaces is proportional to the exposed surface area and local zinc emissions rates. Zinc emissions rates depend on multiple factors, including air pollutant-induced corrosion rates and rainfall volumes. Annual zinc runoff loads are usually calculated on the basis of an annual emission factor (reflecting local washoff rates) and an estimate of exposed zinc surface area in the local watershed:

Zinc Runoff Quantity = Emission Factor x Surface Area

While this simplified approach is appropriate on a watershed scale, additional factors need to be included when developing site-specific estimates. A key site-specific factor is the building material inclination angle, since washoff from vertical surfaces (where water contact times are relatively short) is substantially less than from horizontal surfaces (Bertling 2005; He 2002). For example, zinc emissions from a vertical surface were about 66% less than emissions from an identical nearly horizontal surface (7 degree angle) on the same site (Bertling 2005). Another factor is the quality of the zinc material and the presence of temporary coatings. For example, materials with rough surfaces (e.g., inexpensive galvanized fencing) have larger surface areas than their smooth counterparts.

Emissions factors. A generic zinc runoff estimate can be developed on the basis of emissions factors from the scientific literature. Table 1 summarizes the highest quality available emission factor data, excluding studies that did not control for local air deposition or avoid use of zinc in runoff collection systems. Many additional studies reported zinc concentrations in runoff from outdoor zinc surfaces, but did not provide annual emissions factors, usually because measurements were short term (e.g., a small number of storm events).

Table 1. Summary of Zinc Surface Runoff Annual Emission Factor Data

Material	Emission Factor (g/m^2)	Exposure Location and Time
Galvanized steel	2.5 2.1 1.9 1.9	Stockholm, Sweden, 5 years[a] Stockholm, Sweden, 10 years[b] Créteil, France (urban), 1 year[c] Champs-sur-Marne, France (suburban), 1 year[c]
Galvanized steel / chromate coating	1.8 1.7	Stockholm, Sweden, 5 years[a] Stockholm, Sweden, 10 years[b]
Galvanized steel / TOC coating	0.8 1.0	Stockholm, Sweden, 5 years[a] Stockholm, Sweden, 10 years[b]
Zinc sheet	2.1 1.9 3.9 4.5 3.3 4.2 3.7	Stockholm, Sweden, 5 years[a] Stockholm, Sweden, 10 years[b] Créteil, France (urban), 1 year[c] Créteil, France (urban), 40 years[c] Champs-sur-Marne, France (suburban), 1 year[c] Champs-sur-Marne, France (suburban), 40 years[c] Garching, Germany (Rural) 14 years[d]
Pre-painted galvanized steel	0.07 0.02 0.01	Stockholm, Sweden, 5 years[a] Créteil, France (urban), 1 year[c] Champs-sur-Marne, France (suburban), 1 year[c]
Anthra Zinc	1.4 2.3 2.1	Stockholm, Sweden, 3 years[a] Créteil, France (urban), 1 year[c] Champs-sur-Marne, France (suburban), 1 year[c]
Quartz Zinc	1.5	Stockholm, Sweden, 3 years[a]
Galfan (95% zinc + 5% aluminum)	1.1	Stockholm, Sweden, 5 years[a]
Galfan / TOC coating	0.6	Stockholm, Sweden, 5 years[a]
Galvalume (45% zinc + 55% aluminum)	0.5	Stockholm, Sweden, 5 years[a]
Galvalume / TOC coating	0.3	Stockholm, Sweden, 5 years[a]
Spray coated Zinc-Aluminum (85% zinc + 15% aluminum)	1.7	Stockholm, Sweden, 5 years[a]
Spray coated Zinc-Aluminum post-painted with epoxy	0.09	Stockholm, Sweden, 5 years[a]

Sources: [a]Bertling et al. 2006; [b]Lindstrom and Odnevall Wallinder 2011; [c]Robert-Sainte et al. 2009; [d]Schriewer et al. 2008

The data in Table 1 reveal differences among zinc-containing materials and effects of temporary and permanent coatings. In general, emissions increased with the age of the surface (Robert-Sainte et al. 2009), which could relate either to oxidation patterns or to the loss of temporary surface coatings applied by manufacturers. Zinc sheet and galvanized steel had similar emissions in Sweden, but in France, zinc sheet emissions were nearly twice those of galvanized steel (Bertling et al. 2006; Robert-Sainte et al. 2009; Lindstrom and Odnevall Wallinder 2011). Pre-aged "Anthra Zinc" and pre-patinated "Quartz Zinc" had emissions similar to those from other zinc surfaces.

Three zinc-aluminum alloys were tested: Galvalume (45% zinc + 55% aluminum), Galfan (95% zinc + 5% aluminum), and spray-coated zinc-aluminum (85% zinc + 15% aluminum). With the exception of the spray-coated material, zinc-aluminum alloys had lower emissions than would be expected on the basis of the alloy ratios alone (Bertling et al. 2006).

Permanent coatings nearly eliminate zinc runoff. Swedish scientists measured 97% lower emissions from a pre-painted galvanized surface and 95% lower emissions from a spray-on zinc coating that was subsequently painted with epoxy (Bertling et al. 2006). A French research team found 99% lower emissions from the pre-painted surface in both their urban and suburban testing locations (Robert-Sainte et al. 2009).

Temporary passivation coatings that protect the appearance of galvanized steel prior to installation reduce zinc losses for several years after installation, but eventually wash away (Bertling et al. 2006; Lindstrom and Odnevall Wallinder 2011). Over a 10-year period, zinc emissions from a chromate-coated galvanized panel were about 20% lower than emissions from an uncoated panel (Lindstrom and Odnevall Wallinder 2011). A longer-lasting TOC coating reduced zinc emissions by 52% over a 10-year period (Lindstrom and Odnevall Wallinder 2011).

All of the zinc emission factor data in Table 1 are from Europe. European sulfur dioxide concentrations in air were previously higher than those in California. Current annual average California sulfur dioxide concentrations are relatively low, in the range of 0 to 3 parts per billion (ppb) (ARB 2013), with some locally higher concentrations in areas near large emissions sources such as refineries and ports (ARB 2011). Stockholm, where the bulk of available data were collected, also has relatively low sulfur dioxide concentrations (between 0.2 and 1.1 ppb) (Odnevall Wallinder et al. 1998). Insufficient data are available to compare other air quality characteristics.

Although several equations have been proposed to account for local air quality conditions in Europe (e.g., Reiss et al. 2004; Odnevall Wallinder et al. 1998), three of these equations were developed specifically for Switzerland. The fourth equation accounts only for differences in sulfur dioxide levels (Odnevall Wallinder et al. 1998 as revised by Netherlands 2008a):

Zinc emission factor = 1.36 + 0.43 x Sulfur Dioxide concentration

Where the emissions factor is expressed in grams per square meter (g/m^2) per year and sulfur dioxide concentration is in ppb.

This equation suggests that zinc emissions from uncoated outdoor zinc surfaces in California urban areas might be similar those listed in Table 1. No unifying equation applicable for California conditions (i.e., addressing California ozone and chloride levels, its seasonal rainfall patterns, and lower total rainfall volumes) was identified in the literature review.

In the absence of local data, California emissions, which are primarily from galvanized surfaces, are best estimated on the basis of the emissions factor generated from the longest exposure period for untreated galvanized surfaces, 2 grams per square meter (g/m^2) per year (Lindstrom and Odnevall Wallinder 2011).

Total outdoor watershed zinc use. Estimating total zinc emissions from outdoor surfaces requires an estimate of the surface area of zinc in the watershed. The literature review did not reveal any existing estimates of the use of outdoor zinc materials for California or any of its regions. Neither zinc market data nor data characterizing zinc usage in buildings appear to be available in California. Although total U.S. sales of all galvanized materials have been estimated at about 2.3 million tons per year (American Galvanizers Association 2013), these data reflect all galvanized products—including structural, fasteners, tubing, pipe, wire, nails, reinforcing steel, guardrail, and posts—many of which are not used outdoors.

Other inventories approached the estimation of surface area in various ways, usually relying on a combination of market data and field surveys, sometimes supplemented by local geographic information system data. For example, the Netherlands national zinc runoff estimate accounted for roofs, gutters, greenhouses, nuts and bolts, facades, sheds, structural components, fencing, street furniture, vehicles, road crash barriers, and high-tension poles, relying on an extensive national inventory of zinc-containing construction materials that used commercial data on zinc sales and product replacement frequencies (Netherlands 2008a). To develop Swiss nationwide estimates of zinc runoff from outdoor surfaces, Reiss et al. (2004) used an on-the-ground survey of outdoor zinc surfaces, which focused on large surface area items such as roadway features (bridges, guard rails, signs), rooftops, and utility structures (power transmission line towers, light posts). The survey was supplemented by data provided by the building industry to characterize replacement rates for various materials and the total sales volumes.

Most watershed-specific estimates have focused primarily on roofing:

- The Chollas Creek and Auckland, New Zealand inventories relied on photographic and field assessments of outdoor zinc use, particularly focusing on roofing types (Weston Solutions 2011; Kennedy and Sutherland 2008).
- Similarly, the City of Palo Alto estimated the total area of copper roofing in its watersheds on the basis of a contractor survey, building department staff interviews, and a visual inspection of buildings in Palo Alto (Barron 2001).
- A San Francisco Bay area copper roof runoff estimate used total watershed area by land use, land-use-specific estimated fractions of all directly connected impervious area comprised of roofs (generated from a regional geographic information system), and a rough estimate of the total fraction of all roofs (by land use) that are copper (TDC Environmental 2004).
- The Puget Sound estimate used local geographic information system data to estimate total roof area for each land use category within the watershed. Roofing type frequencies were obtained from assessor's databases for two counties; however, these data did not fully distinguish among the various metals used in roofing (Washington Ecology 2011).

Developing outdoor zinc surface area estimates for California watersheds. Estimates must be developed on a watershed-specific basis. In the absence of market or building permit data, the simplest initial approach entails use of publicly available aerial and street photography. Detailed aerial photography of urban areas, including street-level imagery, is readily available—often at no cost—from various sources, including Internet mapping sites. Random sampling of these photographic data can provide low-cost estimates of building characteristics in urban locations without heavy tree cover. For example, the San Francisco Estuary Institute used randomly sampled aerial images to estimate the total building footprint areas and building heights in San Francisco Bay Area watersheds (Klosterhaus et al. 2011). Computational analysis of high-resolution aerial photography can provide detailed estimates of roofing materials and surface areas at a small watershed scale (Nishimura 2013).

Common outdoor zinc surfaced fixtures should be included in watershed estimates, particularly if these features drain to directly connected impervious areas (i.e., streets and storm drainage channels). Initial rough estimates can be developed with limited photographic or field surveys and the following surface area estimates:

- <u>Galvanized wire fencing</u>. Fencing has a surprisingly large surface area. For example, a 6-foot high industrial gauge (6-gauge) chain link fence has a surface area of 2.2 square meters per meter length (Golding 2006).
- <u>Guardrails</u>. Galvanized guardrail has a surface area of 0.6-1 square meter per meter length (Blok 2005; Kennedy & Sutherland 2008).
- <u>Light standards and sign poles</u>. Light poles have surface areas from 4 square meters (small) to 35 square meters (large) (Kennedy & Sutherland 2008).

Galvanized drainpipes, though not commonly installed today by municipalities, may be used in certain jurisdictions or in highway rights-of-way. In some watersheds, these may have sufficient surface area to be significant contributors to zinc runoff loads. No unit area data were identified for galvanized pipes.

Galvanized pipes often convey stormwater

Most inventories omit materials believed to have relatively small total surface area. For example, building gutters may not be necessary to include in inventories. In New Zealand, a detailed building inventory found unpainted galvanized gutters on fewer than 10% of all structures. In California, vinyl, aluminum, and painted gutters have major market shares due to their attractive appearance and lower prices. Compared to other features, gutters have relatively small surface areas (Barron 2001).

Most regional inventories also omit rooftop equipment like ventilation system equipment, cooling towers, and housings for other building mechanical equipment; flashing; and signs, which usually have total surface areas that are relatively small.

<u>Zinc reductions in drainage systems</u>. Most inventories assume that all zinc emitted from outdoor zinc surfaces is washed into the storm drain system without any zinc losses. There is a potential for significant reduction in zinc levels in runoff if the runoff flows through vegetation or passes through a treatment device. These reductions cannot be predicted on a generic basis, but watershed specific urban design information can provide a reasonable basis for estimates of potential zinc reductions before runoff enters the storm drainage system.

For example, in highly impervious watersheds, building gutters often connect directly to storm drains (this is often required by building codes). However, in less impervious areas, large zinc surfaces like galvanized fences occur primarily over pervious surfaces in the landscaped buffers between properties. Infiltration of runoff into a soil “drip zone” substantially reduces zinc levels in runoff (Blok 2005). Even concrete can reduce zinc levels in low flows until its binding capacity is exceeded, as demonstrated by experimental data showing that sheet flow across 1 meter of fresh concrete removed 7-25% of zinc in roof runoff (Lindstrom and Odnevall Wallinder 2011).

<u>Zinc loads from outdoor zinc surfaces</u>. In the absence of data characterizing the presence of outdoor zinc surfaces in California urban watersheds, it is impossible to create generic load estimates. Using Los Angeles County land use information and data from other inventories, this section illustrates the load estimation method. Load estimates focus on the largest exposed zinc surfaces in the watershed—typically roofs, fencing, guardrails, and large posts.

Table 2 summarizes the illustrative estimate. For purposes of illustration, zinc roof area was estimated on the basis of two previous assessments. In San Diego, Weston Solutions (2011) estimated that galvanized roofs comprised 1% of all roof area in the Chollas Creek watershed. The total watershed roof area was not specified, so roof area estimates for the San Francisco Bay area were substituted (30% of all residential land use area and 50% of commercial/industrial/institutional land use areas are roofs) (Barron 2001). The Washington Department of Ecology estimated that in the Puget Sound region, roofs comprise 8% of residential land use surface area and 24.5% of commercial/industrial land use surface areas (Washington Ecology 2011). Washington estimated that 4.1% of residential roof area and 15% of commercial/industrial roof area are zinc (Washington Ecology 2011). Using Los Angeles County total land use areas (residential - 1 billion square meters; commercial/industrial/institutional – 2 billion square meters) (SCAG 2011), total zinc roof area can be grossly estimated at 11 to 44 million square meters.

Table 2. Illustration of Methodology to Estimate Runoff from Zinc Surfaces

Surface	Quantity	Unit Surface Area (m^2)	Total Surface Area (m^2)	Zinc Emissions Factor (mg /m^2)	Zinc Load (kg)
Roof area	11-44 million m^2	1	11-44 million	2	22,000-88,000
Fencing (length)	2.8 million m	2.2	6.1 million	2	12,000
Guard Rail (length)	2.8 million m	0.8	2.2 million	2	4,000
Large Posts (each)	5,500	35	0.2 million	2	400
Other surfaces	Assumed negligible				--
				Total	**40,000-100,000**

For illustration purposes, it was assumed that total galvanized fencing in Los Angeles County would be equivalent to a six-foot-high galvanized fence spanning the entire length of both sides of all state highways (1385 kilometers) (Caltrans 2011a). Similarly, for illustration purposes, total galvanized guardrail was assumed to be equivalent in length to a guardrail spanning the entire length of both sides of all of the highways in Los Angeles County. Large galvanized posts were assumed to be installed in a quantity equal to four large posts per highway mile. Note that this illustration does not account for zinc removal that may occur between the zinc surface and the storm drain, such as when zinc fencing is installed over pervious surfaces.

Only two previous source inventories—from the Netherlands and Switzerland—provide total estimates of zinc runoff from outdoor zinc surfaces (Netherlands 2008a; Reiss 2004). Both estimates represent entire nations with urban designs very different than those in California's urban areas. Since neither estimate provides land use data comparable to those available in California, comparisons can only be made on the very imperfect basis of population ratios, which provide only a sense of scale of the estimates. Based on Los Angeles County's population of 9,958,091 (DOF 2013), and the Netherlands population of 16,319,868 (World Bank 2013), a scaled zinc runoff emissions estimate would be 47,000 kilograms per year. Based on Switzerland's population of 7,364,100 (Swiss Federal Statistics Office 2012), a scaled zinc runoff estimate would be 190,000 kilograms per year. Although these represent very different land use designs, it is notable that these estimates are in the same relative quantity range as the illustrative estimate above.

Priority Information Needs for Local Watershed Estimates

- Local data characterizing outdoor zinc use in specific watersheds.
- Local urban design information sufficient to estimate the fraction of runoff that drains to pervious surfaces or treatment systems.

Uncertainty

- Uncertainty in local watershed-wide estimates of zinc loads from outdoor zinc surfaces will be driven primarily by the accuracy of outdoor surface area estimates and the estimation of potential zinc reductions provided by typical urban design features (e.g., soil under fencing). Careful assessment can ensure that the estimate will represent the correct order of magnitude of total zinc load.
- While the emissions factors do not represent California conditions, the relatively narrow range of values in the literature (Table 1) suggest an uncertainty of less than 25% (e.g., 2 ± 0.5 g/m^2-year).

6.2.2 Outdoor Rubber Materials

To produce tires and other rubber products, manufacturers mix natural or synthetic raw rubber with chemical additives, shape the product (sometimes inserting other components, like the belts in tires), and cure it. Almost all products contain additives that cause the rubber to “vulcanize” (develop crosslinks) during the curing process, which strengthens the final product. Rubber formulators typically add metal oxides, accelerators, retardants, antioxidants, softeners, fillers, and vulcanizing agents in their formulations (EPA 2008a).

Rubber formulations vary; each is designed to achieve the desired characteristics in the final product. Tires contain multiple rubber formulations in their multi-layer construction (ChemRisk and DIK 2008). Tire tread, which is the portion that wears off on roads, may consists of a mixture of ten or more proprietary ingredients, including rubber, carbon black, zinc oxide, organic acids (e.g., stearic acid), benzothiazoles, sulfur compounds, and various oils and resins (EPA 2008a; Ni et al. 2008; ChemRisk and DIK 2008). In the tire tread, zinc oxide is evenly dispersed, occurring in very small particles averaging less than 1 micrometer in diameter (Adachi and Tainosho 2004).

Nearly all rubber products contain zinc oxide, which accelerates vulcanization (EPA 2008a). A typical passenger tire contains about 100 grams of zinc oxide (IZA 2006a). According to the International Zinc Association, zinc oxide improves tire wear abrasion performance, protects against ultraviolet radiation, reduces thermal effects caused by internal friction, helps bond rubber to metal (such as the steel cord of tires), reduces rubber shrinkage during curing, and helps keep product molds clean (IZA 2006a).

Although zinc oxide is the main zinc compound used in rubber, other zinc compounds may also be used. Zinc dialkyldithiocarbamates are sometimes added to promote vulcanization (IZA 2006a). Zinc palmitate, stearate, and oleate may serve as dusting agents for rubber (WHO 2001).

Rubber Uses

New rubber. In the U.S., rubber’s main outdoor use is in vehicle tires. Other outdoor uses include rubber drainage channel linings, erosion control devices, playground surfaces, traffic control products, and traffic safety products like cushioning for rail grade crossings and wheelchair ramps. These durable products, though subject to rainfall, would be unlikely to release meaningful quantities of zinc into the environment because zinc is physically bound into the polymeric structure of the product, which remains intact through the product life cycle.

Rubber has a broad range of indoor and mechanical uses, such as rubber bands, hoses, gaskets, protective casings, tubing, gloves, and belting (EPA 2005). These products are generally durable products, used primarily indoors, and are not designed to wear off into the environment.

Vehicle Tires

Except for tires, the only other outdoor, dispersive use of new rubber is in shoe soles. U.S. EPA estimates that footwear comprises about 3% of the U.S. rubber market (EPA 2005). Like tires, rubber-soled shoes contain zinc. Because relatively small amounts of material wear off of shoe soles as compared to tires, zinc from shoe wear has been estimated to comprise only about 0.1% of the total amount of zinc in urban runoff (Ingre-Khans et al. 2010).

<u>*Used rubber.*</u> Tires comprise the majority of California's rubber waste, an estimated 370 million kg per year (SAIC 2011). Through strong market efforts by the California Department of Resources Recovery and Recycling (CalRecycle), California reuses about half of its waste tires within the state (see Table 3).

Table 3. California Waste Tire Management Summary 2010

Management Approach	Fraction of Waste Tires
Landfill (disposal, alternative daily cover, landfill civil engineering purposes)	25.3%
Combustion ("tire-derived fuel" used at 5 California facilities)	20.3%
Export	19.8%
Reuse on vehicles (includes retreads)	13.7%
Rubberized asphalt pavement	12.3%
Artificial turf infill (4-30 mesh crumb rubber)	3.3%
Loose mulch (0.25-0.75 inch diameter ground rubber)	2.7%
Molded & extruded products	1.8%
Tire-derived aggregate for civil engineering applications (2-12 inch shreds) (excludes landfill use)	0.1%
Solid surface rubberized playgrounds	0.4%
Other (e.g., rubber bumpers on docks)	0.5%

Source: SAIC 2011

Like virgin rubber uses, most waste tire uses do not disperse zinc into the environment. Three exceptions are re-use as tires, combustion as tire-derived fuel, and tire shred and crumb products that contact water. Tire re-use is considered with rubber tires above. Tire combustion, which occurs at five California facilities, may be a locally important zinc source (see Section 6.3.3). Similarly, tire shred and crumb products may be locally important sources if installed in manners exposed to urban runoff (see Section 6.3.2).

Zinc runoff loads from tires. As described above in the conceptual model, rubber tire tread slowly wears off as tires roll across the pavement, gradually emitting rubber—and its zinc content—into the environment. Almost every zinc emissions inventory has identified tire wear as a major source of zinc in urban runoff (Councell et al. 2004; Hjortenkrans et al. 2007; Kennedy and Sutherland 2008; Vos and Janssen 2008). Many detailed estimates of zinc releases from tires and their contribution to runoff have been performed (Blok 2005; Kennedy and Sutherland 2008; Whiley 2011; Hjortenkrans et al. 2007, Ten Broeke 2008).

Most estimates use emissions factors based on tire zinc content and wear rates. Total zinc runoff loads are usually estimated on the basis of watershed-specific vehicle fleet composition and vehicle kilometers traveled data.

Zinc Runoff Quantity = Zinc Emissions Factor x Distance x Washoff

This simple approach can be used for both watershed scale and site-specific estimates. On a site-specific basis, the best estimates involve site-specific data for tire zinc content and wear rates, because both tire zinc content—particularly for heavy-duty equipment—and wear rates may differ significantly from averages.

Tire tread rubber zinc concentration. Since manufacturers consider tire formulations to be trade secrets and tire composition is not regulated by any government agency, there is no independent central data source for tire zinc content data. Many researchers have measured and reported zinc content of individual tires. Table 4 summarizes available data for samples of tire tread material from new tires. Assuming that wear rates represent losses of rubber tire tread material only, the summary excludes data from used tires (Davis et al. 2001; McKenzie et al. 2009; Fauser 1999), which generally have lower zinc levels in due to the embedding of foreign materials (e.g., road dust) in the tread (Kreider et al. 2010).

Table 4. Summary of Tire Tread Zinc Concentration Data

Tire Type	Mean Zinc Concentration (range) (mg/kg)	Data Source
Car	9,400 (6,100 – 16,000) 8,470 (5,650 – 9,640) 9,500 14,800 (12,700 – 16900) 10,250 9,600 (320 to 23,000)	Sweden, 52 tires (Hjortenkrans et al. 2007) New Zealand, 7 tires (Kennedy et al. 2002) Netherlands Industry data (Blok 2005) Japan, 2 tires (Ozaki et al. 2004) France (Legret and Pagatto 1999) EU Rubber Industry survey (Smolders and Degryse 2002)
Truck	17,000 16,000 (13,800 – 18,300) 17,000 (9,600 to 35,000)	Netherlands Industry Data (Blok 2005) New Zealand, 2 tires (Kennedy et al. 2002) EU Rubber Industry survey (Smolders and Degryse 2002)

The data in Table 4 indicate that car tire zinc content is around 10,000 milligrams per kilogram (mg/kg), consistent with typical tire formulations (Kreider et al 2010). Available data suggest that truck tires have almost twice the zinc content of car tires—about 17,000 mg/kg. Unless local or more recent data become available, these concentrations are reasonable values for preliminary estimates.

Although multiple U.S. studies have examined tire zinc content, none analyzed zinc concentrations in the tread of unused U.S. tires. Since the vehicle parts industry operates internationally, international data provide a reasonable approximation of the U.S. market; however, because U.S. market preferences have driven the formulation of other vehicle parts (e.g., brake pads), the lack of U.S. data represents a source of uncertainty when using international data to estimate U.S. tire zinc content.

Two major reviews of tire zinc concentrations have been conducted. The USGS completed a detailed literature review of publications that primarily reported car tire zinc content, ultimately determining that the best estimate of tire tread zinc content in the U.S. market was 10,000 mg/kg (Councell et al. 2004). The European Environment Agency similarly reviewed available data, again primarily from car tires; it decided to use a slightly lower concentration (7,400 mg/kg) based on a weighted average of all data, including data sets from used tires (European Environment Agency 2009).

Recognizing the higher truck tire zinc content, truck tire zinc emissions should be estimated separately from car tire emissions (e.g. Kennedy and Sutherland 2008; Ten Broeke 2008). While it might be advantageous to break out emissions estimates for other vehicle classes, poor data availability will probably preclude such estimates in most California watersheds. Not breaking out mid-sized vehicles from cars would likely lead to an underestimate of tire zinc emissions because mid-sized vehicle tires appear to have zinc concentrations greater than car tires, but lower than truck tires (Blok 2005; Ten Broeke 2008). Because retread tires appear (on the basis of limited data) to have zinc content similar to that in other tires (Hjortenkrans et al. 2007), separate estimations do not appear to be necessary.

Tire tread rubber wear rate. Over a tire's lifetime, more than 10% of its mass wears away onto road surfaces (Blok 2005; Whiley 2011). The rate of tire wear depends on multiple factors, such as the characteristics of the tire itself, the road surface, vehicle operation, and vehicle design and loading (ChemRisk and DIK 2008; Kennedy et al. 2002). Tire wear levels may be greater in deceleration zones (Drapper et al. 2000). Tire wear rates are generally higher in urban areas, where stops, starts, and turns increase wear rates (Ten Broeke 2008).

Few researchers have measured tire wear rates. Often scientists have collected data characterizing only fine particulate emissions (e.g., Kupiainen et al. 2005; European Environment Agency 2009), which represent only a small fraction of total tire wear (Kreider et al. 2010).

Most tire wear rate estimates are based on tire sales volumes, tire geometry, and assumptions regarding the tire tread depth remaining when tires are replaced. For example, Whiley (2011) estimated tire wear rate at 38 milligrams per kilometer (mg/km) based on measurements of a Toyota Camry tire. Legret and Pagatto (1999) used measurements of French tires to estimate wear rates of 68 mg/km for cars (total for all tires) and 136 mg/km for trucks (total for all tires).

Estimates have also been made on the basis of tire weight loss during use. For example, the New Zealand vehicle industry used tire weight loss data to estimate wear rates of 31 mg/km for car tires, 51 mg/km for light truck tires, and 210 mg/km for heavy truck tires (Kennedy et al. 2002).

The Netherland Water Board completed a detailed summary of available data characterizing fine particulate emissions from tires and used particle size distribution data to estimate the fraction that measured particle emissions represent of total tire wear. Emissions rate estimates were further refined with data characterizing changes in emissions on various road types and under different driving conditions. The final estimates, which best characterize Netherlands vehicles driven in urban areas are: car (all 4 tires) – 158 mg/km; van (all 4 tires) – 190 mg/km; bus (all 6 tires) – 495 mg/km; truck (all 8 tires) – 785 mg/km; and truck (all 10 tires) – 1014 mg/km (Ten Broeke 2008).

In the U.S., vehicles are somewhat larger than European vehicles (particularly trucks) and New Zealand vehicles (particularly passenger cars). Only one thorough evaluation of U.S. vehicle tire wear emissions was identified. Based on literature review, tire geometry calculations, and tire sales estimates, the USGS's best estimate of tire wear was 50 mg/km per tire (Councell et a. 2004). For zinc load estimation purposes, cars were assumed to have 4 tires; vans, buses, and light trucks were assumed to have 6 tires; and large trucks ("semi trucks") were assumed to have 18 tires (Councell et al. 2004).

Zinc emissions factor. Using the USGS wear rate (Councell et al. 2004) and the typical car and truck tire tread zinc concentrations listed above (10,000 mg/kg for cars; 17,000 mg/kg for trucks), emissions factors would be 0.5 mg zinc/km for car tires and 0.9 mg zinc/km for truck tires.

Among the literature, only one study created zinc emissions factors specifically for zinc from tire tread (Blok 2005)—all others explicitly used the wear/concentration approach. The Netherlands estimates were 0.2 to 0.3 mg zinc/km for car and van tires and 0.7 mg zinc/km for truck tires (assuming 10 tires per truck) (Blok 2005). These lower estimates reflect vehicles in the Netherlands, which are smaller than typically found in the U.S. fleet (e.g., trucks with no more than 10 tires and vehicles with lower average gross vehicle weight). Since tires from smaller vehicles are typically smaller, Netherlands emissions factors should be lower than California emissions factors.

Distance. Vehicle travel distance must be obtained on a watershed-specific basis. Air quality and transportation agencies conduct vehicle counts and develop vehicle kilometers traveled estimates for California. Most California data resources provide data by road segment, county, or region. Different regions provide different levels of vehicle classification detail (e.g., truck, car, motorcycle, truck size categories). For example, the Southern California Association of Governments (SCAG) provides summary estimates of vehicle kilometers traveled in its jurisdiction, which includes Los Angeles County. SCAG estimates that vehicles drive an average of 120 billion kilometers per year in Los Angeles County, with trucks comprising 4.0 billion of these kilometers (SCAG 2012a). Assuming, for simplicity, that all non-truck kilometers are cars, this translates to 116 billion car kilometers and 4.0 billion truck kilometers traveled annually in Los Angeles County.

Washoff. The fraction of zinc from tires that is entrained in urban runoff is called "washoff." Not all tire wear debris washes away from the surface on which it lands. Some will be ground into the pavement or deposited on pervious surfaces where the zinc may remain permanently. On the basis of the dispersion of tire wear particles in the environment (see conceptual model above), it is reasonable to assume that most tire wear debris is deposited on impervious surfaces and is subject to washoff into storm drains.

Most studies assume that 100% of emitted tire wear debris may be subject to washoff. Blok (2005) estimated that 50% of tire wear debris remains on roads and that 70% of this material may be washed off by rain, but did not estimate the washoff fraction of the 50% of tire wear debris that deposits away from the immediate road surface. After reviewing data characterizing the distribution of tire wear debris in the environment, Kennedy et al. (2002) made the assumption that 80% of tire wear debris was deposited in the near-road environment and therefore subject to washoff. In the absence of local washoff data or a local watershed analysis of tire deposition and washoff, the Kennedy et al. washoff factor of 80% would be reasonable to use for preliminary estimates.

Zinc loads from tires. Preliminary zinc load estimates can be calculated using the emissions factors and washoff factor developed from the literature and local vehicle kilometers traveled data (Table 5). At a minimum, load estimates should separately estimate emissions from cars from trucks, as shown in Table 5. If vehicle kilometers traveled data have greater specificity, more detailed estimates with the appropriate number of tires for each vehicle category would be preferable.

Table 5. Preliminary Estimate of Zinc Load from Tires in Los Angeles County

Vehicle Class	Tire Emissions Factor (mg Zinc/km)	Number of Tires	Annual Distance Traveled (km)	Washoff Factor	Zinc Load (kg)
Car	0.5	4	116 billion	80%	186,000
Truck	0.9	18	4.0 billion	80%	59,000
				Total	**230,000**

On a vehicle kilometers traveled basis, this estimate is somewhat—but not unreasonably—higher than other estimates. The most directly comparable of past estimates are those from the Netherlands and Washington State. The most recent and complete estimated total emissions of zinc from tires in the Netherlands, where vehicles travel an estimated 130 billion kilometers annually, were about 150,000 kg (Ten Broeke 2008). This lower estimate reflects the lighter, smaller vehicle fleet. Although 100% washoff was assumed in urban areas, Ten Broeke estimated that only about 50,000 kg of this zinc washes into storm drains (sewers) or surface water, reflecting that most of the vehicle kilometers traveled in the Netherlands occur outside of urban areas (Ten Broeke 2008).

In Washington's Puget Sound region, where vehicles travel approximately 58 billion kilometers per year, Washington Department of Ecology estimated tire zinc emissions of 80,000 kg, essentially all of which was assumed to be washed into urban runoff. This lower per kilometer estimate reflects not only the lower level of vehicle use in the watershed, but also a lower estimated average tire zinc concentration.

Priority Information Needs for Local Watershed Estimates

- Vehicle kilometers traveled data for the watershed, preferably data that differentiates between cars and trucks.

Uncertainty

- The greatest sources of uncertainty are the zinc emissions factors, which are based on zinc concentration data primarily from overseas and a gross wear rate estimate. The range of available tire zinc concentration data and wear rate estimates and comparison with other estimates suggests an uncertainty of 25 to 50%.
- Vehicle travel data sources typically have relatively low uncertainties (±10%)
- Zinc washoff rates for tire wear debris is only a gross estimate that could have an error as great as ±25%.

6.3 Potential Major Local Zinc Sources

Other zinc sources do not appear throughout California urban areas, but may occur in one or more local watersheds, where they can provide relatively high zinc concentrations in runoff. Zinc-containing paint and shred and crumb rubber from waste tires appear to be the most common potentially important local sources. These two sources are discussed in detail below. Table 6 lists all identified potentially important local zinc sources and briefly summarizes source control options.

6.3.1 Zinc-Containing Paint

Zinc-based white pigments were once commonly used to formulate paints, including paints used on building exteriors (Buxbaum and Pfaff 1998). Since the 1950s, zinc-based building paint pigments have largely been replaced with titanium dioxide-based pigments due to titanium dioxide's greater opacity (hiding power) (Buxbaum and Pfaff 1998). Since nearly all painted structures are repainted regularly, few structures with outer coatings of zinc paint likely exist today. If structures that have not been painted in more 60 years occur in a watershed, the degraded paint could be a locally significant source of zinc.

Today, zinc-based paint has niche uses only, primarily as an anticorrosion paint for metals (Buxbaum and Pfaff 1998; IZA 2011; European Commission 2008). Anticorrosion paint formulations vary—zinc phosphate paints contain less than 30% zinc, but zinc metal paints may contain 75-90% zinc. Zinc paint may serve as a primer or to touch up minor flaws in galvanized surfaces. Compared to galvanization, zinc paint has relatively limited use for corrosion control. In Europe, zinc paint is estimated to comprise about 2% of all corrosion control coatings (European Commission 2010).

Intermodal Shipping Containers May Be Coated with Zinc Anticorrosion Paint

Where zinc anticorrosion paint is not covered with a protective finish coat, it can be a locally significant source of zinc in runoff. Runoff from zinc-based anticorrosion paint can have concentrations as high as 13,000 µg/L (Kszos 2009). Local use sites may include bridges (FHWA 1995), shipping containers (Vincent 2012), and outdoor industrial storage containers (Kszos 2004).

Ordinary paints may contain lower concentrations of zinc, in the form of an antimicrobial additive that prevents unsightly surface staining. For paints, U.S. EPA has approved three zinc antimicrobial additives: zinc borate (at concentrations of 0.5 to 4%) (EPA 2007), zinc oxide (1.5%) (EPA 2009), and zinc pyrithione (0.75-5%) (EPA 2004). While no runoff data for these paints were identified, since antimicrobial zinc concentrations are about one-tenth of zinc concentrations in zinc-based paints, runoff concentrations are likely to be less than 1,000 µg/L, sufficiently elevated to represent a locally significant zinc source.

The extent of the use of paint with zinc antimicrobial additives is unknown. Although antimicrobial zinc is technically a pesticide, U.S. EPA does not require paint manufacturers to notify customers of paint zinc content. U.S. EPA has approved only a few zinc borate and zinc oxide products (EPA 2007; EPA 2009). Few products sometimes (but not always) correlates with low market penetration. Total national sales of zinc pyrithione, often mentioned as the most common paint additive, were about 110,000 kilograms in 2003. These total sales suggest relatively limited market presence in California (which comprises about 10% of the nation's population), and include other common products, such as marine antifouling paint (EPA 2004).

Priority Information Needs for Local Watershed Estimates

- Local surveys of management practices for bridges, shipping containers used at ports and distribution facilities, and outdoor storage containers at industrial sites to examine outdoor zinc anticorrosion paint use.
- Information characterizing the market presence of paints with antimicrobial zinc additives.
- Zinc concentrations in runoff from new and aged outdoor paints with antimicrobial zinc additives.

6.3.2 Tire Shred and Crumb Products

To facilitate recycling, waste tires are cut into pieces to create two products: tire shreds and tire crumb. Tire shred, or "Tire-Derived Aggregate," consists of 5 to 30-centimeter tire pieces. Mechanical knives cut up whole used tires to create tire shreds, which are subsequently size-segregated to exclude fines. Tire shreds' primary outdoor use is for civil engineering applications, such as in solid waste landfill construction and road base.

Grinding entire used tires generates tire crumb. Unlike tire shreds, tire crumb manufacturers separate the crumb rubber from the tires' steel and fiber belts. The resulting granular material varies in size from fine powder to 1-centimeter pieces (Rhodes et al. 2012). Tire crumb's primary outdoor uses are for artificial turf infill and a mulch-like ground cover (SAIC 2011). Other outdoor products, notably rubberized asphalt, may incorporate crumb rubber (SAIC 2011). Municipalities, transportation agencies, and even private entities may use tire shreds or crumb rubber in areas exposed to runoff. California Public Resources Code Section 42703 (AB 338 Levine, 2005) requires Caltrans to require that a specified percentage of crumb rubber be used in asphalt paving materials for state highway projects.

Limited available data suggest that tire shred and crumb zinc concentrations are similar to those in tire tread (Table 4). Like tire tread, crumb created from truck tires has higher zinc concentrations than crumb from car tires (Lim and Walker 2009).

Zinc leaches from both tire shreds and tire crumb when in contact with water. Zinc leachate levels correlate inversely with particle size—the smaller the particle, the greater the losses of zinc (Rhodes et al. 2012). This indicates that tire crumb is the higher priority from the water quality perspective.

Among all uses of tire shred and crumb, tire crumb use as artificial turf infill is the most common use where urban runoff may flow directly through tire material. Elevated zinc levels occur in water that is exposed to tire-based artificial turf infill material (Simon 2010; Bocca et al. 2009; Vershoor 2008). After passing through rubber infill, runoff has been estimated to have zinc concentrations between 100 µg/L and 1,000 µg/L (Vos 2008). Measurements of runoff from a small number of artificial turf fields have been at the lower end of this range (Connecticut DEP 2010).

Potential zinc loads greatly depend on drainage system design. In some cases, water flows directly to storm drainage systems after passing through a tire crumb infill layer. In other designs, water may subsequently flow through base materials (e.g., aggregate). Some base materials have high zinc retention capacity (e.g., sand, lava) that can nearly eliminate zinc discharges until the material's retention capacity is reached (Verschoor 2008; Hofstra 2009a; Hofstra 2009b). If drainage designs do not effectively collect zinc from infiltrated water, installations could create locally elevated zinc concentrations (Verschoor 2007, Vos 2008).

Priority Information Needs for Local Watershed Estimates:

- Local information about tire shred and crumb installations. Drainage design, particularly for artificial turf fields, should be examined.

6.3.3 Other Local Zinc Sources of Potential Importance

Other zinc sources that may occur in one or more California urban watersheds include drinking water anti-corrosion additives, anti-corrosion additives for water-containing equipment, fireworks, dumping, air deposition from forest fires, de-icing products, motor oil/lubricating oils additives, industrial air emissions, industrial runoff, zinc minerals or wastes in construction materials, mining, soils, volcanic ash, tire-derived fuel, re-suspension of zinc from historic emissions sources, fertilizer and agricultural micronutrient products, and zinc granule-impregnated asphalt roofing shingles. Table 6 summarizes all local zinc sources of potential importance and lists potential source control options for each source where applicable.

Priority Information Needs for Local Watershed Estimates:

- Local surveys to identify whether any of the above sources occur in a watershed.

6.4 Minor Zinc Sources

Zinc has many uses in California urban areas that do not have potential to be major sources of zinc in urban runoff. This section details two such sources—vehicle brake pads and wheel weights—that have received significant attention in relationship to other pollutants. Table 7 describes many other minor sources.

6.4.1 Brake Pads

About half of vehicle brake pads contain zinc, primarily at relatively low concentrations (less than 2%) (Washington Ecology 2014). Each time vehicle brakes engage, a tiny amount of fine dust wears off of the vehicle's brake pads. About half of the dust, called "brake pad wear debris," falls on the road; the rest moves through the air to deposit throughout the region. Depending on where it deposits, much (but not all) of this fine dust washes off into urban runoff.

Other inventories found brake pads to be a relatively small zinc source. Using measurements of zinc in New Zealand brake pad wear debris, Kennedy and Sutherland (2008) estimated that

Vehicle Disc Brake Pads

Table 6. Potential Major Local Zinc Sources

Zinc Use	Analysis	Potential Source Control Options
Zinc-containing paint	See text	Alternative paints; topcoat with non-zinc paint
Tire-derived shred and crumb rubber	See text	Alternative materials; drainage design to prevent zinc discharge
Drinking water anti-corrosion additive	Some potable water suppliers add “zinc orthophosphate” (usually a mixture of a zinc salt and an orthophosphate salt) within the water supply distribution system to control corrosion of piping in service connections and buildings. Where this treatment occurs, zinc concentrations in treated water can be in the range of 100-500 µg/L zinc (Hill 2010). Discharge occurs only indirectly, via drinking water indirect discharge pathways like irrigation overflow, water system flushing, fire hydrant discharges, and emptying of swimming pools, spas, and fountains to storm drains.	Non-zinc corrosion control additives; minimizing drinking water discharges
Anti-corrosion additives for water-containing equipment	Zinc-containing additives are used to control corrosion in water-containing equipment like boilers and cooling water systems. Ordinarily water from these systems is discharged to indoor drains, but discharges, particularly of cooling water system “blow down,” occasionally flow to storm drains.	Non-zinc additives; direct discharges to sewer
Fireworks	In fireworks, zinc creates smoke effects. Fireworks shows are usually a relatively rare event, and thus a relatively small contributor to overall levels of zinc in urban runoff (e.g., Kennedy and Sutherland 2008). For safety reasons, where possible fireworks are often launched such that residuals deposit directly into water, limiting the potential zinc contribution to urban runoff. Firework-related releases of multiple metals have triggered issuance of an NPDES permit in the San Diego area (San Diego Water Board 2011). In locations where fireworks shows over urban land are frequent (e.g., amusement parks), fireworks could potentially be a non-negligible source of zinc in urban runoff.	None
Dumping	Dumping of high-zinc wastes, like motor oil or loads of alkaline batteries, could include meaningful zinc quantities.	None
Air deposition from forest fires	Large-scale fires may deposit zinc on local watersheds, temporarily increasing levels in urban runoff (Sabin et al. 2005; Stein and Brown 2009).	None
De-icing products	Zinc oxide or zinc salts may be added to de-icing salts to reduce corrosivity. When used, deicing salts may be dispersed by traffic onto galvanized surfaces, where their presence enhances corrosion and increases zinc runoff (Legret and Pagatto 1999; Houska undated; Klimaszewska et al. 2007). De-icing products are rarely needed in most California urban areas.	Non-zinc de-icing products

Table 6. Potential Major Local Zinc Sources (Continued)

Zinc Use	Analysis	Potential Source Control Options
Motor oil/ lubricating oil additive	California used motor oil contains an average of 822 ppm zinc (Boughton and Horvath 2004). Quantities of oil in urban runoff have declined in recent years, due to improvements in vehicle design (reflected in extended oil change intervals) and aggressive programs to end motor oil dumping. OEHHA reported that median urban runoff oil and grease concentrations are 4,300 µg/L (Mazur et al. 1996), which corresponds to runoff concentrations of less than 1 µg/L zinc, a small contribution to total zinc concentrations in runoff. The Auckland Regional Council and the Netherlands similarly found that contributions of zinc from oil leaks to zinc levels in urban runoff were small (Kennedy and Sutherland 2008; Netherlands 2008d). At industrial and transportation facilities, leaks and spills may be sufficiently common as to become a major zinc source at the site (Golding 2006; Golding 2008). Waste oil combustion is estimated to emit up to 136 million grams of zinc to air; however, almost all of these emissions occur outside of California's airshed, primarily as emissions from waste oil burning as a ship fuel (Boughton and Horvath 2004).	Minimize leaks and spills
Industrial air emissions	U.S. EPA's Toxics Release Inventory lists few major zinc emitters in California; however, the inventory may not include all zinc-emitting industrial facilities (EPA 2011; ATSDR 2005). Nationally, refuse incineration, coal combustion, smelter operations, and some metal-working industries constitute the major sources of zinc in air (ATSDR 2005). Zinc air deposition is likely elevated around each major emitter.	Air emissions controls systems
Industrial runoff	The primary sources of zinc in industrial runoff are galvanized surfaces, tires, and leaks and spills of motor and hydraulic fluids (Golding 2006; Golding 2008). All of these true zinc sources are described in this report. At specific industries, site-specific sources (e.g., exhaust from on-site galvanizing systems, equipment covered with zinc-containing anticorrosion paint) could contribute to zinc levels in runoff.	Multiple strategies – see Washington Department of Ecology best management practices (Golding 2008)
Zinc minerals or wastes in construction materials	Zinc minerals or high-zinc wastes may in rare instances be used to make bricks or concrete, which could release zinc, particularly during construction and demolition (Perry et al. 2005).	Use best management practices to control dust and debris
Volcanic ash	Some volcano emissions contain relatively large quantities of zinc (ATSDR 2005). Ash may be transported in the upper atmosphere for thousands of kilometers prior to deposition. Ash deposition could temporarily increase levels in urban runoff.	None
Mining	Old mines may exist in some California urban areas and may be a source of zinc leachate or minerals that contribute zinc loads to urban runoff. For example, in the Santa Ana mountains, zinc mines occurred in the zinc-rich Bedford Canyon Formation (Stadum 2013).	Runoff control measures for mine drainage and spoil piles

Table 6. Potential Major Local Zinc Sources (Continued)

Zinc Use	Analysis	Potential Source Control Options
Soils	Typical California soils have a mean zinc concentration of 149 ppm (range 88-236 ppm), with few soil types exceeding 200 ppm zinc (Bradford 1996). However, a few soil formations (e.g., the Bedford Canyon formation and fresh carbon-rich portions of the Monterey formation) have much higher zinc levels, in excess of 300 ppm (Stadum 2013; Isaacs 1999). High-zinc soils may increase zinc levels in urban runoff and creeks where these soils are exposed (LVMWD 2011).	Enhanced erosion control measures (where feasible)
Tire-derived fuel	Waste tires are sometimes used as fuel at large industrial facilities. In California, waste tires currently may burned as a fuel source at five cement kilns and one cogeneration plant (SAIC 2011). If zinc is not fully removed by emissions controls systems, tire burning could create localized zinc deposition that could elevate runoff zinc concentrations in downwind areas.	Air emissions controls systems
Re-suspension of zinc from historic emissions sources	Despite large reductions in industrial zinc emissions since the mid-20th century, monitoring data show no decrease in environmental zinc concentrations in urban areas (Mahler et al. 2006; Casey et al. 2007). For example, in surveys of U.S. lake sediments from 1970 through 2001, USGS scientists found minor (<10%) increases in zinc concentrations in urban lakes and minor (<10%) decreases in sediments in reference lakes (Mahler et al. 2006). These data suggest that no environmental reservoir of zinc from past emissions exists in most locations. In localized areas around past or current major zinc emissions sources, re-suspension and deposition of high zinc concentration surface soils could potentially elevate runoff zinc concentrations in the local area.	None
Fertilizer and agricultural micronutrient	Zinc is one of the essential nutrients included in most fertilizers. It may also be applied separately as a soil micronutrient. Commercial fertilizer zinc concentrations depend on the fertilizer type. For example, compost fertilizers contain 50-750 ppm zinc (Sato 2010; Miller 2010), but chemical fertilizers typically contain 10,000 ppm zinc (IZA 2010). Zinc-specific amendments like zinc sulfate may also be used where zinc deficiencies exist in soils (IZA 2010). Since application rates are low—around a kilogram per acre at most, with the intent of providing a few ppm bioavailable zinc—the potential for fertilizers to increase zinc levels in runoff significantly is low except in special cases, like nurseries or other intensive operations that may have frequent spills.	Where fertilizers are stored outdoors, implement runoff prevention and spill cleanup measures
Zinc granule-impregnated asphalt roofing shingles	In high humidity, high rainfall areas, zinc granules may be impregnated into asphalt roofing shingles to prevent formation of algal black streaks. Although California has not registered zinc for this purpose, zinc-impregnated shingles may be shipped in from other states for use in the few California urban areas with humid, wet environments.	See control measures for outdoor zinc surfaces (Section 7.1)

brake pads comprised <2% of total zinc loads in Auckland watersheds. The Netherlands and Washington Department of Ecology similarly found brake pads to be a relatively small zinc source (Netherlands 2008e; Washington Ecology 2011).

Brake Pad Zinc Emissions. The Brake Pad Partnership completed detailed evaluation of brake pad copper releases, estimating total emissions of 1.08 milligrams of copper per kilometer based on vehicular copper emissions estimates in the Los Angeles area (Rosselot 2006 based on Gillies et al. 2001). Washington Department of Ecology collects brake pad zinc and copper content data under its "Better Brakes Rule" reporting requirement. Washington Ecology data (Washington Ecology 2015) show an average brake pad zinc concentration of 1%, about 13% of the average brake pad copper concentration at the time of the Brake Pad Partnership estimates (Brake Pad Partnership 2008). Based on these data, brake pad zinc emissions should be 13% of the Brake Pad Partnership's estimated copper emissions, or 0.14 mg/km.

Brake Pad Zinc Washoff. Because brake pad wear debris consists of tiny particles averaging only a few micrometers in diameter, it is more broadly dispersed in the urban environment than tire wear debris particles, which are more than 10 times larger. Some brake pad zinc emissions blow out of the watershed; other particles are deposited onto pervious surfaces and subsequently sequestered. Although the detailed Brake Pad Partnership studies do not provide the basis for direct calculation of a washoff factor for a highly urbanized watershed, the modeling shows that washoff is much less than 100% (Donigian and Bicknell 2007). After reviewing data characterizing the distribution of tire wear debris in the environment, Kennedy et al. (2002) made the assumption that 70% of brake wear debris would be washed into urban runoff. In the absence of local washoff data or a local watershed analysis of tire deposition and washoff, the Kennedy et al. washoff factor of 70% would be reasonable to use for preliminary estimates.

Zinc Loads from Brake Pads. In Los Angles County, where vehicles travel 120 billion kilometers annually (SCAG 2012a), zinc emissions from brake pads are estimated to be about 17,000 kilograms per year. Assuming 70% washoff, brake pad zinc loads would be about 12,000 kg per year, about 5% of the estimated load from tires in the county.

6.4.2 Wheel Weights

To keep vehicles rolling smoothly, vehicle wheels are "balanced" with small weights clipped on the inside wheel rim. As a consequence of a vehicle's motion, wheel weights often loosen and may fall off onto roads. Before being collected by street sweepers, captured in catch basins or buried in roadside soils, their surfaces are often abraded by the action of passing vehicles.

In recent years, manufacturers have reformulated wheel weights due to requirements to end use of lead-based weights. In 2011, DTSC evaluated alternatives to lead wheel weights, finding that steel weights were environmentally preferable (DTSC 2011). The current market is dominated by steel weights, but zinc weights (which are larger than steel weights) gain popularity when steel prices rise (Boughton 2011).

Wheel Weights Collected from City Streets

USGS estimated that about 10,000 metric tons of wheel weights sold were sold and installed each year in the U.S. and determined that this sales volume would be unlikely to change with reformulation (Bleiwas 2006). On the basis of a review of all available information (e.g., Root 2000, Bleiwas 2006), DTSC estimated that about 1% of the total volume of annual wheel weight sales (100 metric tons nationally) may be dispersed into the environment, including streets, storm drain systems, and surface waters.

Since wheel weight replacement occurs primarily in conjunction with vehicle servicing (particularly tire replacement), Los Angeles County wheel weight sales can be roughly estimated on the basis of the fraction of nationwide driving (vehicle kilometers traveled) that occurs in Los Angeles County. The ratio of total national vehicle use (an estimated 4,772 billion kilometers) (FHWA 2012) and Los Angeles vehicle use (an estimated 120 billion annual kilometers) (SCAG 2012a) is 2.5%. This suggests that about 2.5 metric tons (2,500 kilograms) of wheel weight material is dispersed into the Los Angeles County environment annually. Even if all of this material were zinc, it would comprise a relatively small load, only about 1% of the estimated zinc load from tires.

6.4.3 Other Minor Zinc Sources

Other minor zinc sources that may occur in one or more California urban watersheds include coins, brass, cosmetics and personal care products, indoor drinking water pipes, die cast zinc products, sacrificial anodes, glow-in-the-dark products, fluorescent tubes, waterproofing agents, glass and ceramics, marine antifouling paint, plastics, sealants, mastics additive / preservative, candle wicks, waxes and polishes, vehicle exhaust, asphalt, grease additive, zinc phosphate cleaners, batteries, zinc-preserved wood, zinc-based moss control products, swimming pool biocide, zinc phosphide rat killer, and non-zinc roofing and siding. Table 7 summarizes all minor zinc sources.

Table 7. Minor Zinc Sources

Zinc Use	Analysis	Conclusion
Vehicle brake pads	See text	Relatively small source.
Wheel weights	See text	Relatively small source.
Coins (metal alloys)	May rarely be left outdoors (e.g., in fountains that are subsequently emptied to storm drains).	Relatively small source.
Brass	Brass is an alloy of copper and zinc, commonly 10-40% zinc (IZA 2011). Outdoor uses of brass are largely ornamental (e.g., doorknobs and other architectural details, sculptures) and limited in size due to cost. Coatings, which are often applied to protect the appearance of the brass (IZA 2011), reduce metal corrosion and washoff (Selwyn 1996). Although zinc runoff from uncoated brass is higher than would be predicted based on zinc's concentration in brass, the overall quantity of zinc washed into urban runoff from brass is less than the quantity washed from the same area of pure zinc (Herting 2008).	Relatively small source.
Cosmetics and personal care products	Sunscreen and other skin-applied products can be washed off, but normally this occurs indoors or directly to surface water at recreational locations. Shampoo (zinc pyrithione in dandruff shampoo) is ordinarily rinsed to indoor drains.	Limited pathway to urban runoff.
Indoor drinking water pipes	Galvanized drinking water pipes are now rarely installed due to corrosion and leakage problems (NSF International 2012). Most water that flows through indoor drinking water pipes is discharged to indoor drains.	Not common. Limited pathway to urban runoff.
Die cast zinc products	Used as "insides" for many manufactured products. Usually under a shell of plastic or an outside coating (Bess 2006).	Limited pathway to urban runoff.
Sacrificial anodes (boats)	Provide protection for in-water galvanic corrosion. Zinc is the preferred metal for salt water applications; other metals are preferred in brackish and fresh water (Singhasemanon et al. 2009). Sacrificial anodes are only needed in the water, where they release zinc directly into the water body to protect other metal elements on the boat. When boats are stored on land, anodes are no different than other small zinc metal pieces, with limited exposure to stormwater and relatively small total surface area.	Limited pathway to urban runoff.
Glow-in-the-dark products like toys	Zinc sulfide is use to make the toys glow in the dark. Such toys have a relatively small market presence and have limited outdoor use.	Not common. Limited pathway to urban runoff.
Fluorescent tubes	Only used in earliest fluorescent tubes. Zinc compounds were replaced by chemicals with more desirable light emissions spectra (Yen et al. 2006).	Not common.
Waterproofing agent	Zinc compounds may serve as a waterproofing agent for textiles, paper and concrete (WHO 2001; IZA 2011). In an Internet search for commercial products, no examples of concrete waterproofing were identified, suggesting that this is not a common practice. Other substances (polymers) appear to be most common approach for waterproofing outdoor fabrics.	Not common.

Table 7. Minor Zinc Sources (Continued)

Zinc Use	Analysis	Conclusion
Glass and ceramics	Zinc oxide is used in some glasses and ceramics. Zinc should be encapsulated in the chemical structure.	Limited pathway to urban runoff.
Marine antifouling paint (zinc biocides)	Release is directly to the water body where the boat is berthed. For cost reasons, boats that are stored on land are usually not treated with antifouling coatings.	Limited pathway to urban runoff.
Plastics, sealants, mastics additive / preservative	Zinc borate (formed by reaction of zinc oxide and boric acid) is used extensively as a fire retardant in plastics (IZA 2011). Zinc stearate is used in PVC (IZA 2011). Zinc oxide, zinc metal, and other zinc compounds may be used as materials preservatives in plastics, mastics (adhesives), carpet, and caulking (IZA 2011; EPA 2009). Most zinc-preserved products are used only indoors (EPA 2009). The polymeric structure of impregnated products used outdoors (e.g., caulk) limits zinc releases into runoff (Pitt and Lalor 2000).	Limited pathway to urban runoff.
Candle wicks	Zinc is sometimes used as core in candle wicks. Some of the zinc may be emitted to air when burned (the rest becomes ash).	Relatively small source.
Waxes and polishes	Zinc is used in some indoor floor waxes designed for high-traffic areas like hospital corridors and retail stores. When floors are cleaned and wax stripped, discharges are usually to indoor drains. Zinc may also occur in some car waxes, but this appears to be rare based on an internet search that identified only one product.	Not common. Relatively small source.
Vehicle exhaust	Zinc may appear as an impurity in gasoline or diesel fuel. Tests of 39 gasoline and diesel fuel samples from San Francisco Bay Area refineries found zinc below detection limit in all samples (Brosseau 2004). A European Commission study based on data from the Netherlands and a study by the Auckland Regional Council (New Zealand) also found negligible quantities of zinc in vehicle exhaust (European Commission 2010; Kennedy and Sutherland 2008).	Relatively small source.
Asphalt	Zinc concentrations reported in asphalt (less than 10 ppm) and used asphalt (about 50 ppm) are lower than typical California soil zinc levels (88-236 ppm) (Kennedy et al. 2002; Ozaki et al. 2004; Bradford et al. 1996). Other inventories have also found road pavement to be a relatively small source of zinc (Kennedy and Sutherland 2008; Netherlands 2008c).	Relatively small source.
Grease additive	Zinc-containing grease additives may be used to prevent joint seizing in specialized applications where contacting moving parts are exposed to highly corrosive conditions. These parts would be unlikely to be exposed to urban runoff. In the Netherlands, nationwide emissions of zinc-containing boat propeller shaft lubricants were estimated to be small (about 133 kg per year) even though these parts are close to the water (Netherlands 2008b).	Relatively small source.
Zinc phosphate cleaners	Used to clean and prepare metal surfaces for plating or painting. Use appears to occur indoors at industrial facilities, e.g., in tanks at manufacturing operations.	Limited pathway to urban runoff.

Table 7. Minor Zinc Sources (Continued)

Zinc Use	Analysis	Conclusion
Batteries	Alkaline and zinc-carbon batteries are used in small appliances, flashlights, and other portable goods. Zinc-air batteries are used in hearing aids. Nickel-zinc batteries appear in cameras and other electronics. These batteries are contained while in use, but can be exposed to urban runoff if improperly disposed (e.g., crushed batteries on roads). Improper disposal occurs, but is assumed to be relatively uncommon (see "dumping" in Table 6).	Limited pathway to urban runoff.
Zinc-preserved wood	Zinc naphthenate, borate, and oxide may be used to preserve wood. California reported small 2011 sales volumes for all three pesticides: zinc naphthenate – 4,300 kilograms, zinc borate – none, and zinc oxide – 3,500 kilograms (DPR 2013). These totals exclude treated wood shipped from out of state. All three appear to be niche products. Zinc borate is not normally used outdoors. Zinc naphthenate is not generally recommended for ground contact. Zinc oxide is a component of the arsenic-containing preservative Ammoniacal Copper Zinc Arsenate (ACZA), which has limited use due to its arsenic content. An informal internet product survey suggests that copper preservatives dominate the market and that zinc preservatives are relatively uncommon.	Relatively small source.
Zinc-based moss control products	Zinc metal, zinc chloride, and zinc sulfate monohydrate may be applied on impervious surfaces like roofs and walkways to control moss. There are no zinc metal or zinc sulfate monohydrate moss control products approved for use in California (DPR 2013). California statewide 2011 sales of zinc chloride products were only 120 kilograms (DPR 2013).	Relatively small source.
Swimming pool biocide	Zinc sulfate monohydrate is a relatively new ingredient in four swimming pool biocide and algaecide products. Pools emptied to gutters can carry any zinc not removed by the pool's filtration system into storm drains. (Pools are usually emptied during dry weather). Current sales of these products are likely small, based on the small number of registered products and total California zinc sulfate monohydrate sales in 2011, which were less than 100 kilograms (DPR 2013).	Relatively small source.
Zinc phosphide rat killer	In urban areas, zinc phosphide is primarily in containerized bait systems for safety reasons (EPA 2008b). Bait systems limit exposure to urban runoff. California statewide 2011 zinc phosphide sales were 12,000 kilograms (DPR 2013).	Limited pathway to urban runoff.
Non-zinc roofing and siding	Roofs other than those composed of zinc-containing metals (or with zinc granules) contain very small quantities of zinc (<3,000 µg/L total leachable zinc) (Clark 2008) and are relatively small sources of zinc in runoff (Washington Ecology 2014c). Unpainted, non-zinc siding materials similarly are not a true source of zinc, though they may contain zinc in runoff from other sources (e.g., air deposition) (Kennedy and Sutherland 2008). Although elevated zinc runoff levels are sometimes reported in the literature (e.g., Chang and Crowley 2003; Chang 2004; Davis 2001), the sampling locations have galvanized materials in roof construction (e.g., flashing), galvanized gutters and downspouts, or air deposition from upwind zinc-emitting industry and/or nearby roads.	Relatively small source.

7.0 CONTROL MEASURE OPTIONS FOR MAJOR ZINC SOURCES

This section presents a brief overview of potential control measures for the major zinc sources identified in this report. In general, controlling zinc at its source is more effective —and usually more cost effective—than using treatment to remove zinc from diluted urban runoff (e.g., Timperley and Green 2005, Seyb and Shaver 2005, Mark-Brown 2011; Ouwejan et al 2006, Golding 2008). All measures below—particularly the more cost effective prevention measures—require further evaluation to determine their feasibility in terms of cost, potential impacts, and public policy considerations.

7.1 Outdoor Zinc and Galvanized Surfaces

7.1.1 Minimize Installation of New Outdoor Zinc Surfaces

Both voluntary and regulatory measures can reduce installation of new outdoor zinc surfaces. On a practical basis, these measures would likely only be able to address projects large enough to require a building permit. Smaller activities like replacing fencing and roof repair cannot readily be identified. Voluntary efforts are particularly challenging in areas served by a regional marketplace.

Public education. Education of architects, planners, and the public has the potential to reduce use of outdoor, uncoated zinc use in new and remodeled buildings. Many alternative materials exist, including coated zinc and galvanized building materials and coated galvanized fencing, which have longer lifetimes than uncoated materials (IZA 2006b). Installing pre-coated materials is less expensive than post-installation coating.

Educational programs are most effective when designed in a targeted manner. In this case, the two key target audiences are (1) permit applicants for projects involving installation of outdoor zinc or galvanized materials and (2) architects. Reaching these audiences would be most effectively accomplished on a regional basis and in collaboration with partners, such as the American Institute of Architects (AIA).

Green building programs usually do not address water pollution from zinc architectural features, which are indirectly incentivized by most green building programs because of their durability (e.g., U.S. Green Building Council Leadership in Energy and Environmental Design). Since green building programs have increasing popularity, it may be worthwhile to consider approaching regional and national green building certification associations, such as the U.S. Green Building Council and Build It Green, with educational information. This would best be done on a regional basis together with other agencies (including water quality regulators).

If a regulatory program is implemented, an education program can usually be downsized or replaced with a compliance assistance program.

Regulatory limitations. Local governments have the authority to regulate the use of building materials on new and remodeled buildings. Regional development of a model ordinance—or incorporation into a statewide model building code like the California Green Building Standards Code—reduces ordinance development and compliance assistance costs.

Regulatory controls have previously been used to limit use of other architectural materials associated with water pollution. For example, the City of Palo Alto adopted an ordinance prohibiting the use of copper for new roofs, with exceptions for copper flashing, ornaments and historic buildings (Palo Alto Municipal Code Section 16.09.160). The Netherlands has proposed tailored, site-specific limitations on use of uncoated zinc materials in constructions that consider surface area, drainage location (e.g., pervious or impervious surface), runoff volumes and drainage characteristics, and other parameters (Verschoor and Brand 2008).

Regulatory measures that do not completely prohibit uncoated outdoor zinc and galvanized materials use are likely to be more politically acceptable than outright prohibitions; however, such ordinances would be more expensive to develop and implement. For example, municipalities could allow installation of only certain types of materials (e.g., galvalume but not pure zinc surfaces), allow zinc and galvanized materials to be installed if accompanied by runoff treatment systems and/or diversion of all runoff to landscaping, or require examination of alternatives if galvanized or zinc materials are proposed to be installed in outdoor locations.

Potential Zinc Reductions. These programs primarily serve to stem the increase in outdoor zinc surfaces associated with new development. At individual locations, not installing outdoor zinc materials prevents all zinc runoff that would have come from these materials. Using pre-coated zinc materials reduces zinc load by 97-99% (see data in Table 1). Watershed zinc reductions depend on the extent to which change occurs throughout the watershed.

Due to the durability of zinc and galvanized materials, voluntary modification of existing installations is unlikely. A highly targeted, well-designed education program for outdoor zinc material could achieve behavior change rates up to 10-15% (Larry Walker Associates 1999). Less targeted programs would have lower effectiveness rates.

Despite low effectiveness, education programs are a common first step because they set the stage for potential future regulatory programs. They make affected parties aware of the link between a pollutant source and a water quality threat. Voluntary actions resulting from an education program provide helpful examples that the requested change is feasible (or occasionally prove that alternatives are impractical for some types of installations). Agencies that operate education programs can clarify the technical and policy issues that need to be faced prior to initiating a regulatory program.

Depending on ordinance design, regulatory controls would reduce or eliminate increases in the zinc load, but would be unlikely to achieve significant zinc load reductions in the next decade. Typical redevelopment rates are unlikely to exceed 10% of developed municipal land area in the next 20 years. To the extent that redevelopment occurs at existing sites with outdoor zinc and/or galvanized materials, regulatory controls could reduce watershed zinc loads.

7.1.2 Retrofits Addressing Existing Outdoor Zinc Surfaces

Coatings. Outdoor zinc materials can be coated to prevent zinc release (IZA 2013; IZA 2006b; Vos and Janssen 2008; Ouwejan et al. 2006). Coating involves careful surface preparation and proper management of wastewater from surface pre-cleaning (Ouwejan et al. 2006). The International Zinc Association provides detailed specifications for field coating of galvanized surfaces, including preparation procedures and recommended maintenance (IZA 2013).

Coating zinc surfaces extends their lifetime by 10-15 years (IZA 2006, IZA 2013), making coating a potentially cost-effective alternative to roof replacement. Coatings require maintenance and repainting from time to time to maintain zinc reduction benefits (Ouwejan et al. 2006; Kennedy and Sutherland 2008).

Galvanized storm drain lines require special coating technology due to the inability to clean lines thoroughly enough for a coating to adhere to the surface. For galvanized drain lines, various cementitious and plastic linings or cured in place pipe can be installed within the existing drain line with little or no excavation. Caltrans has standard lining specifications in its Highway Design Manual, primarily in Chapter 853 (Caltrans 2012) and in a special design information bulletin for culvert repair (Caltrans 2011b). Coatings reduce the pipe diameter, sometimes significantly, but extend pipe lifetimes for as long as 50 years (Caltrans 2012). Coatings cost significantly less than pipe replacement.

Standard coating methods would likely be impractical for galvanized fencing. Replacing the mesh with vinyl-coated mesh might be more cost effective. This change alone (not accompanied by coating or replacement of the remaining fence framework) could reduce exposed surface area by more than 80%.

Due to the cost to coat zinc surfaces, financial incentives or regulatory requirements would likely be necessary to motivate action by private property owners. Any program to encourage or require coating installation should ensure coatings are inspected and maintained.

Runoff treatment. Treatment systems can be very effective for zinc removal (Geosyntec Consultants and Wright Water Engineers 2012), but some types can be costly to install, manage and maintain.

Treatment is most cost effective when conducted on the most concentrated runoff, such as the runoff flowing directly from zinc or galvanized outdoor surfaces. Since zinc in runoff from outdoor zinc surfaces is primarily in the dissolved form (Bertling 2006, Heijerick et al. 2002), systems based on soil contact and infiltration (e.g., swales, filter strips, media filters, porous pavement, retention ponds, and wetland basins) are most effective (Jones et al. 2012). Manufactured devices (e.g., drain inserts), though convenient, are less effective at removing zinc, particularly dissolved zinc (Jones et al. 2012; Geosyntec Consultants and Wright Water Engineers 2012).

A grassy swale treats the runoff from this galvanized fence

A Washington state literature review indicated that passive treatment systems might be useful to treat roof runoff, but that more rigorous testing was needed (Herrera 2011). Subsequent pilot projects in Washington State suggest that high-metal-removal-capacity planter boxes have the potential to provide effective zinc removal from roof runoff at relatively low cost (PPRC 2014; Kalmar 2013).

When infiltrating runoff from zinc surfaces, care must be taken to protect groundwater quality. Although zinc initially stays in upper soil layers in infiltration systems, long-term testing has shown continued zinc transport deeper into subsoils (Mason 1999). Infiltration system designers should consider local site conditions to determine if groundwater quality protection measures should be included in facility designs.

Outdoor zinc and galvanized surfaces occur primarily on private property. Without financial incentives, voluntary implementation of treatment by private property owners would be unlikely due to cost. Enacting treatment requirements for existing outdoor zinc surfaces on private property would pose both political and logistical challenges. A hybrid program, such as a package of financial incentives for treatment and/or retrofit coatings backed by potential regulatory requirements might have success at targeted properties (e.g., those with large exposed zinc/galvanized surface areas); however, the structure, cost, and funding for such a hybrid program would need further exploration prior to considering any potential implementation.

Municipal treatment of urban runoff to remove zinc is also potentially possible, particularly when treatment has multiple benefits; however, treatment of large volumes of dilute runoff poses both funding and logistical challenges.

Potential zinc reductions. Coating zinc surfaces typically reduces zinc runoff load by about 95% (Bertling et al. 2006; Kennedy and Sutherland 2008). Retrofit coating of galvanized highway guardrails reportedly reduced zinc runoff concentrations by >90% (Tobiason and Logan 2004). To achieve the full zinc reductions, retrofit coating of roofs should be accompanied by cleaning of accumulated debris from gutters and drainage systems (Tobiason and Logan 2004).

Coating maintenance is essential (Vos and Janssen 2008; Kennedy and Sutherland 2008; Ouwejan et al. 2006). In Auckland, roofs where the coating had deteriorated to the point of visible paint oxidation with minor flaking have reduced zinc reduction (Kennedy and Sutherland 2008). On some roofs, reductions dropped to as little as 10%, likely due to the presence of zinc-based primers underneath the coating.

Treatment system effectiveness depends on the system selected, its design capacity, and influent zinc concentrations. Ongoing oversight is necessary to ensure that treatment systems are maintained and continue to meet performance standards. For most treatment systems, removal efficiencies are highest with higher influent concentrations (Minton 2005), which indicates that installation close to the zinc runoff source, (e.g., at the gutter discharge point from a galvanized roof), will provide greatest effectiveness. With high zinc influent concentrations such as those in roof runoff, soil-based systems may exhibit greater than 75% zinc removal (Geosyntec Consultants and Wright Water Engineers 2012; Kalmar 2013). At lower zinc concentrations typical in urban runoff, treatment systems may remove less than one-third of all zinc (Geosyntec Consultants and Wright Water Engineers 2012). Poorly maintained systems will provide lower or no zinc reduction.

7.2 Tires

7.2.1 Reducing Tire Zinc Content

Rubber formulation is a complex art (Dick 2001). Tire rubber formulation responds to numerous safety and environmental demands. For example, in recent years, vehicle fuel efficiency requirements have driven tire manufacturers to redesign tires to reduce rolling resistance. Nonetheless, tires have previously been reformulated to remove pollutants. In the European Union, tires were reportedly recently reformulated to reduce their polyaromatic hydrocarbon content (Sadiktis 2012; ChemRisk and DIK 2008).

Low-zinc and zinc-free tires currently have little market presence and are not available for most vehicles (Bauters 2012). To protect water quality, the Netherlands has subsidized research into lower zinc tire rubber formulations (Vos and Janssen 2008). Internationally, many researchers have explored methods to reduce use of zinc oxide in tires. Alternatives investigated include use of nanoparticle zinc oxide, magnesium oxide, and other chemicals as substitutes (Van Baarle 2006; Kim et al 2010; Henning 2007; Heideman 2004; Heideman et al. 2004; Heideman et al. 2006). Even those in the rubber industry have promoted industry efforts to reduce zinc in tires tread (Byers 2007). Zinc reduction appears to be possible within existing vulcanization approaches (e.g., Veyland and Araujo Da Silva 2011, Henning 2007). A completely different vulcanization system would be needed to eliminate zinc (Heideman 2004; Byers 2007).

Any examination of reduced zinc rubber formulations should focus on the rubber used in tire tread, which is the primary source of zinc in urban runoff. Truck tires, which have about 70% higher zinc levels than car tires (Table 4), merit special examination.

Alternative materials may have environmental impacts that should be considered when examining reformulation (Vos and Janssen 2008). California Department of Toxic Substances Control (DTSC) will soon initiate a regulatory program under its Safer Consumer Products Regulations that might be able to require manufacturers to examine the necessity of current levels of zinc in tire tread and to explore the efficacy and safety of potential alternative formulations.

7.2.2 Reducing Tire Emissions

Reducing vehicle use. Reducing vehicle use reduces zinc emissions. In response to Federal and California Clean Air Act requirements and climate change, the California Air Resources Board, regional agencies like the South Coast Air Quality Management District and the Southern California Association of Governments (SCAG), and municipalities have worked for the last several decades to reduce vehicle use. These efforts were largely unsuccessful until the last few years, when California saw its first reduction in vehicle kilometers traveled in decades. The reduction has been attributed to a variety of factors, such as the economic downturn, gasoline price increases, increased investment in public transportation, changes in land use patterns, climate change program implementation, and generational behavior differences (Puentes and Tomer 2008).

Regional Plans mandated by state law (California Senate Bill 375, 2008) call for aggressive efforts to reduce California's per capita vehicle use. For the Los Angeles area, the per capita vehicle kilometers traveled reduction target is a 9% reduction by 2020 and 16% reduction by 2035 compared to a 2005 baseline level (SCAG 2012b). SCAG anticipates significant expenditures to achieve these targets. Population increases (which could be >20% during this time period) may offset these reductions to create a net increase in total vehicle travel in the region (SCAG 2012b).

Population growth and vehicle use reduction actions will vary among individual watersheds. Anticipated local changes in total vehicle use should be tracked and factored into zinc runoff management plans.

Managing use of tire shred and crumb products. Most tire shred and crumb products are used by government agencies or in projects large enough to require government permitting. Voluntary and regulatory measures could seek to ensure that drainage designs avoid zinc discharges, either by eliminating runoff contact with tire material or by employing designs that effectively remove zinc prior to discharge.

Where discharges cannot be avoided, alternative materials can be used and may even be preferable for some agencies. For example, the Los Angeles Unified School District will reportedly be using non-tire infill materials for all new artificial turf fields (SAIC 2011).

Since most installations occur at facilities not regulated at the local level (e.g., Caltrans facilities, school grounds), local regulatory measures would have limited benefits. The Water Boards can regulate agencies' use of tire shred and crumb products through permits or conditional waivers. For example, the San Francisco Bay Water Board determined that use of tire-derived aggregate was a "discharge" potentially subject to a Waste Discharge Requirement under the California Water Code. It issued a Conditional Waiver of Waste Discharge Requirements with a set of conditions detailing placement, drainage, and particle sizes that together minimize the potential losses of zinc and other water pollutants into urban runoff (San Francisco Bay Water Board 2011).

Design changes and alternative materials could substantially eliminate zinc loads from installations of tire shred and crumb products. Actual zinc load reductions cannot be estimated generically, as they depend on site-specific characteristics.

7.2.3 Post-Emission Zinc Management

Street sweeping. Street sweeping collects particles from streets and highways. Since municipalities already sweep most urban streets, increasing zinc removal usually involves improving sweeper efficiency or increasing sweeping frequency. Street sweeping has less zinc reduction potential than often assumed for two major reasons:

- Efficiency. Street sweepers are only moderately efficient in collecting particles in the size range of tire wear debris (Breault et al. 2005).
- Location. Tire wear debris deposits on many urban impervious surfaces not subject to street sweeping, such as sidewalks, driveways, and rooftops.

Ouwejan et al. (2006) estimated that twice-weekly high-efficiency vacuum sweeping in urban areas would reduce zinc loads in an Auckland watershed by only a few percent. A specially designed enhanced street sweeping program in San Diego reduced total zinc in first flush urban runoff by 58-69%, however, it is unclear if these initial reductions were reflected in total annual loads, which were not measured (Weston Solutions 2010). Interestingly, San Diego found that with a mechanical sweeper, dissolved zinc levels in first flush runoff *increased* by more than 20% (this effect did not occur with a vacuum sweeper). The seemingly odd increase in dissolved zinc concentration is consistent with a USGS study that found that street sweeping changed the nature of metals runoff by removing larger particles from the runoff, but ultimately provided little reduction in total zinc runoff (Selbig and Bannerman 2007).

Treating runoff from areas with tire debris. As discussed in Section 7.1.2, treatment systems can be effective for zinc removal, but can be costly to install, manage and maintain. Without financial incentives or regulatory requirements, voluntary implementation of treatment by private property owners would be unlikely due to cost.

Treatment is most effective when conducted on the most concentrated runoff. In the case of tires, the most concentrated runoff would come from high-tire use areas, such as loading facilities. Treating concentrated runoff could achieve zinc reductions as high as 75% (Geosyntec Consultants and Wright Water Engineers 2012). Poorly maintained systems provide lower or no zinc reduction.

Treatment of urban runoff from streets to remove zinc is also potentially possible, particularly when treatment has multiple benefits; however, as mentioned above, treatment of large volumes of dilute runoff poses both funding and logistical challenges.

At the lower zinc concentrations typical of urban runoff, non-infiltration treatment systems may remove less than one-third of all zinc (Geosyntec Consultants and Wright Water Engineers 2012). On roads, use of porous pavement is a potential treatment option; however, this would be costly due to the need to reconstruct road surfaces and to provide regular maintenance (Vos and Janssen 2008) and might itself be a zinc source if the porous pavement were rubberized.

8.0 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

Conclusion 1. The major sources of zinc in urban runoff are outdoor zinc surfaces (including galvanized surfaces) and tire wear debris.

Conclusion 2. Some watersheds contain local zinc sources that could contribute significant quantities of zinc to urban runoff. Local zinc sources that could potentially contribute significant quantities of zinc to urban runoff in specific locations in some California urban watersheds include zinc-containing paint, tire-derived shred and crumb rubber, drinking water anti-corrosion additives, anti-corrosion additives for water-containing equipment, fireworks, dumping, air deposition from forest fires, de-icing products, motor oil/lubricating oils additives, industrial air emissions, industrial runoff, zinc minerals or wastes in construction materials, mining, soils, volcanic ash, tire-derived fuel, re-suspension of zinc from historic emissions sources, fertilizer and agricultural micronutrient products, and zinc granule-impregnated asphalt roofing shingles.

Conclusion 3. Many minor zinc sources that do not contribute significant quantities of zinc to urban runoff exist. These include vehicle brake pads, wheel weights, coins, brass, cosmetics and personal care products, indoor drinking water pipes, die cast zinc products, sacrificial anodes, glow-in-the-dark products, fluorescent tubes, waterproofing agents, glass and ceramics, marine antifouling paint, plastics, sealants, mastics additive / preservative, candle wicks, waxes and polishes, vehicle exhaust, asphalt, grease additives, zinc phosphate cleaners, batteries, zinc-preserved wood, zinc-based moss control products, swimming pool biocides, zinc phosphide rat killer, and non-zinc roofing and siding.

Conclusion 4. Promising source control strategies exist for zinc in urban runoff. For outdoor zinc surfaces, both source control and on-site treatment of concentrated runoff appear to be technically feasible. Reducing zinc from tires will pose a greater challenge, as low-zinc and zinc-free products have little market presence and tire wear debris is widely dispersed across urban environments, making it very difficult to collect.

8.2 Recommendations

Recommendation 1. To identify major zinc sources in specific urban watersheds, develop a watershed-specific zinc source inventory based on local watershed information. For tire wear debris and outdoor zinc surfaces, local zinc loads can be estimated based on data for the local watershed (e.g., vehicle kilometers traveled data, estimated fraction of galvanized roofing, rough estimates of length of galvanized fencing and guard rails, estimated number of galvanized light posts) and the emissions factors in this report. Every urban watershed should be evaluated to determine if any of the potentially major local zinc sources listed in Section 6.3 occur, and if so, local information should be developed to estimate the significance of the source.

Recommendation 2. Integrate source control into zinc load reduction programs. Promising source control strategies exist for outdoor zinc surfaces and for most potentially major local sources. Source control strategies are substantially more cost-effective than urban runoff treatment.

Recommendation 3. Employ source control to reduce zinc in runoff from industrial facilities. Washington Department of Ecology has prepared a guidebook with specific, practical zinc reduction best management practices for industry (Golding 2008).

Potential Statewide Zinc Source Control Actions

Recommendation 4. Develop a menu of zinc source control strategies for municipalities. Menu development should focus on major zinc sources and involve investigation and evaluation of each potential source control strategy to determine its feasibility in terms of cost, potential impacts, and public policy considerations. Like the San Francisco Bay area's Copper Management Strategy Development Resources document (Larry Walker Associates and TDC Environmental 2006), a well-designed zinc source control menu would provide the basic information needed to support local management decisions about the source control portion of zinc reduction program design.

Recommendation 5. Examine the possibility of petitioning the California Department of Toxic Substances Control (DTSC) to require evaluation of zinc in tires under its Safer Consumer Products Regulations. If multiple California agencies determine that zinc reductions are necessary for Clean Water Act compliance and cannot reasonably be achieved from other sources, the potential to reduce zinc concentrations in tires should be evaluated. Reducing zinc in tires would avoid costs associated with removing tire-related zinc from urban runoff. Zinc reductions could relieve manufacturers of liability for the portion of these costs than can be linked specifically to tires.[4]

Before DTSC can bring a product into its Safer Consumer Products regulatory process, it must complete a regulatory rulemaking to justify its selection of the product as a priority. Prior to submitting a petition, agencies would need to invest in the development of high-quality scientific information to form the scientific basis for DTSC's product selection regulation. Since the regulations prioritize petitions from state agencies that relate to the agency's statutory authorities, the petition and supporting scientific information would best be submitted in partnership with the Water Boards. DTSC cannot prioritize zinc-containing products prior to January 2016.

DTSC's regulatory framework is designed to require examination of the major questions related to tire reformulation that were identified in this report, particularly questions about the safety and feasibility of alternatives. The Safer Consumer Products regulatory process, which hinges on the outcomes of each manufacturer's alternatives assessment, ensures full examination of the questions, but does not guarantee that zinc reductions would necessarily occur.

Recommendation 6. Seek integration of water quality considerations into California Department of Resources Recycling and Recovery's (CalRecycle's) waste tire market development programs. CalRecycle seeks to expand markets for reuse of crumb rubber from tires (CalRecycle 2011; SAIC 2011). Its market development activities include grant funding and outreach to user groups. Among CalRecycle's priorities has been promoting new technology that makes it easier to blend tire crumb with asphalt, which may cause tire crumb to appear in asphalt products, like sealants and roofing shingles (SAIC 2011). These activities could potentially conflict with urban runoff zinc reduction efforts. CalRecycle should be provided information about California zinc water pollution, including the Clean Water Act list of impaired waters and Total Maximum Daily Loads. Potential actions that CalRecycle could integrate into its program include development of best management practices for use of tire shred and crumb.

Recommendation 7. Seek integration of water quality considerations into U.S. EPA's review of zinc biocides. U.S. EPA Office of Pesticide Programs reviews pesticide registrations about once every 15 years. The pesticides subject to review include zinc-

[4] If data demonstrating a stronger linkage between tires and urban runoff zinc are needed, consider using substances uniquely emitted from tires into the environment, such as 2-(4-morpholinyl) benzothiazole or N-cyclohexyl-2-benzothiazolamine (NCBA) as tracers (Ni et al. 2008; Kumata et al. 2002).

containing antimicrobial paint additives. In the late 2000s, EPA initiated reviews of zinc oxide and zinc borate preservatives; these reviews should generate draft evaluations of the environmental risks posed by their outdoor uses in 2017. Zinc pyrithione's review started in 2014. Although U.S. EPA pesticide reviews proceed slowly, they provide invaluable scientific information and have the capacity to result in implementation of highly effective mitigation measures. Stormwater participation in zinc biocide review process would provide the opportunity to request that EPA specifically assess the potential for zinc from biocide-containing paints and other outdoor products to contribute meaningful quantities of zinc to urban runoff.

Information Gaps

Recommendation 8. *Investigate runoff from rubberized asphalt pavement*. Rubberized asphalt pavement (often called rubberized asphalt concrete or "RAC") might potentially contribute moderate quantities of zinc into urban runoff where it is installed. The highest potential for zinc release would occur if rubberized asphalt is used in porous pavement systems, where water drains through the material itself and flows directly into a drainage system. This use merits additional research to determine whether it has potential to be a locally major zinc source. Caltrans and other transportation agencies may want to research the potential water quality effects of the state's requirement to use crumb rubber (California Public Resources Code Section 42703).

Recommendation 9. *Determine the market presence of zinc-containing paints, particularly paints with antimicrobial zinc additives, and the zinc concentrations in runoff from new and aged outdoor paints with antimicrobial zinc additives*. Some of this information might be generated through participation in U.S. EPA's reviews of zinc biocides.

Recommendation 10. *If California agencies require more accurate estimates of zinc emissions from tires to support zinc reduction actions, obtain information characterizing California tires*. California tire characterization information that would provide the greatest uncertainty reductions:

> (1) Measurements of zinc concentrations in tread material from new tires representative of new vehicle and aftermarket (replacement) tires in the California market. Measurements should follow vehicle class—at a minimum, car and truck tires should be differentiated.
>
> (2) Wear rate estimates for tires, by vehicle class. Either geometric or weight loss estimation methods could be used. Estimates should follow vehicle class—at a minimum, car and truck tires should be differentiated. Ideally, estimation categories would match vehicle kilometers traveled data categories and would specify the number of tires per vehicle in each class.

Recommendation 11. *If California agencies require more accurate estimates of zinc emissions factors from outdoor zinc surfaces to support zinc reduction actions, develop California-specific zinc emissions factors based on runoff from test panel systems*. Measurements would take several years to complete and would involve construction of one or more field test facilities. To best account for local air quality and rainfall volumes in California's major urban watersheds, measurements should be conducted away from all air deposition sources (particularly streets) and should use aged materials (e.g., removed from existing structures) if possible.

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