State of Knowledge Report

Contribution of Zinc to Watersheds from Building Materials, Consumer Products, Tires and Other Sources

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Shaping the Future

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Appendix A - USTMA Calculation of Tire Wear Rates

Executive Summary

Zinc (Zn) is naturally distributed as minerals and other non-elemental forms in nature in the Earth's crust. Zn is emitted to the environment from a variety of natural and anthropogenic point and non-point (diffuse) sources, and is an essential nutrient found in organisms. In the United States, the vast majority of Zn is used in metals industries, with 85% of Zn used to galvanize metals for corrosion resistance. Only 3% of Zn is used for non-metallic purposes, including as an ingredient in personal care products, such as sunscreen (ZnO) and medicated shampoos (Zn pyrithione), as well as in batteries, a biocide in paints and coatings, rubber vulcanization, pharmaceuticals, and other products. Zn has been measured in industrial wastewater and stack emissions, as well as in natural sources, such as wildfires and native soil runoff. Zn is also commonly found in food products and biological waste, given that it is an essential mineral. In urban environments, each of these sources can contribute variable amounts of Zn, which may eventually reach surface waters. In some areas across the U.S., Zn levels in watershed runoff and point-source effluents have been found to be elevated with respect to background levels in rain or upstream surface water.

Figure ES.1 presents a simplified schematic of the potential emission sources, transport pathways, and entry routes of Zn to surface waters. To date, there have been no publicly-available reports of efforts to create a comprehensive Zn emissions inventory or mass balance in any U.S. city or watershed. The limited inventories of air emissions are not sufficiently complete to allow characterization of sources to water. Comprehensive inventories, however, have been prepared in other countries and indicate that exterior galvanized metals, tires, brakes, engine oil, exhaust, littered items such as batteries and other metal products, and personal care products such as detergents, shampoos, cosmetics and pharmaceuticals, likely contribute quantifiable amounts of Zn to surface water. Given the diversity of sources, different release mechanisms, and local, regional and country controls, it is not possible to generalize these studies to determine specific source contributions in U.S. locations.

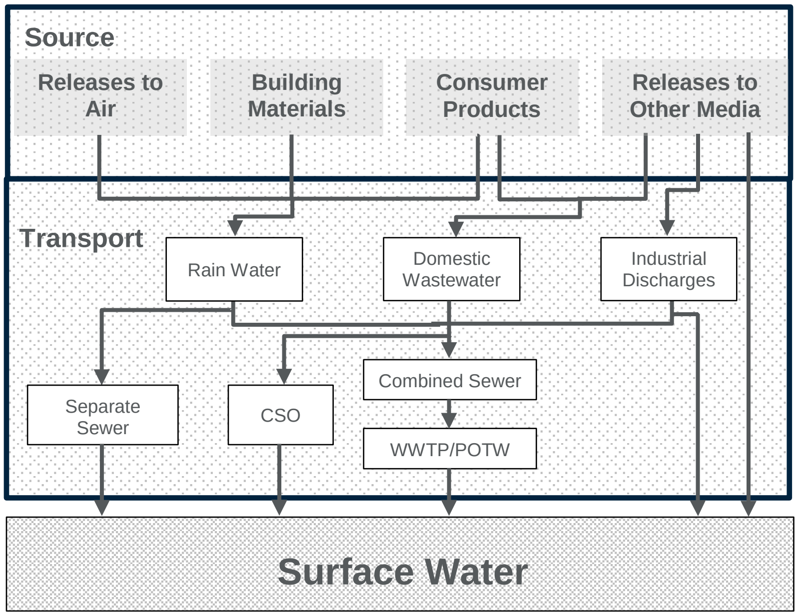

Figure ES-1: Simplified Potential Sources and Transport Pathways of Zn to Surface Waters

In the U.S., the Toxics Release Inventory (TRI) tracks reported emissions from industrial facilities across the country subject to reporting requirements for Zn. The TRI does not estimate non-point (diffuse) sources of Zn and non-reportable quantities. In California, the California Toxics Inventory (CTI) combines the reported industrial emissions for California facilities with estimated emissions of Zn released to the atmosphere from non-point (mobile) sources. The CTI does not estimate diffuse emissions that are not released to the atmosphere but may contribute to sewers and surface waters, and therefore does not account for sources such as galvanized metals and domestic waste. The Netherlands Pollutant Release Transfer Register (PRTR) estimates emissions for all potential sources of Zn to air, water, and soil. In the inventory, galvanized metals account for a quarter of the load to sewers and more than 50% of the load to sewers if domestic wastewater is excluded. Zn resulting from tire wear under urban driving conditions is estimated to account for only 8% of the load to sewers and 1% of the load to surface waters.

In addition to the TRI and the Netherlands PRTR, several studies have been conducted to investigate potential sources of Zn and their contribution to surface water pollution. Runoff from roofing and gutters made of galvanized metals has been associated with elevated levels of Zn in urban areas. In some areas, natural soils, batteries, and wildfires have been identified as major contributors of Zn to runoff. The high variability in source contribution observed in the literature emphasizes the importance of developing location-specific inventories in order to understand the significance of individual sources on a watershed or region. Among the available studies, the Davis et al. (2001) study has been frequently cited in reviews of Zn source allocation. The study used prior literature and limited sampling to prepare a preliminary estimate the loading of lead, copper, cadmium, and Zn to storm water runoff from a few restricted sources. The screening methods used in the study indicate that building runoff and automobile non-exhaust emissions should be considered as potentially important non-point source contributions to urban waterways. However, based on the methods employed and limited analysis conducted, the study is considered to be a hypothesis generating study and therefore cannot be used to draw conclusions about relative importance of sources of Zn locally, regionally, or nationally.

In Los Angeles County, a significant amount of research has been conducted by the Southern California Coast Water Research Project (SCCWRP) to characterize Zn sources including dry and wet atmospheric deposition, runoff from industrial facilities and the discharge from water reclamation plants has been assessed. Loadings based on land use and geographic information system (GIS) software have also been researched. Local watersheds in LA County have initiated enhancement programs with the intent to improve water quality by reducing Zn content in watershed effluents. To date, a comprehensive source inventory has not been prepared.

Based on the prevalence and use of the numerous other sources of Zn and the information found in the available inventories and literature, it is unlikely that the Zn associated with tire wear would show a contribution to surface water exceeding 5 or 10% of all sources in an inventory assessment. Zn loads are highly variable between watersheds, and it is not possible to develop a generic characterization of major or minor sources within U.S. watersheds. Selection of tires for source control prior to completion of a source inventory may result in minimal benefit to the watershed. Therefore, a comprehensive source emission inventory in LA County and other areas of the country considering loading of Zn to the environment is necessary to understand the potential efficacy of mitigation measures regarding galvanized metals, batteries, tires and other consumer products. Source inventories should be based on multiple lines of evidence including sales data, regionally specific leaching studies, and mass-balance assessment. These inventories can be used to determine whether proposed source controls will meaningfully reduce the loading of Zn in urban runoff. A significant amount of site-specific information must be available and analyzed to reliably apportion Zn within an individual watershed or region to individual sources.

1 Conceptual Model

1.1 Overview

Zinc (Zn) is naturally distributed as minerals and other non-elemental forms in nature in the Earth's crust at a concentration of 20 to 200 mg/kg and is an essential nutrient found in organisms (ATSDR, 2005). Zn is emitted to the environment from a multitude of natural and anthropogenic point and non-point (diffuse) sources. Overall, the greatest source of Zn to the worldwide environment are believed to be loading to soil from smelter slags, fly ash, and use of fertilizers (e.g. Zn nutrient crop supplementation) and wood preservatives (e.g. zinc Naphthenate). Zinc releases to soil are most often confined to the area of local release (ATSDR, 2005).

A wide diversity of sources and pathways of Zn release must be considered to obtain an accurate understanding of overall loading to the environment. Figure 1.1 presents a conceptual model of potential emission sources, transport pathways, and entry routes of Zn to surface waters (Hüffmeyer et al., 2009; ATSDR, 2005; Netherlands PRTR, 2015). Potential point sources to surface waters include direct emissions from industrial discharges, domestic water discharges, and rainwater sewer outlets. In locations with combined sewers, domestic discharges, rainwater sewers and some industrial discharges may be treated together by wastewater treatment plants (WWTP) or publicly owned treatment works (POTW). During wet weather conditions, increased flows may cause overflows, known as combined sewer overflows (CSO). In regions with separate sewer systems, rainwater may not be treated at all and may discharge directly into surface waters. Surface waters may also receive loads from non-point sources, including groundwater and diffuse surface runoff. Depending on the local environment, sewer system, and anthropogenic activities, the contribution of each of these sources may vary.

1.2 Production and Consumption in the U.S.

Zn is the fourth most produced metal by tonnage. Metallic Zn is used to galvanize and protect iron and steel, as rolled Zn, and as an ingredient in alloys such as bronze, brass, and Zn-based die casting alloy. In 2012, U.S. mines produced 713,000 metric tons of Zn. Approximately 806,000 tons of Zn was consumed in the U.S. in 2012, with galvanizing accounting for 85% of all uses. Usage of Zn in the U.S. in 2012 is summarized in Table 1.1 (Tolcin 2012). Besides its use in galvanizing and in alloys, Zn is used in pharmaceuticals and supplements, batteries, paint coatings, rubber, cosmetic and sunscreen products, in shampoos, conditioners, and soaps, dental cements, and in many more applications (ATSDR, 2005). International uses of Zn are similar to the United States. For example, in France, 328,000 tons of Zn are used in construction (37%), urban furniture (19%), energy (11%), agriculture (13%), industrial equipment (13%), transport (6%), and screws and bolts (2%) (Chen et al. 2008).

Table 1.1: U.S. Consumption of Zn in 2012

Industry	Usage (metric tons)	Percent Contribution
Galvanizing	685,000	85.0%
Brass and bronze	49,700	6.1%
Zn-based alloys	44,700	5.5%
Other	26,500	3.3%

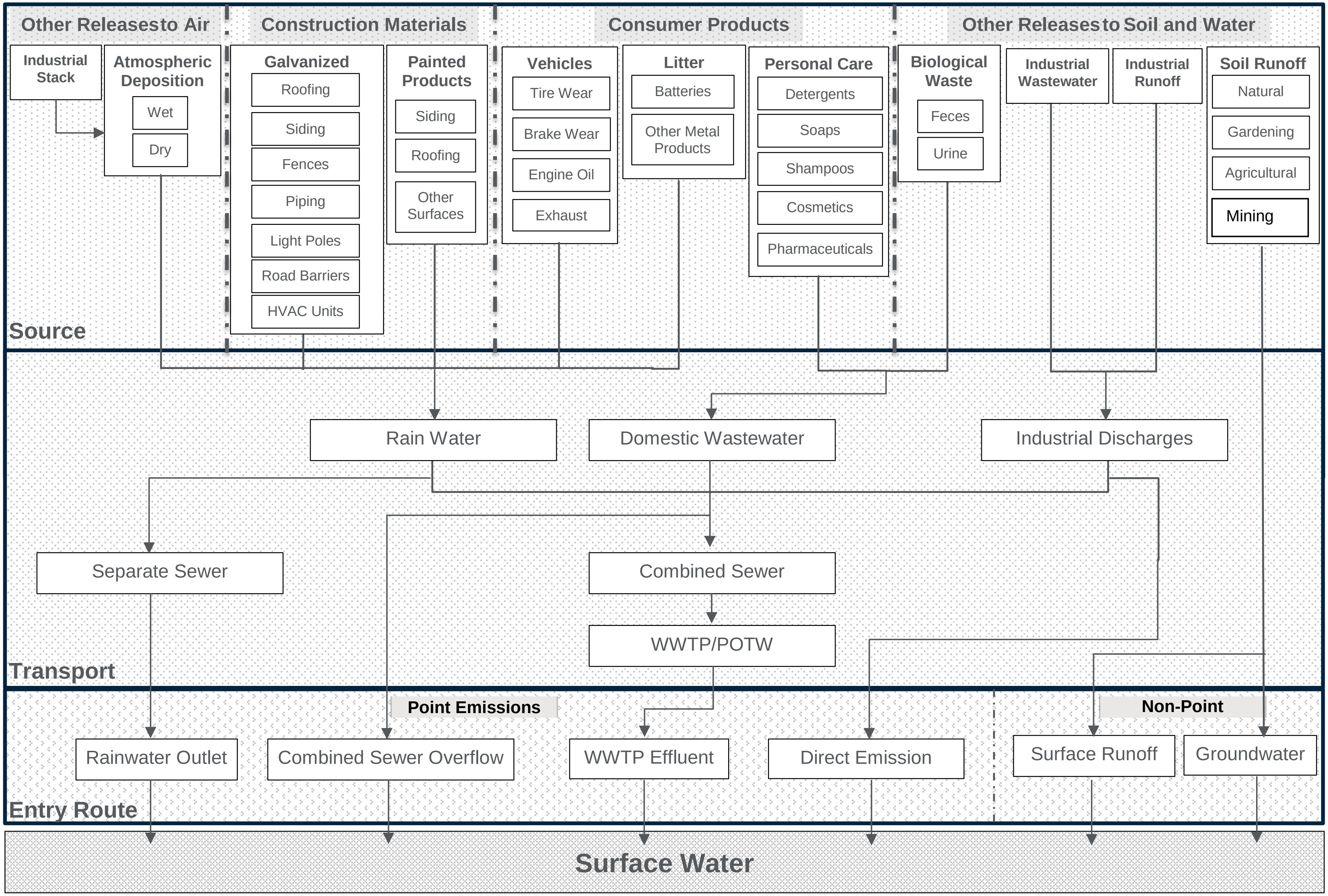

Figure 1.1: Schematic of Potential Emission Sources, Transport Pathways and Entry Routes of Zn to Surface Water (adapted from Hüffmeyer et al., 2009; ATSDR, 2005; Netherlands PRTR, 2015)

2 Review of Emission Inventories

2.1 Overview

An emission inventory is a tabulation of chemical pollutants discharged to the environment from specific point and/or non-point sources for a defined geographical area and time period. There are several emission inventories of varying scopes and complexity maintained by governmental bodies and international agencies. Table 2.1 provides estimates of releases from various sources of zinc from the U.S. EPA TRI and California's CTI, as well as international inventories. Also noted on the table are the methodology used to create the inventory, major and minor emission sources for Zn considered, and emission estimates. The inventories demonstrate the complexity of the contributions of diffuse sources to surface waters. For example, the Netherlands Pollutant Release and Transfer Register (PRTR) considers over a dozen distinct sources of Zn and numerous sub-categories for each source. Each inventory is characterized by data gaps and uncertainty. For example, the Regional Council for Auckland, New Zealand inventory estimates summed greater than 100% of the measured load (Kennedy & Sutherland 2008).

Table 2.1: National and International Inventories of Zinc Emissions

Inventory	Methodology	Sources of Zn Considered	Quantitative Estimates	Notes
United States Toxics Release Inventory	Mandatory reporting for individual industrial facilities that meet reporting requirements	Major: Industrial emissions Minor: Not considered	Tire wear not considered; total off-site disposal or other releases of Zn in the U.S. in 2013 was 136.6 million lbs.	Release rates determined by a variety of methods at each facility, including measurements or engineering estimates.
California Toxics Inventory	TRI data for California facilities combined with emission estimates for mobile air releases	Major: Industrial emissions; wildfires Minor: Mobile sources	All vehicle emissions account for 11% of emissions; "areawide" and "natural" sources account for 46% and 37%, respectively; only source emissions to air are considered.	Factors for particulate matter emissions and the chemical distribution of particulate matter are correlated to determine mobile emissions; sources not emitted to air are not considered.
Washington State Department of Ecology	Published release rates were used to calculate Cu and Zn loading to urban stormwater	Major: moss control products, building siding, parking lots, vehicle tire wear Minor: chain link fencing, roofing material, vehicle brake wear, roof gutters, HVAC, vehicle exhaust, streetlights	Tire wear estimated to contribute 12.6% to overall loading in urban runoff, with moss control and building siding accounting for 68% of load.	Significant number of sources evaluated and considered representative of a typical urban environment. Uncertainty regarding published released rates resulted in recommendations for sampling of run off in a future program.
Netherlands Pollutant Release and Transfer Register	Reported emission data and calculated estimates for diffuse source emissions to air, water, and soil	Major: Galvanized metals; POTW discharges Minor: Tire wear; atmospheric depositions	Tire wear estimated to contribute 8% of the load to sewage waters; galvanized metals and domestic discharge account for 70% of load.	Significant number of sources estimated with detailed emission calculations supported by local sampling and literature reviews.
United Kingdom National Atmospheric Emissions Inventory	Estimated data for emissions to the air from industrial and diffuse sources	Major: Metal production; lubricants Minor: Tire wear; combustion emissions	Tire wear estimated to emit 72 tons Zn in UK in 2012; only source emissions to air are considered.	Source emission calculations supported by local sampling and/or literature reference values; sources not emitted to air are not considered.
United Kingdom Pollutant Release Transfer Registry	Reported emissions from individual industrial sources	Major: Urban wastewater treatment Minor: Power plants; iron and steel production; aquaculture	Tire wear not considered; urban wastewater treatment emitted 227 tons Zn in all of the UK in 2013.	Release rates provided by operators of individual facilities.

Inventory	Methodology	Sources of Zn Considered	Quantitative Estimates	Notes
Australian National Pollutant Inventory	Reported emissions from individual industrial sources and estimated diffuse source emissions	Major: Mining and metal manufacturing; atmospheric deposition	Motor vehicles estimated to release 44 tons Zn to air in 2013/2014 (combination of all vehicle sources); paved/unpaved roads estimated to release 360 tons Zn to air in 2013/2014.	Air, water, and land emission estimates calculated using a variety of techniques. Some industries report data, while other releases are estimated.
		Minor: Motor vehicles; water supply; Wildfires		
Auckland Regional Council	Technical report estimating diffuse source emissions in urban environment	Major: Galvanized roofing	Tires estimated to contribute 0.070 – 0.677 kg/ha-year, depending on the catchment; roof runoff estimated to contribute 0.265 – 4.297 kg/ha-year.	Summation of the sources is greater than assessed loads; overestimation is attributed to the “significant error/uncertainty associated with the emission rates” for metal roofing and tire wear.
		Minor/Major: Tire wear; atmospheric deposition; other galvanized metals		

2.2 United States Toxics Release Inventory (TRI)

The U.S. TRI is a database of reported emissions from facilities in the U.S. (U.S. TRI). The inventory can be used to compare estimated emissions to actual industrial emissions for individual watersheds or regions, and from local individual facilities. It is important to note that TRI releases include Zn from both consumption of defined Zn-containing commodities (e.g. zinc salts), as well as from indirect releases of Zn from recycled materials and plant-based products that contain naturally occurring Zn such as cardboard paper. In addition, TRI release estimates reflect a variety of methods including default emissions factors and site-specific measurements. As such, Zn consumption inventories cannot be directly compared to the TRI release inventory estimate.

In the U.S. in 2013, over 880,000 lbs (>400,000 kg) of Zn is reported to be emitted as surface water discharges, with almost 400,000 lbs (>175,000 kg) released to surface waters by facilities classified as industrial uses in the paper sector. Another 278,000 lbs (126,000 kg) is released to POTWs across the U.S. (U.S. TRI). Industrial emissions vary appreciably between localities. For example, in LA County for year 2013, relatively low direct environmental emissions of zinc (<3 ton/year) have been reported from facilities in various industries (Figure 2.1). The total reported direct emission to surface water in LA Country was 0.4 tons/year in 2013. In comparison, TDC Environmental (2015) estimated that galvanized roofing area alone contributed 22 to 88 tons/year to LA County runoff. It is important to note that since Zn is not required to be reported under all scenarios, and diffuse sources are not considered, the TRI inventory is not comprehensive.

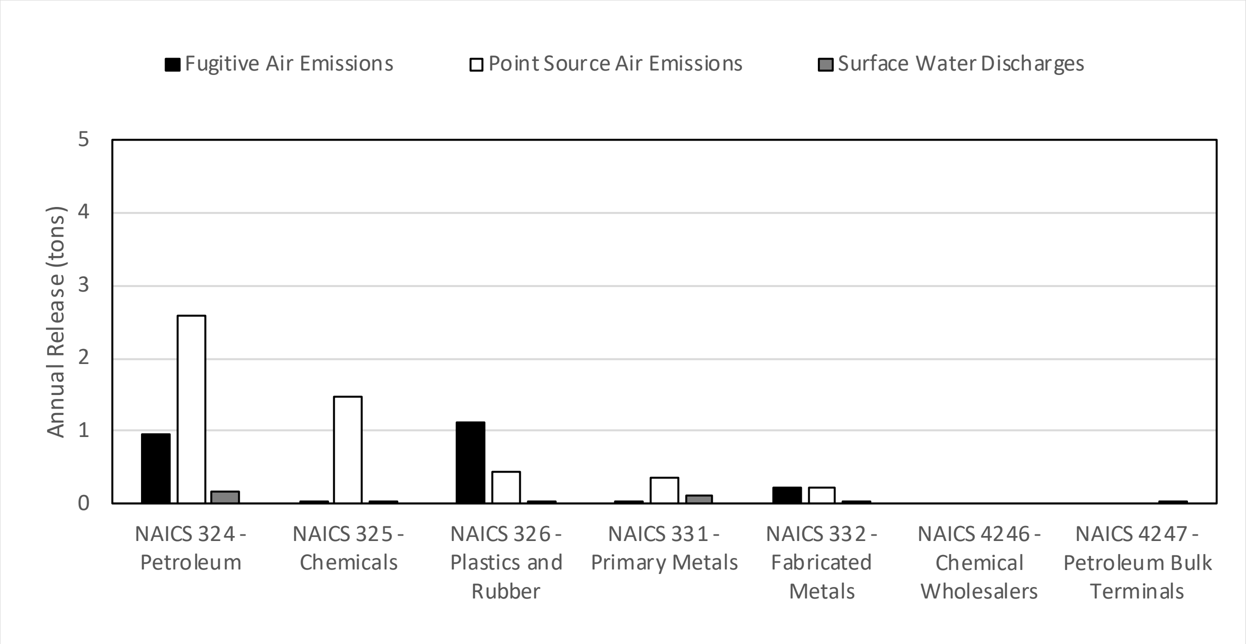

Figure 2.1: TRI Reported Emissions of Zn for LA County

2.3 California Toxics Inventory (CTI)

The CTI aggregates point source emissions reported to the U.S. TRI for California facilities with calculated emissions from a variety of other sources (CTI). Only emissions to the atmosphere are considered, and therefore the inventory does not estimate all diffuse sources to sewers and surface waters. Particulate matter emissions for tire wear are estimated for each motor vehicle class to be 0.008 – 0.012 g/mi (0.005 – 0.009 g/km). This particulate matter release is then combined with an estimated component distribution of the source particulate matter, and activity rate for the source. In the CTI, the concentration of Zn in airborne tire wear particles is estimated to be 0.005% based on an average of values presented by Hildemann, (1991) and Cooper et al., (1987). Sources designated as “areawide” (e.g. farming operations, paved and unpaved road dust, fugitive windblown dust, and construction and demolition) account for 46% of the inventoried emissions, while sources designated as “natural” (e.g. wildfires) account for 37% of the emissions. All road sources combined account for 11% of emissions, while point sources contribute 6% of tabulated emissions (CTI).

2.4 Washington State Department of Ecology

Washington State Department of Ecology (WA DOE) conducted a source inventory of copper and zinc in urban runoff in response to the Puget Sound Toxics Loading Assessment and as well as the recommendation of the CASQA to develop a source inventory based on local watershed information (Booker, 2017; CASQA 2015). The WA DOE goal was to develop a comprehensive data set of the relative importance of individual sources of Cu and Zn within an urban watershed that was representative of urban watersheds statewide. In doing so, they identified the study area in the lower Woodland Creek watershed primarily within the City of Lacey but extending into a portion of Thurston County in Western Washington State. WA DOE selected this area because it is reflective of land use in other Puget Sound suburban areas, the land area was of manageable size to allow a comprehensive review of potential Cu and Zn sources and the location was logistically convenient for sampling stormwater during unpredictable storm events.

The WA DOE compiled literature release rates for known primary sources of Cu and Zn and then calculated loading to the urban environment using surface area (for building materials) or vehicle kilometers traveled for motor vehicle sources. They indicated that the loading values represent worst case estimates that assume complete contact of precipitation with the exposed surface areas. The WA DOE concluded that the primary sources of Cu (in order of mass loading) were: vehicle brake wear, roofing materials, parking lots, treated lumber, building siding and vehicle exhaust. They concluded that the primary sources of Zn (in order of mass loading) were: moss control products, building siding, parking lots, vehicle tire wear, chain link fencing, roofing material and vehicle brake wear. The WA DCOE acknowledged uncertainty in the literature release rates and therefore recommended as second phase of investigation involving sampling of sources with the largest uncertainty. Those sources include: siding materials (including painted wood and metal siding), parking lots (as a secondary source related to motor vehicles), roofing materials (as built to include various structures associated with a full scale building including gutters, downspouts, HVAC system components), roof gutters specifically and streetlights.

2.5 Netherlands Pollutant Release and Transfer Register (PRTR)

The Netherlands PRTR is a compilation of yearly emissions data for over 350 pollutants from 700 sources (Netherlands PRTR). The register tracks emissions to air, water, and soil. The emissions to water are further divided into discharged load to surface waters, load to sewers and surface waters, and load to sewers. Emissions are calculated following UN and EU regulations and directives, as well as national reporting policies, and are evaluated for each of the following sources (bold indicates inventoried Zn emissions):

- **Ammunition from hunting**
- Angling lead
- **Atmospheric deposition**
- Bilge water in inland navigation
- Coatings, inland navigation
- **Coatings, merchant shipping**
- **Coatings, recreational boats**
- **Effluents WWTPs**
- Exhaust from recreational boats
- **Fireworks**
- **Galvanized steel and sheet zinc**
- **Greenhouse cultivation**
- **Heavy metals from farmland**
- **Industry, individual facilities**
- **Industry, statistical estimation**
- Lead sheets
- Nutrient losses from farmland
- Oil spills by inland navigation

- Oil spills on NCP
- Pantographs and overhead wires
- Preserved wood in bank revetments
- **Propeller shaft lubricant**
- Road surface wear
- **Road traffic brake wear**
- **Road traffic engine oil leaks**
- **Road traffic tyre wear**
- **Sacrificial anodes, inland shipping**
- **Sacrificial anodes, merchant shipping**
- **Sacrificial anodes, sluice valves**
- Shipyards
- Stainless steel in industries
- **Transboundary riverine inputs**
- Unintended fertilization of ditches
- Water conduits in office buildings
- Weed control on pavements

The sources listed are further divided where necessary to properly estimate emissions. For example, galvanized steel is sub-divided into many groups, including Zn plated roof and roof-gutters on residential housing, plated roof and roof-gutters on commercial and industrial buildings, plated steel for constructions and structures, plated steel for transporting trailers, plated steel on bolts and nuts, and plated steel on greenhouses.

The Netherlands PRTR lists the top 25 discharge loads of zinc to sewers, surface waters, and sewers and surface waters combined starting in 1990 and as recently as 2012. The top source of Zn in 2012 to sewers and sewers and surface waters combined was discharges of domestic wastewater, comprising 52% and 31% to each respectively. The largest emission sources to surface waters alone are from the leaching of agricultural and natural soils (29%), the corrosion of zinc anodes on ships (23%), and emissions from various point-source facilities (18%). Agricultural and natural soils and ship anodes do not contribute to sewer loads, and point-source facilities only comprise 3% of the total load to sewers. The next largest emission source to sewers after domestic wastewater is from the corrosion of galvanized steel and sheet Zn. Galvanized metals account for 25% of the load to sewers and more than half of the load excluding domestic wastewater. Zn resulting from tire wear under urban driving conditions is estimated to account for only 8% of the load to sewers and 1% of the load to surface waters. Similarly, 7% of the load to sewers is apportioned to atmospheric deposition. Brake wear and motor oil leakage are estimated to account for just over 1% of the load to sewers. Notably, fireworks on New Year's is estimated to contribute over 2% of the yearly load of Zn to the sewers (Netherlands PRTR).

When calculating pollutant emissions from tire wear, the Netherlands PRTR considers vehicle types and driving location (urban, highway, rural). The number of kilometers traveled for each vehicle type in each setting are used as activity rates and were obtained from Statistics Netherlands. Additionally, emissions factors in units of emissions per kilometer were calculated using factors such as tire sales data, average tire weight lost during lifetime, average lifetime mileage of tires, and using direct sampling of particulate matter from roadways. Tire wear rates were selected based on a comprehensive literature review and were sub-divided by the vehicle class and Zn content. For example, a tire wear rate of 100 mg/km was selected for passenger cars, which is slightly higher than the average rate assumed in the Blok (2005) estimate of Zn release from tires in the Netherlands of 87 mg/km. To obtain the total Zn emissions from tire wear for each category, the activity rate, wear rate, and percent content of Zn in tires were multiplied together (ten Broeke et al. 2008). Light and heavy vehicle tire wear under urban driving conditions was estimated to emit 24 tons of Zn to Dutch sewers in 2014. With approximately 4.2 million hectare (ha) of total space and an urban density around 30%, the Netherlands has 1.2 million ha of urban area. This corresponds to ~0.02 kg/ha of Zn from tire wear on urban roads in the Netherlands.

When calculating the runoff emissions of Zn from corrosion of galvanized steel and sheet Zn, the area of material exposed to precipitation and the weight of Zn emitted per unit area per year are two important factors. The area of Zn exposed was calculated using sheet Zn and galvanized steel sales data. The emission factors of Zn from these sources depend on a variety of factors such as SO_2 concentration in precipitation and spatial orientation of the Zn containing product. SO_2 air concentrations and spatial orientation averages per region were obtained and used in calculations. The total emission was calculated as area of exposed Zn multiplied by the respective emission factor (Netherlands Centre for Watermanagement 2008).

Zn emissions from waste water treatment plants were measured by Statistics Netherlands at about 100 treatment plants in urban areas. Metal concentrations in both influents and effluents were measured along with total volume of discharged water and were used in calculating average daily loads of Zn. This data was used to calculate removal rates of Zn from wastewater. The annual Zn load in waste water treatment effluents was then calculated using the Zn load in sewage sludge per year as well as the removal efficiency (Baas 2008).

The Netherlands PRTR is a comprehensive inventory that demonstrates the effectiveness of region-wide apportionments that consider many emission sources. The methodology employed in the database can be applied to other regions by adjusting the location-specific data in order develop a quality inventory of Zn emissions and source contributions.

2.6 United Kingdom National Atmospheric Emissions Inventory (NAEI) and Pollutant Release Transfer Registry (PRTR)

The UK NAEI is a database of emissions to air for a variety of pollutants used in national and international emissions reporting (UK NAEI). The UK NAEI collects and analyzes data and relies on a variety of sources such as national statistics and data collected from industrial plants. The database only includes estimated emissions for sources that release to the air, and therefore, some of the largest potential sources of Zn to sewers and surface waters are not considered. The sources emitting the most Zn to air in the 2012 inventory are lubricants such as motor oils, contributing an estimated 26% (99 tons) of the tabulated emissions and tire wear accounting for 72 tons (19%) in the inventory. The reliability of the tire emission factors, and the fraction of tire wear emissions assumed to occur as PM_{10} are unclear. For example, the European Environment Agency's (EEA) Emission Inventory Guidebook 2009 Tier 2 emission factor for passenger tires (considered in the NAEI) is 10.7 mg TSP/km x 60% PM_{10} fraction or, 6.4 mg/km. Recent data suggest that the central tendency for all vehicles is likely approximately 2.4 mg/km (Panko et al. 2013). Therefore, it seems likely that the release to air is appreciably overstated in the UK air emissions inventory, and that Zn likely accounts for less than 5% to 10% of the Zn PM_{10} release to air.

The UK PRTR is an emission database of pollutants released to water, air, and soil by individual facilities with a requirement to report by the European Union (UK PRTR). The database does not include diffuse sources of release, but can provide a comparison for the UK NAEI. For example, the largest release of Zn to water is from urban wastewater treatment plants, which released over 226 tons of Zn. The products and processing of metals including metal ore roasting and iron and steel facilities, released 25 tons Zn to air and over 52 tons Zn to water. Other major facility releases include thermal and combustion power plants, aquaculture, and industrial wastewater releases (UK PRTR).

2.7 Australian National Pollutant Inventory (NPI)

The Australian NPI contains reported emissions from individual industrial sources and estimated diffuse source emissions by local or state environmental protection agencies (Australian NPI). Paved and unpaved roads and windblown dust account for more than 10 times the amount of Zn released to the air than the emissions estimated for motor vehicles, which may include tire wear, brake wear, and exhaust emissions. However, it is unclear whether the estimated emissions from road dust includes resuspended vehicle wear debris and emissions, or reflects only the contribution of non-vehicle sources.

2.8 Auckland Regional Council, New Zealand

In 2008, the Auckland Regional Council issued a Technical Report titled “Urban Sources of Copper, Lead and Zinc” (Kennedy & Sutherland 2008). Auckland is the largest urban area in New Zealand with over 1.4 million inhabitants represents approximately 30% of the country’s population. The technical report investigated sources in three drainage areas including the commercial central business district, the residential Mission Bay catchment, and the industrial Mt. Wellington catchment. For each catchment, the emissions were estimated for sources including atmospheric deposition, vehicle emissions and wear, soil leaching, building sidings and roofing, public water, garden and household products, litter, and road and pavement wear. Importantly, the report outlines the uncertainty associated with each source, and inherent variability between individual catchments or watersheds. The report notes that the summation of the sources accounts for greater than 100% the assessed loads. This overestimation is attributed to the “significant error/uncertainty associated with the emission rates” for metal roofing and tire wear (Kennedy & Sutherland 2008).

Based on Figure 5.3 in the report which corrects the total mass to 100%, roofing materials were estimated to contribute 75% of the industrial catchment Zn load, 41% of the central business district (CBD) Zn stormwater load, and 33% of the residential catchment Zn load. In comparison, tire wear was estimated to contribute 33% to the residential load, 17% to the CBD load, and only 1% to the industrial catchment load. The authors categorized sources as negligible (<1%), minor, (1-10%), moderate (10-20%), and major (>20%). Zn-containing roofing materials were considered to be a major source (>20%). Other roof infrastructure components, galvanized street infrastructure, and public water supply releases were considered to also be minor sources. Rainfall was classified as either a minor or major source depending on land use. Tires were considered to be a minor (<10%) or major (>20%) source depending on land use characterization. Lastly, rainfall was considered to be minor or major source, roof-top building materials including gutters, heating ventilation and cooling (HVAC) units, and flashing, were considered to be a minor source.

3 Literature Review

3.1 Overview

The published literature confirmed the wide variety of applications for Zn, as shown in Table 3.1. Many of these of potential sources have been identified as important sources of Zn to watersheds. The potential for specific sources to contribute to Zn loading in watersheds has been studied using a variety of techniques. Researchers have conducted sampling, geo-spatial analysis, laboratory tests, pilot field studies, and hypothesis generating investigations. Conceptual models have been presented in some studies to characterize potential sources of zinc to water and the environment. The sources of zinc reviewed below include galvanized metals, piping, domestic wastewater, painted structures, atmospheric deposition, industrial runoff, vehicle traffic, and littered batteries. In addition, the results of watershed-scale source apportionment studies are discussed.

Table 3.1: Potential Sources of Zn (ATSDR, 2005; Blok 2005; Comber & Gunn 1996; Krouse et al. 2009)

Construction Materials		**Consumer Products**		**Other**	
Galvanized metal surfaces	Roofing	Littered products	Batteries	Atmospheric deposition	Wet
	Siding		Other metal products (e.g. coins)		Dry
	Road barriers			Combustion	Coal and waste burning
	Piping				Forest fires
	Light poles	Personal care	Cosmetics	Industrial	Stack emissions
	Fences		Soaps		Wastewater
	Scrap Metal		Shampoos		Runoff
	HVAC units		Detergents	Soil runoff	Agriculture
			Pharmaceuticals		Gardening
		Vehicles	Exhaust		Natural
Painted or coated products	Siding		Brake wear	Biological waste	Urine
	Roofing		Tire wear		Feces
	Other products (e.g. wood preservatives)		Engine Oil		

3.2 Galvanized Metals and Roofing Materials

Many environmentally exposed metal surfaces are galvanized, or coated with Zn, to reduce rusting of the interior metal product. Zn is more resistant to corrosion than steel or iron, which prevents the products from rusting prematurely. Further, if the product is chipped, Zn acts as a sacrificial anode and will corrode before the exposed product (ATSDR. 2005). Despite the ability of galvanization to increase the durability of metal products, the degradation and dissolution of the Zn coating is unavoidable resulting in the release zinc from exposed exterior surfaces. Common exposed galvanized metal structures and products include building sidings, roofing, gutters, and facades, along with street light poles, road crash barriers, fences, metal benches and waste bins, piping, heating, ventilation, and air conditioning units, and sacrificial galvanic anodes used on ships and statues. Since the objective of galvanizing is to release Zn into the environment preferentially to the protected product, galvanized metals have been recognized as a major non-point source contributor of Zn to urban storm water runoff. Other products, such as Zn sheets used for roofing, are constructed of nearly 100% Zn or Zn alloys, and are also potential contributors of Zn in urban areas.

Further, metal surfaces have the potential to accumulate atmospheric deposition that are later released in the first flush of a storm event (Lindstrom & Odnevall Wallinder 2011; Gromaire et al. 2002).

Galvanized metal surfaces, including roofs and gutters, have been associated with elevated Zn levels in water. For example, Davis et al. (2001) measured a Zn concentration of 7,600 µg/L in rain runoff from a galvanized metal roof. In comparison, the mean Zn concentration in 13 samples collected from residential roofs was only 100 µg/L. Also, Tobiszewski et al. (2010) measured Zn levels in galvanized roofing runoff as high as 9,600 µg/L. In a two-year pilot study of a galvanized panel, Clark et al. (2008) measured Zn concentrations in runoff of 5,000 to 30,000 µg/L. The long-term leaching potential of these products may be further enhanced in areas with acid rain (pH less than 5.6) (Clark et al., 2008).

Lindstrom and Odnevall Wallinder (2011) evaluated long-term Zn release over a 10 year period at an urban location in Sweden and determined that galvanized steel and Zn sheets have annual runoff rates of approximately 2 g Zn/m^2/year. In comparison, the runoff rate from a Plexiglas control surface yielded a runoff rate of only 0.02 g Zn/m^2/year. The runoff rate remained nearly constant from years 5-10, despite dropping from >5 to ~2.5 g Zn /m^2/year in the first 2 years of the study. This result indicates that corrosion of a new galvanized product decreases somewhat after initial weathering, but is also likely to persist for the entire service life of the structure. Based on available mass and the observed rates, the authors estimated that the Zn layer on the galvanized steel “should last for more than 200 years.”

Horvath and Buzas 2013 conducted pilot studies in Hungary with a galvanized steel roof near a busy street in an urban location. Similar to the findings of Lindstrom and Odnevall Wallinder (2011), the estimated annual average runoff rate was 0.7 g/m^2/year, and atmospheric deposition rates were minor as compared to dissolution from the gutter materials and roofing. Longer contact times from low intensity rain events or roofing with shallow grades, as well as longer dry periods before rain events resulted in more corrosion products dissolving into the storm runoff. Contact time and dry periods are therefore likely to be important factors contributing to Zn release from galvanized building materials in urbanized areas with flat roofed buildings, and climates with infrequent rain event.

Van Metre and Mahler (2003) estimated that particle-bound Zn from roof washoff accounted for 55% (median value) of the particle-bound Zn load in the Shoal Creek drainage area in Austin, TX. Of the total particle-bound Zn from roof washoff, 20% was attributed to roofing materials and 37% from atmospheric sources (median values). The effect of proximity to a major roadway was eliminated by only using samples collected greater than 100 m from major roadways. Source contributions were calculated using estimated yields (mass release per material area) for asphalt and galvanized metal roofing and total roofing area in the drainage area of asphalt (25% of drainage area) or galvanized metal roofs (4% of drainage area).

Gromaire et al. (2002) estimated the source contribution of Zn roofs in Paris total loading using literature estimates of corrosion and runoff samples collected from four zinc roofs. Rolled Zn roofing material was estimated to comprise 41% of total roof area, and 29% of the total land area in Paris. Approximately 50% of the total yearly Zn runoff in Paris runoff (33 to 60 tons) was estimated to originate from Zn roofing. The conclusion is also consistent with the qualitative findings of Chen et al. (2008), which showed that zinc isotope ratios suggested that roof leaching is a “major source” of Zn in Paris. Similarly, Thevenot et al. (2007) completed a mass-balance assessment of a 0.42 km^2 experimental catchment in Paris, and found that roof runoff accounted for 55% of the Zn in combined sewage (as compared to only 7% for street runoff). Sellami-Kaaniche et al. (2014) evaluated an urban suburb of Paris by visual estimation of rooftop surface area, gutter length, valley length, land use classifications, as well as characterization of material age. The mean annual Zn estimated runoff rate was 0.3 to 0.7 g/m^2/year, which is similar in magnitude to estimates from other studies that have presented material specific runoff rates. The authors also concluded that gutters are an appreciable source of Zn emissions.

Galvanized metals have the potential to be the largest source of Zn to stormwater in many urban environments based on the surface area covered by the products and technical function of Zn as a sacrificial anode. The potential for Zn to leach from aged Zn-based environmentally exposed building materials appears to exist for the lifespan of these products, corresponding to a time period of at least 10 years, and possibly as many as 60 years (Clark et al., 2008).

3.3 Littered Batteries

Discarded batteries first became a concern in 2001 when a group of researches conducting heavy metal sampling of soils near retail parking lots found higher than expected Zn levels and noticed littered batteries throughout the area. Subsequent research discovered that littered batteries may be a primary contributor of metal pollution. Between 2001 and 2006, 179 surveys in Cleveland, OH of parking lots and streets recovered 4,481 batteries. The average pavement survey (of either 1 retail parking lot or a few blocks of urban streets) yielded approximately 25 batteries (range 1-198 batteries). Also noted was that the degree of battery deterioration was likely significant with 70% of the cells leaking or having already discharged their contents upon recovery. The research has resulted in a battery litter mass loading model. An example application of the model resulted in 2.7 kg Zn released per year in a 3.0 ha location in the Cleveland, OH area. This release rate, ~1 kg/ha/year (100 kg/km^2/year), was considered to be the largest source of Zn in runoff in this study area (Krouse et al. 2009). In comparison, the Thevenot et al. (2007) mass-balance assessment of combined sewage system annual fluxes for a 0.42 km^2 experimental catchment in Paris found that roof run-off and street run-off accounted for 10.62 kg/ha/year (1062 kg/m^2/year), and 1.44 kg/ha/year (144 kg/m^2/year), respectively. This suggests that littered batteries may be of equal or greater importance in Zn source contribution than traffic related sources including tires, brakes, and motor oils.

3.4 Vehicle Traffic and Roadway Systems

Vehicle traffic and roadway systems have several potential emission sources for Zn. Components of vehicles that may contain Zn, include motor and diesel oils, tires, paints, metallic trim, and brakes. Further, vehicles have the ability to re-suspend and transport atmospheric deposition of Zn from other sources including exhaust emissions that has accumulated on the roadway, along with the wear of the roadway itself. Table 3.3 summarizes the different types of Zn emissions that vehicle traffic can produce. The release of each of these depends on the type of driving, the road conditions, the Zn content in the materials, and the amount of vehicle traffic (Blok 2005; Sorme & Lagerkvist 2002; Legret & Pagotto 1999).

Table 3.2: Emission Sources of Zn from Vehicle Traffic

Source	**Emission Type**
Oils	Direct release
Brakes	Particle wear
Tires	Particle wear
Metals	Particle wear and wash off
Paints	Particle wear and wash off
Exhaust	Air
Road surfaces	Indirect particle wear
Deposition Re-suspension	Indirect

With the exception of governmental emission inventories, there have been few mass balance studies that present estimates of Zn loads for specific geographical regions for vehicles or roadway systems. Blok (2005) estimated that 140 tons/year of Zn is released from tires in the Netherlands. Of this amount, 6.5 tons/year (5%) of the particulate was estimated to distribute beyond the “technosphere” of the roadway system to a “target zone” of potential ecological impact. An additional 50 tons/year (36%), was assumed to be released to runoff, which is either conveyed to local waterways, or infiltrates in roadside soils and detention ponds. An additional 44 tons/year of Zn was estimated to be released from galvanized roadway safety fences within the roadway technosphere.

Sorme and Lagerkvist 2002 estimated that 10 to 11% of the daily Zn load in the combined sewers of Stockholm, Sweden were from traffic sources. In comparison, households and businesses each accounted for 30%, and building materials accounted for 27%. The major traffic sources considered by Sorme and Lagerkvist 2002 included brake lining, tire rubber, oil and asphalt, with tires estimated to account for approximately 85% of the mass released from these traffic related sources.

Caltrans conducted a comprehensive set of studies designed to characterize stormwater runoff from transportation facilities throughout the state of California (Caltrans 2003a). The goals of their investigation was to achieve compliance with permit requirement, produce data that are scientifically credible and representative of runoff from their facilities and provide information that can be used to design effective stormwater management strategies. Caltrans measured a variety of water quality parameters in this study including conventional indicators, various nutrients and metals such as arsenic, cadmium, chromium, copper, lead, nickel and zinc. Caltrans reported that the highest pollutant concentrations were in runoff from facilities with higher vehicle counts (i.e., highways and toll plazas), and were generally higher in highway runoff located in agricultural and commercial areas than in residential, transportation corridors and open land use areas. Additionally, the researchers found that the concentrations were not predictable by geographic region and that there was no consistent pattern in runoff within a geographic region. The authors reported that the correlation coefficient in regression models for zinc were low; finding that traffic count and precipitation factors explained some but not all of the variability and that there were other unaccounted for factors contributing to the variability in the runoff. This study was not designed to evaluate contributions of individual sources and does not provide data on relative importance of different types of sites.

In another study related to stormwater management practices, Caltrans assessed the use of roadside vegetated treatment (Caltrans 2003b). In this study, Caltrans again assessed water quality parameters including conventional indicators, nutrients and metals and evaluated the reduction between the concentrations of the parameters in runoff water collected at the edge of the pavement and at varying distances from the roadway within the vegetative cover. Monitoring was conducted at 8 sites during 9-26 storm events based on location. For nearly all sites, Zn concentration were lower in runoff collected in the vegetative cover areas than at the edge of the pavement. These findings supported the use of roadside vegetative cover for metals reduction in runoff. As with the other Caltrans study, the researchers did not design the vegetative cover study, nor do the measurements that were made provide data to evaluate contributions of individual sources of Zn on the road such as tires, galvanized crash barriers, fencing, road signs, etc that were present in the study areas.

TDC Environmental (2015) estimated that tires contribute 230 tons/year to LA County, California runoff based on a number of assumptions used to estimate an order of magnitude contribution. This estimate likely overstates the load of Zn from tires because a washoff factor of 80% was assumed, and the Zn generation rate of 2 mg/km (200 mg tread/km) for passenger cars likely overstates modern tread wear rates. In comparison, Blok (2005), estimated wear rates of 1.53 mg/km, 0.93 mg/km, and 0.31 mg/kg for urban, regional, and highway driving, respectively. The TDC Environmental passenger car estimate of 200 mg tread/kg was taken from Councell (2004), which cited road simulator data for gentle, normal and hard driving corresponding to a passenger car (4 tire) rate of 92 mg/km, 168 mg/kg and 292 mg/km. With regard to washoff, the assumed fraction of 80% does not account for Zn sequestered within the “technoshpere” of the roadway systems, or otherwise removed by detention pond/storm basin sedimentation, and street cleaning. Considering these factors, the contribution of Zn from tires to urban runoff in LA County is likely overestimated by a factor of 4 or more.

Permeable friction courses (PFC) are used increasingly on roadway systems as a mechanism to improve roadway safety by allowing stormwater to flow through it to the roadside. An additional benefit associated with the use of PFC has been reductions in water quality parameters of storm water runoff (Stolz and Krauth, 1994; Berbee et al., 1999; Pagotto et al., 2000; Roseen et al., 2009; Eck et al.,2012). One binder used in PFC is crumb rubber and recently Barrett and Sampson (2013) published a study on the impact of different binder materials in PFC in reducing water quality impacts compared to conventional pavements. These researchers found that both the Performance Grade (PG-76) binder and the asphalt-rubber (A-R) binder, which contains crumb rubber from recycled tires significantly reduced TSS, Kjeldahl nitrogen (TKN) and total an dissolved phosphorous, copper, lead and zinc as compared to conventional pavement. A summary of the reductions observed is presented in Table 3.4. Specifically for zinc, the PFC with A-R binder reduced the median total zinc in the run-off by 70% compared to conventional pavements. Additionally, Sampson and Barrett (2013) reported approximately 40% reduction in dissolved zinc concentrations for the PFC with A-R binder.

Table 3.3 Summary of Water Quality Parameter Measurements (Adapted from from Barrett and Sampson, 2013

Constituent	Median Concentration			Percent Reduction	
	Conventional Pavement	PG-76 Binder (Camp Mabry Site)	A-R Binder (Camp Hubbard Site	PG-76 Binder (Camp Mabry Site)	A-R Binder (Camp Hubbard Site
TSS (mg/L)	152.0	12.0	12.0	92	92
NO_3^+/NO_2^- (mg/L)	0.7	0.3	0.3	61	56
Total P (mg/L)	0.5	0.1	0.1	81	86
Total Copper (ug/L)	50	12.7	13.1	75	74
Total Lead (ug/L)	130	1.6	2.4	99	98
Total Zinc (ug/L)	285	37.4	85.8	87	70

3.5 Piping and Domestic Wastewater

Galvanized steel piping was used for drinking water and other water supplies in structures built prior to the 1960s (McFadden et al. 2011; Comber & Gunn 1996). Similar to other galvanized metals, galvanized piping has the potential to corrode and contaminate the liquid flowing through the pipes. The amount of Zn emitted by piping depends on the properties of the piping including pH level of the water and age of the pipes, as well as the length of the piping network (Zhang et al. 2008).

The sources of Zn in domestic wastewater have been largely attributed to anthropogenic sources including personal care products and human waste (Comber & Gunn 1996; Sorme & Lagerkvist 2002; Houhou et al. 2009). Additionally, laundry detergents have also been found to contain Zn, which raises Zn concentrations in greywater (Aonghusa & Gray 2002). Municipal waste water has been found to contain elevated levels of Zn in several sampling programs (Comber & Gunn 1996; Aonghusa & Gray 2002). Zn has been found to be the most abundant metal in laundry water (Aonghusa & Gray 2002; Braga & Varesche 2014). In total, over 50% of domestic wastewater has been attributed to anthropogenic sources (Comber & Gunn 1996). The remainder of the Zn in domestic wastewater can be attributed to Zn from the water inlet, corrosion from piping and taps, release of amalgam from dental fillings, and food products (Comber & Gunn 1996; Sorme

& Lagerkvist 2002). Sorme and Lagerkvist 2002 estimated that 30% of the daily Zn load in the combined sewers of Stockholm, Sweden were from household sources.

3.6 Painted Structures

Sampling research suggests that runoff from painted structures may contribute to urban storm water pollution. Kszos et al. (2004) traced the aquatic toxicity of storm water runoff to the paint used on thousands of cylinders at a depleted uranium hexafluoride holding site that had been recently painted to ensure containment of the materials. Therefore, painted surfaces distributed over large land areas may be an important source of leachable Zn. Davis et al. (2001) sampled painted and unpainted wood building sidings and found that runoff from painted wood siding was more than 8 times higher than unpainted wood siding.

3.7 Atmospheric Deposition

Atmospheric deposition of Zn occurs from many sources of natural and anthropogenic origins. Anthropogenic sources include industrial emissions such as stack emissions, and the transport of aerosolized diffuse emissions such as vehicle exhaust. Natural sources of deposition include forest fires, volcanic ash and eroded natural soils. Atmospheric deposition is classified as either dry deposition attributable to particle transport, or wet deposition attributable to scavenging by rain, snow or fog. Deposition rates vary across and within regions (Wu et al. 1994; Scudlark et al. 1994; Sabin et al. 2005; Horvath & Buzas 2013). Sabin et al. (2006) demonstrated that deposition fluxes can vary between seasons, even in locales with relatively stable climates. In southern California, the average dry deposition of Zn ranged from 0.10 kg/ha-year in the spring to 0.14 kg/ha-year in the summer. Also, dry deposition may be highly dependent on the antecedent dry days (Sabin et al. 2006). Table 3.2 summarizes selected rates of atmospheric deposition of Zn.

Table 3.4: Selected Atmospheric Deposition Rates of Zn

Source	**Location**	**Wet (kg/ha-year)**	**Dry (kg/ha-year)**
Wu et al. 1994	Chesapeake Bay	N/A	0.02
Scudlark et al. 1994	Chesapeake Bay	0.013	N/A
Sabin et al. 2005	Los Angeles	0.015	0.13
Sabin et al. 2006	Los Angeles Area	N/A	0.069 – 0.230
Paode et al. 1998	Chicago	N/A	0.20

3.8 Industrial Facilities

Industrial sites emit Zn indirectly though fugitive and stack emissions to the atmosphere and discharges of treated process and facility water. Many facilities also release Zn directly through surface runoff emissions to stormwater. Stormwater runoff from industrial sites has been reported in the literature to be elevated with Zn (Line et al. 1996; Sorme & Lagerkvist 2002; Comber et al. 2015). For example, Line et al. 1996 measured runoff concentrations in North Carolina from each of two industrial locations described as auto salvage yards, metal fabricating sites, scrap and recycling sites, vehicle maintenance sites, and wood preserving sites. Of the 10 sites, only one site did not have exposed materials that were used, sold, or serviced by the business. Concentrations of Zn were elevated at all of the sampled sites, and were especially high at the auto salvage yards and scrap metal yards, indicating that galvanized metal products were the primary source of Zn in the industrial runoff. In the U.S. stack and direct discharges are inventoried in the U.S. Toxics Release Inventory (see Section 2.2).

3.9 Watershed Inventories

Several studies are available that present conceptual models of pollutant loading and distribution in order to characterize potential sources of Zn and/or develop water quality improvement methods by targeting Zn sources. Although varying in complexity, these studies often employ GIS and site-specific sampling.

Gromaire et al. 2001 performed selective sampling in the Marais catchment of Paris and estimated that roof runoff contributed 88-96% of Zn runoff to the sewers, and that street runoff and courtyard runoff contributed 2-7% and 1-5%, respectively. As discussed in a previous section, Thevenot et al., 2007 utilized flow and emission estimates to calculate source contributions of Zn to the combined sewers of the Seine River basin in Paris. Roof runoff, domestic wastewater, and street runoff contributed 55%, 37%, and 7%, respectively. Utilizing a similar method to Thevenot et al. 2007, Sorme and Lagerkvist, 2002 estimated the loadings of Zn to the combined sewers in Stockholm and determined that sewage water (household, businesses, drainage water, and pipe sediments) contributed 91% of Zn, while buildings and road traffic contributed 13-17% and 5%, respectively. Hüffmeyer et al. (2009) utilized the Geo-referenced Regional Exposure Assessment Tool for European Rivers (GREAT-ER) to estimate the Zn loading to the Ruhr river basin. Roofs and gutters were estimated to contribute 57% of the Zn in rainwater and 22% of the Zn in WWTP influent. Road surfaces were estimated to account for the remainder of Zn in rainwater (43%) and 17% of the WWTP influent. Private households were estimated to contribute the remainder of the Zn to the WWTP influent. Comber et al. 2015 conducted sampling in 9 cities in the UK and reported that the Zn loading estimates varied by city, with domestic sewage contributing between ~15-65%, trade effluent (i.e., industrial discharge) contributing ~5-80%, town centre runoff contributing <10%, light industry contributing <5-40%, and runoff was contributing <5-40%.

The inventories and budgets in the literature suggest that a source apportionment must be conducted for each individual watershed or region due to variances in galvanized metal usage, atmospheric depositions, domestic and industrial discharges, road traffic, and other differences. However, similarly to the inventories described in Section 2, the published inventories demonstrate that domestic wastewater and galvanized metals are likely the major sources of Zn in urban watersheds.

3.10 Conclusions Regarding Literature

A consensus or generic determination of the source apportionment of Zn in urban watersheds cannot be derived from the available literature. In general, galvanized metal and other zinc-based building materials, as well as, municipal wastewater appear to be the primary sources of Zn to waterways. Minor sources of zinc include vehicle components include brakes and tires, atmospheric deposition, agricultural treatments, and paints and other environmentally exposed consumer products, although these will certainly vary by location. A recent study suggested that improperly disposed batteries may be the largest source of Zn in some catchment areas. The high variability in the literature suggests that a region-specific source inventory is necessary to understand the sources of Zn in an individual watershed.

4 Davis et al. (2001)

4.1 Overview

Davis et al. 2001 used literature and limited sampling to estimate the loading of lead, copper, cadmium, and Zn to storm water runoff from several specific sources. Building runoff (siding and roofing) and automobile non-exhaust emissions (brakes, tires, and oil leakage) were investigated as Zn sources through a series of sample collection activities. The sample collection generally consisted of simple leaching experiments with synthetic or natural rainwater collection. Wet and dry atmospheric deposition rates were estimated using published estimates from the Chesapeake Bay (Wu et al. 1994; Scudlark et al. 1994). This review focuses on the purpose, scope, and reliability of the Zn loading estimates presented by the authors.

After completing the experimental data collection, the authors developed a residential scenario to characterize a theoretical urban hectare of land. Assumptions were made for the amount and intensity of rainfall per year, the number of houses per hectare, the surface area of siding and roofing per house, the number of vehicles per house, the amount of distance driven per vehicle, and the tire wear and oil leakage per distance. Building siding and tire wear comprised 58% and 25% of total Zn load, respectively. A limited sensitivity analysis suggested that the percent contribution did not vary appreciably with minor, arbitrary adjustments to the assumptions. However, in two alternative scenarios developed after the sensitivity analysis, the total Zn load estimated for a commercial land use scenario was 700% greater than the residential scenario that assumed buildings had predominately vinyl siding, and the building roofing contribution ranged from 18% to 58% of total Zn load. Thus, it can be concluded that the sensitivity analysis failed to address the true uncertainty in the percent contributions, because it only assessed small perturbations in input parameters, rather than characterizing parameter uncertainty and variability.

The authors performed a limited comparison of their Zn loading estimates to the estimates of Wong et al. 1997, who used empirical models and a geographic information system (GIS) to estimate pollutant loadings to the Santa Monica Bay. The results from each land use designation and scenario from Davis et al.2001 accounted for more than 100% of the total Zn load estimated by Wong et al. 1997, despite accounting for only three potential sources of Zn (automobiles, buildings, and atmospheric depositions). This overestimate is notable because several potentially major sources were not included in the Davis et al. 2001 emission inventory, including combustion emissions, fires of natural and anthropogenic origin, industrial releases, agricultural runoff, littered product, and upstream domestic wastewater discharge. In summary, the loading estimate methodology consisted of basic sampling and laboratory experiments paired with calculations based on simplifying assumptions with significant uncertainty and variability.

This study demonstrated that the source apportionment of Zn in urban storm water runoff is complex and requires a substantial understanding of the area surrounding the specific watershed(s). The authors characterize their work as an “initiatory study” and “preliminary investigation.” As noted by the authors in the Summary and conclusions, “[t]his work was designed as an introductory study to estimate metal loadings. Improved information on the metal release and distributions from the specific sources with focused subsequent research, along with detailed characterization of drainage areas will allow refinements in the predictions” (p. 1009). The goal of the work was to “estimate metal loadings from individual components of automobiles and buildings”, but the authors clearly characterize their work as hypothesis generating. The intent of the study design was to “identify important sources of metals” that should be the focus of future investigations specifically designed to quantify origin and release. As such, Davis et al. 2001 demonstrates the need for documented and defensible quantitative emissions inventories, as well as, local source apportionment and mass balances studies of Zn in storm water runoff. The study shows that automobile wear and building runoff should be considered as potential quantifiable sources of Zn. However, given the exploratory nature of this research, it would be inappropriate to use the results from this study for specific source apportionment of Zn load in any watershed, regardless of land use.

4.2 Sampling Methods

Davis et al. 2001 used pilot aqueous extraction studies to estimate metal content in storm water resulting from tire and break wear, engine oil, and building sidings. The aqueous extraction studies were not performed according to standard methods, and therefore represent a qualitative indicator of availability of soluble metal rather than a quantitative measure of emission. Limited roof sampling during rain events was conducted in an attempt to characterize runoff from building roofs. Wet and dry deposition values were taken from literature. The pilot studies were combined with simplified calculations in an attempt to estimate loading to storm water. The sampling methods and calculations are simplistic, and reflect the hypothesis generating nature of this paper. Table 4.1 outlines the sampling methods for each source, and the critical uncertainties that prevent the generalization the results of this study to specific regions or localities.

Table 4.1: Methods and Uncertainties of Sampling

Source	Sampling Methods	Uncertainties
Building roofing	• Runoff from 38 roofs were sampled • Roof types were divided into three categories: residential, commercial, institutional • “In some cases, the type of roof was known” (p. 1001)	• One of the four rain water blanks had higher Zn levels than the median level measured in residential area • Type and age of roof materials unknown • Sampling location and antecedent dry period unknown • Season unknown
Building siding	• Synthetic rain water sprayed on sidings of six materials and collected • Brick, vinyl, concrete, metal, and painted and unpainted wood	• Age of materials unknown • Sampling location and antecedent dry period unknown • Season unknown
Tire wear	• Steel brush used to abrade tires • Abraded particles extracted in synthetic rain water • 4 brands of tires investigated	• Vehicle type unknown • Age of tire unknown • Brand representativeness unknown
Brake wear	• 54 front brake dust samples • Synthetic rain water sprayed on brake parts and collected	• Brake type and manufacturer unknown • Age of brakes unknown
Engine oil	• 13 used engine oil samples obtained from local repair shops • Mixed with synthetic rain; water phase separated from oil	• Type of oil unknown • Age of oil unknown • Brand unknown
Wet deposition	• Literature values from 3 sites surrounding Chesapeake Bay (Scudlark et al. 1994)	• Deposition fluxes vary appreciably based on local source, weather, and watershed characteristics
Dry deposition	• Literature values from 2 sites surrounding Chesapeake Bay (Wu et al. 1994)	

Considering the methods and uncertainties summarized in Table 4.1, a few important themes are evident. First, the representativeness of the products selected for testing is unknown with respect to national, regional, or local distribution of product type. The authors made no attempt to characterize the market-share distribution of roof type, brake pad alloy, oil and tire tread formulation, and building siding material. For example, the authors were unable to document the type of roof where runoff was collected, which is a critical determinant in expected Zn load. Second, other important determinants were not controlled in the study including the age of the materials tested, the season of sample collection, and the duration of the dry period before sampling was performed. Finally, while the wet and dry deposition rates appear to be reflective of the region of the country where the study was performed, there is no characterization of variability in these rates, and the other aspects of the study were not controlled to be representative of regional characteristics. In summary, the study methods and uncertainties reflect the qualitative and exploratory nature of the study, and the limitations that prevent extrapolation of the results to specific regions or localities.

4.3 Emission Calculations

The measured metal concentrations were normalized by surface area or component to facilitate the calculation of annual metal loadings to a hypothetical watershed. Key assumptions included the surface area of building surfaces, the number of vehicles per household, and annual vehicle miles traveled. Table 4.2 summarizes the assumptions that were used for each emission calculation and the uncertainties corresponding to each source. Several limitations regarding the emission calculation are apparent when comparing the approach used for each source. In particular, the assumed building material types and density, surface areas, and traffic densities were arbitrarily selected and not well documented. These assumptions are not necessarily representative of the region where sampling was conducted. The limited documentation and bounding nature of the assumptions are consistent with the objectives of the authors to identify potentially important sources of metals to watersheds. However, because the collective assumptions are not representative of any particular region or locality, it is not possible to extrapolate or adjust the results of the emissions estimates to draw conclusions about source apportionment at a specific location.

It is important to note that the tread wear rate assumed by Davis et al. 2001 is implausible because it likely represents the loss of approximately 50% of the entire mass of the tire including sidewall and tread. Assuming a nominal tire service life of 75,000 km, the Davis et al. 2001 rate of 0.05 g/km/tire would equate to a loss of 0.05 g/km/tire x 75,000 km x 0.001 kg/g = 3.75 kg/tire. In comparison, a modern passenger tire has a mass of only 7.5 kg on average (ETRMA 2009; Blok 2005). Therefore, the emission rate used by Davis et al. 2001 represents a loss of approximately 50% (3.75 kg wear/7.5 kg total tire) of the mass of the entire tire, which would include the entire mass of tread and part of the sidewall. Mass balance calculations have shown that approximately 11.5% of the total 7.5 kg mass of tire is released to the environment as a particulate, or about 0.9 kg (ETRMA, 2009; Blok, 2005). The emission rate for tires used in the Davis et al. 2001 study represents a historical situation where tire mass was 10 kg or greater, and wear rates were higher than in modern tires. As such, considering just emission rate, the importance of tires as a source of Zn to the environment was likely overstated by at least a factor of approximately four.

Table 4.2: Assumptions and Uncertainties of Emission Calculations

Source	Assumptions	Uncertainties
Building roofing	• Building density* • Surface area of roofing per building* • Amount of yearly rainfall*	• Building density not justified • Surface area of roofing not justified • Distribution of roofing materials for each land use unknown • Amount of rainfall is not applicable to other climates • First-flush principles unaccounted
Building siding	• Building density* • Surface area of siding per building* • Rainfall events[1]	• Building density not justified • Surface area of siding not justified • Distribution of siding materials not representative of regional scale • Amount of rainfall is not applicable to other climates • First-flush principles unaccounted
Tire wear	• Housing density* • Vehicles per house* • km travelled per vehicle* • Tire wear rate per km*	• Traffic density not justified • Tire wear rate not justified and likely a significant overestimation, if not physically impossible
Brake wear	• Housing density* • Vehicles per house* • km travelled per vehicle* • Dust release rate per km[2]	• Traffic density not justified • Brake wear rate applied as a comparison to literature values of Cu wear
Engine oil	• Housing density* • Vehicles per house* • km travelled per vehicle* • Oil release rate per km*	• Traffic density not justified • Oil release rate is not based on a mass balance approach
Wet deposition and dry deposition	• Flux is constant and homogeneous under all scenarios* • Other sources must not be contributors to deposition to avoid double-counting*	• Deposition fluxes are dependent on the characteristics of the area surrounding the watershed • Important factors ignored in the assumption of constant and homogenous flux includes variations in industrial and commercial emissions, nearby fires (of natural and anthropogenic origin), surrounding land uses, local water bodies, and climate

*Arbitrary value assigned to variable and/or no citation or justification provided for assumption.

[1] Assumed 60 rainfall events per year (Urbonas 1999).

[2] Assumed 1.5 mg/km-vehicle dust release and 5% of dust particles are Cu (Malmqvist 1983; Hewitt and Rashed 1990); correlated measured values of other metals to Cu and standardized each to this Cu release.

4.4 Source Contributions

The authors used the emission assumptions described above for “demonstration purposes” to estimate loadings for each metal, including Zn. As noted above, many of the assumptions were arbitrary or not justified with respect to an actual exposure scenario. The authors acknowledge that the densities assumed could be refined, however, it is unclear that a more reliable estimate of loading would be obtained given that standard methods were not used for the extraction studies, and the materials tested are not well characterized.

Source contributions were presented for a hypothetical urban residential community with 5 homes per hectare (2 units/acre, or 1295 units/square mile). The source contribution calculation also assumed 2 vehicles per household, brick buildings, and residential roofs of unknown composition. Historical wet and dry deposition rates for the Chesapeake Bay region was assumed. Based on these assumptions and the previous compounded uncertainties, the sources of zinc identified were allocated to siding and roofs (66%), tire wear (25%), brake wear (3%), atmospheric deposition (5%) and oil (1%). It is important to note that any of these contributions could misrepresent actual source contributions by a factor of 10 or more in consideration of the methodology that was used. Therefore, the primary conclusion of this calculation is that each these sources have the potential to contribute measurable Zn to the watersheds. The magnitude of the contribution at a specific region or locality is not determinable from this study.

4.5 Sensitivity Analysis

Davis et al. 2001 completed a limited local sensitivity analysis, and concluded that the “source results are not particularly sensitive to the assumptions” and that “the same basic conclusions” are appropriate “for other, somewhat different watersheds” (p. 1007). The purpose of a sensitivity analysis is to determine the impact of uncertainty in model input assumptions on the estimated quantities, such as the mass loadings and source contributions presented by Davis et al. 2001. Sensitivity analyses may consider local sensitivity, where small changes in input assumptions are evaluated, or global sensitivity where the overall importance of uncertainty in each parameter is ranked and quantified (U.S. EPA 2001).

The Davis et al. 2001 sensitivity analysis provides an indication that the results are not exceptionally sensitive to small changes in inputs, which was not unexpected given the general use of linear relationships used in the model. However, the sensitivity analysis does not address global uncertainty in the input parameters. For example, the minimum and maximum annual wet and dry metal deposition rates in the continental United States were not considered in the sensitivity analysis. As such, it is impossible to determine whether misspecification of the atmospheric deposition rates is relatively important or unimportant to the accuracy of the source contribution calculations.

Davis et al. 2001 considered three assumptions in the local sensitivity analysis (see Table 4.3), but failed to consider many of the other assumptions needed for the calculation (see Table 4.4). For each of the three adjusted variables, no justification is given for the original value, the adjusted value, or the expected variation in the assumption within a watershed or between watersheds. Thus, it can be concluded that the sensitivity analysis failed to clarify the most sensitive input assumptions which would be priorities for refinement.

Table 4.3: Assumptions Adjusted in the Sensitivity Analysis

Assumption	Adjustment	Uncertainty and/or Variability
Housing/building density	Doubled building density from 5 buildings/houses per ha to 10 buildings/houses per ha	No justification is provided for the original value, the adjusted value, or the expected variation within a watershed or between watersheds. This adjustment also impacts auto density, which was not considered.
Auto density	Doubled vehicle traffic from 240,000 km/ha-year to 480,000 km/ha-yea	Traffic density is not compared to literature and does not capture the expected variation within a watershed, between watersheds, or under varying land uses.
Atmospheric deposition	Dry deposition doubled from 0.020 kg/ha-yea to 0.040 kg/ha-yea Wet deposition doubled from 0.013 kg/ha-yea to 0.026 kg/ha-yea	Atmospheric deposition is highly variable between watersheds based on a variety of factors. For example, Sabin et al. 2005 determined the dry deposition in LA County to be 0.13 kg/ha-year; five-fold higher than the baseline dry deposition value used in the sensitivity analysis.

Table 4.4: Assumptions Not Considered in the Sensitivity Analysis

Assumption	Variable or Uncertain Parameter	Included in Sensitivity Analysis	Uncertainty and/or Variability
Tire wear rate	Yes	No	Assumption used not representative of modern tires (see text). Tire wear rate depends on vehicle type, traffic type, and road types.
Brake wear rate	Yes	No	Brake wear composition was correlated to data from a limited study. Brake wear rate depends on the vehicle type, traffic type, and brake type.
Oil leakage rate	Yes	No	Oil leakage rate depends on the vehicle type and traffic type.
Building siding surface area	Yes	No	No justification is provided for the baseline value. Siding surface area is dependent on the size of the building. This value is not adjusted to account for larger buildings, e.g. apartment buildings.
Building siding material distribution	Yes	No	Davis et al. 2001 reported that Zn from building siding washes ranged from 24 to 23,000 µg/m^2 depending on the material.
Building roofing surface area	Yes	No	In highly dense urban area, roofing may cover a large percentage of area. Under the highest density scenario investigated (10 buildings/ha with 100 m^2/building), only 10% of the area is exposed to roofing.
Building roofing material distribution	Yes	No	Davis et al. 2001 noted that runoff from galvanized metal roofing had a Zn concentration 7 times higher than the value used for the commercial scenario, and 76 times higher than the value used for the residential scenario.
Rainfall events and intensity	Yes	No	Rainfall frequency and amount is highly dependent on climate and impacts building runoff and first-flush concentrations.

The shortcomings in the sensitivity analysis are readily illustrated by adjusting two critical parameters assumed in the baseline Davis et al. scenario, including dry deposition rate and the tire wear rate. First, the dry deposition rate can be increased from 0.02 kg/hr-year to 0.13 kg/hr-year to represent a heavily urbanized area such as Los Angeles County (Sabin et al. 2005). Second, the rate of tire wear can be reduced by 4-fold to reflect the current passenger tire characteristics (see Section 4.2). Based on Figure 4.1, it can be concluded that the sensitivity analysis performed was consistent with the exploratory nature of the study, but was insufficient to conclude that the results of the study provide a reliable characterization of watersheds in Maryland or elsewhere.

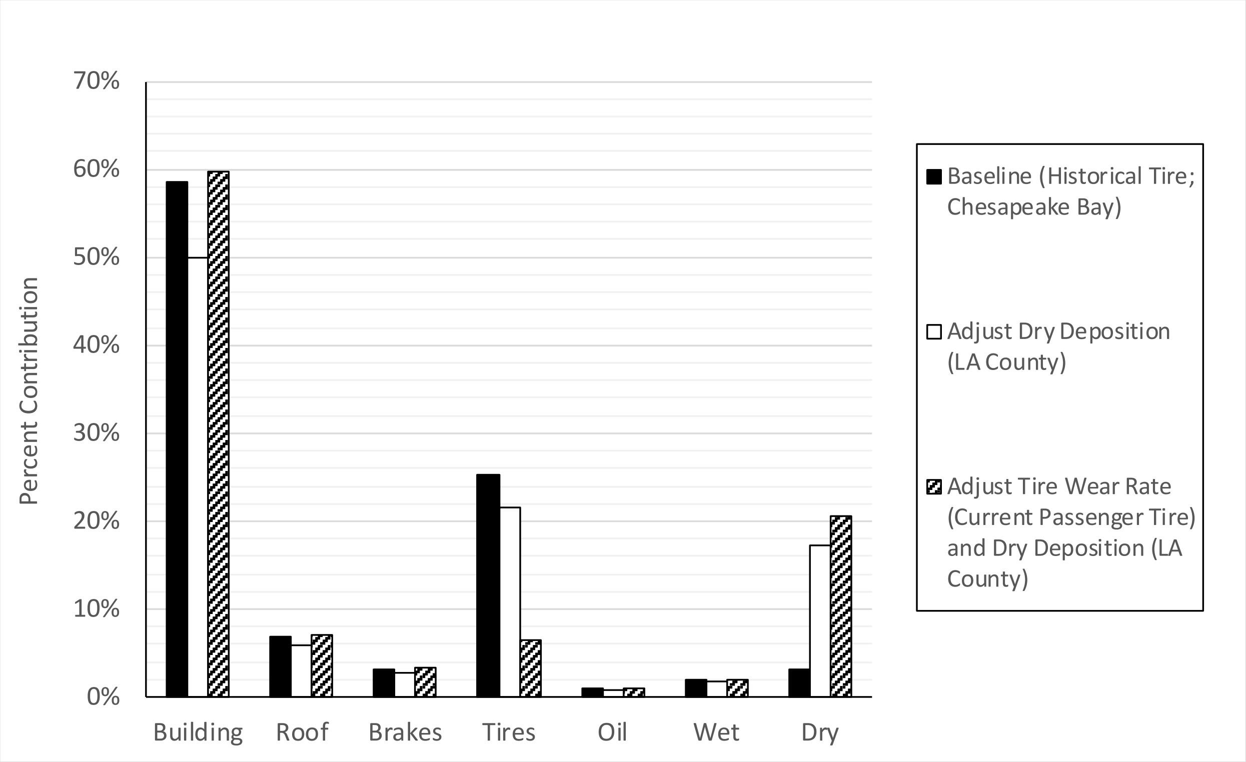

Figure 4.1: Example illustrating impact of adjusting two critical parameters on conclusions about source contribution (see text for basis of adjustments). Arbitrary adjustment of dry deposition rate was considered in Davis et al. 2001 sensitivity analysis, and tire wear rate was not considered. This example demonstrates the importance of considering non-arbitrary adjustments to input parameters.

4.6 Alternative Land Use Scenarios

Davis et al. 2001 also presented source contributions for two alternate land uses. In the first scenario, the “dominant building type” was changed from brick to vinyl. For these analyses, 100% of the building siding was assumed to be constructed of the respective materials. Since Zn levels from vinyl siding were two orders of magnitude lower than brick, the contribution from building siding dropped from 58% to only 4%. However, Davis et al. 2001 did not evaluate land uses with buildings of mixed materials or with buildings of other types of building siding that had Zn levels as high as or higher than brick, e.g. painted wood, concrete, or metal. In a second commercial land use scenario, the building density was doubled to 10 buildings per ha and commercial roof runoff concentrations were used. Since the sampling of commercial roofing runoff resulted in significantly higher Zn levels (ten times higher than residential), the contribution from roofing increased from 7% in the high density residential scenario to 45% in the commercial land use (buildings accounted for 80% of the total Zn load in the commercial land use scenario). These alternative scenarios emphasize the rudimentary and incomplete nature of the scenarios evaluated by Davis et al. 2001. For example, these alternative scenarios did not account for changes in building siding materials, the surface area of building siding, or the vehicle traffic for the commercial land use scenario from the residential assumptions. The alternative scenarios also emphasize the wide range of potential source contributions that can be calculated from the data set. For example, in a scenario with all galvanized metal roofing materials, 85% of the total Zn load would be attributed to building roofing materials, or twelve times the Zn load of the residential scenario[10]. Similar to other aspects of the study, the limited sensitivity analysis and simple alternative land use scenario analysis emphases the exploratory and preliminary nature of the study.

4.7 Applications of the Davis et al. Study

The Davis et al. 2001 study establishes that the source apportionment of Zn in urban storm water runoff is complex and can be highly variable in differing environments based on land uses, building densities, building materials, and traffic densities. The study is considered to be exploratory, and Davis et al. 2001 noted in the Summary and conclusions that "[t]his work was designed as an introductory study to estimate metal loadings. Improved information on the metal release and distributions from the specific sources with focused subsequent research, along with detailed characterization of drainage areas will allow refinements in the predictions" (p. 1009). The main conclusion of Davis et al. 2001 that building runoff and automobile wear can result in appreciable metal load in urban areas has been widely cited.

Given the preliminary nature of the Davis et al. 2001 methodology, most investigators have referred in general to the Davis et al. 2001 study to provide background for their study (Yoon & Stein 2008; Tiefenthaler et al. 2008; Kszos et al. 2004; Birch & Rochford 2010). In some cases, the limitations have not been fully acknowledged. For example, Birch and Rochford 2010 indicated that Davis et al. 2001 showed that "tyre wear is a significant source of Zn in catchments", which fails to adequately acknowledge that methodology and assumptions used were not sufficiently robust to make conclusions about significant or insignificant contributions. The identity of significant sources likely varies by population density, land use, region, construction materials, and consumer product preferences.

The steps employed by Davis et al. 2001 to calculate loading estimates from a series of non-standardized extraction tests does not appear to have been repeated by other investigators. However, at least one study considered the measured water concentrations as part of a pooled estimate of expected concentrations for use in a model comparison. Park et al. 2009 pooled the Davis et al. 2001 measured Zn and other metal water concentrations with other data from other studies to develop an estimate of event mean concentration (EMC). The EMCs from literature were compared to the results of multiple urban stormwater loading models for the Upper Ballona Creek Watershed in Los Angeles, CA. Park et al. 2009 noted that "careful review of the estimates for the same land use and pollutants show variability which suggests the need for site-specific calibration and comparison, as performed in this study" (p. 2775). The Davis et al. 2001 loading estimate methodology was not one of the models considered by Park et al. 2009, as it is not sufficiently detailed for a watershed-scale analysis. In general, the references to the Davis et al. 2001 study in the literature reflect the preliminary and exploratory nature of the work. In summary, there are no indications in the peer-reviewed literature that suggest that the Davis et al. 2001 source contributions are considered definitive estimates of the true source contributions.

4.8 Conclusions Regarding Davis et al. 2001

Davis et al. 2001 conducted an exploratory study that indicates that building runoff and automobile non-exhaust emissions should be considered as important potential non-point source contributions to urban runoff. However, the study does not quantitatively apportion Zn loads to specific non-point sources, such as tire wear, over mixed use or large areas. Source contributions vary due to a number of factors that were not considered in the Davis et al. 2001 study. Therefore, the estimated source contributions presented in the study should be considered illustrative, and should not be used to draw conclusions about important or significant sources of Zn locally, regionally, or nationally. As discussed elsewhere in this report, there are several reliable mass-balance based approaches which can be used over different scales of concern (e.g. stream, river, lake, watershed) to better understand Zn source contribution.

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[10] The total Zn load for the residential scenario is 0.646 kg/ha-yr. The contribution of roofing is 0.045 kg/ha-yr; excluding roofing, the total Zn load is 0.601 kg/ha-yr. If the roofing runoff concentration is changed from residential (100 µg/L) to the galvanized metal roof sample mentioned (7600 µg/L), then the roof loading becomes 3.42 kg/ha-yr. The total loading for this scenario is therefore 4.021 kg/ha-yr. The contribution of roofing is 3.42/4.021, or 85%.

5 Los Angeles County

5.1 Overview

In order to understand the major and minor sources of Zn in a specific watershed, it is critical to accurately characterize specific sources, land use, and drainage characteristics. Some sources of Zn such as reported industrial releases are easily tabulated from available sources, or are readily measured such as the mass loading from treated municipal or industrial wastewater. However, most sources require significant work to reliably estimate, including in particular, the contribution of galvanized metal corrosion, littered consumer products, and tire wear. It is necessary for this research to be conducted for each individual watershed or region in order to dependably apportion Zn loads to specific sources.

5.2 California Stormwater Quality Association

The California Stormwater Quality Association (CASQA) is a non-profit professional member association with representatives from cities, counties, industries and consulting firms. The CASQA and the LA River Metals TDML Steering/Technical Committee funded a literature review completed by TDC Environmental (2015) of the sources of Zn in Californian Urban Runoff. The review concluded that:

> Outdoor zinc surfaces and tire wear are the major sources of Zn;
> Some watersheds contain other local major sources of Zn; and
> A number of minor sources do not contribute significantly to Zn load.

In addition, several recommendations were presented, including:

> Development of watershed-specific emission inventories using local information;
> Integrate source control into Zn load reduction programs;
> Use source control at industrial facilities;
> Develop a “source-control menu” for municipalities;
> Research a petition for evaluating Zn in tires under the Safe Consumer Products (SCP) process;
> Consider water quality in the waste tire market programs of CalRecycle;
> Petition for inclusion of water quality in U.S. EPA registration of Zn biocides in paint;
> Measure runoff from rubberized asphalt;
> Characterize Zn-containing paints in the marketplace;
> Characterize Zn in tread and develop wear-rate estimates by class; and
> Develop California-specific emissions factors for outdoor Zn surfaces.

The report included “order-of-magnitude” estimates of Zn release in LA Country for galvanized metals, tire wear and brake wear as shown in Table 5.1. TDC Environmental characterizes these estimates as “illustrative” and in fact, a number of refinements to these estimates are required to yield reliable loading values. In addition, quantitative estimates have not been provided for a number of potentially significant sources, such as littered batteries and discharge from treated municipal and industrial waste.

The authors concluded that tires and outdoor zinc surfaces were “major” sources of zinc in all Californian urban areas. In addition, several other sources were characterized as potentially major sources in local areas, including zinc-containing paint, recycled rubber, anti-corrosion additives in water, fireworks, dumping/littering, forest fires, motor oils, industrial runoff, soils, fertilizer, and zinc granule impregnated asphalt roofing. Finally a number of minor sources were identified including brake pads, wheel weights, cosmetics, sacrificial anodes, waterproofing agents, waxes, vehicle exhaust, batteries, zinc-preserved wood, swimming pool biocides, rodenticides, and non-zinc roofing.

It is important to note that identifying sources as major or minor in the absence of a complete emission inventory may lead to incorrect conclusions about the efficacy of source control options. For example, as noted previously in this report, in some areas, littered batteries crushed on road surfaces may represent the most significant source of Zn to runoff in some local areas. The contribution from Zn biocides in exterior paint was not estimated. Furthermore, in large urban areas, it is important to take into account the cumulative effect of small surfaces. For example, the estimate in Table 5.1 neglects rooftop heating, ventilation and cooling units, which likely represent a meaningful and important surface area in warm climates. This equipment, assumed to be of negligible importance, may, in fact, be of equal or greater importance than tire wear.

The effluent from water treatment plants is notably not quantified this report, despite having been shown to be of high importance in other assessments and inventories. Wastewater effluent was excluded because it is not an “ordinary part of urban runoff.” While it is acknowledged that the scope of the report was limited to urban runoff rather than total loading to surface water, it is important to note that wastewater treatment effluent is likely a major source of loading of Zn to surface water in LA County. Accounting for the wastewater treatment loads is important when evaluating the efficacy of potential mitigation measures on overall loads to surface water.

In general, the recommendations in the TDC Environmental report emphasize the importance of watershed-specific inventories, and note that there are important information gaps, such as the use of Zn as a biocide in paint. The recommendations suggest that California-specific emission factors for Zn-containing surfaces are necessary for a reliable estimate of the contribution from these sources. As noted in Section 1, 85% of Zn is used in galvanizing applications, with most applications likely representing protection from exterior corrosion. Given the long service life and ongoing dissolution of Zn as part of the intended function of corrosion protection, it is unclear whether tire wear represents a major or minor source in LA County. Based on usage rate, and greater likelihood of particulate Zn being contained with the roadway “technosphere” as compared to Zn solubilized from galvanized and other Zn-containing exterior surfaces, it seems unlikely that a comprehensive emission inventory would allow one to reach a conclusion that tire wear and galvanized metals were of equal importance to runoff. As such, the recommendation to consider Zn in tires under the SCP legislation appears to be premature. Furthermore, until a complete inventory is completed, the importance of potentially major sources is unclear. For example, the TDC Environmental report identifies dumping of alkaline batteries as both a potential major source, and a minor source because dumping is “assumed to be relatively uncommon.” As discussed in Section 3.2, investigators in one urban area have concluded that battery littering is more common than previously thought (Krouse et al., 2009).

Table 5.1: Overview of Quantitative Estimates of Zn to Runoff in the TDC Environmental Report

Source	**Zinc Load (tons/year)**	**Reliability**	**Necessary Refinements**
Zinc surfaces including roofs, fencing, guard rail, large posts, and other surfaces	40 to 100	Low: Calculations were "illustrative". Roof parameter estimates were from San Francisco Bay and San Diego; incomplete inventory	Test panel runoff data of new and aged materials; exterior area of Zn surfaces in LA Country; sales data
Tire wear from cars and trucks	230	Low: Vehicles were classified as only passenger or truck; wear rates appear to be overestimated (see section 3.3); washoff rate was not specific to land use or watershed	Wear rate and mileage estimates by specific vehicle classification and driving characteristics; verification of release rates using sales data.
Brake wear	12	Low: Vehicles were classified as only passenger or truck; washoff rate was not specific to land use or watershed	Wear rate and mileage estimates by specific vehicle classification and driving characteristics; verification of release rates using sales data.

The USTMA has recently calculated tire wear using the sales approach and concluded that an average wear rate for passenger cars was 74 mg/vkm and 892 mg/vkm for truck tires. These wear rates are similar to that calculated by the Netherlands in the PRTR and by the ETRMA based on Blok et al.(2005). Ultimately, use of an incorrect wear rate leads to more than double the amount of Zn predicted to be released into the environment from tire wear (Appendix A).

5.3 Literature Specific to LA County

Due to the size, regional importance, and unique climate of Los Angeles, a relatively large amount of research has been conducted in the region. Further, the California Toxics Inventory has regional data for the South Coast Air Basin, which includes most of LA County, San Bernardino County, and Riverside County, and all of Orange County (the northeastern portion of LA County is in the Mojave Desert Air Basin). The available information is useful in understanding the local environment and potential sources of Zn in LA County, but is not sufficiently comprehensive to apportion all sources of Zn.

The Southern California Coastal Water Research Project (SCCWRP) has been conducting research in the Los Angeles County region since 1969 (Southern California Coastal Water Research Program). Their research involves stormwater, atmospheric deposition, and heavy metal investigations. For example, Sabin et al. 2005 conducted sampling in San Fernando County to determine the wet and dry deposition fluxes of the local area. The annual wet deposition flux was determined to be 0.015 kg/ha-yr. Dry deposition was calculated to have an annual flux of 0.13 kg/ha-year. Dry deposition was later shown to vary by location in the Los Angeles basin (range 0.069 – 0.230 kg/ha-year) and by the number of antecedent dry days (0.050 and 0.150 kg/ha-year for less than and greater than 5 antecedent dry days, respectively) (Sabin et al. 2006). Further, the total deposition was estimated to contribute 57% of the Zn in the local stormwater (Sabin et al. 2005). Sabin et al. 2005 noted that "the finding that atmospheric deposition and stormwater loadings were on the same order of magnitude is in agreement with previous studies in this region, and further demonstrates atmospheric deposition should not be ignored when assessing sources of trace metal pollution to contaminated water bodies near urban centers". It is important to note that while atmospheric deposition is a potentially important source, it is often difficult to apportion deposition to the primary natural or anthropogenic source without sophisticated modeling or isotope analyses.

Stein et al. (2012) investigated the impact of wildfires on stormwater contaminant loadings. The authors determined that wildfires may greatly impact stormwater quality, stating that “postfire runoff is a significant source of contaminants to downstream areas and is worthy of management attention”. Further, the authors noted that aerial deposition has the potential to impact catchments outside the burned area’s watershed. The authors stated that the wind patterns may carry ash directly over the Ballona Creek watershed and that the peak Zn concentration in the Ballona Creek stormwater of the first storm following the events was triple those seen in typical stormflow in the watershed.

SCCWRP research has also examined the water quality of rivers and receiving bodies in Los Angeles County. The Los Angeles River and its watershed stretches from the San Fernando Valley through Los Angeles and drains into San Pedro Bay. The LA River receives input from the municipal storm drainage system, as well as from three water reclamation plants and numerous industrial facilities, which may discharge emissions and surface runoff during storm events. Despite Zn concentrations being similar between the water reclamation plant effluents and the storm drains, 0.04 mg/L and 0.01 mg/L, respectively, nearly 80% of the daily Zn load was contributed by the water treatment plants because of the significantly larger flow in their effluent. Further, a value of zero was chosen in cases of non-detect for heavy metals in the plant effluents rather than an estimate based on the limit of detection or expected distribution of the metal. Accounting for Zn present below the detection limit would increase the load from plant effluents (Ackerman et al., 2003).

Researchers at SCCWRP have also investigated metal loading in urban storm water based on land use (Tiefenthaler et al. 2008). Although the model is unable to apportion Zn to individual sources in each land use, the results can be used to target the land use type of most importance to a specific watershed. For example, runoff from industrial land uses had the greatest mean concentration (in mg/L) and the greatest flux (in g/km^2). Commercial land uses had the next highest concentration, but had a flux lower than agricultural, recreational, open-space, and high-density residential land uses. The authors stated that ANOVA indicated that both industrial and recreational sites were significantly different than open-space sites, but that all other land uses were indistinguishable.

Other literature has been applied to LA County and its watersheds. For example, Park et al. 2009 investigated six different models and their application to the Ballona Creek watershed. The authors noted that “careful review of the estimates for the same land use and pollutants shows variability which suggest the need for site-specific calibration and comparison” and added that “[event mean concentrations (EMCs) that fit Los Angeles data well can be different than EMCs reported in other areas, which suggest that climate, geography and cultural differences will require site-specific calibration [of models]”.

The California Toxics Inventory is a combination of the industrial emissions reported to the U.S. Toxics Release Inventory and estimated releases of Zn to the atmosphere from non-point sources. The inventory only considers emissions to the air, i.e. emission sources such as galvanized metals are not considered because they release directly to surface water runoff (see Section 2.2 for more information). The inventory is characterized by individual air basins. LA County includes both the South Coast Air Basin and the Mojave Desert Air Basin. In the South Coast region, sources designated as “areawide” comprised 53% of emissions to the air in 2010. Areawide sources include farming operations, construction and demolition, and fugitive windblown dust. 16% of the emissions reported in the inventory for 2010 were sourced to “natural” sources; the only natural source investigated that emits particulate matter is wildfires.

5.4 Local Watershed Management Programs

Several watersheds in LA County have initiated enhanced watershed management programs (EWMPs) to improve water quality and reduce Zn levels to meet their respective total maximum daily loads (TMDLs). Nearly every watershed plans to improve storm runoff by implementing “green streets” throughout the watershed that will decrease the impervious surfaces in the watershed and allow for better water filtration. Some programs have indicated plans to install subsurface infiltration and improved storage and holding systems. Table 5.1 summarizes the plans for each watershed.

Table 5.1: Enhanced Watershed Management Programs for Major LA County Watersheds

Watershed	**Priority Pollutants**[1]	**Strategies for Water Quality Improvement**	**Comments on Zn Sources**
Upper Los Angeles River	Bacteria, Toxics, Zn	Green streets; Rainfall retention/storage programs; Significant regional projects	Compared land-use based modeled Zn load results to SCCWRP and LA County stormwater measurements; diffuse source apportionment not attempted
Ballona Creek	Bacteria, Toxics, Zn	Green streets; Rainfall retention/storage programs; Significant regional projects; Improved street cleaning	“Targeted Zn Reduction Program” being formalized to understand diffuse sources of Zn; “Nationwide, watershed management plans identify vehicle brake pads, tire tread, roadway sediment, used motor oil, and building materials as significant sources of metals in urbanized watersheds (uncited)”.
Marina Del Rey	Bacteria, Toxics, Metals	Green streets; Subsurface infiltration and stormwater holding; Improved street cleaning	Stated priority sources of Zn: commercial contributions, stormwater runoff; “Certain building materials can contribute loads” of Zn through urban runoff; Seeking to reduce sources of Zn, including “replacing galvanized metal products” and “the reduction of Zn in tires”.
Dominguez Channel	Bacteria, Toxics, Lead	Green streets; Subsurface storage projects	N/A
Santa Monica Bay	Bacteria	Green streets; Subsurface infiltration projects	N/A

[1] Los Angeles County Department of Public Works Enhanced Watershed Management Programs Impact Report 2015

None of the watershed plans attempt to determine the sources of Zn in the runoff. Despite not having an understanding of the impact of specific source mitigation, several watershed plans comment that measures patterned after SB 346 (the reduction of copper in brake pads in California) may be implemented in order to support the financial burdens of the management programs; some plans mention a reduction of Zn in tires or a fee assessment. However, lacking a complete Zn source inventory, none of the watershed plans have suggested – or are able to suggest – that even a complete removal of Zn from tires would noticeably improve their water quality.

5.5 Recommendations for LA County

There are many sources of Zn to LA County waterways and more research must be conducted in order to fully characterize the source contributions to individual watersheds in LA County. Potential sources identified in the literature and other national and regional inventories include the corrosion of galvanized and other exterior exposed Zn-containing metals, littered batteries, tire wear industrial and domestic wastewater discharge, and wildfires. Since the primary use of Zn appears to be in galvanized metal applications, a priority should be the determination of the fraction of runoff load than can be explained by this source in each watershed. It is possible that the most significant anthropogenic source with the potential for reduction or modification by coatings is the use of galvanized metals on roofing, gutters, road barriers, fences, and piping. Additionally, roadside and parking lot battery disposal should be inventoried. The potential contribution of consumer products and building materials should be quantified using sales data. For mobile sources including tires and brakes, the fraction of Zn released beyond the “technosphere” of the roadway system should be taken into account. In summary, mass-balance of Zn in LA County must be conducted before any impact of source reduction can be quantified. Several methods for conducting inventories have been discussed in this report (see Sections 2 and 3). In LA County, population surveys combined with GIS should give reliable estimates of source emissions to stormwater. Additionally, as described by Chen et al., 2008, Zn isotope profiles for various sources could be developed and used as a marker for specific anthropogenic sources of Zn.

6 Reduction of Zn in Tires

6.1 Published Information

No publically available information regarding tire industry sponsored evaluations of zinc usage has been identified. One research thesis entitled “Reduced zinc oxide levels in sulfur vulcanization of rubber compounds; mechanistic aspects of the role of activators and multifunctional additives” prepared by G. Heideman (2004) was identified. This research included a comprehensive review of the use of ZnO as an activator in rubber vulcanization and an evaluation of options for reducing ZnO through use of other zinc complexes as well zinc-free systems. The conclusions of the research were:

- Zinc-m-glycerolate in particular was a good substitute for ZnO as an activator for sulfur vulcanization, in EPDM as well as s-SBR rubber, without detrimental effects on the cure and physical properties. The properties after ageing suggest that the addition of zinc-m-glycerolate in EPDM compounds leads to a considerable improvement of the thermal stability. Furthermore, the results in s-SBR indicate that depending on the intended applications, zinc-2-ethylhexanoate and zinc stearate might represent substitutes for the commonly used activator ZnO, although zinc stearate is considerably less effective than ZnO *per se*. Overall, it is anticipated that a significant reduction of zinc content can be achieved by optimization of the zinc complex levels.
- It was observed that other metal oxides including CdO, PbO, BaO, CaO, MgO, and BeO are not proper substitutes for ZnO as activator in thiuram-accelerated vulcanization of EPDM, nor do they show a synergistic effect with ZnO. In s-SBR compounds, however, it is demonstrated that CaO and MgO can function as activator of cure for sulfur vulcanization, retaining the curing and physical properties of the rubber vulcanizates.
- MultiFunctional Additives (MFA), amines complexed with fatty acids, for sulfur vulcanization of rubbers were developed to function both as an activator and accelerator for sulfur vulcanization. Good physical properties can be obtained in s-SBR compounds using the MFA/S cure system, albeit at the cost of a shortened scorch time as compared to a regular ZnO/stearic acid system. Inclusion of ZnO lengthens the scorch time, though it reduces the state of cure and ultimate properties. The introduction of metal oxides other than ZnO, *viz.* CaO and MgO, leads to an appreciable improvement in the state of cure. The physical properties are grossly comparable with those obtained with commonly employed vulcanization ingredients. In summary, the results indicate that depending on the intended applications (*e.g.* tyres or roofing foils) there exists a potential to significantly or even completely reduce the need for ZnO.
- A mineral clay, *viz.* Montmorillonite, was used as carrier material and loaded with Zn2+-ions via an ion-exchange process. Application in a wide range of natural and synthetic rubbers was been explored. Results demonstrate that this ZnClay can substitute conventional ZnO, grossly retaining the curing and physical properties of the rubber products but reducing the zinc concentration with a factor 10 to 20. Based on all the results, it can be concluded that systems with Zn2+-ions provided on a support can be regarded as potential substitutes for ZnO commonly used in rubber vulcanization.

Overall, it was found that ZnO and zinc-containing species are considered indispensable for the vulcanization process and difficult to substitute. To date, no published studies have been identified to indicate the possibility or the commercialization of zinc-free vulcanization systems.

7 References

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Appendix A
USTMA Calculation of Tire Wear Rates

Introduction

The TRWP emission rate to the environment for the service life of the tire can be calculated using either a sales approach or a distance travelled approach. The sales approach relies on estimates of the number of tires sold by broad category (e.g. car, van, truck tire) and an estimate of the fraction of the mass lost over the service life of the tire. Assumptions about wear rate (i.e. mg TRWP/km) are not required for the sales approach. The distance traveled approach relies on total distance traveled by broad category of tire and an estimate of the wearing rate of the tire. Past research has shown that similar annual regional TWP emission rates are estimated using either approach (Blok 2005). The current average tire weight loss over the service life of a tire has been estimated to range from 10% to 12% (Camatini et al., 2001, Blok 2005, OECD 2004). Historical estimates of tread wear rates from the 1970s are not reliable because modern radial tires are characterized by a lower wear rate than the bias ply tires used in the earlier time period (Veith 1992). The recommended loss fraction, representing a real-world end of life state for a modern tire, is 11.5% for passenger and truck tires (Blok 2005).

Wear Rate Calculation

The USTMA calculated a tire wear rate for passenger cars, light trucks and heavy duty vehicles (truck/busses) based on both the sales and the distance travelled approaches. Table A.1 provides the details of the calculation. The results indicate average wear rates for passenger car, light truck, and truck/bus tires of 74 mg/vkm, 104 mg/vkm and 758 vkm, respectively. The wear rates calculated indicate 11.5%, 12% and 13% average tire weight loss from tread wear for passenger car, light truck and truck/bus tires, respectively. These values are consistent with the recommended European loss fraction of 11.5%.

U.S. WEAR RATE CALCULATION

FACTOR	Tire Type			Notes
	Passenger Car	Light Truck	Truck/Bus	
AVERAGE WEIGHT OF TIRE (LBS)	26.33	48.18	117.19	USTMA member assumption
TREAD WEIGHT (LBS)	8.59	15.83	29.64	USTMA member assumption
TREAD DEPTH (IN)	9.5	14.5	18	USTMA member assumption
UNDER TREAD (IN)	2	2	3	USTMA member assumption
TOTAL TREAD (IN)	11.5	16.5	21	USTMA member assumption
WEAR TO DEPTH (4/32 FOR PASSENGER CARS AND LIGHT TRUCKS; 6/32 FOR TRUCK-BUS) (IN)	5.5	10.5	12	USTMA assumption not reflective of removal depth recommendation
PERCENT TREAD WORN (%)	48%	64%	57%	Percent worn = Wear to Depth / Total Depth
POTENTIAL WORN TREAD WEIGHT (LBS)	4.11	10.07	16.94	Worn tread = % tread worn * tread weight
TREAD GROOVE VOID FACTOR (%)	25%	35%	15%	USTMA member assumption
TOTAL WORN TREAD WEIGHT (LBS)	3.08	6.55	14.39	Total Tread Worn = (1-Groove factor void)*Potential Worn Tread Weight
NUMBER OF TIRES SHIPPED	254,800,000	36,300,000	49,000,000	USTMA member assumption
DISTANCE TRAVELED (MILES)	2,191,764,000,000	657,954,000,000	304,245,000,000	Federal Highway
WEAR RATE (LB/VMT)	0.0004	0.0004	0.0023	Wear Rate = Total Tread Worn * Number of tires shipped / Distance traveled
WEAR RATE (G/KM)	0.10	0.10	0.66	Wear Rate (g/km) = Wear Rate (lb/vmt) * 454 / 1.6