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November 21, 2009

Metals Background Report
- Sources of Metals in Watersheds -

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1.0 Summary and Conclusions Applied to Santa Susana Field Laboratory

The purpose of this report is to examine likely "background" sources and concentrations of metals in stormwater runoff at The Boeing Company's (Boeing) Santa Susana Field Laboratory (SSFL), located in the Simi Hills near the Los Angeles/Ventura County line, with focus on NPDES stormwater monitoring Outfalls 008 and 009, and to a lesser extent, Outfalls 001 and 002 (using data collected between August 2004 and March 2009). "Background" is defined here as stormwater runoff conditions that would be expected at natural, undisturbed reference watersheds with similar geology, rainfall, sediment yields, and other key characteristics to the SSFL site. Metal concentrations from typical urban runoff are also discussed. The intended use of this information is for comparison with runoff quality at the SSFL as well as with the SSFL NPDES permit limits[1], for submittal to Regional Board NPDES staff for their consideration. An important aspect of likely background metal concentration descriptions is an understanding of the sources of the contaminants of interest. If the sources are natural or uncontrollable, such as uncontaminated soils or atmospheric deposition from regional sources, these should also be recognized.

Stormwater heavy metals have long been investigated as important pollutants discharged to urban receiving waters. The effects of metals on urban water resources and the environment, especially through contaminated stream sediments and effects on the benthos, are summarized by Burton and Pitt (2001) and Burton, *et al.* (2000), amongst others. Appropriate interest is therefore directed towards identifying the sources of these urban heavy metals and their treatability. This paper reviews SSFL stormwater metal characteristics, mostly as reported by the SSFL stormwater outfall monitoring, as well as regional (e.g., published data from the Southern California Coastal Water Research Project [SCCWRP] and Los Angeles County) and nationwide (e.g., the National Stormwater Quality Database [Pitt, *et al*. 2009]) stormwater monitoring data. Heavy metals in stormwater originate from several sources, including natural soil components, rainfall and dry atmospheric deposition from regional activities, and local activities taking place in the land uses in the watershed. ***There is substantial information describing these different sources and activities, but there is much confusion and misunderstanding concerning how the metals from these different sources move through the system and contribute to outfall discharges.*** Some of this supporting information is therefore also presented in appendices to this report.

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[1] The terms "permit limits" and "benchmarks" are used interchangeably throughout this report because the SSFL NPDES permit threshold values are currently benchmarks for some outfalls and effluent limits for others. This report is not intended to be a regulatory guidance or compliance assessment document. It is a technical study that compares these NPDES permit threshold values, along with SSFL stormwater discharge monitoring data, to stormwater quality monitoring results from various nationwide and regional studies, for the purpose of addressing key issues related to the problem of defining "background" levels in stormwater.

The following are the major conclusions from this evaluation of site metal conditions, pertaining to typical background conditions and sources of the heavy metals at the SSFL watersheds draining to Outfalls 008 and 009.

1) Metal concentrations at SSFL Outfalls 008 and 009 compared to other land uses:

- The metals with the most frequent exceedances[2] of the current permit limits at the SSFL 008 and 009 outfalls include lead, mercury, and copper. Antimony, nickel, thallium, and zinc have no measured concentrations above these benchmarks. Cadmium was measured above its benchmark value once in 30 total observations at outfall 009 and at no time in 19 observations at outfall 008. In all cases, except for mercury, the percentage of historic concentrations above current SSFL benchmarks at Outfall 008 and 009 are less than, or the same, as the lowest exceedance percentages shown for any of the NSQD (National Stormwater Quality Database) land uses. Also, the mercury median and average values for the detected site data are less than the median and average concentrations contained in the NSQD for any land use category, including open space.

- Data from a 2007 SCCWRP study showed that the regional wet weather metals concentrations in the creeks studied within natural watersheds were significantly less than the values obtained from the regional developed watersheds. The natural area stormwater metals concentrations were generally one order of magnitude lower compared to the concentrations from the developed areas (with the exception of TSS). The SCCWRP monitoring sites within these natural watersheds were between 700 and 2,300 acres, while SSFL Outfall 1, 2, 8, and 9 watersheds were 603, 914, 62, and 536 acres, respectively. SSFL outfall metal concentrations were comparable to the concentrations measured at these undeveloped watersheds.

- SCCWRP researchers also noted that the California Toxic Rules (CTR) criteria were originally based on dissolved concentrations and that the rule includes a simple conversion procedure to estimate applicable total concentrations. However, the dissolved fraction of the metals monitored by the SCCWRP were seen to vary greatly during the individual storms, making a simple comparison of the total metals concentrations to the criteria difficult. They concluded that estimates of metal toxicity should therefore be based on direct measurements of the dissolved metal concentrations. The SSFL permit uses total metal permit limits, so total metals are monitored and used for compliance determination purposes.

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[2] The term "exceedances" is used throughout this report to describe a statistical condition where measured values "exceed" or are greater than a regulatory threshold (e.g., effluent limits or benchmarks), for the purpose of comparing various datasets relative to one another and relative to current permit thresholds. The reported "exceedance frequencies" do not reflect compliance histories for these outfalls since SSFL permit limit values and enforceable status (e.g., effluent limits vs benchmarks) have changed over the course of the 2004 to 2008 monitoring period.

- During their regional monitoring, SCCWRP researchers also concluded that the geological characteristics of the drainage areas were a significant factor affecting the metal, nutrient, and TSS concentrations: areas underlain by sedimentary rock had higher concentrations of these constituents compared to areas underlain by igneous rock. This likely has a significant effect on the SSFL runoff water quality compared to other natural areas, as the SSFL is comprised of sedimentary rock of the Chatsworth formation -- sandstone and siltstone with alluvial deposits of silty sand and sandy silt. Based on analyses conducted in later sections of this report, natural soils were found to be the likely primary sources of the metals in runoff at SSFL Outfalls 008 and 009, so the geological formation of the site is of great importance.

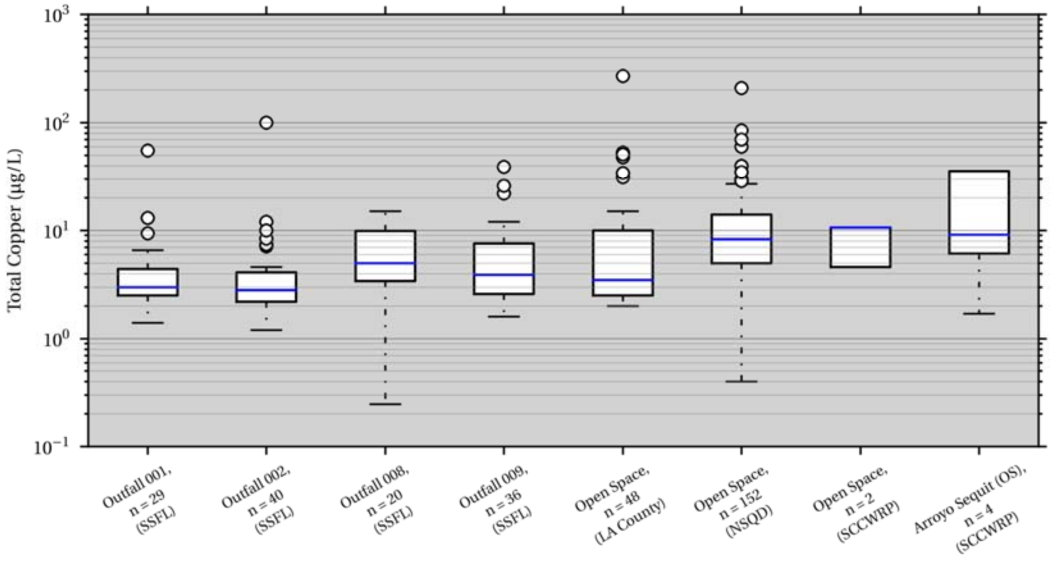
- Overall, the cadmium, copper, lead, and zinc SSFL Outfall 008 and 009 concentrations in stormwater runoff are relatively low compared to published source area data for these metals (the metals with commonly available source area data) and are similar to the concentrations observed in undeveloped areas based on regional and nationwide land use runoff monitoring data, and were even less than urban rain quality. Source area data in undeveloped land uses are summarized later in this report and were obtained by sampling runoff close to points of origin (such as landscaped areas, dirt paths, general undeveloped areas, etc.) and not at the outfalls.

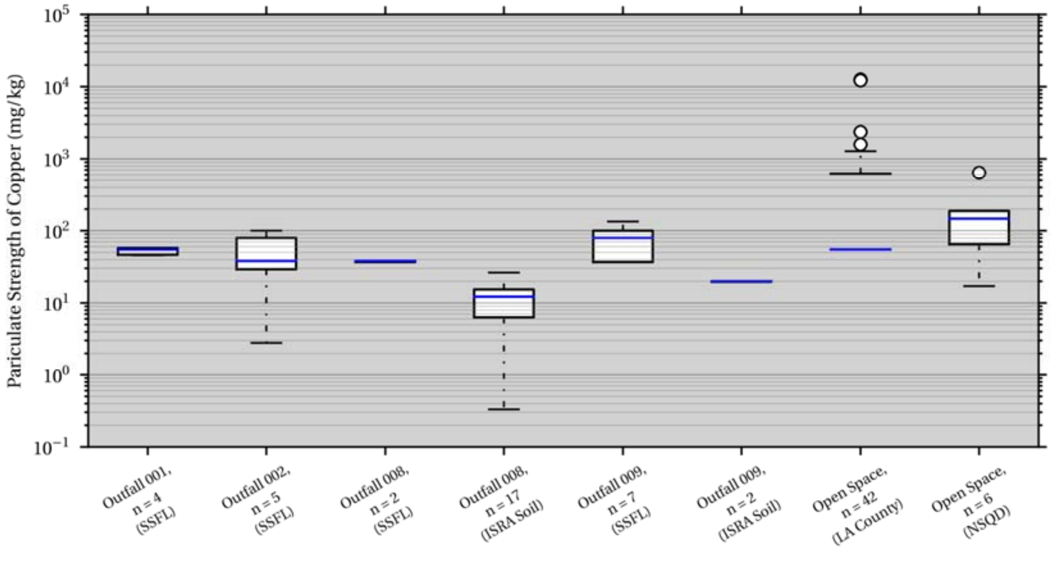
2) Pollutant strengths and sources of SSFL Outfall 008 and 009 heavy metals:

- There is substantial information describing different pollutant sources and related activities, but there is much confusion and misunderstanding concerning how the metals from these different sources move through the system and contribute to outfall discharges.

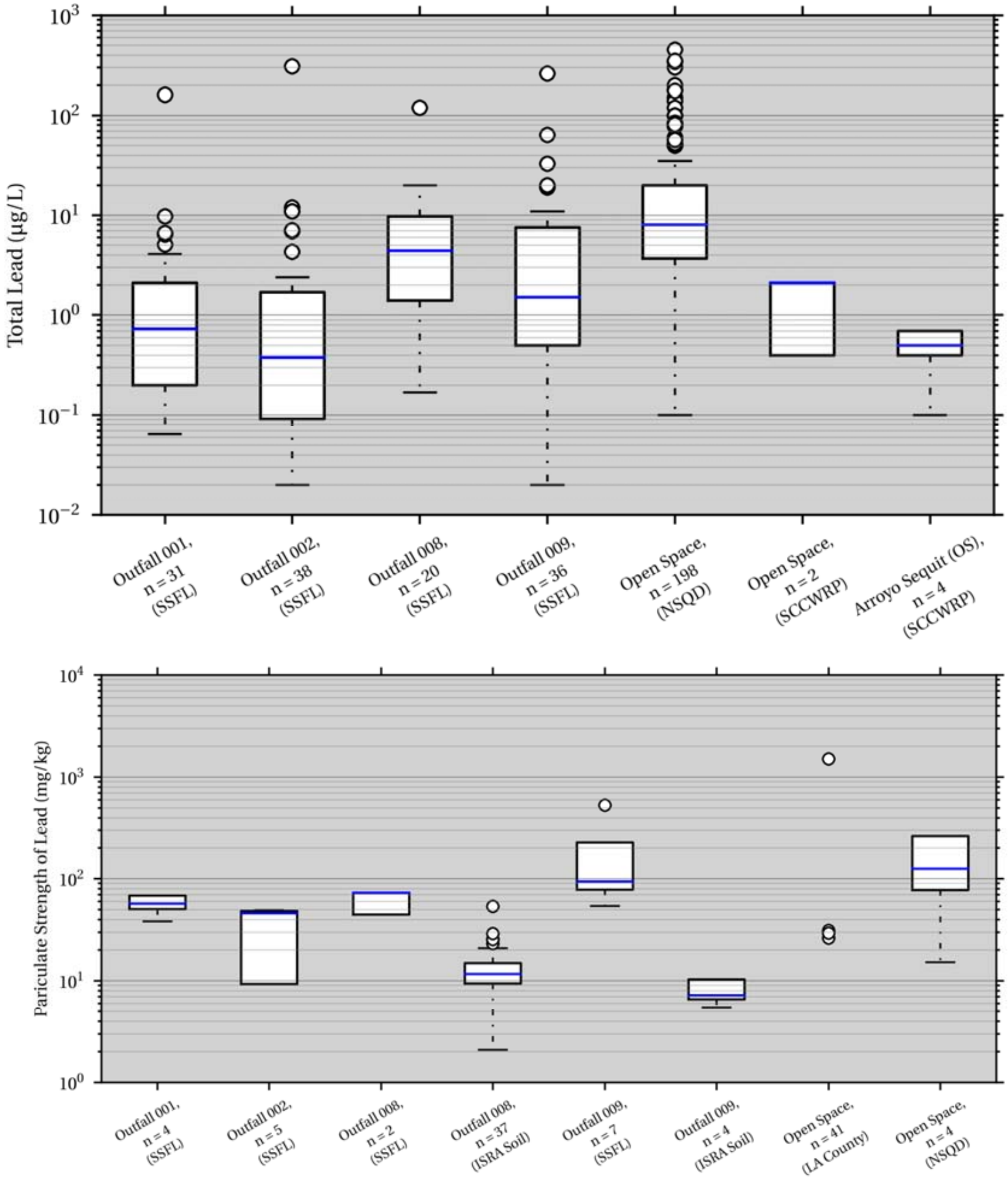
- When preparing their *Soils Background Report* for SSFL, MWH evaluated the spatial and vertical distribution of the metal data from soils collected on and near the SSFL. They found no consistent pattern in observed concentrations and therefore concluded that there was no significant airborne dispersion and deposition of metal contaminants from SSFL operations at these sampling locations nearby and on the SSFL property in areas where no site activity was occurring.

- The SSFL copper particulate strengths (i.e., total metal concentrations minus dissolved metal concentrations divided by total suspended solids, or mass of particulate metal per mass of suspended sediment) calculated from the outfall monitoring data are intermediate compared to the reported values for open space and undeveloped land particulate strength data for soils and other source area particulates and indicate relatively little potential contamination. However, the lead particulate strength data for Outfall 009 is relatively large and indicates potential contamination (which is consistent with known issues that are currently being addressed upstream in the drainage where an ongoing cleanup action is occurring in and near the channel). Zinc particulate strength data from Outfall 009 (and Outfall 002) are also relatively high compared to the other open space/undeveloped data. The high zinc conditions are more in line with observations obtained from residential, commercial, and freeway land uses, and are likely from galvanized metals that are used in buildings and equipment/material storage areas on the site, rather than from areas of soil contamination. However it should be noted that zinc in stormwater has not been observed at concentrations above the SSFL current permit daily maximum benchmarks at Outfalls 001, 002, 008, or 009 (the outfalls studied here) except for one event in September 2007 due to a mudslide immediately upstream of Outfall 002 that resulted in a TSS measurement of 33,000 mg/L. In addition, the SSFL site background soil samples and the more recent ISRA soil samples have particulate strength concentration values amongst the lowest compared to all of the open space and undeveloped land sample data reported. These site soil data are lower than the outfall particulate strength data, likely because they are bulk soil samples and include all of the soil particle sizes, while the outfall sample particulate strengths are more greatly influenced by the smallest particle sizes, usually having the highest pollutant strengths.





Figures ES-1a and ES-1b. Copper: Total Metal Concentrations and Particulate Strength Data for SSFL Outfalls and LA County/Nationwide Open Space Land Use Sites, for comparison (centerlines represent medians, boxes represent interquartile range, and whiskers represent 5th/95th percentile values; missing boxes indicate insufficient data)



Figures ES-2a and ES-2b. Lead: Total Metal Stormwater Concentrations and Particulate Strength Data for SSFL Outfalls and LA County/Nationwide Open Space Land Use Sites, for comparison (centerlines represent medians, boxes represent interquartile range, and whiskers represent 5th/95th percentile values; missing boxes indicate insufficient data)

- Another comparison was made using the site background soil concentrations and multiplying them by the average TSS outfall concentrations to estimate the average outfall total metal concentrations in stormwater under these background conditions. ***The***

resulting lead concentrations are predicted to exceed the SSFL permit limit by about 1.7 times, even with the suspended soils at the background lead concentration. The calculated copper concentrations are about half of the site permit limit, while antimony is about 40% of the permit limit, and mercury and zinc are about 20% of their permit limits. The other metals (cadmium, nickel, and thallium) are about 5 to 10% of their permit limits.

- The observed sediment yields from the site watersheds, based on outfall monitoring and calibrated modeling of runoff quantities, are about 4 tons per year for watershed 008 and 30 tons per year for watershed 009 (Geosyntec, 2009). However, these sediment yields are much smaller than the calculated erosion rates for these watersheds using the Revised Universal Soil Loss Equation (RUSLE). It is likely that less than 1% of the eroded material actually is discharged from the watersheds at the outfalls, with the remaining material being deposited on lower slopes below the steep areas, and in the channels.

- SSFL site slopes can vary significantly, from less than 1% in the main drainage channels to approaching 50% on the steep hillsides. The flow depths can be several feet deep in the main channels during large rains, while they would only be a fraction of an inch on the steep slopes. Therefore, the shear stresses would also vary greatly on the site, possibly being in the order of about 0.1 to 1 lb/ft^2 on the steep slopes and about 1 to 5 lb/ft^2 in the main channels during the larger rains. Therefore, much of the eroded material from the steep slopes will tend to accumulate on the lower slopes and channels during most rains, while periodic very large events are quite capable of moving much of the deposited material.

- The erodible soils at SSFL tend to be characterized by very fine soils that have generally been found to have higher metal concentrations compared to larger particles. These particles preferentially erode, and cause the outfall particle strength metal data to be higher than the bulk soil samples would indicate.

- Although little stormwater monitoring data is available for dissolved (filtered) metals, the data indicates that the vast majority of metal mass in SSFL runoff from Outfalls 001, 002, 008, and 009 appears to be in the particulate phase. Also, the dissolved concentrations of the metals have never been measured at concentrations above benchmarks at these outfalls. As noted above, the benchmarks were originally established based on the toxicology of the dissolved forms of the metals, and then a coefficient was used to attempt to relate these to the total recoverable forms. Unfortunately, although the fraction of the filterable metals is low, the ratio compared to the total forms is highly irregular, making the comparison of the concentrations of the total recoverable forms of the metals to the filterable forms used in the development of the benchmarks highly uncertain.

3) Fingerprinting potential watershed metal sources:

- Regional data shows that the atmospheric deposition flux is quite large compared to the total LA River discharge, especially for copper and zinc. This has lead to the conclusion that the atmospheric flux is the most important source of metals to the river.

Unfortunately, this does not consider the imbalance in other constituents, or, more importantly, the retention of the depositional material in the watershed, and the other obvious sources of metal pollutants in most land uses.

- The zinc to copper ratios at Outfall 009 are very high and indicate additional zinc contamination besides atmospheric deposition, compared to the copper values. It is possible that galvanized metal in the Outfall 009 watershed is responsible for these higher than expected zinc concentrations. However, it is interesting to note that the Outfall 008 particulate strength ratios are very similar to the ratios for the background soil metal ratios, indicating the soil is the likely major source of the metals at Outfall 008.

- With the limited data available, it seems likely that copper concentrations at both Outfalls 008 and 009, and lead and zinc concentrations at Outfall 008, are likely primarily due to erosion of natural site soils, while the elevated Outfall 009 lead concentrations (which are also partly due to erosion of natural soils) are likely affected by the site lead contamination in the northern drainage area, which is currently being addressed by an ongoing cleanup action. The higher zinc particulate strength concentrations observed at Outfall 009 may be associated with galvanized metals in the drainage area in addition to erosion of natural soils. However zinc, unlike lead, has not been observed at concentrations above the current NPDES benchmarks at Outfalls 008 or 009.

Additional information from the literature is presented in the appendices. Noteworthy comments are highlighted there, but are not repeated in this section. Many of the appendix comments substantiate the findings listed above. Some of these issues have been confusing for the public, regulators, and others in terms of their general understanding of stormwater sources and water quality patterns at the site. One issue pertains to the importance of atmospheric deposition. As an example, studies that only measured atmospheric deposition and watershed yield commonly conclude that the deposition is the major source of contamination at the outfall. In contrast, those that also measure source area flow quality realize that other significant sources of contaminants obviously occur in the watershed and that not all of the deposition is mobilized and transported in the runoff. In other situations, large waterbodies (such as SF Bay) can have significant deposition directly falling onto the receiving water. Another issue relates to “first flushes” of contaminants at stormwater monitoring outfalls. First flushes are common for small, mostly paved areas under relatively consistent rain intensities, however first flushes are less common for larger areas that have little impervious areas and for areas that have periods of high intensity rainfall later in the event. Source-limited pollutants/areas (such as those for which atmospheric deposition is a primary source) also more commonly experience first flushes. The SSFL watersheds 001, 002, 008, and 009, by contrast, are likely flow-limited in that metal concentrations are likely correlated to TSS concentrations, rainfall depth/intensity, and runoff flow rate.

2.0 Metals Concentrations at Outfalls 008 and 009 at Santa Susana Field Laboratory Compared to Other Land Uses

This section of the background metals report discusses stormwater metal concentrations observed at Outfalls 008 and 009 at the Santa Susana Field Lab. In addition, a brief summary comparing these observations with stormwater characteristics from other locations, and from a range of land uses, is also shown to indicate how the site stormwater compares to typical runoff conditions.

The most comprehensive database of stormwater characteristics is the National Stormwater Quality Database (NSQD), described in Appendix A. Version 3 of the NSQD contains data from more than 8500 events from around the US and represents most land uses. Most of the data contained in the NSQD is from outfall monitoring associated with Phase 1 MS4 stormwater permits. It also contains selected data from the Environmental Protection Agency (EPA)'s Nationwide Urban Runoff Program (NURP) project and from the International Best Management Practices (BMP) Database, along with selected data from special Unites States Geological Survey (USGS) studies. All of the data in the NSQD is from outfall monitoring, and before the implementation of any outfall stormwater control practice, if present. The database includes extensive descriptions of the monitoring procedures and sites, and underwent extensive QA/QC reviews as part of the EPA-supported project.

Table 1 summarizes the expected long-term frequencies that current permit limits may be exceeded, while Tables 2 through 9 summarize and compare the SSFL Outfall 008 and 009 and the NSQD heavy metal concentration data (all sites combined and by major land use). Because of the presence of non-detectable values, the statistical descriptions (minimum, coefficient of variation, standard deviation, average, median, and maximum) are only based on concentrations measured above the detection limit. Except for the median, these values would be greatly distorted if any substitution scheme was used to replace the non-detected values, especially since the NSQD usually has several limits of detection for each constituent (Berthoux and Brown 2004, Burton and Pitt 2001, and Maestre 2005). The other values on the tables (% of observations with detected values, number of total observations, number of observations having detected concentrations, SSFL permit limits, number of observations exceeding the permit limits, and the percentage of the total observations exceeding the permit limits) are based on the complete data set.

These tables show summaries for the complete NSQD data set and for the six major land uses. Within each land use group, homogeneous land use sites are included, along with sites having the designated land use as the predominate land use. As further described in Appendix A, ***there are significant differences in the metal concentrations between the different land uses. Generally, the largest metal concentrations are observed in the commercial, industrial, or freeway land uses, and the smallest metal concentrations are observed in the open space and residential land uses.*** For some metals, very few data are available for institutional land uses.

Each of these data sets (the SSFL Outfalls 008 and 009, along with each land use in the NSQD) were separately compared to the SSFL permit limits, as shown on these tables. ***In all cases, except for mercury, the SSFL 008 and 009 Outfalls exceedance percentages of the current***

permit limits are less than, or the same, as the lowest levels for any of the NSQD land uses. Furthermore, the observed mercury median and average values for the site data are less than the median and average concentrations contained in the NSQD for any land use category, including open space. This discrepancy is likely due to differences in detection limits in the data sets. Figures 3 through 9 are probability plots of the SSFL 008 and 009 metal concentration data (antimony, cadmium, copper, lead, mercury, nickel, and zinc; too few data are available to prepare a probability plot for thallium). These plots also show the current permit limits as references.

Probability plots are prepared by ranking the available data and calculating their probability of occurrence. These probability values (shown on the vertical axis) are plotted against their concurrent concentrations. As an example, Figure 3 shows that the 90th percentile antimony value (90% of the observations have equal or lower concentrations, and 10% are greater) observed at Outfall 008 was about 0.35 µg/L. This plot also indicates that about 60% of the samples had non-detected concentrations, and that the lowest detected value was about 0.19 µg/L. This is a very useful way to present data that has non-detected values and when comparing observations from multiple locations. It is also useful to estimate the approximate likelihood of exceeding a critical value, such as the current benchmark concentrations. In this example, it is extremely unlikely that Outfall 008 concentrations would exceed the benchmark value of 6 µg/L for antimony, while Outfall 009 concentrations may be larger than this value at a frequency of about 1%.

These plots show the observed values starting at the detection frequency, indicating that the limit of detection is well below the permit limit values. Also, these plots are log-normal probability plots and the straight line nature of the observed values indicate that the observed metal concentrations at the site outfalls are roughly log-normally distributed, as is typical for most stormwater constituents, but some skewness is usually still observed. Table 1 summarizes the exceedances for the available samples, along with calculated expected exceedances based on long term data, from probability plots. ***The metals with the most frequent observed and projected exceedances include lead, mercury, and copper, with cadmium, nickel and zinc having much lower observed and projected exceedances expectations. Consistent with observed data, antimony and thallium are not expected to have any notable projected exceedances.***

Table 1. SSFL Outfall Metal Data Compared to Permit Limits and Projected Exceedances

Parameter	Actual % of available samples exceeding site permit limits (008 and 009)	Projected % of samples that may exceed site permit limits over the long term (008 and 009) based on assumption of log-normality
Antimony	0 and 0%	<0.01 and 1%
Cadmium	0 and 3.3%	5%
Copper	10.5 and 10%	8 and 10%
Lead	42.1 and 22.6%	35 and 25%
Mercury	21.1 and 16.1%*	15%
Nickel	0 and 0%	<0.01 and 1%
Thallium	0 and 0%	n/a (too few data)
Zinc	0 and 0%	<0.01 and 8%

* There also appears to be a temporal trend for mercury concentrations, with a lower frequency of observed exceedances at these outfalls since the last major wildfires on the site.

Table 2. Antimony (concentrations in µg/L) at SSFL and as Contained in the NSQD

	SSFL Outfall 008	SSFL Outfall 009	NSQD all sites combined	NSQD open space	NSQD residential	NSQD institutional	NSQD commercial	NSQD industrial	NSQD freeways
Minimum*	0.19	0.3	0.7	1	1	n/a	2	0.7	1.7
COV*	0.3	0.9	1.7	n/a	1.6	n/a	1.1	1.5	0.3
St dev*	0.12	0.84	11.7	n/a	15.3	n/a	30.5	10.9	0.7
Average*	0.35	0.9	11.3	1	9.7	n/a	27.5	7.4	2.7
Median*	0.31	0.76	3	1	1	n/a	20	3.4	3
Maximum*	0.54	4.2	100	1	40	n/a	100	46	3.4
% of obs with detected values	36.8	66.7	6.2	5.7	3.8	n/a	4.5	9.2	41.2
# of obs	19	30	1022	52	395	0	291	251	17
# obs with values > DL	7	20	63	3	15	n/a	13	23	7
SSFL current permit limits	6	6	6	6	6	6	6	6	6
# exceeding current permit limit	0	0	23	0	4	n/a	9	9	0
% of obs exceeding current permit limit**	***0***	***0***	2.3	***0***	1.0	n/a	3.1	3.6	***0***

* Based on observed values only (does not include non-detects)

** The ***bold italycs*** values are the lowest percentage exceedance values compared to the SSFL current permit limits

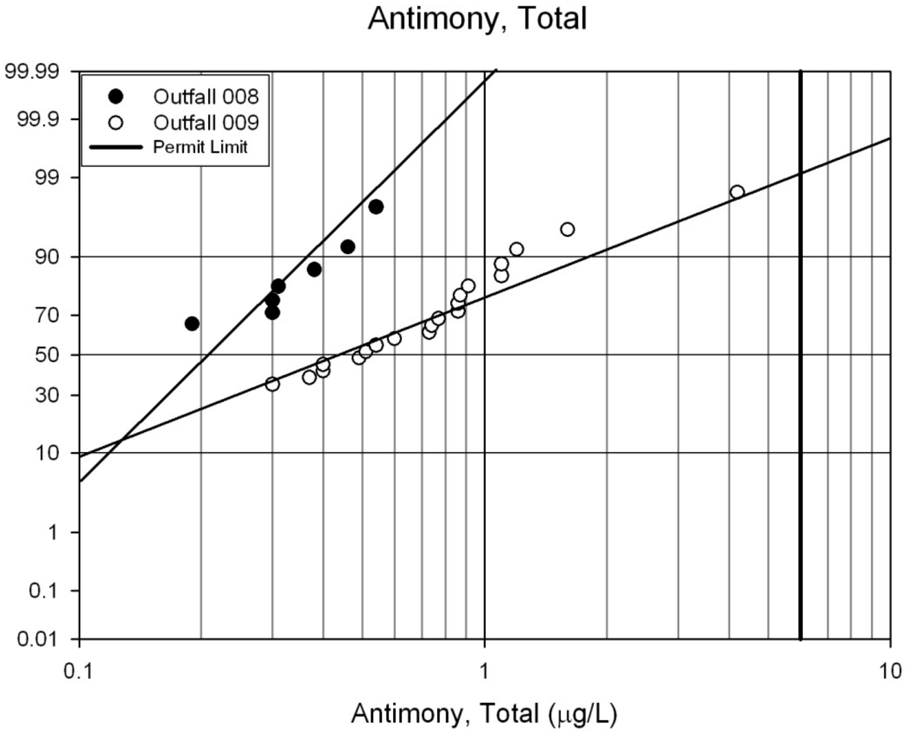


Figure 3. SSFL antimony concentrations at Outfalls 008 and 009, compared to current permit limit (the vertical axis is a normal probability scale, or the measurement percentile which indicates the probability of an equal or lower concentration).

Table 3. Cadmium (concentrations in µg/L) at SSFL and as Contained in the NSQD

	SSFL Outfall 008	SSFL Outfall 009	NSQD all sites combined	NSQD open space	NSQD residential	NSQD institutional	NSQD commercial	NSQD industrial	NSQD freeways
Minimum*	0.02	0.02	0.04	0.04	0.04	0.1	0.04	0.1	0.09
COV*	1.8	3.3	4.1	2.3	5.0	0.7	2.2	4.2	1.2
St dev*	0.38	2.0	14.3	19.3	15.3	0.5	6.0	19.8	4.3
Average*	0.21	0.62	3.5	8.6	3.1	0.7	2.8	4.8	3.6
Median*	0.11	0.054	0.92	2	0.5	0.6	1.0	1.8	1
Maximum*	1.5	9.2	334	90	275	2.1	80	334	16.1
% of obs with detected values	73.7	66.7	43	27.7	39.4	71.2	39.8	47.5	78.5
# of obs	19	30	3600	148	1658	52	757	724	214
# obs with values > DL	14	20	1562	41	653	37	301	344	168
SSFL current permit limits	4	4	4	4	4	4	4	4	4
# exceeding current permit limit	0	1	309	11	99	0	63	82	53
% of obs exceeding current permit limit**	***0***	***3.3***	8.6	7.4	6.0	***0***	8.3	11.3	24.8

* Based on observed values only (does not include non-detects)

** The ***bold italycs*** values are the lowest percentage exceedance values compared to the SSFL current permit limits

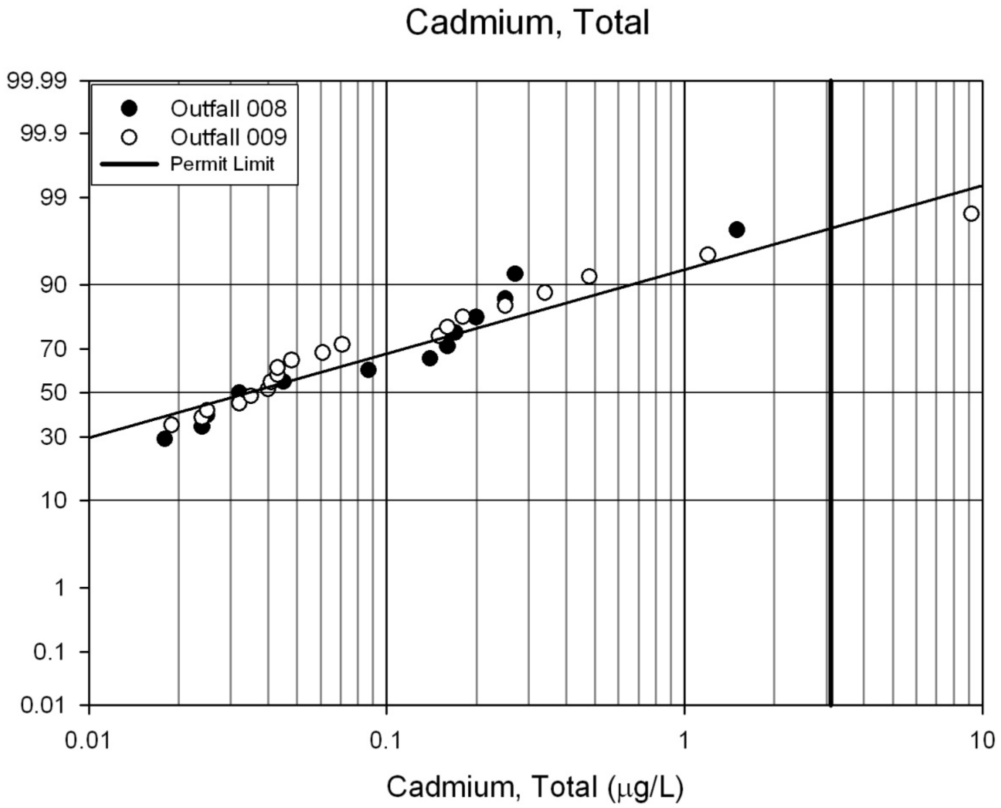


Figure 4. SSFL cadmium concentrations at Outfalls 008 and 009, compared to current permit limit (the vertical axis is a normal probability scale, or the measurement percentile which indicates the probability of an equal or lower concentration).

Table 4. Copper (concentrations in µg/L) at SSFL and as Contained in the NSQD

	SSFL Outfall 008	SSFL Outfall 009	NSQD all sites combined	NSQD open space	NSQD residential	NSQD institutional	NSQD commercial	NSQD industrial	NSQD freeways
Minimum*	2.4	1.6	0.2	2	0.3	2.1	0.2	0.4	0.4
COV*	0.61	1.2	2.1	1.5	1.8	0.8	2.3	2.1	2.2
St dev*	4.1	8.3	62	21.2	48.3	17.3	83.7	74.3	70.8
Average*	6.8	6.8	30	14.1	27.3	21.1	36.7	36.3	32.5
Median*	5.3	3.5	15	9	14	18.0	18.0	19.2	15.4
Maximum*	15	39	1360	210	753	90.8	1300	1360	800
% of obs with detected values	94.7	100	88	83.9	87.7	85.1	87.6	86.0	98.1
# of obs	19	30	5165	155	2613	67	1068	769	364
# obs with values > DL	18	30	4544	130	2291	57	936	661	357
SSFL current permit limits	14	14	14	14	14	14	14	14	14
# exceeding current permit limit	2	3	2406	40	1159	33	547	415	190
% of obs exceeding current permit limit**	***10.5***	***10.0***	46.6	25.8	44.4	49.3	51.2	54.0	52.2

* Based on observed values only (does not include non-detects)

** The ***bold italycs*** values are the lowest percentage exceedance values compared to the SSFL current permit limits

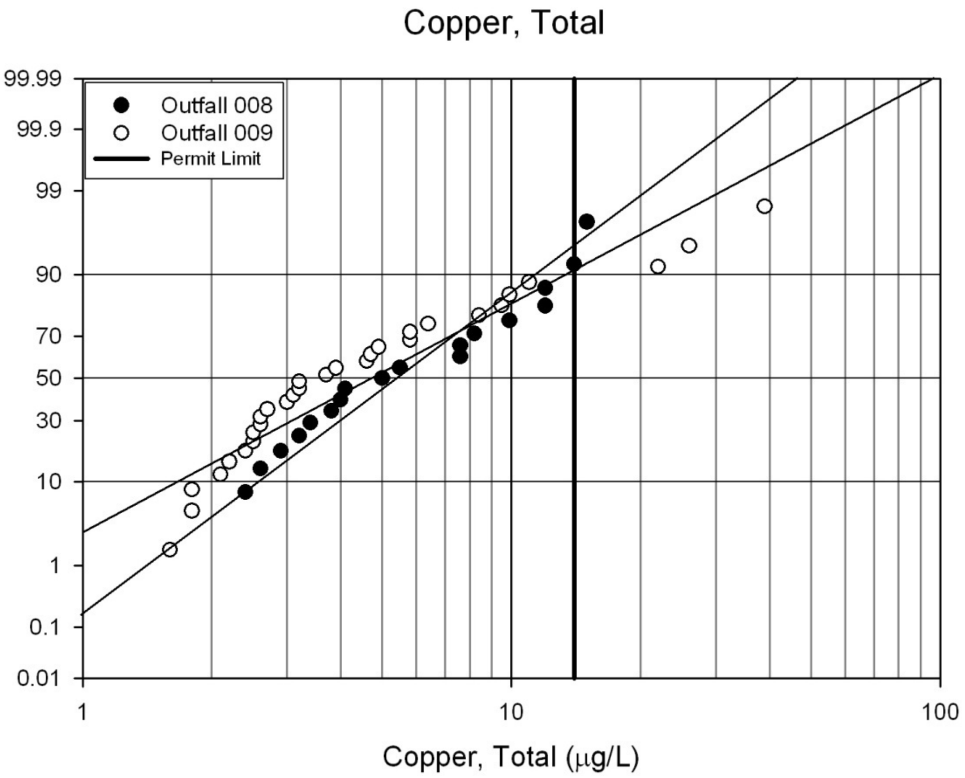


Figure 5. SSFL copper concentrations at Outfalls 008 and 009, compared to current permit limit (the vertical axis is a normal probability scale, or the measurement percentile which indicates the probability of an equal or lower concentration).

Table 5. Lead (concentrations in µg/L) at SSFL and as Contained in the NSQD

	SSFL Outfall 008	SSFL Outfall 009	NSQD all sites combined	NSQD open space	NSQD residential	NSQD institutional	NSQD commercial	NSQD industrial	NSQD freeways
Minimum*	0.17	0.08	0.05	0.2	0.1	1.9	0.05	0.5	0.4
COV*	2.3	3.4	2.0	2.2	2.6	1.5	1.6	1.9	1.1
St dev*	26.8	54.4	74	68.0	65.9	44.2	54.5	102	79.1
Average*	11.9	16.1	37	30.5	25.8	30.3	34.3	54.5	70.8
Median*	4.4	1.3	14	10	10	18.3	15	20	43.5
Maximum*	120	280	1200	450	1200	269	689	1200	660
% of obs with detected values	100	87.1	78	66.5	76.9	92.3	79.9	75.9	97.1
# of obs	19	31	4694	203	2142	52	915	848	379
# obs with values > DL	19	27	3684	135	1648	48	731	644	368
SSFL current permit limits	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2	5.2
# exceeding current permit limit	8	7	2714	97	1042	36	584	559	341
% of obs exceeding current permit limit**	***42.1***	***22.6***	57.8	47.8	48.6	69.2	63.8	65.9	90.0

* Based on observed values only (does not include non-detects)

** The ***bold italycs*** values are the lowest percentage exceedance values compared to the SSFL current permit limits

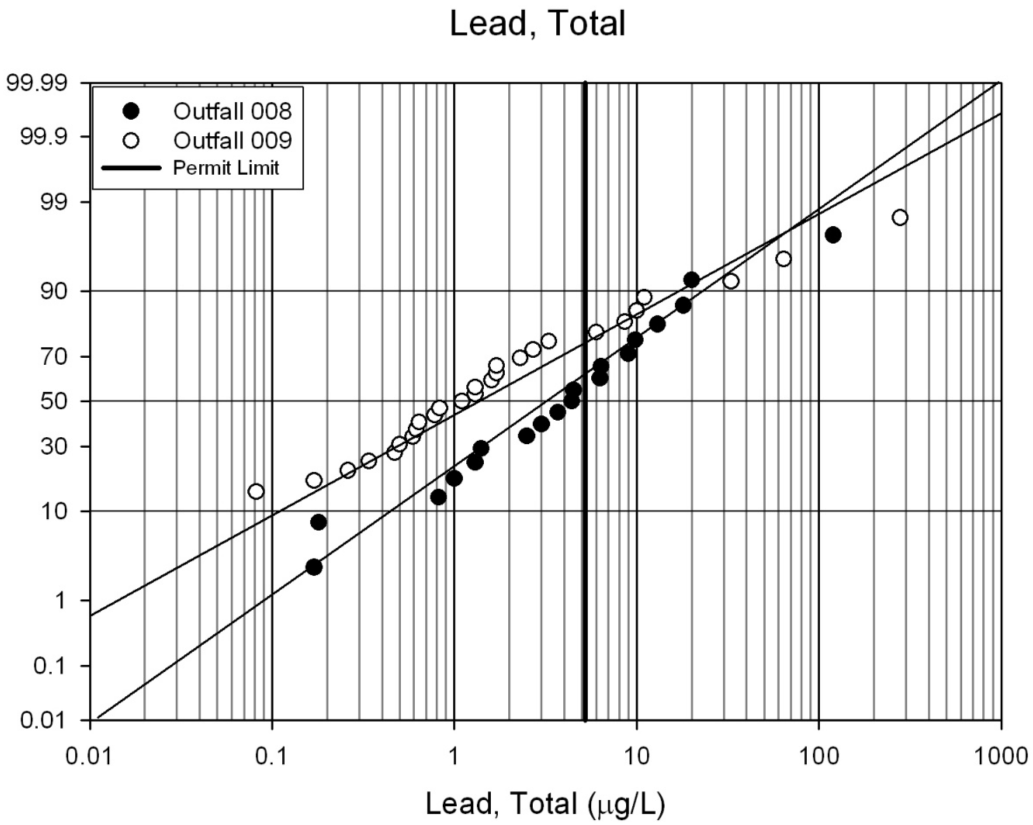


Figure 6. SSFL lead concentrations at Outfalls 008 and 009, compared to current permit limit (the vertical axis is a normal probability scale, or the measurement percentile which indicates the probability of an equal or lower concentration).

Table 6. Mercury (concentrations in µg/L) at SSFL and as Contained in the NSQD

	SSFL Outfall 008	SSFL Outfall 009	NSQD all sites combined	NSQD open space	NSQD residential	NSQD institutional	NSQD commercial	NSQD industrial	NSQD freeways
Minimum*	0.066	0.066	0.03	0.1	0.03	n/a	0.03	0.1	0.08
COV*	0.29	0.34	2.5	0.4	0.9	n/a	1.0	2.8	0.8
St dev*	0.036	0.046	0.93	0.058	0.25	n/a	0.24	1.4	0.15
Average*	0.12	0.13	0.37	0.15	0.29	n/a	0.25	0.5	0.2
Median*	0.14	0.13	0.2	0.15	0.2	n/a	0.2	0.2	0.2
Maximum*	0.17	0.21	9.2	0.2	1.3	n/a	1	9.2	0.3
% of obs with detected values	36.8	32.3	9.0	9.8	8.5	n/a	6.1	13.4	5.9
# of obs	19	31	1162	41	422	0	314	328	34
# obs with values > DL	7	10	105	4	36	n/a	19	44	2
SSFL current permit limits	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
# exceeding current permit limit	4	5	74	2	28	n/a	12	31	1
% of obs exceeding current permit limit**	21.1	16.1	6.4	4.9	6.6	n/a	***3.8***	9.5	***2.9***

* Based on observed values only (does not include non-detects)

** The ***bold italycs*** values are the lowest percentage exceedance values compared to the SSFL current permit limits

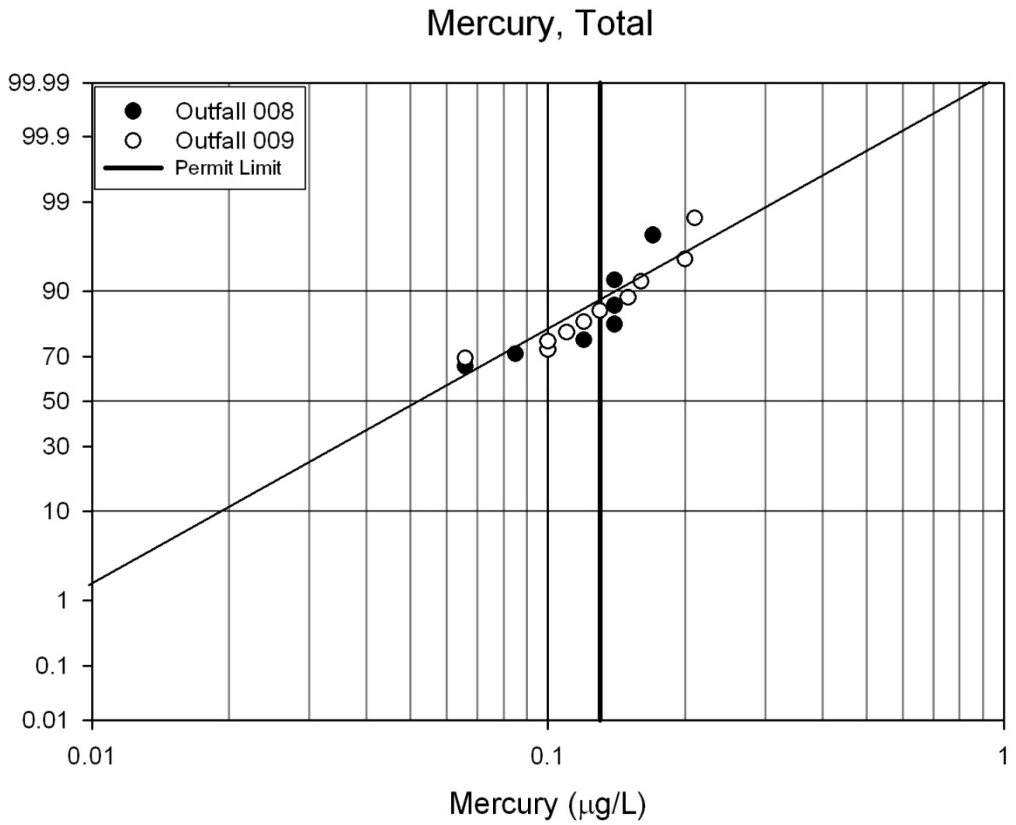


Figure 7. SSFL mercury concentrations at Outfalls 008 and 009, compared to current permit limit (the vertical axis is a normal probability scale, or the measurement percentile which indicates the probability of an equal or lower concentration).

Table 7. Nickel (concentrations in µg/L) at SSFL and as Contained in the NSQD

	SSFL Outfall 008	SSFL Outfall 009	NSQD all sites combined	NSQD open space	NSQD residential	NSQD institutional	NSQD commercial	NSQD industrial	NSQD freeways
Minimum*	4.3	2	1	1	1	n/a	1	1	2.8
COV*	0.32	0.92	1.2	1.1	1.1	n/a	1.2	1.1	0.9
St dev*	1.9	4.5	16.2	20.4	10.3	n/a	12.2	21.8	12.0
Average*	5.7	4.9	13.6	18.1	9.5	51	10.0	20.4	13.2
Median*	5	2.6	8	11	6	n/a	7	11	9
Maximum*	7.8	10	120	100	100	n/a	110	120	87
% of obs with detected values	100	75.0	54.7	47.8	46.4	n/a	55.8	63.0	87.3
# of obs	3	4	1602	92	580	19	403	389	102
# obs with values > DL	3	3	876	44	269	1	225	245	89
SSFL current permit limits	100	100	100	100	100	100	100	100	100
# exceeding current permit limit	0	0	6	1	1	0	1	3	0
% of obs exceeding current permit limit**	***0***	***0***	0.4	1.1	0.2	***0***	0.2	0.8	***0***

* Based on observed values only (does not include non-detects)

** The ***bold italycs*** values are the lowest percentage exceedance values compared to the SSFL current permit limits

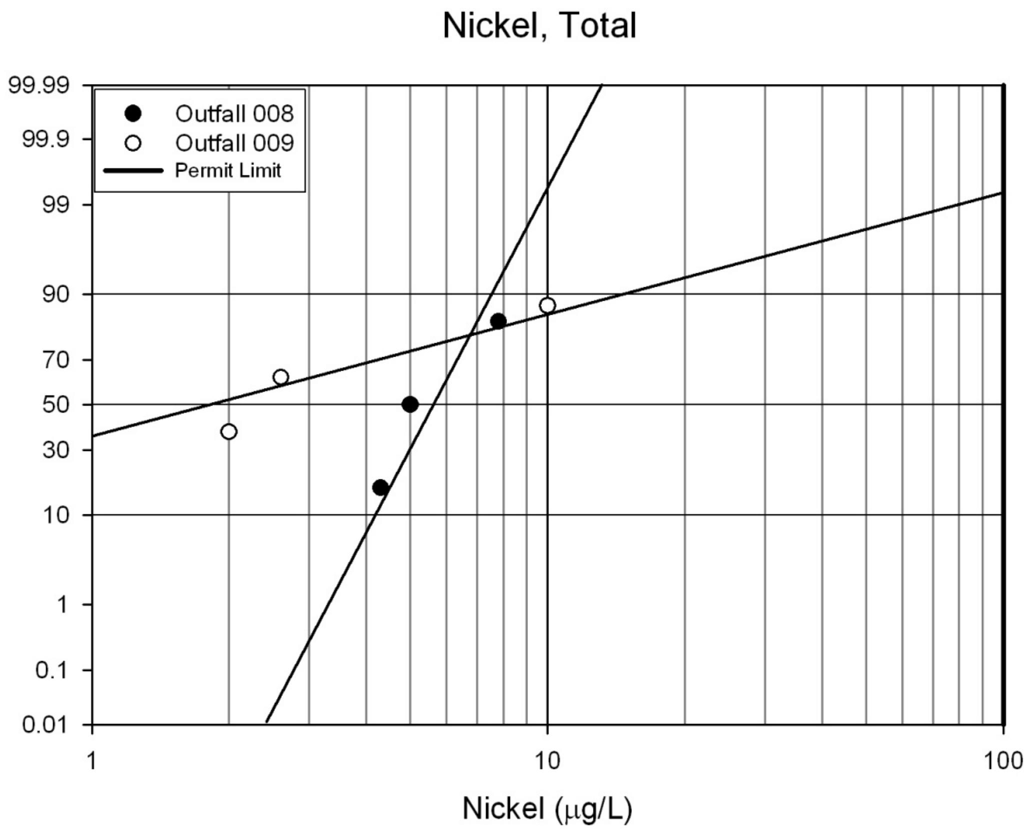


Figure 8. SSFL nickel concentrations at Outfalls 008 and 009, compared to current permit limit (the vertical axis is a normal probability scale, or the measurement percentile which indicates the probability of an equal or lower concentration).

Table 8. Thallium (concentrations in µg/L) at SSFL and as Contained in the NSQD

	SSFL Outfall 008	SSFL Outfall 009	NSQD all sites combined	NSQD open space	NSQD residential	NSQD institutional	NSQD commercial	NSQD industrial	NSQD freeways
Minimum*	n/a	n/a	0.01	n/a	n/a	n/a	n/a	0.01	n/a
COV*	n/a	n/a	4.0	n/a	n/a	n/a	n/a	3.5	n/a
St dev*	n/a	n/a	286	n/a	n/a	n/a	n/a	361	n/a
Average*	n/a	0.41 (only obs)	71.5	1	26.5	n/a	2	104	1
Median*	n/a	n/a	1	n/a	n/a	n/a	n/a	0.2	n/a
Maximum*	n/a	n/a	1250	n/a	n/a	n/a	n/a	1250	n/a
% of obs with detected values	0	7.1	2.2	1.9	0.6	n/a	0.5	5.9	6.7
# of obs	8	14	864	53	351	0	224	205	n/a
# obs with values > DL	0	1	19	1	2	0	1	12	15
SSFL current permit limits	2	2	2	2	2	2	2	2	2
# exceeding current permit limit	0	0	6	0	2	n/a	1	1	0
% of obs exceeding current permit limit**	***0***	***0***	0.7	***0***	0.6	n/a	0.4	0.5	***0***

* Based on observed values only (does not include non-detects)

** The ***bold italycs*** values are the lowest percentage exceedance values compared to the SSFL current permit limits

Not enough SSFL data for probability plots

Table 9. Zinc (concentrations in µg/L) at SSFL and as Contained in the NSQD

	SSFL Outfall 008	SSFL Outfall 009	NSQD all sites combined	NSQD open space	NSQD residential	NSQD institutional	NSQD commercial	NSQD industrial	NSQD freeways
Minimum*	15	6.3	0.4	5	0.4	18	0.4	0.4	0.4
COV*	0.46	0.93	3.3	1.1	2.8	1.0	1.4	3.5	1.4
St dev*	11	37	593	122	347	204	278	1330	223
Average*	24	40	181	109	125	210	197	381	160
Median*	21	33	90	70	76	138	120	156	97
Maximum*	40	88	22,500	840	14,700	1300	4600	22,500	2100
% of obs with detected values	80	100	97.5	90.7	96.7	100	99.1	98.9	99.3
# of obs	5	4	6184	214	3028	68	1201	898	611
# obs with values > DL	4	4	6030	194	2927	68	1190	888	607
SSFL current permit limits	159	159	159	159	159	159	159	159	159
# exceeding current permit limit	0	0	1781	34	588	31	474	441	192
% of obs exceeding current permit limit**	***0***	***0***	28.8	15.9	19.4	45.6	39.5	49.1	31.4

* Based on observed values only (does not include non-detects)

** The ***bold italycs*** values are the lowest percentage exceedance values compared to the SSFL current permit limits

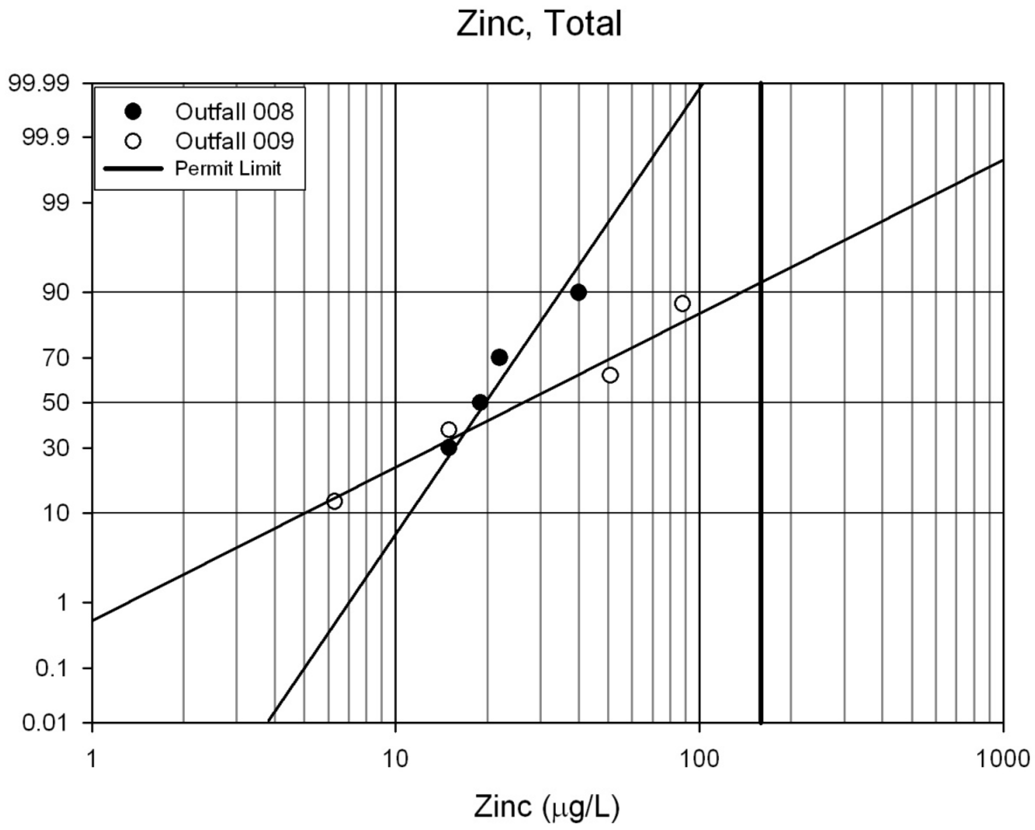


Figure 9. SSFL zinc concentrations at Outfalls 008 and 009, compared to current permit limit (the vertical axis is a normal probability scale, or the measurement percentile which indicates the probability of an equal or lower concentration).

The Southern California Coastal Water Research Project (SCCWRP) recently prepared Technical Report 500: *Assessment of Water Quality Concentrations and Loads from Natural Landscapes (*Stein and Yoon 2007). They reviewed existing watershed characteristics and associated stream water quality data. They identified natural watersheds that were at least 95% undeveloped and had no obvious evidence of human use and no excessive channel erosion. The streams were also relatively large, being at least 3rd order streams in order to be more likely of having dry weather base flows. They also eliminated any areas that were affected by wildfires within the three years before the study. Safety and access were also critical factors. Twenty-two sites were selected, out of the original 45 candidates, and were located in six counties and 12 different major watersheds. Each site was sampled during two or three storms in the period of December 2004 to April 2006. A total of about 30 events were included during the wet weather portion of the study (dry weather sampling was also conducted). Samples were collected manually from within the streams during the events, along with concurrent flow measurements. Each event included several samples during each event, and flow-weighted concentrations were then calculated, along with mass discharges. Figure 10 shows the flow-weighted mean heavy metals concentrations observed during these undeveloped stream sampling efforts during wet weather, along with regional data from developed watersheds. With only a very few events sampled from each site, these samples do not represent seasonal or different rain characteristic effects. However, the range of sampling site characteristics represented in this monitoring program did allow SCCWRP to make a number of conclusions from these natural vs. developed watershed monitoring data:

- ***For almost all constituents, the observed concentrations from the natural areas were significantly different from the values obtained from developed watersheds. The natural area stormwater concentrations were generally one order of magnitude lower compared to the concentrations from the developed areas.***

- Metal concentrations were consistently below the California Toxic Rules (CTR) acute toxicity criteria for freshwater aquatic life, except for some exceedances for copper (15 out of 133 individual samples for total copper exceeded the acute criteria, while none of the flow-weighted total copper concentrations exceeded the acute criteria; only one of the 133 individual dissolved copper concentrations exceeded the acute criteria).

- ***The CTR criteria are originally based on dissolved concentrations and the rule includes a simple conversion procedure to estimate applicable total concentrations. However, the dissolved fraction of the metals were seen to vary greatly during the individual storms, making a simple comparison of the total metals concentrations to the criteria difficult. They concluded that estimates of metal toxicity should therefore be based on direct measurements of the dissolved metal concentrations.***

- ***The geological characteristics of the drainage areas were a significant factor affecting the metal, nutrient, and TSS concentrations: areas underlain by sedimentary rock had higher concentrations of these constituents compared to areas underlain by igneous rock.***

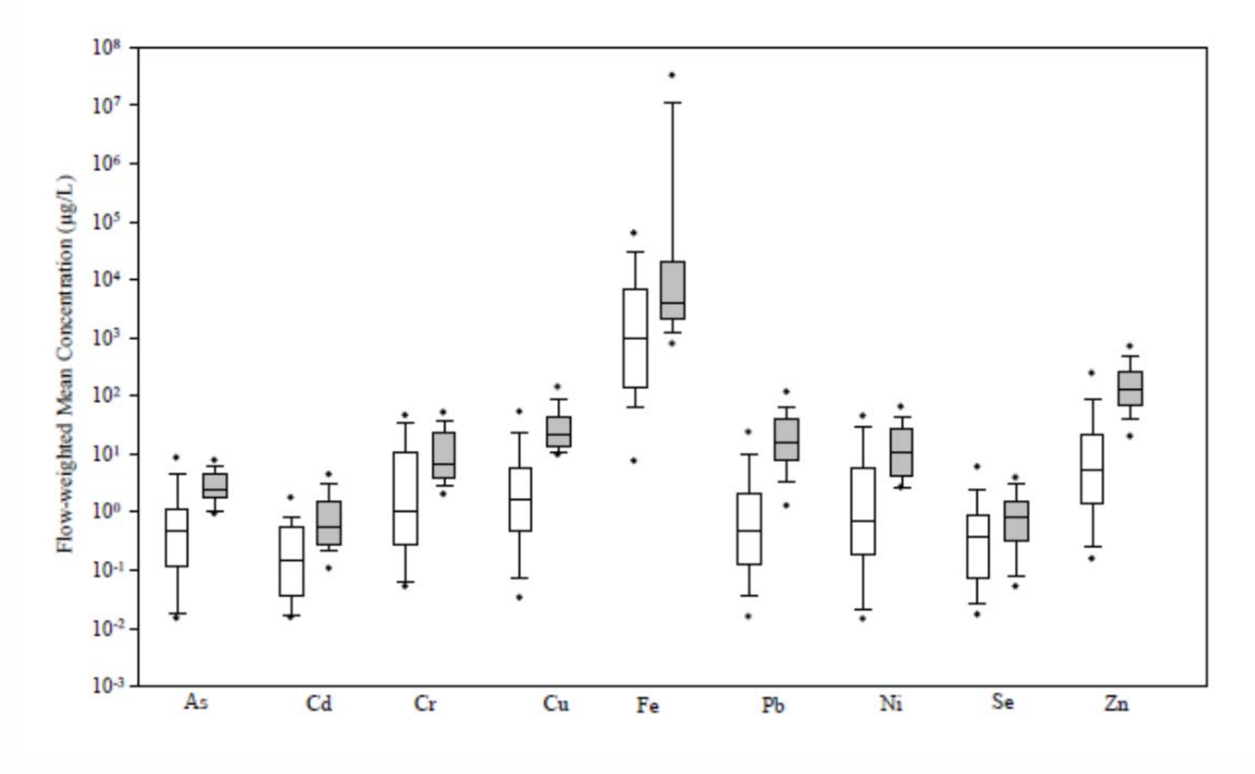


Figure 10. Natural (white boxes) and developed (shaded boxes) stormwater heavy metal concentrations in southern California (Stein and Yoon, SSWRP 2007) [<5 (lower star), 5 (lower bar), 25 (low side of box), 50 (line inside box), 75 (upper side of box), 95 (top bar), >95 (upper star) percentile values indicated]

Figures 11 through 14 present box and whiskers plots for total cadmium, copper, zinc and lead to illustrate the range of measured stormwater concentrations at the SSFL Outfalls relative to open space data from LA County, NSQD, and SCCWRP. Other metals were not included due to limited data. For these box and whisker plots, the centerlines represent median values (50th percentile concentrations), the boxes indicate the interquartile range (or the 25th and 75th percentile concentrations), the whiskers represent the 5th and 95th percentile values, and the dots represent results beyond the whiskers; missing boxes indicate insufficient data to compute accurate percentile values.

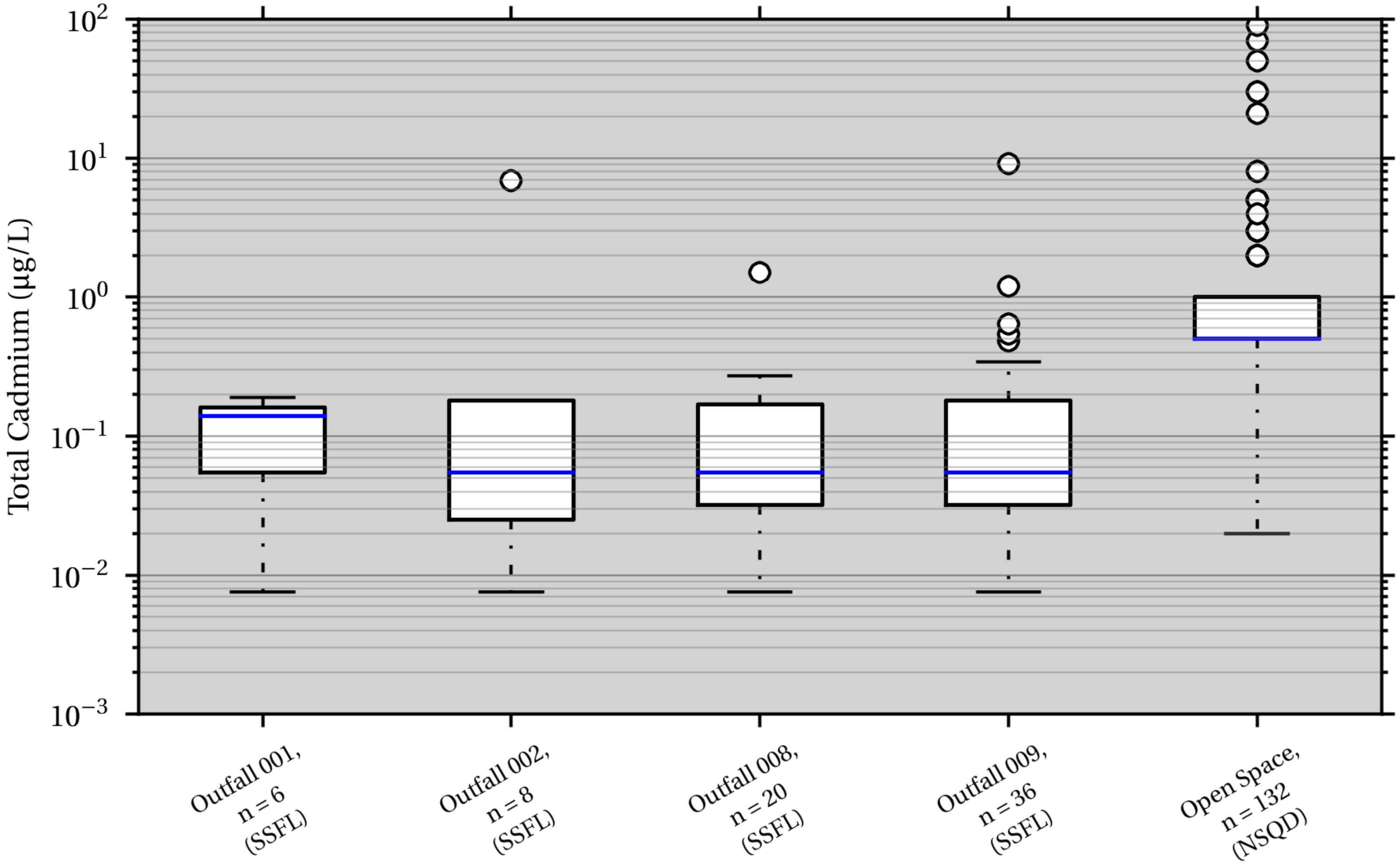


Figure 11. Cadmium concentrations at SSFL Outfalls compared to NQSD open space observations.

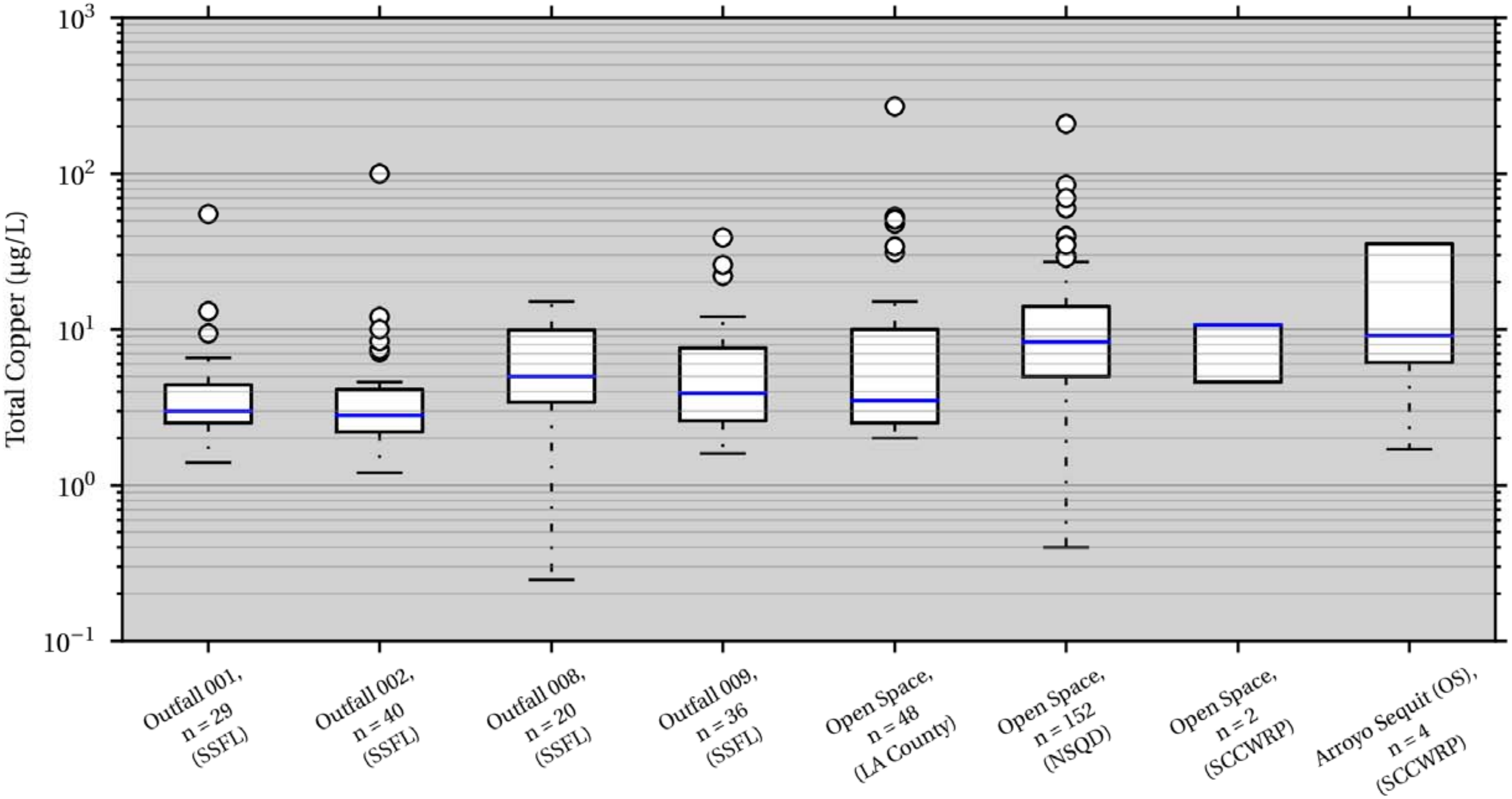


Figure 12. Copper concentrations at SSFL Outfalls compared to LA County, SCCWRP, and NQSD open space observations.

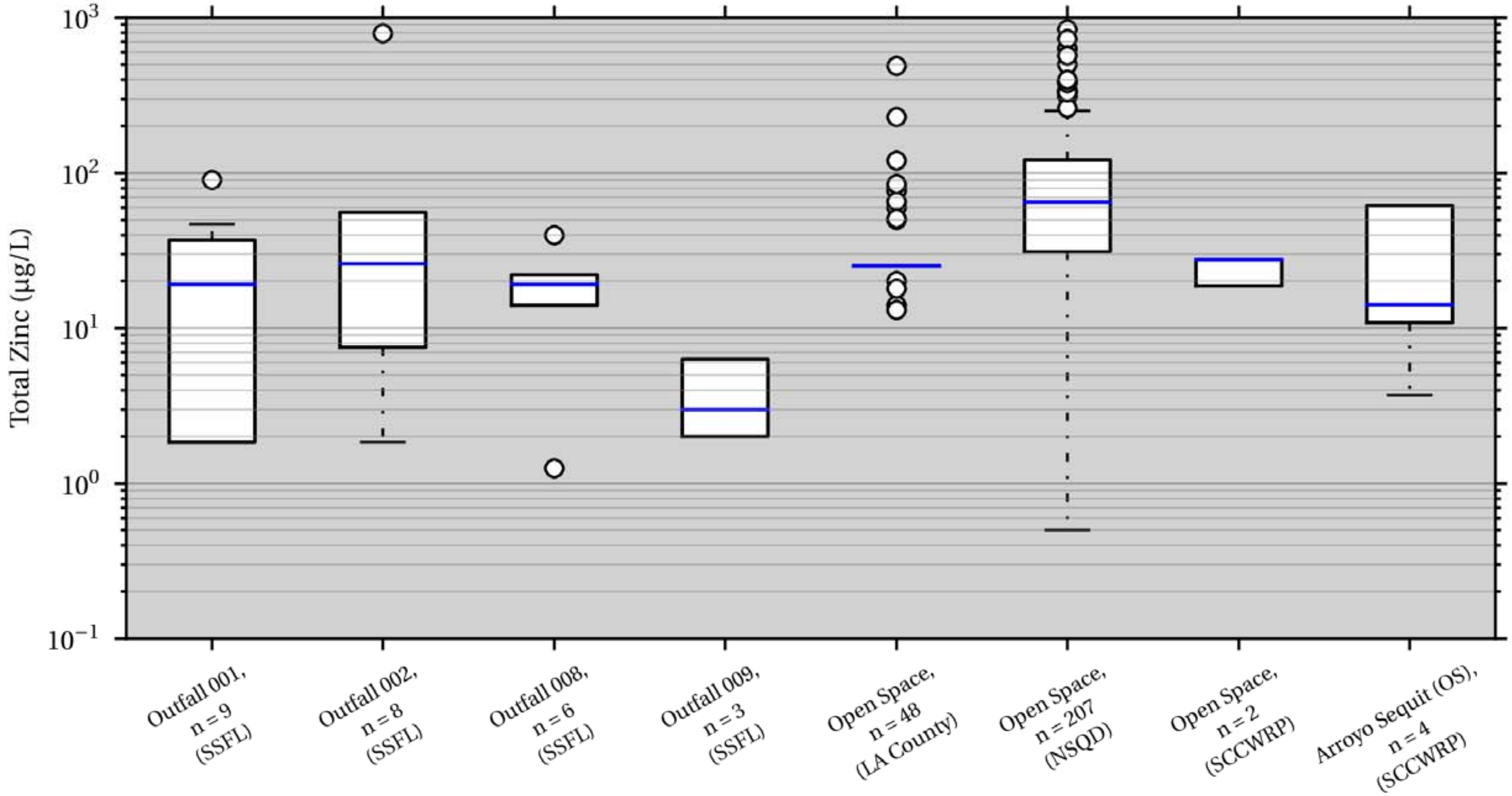


Figure 13. Zinc concentrations at SSFL Outfalls compared to LA County, SCCWRP, and NQSD open space observations.

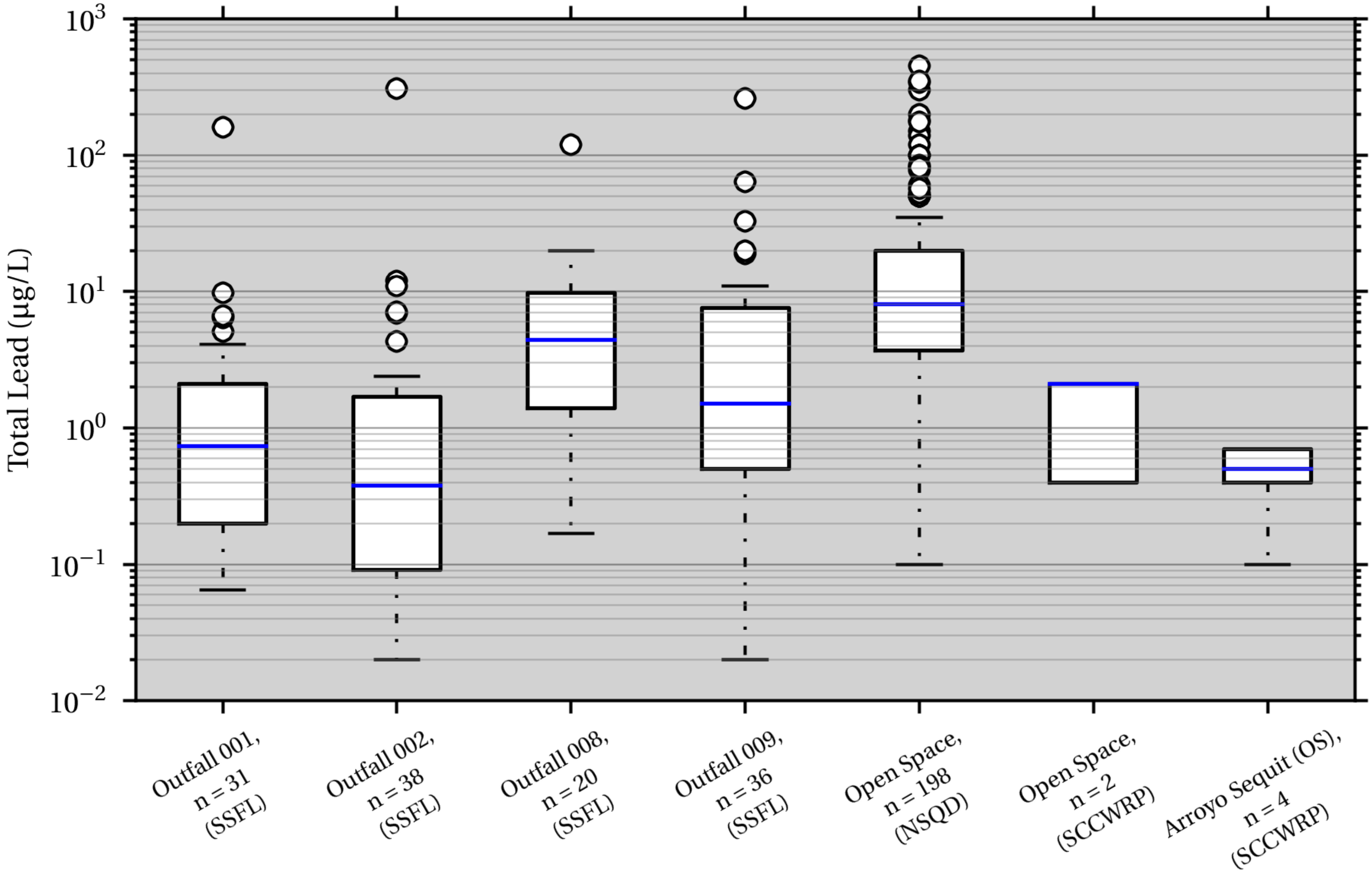


Figure 14. Lead concentrations at SSFL Outfalls compared to SCCWRP and NQSD open space observations.

3.0 Potential Sources of Contaminants

Rainfall and associated constituents (sometimes reported as “wet fall”) affect the complete watershed relatively evenly. Contamination of the rain occurs with regional (to global) scale atmospheric gaseous and fine particulate emissions. Much information is available concerning this degradation, including such things as acid rain and contamination associated with aerial spraying of pesticides and wind-blown pesticides from distant locations. Irrespective of this contamination, rainfall is usually the least contaminated source of metals and other pollutants in urban watersheds. The contributions of rainfall contaminants to outfall discharges is relatively straight-forward, especially for the conservative metals, and is simply related to the fraction of the rainfall that occurs as direct runoff. An interesting exception is for rainfall acidity and pH. Natural rainfall is in equilibrium with atmospheric CO_2 and is therefore slightly acidic, at a pH of about 5.6. “Acid rain” can have substantially lower pH levels. In urban areas, the pH of stormwater is usually relatively close to neutral, even if the rain water is acidic, possibly due to the neutralizing effects of urban surfaces, especially concrete. This is fortunate, as the toxicity of heavy metals increases under acidic conditions. In natural areas, rainfall can also be quickly neutralized upon interacting with the ground, depending on the alkalinity of the soils. Only about 1.5% of the stormwater observations in the National Stormwater Quality Database have pH values less than 5.6, the natural pH of rainwater, for example.

Dry atmospheric deposition (“dust fall” occurring between rains) has also been monitored in many locations. Sources of contaminated dry deposition can be both regional and local. It is possible that some of the dry deposition can be associated with close-by fugitive dust (nonpoint source air pollution emissions originating from relatively large areas, such as from unpaved roads). In some cases, dry deposition measurements may be double-counting these contributions as the fugitive dust original source may have been influenced by previous dry deposition. Like rainfall, dry deposition falls on all surfaces, but may not be evenly deposited. Dust fall near major fugitive dust sources will likely be greater than in locations surrounded by well-vegetated areas. In addition, washoff of previously deposited dry deposition material varies greatly depending on the type of surface the material falls onto and the rainfall characteristics. Even on smooth impervious surfaces, the washoff yield of this material can be low. On natural surfaces, the washoff yield is even less. Monitored outfall yield of metals can be less than the total measured dry deposition of metals in an area due to the permanent retention of this material on many surfaces. Complete urban area mass balance monitoring is needed in order to understand these complicated processes and the role of dry deposition to outfall metal yields.

Natural soils can also be a source of stormwater contaminants. Many heavy metals are present in the minerals in an area’s soils and are subject to erosion. The loss of these materials, and their subsequent transport through a drainage system, are highly dependent on the rainfall and runoff energy. The natural soils in an area can be affected by the above described atmospheric processes and by activities in the area. When source tracking stormwater particulates (such as by studying particle morphology and mineralogy using polarizing microscopes, or by thermal chromatography, for example), most of the particulate matter being discharged is found to be erosion products of the local soils. These particles, however, can become contaminated by other processes and sources as they (sometimes slowly) move through an area. The pollutant strength of the particulates in an area (usually expressed as mg pollutant/kg sediment, or ppm) can usually be seen to increase at locations subject to stormwater contamination.

This summary examines potential processes that affect the heavy metal concentrations in the stormwater at the SSFL site. Specifically, erosion processes on the site are responsible for the loss of soils. Atmospherically deposited materials are also moved through erosion processes. Deposition and subsequent resuspension of eroded material are other processes that are involved in the loss of these materials from the site. The heavy metal content of the site soils that are transported in the runoff is compared below with typical soil heavy metal content and particulate matter associated with stormwater from a variety of land uses.

This section compares SSFL Outfalls 008 and 009 data to different source area stormwater data from regional and nationwide stormwater monitoring sites. These published observations were obtained during actual storms by sampling at specific source areas at different land uses under a wide range of conditions. These comparisons are useful because they show that rain water and most roof runoff has the best water quality compared to other areas and that the runoff becomes more contaminated as it travels through more developed locations. As an example, atmospheric deposition affects all of the source areas in an area in a similar manner. If that was the most important source of stormwater contaminants, then it is expected that all of the source area stormwater concentrations would be similar. Some areas and constituents are similar to the rain water, but the majority show large concentration increases that must be associated with contamination at the source areas due to activities or materials present in those areas.

These data also show that the undeveloped, landscaped, and otherwise less intensively developed land uses have runoff with the best water quality. Tables 10 through 14 provide summaries of the full data set presented in Appendix B of concentrations of total forms of cadmium, copper, lead, and zinc . These data are separated by land use and are sorted by source area concentrations (from the lowest copper to the highest copper concentrations). The references are shown for each line and are generally grouped by date of research and/or location, and therefore, there may be several instances of the same type of area represented for each land use.

Also included on these tables are summaries for Outfall 008 and 009 observations. As noted in Appendix B, the source area samples were obtained as sheetflows during actual rains. Several studies are represented in these data, with most from Wisconsin, Alabama, Toronto, California, and Washington. However, most of the studies only included few samples from each source area (usually about 10). Stormdrain outfall monitoring data is also shown from the NSQD for each of these land uses. In most cases, the outfall concentrations are intermediate in the overall range represented by the source areas, as would be expected as the outfall flows are made up of mixtures of the source area data. Many of the lead source area data however are relatively high compared to the outfall data, as some of the source area observations were obtained during periods of high leaded gasoline use. Runoff from galvanized metal has extremely high zinc concentrations, while runoff that was in contact with CCA-treated wood also has very high copper concentrations. The rain quality data is similar to the lowest concentrations observed across all areas, with runoff from other source areas obviously being contaminated by local or regional sources (i.e., materials or activities). Outfall 008 and 009 data are also shown on all of the tables as a reference. ***Overall, the cadmium, copper, lead, and zinc SSFL Outfall 008 and***

009 concentrations are relatively low compared to the source area data for these constituents and are similar to the concentrations observed in undeveloped areas.

Table 10. Average Total Metal Concentrations in Stormwater for Open Space, Undeveloped Land, Bare Soil, and Landscaped Areas

Average (COV)	**Cadmium (µg/L)**	**Copper (µg/L)**	**Lead (µg/L)**	**Zinc (µg/L)**
Undeveloped areas (Pitt, *et al.* 2005 WI and MN)	n/a	5	1.3	n/a
Rain quality (Rubin 1976 rural WA and NY)	n/a	5.7	n/a	25
Outfall 008	<0.21 (1.8)* [74%]	<6.8 (0.6) [95%]	11.9 (2.3) [100%]	<24 (0.5) [80%]
Outfall 009	<0.62 (3.3) [67%]	6.9 (1.2) [100%]	<17.5 (3.1) [89%]	36 (1.2) [100%]
Small landscaped areas in developed land uses (Pitt, *et al.* 2005 WI and MN)	0.6 (0.4)	12 (0.4)	54 (0.9)	67 (0.4)
Open space outfall (NSQD national data)	n/a	14.1 (1.5)	30.5 (2.2)	109 (1.1)
Landscaped areas in developed land uses (Pitt 1983, Ottawa; Pitt and Bozeman 1982, San Jose; Pitt and McLean 1986, Toronto)	<3	<20	25	10
Residential dirt walks in developed areas (Pitt and McLean 1986 Toronto)	<1	20	30	40
Rain quality (Rubin 1976 continental average)	n/a	21	n/a	107
Undeveloped areas (Denver Regional Council of Governments 1983; Pitt 1983, Ottawa; Pitt and Bozeman 1982, San Jose; Pitt and McLean 1986, Toronto)	<4	30	50	100
Landscaped areas in developed land uses (Pitt, *et al*. 1995 Birmingham)	0.5	81	24	230

* Average value followed by coefficient of variation, if available. Also shows the percentage of samples that had values greater than the detection limit for Outfall 008 and 009. When detection percent is <100%, average values are preceded with < signs indicating that the value shown is larger than the actual average, as non-detected observations were not used in the calculations.

Table 11. Average Total Metal Concentrations in Stormwater for Residential Areas

Average (COV)	Cadmium (µg/L)	Copper (µg/L)	Lead (µg/L)	Zinc (µg/L)
Residential roofs (Bannerman, *et al.* 1983, Milwaukee, WI; Pitt 1983 Ottawa; Pitt and Bozeman 1982, San Jose; Pitt and McLean 1986 Toronto)	0.3	5	30	390
Rain quality urban (Wilber and Hunter 1980 NJ)	n/a	6	45	44
Rain quality urban (Pitt and Bozeman 1982 San Jose)	n/a	10	<10	40
Residential streets (Pitt, *et al.* 2005 WI and MN)	0.6 (0.9)	18 (0.6)	24 (0.7)	151 (0.7)
Residential paved sidewalks (Pitt and McLean 1986 Toronto)	<4	20	80	60
Residential roofs (Pitt, *et al.* 2005 WI and MN)	0.5 (1.8)	21 (1.6)	43 (2.2)	185 (1.1)
Residential outfall, NSQD	n/a	27.3 (1.8)	25.8 (2.6)	125 (2.8)
Residential streets (Pitt and Bozeman 1982 San Jose; Pitt and McLean 1986 Toronto)	<5	35	425	160
Driveways (Pitt, *et al.* 2005 WI and MN)	0.9 (1.1)	37 (1.0)	57 (1.3)	164 (0.8)
Residential paved parking/storage (Pitt and McLean 1986 Toronto)	2	60	500	450
Roof runoff (Pitt, *et al.* 1995 Birmingham)	3.4	110	41	250
Residential paved driveways (Pitt and McLean 1986 Toronto)	5	210	1400	1000
Street runoff (Pitt, *et al*. 1995 Birmingham)	37	280	43	58
Outfall 008	<0.21 (1.8) [74%]**	<6.8 (0.6) [95%]	11.9 (2.3) [100%]	<24 (0.5) [80%]
Outfall 009	<0.62 (3.3) [67%]	6.8 (1.2) [100%]	<6.1 (3.4) [87%]	40 (0.9) [100%]

* Outfall 008 and 009 data are also shown on this table as a reference.

** Average value followed by coefficient of variation, if available. Also shows the percentage of samples that had values greater than the detection limit for Outfall 008 and 009. When detection percent is <100%, average values are preceded with < signs indicating that the value shown is larger than the actual average, as non-detected observations were not used in the calculations.

Table 12. Average Total Metal Concentrations in Stormwater for Commercial Areas

Average (COV)	**Cadmium (µg/L)**	**Copper (µg/L)**	**Lead (µg/L)**	**Zinc (µg/L)**
Commercial roofs (Pitt, *et al.* 2005 WI and MN)	0.7 (1.0)	19 (0.8)	58 (1.1)	322 (0.54)
Commercial parking (Pitt, *et al.* 2005 WI and MN)	1.0 (0.7)	30 (0.8)	51 (0.8)	292 (0.9)
Commercial streets (Pitt, *et al.* 2005 WI and MN)	1.0 (0.7)	34 (0.6)	39 (0.7)	302 (1.0)
Commercial outfall (NSQD)	n/a	36.7 (2.3)	34.3 (1.6)	197 (1.4)
Commercial streets (Pitt and McLean 1986 Toronto)	<5	40	180	180
Commercial paved parking (Bannerman, *et al.* 1983 Milwaukee, WI; Denver Regional Council of Governments 1983; Pitt 1983 Ottawa; Pitt and Bozeman 1982 San Jose; Pitt and McLean 1986 Toronto; STORET*** Site #590866-2954309 Shop-Save-Durham, NH; STORET Site #596296-2954843 Huntington-Long Island, NY)	3	65	350	290
Commercial roofs (Bannerman, *et al.* 1983 Milwaukee, WI; Pitt and Bozeman 1982 San Jose)	n/a	110	25	200
Commercial paved parking (Pitt, *et al.* 1995 Birmingham)	6.3	116	46	110
Commercial vehicle service areas(Pitt, *et al.* 1995 Birmingham)	9.2	135	63	105
Outfall 008	<0.21 (1.8) [74%]**	<6.8 (0.6) [95%]	11.9 (2.3) [100%]	<24 (0.5) [80%]
Outfall 009	<0.62 (3.3) [67%]	6.8 (1.2) [100%]	<6.1 (3.4) [87%]	40 (0.9) [100%]

* Outfall 008 and 009 data are also shown on this table as a reference.

** Average value followed by coefficient of variation, if available. Also shows the percentage of samples that had values greater than the detection limit for Outfall 008 and 009. When detection percent is <100%, average values are preceded with < signs indicating that the value shown is larger than the actual average, as non-detected observations were not used in the calculations.

*** STORET data are from the EPA's STORET water quality database. These sites were NURP 1983 monitoring locations.

Table 13. Average Total Metal Concentrations in Stormwater for Industrial Areas

Average (COV)	**Cadmium (µg/L)**	**Copper (µg/L)**	**Lead (µg/L)**	**Zinc (µg/L)**
Industrial roofs (Pitt, *et al.* 2005 WI and MN)	0.3 (0.5)	9 (0.6)	8.3 (0.3)	319 (1.5)
Industrial roofs (Pitt and McLean 1986 Toronto)	<4	<20	<40	70
Industrial loading docks (Pitt, *et al*. 1995 Birmingham)	1.4	22	55	55
Industrial streets (Pitt, *et al.* 2005 WI and MN)	1.1 (0.8)	22 (0.6)	87 (0.7)	593 (0.5)
Industrial paved sidewalks (Pitt and McLean 1986 Toronto)	<4	30	<40	60
Industrial parking (Pitt, *et al.* 2005 WI and MN)	1.5 (0.5)	33 (0.5)	53 (0.5)	228 (0.7)
Industrial outfall (NSQD)	n/a	36.3 (2.1)	54.5 (1.86	382 (3.5)
Industrial paved driveways (Pitt and McLean 1986 Toronto)	<4	40	260	310
Galvanized metal runoff (Clark 2000)	n/a	41	32	10,200
Industrial unpaved storage (Pitt and McLean 1986 Toronto)	<4	120	210	410
Industrial unpaved driveways (Pitt and McLean 1986 Toronto)	<4	140	340	690
Industrial streets (Pitt and McLean 1986 Toronto)	<4	220	560	910
Industrial storage areas (Pitt, *et al.* 1995 Birmingham)	5.9	290	105	1730
Industrial paved parking/storage (Pitt and McLean 1986 Toronto; STORET*** Site #590866-2954309 Shop-Save-Durham, NH)	<4	370	250	480
CCA-treated plywood runoff (Clark 2000)	n/a	1,300	33	93
Outfall 008	<0.21 (1.8) [74%]**	<6.8 (0.6) [95%]	11.9 (2.3) [100%]	<24 (0.5) [80%]
Outfall 009	<0.62 (3.3) [67%]	6.8 (1.2) [100%]	<6.1 (3.4) [87%]	40 (0.9) [100%]

* Outfall 008 and 009 data are also shown on this table as a reference.

** Average value followed by coefficient of variation, if available. Also shows the percentage of samples that had values greater than the detection limit for Outfall 008 and 009. When detection percent is <100%, average values are preceded with < signs indicating that the value shown is larger than the actual average, as non-detected observations were not used in the calculations.

*** STORET data are from the EPA's STORET water quality database. These sites were NURP 1983 monitoring locations.

Table 14. Average Total Metal Concentrations in Stormwater for Freeways

Average (COV)	Cadmium (μg/L)	Copper (μg/L)	Lead (μg/L)	Zinc (μg/L)
Freeways outfall, NSQD	n/a	32.5 (2.2)	70.8 (1.1)	160 (1.4)
Freeways (Pitt, *et al.* 2005 WI and MN)	0.7 (0.4)	59 (0.6)	34 (1.2)	233 (0.8)
Freeway paved lane and shoulders (Shelly and Gaboury 1986 Milwaukee)	60	120	2000	460
Outfall 008	<0.21 (1.8) [74%]**	<6.8 (0.6) [95%]	11.9 (2.3) [100%]	<24 (0.5) [80%]
Outfall 009	<0.62 (3.3) [67%]	6.8 (1.2) [100%]	<6.1 (3.4) [87%]	40 (0.9) [100%]

* Outfall 008 and 009 data are also shown on this table as a reference.

** Average value followed by coefficient of variation, if available. Also shows the percentage of samples that had values greater than the detection limit for Outfall 008 and 009. When detection percent is <100%, average values are preceded with < signs indicating that the value shown is larger than the actual average, as non-detected observations were not used in the calculations.

3.1 Pollutant Strengths of Stormwater Particulates and Sources of Contaminants

Pollutant strengths are the contaminant concentrations associated with the particulate matter in the stormwater. As such, these values can be used to help identify sources of these contaminants, based on their similar values to particulates found within the watershed. Particulate strengths are determined by calculating the pollutant concentration only associated with the particulates (measured as TSS or SSC) in the runoff water. They are calculated by the following equation:

$$\frac{(total\ conc. - filterable\ conc.)}{particulate\ solids\ conc.}$$

As an example, if the total copper concentration was 50 μg/L, the filterable (“dissolved”) copper concentration was 10 μg/L, and the TSS concentration was 150 mg/L, the particulate strength for this sample would be:

$$\frac{\left(50\ \mu\frac{gCu}{L} - 10\mu\frac{gCu}{L}\right)}{150\ mg/L} = 0.26\ \mu\frac{gCu}{mg\ solids} = 260\ \mu\text{g Cu/g solids} =$$

260 mg Cu/kg solids (also = 260 ppm)

This value is therefore the metal concentration associated with the particulate matter in the runoff sample. These values are very useful when identifying erosion and other sources of the particulate-bound pollutants in the runoff, in contrast to the μg/L concentration values that are affected by dilution and site hydrology. As an example, the particulate strength data presented in this report for the outfall samples are compared to typical particulate strength data for soils and for regional dry atmospheric deposition material. These values are also compared to different land uses to show how they are affected by increasing site activities. Finally, values for background soil concentrations are used in conjunction with site TSS observations to calculate metal concentrations for comparison to the current site permit limits.

Tables 18 through 22 summarize pollutant strengths that are presented in Appendix B of this report. These are divided by general land use categories and data are summarized for copper, lead, nickel, zinc, and chromium, the most commonly available data for particulate strength, although nickel is frequently missing. The rows are sorted based on the copper concentrations, from smallest to largest observed average concentrations, except that any n/a copper sources are listed last.

There are relatively few SSFL particulate strength data available since dissolved/filterable metals were only recently incorporated into their monitoring suite, and observed concentrations for TSS, total and filterable forms of the metals are all necessary for each individual sample in order to calculate these values. This paucity of data makes overall comparisons difficult. For Outfall 009, four events had total cadmium observations, while all the filtered cadmium values were less than the detection limit. The situation was similar for chromium. The calculations substituted half of the detection limit for the non-detected values, which is considered acceptable given the low dissolved fraction of these total metal results. This increases the uncertainty of the particulate strength results, but does provide values that are similar to the values obtained using a Monte Carlo analysis with wide ranging substitutions over the complete range of possible values. In contrast to cadmium and chromium, all of the copper, lead, and 2 of 3 of the filtered zinc were above the detection limits. There were also a few TSS values that were below the detection limits. Additional data, especially with lower detection limits, would improve these analyses. However, these data are still very useful for comparisons to the values for other conditions and land uses.

An important comparison is with on-site and nearby data obtained as part of the Soils Background Report (MWH 2005). Sampling locations were selected within and surrounding the SSFL in areas not impacted by site activities to provide data representative of ambient or local soil conditions. As part of the MWH study, forty-one soil samples were collected at 29 agency-approved locations during several sampling periods, as described below:

- Nine samples collected by McLaren/Hart in 1992 for analyses of 13 metals (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc);

- Seven samples collected by ICF Kaiser in 1995 for analyses of 17 metals (barium, cobalt, molybdenum, and vanadium in addition to the target list utilized by McLaren/Hart);

- Fifteen samples collected by Ogden in 1996 for analyses of 18 metals (aluminum added to the analytical suite);

- Seven samples collected by Ogden in 1998 for analyses of 19 metals (boron added to the analytical suite);

- Three samples collected by Ogden in 2000 and analyzed for the same 19 metals; and

- Forty supplemental samples collected by MWH in 2005, which added fluoride and six metals (iron, lithium, manganese, potassium, sodium, and zirconium) to the target list, resulting in a total of 25 metals in the validated analyses.

Using these soil sampling results, MWH (2005) evaluated the spatial and vertical distribution of the metal data and found no consistent pattern in observed concentrations. They therefore concluded that there was no airborne dispersion and deposition of metal contaminants from SSFL operations at these sampling locations nearby and on the SSFL property in areas where no site activity was occurring. It was determined that the entire metals background data set (shown in Table 15 for selected heavy metals) was representative of ambient conditions (i.e., background) based on the overall consistency in the observed concentrations (narrow range of COV values), and because the detected concentrations were within the range of concentrations observed for California soils. The reference background soil concentrations used to evaluate potentially contaminated areas on the SSFL are the maximum values shown on this table.

Table 15. SSFL Background Metal Analyses for Soil Samples (summarized by MWH 2005)

Metal (mg/kg)	# of samples (detected/total)	Minimum detected	Maximum	Mean*	COV*
Aluminum	38/38	5600	20,000	12,000	0.26
Antimony	13/37	3.1	8.7	2.4	1.2
Arsenic	33/38	1.7	15	4.4	0.73
Beryllium	36/38	0.28	1.1	0.58	0.39
Cadmium	9/38	0.22	1	0.25	0.89
Chromium	38/38	8.8	36.8	19	0.3
Copper	38/38	3.8	29	11	0.49
Iron	37/37	12,000	28,000	20,000	0.24
Lead	38/38	4.2	34	15	0.50
Manganese	37/37	190	495	319	0.21
Mercury	22/37	0.019	0.09	0.044	0.46
Nickel	38/38	5.2	29	13	0.33
Selenium	16/37	0.21	0.65	0.44	0.71
Thallium	13/37	0.13	0.46	0.19	0.56
Zinc	38/38	32	110	57	0.27
Zirconium	30/37	1.7	8.6	3.2	0.64

* Using ½ of the detection limit for non-detected values

Other site soil data were recently obtained as part of the Final ISRA Report: Interim Source Removal Action (ISRA) Workplan (MWH 2009). During this data collection effort, samples were collected from 52 locations between February and April 2009 on the SSFL site in watersheds draining to Outfalls 008 and 009. The low number of subsurface samples is due to the presence of bedrock at depths less than three feet below the ground surface at most of the sample locations. Available data for these samples are shown in Tables 16 and 17.

Table 16. Metal Concentrations in 008 Drainage Area Soil Samples (mg/kg) (MWH 2009)

	# of samples	Minimum	Maximum	Mean	COV
Arsenic	9	2.1	5.4	4.3	0.21
Cadmium	17	0.096	0.41	0.30	0.38
Copper	17	0.33	26	11	0.63
Lead	37	2.1	54	14	0.65
Zinc	11	46	78	57	0.19

Table 17. Metal Concentrations in 009 Drainage Area Soil Samples (mg/kg) (MWH 2009)

	# of samples	Minimum	Maximum	Mean	COV
Cadmium	4	0.095	0.17	0.12	0.31
Copper	2	20	21	20	0.042
Lead	4	5.5	10	7.4	0.28
Mercury	4	0.0039	0.017	0.011	0.52

Table 18 summarizes the SSFL sotrmwater particulate strength data for outfalls 001, 002, 008, and 009. The Outfall 001 and 002 drainage areas are similar to the 008 and 009 areas in that they don't have any stormwater controls in place, they are large open space watersheds, and they are entirely in the SSFL buffer zone, so they have never had historic industrial activities occurring there. However, they do receive discharges from the treatment controls at Outfalls 011 and 018, so they are not completely unaffected by site activities. Background soil concentrations for the site are also included in Table 18 for comparison, as well as stormwater monitoring data for open space land use sites from various studies.

As shown in Table 18, ***the SSFL copper particulate strength data are intermediate compared to the reported values for open space and undeveloped land and indicate relatively little potential contamination. However, the lead particulate strength data for Outfall 009 is relatively large and indicates potential contamination (which is consistent with known issues that are currently being addressed upstream in the drainage and an ongoing cleanup action is occurring in and near the channel), although the total lead outfall concentrations are low compared to the other open space and undeveloped areas. Zinc particulate strength data from Outfall 009 (and Outfall 002) are also relatively high compared to the other open space/undeveloped data. Both of these high lead and zinc conditions are more in line with observations obtained from other developed land uses, as shown on the other tables. It is interesting to note that the SSFL site background soil samples and the more recent ISRA soil samples have particulate strength concentration values amongst the lowest compared to all of the open space and undeveloped land sample data shown on Table 18. These site soil data are lower than the outfall particulate strength data, likely because they are bulk soil samples and include all of the soil particle sizes, while the outfall sample particulate strengths (representing eroded/resuspended particles) are more greatly influenced by the smallest particle sizes, usually having the highest pollutant strengths.*** Again, the few outfall data observations (mostly limited by number of dissolved metal results) result in more uncertainty than desired, but the additional site data substantiate these results through their weight-of-evidence.

In some cases, such as the mass balance studies conducted in Toronto, Wisconsin, and Birmingham, the particle strength data were an important aspect of the field monitoring activities and therefore are better represented. In other studies, such as the San Jose and Castro Valley, CA, and Bellevue, WA, projects, most of the field activities involved extensive street dirt measurements for the major land uses, and a great amount of these data are represented in the tables. In many cases, average and COV (coefficient of variation, or the standard deviation divided by the mean) values are given for the values where enough data is represented, or the data was available to calculate the values. In other cases, where only data summaries were available, only averages are presented.

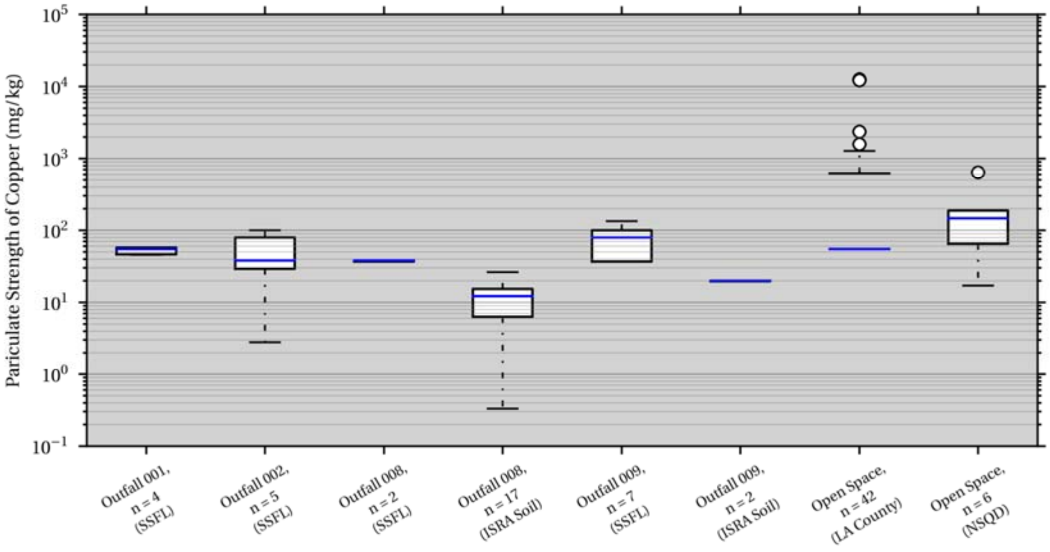
This is further shown in Figures 15 through 18, which compare particulate strength data from the SSFL outfalls with runoff monitoring data for other land uses from the NSQD. In most cases, based on the land use datasets summarized above, obvious trends are seen with increasing particulate strengths for all of the metals as the site activities (such as vehicle usage) increase, as was indicated in the summaries for the total forms of the metals.

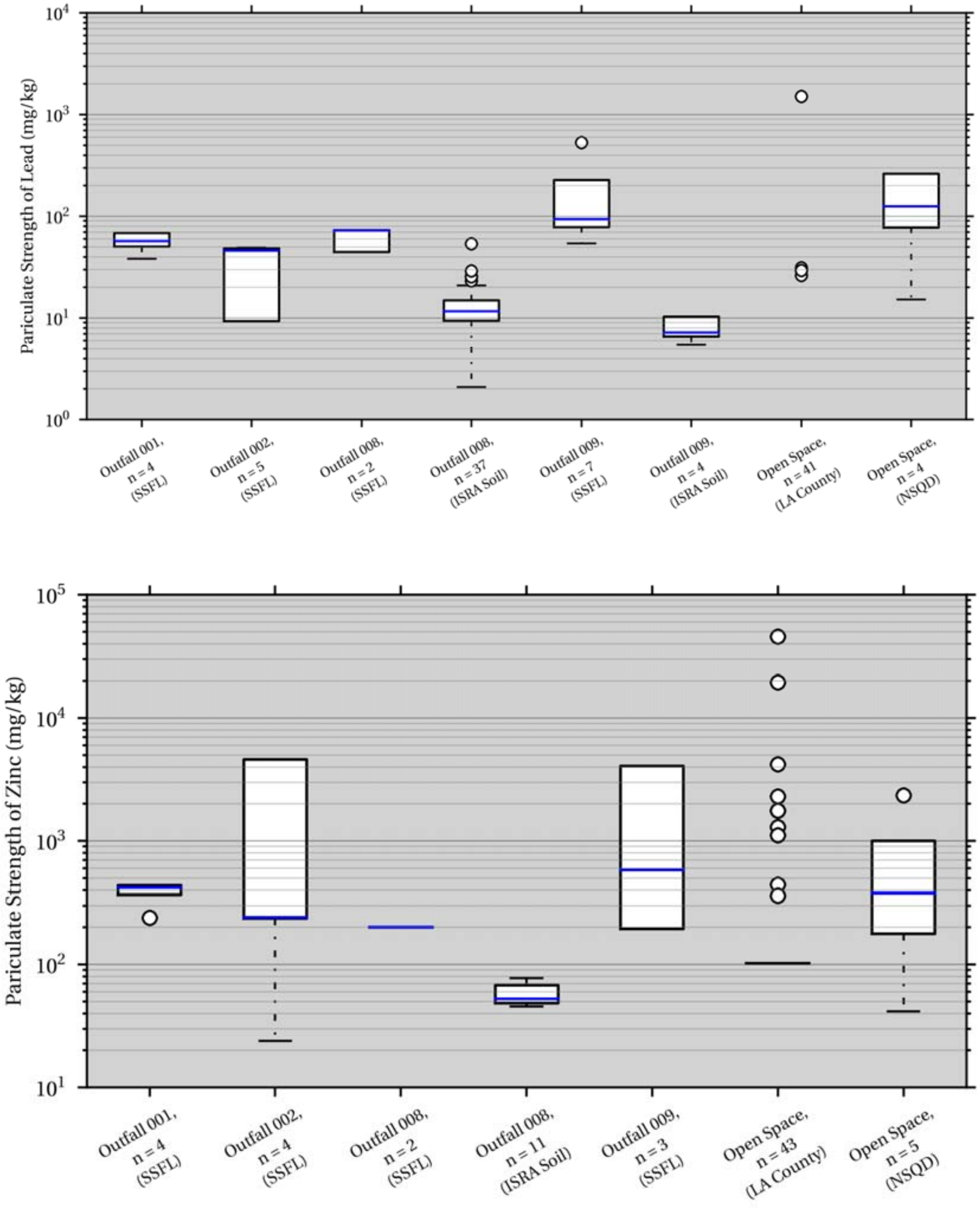
Table 18. Open Space, Undeveloped Land, Bare Soil Samples Particulate Strengths

	Copper (mg Cu/kg SS)	Lead (mg Pb/kg SS)	Nickel (mg Ni/kg SS)	Zinc (mg Zn/kg SS)	Chromium (mg Cr/kg SS)
SSFL background soil samples (MWH 2005)	11 (0.5)*	15 (0.5)	14 (0.3)	57 (0.3)	19 (0.3)
SSFL ISRA soil samples in watershed 008 (MWH 2009)	11 (0.6)	14 (0.7)	n/a	57 (0.2)	n/a
Small landscaped areas (Pitt 2004 WI and MN sheetflow)	14 (0.4)	250 (1.1)	n/a	160 (1.3)	20
Resid./Commer. dirt path (Pitt and McLean 1986, Toronto, Ontario 125μm)	15	38	n/a	50	25
SSFL ISRA soil samples in watershed 009 (MWH 2009)	20 (0.04)	7.4 (0.3)	n/a	n/a	n/a
Soils (Hurley 2009)	25	19	19	60	54
California benchmark soils (Kearney 1996)	29 (9.1 to 96)	24 (12 to 97)	57 (9 to 510)	150 (88 to 240)	120 (23 to 1600)
Resid./Commer. garden soil (Pitt and McLean 1986, Toronto, Ontario 125μm)	30	50	n/a	120	35
Santa Susana Field Laboratory Outfall 008 samples	37 (37 and 38)	59 (45 and 73)	n/a	200 (both at 200)	28 (nd and 57)
Santa Susana Field Laboratory Outfall 002 samples	50 (3 to 100)	31 (nd to 49)	n/a	1280 (24 to 4600)	87 (nd to 220)
Santa Susana Field Laboratory Outfall 001 samples	51 (45 to 58)	53 (38 to 68)	n/a	370 (240 to 440)	75 (nd and 150)
Santa Susana Field Laboratory Outfall 009 samples	70 (37 to 130)	170 (54 to 530)	n/a	1620 (190 to 4100)	63 (nd to 150)
Industrial bare ground (Pitt and McLean 1986, Toronto, Ontario 125μm)	91	135	n/a	270	38
Open Space NSQD outfalls	188 (1.2)	120 (0.9)	n/a	789 (1.2)	n/a
Dustfall Oceanic (Rubin 1976)	4500	n/a	n/a	230	38
Undeveloped (Pitt 2004 WI and MN sheetflow)	n/a	48	n/a	n/a	n/a

* Average and coefficient of variation values (where available). In some cases (XX to YY), the parenthetical values show the range.

Figure 15 presents particulate strength box and whisker plots for cadmium, chromium, copper, lead, and zinc indicating the observed ranges and comparisons of these data for the different sites. For these box and whisker plots, the centerlines represent median values (50th percentile concentrations), the boxes indicate the interquartile range (or the 25th and 75th percentile concentrations), the whiskers represent the 5th and 95th percentile values, and the dots represent results beyond the whiskers; missing boxes indicate insufficient data to compute accurate percentile values. There are few data available, but it is clear the Outfall 009 lead particulate strength values are noticeably larger than for the other three site outfalls shown. This may be associated with the known lead contamination issues in the Northern Drainage area within the Outfall 009 watershed that are in the process of being addressed. Los Angeles undeveloped watershed particulate strength data (calculated from data presented by Stein and Yoon, SSWRP 2007) is also shown for copper, zinc, and lead (not available for the other metals plotted). The regional LA County particulate strength data for copper appears to be noticeably larger than for the site outfall data, while the regional zinc data tends to mostly overlap the observed site data, but with some higher values.





Figures 15a, 15b, and 15c. Particulate strength data for copper, lead, and zinc, respectively, for SSFL outfalls compared with LA County and NSQD open space areas.

Table 19. Residential Area Samples Particulate Strengths

	Copper (mg Cu/kg SS)	Lead (mg Pb/kg SS)	Nickel (mg Ni/kg SS)	Zinc (mg Zn/kg SS)	Chromium (mg Cr/kg SS)
Resid./Commer. road shoulder (Pitt and McLean 1986, Toronto, Ontario 125µm)	35	230	n/a	120	25
Residential streets (Pitt 2004 WI and MN sheetflow)	39 (0.6)*	87 (0.6)	n/a	350 (0.6)	11 (0.8)
Resid./Commer. pvd sidewalk (Pitt and McLean 1986, Toronto, Ontario 125µm)	44	1200	n/a	430	32
Resid./Commer. unpvd parking (Pitt and McLean 1986, Toronto, Ontario 125µm)	45	160	n/a	170	20
Paved driveways (Pitt 2004 WI and MN sheetflow)	89 (1.0)	240 (0.8)	n/a	650 (0.5)	11 (0.1)
Resid./Commer. roofs (Pitt and McLean 1986, Toronto, Ontario 125µm)	130	980	n/a	1900	77
Resid./Commer. pvd parking (Pitt and McLean 1986, Toronto, Ontario 125µm)	145	630	n/a	420	47
Residential roofs (Pitt 2004 WI and MN sheetflow)	160 (1.3)	870 (0.8)	n/a	2900 (0.6)	n/a
Resid./Comer. pvd driveways (Pitt and McLean 1986, Toronto, Ontario 125µm)	170	900	n/a	800	70
Street Dirt Residential (Pitt 1979, San Jose, CA <45 µm; Pitt 1985, Bellevue, WA) <63 µm; Pitt and McLean 1986, Toronto, Ontario <125 µm, Pitt and Sutherland 1982, Reno/Sparks, NV <63 µ)	230	1615	n/a	431	81
Residential NSQD outfalls	431 (2.6)	358 (2.1)	48 (1.4)	1262 (1.4)	n/a
Dustfall Urban (Rubin 1976)	1900	n/a	950	6700	190
Dustfall Suburban (Rubin 1976)	2700	n/a	1400	1400	270
Santa Susana Field Laboratory Outfall 008 samples**	37 (37 and 38)	59 (45 and 73)	n/a	200 (both at 200)	28 (nd and 57)
Santa Susana Field Laboratory Outfall 009 samples**	70 (37 to 130)	170 (54 to 530)	n/a	1620 (190 to 4100)	63 (nd to 150)

* Average and coefficient of variation values (where available). In some cases (XX to YY), the parenthetical values show the range.

**SSFL Outfall 008 and 009 samples shown for comparison

Table 20. Commercial Area Samples Particulate Strengths

	Copper (mg Cu/kg SS)	**Lead (mg Pb/kg SS)**	**Nickel (mg Ni/kg SS)**	**Zinc (mg Zn/kg SS)**	**Chromium (mg Cr/kg SS)**
Commercial parking (Pitt 2004 WI and MN sheetflow)	100 (0.7)*	320 (0.4)	n/a	802 (0.6)	47 (0.4)
Commercial streets (Pitt 2004 WI and MN sheetflow)	140 (1.3)	210 (0.5)	n/a	1150 (1.2)	38 (0.3)
Street Dirt Commercial (Bannerman, *et al*. 1983, Milwaukee, WI <31μm; Pitt 1979, San Jose, CA <45 μm; Pitt and Sutherland 1982, Reno/Sparks, NV <63 μm; Terstrip, *et al*. 1982, Champaign/Urbana, IL <63 μm)	175	4000	n/a	975	122
Commercial roofs (Pitt 2004 WI and MN sheetflow)	180 (1.0)	750 (0.5)	n/a	3500 (1.0)	n/a
Commercial NSQD outfalls	358 (1.8)	678 (1.1)	46 (1.4)	1218 (1.4)	n/a
Santa Susana Field Laboratory Outfall 008 samples**	37 (37 and 38)	59 (45 and 73)	n/a	200 (both at 200)	28 (nd and 57)
Santa Susana Field Laboratory Outfall 009 samples**	70 (37 to 130)	170 (54 to 530)	n/a	1620 (190 to 4100)	63 (nd to 150)

* Average and coefficient of variation values (where available). In some cases (XX to YY), the parenthetical values show the range.
**SSFL Outfall 008 and 009 samples shown for comparison

Table 21. Industrial Area Samples Particulate Strengths

	Copper (mg Cu/kg SS)	**Lead (mg Pb/kg SS)**	**Nickel (mg Ni/kg SS)**	**Zinc (mg Zn/kg SS)**	**Chromium (mg Cr/kg SS)**
Industrial streets (Pitt 2004 WI and MN sheetflow)	74 (0.4)*	100 (0.3)	n/a	540 (0.4)	24 (0.6)
Industrial parking (Pitt 2004 WI and MN sheetflow)	83 (0.5)	180 (0.5)	n/a	490 (0.5)	24 (0.4)
Industrial pvd path (Pitt and McLean 1986, Toronto, Ontario 125μm)	280	460	n/a	1300	63
Industrial NSQD outfalls	281 (0.6)	664 (0.9)	76 (0.6)	7147 (1.6)	n/a
Industrial street dirt (Pitt and McLean 1986, Toronto, Ontario <125 μm)	360	900	n/a	500	70
Industrial pvd parking (Pitt and McLean 1986, Toronto, Ontario 125μm)	1110	650	n/a	930	98
Industrial unpvd parking (Pitt and McLean 1986, Toronto, Ontario 125μm)	1120	2050	n/a	1120	62
Industrial roofs (Pitt 2004 WI and MN sheetflow)	n/a	220 (1.1)	n/a	n/a	n/a
Santa Susana Field Laboratory Outfall 008 samples**	37 (37 and 38)	59 (45 and 73)	n/a	200 (both at 200)	28 (nd and 57)
Santa Susana Field Laboratory Outfall 009 samples**	70 (37 to 130)	170 (54 to 530)	n/a	1620 (190 to 4100)	63 (nd to 150)

* Average and coefficient of variation values (where available). In some cases (XX to YY), the parenthetical values show the range.
**SSFL Outfall 008 and 009 samples shown for comparison

Table 22. Freeway Samples Particulate Strengths

	Copper (mg Cu/kg SS)	Lead (mg Pb/ kg SS)	Nickel (mg Ni/ kg SS)	Zinc (mg Zn/kg SS)	Chromium (mg Cr/kg SS)
Freeways NSQD outfalls	244 (0.7)*	375 (1.2)	51 (1.4)	1318 (0.6)	n/a
Freeways (Pitt 2004 WI and MN sheetflow)	300 (0.5)	230 (0.4)	n/a	1330 (0.4)	n/a
Dustfall (Spring 1978)	n/a	500 – 2800 (550 from and near LA freeway)	n/a	n/a	n/a
Santa Susana Field Laboratory Outfall 008 samples**	37 (37 and 38)	59 (45 and 73)	n/a	200 (both at 200)	28 (nd and 57)
Santa Susana Field Laboratory Outfall 009 samples**	70 (37 to 130)	170 (54 to 530)	n/a	1620 (190 to 4100)	63 (nd to 150)

* Average and coefficient of variation values (where available). In some cases (XX to YY), the parenthetical values show the range.
**SSFL Outfall 008 and 009 samples shown for comparison

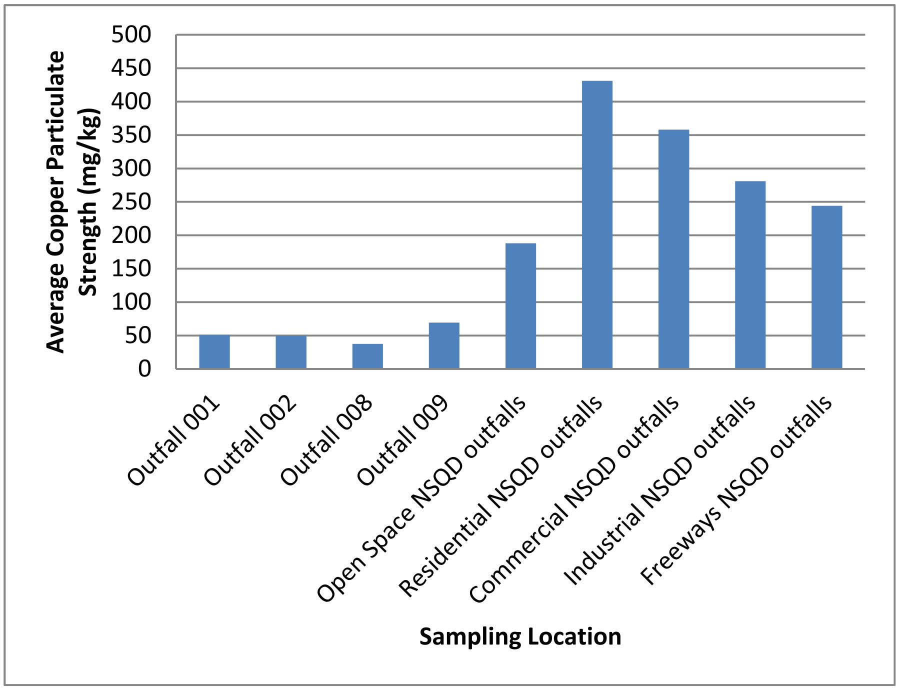


Figure 16. SSFL outfall copper particulate strength average values compared to outfall data from other land uses.

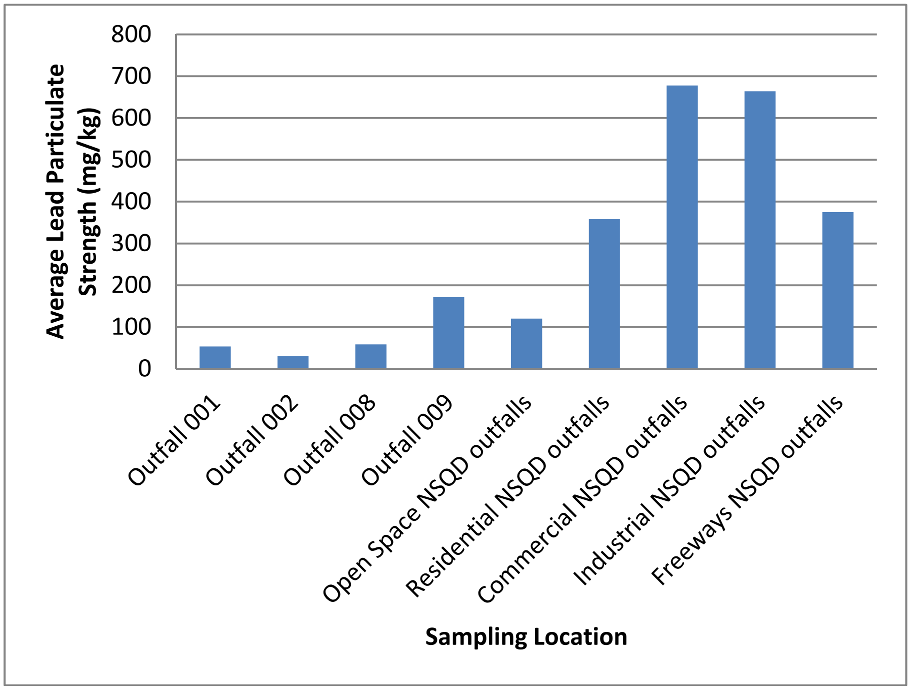


Figure 17. SSFL outfall lead particulate strength average values compared to outfall data from other land uses.

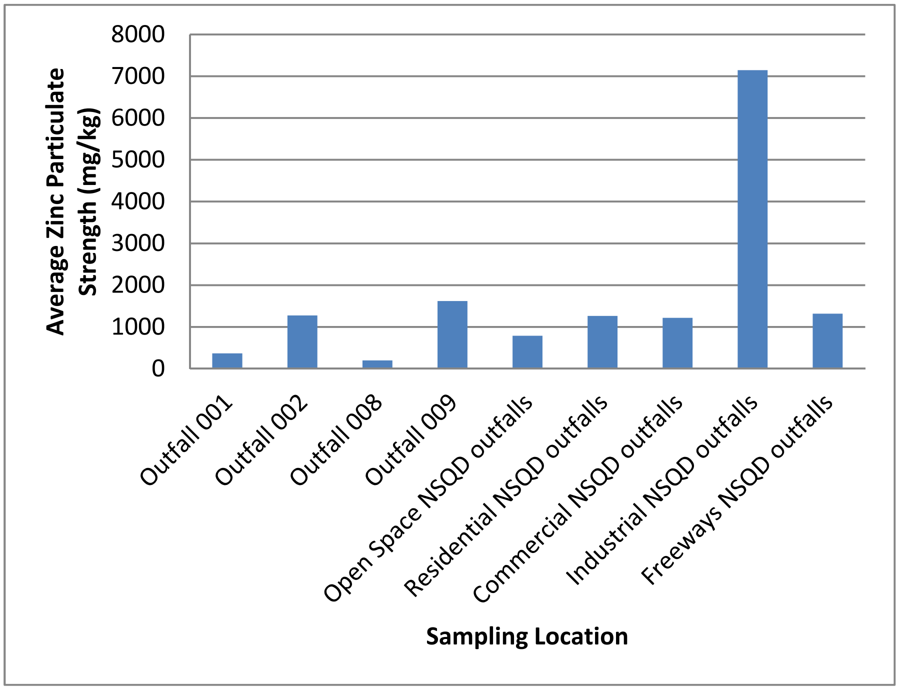


Figure 18. SSFL outfall zinc particulate strength average values compared to outfall data from other land uses.

3.1.1 Background Soils Concentrations Compared to Current Site Permit Limits

Table 23 shows the resulting outfall concentrations when the background average metal particulate strength values (from the MWH 2005 report) are used in conjunction with the overall average TSS concentrations at Outfalls 008 and 009. The metal concentrations are calculated by multiplying the TSS concentration by the particle strength, and then applying appropriate unit conversions. The resulting concentrations of the metals are compared to the existing permit limits on Table 23.

At Outfall 008, 10 of the 11 TSS outfall concentrations were greater than the 10 mg/L detection limit. The calculated average value of 257 mg/L was the same if the non-detected value was either 0 or 10 mg/L. At Outfall 009, only 6 of the 20 outfall TSS observations had detected values. When 0 or 10 mg/L were substituted for the non-detected values, the resulting average TSS ranged from only 250 to 257 mg/L, so an intermediate value of 253 is used in these calculations. Even though the number of non-detected observations were relatively large at Outfall 009, they had little effect on the calculated average TSS because the detection limit was relatively small compared to the observed values.

The calculate average lead concentrations are shown to exceed the SSFL permit limit by about 1.7 times, even if the site soils meet the background concentration criterion, as presented in the MWH (2005) report. The calculated copper concentrations are about half of the site permit limit, while antimony is about 40% of the permit limit, and mercury and zinc are about 20% of their permit limits. The other metals (cadmium, nickel, and thallium) are about 5 to 10% of their permit limits.

Table 23. Estimated SSFL Metal Concentrations in Stormwater Assuming Background Soils Resuspended at Average Stormwater TSS Concentrations

	Average TSS conc. (mg/L)	Average background metal particulate strength (mg metal/kg TSS)	Calculated average metal concentrations (μg/L)	Current Permit limit (μg/L)
Antimony				
008	257	8.7	2.2	6
009	253	8.7	2.2	6
Cadmium				
008	257	1	0.26	4
009	253	1	0.25	4
Copper				
008	257	29	7.5	14
009	253	29	7.3	14
Lead				
008	257	34	8.7	5.2
009	253	34	8.6	5.2
Mercury				
008	257	0.09	0.023	0.13
009	253	0.09	0.023	0.13
Nickel				
008	257	29	7.5	100

	Average TSS conc. (mg/L)	Average background metal particulate strength (mg metal/kg TSS)	Calculated average metal concentrations (μg/L)	Current Permit limit (μg/L)
009	253	29	7.4	100
Thallium				
008	257	0.46	0.12	2
009	253	0.46	0.12	2
Zinc				
008	257	110	28	159
009	253	110	28	159

3.2 Fingerprinting Potential Watershed Metal Sources

One of the traditional methods used to identify potential sources of contamination of environmental sources is through fingerprinting, or comparing patterns of relationships in concentrations between different samples. This technique has been extensively used in air quality studies to identify sources of dustfall contamination, for example. The Center for Watershed Protection and Pitt (2004) and Pitt, *et al.* (1993) have used these techniques for identifying sources of inappropriate discharges to storm drainage systems. The basic method is a linear algebra solution of simultaneous equations. Because of the uncertainty in the characteristics of the potential sources (and their likelihood of changing with time), a stochastic component is also added to the method, resulting in a description of the probability of the source components. A common feature of this method is having a comprehensive "library" of characteristics of potential sources, and extensive data for the receptor being studied.

Unfortunately, neither source nor receptor data is well described to identify potential metal sources at the SSFL. However, a preliminary assessment can be made to help substantiate findings from other approaches. One issue is the potential of atmospheric dustfall being a major source of heavy metals found at the site. Extensive regional air deposition measurements are available and have been used to calculate the total deposition to the Los Angeles River watershed by local water agencies (LA RWQCB and DPW) and research groups (SCCWRP). Their data is shown on Table 24, along with some calculated ratios. ***The most significant conclusion usually made is that the deposition flux is quite large compared to the total river discharge, especially for copper and zinc. This leads to the premature conclusion that the atmospheric flux is the most important source of metals to the river. Unfortunately, this does not consider the imbalance in other constituents, or, more importantly, the retention of the depositional material in the watershed, and the significance of other sources of metal pollutants in most land uses.***

Table 24. Los Angeles River Watershed Loads and Deposition Flux

	Annual average wet weather loads (kg/yr)	**Ratio of discharges compared to Cu**	**Atmospheric deposition flux to watershed (kg/yr)**	**Ratio of deposition flux compared to Cu**	**Ratio of atm. deposition flux to discharge load**
Copper	6,140	1.0	16,000	1.0	2.6
Lead	15,500	2.5	3,000	0.2	0.2
Zinc	32,800	5.3	28,200	1.8	0.9

Table 25 shows the particulate strengths, and their ratios compared to copper, for the background soils on the SSFL, the other obvious source of sediment and metals in the 008 and 009 stormwater. ***These ratios, especially for lead, are quite different compared to the ratios of the atmospheric deposition flux values. Therefore, comparing the outfall 008 and 009 lead and zinc to copper ratios enables the major sources to be identified (atmospheric deposition, site background soils, or other site contamination).***

Table 25. SSFL Background Soil Particulate Strengths (mg/kg TSS)

	Particulate strengths (mg/kg and COV)	**Ratio of particulate strengths compared to Cu**
Copper	11 (0.5)	1.0
Lead	15 (0.5)	1.4
Zinc	57 (0.3)	5.2

Tables 26 and 27 show the particulate strength ratios of lead and zinc to copper for outfall 008 and 009 stormwater samples for comparison to the ratios for atmospheric deposition and site background soil concentrations.

Table 26. Outfall 008 Lead and Zinc Particulate Strengths Compared to Copper Particulate Strength

Outfall 008	**Particulate strength**	**Ratio of particulate strengths compared to Cu**
Copper strength	37 (37 and 38) mg Cu/kg SS	1.0
Lead strength	59 (45 and 73) mg Pb/kg SS	1.6 ratio of Pb to Cu particulate strength
Zinc strength	200 (both 200) mg Zn/kg SS	5.4 ratio of Zn to Cu particulate strength

Table 27. Outfall 009 Lead and Zinc Particulate Strengths Compared to Copper Particulate Strength

Outfall 009	**Particulate strength**	**Ratio of particulate strengths compared to Cu**
Copper strength	70 (37 to 130) mg Cu/kg SS	1.0
Lead strength	170 (54 to 530) mg Pb/kg SS	2.4 ratio of Pb to Cu particulate strength
Zinc strength	1620 (190 to 4100) mg Zn/kg SS	23 ratio of Zn to Cu particulate strength

Tables 28 and 29 show the total lead and zinc to copper ratios for the outfall stormwater samples. Both outfalls have total copper, lead, and zinc concentrations for stormwater discharges (from grab samples).

Table 28. Outfall 008 Stormwater Total Lead and Zinc to Copper Ratios

Outfall 008	**Average total metal concentrations, detected only (COV) [%detected]**	**Ratio of avg total concentrations compared to Cu**
Total copper concentration	6.8 (0.6) [95%] µg/L	1.0
Total lead concentration	11.9 (2.3) [100%] µg/L	1.8 ratio of Pb to Cu total concentration
Total zinc concentration	24 (0.5) [83%] µg/L	3.5 ratio of Zn to Cu total concentration

Table 29. Outfall 009 Stormwater Total Lead and Zinc to Copper Ratios

Outfall 009	Average total metal concentrations, detected only (COV) [%detected]	Ratio of avg total concentrations compared to Cu
Total copper concentration	6.9 (1.3) [100%] µg/L	1.0
Total lead concentration	17.5 (3.1) [89%] µg/L	2.5 ratio of Pb to Cu total concentration
Total zinc concentration	36 (1.2) [100%] µg/L	5.2 ratio of Zn to Cu total concentration

If both metals were strongly associated with the atmospheric deposition, the lead particulate strength would either be much less than (i.e. about 20% of) the copper strengths, or other sources would be contributing to the lead discharges. However, the Outfall 009 copper particulate strength value is near the low end of typical soil values while the lead is much greater, not less. ***The high Outfall 009 lead particulate strength is not surprising, considering the lead cleanup activities that have been on-going in the northern drainage section of this area due a historic shooting range located there***. The ratios for the total copper to total lead concentrations at both outfalls also show high ratios, also indicating that atmospheric deposition can't be responsible for both metals. The ratios for Outfall 008 stormwater particulate strengths offer similar findings, but the lead values are not as great as for Outfall 009. ***The zinc particulate strength values at Outfall 009 are also high and indicate additional contamination compared to the copper values. It should be noted that zinc in stormwater has not been observed at concentrations above the SSFL current permit daily maximum benchmarks at Outfalls 001, 002, 008, or 009 (the outfalls studied here) except for one event in September 2007 due to a mudslide immediately upstream of Outfall 002 that resulted in a TSS measurement of 33,000 mg/L. It is also interesting to note that the Outfall 008 particulate strength ratios are very similar to the ratios for the background soil metal ratios, indicating the soil is the likely major source of the metals at Outfall 008.***

Retention of atmospheric deposition material in the watershed is very likely due to the erosion/sedimentation processes. It is expected that the very small sized deposition material may have a yield from <1 to 10% from the pervious areas of the watershed and up to about 50% from the impervious areas, based on historical washoff observations and mass balance monitoring in urban areas (summarized in the appendix; Pitt 1979; 1983; with McLean 1986; 1987, amongst others). With the watersheds being about 80 to 90% pervious, it is expected that most of the depositional material would be retained with the site soils. This is more obvious when conducting a full mass balance in an urbanized watershed where runoff samples are obtained from many source areas, and from the outfall. In these cases, roof runoff usually has the lowest concentrations of most pollutants (a common exception is for zinc when galvanized metals are used as part of the roof, or sometimes elevated copper when that metal is used as a roof flashing), and runoff from other surfaces show obvious contamination from other site activities. If atmospheric deposition was the most important source of the stormwater metals, then the runoff quality from all of the areas would not differ significantly from the roof runoff.

In a heavily urbanized region, such as the Los Angeles area, it is likely that atmospheric deposition materials do contribute important stormwater pollutants; however, they are not likely the most important source of most contaminants. Close-by fugitive dust sources (such as major roadways or manufacturing industrial areas) likely have a much greater effect than the regional fugitive dust sources (such as industrial atmospheric particulates or heavy vehicle particulate emissions from major roads). However, unique emissions of certain pollutants, such as mercury and some organics from regional fossil fuel fired power plants, may be the most important source of some stormwater pollutants that do not have major local sources.

The data shown for treated wood and galvanized metals also indicate that they may be important sources of copper/chromium/arsenic and zinc in areas where these materials may be found. CCA-treated wood is seldom used in current construction, but historically, it was commonly used in many areas. Current research investigating ash from burned CCA-treated wood also indicates that these metals can be easily transported in the runoff from the burn areas. Similar sources may be associated with ash from combustion of creosote treated wood (utility poles).

With the limited data available, it seems likely that copper concentrations at both Outfalls 008 and 009, and lead and zinc concentrations at Outfall 008, are likely primarily due to erosion of natural site soils, while the elevated Outfall 009 lead concentrations (which are also partly due to erosion of natural soils) are likely affected by the site lead contamination in the northern drainage area, which is currently being addressed by an ongoing cleanup action. The elevated zinc concentrations observed at Outfall 009 may be associated with galvanized metals in the drainage area, although it should be noted that the zinc concentrations in the stormwater has not been observed at concentrations above the SSFL current permit daily maximum benchmarks at this outfall. Currently, there is insufficient data for the other metals due to the large fraction of undetected concentrations reported, especially for the filtered metals. It is hoped that future data will result in additional information that can be used to extend these analyses and decrease the uncertainty.

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Appendix A: National Stormwater Quality Database Metals Data

The University of Alabama and the Center for Watershed Protection were awarded a U.S. Environmental Protection Agency, Office of Water 104(b)3 grant in 2001 to collect and evaluate stormwater data from a portion of the NPDES (National Pollutant Discharge Elimination System) MS4 (municipal separate storm sewer system) stormwater permit holders. Version 3 of this database has recently been completed under continued 104(b)3 support from the EPA. These stormwater quality data and site descriptions were collected and reviewed to describe the characteristics of national stormwater quality, to provide guidance for future sampling needs, and to enhance local stormwater management activities in areas having limited data. The monitoring data collected over nearly a ten-year period from more than 200 municipalities throughout the country have a great potential in characterizing the quality of stormwater runoff and comparing it against historical benchmarks. This project is creating a national database of stormwater monitoring data collected as part of the existing stormwater permit program, providing a scientific analysis of the data, and providing recommendations for improving the quality and management value of future NPDES monitoring efforts. Version 3 contains data from more than 8,500 events from about 100 municipalities throughout the country, representing several land uses.

The complete National Stormwater Quality Database (NSQD) Version 3 is available as a large (7.5Mb) Excel spreadsheet at: http://unix.eng.ua.edu/~rpitt/Research/ms4/mainms4.shtml. Detailed statistical analyses and site descriptions are available in the EPA final report for the version 1.1 database located at:
http://unix.eng.ua.edu/~rpitt/Publications/Stormwater%20Characteristics/NSQD%20EPA.pdf

The NSQD Version 3 is a compilation of data collected from various stormwater sampling efforts including; the Nationwide Urban Runoff Program (NURP) (EPA 1983) [excluding lead data which has significantly reduced with time as a result of the elimination of lead in gasoline]; the International BMP Database (ASCE 2002) [only influent data to stormwater controls located at outfall locations]; the U.S. Geological Survey (USGS) Urban-Stormwater Database (Smullen and Case, 2002; Driver, *et al.* 1985) [associated with MS4 monitoring activities conducted by the USGS]; the data from the earlier National Stormwater Quality Database NSQD ver. 1.1, and additional data collected from other Phase 1 NPDES MS4 stormwater permit holders as part of this newer effort. Most of the data are from MS4 communities from their current permits. The earlier NURP data was extremely helpful in obtaining needed data from the upper Midwest and northeastern areas of the country. The other databases also helped in obtaining information for under-represented situations. All of the data underwent extensive quality control/quality assurance reviews before it was added to the NSQD.

More than 8,500 events are now in Version 3 of the NSQD. Table A1 shows the 12 land uses, 9 EPA Rain Zones and four seasons identified in the assembled database. The land uses were assigned categories according to their predominant land use in the watershed. When more than one land use was present it was considered a mixed site with the major land use noted. About 30% of the storm events stored in the database were collected in residential land use areas, followed by mixed residential and commercial areas with 16% and 15% of the total events respectively. More than 5,800 events represent single land use areas, as shown in Table A2.

More than 100 events represent each EPA Rain Zone, except for rain zone 8, where very few single land use sites are available. Most of the single land use sites represent residential, commercial, and industrial areas in EPA Rain Zones 1, 2, 3, 4, 5, 6, and 7, with 32 to 1,470 events per rain zone per land use. Many freeway data are also available, but they only represent EPA Rain Zones 2, 5, and 6. Figure A1 is a map showing the EPA Rain Zones in the U.S., along with the locations of the communities represented in the database.

Table A1. Main land uses, EPA Rain Zones and seasons identified in the assembled database

LAND USE	EPA RAIN ZONE	SEASON
Commercial	Zone 1 – Great Lakes	Spring: February – April
Freeway	Zone 2 – Northeast	Summer: May – July
Industrial	Zone 3 – Southeast	Fall: August – October
Institutional	Zone 4 – Lower Mississippi Valley	Winter: November – January
Open Space	Zone 5 – Texas	
Residential	Zone 6 – Southwest	
Mixed Commercial	Zone 7 – Northwest	
Mixed Freeway	Zone 8 – California	
Mixed Industrial	Zone 9 – Rocky Mountains	
Mixed Institutional		
Mixed Open Space		
Mixed Residential		

Table A2. Number of events for EPA Rain Zone for single land use sites

Single land use	1	2	3	4	5	6	7	8	9	Total
Commercial	234	484	131	66	42	37	64	0	22	1080
Freeways	0	241	14	0	262	189	28	0	0	734
Industrial	100	327	90	51	83	74	146	0	22	893
Institutional	9	46	0	0	0	0	0	0	0	55
Open Space	68	37	0	18	0	2	0	0	0	125
Residential	294	1470	290	122	105	32	532	7	81	2933
Total	705	2605	525	257	492	334	770	7	125	5820

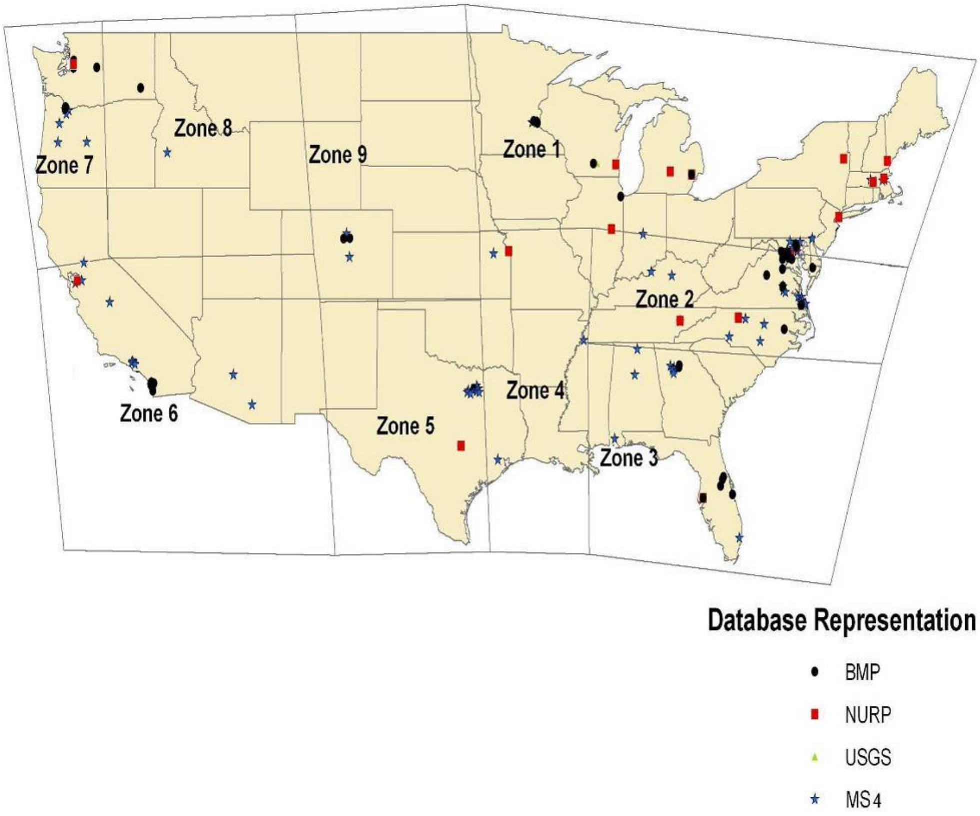


Figure A1. Sampling Locations for Data Contained in the National Stormwater Quality Database, Version 3.

These data were extensively reviewed, and additional NPDES data were collected from the northeast for this project phase for the completion of NSQD Version 3. The EPA's NURP data (EPA, 1983) was found to be a good source of this additional information, and after extensive reviews, that data was entered in the NSQD (except for lead). The NSQD Version 3 now contains extensive data for: total suspended solids (TSS), 5-day biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total phosphorus (TP), Total Kjeldahl Nitrogen (TKN), nitrite plus nitrate (NO2+NO3), total copper (Cu), total lead (Pb), and total zinc (Zn), and less data for many other constituents. Table A3 is a summary of the stormwater data included in NSQD Version 3. This table describes the total number of observations, the percentage of observations above the detection limits, average, median, and coefficients of variations for TSS, COD, fecal coliforms, total phosphorus, total copper, and total zinc for residential, commercial, industrial, institutional, freeways, and open space single land use categories, although relatively few data are available for institutional and open space areas. About 5,800 samples represent these single land use areas, with a total of 8,139 events when the mixed land use sites are included.

Table A3. Summary of Selected Stormwater Quality Data Included in NSQD, Version 3.0

	TSS (mg/L)	COD (mg/L)	Fecal Colif. (mpn/100 mL)	Phosphorus, total (mg/L)	Cu, total (µg/L)	Zn, total (µg/L)
All Areas Combined (8,139 events)						
Average	137.0	77.6	47665	0.4	30.1	181.1
Coef. of variation (COV)	2.2	1.1	5.0	2.8	2.1	3.3
Median	62.0	53.0	4300	0.2	15.0	90.0
Number of samples	6780	5070	2154	7425	5165	6184
% of samples above detection	99	99	91	97	88	98
All Residential Areas Combined (2,586 events)						
Average	122.7	68.8	55891	0.4	27.1	123.2
Coef. of variation (COV)	2.0	1.0	5.7	1.6	1.9	3.3
Median	59.0	50.0	4200	0.3	12.0	70.0
Number of samples	2167	1473	505	2286	1640	1912
% of samples above detection	99	99	89	98	88	97
All Commercial Areas Combined (916 events)						
Average	118.2	90.7	26065	0.3	31.4	197.5
Coef. of variation (COV)	1.7	1.0	3.0	1.2	1.4	1.4
Median	55.0	63.0	3000	0.2	17.9	110.0
Number of samples	843	640	270	920	753	839
% of samples above detection	97	98	89	95	85	99
All Industrial Areas Combined (719 events)						
Average	171.0	97.6	47329	0.4	40.6	243.9
Coef. of variation (COV)	1.7	1.3	6.1	1.4	2.1	1.7
Median	73.0	59.0	2850	0.2	19.0	156.2
Number of samples	594	474	317	605	536	596
% of samples above detection	98	98	94	95	86	99
All Freeway Areas Combined (680 events)						
Average	113.7	88.2	8553	0.7	33.7	162.4
Coef. of variation (COV)	2.6	1.0	2.7	5.2	2.2	1.4
Median	53.0	64.0	2000	0.3	17.8	100.0
Number of samples	360	439	67	585	340	587
% of samples above detection	100	100	100	99	99	99
All Institutional Areas Combined (24 events)						
Average	47.0	62.6	3100	0.2	24.7	308.7
Coef. of variation (COV)	1.1	1.0	0.4	0.9	0.6	0.9
Median	18.0	37.5	3400	0.2	21.5	198.0
Number of samples	23	22	3	23	21	22
% of samples above detection	96	91	100	96	57	100
All Open Space Areas Combined (79 events)						
Average	36.5	22.3	7323	0.1	9.2	59.1
Coef. of variation (COV)	1.8	0.6	1.2	1.5	0.4	0.8
Median	10.5	21.3	2300	0.0	9.0	57.0

Number of samples	72	12	7	77	15	16
% of samples above detection	97	83	100	97	47	50

Probability plots, comparisons with other data, logical plots, and transcription reviews were some of the methods used to review the data.

A.1. Observations

There are many factors that can be considered when examining the quality of stormwater. These factors include, but are not limited to the following; land use, geographical region (EPA Rain Zone), and season. The NSQD includes sampling location information such as city, state, land use, drainage area, and EPA Rain Zone. The database also includes sampling information such as date, season, and rain depth, as well as concentrations of many constituents. Supplemental information available on each sampling location includes the exact sampling locations (street intersections or longitude/latitude), breakdown of land use by percentage, aerial photographs, topographic maps, and information on sampling procedures, and quality control. It is important to note that the supplemental information can vary depending on availability of the information. All information contained in the database is useful in characterizing stormwater on a national basis, and will provide assistance for the many municipalities that are affected by the NPDES stormwater permit program, and researchers.

Land use has an important impact on the quality of stormwater. For example, the concentrations of heavy metals are higher for industrial land use areas due to manufacturing processes and other activities that generate these materials. Seasons could also be a factor in the variation of nutrient concentrations in stormwater due to seasonal uses of fertilizers and leaf drop occurring during the fall season. Most studies also report lower bacteria concentrations in the winter than in the summer. Most of the statistical tests used multivariate statistical evaluations that compared different constituent concentrations with land use and geographical location.

The following grouped box and whisker plots (Figures A2 through A9) illustrate the variability of the concentrations of TSS, and the total forms of As, Cd, Cu, Cr, Ni, Pb, and Zn for the different land use categories. These plots are for each major land use and some combined land uses where one was predominate, but only include data above the detection limit (non-detected values were not used in these plots due to problems in representing the missing data on the graphs). The concentrations are log-normally distributed and are plotted with a $\log_{10}$ scale. The central box defines the 25th to 75th percentile values, and the central line in the box represents the median value. The lines on the upper and lower line extensions (the “whiskers”) represent the 5th and 95th percentile values. The individual circles represent values less than and greater than these values. The land use-sorted data were evaluated by one-way ANOVA to determine if any significant differences existed between the groups, compared to within the groups. Since the concentrations were log-normally distributed, the ANOVA tests were applied to the $\log_{10}$ values. In all cases for these constituents, the calculated p values were all highly significant, at $p < 0.001$, much less than the typically accepted level of significance of $p = 0.05$. These results signify that there was at least one member of the group that was significantly different from the others. Unfortunately, ANOVA does not directly calculate if more than one member is different, or which one(s) was different. Observing the grouped box and whisker plots and the variance of the individual groups resulted in the following possible groupings of these data, by constituent, ranked by lowest to highest average values, and combined on the same line if there are small variance differences:

TSS:
    Institutional
    Freeways, residential, open space, and commercial
    Industrial

Arsenic:
    Commercial
    Freeways
    Open space and residential
    Industrial

Cadmium:
    Residential and institutional
    Commercial
    Open space and freeways
    Industrial

Copper:
    Open space
    Freeways
    Residential and institutional
    Industrial and commercial

Chromium:
    Residential and commercial
    Open space
    Freeways
    Industrial

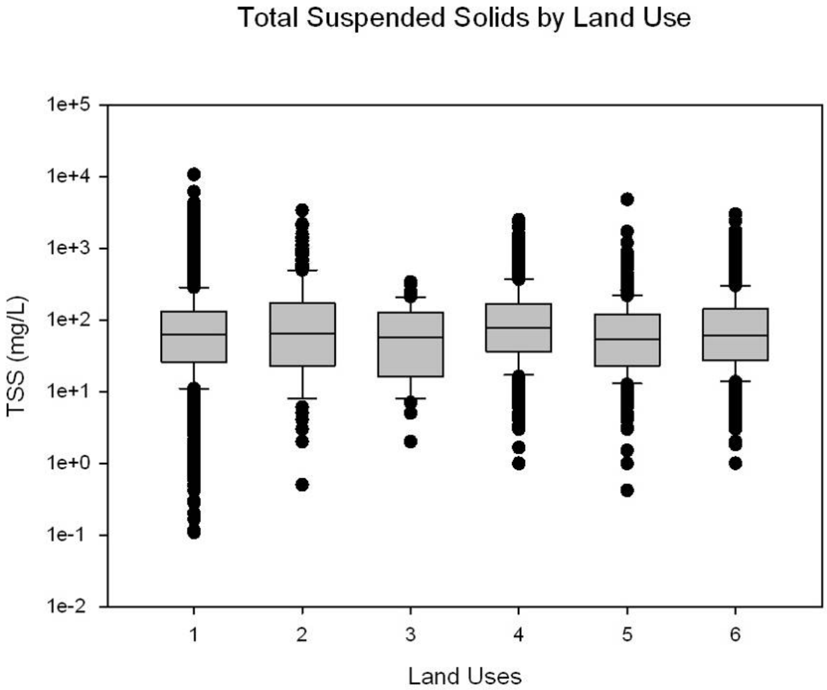
Nickel:
    Residential and commercial
    Open space, industrial, and freeways

Lead:
    Residential and open space
    Institutional and commercial
    Industrial
    Freeways

Zinc:
    Residential, open space, and freeways
    Commercial

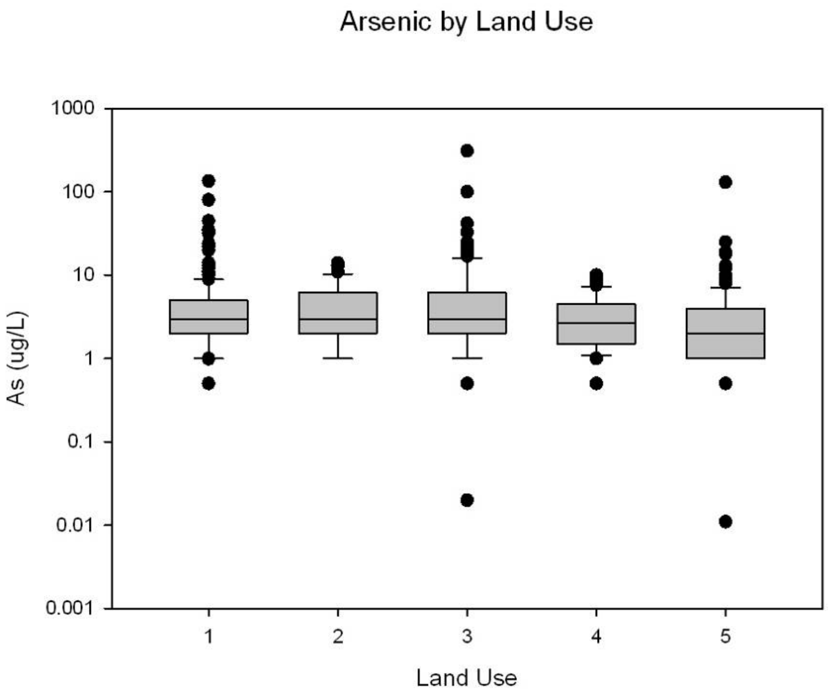
Institutional and industrial

In most cases, open space and residential land uses are associated with the lowest concentrations, while freeways and industrial areas are associated with the highest concentrations. Industrial land use samples also usually had the largest variability and the highest observed concentrations. Typically, industrial areas have the greatest range of activities present and include some of the most contaminated areas, while open space runoff is mostly affected by the area's soils and regional air pollution depositional sources and rain quality.



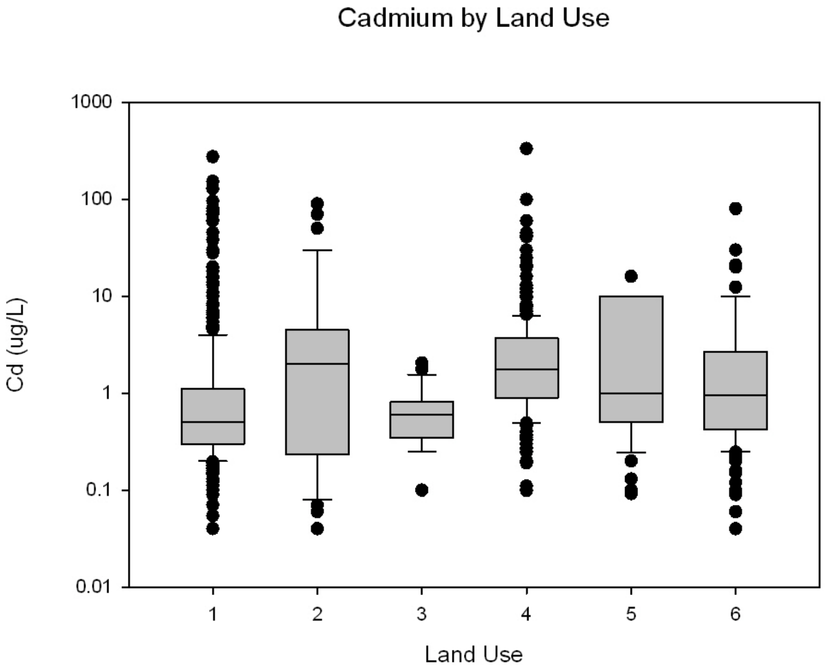
Note: 1: residential; 2: open space; 3: institutional; 4: industrial; 5: freeways; 6: commercial

Figure A2. TSS by land use.



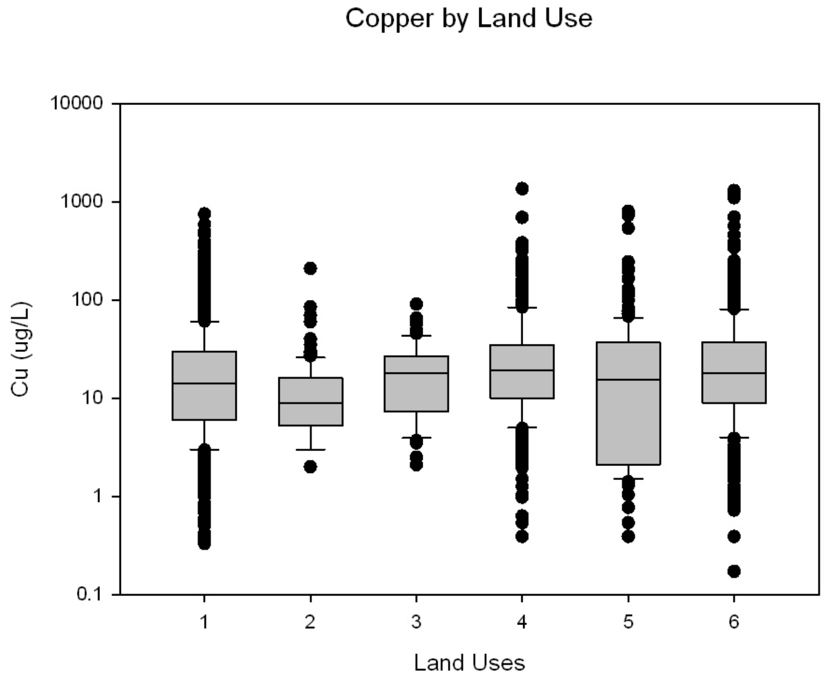
Note: 1: residential; 2: open space; 3: industrial; 4: freeways; 5: commercial

Figure A3. Arsenic by land use.



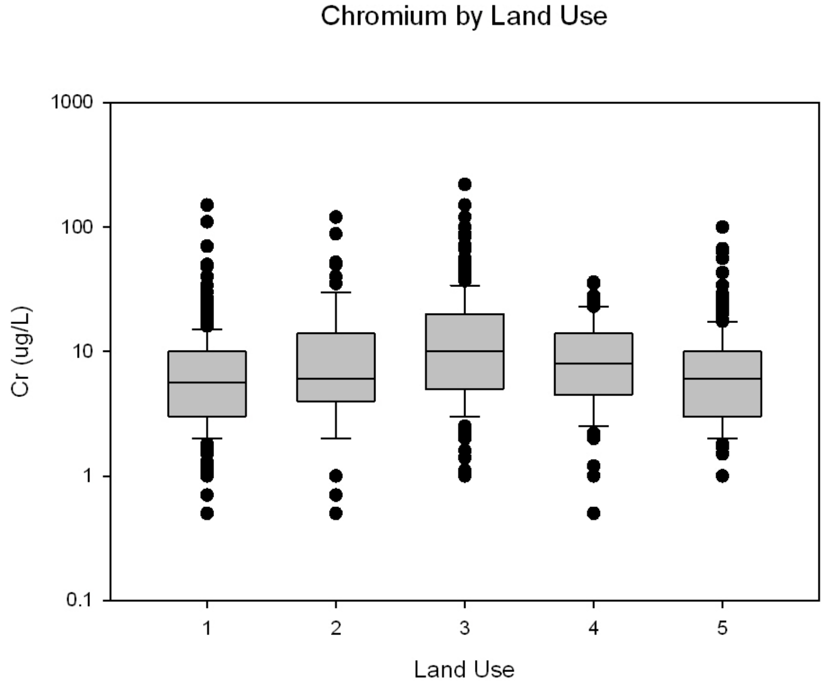
Note: 1: residential; 2: open space; 3: institutional; 4: industrial; 5: freeways; 6: commercial

Figure A4. Cadmium by land use.



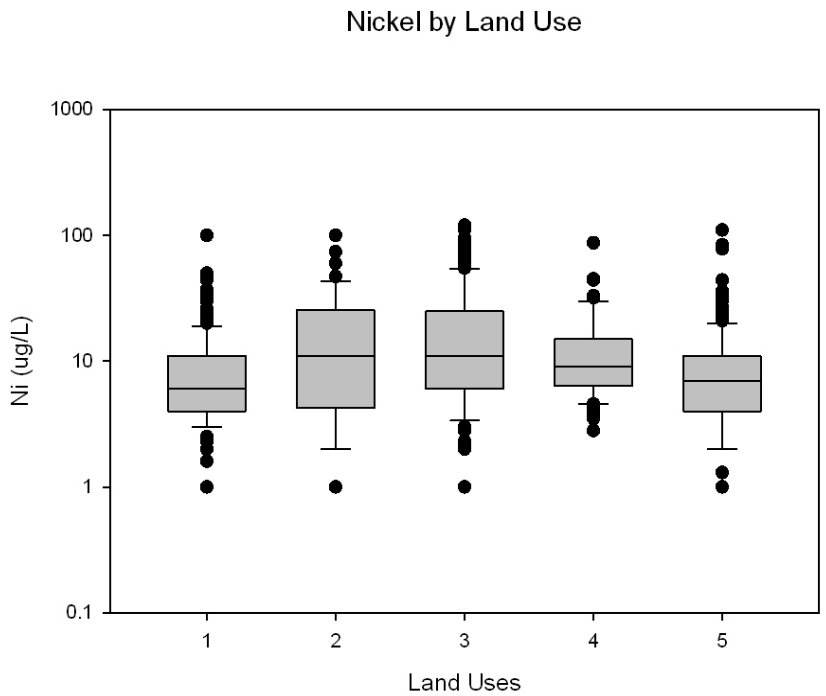
Note: 1: residential; 2: open space; 3: institutional; 4: industrial; 5: freeways; 6: commercial

Figure A5. Copper by land use.



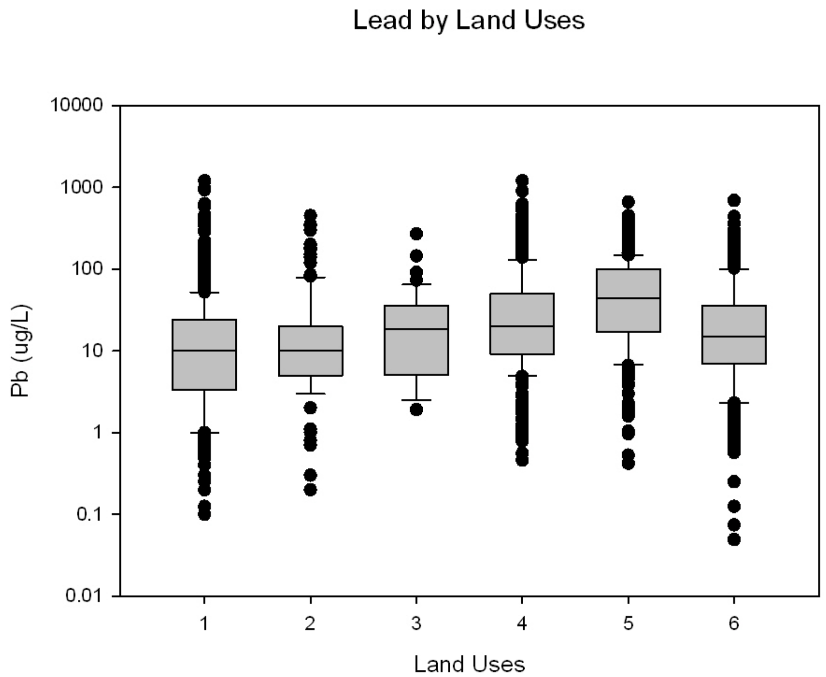
Note: 1: residential; 2: open space; 3: industrial; 4: freeways; 5: commercial

Figure A6. Chromium by land use.



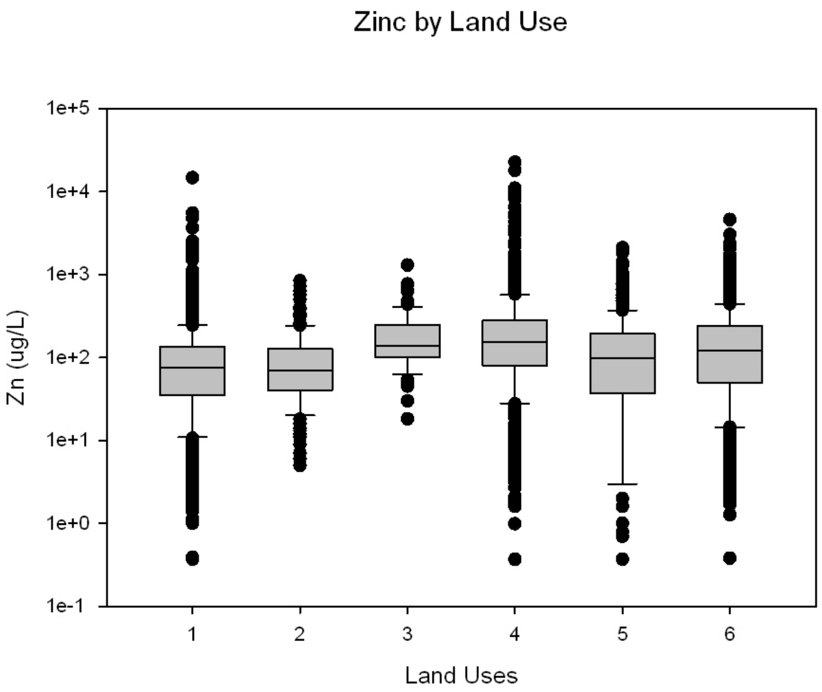
Note: 1: residential; 2: open space; 3: industrial; 4: freeways; 5: commercial

Figure A7. Nickel by land use.



Note: 1: residential; 2: open space; 3: institutional; 4: industrial; 5: freeways; 6: commercial

Figure A8. Lead by land use.



Note: 1: residential; 2: open space; 3: institutional; 4: industrial; 5: freeways; 6: commercial

Figure A9. Zinc by land use.

As noted during earlier NSQD data analyses, lower concentrations for TDS, BOD$_5$, and fecal coliforms were observed in industrial land use areas. Fecal coliform concentrations are relatively high for residential and mixed residential land uses, and nitrate concentrations are higher for the freeway land use. Open space land use areas show consistently low concentrations for the constituents examined.

A.2. Land Use and Geographical Region Analyses

Maestre and Pitt (2007) prepared a general linear model (GLM) using version 1.1 NSQD data that also included the interaction effects between land use, geographical region, and season using the complete database. Doing this analysis requires sufficient sample observations representing each group to result in sufficient statistical power. Table A4 shows the main three factors and levels used in the GLM. This analysis examined only a selection of constituents that were well represented in each category and included: TSS, BOD, COD, TP, NO2+NO3, TKN, Cu, Pb, and Zn. Unfortunately, other data and all rain zones could not be evaluated due to limited observations in all cases.

Table A4. Main land uses, EPA Rain Zones and seasons identified

LAND USE	EPA RAIN ZONE	SEASON
Commercial	Zone 1 – Great Lakes	Spring: February – April
Freeway	Zone 2 – Northeast	Summer: May – July
Industrial	Zone 3 – Southeast	Fall: August – October
Open Space	Zone 4 – Lower Mississippi Valley	Winter: November – January
Residential	Zone 5 – Texas	
	Zone 6 – Southwest	

	Zone 7 – Northwest	
	Zone 9 – Rocky Mountain	

Mixed land uses were excluded from these analyses to eliminate the confusing effects of different land uses in the same area. Rain zone 8 was also eliminated because none of the single land uses have observations in this EPA Rain Zone. All four seasons were selected as they were well represented in all of the selected land uses and EPA Rain Zones.

Two-way and three-way interactions were included in the model. Table A5 shows the results from the model analyses. A p-value smaller than 0.05 indicates that the factor, or interaction of factors, was found to be significant at least at the 5% significance level.

The results indicated that the factors for land use, and the EPA Rain Zone, plus the interaction land use–rain zone were the most important factors used in the model. There were significant differences by EPA Rain Zone, and land use for all the constituents examined. The interaction of these two factors was also significant. Using the GLM and all the data, it was found that season alone was not significant for any constituent except for TKN. Note that bacteria were not evaluated due to missing data in some of the important categories. Historically, bacteria have been found to vary by season (lower in colder seasons). The interaction between land uses and EPA Rain Zone is very important and must be considered when determining likely stormwater concentrations for a site. For all the constituents except TSS, concentrations in the open space land use were lower than for the other land uses, while, samples collected at freeways and industrial sites had the highest concentrations, as previously noted.

Samples collected in EPA Rain Zone 3 (the southeast) had the lowest concentrations for all the constituents. The largest concentrations were observed in EPA Rain Zone 6 (the southwest) followed by rain zones 1 (Great Lakes and northeast) and 4 (Mississippi valley).

Table A5. p-values for main factors and interactions

Constituent	Land Use (LU)	Season (SN)	EPA Rain Zone (EPA)	LU*SN	LU*EPA	SN*EPA	LU*EPA*SN
TSS, mg/L	<0.0001	0.737	<0.0001	0.017	<0.0001	0.1836	<0.0001
BOD, mg/L	<0.0001	0.1551	<0.0001	0.0008	<0.0001	0.0011	0.2209
COD, mg/L	<0.0001	0.1341	<0.0001	0.0343	<0.0001	0.0137	0.0085
TP, mg/L	<0.0001	0.6869	<0.0001	0.0551	<0.0001	0.0004	<0.0001
NO2+NO3, mg/L	<0.0001	0.1075	<0.0001	0.0524	<0.0001	0.0343	0.057
TKN, mg/L	0.0026	0.0235	<0.0001	0.9989	<0.0001	<0.0001	0.1671
Cu, µg/L	<0.0001	0.1123	<0.0001	0.6226	<0.0001	0.0382	0.1405
Pb, µg/L	<0.0001	0.7645	<0.0001	0.4203	<0.0001	0.2854	0.0117
Zn, µg/L	<0.0001	0.91	<0.0001	0.9362	<0.0001	0.0139	<0.0001

Ignoring the interactions between land use and EPA Rain Zone can mislead the interpretation of the factors that affect stormwater concentrations around the continental U.S. The EPA Rain Zone factor followed by the interaction between EPA Rain Zone and the land use, and the factor representing land use alone were all significant when examining the variations in concentrations of the nine stormwater constituents evaluated.

Season alone is not a significant factor in the variability of these stormwater constituent concentrations. However, the interactions between season and EPA Rain Zone are significant for all these pollutants except for TSS and total lead. The variability between sampling locations for any land use category is greater than the variability between land uses, signifying the need to have many sampling sites to represent each land use category for any one geographical area.

A.3. Observed Heavy Metals for Different Land Uses

A.3.1. Particulate Strength Data for Different Land Used from National MS4 Data

The following figures and tables were prepared using the complete NSQD Version 3 data set for TSS and for arsenic, cadmium, copper, chromium, nickel, lead, and zinc for this metals background report. These calculations were made to estimate the particulate strengths of the stormwater samples for comparison to literature values of typical soil metal values. The other metals contained in the NSQD had relatively low detection limits (<40%). For these calculations, non-detected total forms of the metals were eliminated from the calculations, and half of the detection limits were substituted for the non-detected filtered metal values. If the total metal concentration was close to the detection limit and the filtered metal was non-detected, that specific set of data were eliminated from these calculations. These calculations determined the particulate strength of the metals by subtracting available filterable metal concentrations from the total metal concentrations and then dividing the result by the suspended solids concentration. All three of these values were needed for any sample in order for the calculation to be made, resulting in many fewer data sets.

One-way ANOVA tests examining the particulate strengths for these constituents for the land use categories were all significant, with p values < 0.05, except for arsenic. Observing the grouped box and whisker plots and the variance of the individual groups resulted in the following possible groupings of these data, by constituent, ranked by average particulate strength values (lowest to highest) and grouped on the same line if they had small variance differences. Not all land uses are listed for each constituent, as some had too few data.

Arsenic:

Not enough samples to indicate any differences between land use groupings (9 to 24 samples for each land use group were available)

Cadmium:

Freeway and residential
Industrial and commercial

Copper:

Residential and ***open space***
Industrial, commercial, and freeways

Chromium:

Freeways, residential and commercial
Industrial

Lead:

Open space
Freeways and residential
Industrial and commercial

Nickel:

Residential and commercial
Industrial and freeways

Zinc:

Open space
Residential
Freeways and commercial
Industrial

Unfortunately, only copper, lead, and zinc had any open space particulate strength observations in the NSQD Version 3 that could be summarized in the following tables showing metal particulate strengths by both land use and geographical area, the preferred approach. ***When the data were available, open space areas had the lowest particulate strengths compared to samples from other land uses. In most cases, industrial, commercial, and freeway samples had substantially higher particulate strengths, also as expected.***

The following tables summarize these TSS and metals data by land use and EPA rain zone. There were few data available to separate by land use, and even fewer to also separate by rain zone. As an example, of the 342 data sets available for copper particulate strength calculations, only 6 are available for all open space sites, and more than 90 are available for residential and freeway sites. This is similar for the lead and zinc data sets also. The available open space data do consistently indicate low particulate strengths, however, there is substantial uncertainty associated with the actual values. The following plot from Burton and Pitt (2001) (Figure A10) can be used to estimate the expected errors associated with different numbers of available samples, assuming a 95% confidence and 80% power in the characterization of the average value of the data set. With only 6 samples and a COV of about 1.3 (corresponding to the copper particulate strength for open space areas), the expected error level may be about 150%. However, the 340 samples available from the complete data set (with a COV of about 1.0) would result in an expected error that is very small (less than 10%). Obviously, lower levels of error are desired, but it is usually difficult to obtain sufficient data to break the 25% error level (would require more than 50 samples per sample set category). This figure assumes that the available data are randomly obtained from the complete sub-population of interest, which is difficult and not likely. However, when examining the complete data set containing several thousand data observations, repeatable trends are observed: open space areas have the lowest stormwater concentrations for the total metals (and likely have the lowest particulate strength values), while local and nearby activities further degrade these conditions as indicated by higher values for the other land use samples.

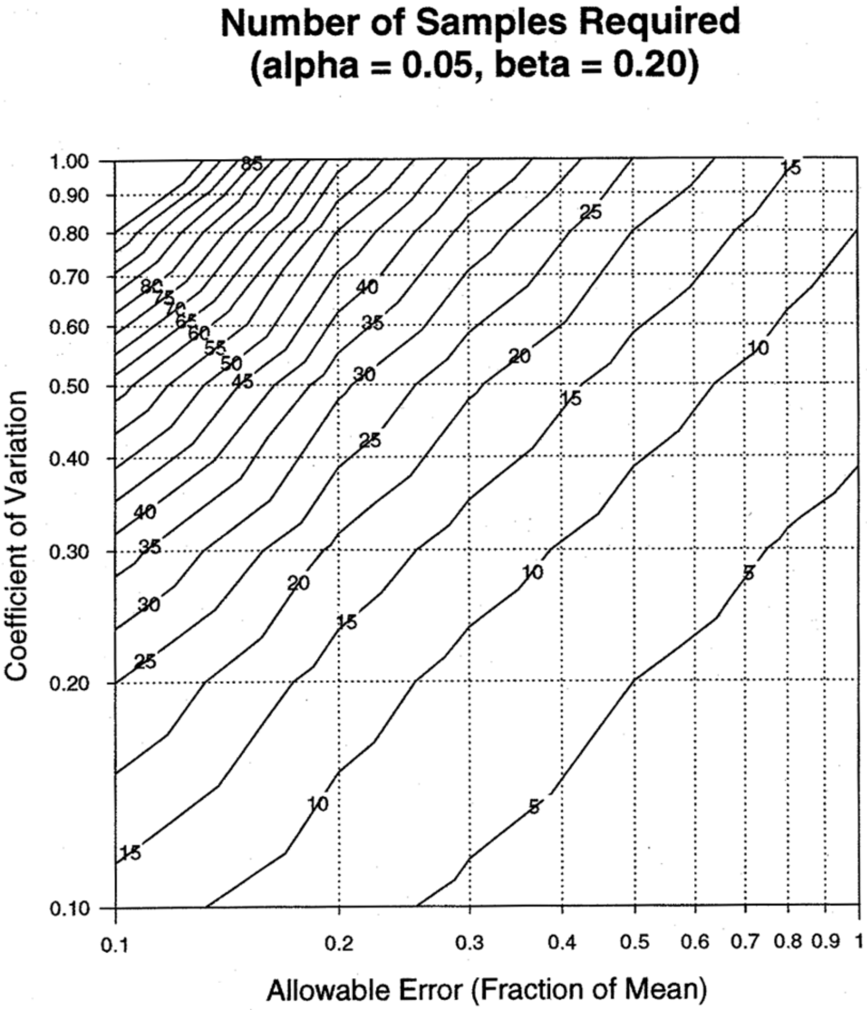
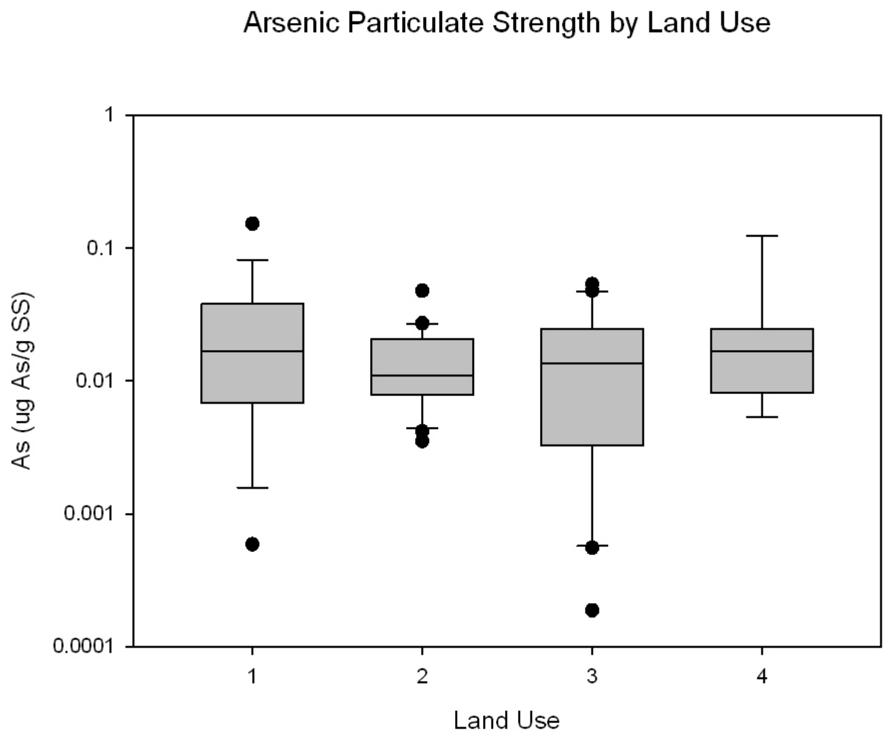
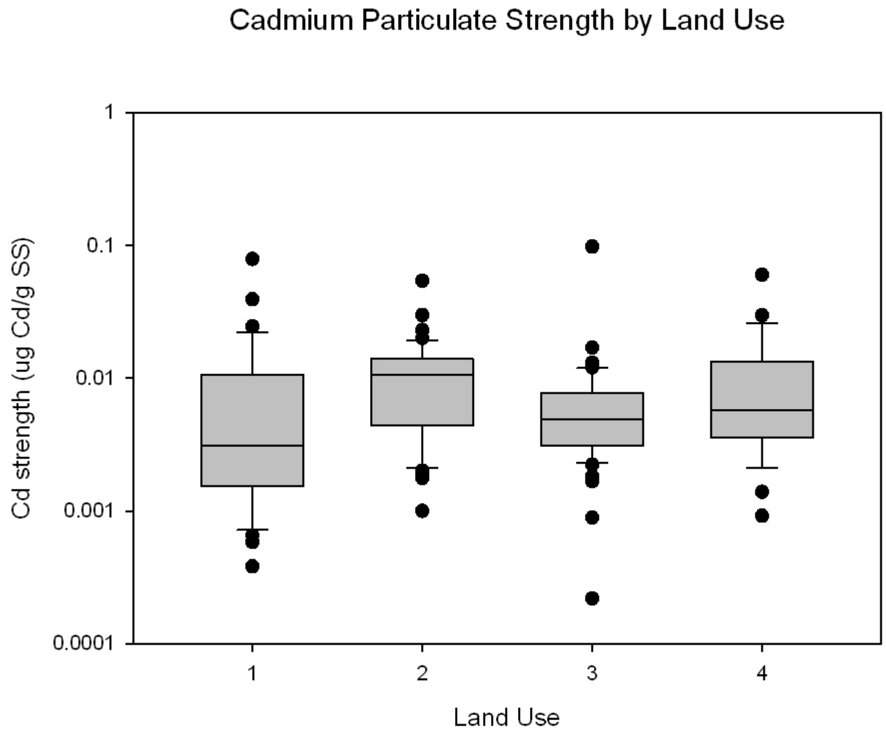


Figure A10. Sample Requirements for Confidence of 95% (α= 0.05) and Power of 80% (β= 0.20) (Burton and Pitt 2001).



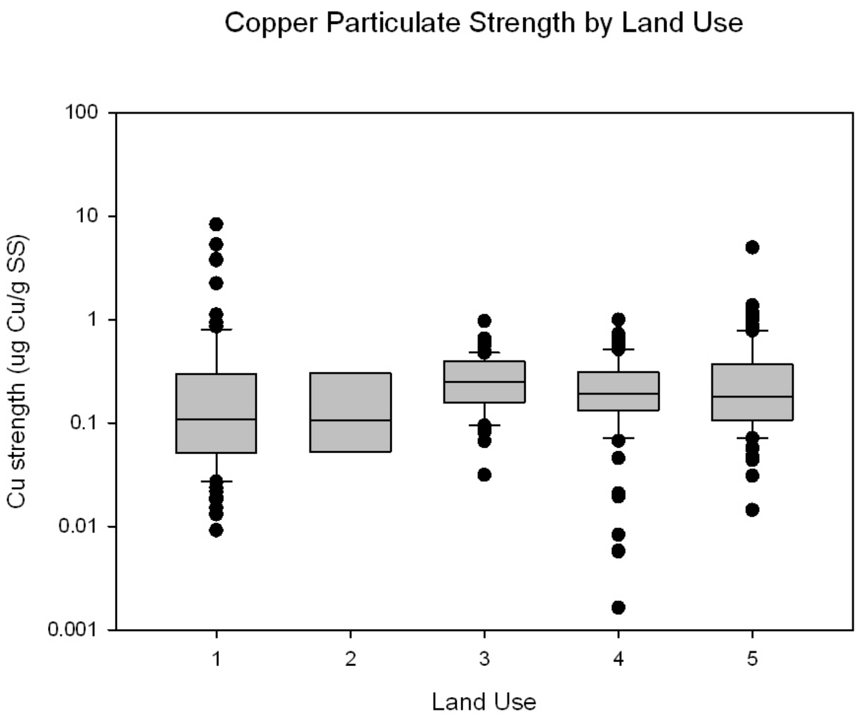
Note: 1: residential; 2: industrial; 3: freeways; 4: commercial

Figure A11. Aresenic Particulate Strength by Land Use



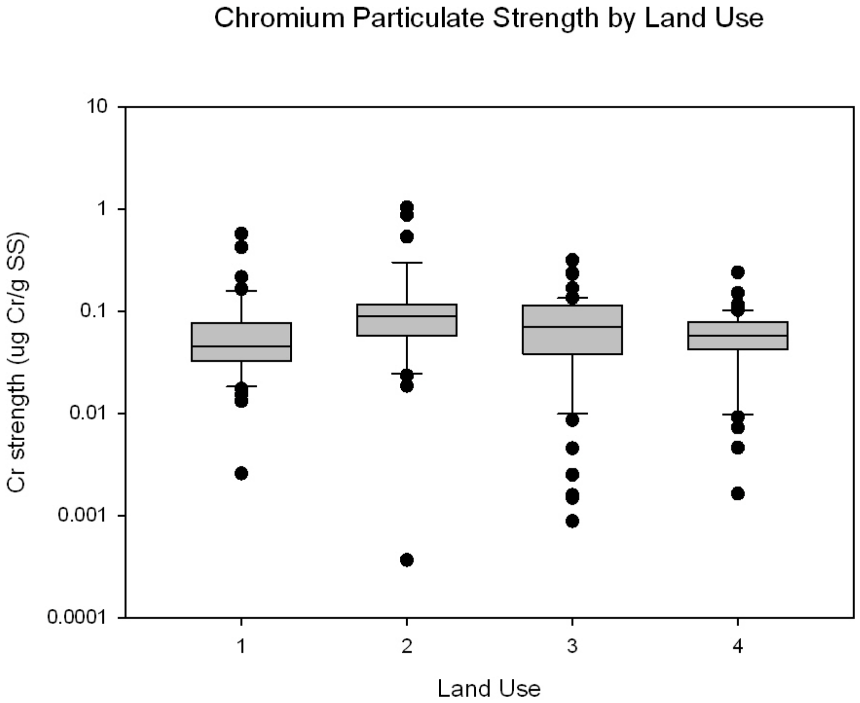
Note: 1: residential; 2: industrial; 3: freeways; 4: commercial

Figure A12. Cadmium Particulate Strength by Land Use



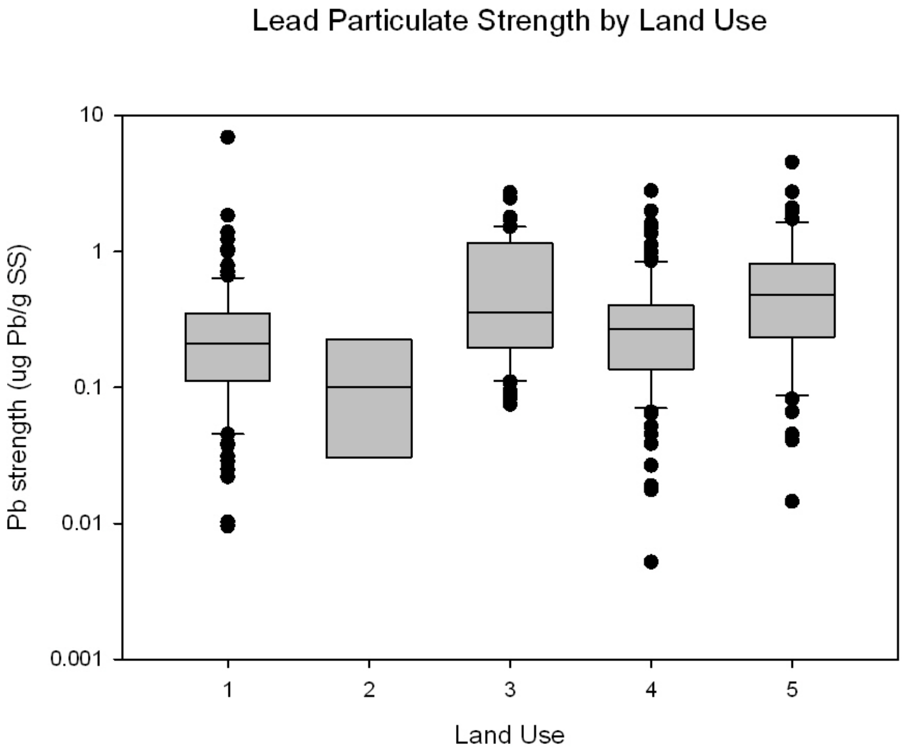
Note: 1: residential; 2: open space; 3: industrial; 4: freeways; 5: commercial

Figure A13. Copper Particulate Strength by Land Use



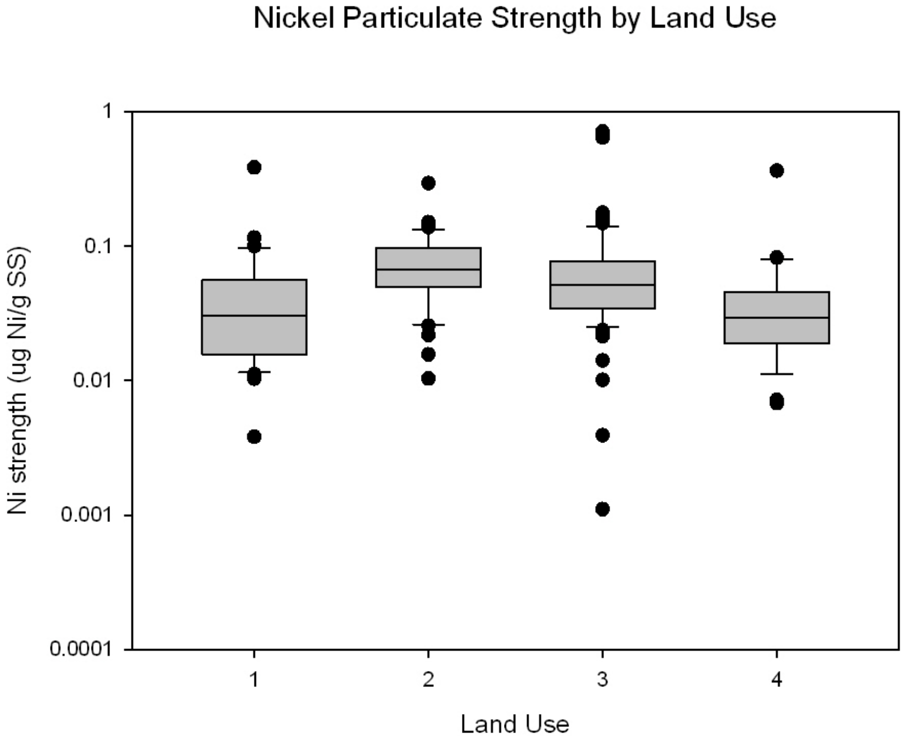
Note: 1: residential; 2: industrial; 3: freeways; 4: commercial

Figure A14. Chromium Particulate Strength by Land Use



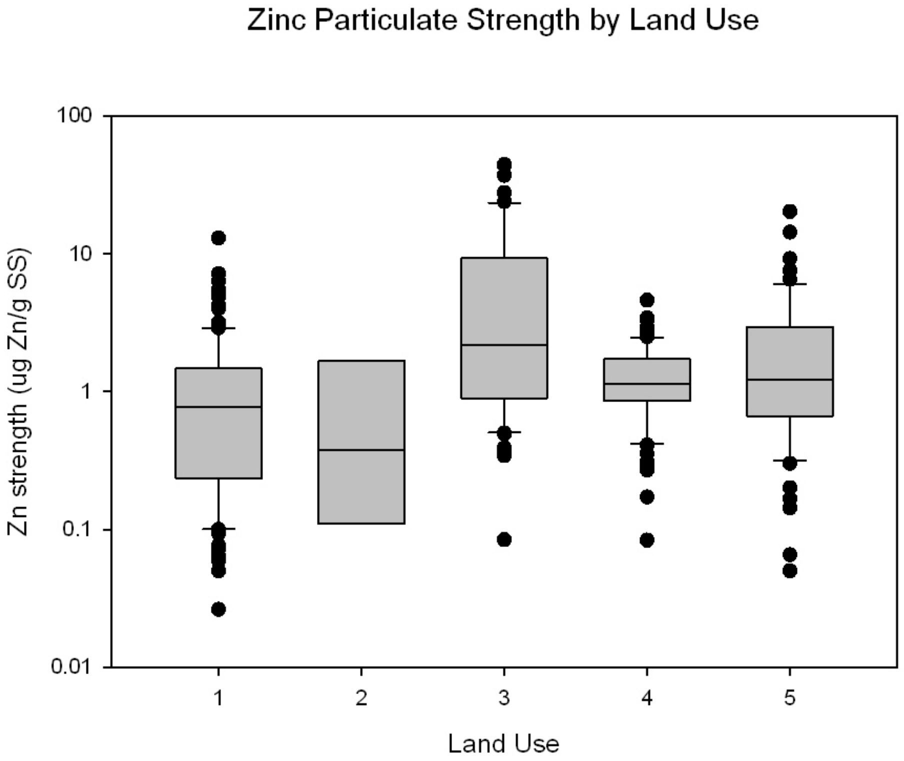
Note: 1: residential; 2: open space; 3: industrial; 4: freeways; 5: commercial

Figure A15. Lead Particulate Strength by Land Use



Note: 1: residential; 2: industrial; 3: freeways; 4: commercial

Figure A16. Nickel Particulate Strength by Land Use



Note: 1: residential; 2: open space; 3: industrial; 4: freeways; 5: commercial

Figure A17. Zinc Particulate Strength by Land Use

Table A6. NSQD Suspended Solids (mg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	median = 47 average = 176 COV = 2.37 numb = 128	median = 82.5 average = 135 COV = 1.16 numb = 507	median = 126 average = 201 COV = 1.45 numb = 310	median = 85.8 average = 177 COV = 1.42 numb = 100	few samples	
2	median = 53 average = 98.2 COV = 1.45 numb = 107	median = 45 average = 102 COV = 1.73 numb = 1893	median = 49 average = 101 COV = 1.68 numb = 669	median = 53.5 average = 97.2 COV = 1.56 numb = 375	median = 36.3 average = 80.3 COV = 1.55 numb = 225	
3	no samples	median = 32 average = 102 COV = 1.65 numb = 207	median = 25 average = 56 COV = 1.98 numb = 55	median = 53.5 average = 105 COV = 1.19 numb = 105	median = 24.6 average = 36.2 COV = 1.42 numb = 13	
4	median = 300 average = 370 COV = 0.84 numb = 18	median = 102 average = 374 COV = 1.81 numb = 140	median = 41 average = 233 COV = 1.85 numb = 67	median = 83.5 average = 164 COV = 1.42 numb = 68	no samples	
5	median = 101 average = 202 COV = 1.60 numb = 67	median = 86 average = 129 COV = 0.93 numb = 203	median = 52 average = 108 COV = 1.64 numb = 100	median = 86 average = 156 COV = 1.70 numb = 106	median = 93 average = 114 COV = 1.09 numb = 12	
6	few samples	median = 113 average = 162 COV = 0.97 numb = 75	median = 106 average = 132 COV = 0.99 numb = 41	median = 200 average = 385 COV = 1.16 numb = 95	median = 97 average = 183 COV = 2.76 numb = 105	
7	no samples	median = 87.0 average = 130.4 COV = 1.82 numb = 315	median = 65.0 average = 86.9 COV = 0.96 numb = 61	median = 115 average = 164 COV = 1.23 numb = 30	median = 109 average = 151 COV = 0.86 numb = 26	
8	no samples	median = 79 average = 140 COV = 0.90 numb = 16	median = 89 average = 98 COV = 0.77 numb = 7	few samples	no samples	
9	median = 826 average = 846 COV = 0.44 numb = 7	median = 113 average = 528 COV = 2.50 numb = 116	median = 242 average = 224 COV = 0.50 numb = 7	median = 260 average = 360 COV = 0.87 numb = 39	no samples	
Total	median = 65 average = 182 COV = 1.88 numb = 329	median = 61.8 average = 137 COV = 2.44 numb = 3,452	median = 61 average = 133 COV = 1.71 numb = 1,342	median = 78 average = 160 COV = 1.57 numb = 919	median = 54 average = 113 COV = 2.53 numb = 384	median = 62 average = 137 COV = 1.01 numb = 6,781

Table A7. NSQD Copper, total (µg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	median = 9.1 average = 9.1 COV = 0.14 numb = 6	median = 18.6 average = 33.8 COV = 1.78 numb = 333	median = 48.5 average = 58.5 COV = 0.82 numb = 141	median = 13.0 average = 25.1 COV = 1.52 numb = 83	few samples	
2	median = 7.0 average = 9.0 COV = 0.85 numb = 58	median = 17.3 average = 29.9 COV = 1.59 numb = 1340	median = 20.6 average = 32.6 COV = 1.23 numb = 502	median = 14 average = 21.2 COV = 1.34 numb = 257	median = 17.8 average = 28.4 COV = 1.99 numb = 103	
3	no samples	median = 6.0 average = 10.1 COV = 2.55 numb = 396	median = 4.0 average = 7.4 COV = 1.45 numb = 106	median = 12 average = 17.5 COV = 0.99 numb = 106	median = 1.2 average = 52.9 COV = 3.67 numb = 14	
4	median = 15 average = 20 COV = 0.85 numb = 12	median = 20 average = 51.5 COV = 1.77 numb = 111	median = 30 average = 68.5 COV = 1.22 numb = 47	median = 30 average = 98.8 COV = 2.29 numb = 49	no samples	
5	median = 9.0 average = 12.4 COV = 0.98 numb = 70	median = 10.0 average = 16.3 COV = 1.80 numb = 164	median = 10.0 average = 61.4 COV = 3.48 numb = 109	median = 14.0 average = 16.7 COV = 0.75 numb = 107	median = 1.5 average = 7.4 COV = 1.68 numb = 117	
6	few samples	median = 24.5 average = 35.8 COV = 1.38 numb = 66	median = 14 average = 20.9 COV = 1.14 numb = 40	median = 55 average = 78.2 COV = 0.85 numb = 93	median = 40 average = 62.1 COV = 1.43 numb = 101	
7	no samples	median = 11.7 average = 16.2 COV = 0.81 numb = 85	median = 21.0 average = 28.9 COV = 1.13 numb = 84	median = 29.0 average = 42.1 COV = 0.80 numb = 34	median = 24.0 average = 32.0 COV = 0.81 numb = 26	
8	no samples	median = 20.0 average = 21.9 COV = 0.44 numb = 15	median = 25.0 average = 42.0 COV = 1.15 numb = 7	few samples	no samples	
9	median = 18 average = 27.7 COV = 0.70 numb = 7	median = 22 average = 27.6 COV = 0.87 numb = 103	median = 13 average = 63.4 COV = 1.93 numb = 7	median = 27.9 average = 44.6 COV = 1.04 numb = 39	no samples	
Total	median = 9.0 average = 14.1 COV = 1.50 numb = 155	median = 14.0 average = 27.3 COV = 1.77 numb = 2,594	median = 17.9 average = 36.7 COV = 2.28 numb = 1,068	median = 19.2 average = 36.3 COV = 2.05 numb = 769	median = 15.4 average = 32.5 COV = 2.18 numb = 364	median = 15.0 average = 30.1 COV = 1.14 numb = 5,165

Table A8. NSQD Copper, filtered (µg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	median = 2.0 average = 2.6 COV = 0.75 numb = 6	median = 1.1 average = 19.8 COV = 2.41 numb = 20	no samples	no samples	few samples	
2	median = 1.0 average = 1.4 COV = 0.73 numb = 5	median = 2.5 average = 7.7 COV = 1.31 numb = 53	median = 6.0 average = 7.1 COV = 0.63 numb = 22	no samples	no samples	
3	no samples	no samples	no samples	no samples	no samples	
4	no samples	no samples	no samples	no samples	no samples	
5	no samples	no samples	no samples	no samples	no samples	
6	few samples	median = 5.0 average = 5.2 COV = 0.25 numb = 14	median = 5.0 average = 6.4 COV = 0.42 numb = 11	median = 7.0 average = 8.7 COV = 0.61 numb = 46	median = 11.6 average = 23.2 COV = 1.44 numb = 104	
7	no samples	median = 4.0 average = 4.8 COV = 0.64 numb = 39	median = 6.1 average = 9.5 COV = 0.90 numb = 39	median = 7.0 average = 8.7 COV = 0.79 numb = 20	median = 6.0 average = 8.7 COV = 0.98 numb = 26	
8	no samples	median = 7.5 average = 11.9 COV = 0.74 numb = 10	median = 12.4 average = 12.1 COV = 0.60 numb = 5	few samples	no samples	
9	no samples	no samples	no samples	no samples	no samples	
Total	median = 2.0 average = 2.3 COV = 0.78 numb = 12	median = 4.0 average = 8.7 COV = 2.28 numb = 122	median = 6.1 average = 8.5 COV = 0.81 numb = 77	median = 7.0 average = 8.6 COV = 0.66 numb = 67	median = 10.7 average = 20.3 COV = 1.51 numb = 130	median = 6.0 average = 11.9 COV = 1.00 numb = 434

Table A9. NSQD Copper, particulate strength (µg Cu/g SS)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	no samples	median = 37.5 average = 799 COV = 2.71 numb = 15	no samples	no samples	few samples	
2	median = 65.2 average = 90.0 COV = 0.98 numb = 3	median = 211 average = 649 COV = 1.79 numb = 39	median = 200 average = 344 COV = 1.02 numb = 19	no samples	no samples	
3	no samples	no samples	no samples	no samples	no samples	
4	no samples	no samples	no samples	no samples	no samples	
5	no samples	no samples	no samples	no samples	no samples	
6	few samples	median = 182 average = 283 COV = 0.70 numb = 9	median = 95.7 average = 730 COV = 1.16 numb = 7	median = 303 average = 310 COV = 0.60 numb = 40	median = 240 average = 270 COV = 0.73 numb = 66	
7	no samples	median = 65 average = 104 COV = 0.92 numb = 36	median = 200 average = 415 COV = 1.93 numb = 39	median = 216 average = 234 COV = 0.51 numb = 19	median = 160 average = 180 COV = 0.46 numb = 25	
8	no samples	median = 93.4 average = 243 COV = 1.43 numb = 5	median = 203 average = 236 COV = 0.84 numb = 5	few samples	no samples	
9	no samples	no samples	no samples	no samples	no samples	
Total	median = 107 average = 188 COV = 1.23 numb = 6	median = 108 average = 431 COV = 2.57 numb = 95	median = 180 average = 358 COV = 1.76 numb = 70	median = 251 average = 281 COV = 0.61 numb = 60	median = 191 average = 244 COV = 0.72 numb = 91	median = 185 average = 356 COV = 1.00 numb = 342

Table A10. NSQD Lead, total (µg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	no samples	median = 22.2 average = 65.5 COV = 2.31 numb = 287	median = 7.7 average = 17.3 COV = 1.28 numb = 101	median = 11.1 average = 14.6 COV = 0.78 numb = 77	few samples	
2	median = 9.0 average = 11.5 COV = 1.18 numb = 107	median = 7.0 average = 19.4 COV = 2.07 numb = 1052	median = 15.0 average = 33.7 COV = 1.69 numb = 438	median = 10.5 average = 21.4 COV = 2.28 numb = 327	median = 100 average = 57.5 COV = 0.78 numb = 100	
3	no samples	median = 2.3 average = 9.6 COV = 3.54 numb = 317	median = 5.0 average = 9.1 COV = 1.49 numb = 71	median = 16 average = 21.5 COV = 1.10 numb = 89	no samples	
4	few samples	median = 13 average = 25.0 COV = 1.66 numb = 96	median = 34.8 average = 63.5 COV = 1.03 numb = 45	median = 19.5 average = 113 COV = 2.05 numb = 48	no samples	
5	median = 9.0 average = 27.0 COV = 2.44 numb = 70	median = 13.0 average = 24.5 COV = 1.55 numb = 183	median = 20.0 average = 37.0 COV = 1.24 numb = 111	median = 23.0 average = 35.5 COV = 1.38 numb = 108	median = 57.0 average = 81.3 COV = 0.83 numb = 138	
6	few samples	median = 27 average = 45 COV = 0.97 numb = 56	median = 12.0 average = 31.8 COV = 2.21 numb = 42	median = 106 average = 148 COV = 0.90 numb = 101	median = 28.5 average = 72.4 COV = 1.51 numb = 112	
7	no samples	median = 15.5 average = 30.3 COV = 1.30 numb = 85	median = 20.0 average = 43.7 COV = 1.39 numb = 84	median = 33.5 average = 45.1 COV = 0.75 numb = 74	median = 32.5 average = 55.1 COV = 1.33 numb = 26	
8	no samples	median = 13.8 average = 21.8 COV = 0.79 numb = 15	median = 49.0 average = 65.0 COV = 1.21 numb = 7	few samples	no samples	
9	median = 200 average = 225 COV = 0.47 numb = 7	median = 10 average = 28.8 COV = 1.16 numb = 51	median = 60 average = 87.1 COV = 0.73 numb = 7	median = 97 average = 157 COV = 1.17 numb = 23	no samples	
Total	median = 10.0 average = 30.5 COV = 2.23 numb = 203	median = 10.0 average = 25.8 COV = 2.55 numb = 2,129	median = 15.0 average = 34.3 COV = 1.59 numb = 915	median = 20.0 average = 54.5 COV = 1.86 numb = 848	median = 43.5 average = 70.8 COV = 1.12 numb = 379	median = 14.0 average = 37.2 COV = 1.27 numb = 4,694

Table A11. NSQD Lead, filtered (µg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	no samples	median = 0.8 average = 0.7 COV = 0.56 numb = 8	no samples	no samples	few samples	
2	median = 2.0 average = 1.9 COV = 0.43 numb = 5	median = 2.5 average = 2.8 COV = 1.13 numb = 53	median = 2.5 average = 4.7 COV = 1.07 numb = 22	no samples	no samples	
3	no samples	no samples	no samples	no samples	no samples	
4	no samples	no samples	no samples	no samples	no samples	
5	no samples	no samples	no samples	no samples	no samples	
6	few samples	median = 5.0 average = 18 COV = 1.332 numb = 35	median = 10.0 average = 20.1 COV = 1.32 numb = 21	median = 5.0 average = 14.4 COV = 1.80 numb = 56	median = 0.63 average = 1.82 COV = 1.99 numb = 100	
7	no samples	median = 1.0 average = 1.5 COV = 1.11 numb = 39	median = 2.0 average = 3.6 COV = 1.11 numb = 40	median = 1.0 average = 2.3 COV = 1.18 numb = 20	median = 1.0 average = 3.2 COV = 2.60 numb = 26	
8	no samples	median = 1.0 average = 1.4 COV = 1.34 numb = 11	median = 1.0 average = 1.4 COV = 0.66 numb = 5	few samples	no samples	
9	no samples	no samples	no samples	no samples	no samples	
Total	median = 2.3 average = 2.4 COV = 0.61 numb = 6	median = 2.0 average = 5.8 COV = 2.34 numb = 138	median = 3.0 average = 7.7 COV = 1.95 numb = 88	median = 5.0 average = 11.1 COV = 2.06 numb = 77	median = 0.63 average = 2.1 COV = 2.36 numb = 126	median = 1.9 average = 5.9 COV = 1.00 numb = 455

Table A12. NSQD Lead, particulate form (µg Cu/g SS)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	no samples	median = 47.3 average = 73.8 COV = 0.99 numb = 5	no samples	no samples	few samples	
2	median = 125 average = 154 COV = 0.62 numb = 3	median = 168 average = 435 COV = 2.85 numb = 30	median = 388 average = 405 COV = 0.72 numb = 17	no samples	no samples	
3	no samples	no samples	no samples	no samples	no samples	
4	no samples	no samples	no samples	no samples	no samples	
5	no samples	no samples	no samples	no samples	no samples	
6	few samples	median = 372 average = 565 COV = 0.78 numb = 11	median = 213 average = 444 COV = 1.53 numb = 7	median = 850 average = 865 COV = 0.75 numb = 43	median = 230 average = 380 COV = 1.25 numb = 72	
7	no samples	median = 238 average = 307 COV = 1.00 numb = 38	median = 602 average = 845 COV = 1.00 numb = 40	median = 241 average = 239 COV = 0.42 numb = 19	median = 300 average = 360 COV = 0.80 numb = 26	
8	no samples	median = 161 average = 205 COV = 0.49 numb = 8	median = 552 average = 595 COV = 0.41 numb = 5	few samples	no samples	
9	no samples	no samples	no samples	no samples	no samples	
Total	median = 101 average = 120 COV = 0.87 numb = 4	median = 211 average = 358 COV = 2.10 numb = 87	median = 483 average = 678 COV = 1.06 numb = 69	median = 359 average = 664 COV = 0.93 numb = 63	median = 267 average = 375 COV = 1.15 numb = 98	median = 284 average = 500 COV = 1.00 numb = 338

Table A13. NSQD Nickel, total (µg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	no samples	median = 23.0 average = 21.2 COV = 0.77 numb = 55	median = 32.0 average = 31.0 COV = 0.37 numb = 77	median = 2.8 average = 10.9 COV = 1.64 numb = 50	few samples	
2	median = 7.0 average = 9.6 COV = 0.76 numb = 42	median = 7.3 average = 10.1 COV = 0.84 numb = 285	median = 7.0 average = 11.4 COV = 1.34 numb = 151	median = 7.7 average = 11.4 COV = 0.93 numb = 131	no samples	
3	no samples	few samples	median = 19.0 average = 19.8 COV = 0.20 numb = 6	few samples	no samples	
4	median = 40 average = 43.3 COV = 0.35 numb = 12	median = 7.8 average = 14.1 COV = 1.02 numb = 57	median = 10.9 average = 10.5 COV = 0.25 numb = 25	median = 10.3 average = 16.2 COV = 0.84 numb = 28	no samples	
5	median = 8.0 average = 14.4 COV = 1.12 numb = 33	median = 4.0 average = 5.6 COV = 0.69 numb = 69	median = 5.0 average = 5.4 COV = 0.89 numb = 47	median = 5.5 average = 7.6 COV = 1.20 numb = 48	no samples	
6	few samples	median = 11.5 average = 16.4 COV = 1.12 numb = 31	median = 9.0 average = 14.6 COV = 1.05 numb = 31	median = 24.0 average = 33.8 COV = 0.74 numb = 89	median = 9.0 average = 13.5 COV = 0.92 numb = 88	
7	no samples	median = 4.0 average = 5.4 COV = 0.95 numb = 56	median = 4.0 average = 4.7 COV = 0.68 numb = 47	median = 14.0 average = 26.2 COV = 1.15 numb = 24	median = 7.0 average = 10.5 COV = 0.82 numb = 8	
8	no samples	median = 6.4 average = 7.0 COV = 0.53 numb = 15	median = 8.3 average = 11.9 COV = 1.01 numb = 7	few samples	no samples	
9	few samples	median = 7.0 average = 6.7 COV = 0.42 numb = 9	median = 5.0 average = 7.3 COV = 0.55 numb = 3	median = 14.0 average = 16.1 COV = 0.61 numb = 15	no samples	
Total	median = 11.0 average = 18.1 COV = 1.13 numb = 92	median = 6.0 average = 9.5 COV = 1.08 numb = 574	median = 7.0 average = 9.6 COV = 1.22 numb = 403	median = 11.0 average = 20.4 COV = 1.07 numb = 389	median = 9.0 average = 13.2 COV = 0.91 numb = 102	median = 3.0 average = 5.8 COV = 1.03 numb = 247

Table A14. NSQD Nickel, filtered (µg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	few samples	no samples	no samples	no samples	few samples	
2	few samples	no samples	no samples	no samples	no samples	
3	few samples	no samples	no samples	no samples	no samples	
4	few samples	no samples	no samples	no samples	no samples	
5	few samples	no samples	no samples	no samples	no samples	
6	few samples	median = 5.0 average = 7 COV = 0.76 numb = 14	median = 5.0 average = 4.5 COV = 0.59 numb = 11	median = 5.0 average = 4.9 COV = 0.57 numb = 37	median = 2.5 average = 6.2 COV = 1.76 numb = 87	
7	few samples	median = 2.0 average = 2.3 COV = 0.61 numb = 25	median = 2.0 average = 2.4 COV = 0.84 numb = 27	median = 11.0 average = 18.8 COV = 1.19 numb = 14	median = 3.5 average = 5.8 COV = 1.04 numb = 8	
8	no samples	median = 6.5 average = 6.7 COV = 0.59 numb = 11	median = 5.0 average = 6.1 COV = 0.31 numb = 5	few samples	no samples	
9	no samples	no samples	no samples	no samples	no samples	
Total	few samples (n = 1)	median = 3.0 average = 4.3 COV = 0.94 numb = 50	median = 3.0 average = 3.3 COV = 0.76 numb = 43	median = 5.0 average = 8.6 COV = 1.53 numb = 52	median = 2.6 average = 6.1 COV = 1.71 numb = 95	median = 1.9 average = 5.9 COV = 1.00 numb = 455

Table A15. NSQD Nickel, particulate strength (µg Ni/g SS)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	few samples	no samples	no samples	no samples	few samples	
2	few samples	no samples	no samples	no samples	no samples	
3	few samples	no samples	no samples	no samples	no samples	
4	few samples	no samples	no samples	no samples	no samples	
5	few samples	no samples	no samples	no samples	no samples	
6	few samples	no samples	median = 77.6 average = 124 COV = 0.95 numb = 6	median = 75.5 average = 88.3 COV = 0.55 numb = 33	median = 50 average = 80 COV = 1.36 numb = 66	
7	few samples	median = 17.5 average = 21.4 COV = 0.57 numb = 17	median = 23.1 average = 23.9 COV = 0.42 numb = 20	median = 42.0 average = 44.8 COV = 0.53 numb = 11	median = 30.0 average = 40.0 COV = 0.59 numb = 8	
8	no samples	median = 30.2 average = 32.0 COV = 0.44 numb = 5	median = 40.0 average = 34.2 COV = 0.46 numb = 3	few samples	no samples	
9	no samples	no samples	no samples	no samples	no samples	
Total	few samples (n = 1)	median = 30.2 average = 47.6 COV = 1.40 numb = 33	median = 29.4 average = 45.7 COV = 1.42 numb = 29	median = 66.6 average = 75.9 COV = 0.63 numb = 45	median = 51.2 average = 77.3 COV = 1.39 numb = 74	median = 47.8 average = 65.7 COV = 1.01 numb = 185

Table A16. NSQD Zinc, total (µg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	median = 40 average = 52.7 COV = 0.82 numb = 10	median = 97 average = 134 COV = 1.16 numb = 351	median = 104 average = 196 COV = 1.39 numb = 225	median = 45.4 average = 106 COV = 1.21 numb = 84	few samples	
2	median = 80 average = 93.2 COV = 0.76 numb = 109	median = 33 average = 125 COV = 3.57 numb = 1471	median = 160 average = 237 COV = 1.20 numb = 513	median = 142 average = 172 COV = 0.92 numb = 326	median = 100 average = 186 COV = 1.29 numb = 203	
3	no samples	median = 40 average = 61.4 COV = 1.18 numb = 384	median = 40 average = 60 COV = 1.43 numb = 136	median = 120 average = 166 COV = 1.33 numb = 107	median = 6.2 average = 7.5 COV = 0.97 numb = 14	
4	median = 65 average = 98 COV = 0.97 numb = 17	median = 120 average = 264 COV = 2.25 numb = 120	median = 171 average = 270 COV = 0.92 numb = 51	median = 200 average = 513 COV = 2.87 numb = 54	no samples	
5	median = 60 average = 100 COV = 1.30 numb = 69	median = 70 average = 95 COV = 0.86 numb = 183	median = 80 average = 116 COV = 0.83 numb = 111	median = 110 average = 169 COV = 1.07 numb = 107	median = 50 average = 89 COV = 1.24 numb = 267	
6	few samples	median = 160 average = 260 COV = 1.21 numb = 76	median = 210 average = 343 COV = 2.03 numb = 42	median = 560 average = 1,720 COV = 2.01 numb = 100	median = 200 average = 304 COV = 1.09 numb = 99	
7	no samples	median = 99 average = 120 COV = 0.76 numb = 328	median = 60 average = 138 COV = 1.04 numb = 84	median = 154 average = 306 COV = 2.92 numb = 81	median = 178 average = 211 COV = 0.78 numb = 25	
8	no samples	median = 179 average = 185 COV = 0.56 numb = 15	median = 306 average = 434 COV = 1.11 numb = 7	few samples	no samples	
9	median = 340 average = 439 COV = 0.43 numb = 7	median = 110 average = 139 COV = 0.99 numb = 100	median = 190 average = 261 COV = 0.80 numb = 7	median = 350 average = 486 COV = 0.92 numb = 39	no samples	
Total	median = 70.0 average = 109 COV = 1.12 numb = 214	median = 76 average = 125 COV = 2.76 numb = 3,009	median = 120 average = 197 COV = 1.41 numb = 1,201	median = 156 average = 382 COV = 3.49 numb = 898	median = 97.0 average = 160 COV = 1.39 numb = 611	median = 90.0 average = 181 COV = 1.03 numb = 6,184

Table A17. NSQD Zinc, filtered (µg/L)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	median = 5.0 average = 30.3 COV = 2.09 numb = 6	median = 6.6 average = 30 COV = 2.02 numb = 20	no samples	no samples	few samples	
2	median = 14.0 average = 14.6 COV = 0.61 numb = 5	no samples	median = 134 average = 142 COV = 0.64 numb = 22	no samples	no samples	
3	no samples	no samples	no samples	no samples	no samples	
4	no samples	no samples	no samples	no samples	no samples	
5	no samples	no samples	no samples	no samples	no samples	
6	few samples	median = 33.5 average = 59.5 COV = 1.10 numb = 14	median = 40.0 average = 75.2 COV = 1.02 numb = 11	median = 130 average = 1,378 COV = 1.90 numb = 46	median = 50 average = 143 COV = 1.85 numb = 79	
7	no samples	median = 40.0 average = 39.7 COV = 0.60 numb = 39	median = 64.0 average = 99.1 COV = 1.56 numb = 40	median = 228 average = 582 COV = 2.73 numb = 20	median = 51 average = 74 COV = 1.23 numb = 26	
8	no samples	median = 75.5 average = 74.6 COV = 0.58 numb = 8	median = 126 average = 131 COV = 0.65 numb = 4	few samples	no samples	
9	no samples	no samples	no samples	no samples	no samples	
Total	median = 5.5 average = 21.4 COV = 2.07 numb = 12	median = 28.0 average = 37.2 COV = 1.05 numb = 118	median = 70.0 average = 110 COV = 1.16 numb = 77	median = 155 average = 1,137 COV = 2.08 numb = 66	median = 51.0 average = 126 COV = 1.87 numb = 105	median = 46.0 average = 254 COV = 1.00 numb = 404

Table A18. NSQD Zn, particulate form (µg Zn/g SS)

EPA Rain Zone	Open Space	Residential	Commercial	Industrial	Freeways	All combined
1	no samples	median = 160 average = 478 COV = 1.51 numb = 14	no samples	no samples	few samples	
2	median = 1,000 average = 1,243 COV = 0.81 numb = 3	no samples	median = 3,149 average = 3,660 COV = 0.97 numb = 20	no samples	no samples	
3	no samples	no samples	no samples	no samples	no samples	
4	no samples	no samples	no samples	no samples	no samples	
5	no samples	no samples	no samples	no samples	no samples	
6	few samples	median = 1,846 average = 2,291 COV = 0.79 numb = 11	median = 1,237 average = 3,975 COV = 1.81 numb = 7	median = 3,242 average = 9,832 COV = 1.31 numb = 42	median = 1,190 average = 1,420 COV = 0.58 numb = 62	
7	no samples	median = 573 average = 862 COV = 0.86 numb = 38	median = 1,005 average = 1,450 COV = 1.11 numb = 38	median = 1,125 average = 1,214 COV = 0.65 numb = 19	median = 930 average = 1,070 COV = 0.61 numb = 25	
8	no samples	median = 828 average = 823 COV = 0.28 numb = 7	median = 2,470 average = 2,951 COV = 0.70 numb = 4	few samples	no samples	
9	no samples	no samples	no samples	no samples	no samples	
Total	median = 379 average = 789 COV = 1.20 numb = 5	median = 768 average = 1,262 COV = 1.39 numb = 102	median = 1,218 average = 2,435 COV = 1.36 numb = 69	median = 2,162 average = 7,147 COV = 1.59 numb = 61	median = 1,128 average = 1318 COV = 0.60 numb = 87	median = 1,090 average = 2,550 COV = 1.00 numb = 344

A.4. Stormwater Heavy Metals and Land Use Relationships as Described in the Literature

Heavy metal concentration variations with land use have long been studied and acknowledged. The following is a summary describing these relationships from the recent literature. Schueler (1996b) summarized the effort to characterize metal and organic toxicants in stormwater discharges in the 700 mi^2 Santa Clara Valley, CA watershed. ***The highest Zn, Cd, Ni (nickel), Pb, and Cu concentrations were associated with industrial-land uses and all of the heavy industrial-area samples were found to be extremely toxic; probably from the dissolved metal fractions. Pesticides and nonpolar hydrocarbons were probably responsible for the moderate to toxic samples obtained from the mixed-land-use areas.***

Solo-Gabriele and Perkins (1997) quantified metal transport (i.e. Fe, Cu, chromium [Cr] and arsenic [As]) for the Aberjona-River watershed in Massachusetts and proposed storm sewer overflows (SSOs) and direct urban stormwater runoff as mechanisms of metal transport. ***The runoff from roofs and streets contributed 50% — 80% of heavy metals, i.e., Cd, Cu, Pb and Zn, to the total mass flow in the domestic wastewater of the combined sewerage system*** (Boller 1997).

Concentrations of Cu, Zn, Pb, Cd and Ni measured in the headwaters of the Hawkesbury-Nepean River, Australia, were amongst the lowest reported in the literature for freshwater systems, and will be used as a benchmark for assessing the effects of increasing urbanization in the catchment

(Markich and Brown 1998). Samples of Hg and methyl-mercury (MMHg) were collected during baseflow and storm flow from the Anacostia River, an urban, impacted river of greater Washington, D.C. (Mason and Sullivan 1998). ***Total concentrations of Hg during the storm flow measured 3—5 times that of the baseflow indicating storm flow is the major vector for Hg in the Anacostia.***

A sampling program in North Carolina collected the first flush at 20 different sites covering ten different industrial groups (Line, *et al.* 1997). Zn and Cu were the most common metals found while other contaminants included volatile and semivolatile organics, pesticides, and conventional pollutants, especially, nutrients and solids, which had high concentrations when a significant amount of biological waste or exposed soil was present.

Bonzongo, *et al.* (1999) studied the impacts of land use and physicochemical settings on methyl mercury levels in the Mobile-Alabama River system. In the Coastal Plain portion of the state, Hg concentrations above the FDA's safe limit have been found in tissues of some fish species in both Fish River and Mobile Bay, Alabama. ***These rivers/streams receive most of their Hg from nonpoint sources (e.g. atmospheric deposition and inputs related to land use within the watersheds).*** They reported results of detailed investigations aimed to study the biogeochemistry of Hg and other trace metals, specifically the impact of different land-use types within the watersheds on Hg speciation. Baloch (1997) observed large seasonal differences in river-mercury (Hg) concentrations and loadings showing dramatic increases in response to spring snowmelt and precipitation events. ***Results revealed total Hg concentrations were highly correlated with SS.***

van Geen and Luoma (1999) conducted a five-year study of dissolved Cd in San Francisco Bay, California and adjacent coastal waters. They showed that the composition of surface waters towards the mouth of the estuary was determined largely by the effect of coastal upwelling. However, surface samples collected throughout San Francisco Bay confirmed an internal Cd source unrelated to river discharge. The Cd content of a benthic foraminifer (*Elphidiella hannai*) in a dated sediment core from San Francisco Bay was used to determine that ***the water column Cd enrichments in San Francisco Bay were related to the rapid development of the watershed.***

Schaefer, *et al.* (1999) studied the increasing concentrations of platinum (Pt), rhodium (Rh), and palladium (Pd) in urban areas associated with increased use of catalytic converters on automobiles. At a typical urban site, the daily deposition rate of Pt in airborne dust was up to 23 ng/m^2.

Sanudo-Wilhelmy and Gill (1999) examined dissolved (< 0.45 μm) trace metals and phosphate concentrations in surface waters collected along the Hudson River estuary, New York, between 1995 and 1997 and compared them with samples collected in the mid-1970s. They concluded that the release of ***Pb and Hg from watershed soils, and Ni and Cu from estuarine sediments, may represent the primary contemporary sources of these metals to the estuary.***

Land applications of organic soil amendments can increase runoff concentrations of metals such as Fe and Zn, metalloids such as B and As, and non-metals such as P and S that have the potential for causing adverse environmental impacts. Aluminum sulfate, or alum

($Al_2(SO_4)_3C(14H_2O)$), can reduce concentrations of some materials in runoff from sites treated with organic amendments (Edwards, *et al.* 1999).

Birch, *et al.* (1999) investigated the sources of heavy metals in stormwater draining into Port Jackson, Sydney, Australia. ***Road dust from streets with different traffic densities in the catchment were highly enriched with Cu, Pb, and Zn. Soils also contained high concentrations of these metals over extensive areas of the catchment.*** Preliminary data suggests that ***roads and soils were probably important in supplying heavy metals to the estuary but the contributions of atmospheric deposition and contaminated sites had not yet been evaluated.***

Webster, *et al.* (2000) analyzed the sources and transport of trace metals in the Hatea River catchment and estuary in New Zealand. They found that the recently deposited estuarine sediment has elevated levels of Cu, Pb, and Zn from the more densely-populated areas, city stormwater drains and the Cu-containing antifoulants used in the marina. All metals were transported in both dissolved and particulate form in the tributaries, with lead being shown to bind most effectively to the sediment. Levesque and De Boer (2000) investigated the impact of a large urban center on the trace metal chemistry of a surficial fine-grained sediment in the South Saskatchewan River, Canada. No effect from the urban center on the metals content of the sediment was seen - with the exception of uranium, whose concentration was measurably greater below the urban center. Smith and Swanger (2000) investigated the impact of ***leaching of lead-free solders in construction waste and found that alloys containing antimony had leachate concentrations above regulatory limits. Alloys containing silver also potentially could impact the environment if entrained in stormwater runoff.***

Nonpoint sources of heavy metals (Hg, Cd, Cu, Zn, Pb, Ni) in the Rhine River watershed were investigated by Mohaupt, *et al.* (2001). ***They found that urban stormwater was the primary source of these metals in the Dutch portion of the watershed. Erosion was of lesser importance, while atmospheric deposition onto open water the least important source.*** Anthropogenic nonpoint sources accounted for 40 to 80% of the total sources for some metals. They recommended further studies of urban nonpoint sources of heavy metals and on ways to improve urban stormwater management. A mass balance of all known sources and sinks for heavy metals (Ag, Cd, Cu, and Pb) in New Haven Harbor, CT, was conducted by Rozan and Benoit (2001). Sources included direct atmospheric deposition, rivers, treated sewage effluent, combined sewer overflows, and permitted industrial discharges. All of the fluxes were directly measured, and the uncertainties were quantified. River inputs accounted for most of the total yearly metal discharges, while the salt marshes removed about 20 to 30% of the metals from the rivers before reaching the harbor. ***Atmospheric deposition is of minor importance, and is comparable to sewage effluent discharges.***

Davis and Burns (1999) ***examined lead concentrations in runoff from painted surfaces. In many tests, high Pb concentrations were found*** (using 100 mL of wash water over 1600 cm^2 of surface). Pb concentrations from 169 different structures followed the following order (median concentrations in the wash water): wood (49 µg/L) > brick (16 µg/L) > block (8.0 µg/L). Pb concentration depended strongly on paint age and condition, with the lead levels from washes of older paints being much higher than from freshly painted surfaces. Lead from surface washes were found to be 70%, or greater, in particulate lead form, suggesting the release of lead pigments from the weathered paints. Davis, *et al.* (2001a) presented loading estimates of lead, copper, cadmium, and zinc in stormwater from different sources. They reviewed available data from the literature, and ***conducted controlled experiments and other sampling. Specific sources that they examined included building siding and roofs; automobile brakes, tires, and oil leakage; and wet and dry atmospheric deposition. The most important sources they identified were building siding for all four metals, vehicle brake emissions for copper, and tire wear for zinc. Atmospheric deposition was an important source for cadmium, copper, and lead.***

Robertson, *et al.* (2002) characterized the geochemical and mineral magnetic qualities of urban sediment particulates from both inner and outer city road surfaces in Manchester, UK. High metal concentrations, coupled with the largely ferrimagnetic multi-domain (MD) mineral magnetic composition of the particulates, indicated anthropogenic origin, primarily particulates derived from automobiles. Iron and Pb concentrations showed a clear spatial trend, whereby concentrations were enhanced in the inner city samples. Lead concentrations for inner and outer city samples averaged 354 and 185 $\mu g\ g^{-1}$, respectively. Iron concentrations for inner and outer city samples average 11302 and 6486 $\mu g\ g^{-1}$, respectively. Sequential extraction analysis showed Mn, Fe, Zn and Pb were largely associated with the reducible fraction, whereas Cu was largely associated with the oxidizable fraction. ***Zinc was the only metal showing significant association with the exchangeable fraction (up to 33%), suggesting that it may be the most susceptible metal to mobilization during runoff.***

Ramessur and Ramjeawon (2002) determined the lead, chromium and zinc concentrations in sediments from the St. Louis River in Mauritius. The mean concentration of Cr (105 ± 30 mg kg^{-1}), Zn (167 ± 30 mg kg^{-1}) and Pb (14 ± 7 mg kg^{-1}) in sediments in an urbanized and industrialized region were well below the limits of 600, 2500 and 700 mg kg^{-1} in the draft standards (24% clay and 10% organic matter by weight) from the Netherlands. Industrial contamination appeared to undergo rapid dilution in the estuary as Cr had high levels near point sources from industries, but decreased rapidly in amount in the estuary possibly because of dilution by other sediments. ***The significant Zn levels from upstream to the estuary suggest that the potential sources could be the adjacent motorway and road runoff. Pb was two folds higher in the sediments in the estuary of St. Louis River compared to upstream and downstream indicating accumulation of Pb in estuarine sediments.*** The potential sources of sediment Pb were from the adjacent motorway and road runoff.

Buffleben, *et al.* (2002) investigated the concentrations of hazardous metal pollutants associated with the aqueous and suspended solids phases entering Santa Monica Bay from the Ballona Creek watershed during wet weather flow. Other objectives of this study were to evaluate during a storm event the relationship between (1) soluble and sorbed metals, (2) storm flow and pollutant loading, including a determination of a first flush was present, and (3) total mass loading of pollutants and relative pollution loading from three watershed sub-basins. The results indicated ***the suspended solids phase primarily transported the mass for five of the six hazardous metals studied: cadmium, chromium, copper, lead, and nickel. Arsenic was found primarily in the aqueous phase.***

Fatoki, *et al.* (2002) investigated trace metal pollution in the Umtata River in South Africa. High levels of Al, Cd, Pb, Zn and Cu were observed, which may affect the “health” of the aquatic ecosystem. Generally the sources of the metals in the river appeared to be diffuse, including rural, urban and agricultural runoff sources in the catchment. Tuccillo (2002) analyzed heavy metals in stormwater at six outfalls draining nonindustrial land uses in Monmouth County, New Jersey. Of the heavy metals, only Cu and Zn were found in all samples, mostly in dissolved form. Larger colloids (≥0.45 µm) were composed mostly of Fe, Al, and Si. Organic colloids were found mostly in the 0.01-0.45-µm-size range.

Glenn, *et al.* (2002) investigated the influence of chemistry, hydrology and suspended solids concentration on partitioning of heavy metals to particles and the applicability of this information to design of on-site controls for stormwater quality. Aqueous chemistry and residence time characteristics such as low alkalinity, low hardness and short pavement residence time (less than 30 minutes) could result in a majority of the heavy metal mass remaining in solution at the edge of the pavement with trends in partitioning only approaching equilibrium conditions towards the end of the event as heavy metals partition to entrained solids.

Mumley and Abu-Saba (2002) investigated the sources of mercury in San Francisco Bay as part of the TMDL development for mercury. ***Half of the contemporary excess mercury concentration in Bay sediments is accounted for by background processes, including shifts in the mineralogy of watershed source sediments and atmospheric deposition of global air sources. The other half of the excess mercury in Bay sediments is mostly attributed to mining legacy sources, with lesser fractions attributed to wastewater discharge (1-3%) and urban runoff (3-10%). Water column mercury concentrations in the turbid Bay waters are directly proportional to mercury concentrations of suspended sediments.***

Rose (2002) compared the major ion geochemistry of Piedmont streams in the Atlanta, Georgia region in order to investigate the effects of urbanization. The regression correlation coefficients for the ions that would evolve through mineral weathering (Ca, Mg, Na, and HCO_3) were much higher in urban stream flow than in the less urbanized waters. This potentially indicated that stormwaters in the urban basin were more closely derived from a two-end member mixture (groundwater and street runoff) than waters from the less developed area, which represented a more complex mixture.

Research by McPherson, *et al.* (2002) compared the pollutant loads in wet and dry weather in the highly urbanized Ballona Creek watershed. Models were used to compare the loading of the following pollutants: total suspended solids, biochemical oxygen demand, total nitrogen, total inorganic nitrogen, total Kjeldahl nitrogen, total phosphorus, copper, lead, arsenic, nickel, cadmium, and chromium. The results indicated that ***dry-weather flow contributed approximately 10-30% of the total annual flow discharged from Ballona Creek.*** The relative contribution to the annual pollutant load varied considerably between each pollutant. In general, the dry-weather-flow load was found to be significant, especially in years with lower precipitation totals.

De Vos, *et al.* (2002) performed a survey of the distribution and origin of platinum group elements (PGE), which includes platinum, palladium, rhodium, iridium, osmium, and ruthenium, in contemporary fluvial sediments in the Kentish Stour, England. The main factor responsible for the dispersion of these elements is their extensive anthropogenic use, and significant quantities enter fluvial systems via road runoff, storm drains, and wastewater and sewage treatment systems. The highest element abundances occur in the motorway-runoff sediments (maximum total PGE content of 55 ng/g), whilst the lowest values were recorded in the sedimentary rocks, where some samples contain PGE at concentrations below the limit of detection. The total PGE content of the river sediments ranged from 0.4 to 10.8 ng/g. The distribution and variation in concentrations and ratios of the PGE in the contemporary fluvial sediments correspond strongly with land-use changes (urban versus rural) and with points of discharge from sewage works.

In-stream metal loadings in the Tijuana River watershed were characterized by Gersberg, *et al.* (2002). In general, ***metal-loading trends could be ascertained from the shape of the storm hydrographs. Elevated metal concentrations existed in base and storm flow conditions.***

Sorme and Lagerkvist (2002) investigated the sources of heavy metals in urban wastewater in Stockholm, Sweden. Results showed that it was possible to track the sources of heavy metals for some metals such as Cu and Zn (110 and 100% found, respectively) as well as Ni and Hg (70% found). Other metals sources are still poorly understood or underestimated (Cd 60%, Pb 50%, Cr 20% known). ***The largest sources of Cu were tap water and roofs. For Zn the largest sources were galvanized material and car washes. For Pb, Cr and Cd, where sources were more poorly understood, the largest contributors for all were car washes.*** Vink and Behrendt (2002) investigated the heavy metal emissions, loads and transport in the Rhine and Elbe river basins. In most cases the measured heavy metal loads at monitoring stations were lower than the sum of the heavy metal emissions. This behavior in large river systems could largely be explained by retention processes (e.g. sedimentation) and was dependent on the specific runoff of a catchment. Between 51% (for Hg) and 74% (for Pb) of the total transport in the Elbe basin was supplied by inputs from diffuse sources. In the Rhine basin diffuse source inputs dominated the total transport and deliver more than 70% of the total transport. The diffuse hydrological pathways with the highest share were erosion and urban areas. Boller and Steiner (2002) investigated the emission and control of copper from roofs and roads in urban surface runoff. A large copper façade was used to investigate the concentrations of copper emitted. The concentrations ranged from 1 – 10 mg/L.

Robertson, *et al.* (2003) analyzed urban sediment samples from roadways in the UK and determined that most sediment had an anthropogenic origin, primarily from automobiles. Mn, Fe, Zn and Pb were largely associated with the reducible fraction, whereas Cu was largely associated with the oxidizable fraction. Zn was the only metal with significant association with the exchangeable fraction.

Morquecho and Pitt (2003) investigated the associations of heavy metals in stormwater with particulate and colloidal fractions. Turbidity, phosphorus, phosphate, magnesium, chromium, copper, iron, lead, and zinc had large decreases with filtration, especially for the more contaminated samples, while total solids and COD had much smaller changes with filtration, with substantial fractions associated with the filterable (<0.45 µm) fraction.

Schiff, *et al.* (2003) performed a retrospective evaluation of shoreline water quality along Santa Monica Bay beaches and showed that ***most of the water quality exceedances occurred near urban runoff drains even though the area represented by drains represent only a small part of the shoreline.*** Lim (2003) found that storm event characteristics and anthropogenic activities most influenced the loads of suspended sediment, nutrients and inorganics. The authors also suggested that the most appropriate sampling of stormwater quality should focus on conducting small-scale, relatively short-term studies to identify and assess specific water quality problems facing each catchment.

Sansalone and Dean (2003) studied the metal and particulate relationships at the upper end of an urban watershed in Baton Rouge, LA. Results indicated that mass-limited events generally exhibited similar but temporally disproportionate mass deliveries for Cd, Cu, Pb and Zn and an initial rapidly declining concentration profile (a strong "first flush"). In contrast, flow-limited events produced mass deliveries that were strongly proportional to the hydrograph flows. Mass-limited events are capable of washing off the complete contaminant load available in the watershed, and are mostly associated with highly impervious areas with very high rain intensities. In contrast, flow-limited events have adequate supplies of contaminants, but the energy of the rainfall and runoff are the limiting factors. Flow-limited events would be most common in more undeveloped areas, especially related to soil erosion. They also found that the partitioning of Cd, Cu, Pb and Zn in runoff was predominately to the particulate fraction.

Graves, *et al*. (2004) investigated the relationship between land use and stormwater quality in South Florida. Runoff from most land uses had low dissolved oxygen, and sediment and nutrient concentrations were closely related to land use, particularly to the amount of fertilizer applied in each land use. ***Copper was the most frequently detected metal and was, along with arsenic, associated with golf course runoff.***

Ramessur (2004) quantified Cr, Zn and Pb in rural and urban estuarine sediments on the island Republic of Mauritius and found that Zn and Pb were significantly higher in urban sediments. Sources were thought to be road runoff.

Selenium and mercury accumulations in the sediment, groundwater and surface water in the Las Vegas Wash were measured by Cizdziel and Zhou (2005). Selenium was higher in samples influenced by urban runoff and groundwater resurfacing.

Dean, *et al.* (2005) investigated the partitioning of metals in runoff from a Portland cement watershed. Zinc was found equally between the particulate and dissolved species, while lead was highly particulate-bound.

The sources of heavy metals and PAHs in urban runoff were investigated by Brown and Peake (2006) in New Zealand. ***Observed elevated lead and copper levels likely originated from industrial land uses, while zinc was attributed to residential galvanized roofing. The PAH observations suggested that an idle gasworks plant was contributing PAHs to runoff.***

Tucillo, *et al.* (2006) investigated the size fractionation of metals in runoff from residential and highway storm sewers. Pb and Cr were associated exclusively with particles > 5 μm in size. Fe, Al, and Si were found mostly in larger size fractions (> 70%), with lesser amounts in the smaller particles (0.45-5 μm in size).

Duke (2007) described the “intensity of industrial activity” method devised for the City of Jacksonville. This method uses a point scale system to visually score each facility based on the intensity of the industrial activities exposed to stormwater, and groups the results into categories A, B, C, or D in increasing order of intensity (Cross and Duke 2008). The categories are designed to distinguish high-concern facilities from low-concern facilities, and not to make fine distinctions among facilities with similar characteristics. This method is sufficient to distinguish facilities with little or no potential for discharging pollutants associated with stormwater from facilities that might discharge those pollutants. A key conclusion was that more than half of the facilities that were subject to Florida’s Multi-Sector Generic Permit (MSGP) were determined to be low-risk and those efforts could have been more effectively directed to higher risk industries (Cross and Duke 2008).

Appendix B: Sources of Urban Stormwater Heavy Metals

It has long been acknowledged that heavy metals found in stormwater mostly originate from automobile use activities, including gasoline combustion, brake lining, fluids (brake fluid, transmission oil, anti-freeze, grease, etc.), undercoatings, and tire wear (early reports by Durum 1974, Koeppe 1977, Rubin 1976, Shaheen 1975, Solomon and Natusch 1977, and Wilbur and Hunter 1980). Auto repair, pavement wear, and deicing compound use also contribute heavy metals to stormwater (Field, *et al*. 1973, and Shaheen 1975). ***All areas are affected by atmospheric deposition, while other sources of pollutants are specific to local activities.*** As examples, the ground surfaces of unpaved equipment or material storage areas can become contaminated by spills and debris, while undeveloped land remaining relatively unspoiled by activities can still contribute runoff solids, organics, and nutrients, if eroded. Atmospheric deposition, deposition from activities on paved surfaces, and the erosion of material from upland unconnected areas are the major sources of pollutants in urban areas.

Natural weathering and erosion products of rocks contribute the majority of the hardness and iron in urban runoff pollutants. Road dust and associated automobile use activities (gasoline exhaust products) historically contributed most of the lead in urban runoff. However, the decrease of lead in gasoline has resulted in current stormwater lead concentrations being about 1/10 of the levels found in stormwater in the early 1970s (Bannerman, *et al*. 1993). In certain situations, paint chipping can also be a major source of lead in urban areas. Road dust contaminated by tire wear products, and zinc plated metal erosion material, contribute most of the zinc to urban runoff. Urban landscaping activities can be a major source of cadmium (Phillips and Russo 1978). Electroplating and ore processing activities can also contribute chromium and cadmium.

Many pollutant sources are specific to a particular area and on-going activities. For example, iron oxides are associated with welding operations and strontium, used in the production of flares and fireworks, would probably be found on the streets in greater quantities around holidays, or at the scenes of traffic accidents. The relative contribution of each of these potential urban runoff sources is therefore highly variable, depending upon specific site conditions and seasons.

Zaman (1999) found that the ***catchments with high intensities of development in close proximity to stormwater systems were found to be transporting more pollutants to receiving waters than other catchments.*** Gromaire-Mertz, et al. (1999) collected stormwater runoff from roofs, courtyards and streets in an experimental catchment in central Paris, France, and analyzed the samples for SS, VSS, COD, BOD5, hydrocarbons, and heavy metals both in dissolved and particulate fractions. The street runoff showed large SS, COD and hydrocarbon loads, but the roof runoff had high concentrations of heavy metals. Wiese and Scmitt (1999) described urban stormwater contributions to large river systems. Their purpose was to develop a mass balance model for many stormwater pollutants, stressing nitrogen and phosphorus, the oxygen depleting substances and some heavy metals.

B.1. Chemical Quality of Rocks and Soils

As noted in the introduction of this report, soils contain varying amounts of heavy metals that can be eroded and contribute to the heavy metal discharges from an area. These “base” values can also be compared to the metal content of other particulates in an urban area to indicate possible contamination. The abundance of common elements in the lithosphere (the earth’s crust) is shown in Table B1 (Lindsay l979). Almost half of the lithosphere is oxygen and about 25 percent is silicon. Approximately 8 percent is aluminum and 5 percent is iron. Elements comprising between 2 percent and 4 percent of the lithosphere include calcium, sodium, potassium and magnesium. Because of the great abundance of these materials in the lithosphere, urban runoff transports only a relatively small portion of these elements to receiving waters, compared to natural processes. Fe and Al can both cause detrimental effects in receiving waters, if in their dissolved forms. A reduction of the pH substantially increases the abundance of dissolved metals. Table B2, also from Lindsay (1979), shows the rankings for common elements in soils. These rankings are quite similar to the values shown previously for the lithosphere. Natural soils can contribute pollutants to urban runoff through erosion. Again, Fe and Al are very high on this list and receiving water concentrations of these metals are not expected to be significantly affected by urban activities alone. Table B4 lists the means and ranges of soil concentrations determined during the California Benchmark Soil Survey (Kearney Foundation 1996, summarized by MWH 2005). A recent summary of heavy metal concentrations in soils (Table B3) was prepared by Hurley (2009) and is similar to these earlier reported values.

The values shown on Tables B1 and B2 are expected to vary substantially, depending upon the specific mineral types. Arsenic is mainly concentrated in iron and manganese oxides, shales, clays, sedimentary rocks and phosphorites. Mercury is concentrated mostly in sulfide ores, shales and clays. Lead is fairly uniformly distributed, but can be concentrated in clayey sediments and sulfide deposits. Cadmium can also be concentrated in shales, clays and phosphorites (Durum 1974).

Table B1. Common Elements in the Lithosphere (Lindsay 1979)

Abundance Rank	Element	Concentration in Lithosphere (mg/kg)
1	O	465,000
2	Si	276,000
3	Al	81,000
4	Fe	51,000
5	Ca	36,000
6	Na	28,000
7	K	26,000
8	Mg	21,000
9	P	1,200
10	C	950
11	Mn	900
12	F	625
13	S	600
14	Cl	500
15	Ba	430
16	Rb	280
17	Zr	220
18	Cr	200
19	Sr	150
20	V	150
21	Ni	100

Table B2. Common Elements in Soils (Lindsay 1979)

Abundance Rank	Element	Typical Minimum (mg/kg)	Typical Maximum (mg/kg)	Typical Average (mg/kg)
1	O			490,000
2	Si	230,000	350,000	320,000
3	Al	10,000	300,000	71,000
4	Fe	7,000	550,000	38,000
5	C			20,000
6	Ca	7,000	500,000	13,700
7	K	400	30,000	8,300
8	Na	750	7,500	6,300
9	Mg	600	6,000	5,000
10	Ti	1,000	10,000	4,000
11	N	200	4,000	1,400
12	S	30	10,000	700
13	Mn	20	3,000	600
14	P	200	5,000	600
15	Ba	100	3,000	430
16	Zr	60	2,000	300
17	F	10	4,000	200
18	Sr	50	1,000	200
19	Cl	20	900	100
20	Cr	1	1,000	100
21	V	20	500	100

Table B3. Trace Elements in the Earth's Crust and Soils

	Earth's Crust (mg/kg)	Soils (mg/kg)
Aluminum (AL)	82,300	72,000
Antimony (Sb)	0.2	0.66
Arsenic (As)	1.8	7.2
Beryllium (Br)	2.8	0.92
Cadmium (Cd)	0.15	-
Chromium (Cr)	102	54
Copper (Cu)	60	25
Iron (Fe)	56,300	26,000
Lead (Pb)	14	19
Mercury (Hg)	0.085	0.090
Nickel (Ni)	84	19
Selenium (Se)	0.05	0.39
Silver (Ag)	0.075	-
Strontium (Sr)	370	240
Zinc (Zn)	70	60

Summary from Hurley 2009

Table B4. California Benchmark Soils (Kearney Foundation 1996)

mg/kg	Mean	Minimum	Maximum
Aluminum	73,000	30,000	106,000
Antimony	0.6	0.15	1.95
Arsenic	3.5	0.6	11
Beryllium	1.28	0.25	2.7
Cadmium	0.36	0.05	1.7
Chromium	122	23	1579
Copper	28.7	9.1	96.4
Iron	37,000	10,000	87,000
Lead	23.9	12.4	97.1
Manganese	646	253	1687
Mercury	0.26	0.05	0.9
Nickel	57	9	509
Selenium	0.058	0.015	0.43
Silver	0.8	0.1	8.3
Thallium	0.56	0.17	1.1
Zinc	149	88	236
Zirconium	93	19	610

Summarized by MWH 2005

B.2. Atmospheric Sources of Urban Runoff Pollutants

Atmospheric sources affecting urban stormwater include dry dustfall and pollutants transported by precipitation. These have been monitored in many urban and rural areas. In some instances, however, the samples were combined as a bulk precipitation sample before processing. Automatic precipitation sampling equipment can distinguish between dry periods of fallout and precipitation. These devices cover and uncover appropriate collection jars exposed to the atmosphere. Much of this information was collected as part of the Nationwide Urban Runoff Program (NURP) and the Atmospheric Deposition Program, both sponsored by the U.S. Environmental Protection Agency.

One must be careful in interpreting the dry dustfall information because much of the polluted dust and dirt particles can be resuspended and then redeposited within the urban area several times as fugitive dust. In some cases, the measured atmospheric deposition values include material that was previously residing and measured in other urban runoff pollutant source areas. ***Only small fractions of the total atmospheric dustfall material would directly contribute to runoff, as much is apparently incorporated into the soil. Any dustfall material falling directly on the water (very important for lakes having small drainages, for example) obviously would be completely "discharged" to the receiving waters. Rain is subjected to infiltration, while the dry fall particulates are mostly incorporated with surface soils with only small fractions eroded during rains. Therefore, mass balances and determinations of urban runoff deposition and accumulation from different source areas can be highly misleading, unless transfer of material between source areas and the effective yield of this material to the receiving water is considered.*** Depending on the land use, relatively little of the dustfall in urban areas likely contributes to stormwater discharges (larger fractions with more pavement, less with more soil). Most of the atmospheric deposition material accumulates onto soil and vegetated surfaces where it is incorporated into the soil. If deposited onto pavement, it is more subject to washoff, but substantial amounts may still reside on the pavement and it becomes subject to wind erosion when large accumulations occur, where it is blown onto the surrounding unpaved areas. During many washoff tests and pavement loading measurements before and after rains, Pitt (1979, 1983, with McLean 1983, 1986, and others) found substantial amounts of material on the pavement after the rains. Rough pavement, light rains, and larger particulates cause more material to be left behind, while smooth pavement, very intense rains, and smaller particles are more effectively removed.

Table B5 summarizes rain quality reported by several early urban researchers. As expected, the non-urban area rain quality can be substantially better than urban rain quality. Many of the important heavy metals, however, have not been measured in rain in many areas of the country. The most important heavy metals found in rain have been Pb and Zn, both being present in rain in concentrations from about 20 up to several hundred μg/L. It is expected that more recent Pb rainfall concentrations would be substantially less than these older values, reflecting the decreased use of leaded gasoline since these measurements were taken. Iron is also present in relatively high concentrations in rain (about 30 to 40 μg/L).

Table B5. Summary of Reported Rain Heavy Metal Quality

	Rural-Northwest (Quilayute, WA)[1]	**Rural-Northeast (Lake George, NY)[1]**	**Urban-Northwest (Lodi, NJ)[2]**	**Continental Avg. (32 locations)[1]**
Scandium, μg/L	<0.002	nd		nd
Titanium, μg/L	nd	nd		nd
Vanadium, μg/L	nd	nd		nd
Chromium, μg/L	<2	nd	1	nd
Manganese, μg/L	2.6	3.4		12
Iron, μg/L	32	35		
Cobalt, μg/L	0.04	nd		nd
Nickel, μg/L	nd	nd	3	43
Copper, μg/L	3.1	8.2	6	21
Zinc, μg/L	20	30	44	107
Lead, μg/L			45	

Sources:
[1] Rubin 1976
[2] Wilbur and Hunter 1980

The concentrations of various urban runoff pollutants associated with dry dustfall are summarized in Table B6. Urban, rural and oceanic dry dustfall samples contained more than 5,000 mg iron/kg total solids. Zinc and lead were present in high concentrations. These constituents can have concentrations of up to several thousand mg of pollutant per kg of dry dustfall (ppm). Spring, *et al.* (1978) monitored dry dustfall near a major freeway in Los Angeles, CA. Based on a series of samples collected over several months, they found that Pb concentrations on and near the freeway can be about 3,000 mg/kg, but as low as about 500 mg/kg 150 m (500 feet) away. In contrast, the Cr concentrations of the dustfall did not vary substantially between the two locations and approached oceanic dustfall Cr concentrations.

Table B6. Atmosphere Dustfall Quality

Constituent, (mg constituent/ kg total solids)	Urban[1]	Rural/ suburban[1]	Oceanic[1]	Near freeway (LA)[2]	500' from freeway (LA)[2]
Scandium	5	3	4		
Titanium	380	810	2700		
Vanadium	480	140	18		
Chromium	190	270	38	34	45
Manganese	6700	1400	1800		
Iron	24000	5400	21000		
Cobalt	48	27	8		
Nickel	950	1400			
Copper	1900	2700	4500		
Zinc	6700	1400	230		
Lead				2800	550

Sources:
[1] Summarized by Rubin 1976
[2] Spring 1978

Much of the monitored atmospheric dustfall and precipitation would not reach urban receiving waters. The percentage of dry atmospheric deposition retained in a rural watershed was extensively monitored and modeled in Oakridge, TN (Barkdoll, *et al.* 1977). ***They found that about 98 percent of the Pb in dry atmospheric deposits was retained in the watershed, along with about 95 percent of the Cd, 85 percent of the Cu, 60 percent of the Cr and Mg and 75 percent of the Zn and Hg.*** Therefore, if the dry deposition rates were added directly to the yields from other urban runoff pollutant sources, the resultant urban runoff loads would be very much overestimated.

Tables B7 and B8 report bulk precipitation (dry dustfall plus rainfall) quality and deposition rates as reported by several researchers. Table B8 also presents the total watershed bulk precipitation, as the percentage of the total stream flow output for the three Knoxville watersheds studies. This shows that almost all of the pollutants presented in the urban runoff streamflow outputs could easily be accounted for by bulk precipitation deposition alone. Betson (1978) concluded that bulk precipitation is an important component for some of the constituents in urban runoff, but the transport and resuspension of particulates from other areas in the watershed are overriding factors.

Table B7. Bulk Precipitation Quality

Constituent (all units mg/L except pH)	Urban (average of Knoxville St. Louis & Germany[1]	Rural (Tennessee)[1]	Urban (Guteburg, Sweden)[2]
Total iron	0.8	0.7	
Manganese	0.03	0.05	
Lead	0.03	0.01	0.05
Mercury	0.01	0.0002	
Zinc			0.08
Copper			0.02

Sources:
[1]Betson 1978
[2]Malmquist 1978

Table B8. Urban Bulk Precipitation Deposition Rates (Source: Betson 1978)[a]

Constituent	Average Bulk Deposition Rate (kg/ha/yr)	Average Bulk Prec. as a % of Total Streamflow Output
Magnesium	9	180
Total Iron	1.9	47
Lead	1.1	650
Manganese	0.54	270
Arsenic	0.07	720
Mercury	0.008	250

[a] Average for 3 Knoxville, KY, watersheds.

Many of the recent atmospheric deposition studies apparently have not considered the relatively low delivery of these materials to receiving waters. Obviously, dry deposition directly on the surface of the receiving water would be much more important that dry deposition of heavy metals on natural soils and landscaped areas. Wet deposition yield would be similar to the fraction of the rainfall that occurs as runoff.

Atasi, *et al.* (1998, 1999, 2000, and 2001) analyzed atmospheric and runoff samples to determine wet and dry deposition and the relative contribution of deposition to runoff pollutant mass. They used specialized sampling equipment and ultra-clean analytical methodology to quantify the concentrations or fluxes of mercury, cadmium, and polychlorinated biphenyl in ambient air, precipitation, runoff, sanitary sewage, and treated sewage in Detroit, Michigan. They concluded that ***atmospheric deposition was the primary source of these compounds in runoff from controlled surfaces.*** The authors argued that the contribution of atmospheric deposition must be accounted for both in modeling of pollutant sources, but also in planning for pollution prevention.

Ahn (1998) recorded the total phosphorus (P) concentrations in south Fla. rainfall at weekly intervals with a detection limit of 3.5 µg/L. Air deposition was found to be the primary source of Cd, Hg, and PCB mass in runoff at the controlled sites in the study.

Glass and Sorensen (1999) examined a six-year trend (1990-1995) of wet mercury deposition in the Upper Midwest of the United States. The annual wet mercury deposition averaged 7.4 µg Hg/m^2-yr and showed significant variations between sites and illustrated significant increasing trends over the monitoring period. Warm (rain) season wet mercury deposition was found to average 77% of total annual wet deposition. Mason, *et al.* (1999) showed that the Chesapeake Bay was an efficient trap for mercury. However, in the estuary, methylation of the mercury occurred, the Bay became a source of methylmercury, and on a watershed scale, only about 5% of the total atmospheric deposition of mercury was exported to the ocean.

Tsai, *et al*. (2001) described their pilot study, conducted from August 1999 through August 2000, that estimated the loading of heavy metals from the atmosphere to San Francisco Bay. Dry deposition flux of Cu, Ni, Cd, and Cr was approximately 1100 +/- 73, 600 +/- 35, 22 +/- 15, and 1300 +/- 90 µg/m^2/year, respectively. The volume-weighted average concentrations of these trace metals in the rain water were 1.2, 0.4, 0.1, and 0.2 µg/L, respectively. Direct atmospheric deposition onto Bay waters, from both dry deposition and rainfall, contributed approximately 1900, 930, 93 and 1600 kg/yr of Cu, Ni, Cd and Cr, respectively. ***Stormwater runoff contributed approximately twice as much as the loading from direct atmospheric deposition. Direct***

atmospheric deposition was therefore found to be a relatively small contributor to the total load of these pollutants to the Bay.

Garnaud, *et al.* (1999) studied heavy metal concentrations in dry and wet atmospheric deposits in Paris, France, for comparison with urban runoff. Samples were continuously collected for 2 to 13 months at each of four test sites. Comparisons of median values of metal concentrations showed that rainwater contamination with heavy metals was only slightly higher in the center of Paris than at Fontainebleau (48 km SE of the city), which illustrates the medium range transport of atmospheric contaminants.

Gabriel, *et al.* (2002) investigated the availability of atmospherically deposited mercury to runoff and receiving waters. The review illustrated the importance of the relationship between mercury deposition and runoff efficiency for common watershed surfaces. The purpose of the review was to illustrate that ***the availability of atmospherically deposited mercury is a function of watershed characteristics including: terrestrial sorption properties, surface water chemistry, rainfall intensity, antecedent dry weather periods, and photochemical reactions.***

Schiff and Stolzenbach (2003) investigated the heavy-metal contributions of atmospheric deposition to Santa Monica Bay and compared the atmospheric deposition loading to the loading from other sources. The annual atmospheric deposition of chromium, copper, lead, nickel and zinc exceeded the estimated annual effluent loads from industrial and power generating stations to Santa Monica Bay. It is interesting to note that the prior noted study by Tsai, *et al.* (2001) had a conflicting conclusion for San Francisco Bay. Obviously, the mix of emission sources are different for the two locations, but this also indicates likely variability in how the studies were conducted. As an example, if only the deposition was measured along with the runoff discharges, it would be easy to conclude that the atmospheric deposition can account for much, if not most, of the runoff metals. However, it is necessary that complete watershed mass balances with many monitoring locations at all likely sources, be conducted. In this way, ***it is possible to determine the likely effective yield of contaminants from each source, which can be substantially different from the deposition rate which does not consider transport losses.*** As an example, Sabin, *et al.* (2005 and 2006b) studied the contribution from atmospheric deposition to the trace metal loadings in stormwater runoff in an impervious urban catchment. Atmospheric deposition accounted for over half, up to almost all, of the total trace metal loads in the runoff. Mean concentrations and fluxes were significantly higher at urban sites compared with the nonurban sites, although differences between urban and nonurban sites were reduced when sampling took place within 5 days after rainfall.

Local anthropogenic sources were found to be substantial contributors to wet deposition of mercury in southern Florida (Dvonch, *et al.* 2005). Higher concentrations were also found during the spring and summer compared to winter. Wang, *et al.* (2005a) investigated the exchange flux of mercury from coal-burning power plants in China. Mercury accumulation was measurable in waters, soils and plants.

B.3. Street Dust and Dirt Pollutant Sources

Most of the street surface dust and dirt material (by weight) are local soil erosion products, while some materials are contributed by motor vehicle emissions and wear (Shaheen 1975). Minor contributions are made by erosion of street surfaces in good condition. The specific makeup of street surface contaminants is a function of many conditions and varies widely (Pitt 1979).

Automobile tire wear is a major source of zinc in urban runoff (after the use of galvanized metals) and is mostly deposited on street surfaces and nearby adjacent areas. About half of the airborne particulates lost due to tire wear settle out on the street and the majority of the remaining particulates settle within about 6 meters of the roadway. Exhaust particulates, fluid losses, drips, spills and mechanical wear products can all contribute lead to street dirt. Many heavy metals are important pollutants associated with automobile activity. Most of these automobile pollutants affect parking lots and street surfaces. However, some of the automobile related materials also affect areas adjacent to the streets after being transported by wind after being resuspended from the road surface by traffic-induced turbulence.

Automobile exhaust particulates contribute many important heavy metals to street surface particulates and to urban runoff and receiving waters. The most notable of these heavy metals has been lead. However, by the late 1980s, the concentrations of lead in stormwater has decreased substantially (by about ten times) compared to early 1970 observations. This decrease, of course, is associated with significantly decreased use of leaded gasoline. Solomon and Natusch (1977) studied automobile exhaust particulates in conjunction with a comprehensive study of lead in the Champaign-Urbana, Illinois area. They found that the exhaust particulates existed in two distinct morphological forms. The smallest particulates were almost perfectly spherical, having diameters in the range of 0.1 to 0.5 μm (nanoparticles). These small particles consisted almost entirely of PbBrCl at the time of emission. Because they are small, they are expected to remain airborne for considerable distances and can be captured in the lungs when inhaled. They concluded that the small particles are formed by condensation of PbBrCl vapor onto small nucleating centers, which are probably introduced into the engine with the filtered engine air.

Solomon and Natusch (1977) found that the second major form of automobile exhaust particulates were rather large, being roughly 10 to 20 μm in diameter. These had typically irregular shapes, with somewhat smooth surfaces. They found that the elemental compositions of these irregular particles were quite variable, being predominantly Fe, Ca, Pb, Cl and Br. They found that individual particles did contain Al, Zn, S, P and some C, Cr, K, Na, Ni and thallium. Many of these elements (bromine, carbon, chlorine, chromium, potassium, sodium, nickel, phosphorus, lead, sulfur, and thallium) are most likely condensed, or adsorbed, onto the surfaces of these larger particles during passage through the exhaust system. They believed that these large particles originate in the engine or exhaust system because of their very high iron content. They found that 50 to 70 percent of the emitted lead was associated with these large particles, which would be deposited within a few meters of the emission point onto the roadway, because of their aerodynamic properties.

Solomon and Natusch (1977) also examined urban particulates near roadways and homes in urban areas. They found that lead concentrations in soils were higher near roads and houses. This indicated the ability of road dust and peeling house paint to contaminate nearby soils. The lead content of the soils ranged from 130 to about 1,200 mg/kg. Koeppe (1977), during another element of the Champaign-Urbana lead study, found that lead was tightly bound to various soil components. However, the lead did not remain in one location, but it was transported both downward in the soil profile and to adjacent areas through both natural and man-assisted processes.

B.4. Source Area Sheetflow and Particulate Quality Observations during Urban Mass Balance Studies

The following discussion briefly summarizes the source area sheetflow and particulate quality data obtained from several studies conducted in California, Washington, Nevada, Wisconsin, Illinois, Ontario, Colorado, New Hampshire, and New York since 1979. Most of the data obtained was for street dirt chemical quality, but a relatively large amount of parking and roof runoff quality data has also been obtained, along with some data pertaining to area soils. Only a few of these studies evaluated a broad range of source areas or land uses which would be needed to conduct a comprehensive mass balance; however, the consistent results from the different source areas in many locations help verify the contamination and transport processes.

B.4.1. Early Source Area Particulate Quality Observations

Particulate potency factors, or strengths, (usually expressed as mg pollutant/kg dry particulate residue, or ppm) for several research projects are summarized on Tables B9 and B10. These data can help recognize critical source areas, but care must be taken if they are used for predicting runoff quality because of likely differential effects due to washoff and erosion from the different source areas. These data show the variations in chemical quality between particles from different land uses and source areas. Typically, the potency factors increase as the use of an area becomes more intensive, but the variations are slight for different locations throughout the country. Increasing concentrations of heavy metals with decreasing particle sizes is also evident, for those studies that included particle size information. Only the quality of the smallest particle sizes (less than about 100 µm) are shown on these tables because they best represent the particles that are washed off different surfaces or eroded during rains.

Table B9. Summary of Observed Street Dirt Heavy Metal Chemical Quality (means) (mg constituent/kg solids)

Constituent	Residential	Commercial	Industrial
Cu	162 (4) 110 (6) 420 (2)	130 (6) 220 (2)	360 (4)
Pb	1010 (4) 1800 (6) 530 (5) 1200 (1) 1650 (3) 3500 (2)	3500 (6) 2600 (5) 2400 (1) 7500 (2)	900 (4)
Zn	460 (4) 260 (5) 325 (3) 680 (2)	750 (5) 1200 (2)	500 (4)
Cd	<3 (5) 4 (2)	5 (5) 5 (2)	
Cr	42 (4) 31 (5) 170 (2)	65 (5) 180 (2)	70 (4)

References; location; particle size described:

(1) Bannerman, *et al*. 1983 (Milwaukee, WI) <31µm

(2) Pitt 1979 (San Jose, CA) <45 µm

(3) Pitt 1985 (Bellevue, WA) <63 µm

(4) Pitt and McLean 1986 (Toronto, Ontario) <125 µm

(5) Pitt and Sutherland 1982 (Reno/Sparks, NV) <63 µm

(6) Terstrip, *et al*. 1982 (Champaign/Urbana, IL) <63 µm

Table B 10. Summary of Observed Heavy Metal Quality for Other Source Area Particulates (means for <125 μm particles) (mg constituent/kg solids)

	Cu	Pb	Zn	Cr
Residential/Commercial Land Uses				
Roofs	130	980	1900	77
Paved parking	145	630	420	47
Unpaved driveways	45	160	170	20
Paved driveways	170	900	800	70
Dirt footpath	15	38	50	25
Paved sidewalk	44	120	430	32
Garden soil	30	0	120	35
Road shoulder	35	50	120	25
		230		
Industrial Land Uses				
Paved parking	1110	650	930	98
Unpaved parking/storage	1120	205	1120	62
Paved footpath	280	0	1300	63
Bare ground	91	135	270	38

Source: Pitt and McLean 1986 (Toronto, Ontario)

B.4.2. Early Warm Weather Sheetflow Quality Observations

Sheetflow data, collected during actual rains, are probably more representative of runoff conditions that the dry particulate quality data presented above because they are not further modified by washoff mechanisms. These data, in conjunction with source area flow quantity information, can be used to predict outfall conditions and the magnitude of the relative sources of critical pollutants. Tables B11 through B13 summarize warm weather sheetflow observations, separated by source area type and land use, from many locations, obtained a number of early research projects.

Table B11. Sheetflow Quality Summary for Other Source Areas (mean concentration and reference)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
Aluminum (μg/L)									
Residential:	0.4 (5)	3.2 (5)	0.38 (5)		5.3 (5)		<0.03 (5)	0.5 (5)	1.5 (5)
Industrial:	<0.2 (5)	3.5 (5)	3.1 (5)	9.2 (5)	3.4 (5)	41 (5)		1.2 (5)	14 (5)
Cadmium (μg/L)									
Residential:	<4 (5) 0.6 (1)	2 (5)	<5 (5)		5 (5)		<1 (5)	<4 (5)	<5 (5)
Commercial:		5.1 (7) 0.6 (8)							<5 (5)
Industrial:	<4 (5)	<4 (5)	<4 (5)	<4 (5)	<4 (5)	<4 (5)		<4 (5)	<4 (5)
Chromium (μg/L)									
Residential:	<60 (5) <5 (4)	20 (5) 71 (4)	<10 (5)		<60 (5)		<10 (5)	<60 (5)	<60 (5) 49 (4)
Commercial:	<5 (4)	19 (7) 12 (8)							<60 (5)
Industrial:	<60 (5)	<60 (5)	<60 (5)	<60 (5)	<60 (5)	70 (5)		<60 (5)	<60 (5)

Table B11. Sheetflow Quality Summary for Other Source Areas (mean concentration and reference) (Continued)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
Copper (µg/L)									
Residential:	10 (5) <5 (4)	100 (5)	20 (5)		210 (5)		20 (5)	20 (5)	40 (5) 30 (4)
Commercial:	110 (4)	40 (2) 46 (4) 110 (7)							40 (5)
Industrial:	<20 (5)	480 (5)	260 (5)	120 (5)	40 (5)	140 (5)		30 (5)	220 (5)
Lead (µg/L)									
Residential:	<40 (5) 30 (3) 48 (1) 17 (4)	250 (5)	760 (5)		1400 (5)		30 (5)	80 (5)	180 (5) 670 (4)
Commercial:	19 (4) 30 (1)	200 (2) 350 (3) 1090 (4) 146 (1) 255 (7) 54 (8)							180 (5)
Industrial:	<40 (5)	230 (5)	280 (5)	210 (5)	260 (5)	340 (5)		<40 (5)	560 (5)

Table B11. Sheetflow Quality Summary for Other Source Areas (mean concentration and reference) (Continued)

Pollutant and Land Use	Roofs	Paved Parking	Paved Storage	Unpaved Parking/Storage	Paved Driveways	Unpaved Driveways	Dirt Walks	Paved Sidewalks	Streets
<u>Zinc (μg/L)</u>									
Residential:	320 (5) 670 (1) 180 (4)	520 (5)	390 (5)		1000 (5)		40 (5)	60 (5)	180 (5) 140 (4)
Commercial:	310 (1) 80 (4)	300 (5) 230 (4) 133 (1) 490 (7)							180 (5)
Industrial:	70 (5)	640 (7)	310 (5)	410 (5)	310 (5)	690 (5)		60 (5)	910 (5)

References:

(1) Bannerman, *et al.* 1983 (Milwaukee, WI) (NURP)
(2) Denver Regional Council of Governments 1983 (NURP)
(3) Pitt 1983 (Ottawa)
(4) Pitt and Bozeman 1982 (San Jose)
(5) Pitt and McLean 1986 (Toronto)
    (1) STORET Site #590866-2954309 (Shop-Save-Durham, NH) (NURP)
    (2) STORET Site #596296-2954843 (Huntington-Long Island, NY) (NURP)

Table B12. Sheetflow Quality Summary for Undeveloped Landscaped and Freeway Pavement Areas (Mean Observed Concentrations and reference)

Pollutants	Landscaped Areas	Undeveloped Areas	Freeway Paved Lane and Shoulder Areas
Aluminum, μg/L	1.5 (5)	11 (5)	- - - -
Cadmium, μg/L	<3 (5)	<4 (5)	60 (6)
Chromium, μg/L	10 (4)	<60 (5)	70 (6)
Copper, μg/L	<20 (5)	40 (2) 31 (4) <20 (5)	120 (6)
Lead, μg/L	30 (3) 35 (4) <30 (5)	100 (2) 30 (3) <40 (5)	2000 (6)
Zinc, μg/L	10 (4)	100 (2) 100 (5)	460 (6)

References:

(2) Denver Regional Council of Governments 1983 (NURP)
(3) Pitt 1983 (Ottawa)
(4) Pitt and Bozeman 1982 (San Jose)
(5) Pitt and McLean 1986 (Toronto)
(6) Shelly and Gaboury 1986 (Milwaukee)

Table B13. Source Area Filterable Pollutant Concentration Summary (means)

	Residential			Commercial		
	Total	**Filterable**	**% Filt.**	**Total**	**Filterable**	**% Filt.**
Roof Runoff						
Lead (μg/L)	48	4	8 (1)			
Paved Parking						
Lead (μg/L)				146 54	5 8.8	3 (1) 16 (8)
Arsenic (μg/L)				0.38	0.095	25 (8)
Cadmium (μg/L)				0.62	0.11	18 (8)
Chromium (μg/L)				11.8	2.8	24 (8)

References:
(1) Bannerman, *et al*. 1983 (Milwaukee) (NURP)
(8) STORET Site #596296-2954843 (Huntington-Long Island, NY) (NURP)

Toronto sheetflow water quality data during rain events were plotted against the rain volume that had occurred before the samples were collected to identify any possible trends of concentrations with rain volume. No statistically significant trends were observed (Pitt and McLean 1986). Lead and zinc concentrations were highest in sheetflows from paved parking areas and streets, with some high zinc concentrations also found in roof drainage samples. However, some of the Toronto sheetflow contributions were not sufficient to explain the concentrations of some constituents observed in runoff at the outfall. As an example, ***the high concentrations of dissolved Cr, dissolved Cu, and dissolved Zn in the Toronto industrial outfall during both wet and dry weather could not be explained by the wet weather sheetflow observations. It is expected that some industrial wastes, possibly originating from metal plating operations, were the cause of these high concentrations of dissolved metals at the outfall and that some sanitary sewage was entering the storm drainage system.***

B.4.3. Source Area Sheetflow Observations during Mass Balance Studies in Birmingham, AL

Pitt, *et al.* (1995) collected and analyzed 87 urban stormwater runoff samples from a variety of source areas under different rain conditions for many organic and metallic toxicants. All of the samples were analyzed in filtered (0.45 μm filter) and non-filtered forms to enable partitioning of the toxicants into "particulate" (non-filterable) and "dissolved" (filterable) forms. Samples were obtained from shallow flows originating from homogeneous source areas by using several manual grab sampling procedures. Table B14 summarizes the source area sample data (mean, maximum, and minimum concentrations) for the heavy metals analyzed. The heavy metals analyzed were detected in almost all samples, including the filtered sample portions. ***The***

particulate sample fractions generally had much higher concentrations than the filtered sample fractions, with the exception of Zn which was mostly associated with the dissolved sample portion (i.e., not associated with the SS). The detection frequencies for the heavy metals are all close to 100 percent for all source areas. Roof runoff, along with storage areas, generally had the highest concentrations of Zn, probably from galvanized roof drainage and building components, as previously reported by Bannerman, *et al*. (1983). Parking and storage areas had the highest Ni concentrations, while vehicle service areas and street runoff had the highest concentrations of Cd and Pb. Street and storage area runoff samples had the highest Cu concentrations.

Table B14. Stormwater toxicants detected in at least 10% of the source area sheetflow samples (μg/L, unless otherwise noted).

	Roof areas		Parking areas		Storage areas		Street runoff		Loading docks		Vehicle service area		Landscape areas		Urban creeks		Detention ponds	
	N.F.[a]	F.[b]	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.
Total samples	**12**	**12**	**16**	**16**	**8**	**8**	**6**	**6**	**3**	**3**	**5**	**5**	**6**	**6**	**19**	**19**	**12**	**12**
Metals (detection limit = 1 μg/L)																		
Lead detection frequency = 100% N.F. and 54% F.																		
No. detected	12	1	16	8	8	7	6	4	3	1	5	2	6	1	19	15	12	8
Mean	41	1.1	46	2.1	105	2.6	43	2	55	2.3	63	2.4	24	1.7	20	1.4	19	1
Max.	170		130	5.2	330	5.7	150	3.9	80		110	3.4	70		100	1.6	55	1
Min.	1.3		1	1.2	3.6	1.6	1.5	1.1	25		27	1.4	1.4		1.4	<1	1	<1
Zinc detection frequency = 99% N.F. and 98% F.																		
No. detected	12	12	16	16	8	7	6	6	2	2	5	5	6	6	19	19	12	12
Mean	250	220	110	86	1730	22	58	31	55	33	105	73	230	140	10	10	13	14
Max.	1580	1550	650	560	13100	100	130	76	79	62	230	230	1160	670	32	23	25	25
Min.	11	9	12	6	12	3	4	4	31	4	30	11	18	18	<1	<1	<1	<1
Copper detection frequency = 98% N.F. and 78% F.																		
No. detected	11	7	15	13	8	6	6	5	3	2	5	4	6	6	19	17	12	8
Mean	110	2.9	116	11	290	250	280	3.8	22	8.7	135	8.4	81	4.2	50	1.4	43	20
Max.	900	8.7	770	61	1830	1520	1250	11	30	15	580	24	300	8.8	440	1.7	210	35
Min.	1.5	1.1	10	1.1	10	1	10	1	15	2.6	1.5	1.1	1.9	0.9	<1	<1	0.2	<1
Aluminum detection frequency = 97% N.F. and 92% F.																		
No. detected	12	12	15	15	7	6	6	6	3	1	5	4	5	5	19	19	12	12
Mean	6850	230	3210	430	2320	180	3080	880	780	18	700	170	2310	1210	620	190	700	210
Max.	71300	1550	6480	2890	6990	740	10040	4380	930		1370	410	4610	1860	3250	500	1570	360
Min.	25	6.4	130	5	180	10	70	18	590		93	0.3	180	120	<5	<5	<5	<5
Cadmium detection frequency = 95% N.F. and 69% F.																		
No. detected	11	7	15	9	8	7	6	5	3	3	5	3	4	2	19	15	12	9
Mean	3.4	0.4	6.3	0.6	5.9	2.1	37	0.3	1.4	0.4	9.2	0.3	0.5	0.6	8.3	0.2	2	0.5
Max.	30	0.7	70	1.8	17	10	220	0.6	2.4	0.6	30	0.5	1	1	30	0.3	11	0.7
Min.	0.2	0.1	0.1	0.1	0.9	0.3	0.4	0.1	0.7	0.3	1.7	0.2	0.1	0.1	<0.1	<0.1	0.1	0.4
Chromium detection frequency = 91% N.F. and 55% F.																		
No. detected	7	2	15	8	8	5	5	4	3	0	5	1	6	5	19	15	11	8
Mean	85	1.8	56	2.3	75	11	9.9	1.8	17		74	2.5	79	2	62	1.6	37	2
Max.	510	2.3	310	5	340	32	30	2.7	40		320		250	4.1	710	4.3	230	3
Min.	5	1.4	2.4	1.1	3.7	1.1	2.8	1.3	2.4		2.4		2.2	1.4	<0.1	<0.1	<0.1	<0.1

	Roof areas		Parking areas		Storage areas		Street runoff		Loading docks		Vehicle service area		Landscape areas		Urban creeks		Detention ponds	
	N.F.[a]	F.[b]	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.	N.F.	F.
Total samples	**12**	**12**	**16**	**16**	**8**	**8**	**6**	**6**	**3**	**3**	**5**	**5**	**6**	**6**	**19**	**19**	**12**	**12**
Metals (detection limit = 1 μg/L)																		
Nickel detection frequency = 90% N.F. and 37% F.																		
No. detected	10	0	14	4	8	1	5	0	3	1	5	1	4	1	18	16	11	8
Mean	16		45	5.1	55	87	17		6.7	1.3	42	31	53	2.1	29	2.3	24	3
Max.	70		130	13	170		70		8.1		70		130		74	3.6	70	6
Min	2.6		4.2	1.6	1.9		1.2		4.2		7.9		21		<1	<1	1.5	<1

[a] N.F.: concentration associated with a nonfiltered sample.

[b] F.: concentration after the sample was filtered through a 0.45 μm membrane filter.

[c] Number detected refers to the number of samples in which the toxicant was detected.

[d] Mean values based only on the number of samples with a definite concentration of toxicant reported (not on the total number of samples analyzed).

[e] The minimum values shown are the lowest concentration detected, they are not necessarily the detection limit.

source: Pitt, *et al.* 1995

Malmquist, *et al.* (1999) investigated the sources of pollutants discharging to Lake Trekanten, Stockholm, which receives stormwater from residential and traffic areas. Pb, Cd, Cu, Zn, P, and PAH in the stormwater from the catchment area were quantified by a source model. It was concluded that building materials were the dominant sources for Cu and important sources for Zn. Source control measures, including covering copper-plated roofs, decreasing traffic, and changes of vehicle materials, were expected to reduce discharges of Cu to less than a third of current levels.

Birch, *et al.* (1999) investigated the sources of heavy metals in stormwater draining into Port Jackson, Sydney, Australia. Road dust from streets with different traffic densities in the catchment were highly enriched with Cu, Pb, and Zn. Soils also contained high concentrations of these metals over extensive areas of the catchment. Preliminary data suggests that roads and soils were probably important in supplying heavy metals to the estuary but the contributions of atmospheric deposition and contaminated sites had not yet been evaluated.

Sanudo-Wilhelmy and Gill (1999) compared current pollutant concentrations in the Hudson River Estuary, New York with concentrations measured in the 1970s. The concentrations of Cu, Cd, Ni, and Zn have declined, while concentrations of dissolved nutrients (PO4) have remained relatively constant during the same period of time, suggesting that wastewater treatment plant improvements in the New York/New Jersey Metropolitan area have not been as effective at reducing nutrient levels within the estuary. Rather than inputs from point sources, the release of Pb and Hg from watershed soils, and Ni and Cu from estuarine sediments, may represent the primary contemporary sources of these metals to the estuary.

B.4.4. Source Area Sheetflow Pollutant Concentrations during Wisconsin Urban Area Mass Balance Studies

This section presents source area data summaries from seven monitoring projects conducted in Wisconsin, and one associated project conducted in Michigan. The monitoring was conducted by the United States Geological Survey (USGS) in cooperation with the Wisconsin Department of Natural Resources (WI DNR). These monitoring projects were carried out between 1991 and 1997 as urban area mass balance projects and were conducted to calibrate WinSLAMM, the Source Loading and Management Model (Pitt and Voorhees 1995).

Madison, WI, runoff samples were collected during the summer of 1991 (Bannerman, *et al.* 1993) to identify the relative pollutant loads from the most common source areas in two study areas. One study area was mostly residential with some commercial land use, while the second area was an all light industrial land use. Sheetflow samples were collected from 46 sites representing roofs, streets, driveways, parking lots, and lawns. The sheetflow samplers were simple in design and were positioned to isolate the runoff from each type of source area, and the collected samples represented runoff composites occurring during the sampled events. Automated flow meters and water samplers were also installed at the storm drain outfalls for each study area to quantify the total mass balance for the area for each event. The sheetflow samples were analyzed for total suspended solids, total solids, total phosphorus, dissolved phosphorus, dissolved and total recoverable zinc, copper, cadmium, chromium, and lead, hardness, and fecal coliform bacteria. Between 7 and 10 runoff samples were collected at all of the sites, except for lawns and commercial parking areas where fewer samples were collected.

Milwaukee and Madison, WI, runoff samples were collected during 1993 (Roa-Espinosa and Bannerman 1994) to evaluate different methods for collecting source area runoff samples at industrial sites. A total of 50 sampling locations at roofs, paved areas, and lawns were sampled at five industrial facilities. The composite samples were analyzed for chemical oxygen demand, suspended solids, total solids, total recoverable zinc, lead, nickel, and copper, and hardness. Depending on the location, samples were collected during 5 to 7 runoff events at each area.

Marquette, MI, runoff samples were collected during 1993 and 1994 (Steuer, *et al.* 1997) to characterize contaminant concentrations for eight sources in one study area. The study area (297 acres) contained a mixture of land uses including residential, open space, commercial and institutional. A total of 33 sheetflow sampling sites were located at streets, parking lots, driveways, rooftops, and grass areas. Samples were analyzed for total solids, suspended solids, ammonia N, nitrate plus nitrite, total Kjeldahl nitrogen, total phosphorus, dissolved phosphorus, hardness, total recoverable and dissolved zinc, lead, cadmium, and copper, fecal coliform, BOD, COD, and PAHs. Sheetflow samples were collected for 12 runoff events at each site. Flow and water quality were measured at the storm drain outfall for the study area.

Madison, WI, runoff samples were collected during 1994 and 1995 (Waschbusch, *et al.* 1999) to estimate the sources of phosphorus in two residential areas for further detailed calibration of WinSLAMM. All the source areas were in two drainage areas. One was 232 acres, with mostly residential and some commercial land uses, while the other was 41 residential acres. Sheetflow samples were collected from roofs, streets, driveways, parking lots, and lawns in residential and commercial land uses. Twenty five storms were sampled in both basins. The sheetflow samples were analyzed for total suspended solids, total solids, dissolved phosphorus, and total phosphorus. Flow and water quality were measured at the storm drain outfalls for both study areas.

Madison, WI, runoff samples were collected during 1994 and 1995 (Waschbusch, *et al.* in press) to evaluate the effects of various environmental factors on the yields of pollutants washed off city streets. The environmental factors included average daily traffic count, antecedent dry time, rainfall intensity, rainfall depth, season, and tree canopy. Street pollutant concentrations were also used to calibrate WinSLAMM. Sheetflow samples were collected from five streets with different daily traffic counts. A total of 11 or 12 runoff samples were collected at each site. Samples were analyzed for suspended solids, PAHs, hardness, and total and dissolved cadmium, lead, copper, zinc, and phosphorus.

Superior, WI, runoff samples were collected during 1995 and 1996 (Holstrom, *et al.* 1995 and 1996) to measure flow rates and water quality for runoff from an undeveloped site. The drainage area of the wooded lot is 76.2 acres. Flow was measured with a Parshall flume and runoff samples were collected with a volume activated water quality sampler. Sixteen storm-composite samples were analyzed for suspended solids, total solids, and total phosphorus. Samples were less frequently analyzed for COD, BOD, sulfate, chloride, nitrogen compounds, and total copper, lead, and zinc.

Madison, WI, runoff samples were collected during 1996 and 1997 (Waschbusch, *et al*. 1999) to verify the pollutant removal efficiency of a stormwater treatment device (Stormceptor). The device was located to treat the runoff from a 4.3 acre (1.7ha) city maintenance yard. Inlet and outlet runoff samples were collected for 45 runoff events. Samples were analyzed for total solids, suspended solids, total and dissolved phosphorus, nitrate plus nitrite, ammonia N, chloride, hardness, alkalinity, organic carbon, particle sizes, PAHs, and total and dissolved copper, cadmium, lead, and zinc. Automated sampling equipment was used to measure flow and collect flow–weighted composite samples. The inlet pollutant concentrations were used to calibrate WinSLAMM for industrial parking lots.

Milwaukee, WI, runoff samples were collected during 1996 (Corsi, *et al*. 1999) to measure the pollutant removal efficiency of a stormwater treatment device (the Multi-Chamber Treatment Train). The device was located to treat the runoff from 0.10 acres of parking lot at a city maintenance facility. Inlet and outlet samples were collected for 15 runoff events. Flow meters and automatic water samplers were used to measure flow rates and collect flow-weighted composite water samples in the inlet and outlet pipes. Samples were analyzed for total solids, suspended solids, alkalinity, BOD, COD, volatile suspended solids, ammonia as N, nitrate plus nitrite as N, chloride, sulfate, hardness, PAHs, TOC, total and dissolved phosphorus, total and dissolved zinc, cadmium, lead, chromium, and copper. The inlet pollutant concentrations were used to calibrate WinSLAMM for industrial parking lots.

Results from the eight Wisconsin studies were combined to create an average concentration for each source area (Table B15). Almost all of the average concentration values represent the results from more than one study. Because the constituent list was different for each study, the sample count varies between the types of source areas. Sample counts are high for suspended solids and phosphorus, since they were analyzed during all the studies. Only one project (Marquette, MI) analyzed COD and PAHs for all the source areas, so these constituents have a low sample count. Censored values (samples having less than the detection limit) are included as one-half the detection limit for some of the constituents having low sample counts. Although loads from a source area are greatly influenced by the volume of runoff, the large differences in some of the source area concentrations can decrease the importance of volume when comparing the loads from different source areas. For example, the volume of runoff from lawns is expected to be relatively low, but concentrations of phosphorus in lawn runoff are 2 to 10 times higher than for other source areas. Because of these relatively high concentrations, lawns can contribute as much as 50% of the annual total phosphorus load in a residential area (Washbusch, *et al*. 1999). With PAH levels from commercial parking lots 10 to 100 times higher than from any other source area, commercial parking lots representing only 3% of an urban drainage area can contribute 60% of the annual PAH load (Steuer, *et al*. 1997).

Concentrations for some of the pollutants can be compared between roofs and streets for all three land uses. Streets in industrial areas are likely important sources of suspended solids, total phosphorus, and zinc whenever they are compared to commercial and residential streets. But concentrations of these three pollutants in industrial roof runoff is similar to, or lower than, the other two land uses.

Table B15. Wisconsin Source Area Sheet Flow Concentrations and Particulate Strengths (Pitt, et al. 2004)

Source Area	Suspended Solids (mg/L)	Cd, Total (µg/L)	Cd, Part.* (mg/Kg)	Cd, Dis. (µg/L)	Cr, Total (µg/L)	Cr, Part.* (mg/Kg)	Cr, Dis. (µg/L)
Residential Roofs							
Sample Count	81	21	5	14	n/a	n/a	n/a
Average	36.7	0.54	9.0	0.15	n/a	n/a	n/a
COV**	2.07	1.78	0.67	0.67	n/a	n/a	n/a
Commercial Roofs							
Sample Count	34	12	5	9	n/a	n/a	n/a
Average	32.8	0.65	12.45	0.73	n/a	n/a	n/a
COV	1.25	1.03	1.00	1.06	n/a	n/a	n/a
Industrial Roofs							
Sample Count	42	4	1	4	n/a	n/a	n/a
Average	15.8	0.30	1.56	0.28	n/a	n/a	n/a
COV	1.7	0.47	n/a	0.75	n/a	n/a	n/a
Commercial Parking							
Sample Count	44	19	16	19	13	11	14
Average	130	0.95	4.65	0.48	9.8	47	2.46
COV	1.15	0.69	0.59	1.33	0.81	0.40	0.83
Industrial Parking Lots							
Sample Count	90	27	20	24	27	12	13
Average	244	1.5	4.2	0.49	11	24	1.26
COV	0.96	0.53	0.55	1.11	0.84	0.42	0.75
Driveways							
Sample Count	69	19	14	14	9	2	2
Average	154	0.91	2.88	0.25	1.94	11	1.5
COV	1.10	1.06	0.79	0.74	0.47	0.01	0.00
Small Landscape Areas							
Sample Count	40	3	3	3	1	1	1
Average	227	0.63	1.51	0.30	19	20	1.5
COV	1.25	0.40	0.69	0.99	n/a	n/a	n/a
Commercial Streets							
Sample Count	75	39	36	38	10	10	10
Average	176	1.03	4.81	0.38	18	38	8.6
COV	1.17	0.67	0.74	1.54	0.47	0.28	0.81
Residential Streets							
Sample Count	131	14	9	9	16	14	16
Average	183	0.6	2.25	0.14	6	11	1.5
COV	1.7	0.85	0.80	0.37	0.64	0.82	0.00
Industrial Streets							
Sample Count	15	13	10	10	15	15	15
Average	894	1.1	1.15	0.29	20	24	3
COV	0.69	0.82	0.88	0.60	0.53	0.56	0.86
Freeways							
Sample Count	66	21	11	11	n/a	n/a	n/a
Average	138	0.71	4.64	0.22	n/a	n/a	n/a
COV	1.17	0.36	0.34	0.39	n/a	n/a	n/a
Undeveloped Areas							
Sample Count	5	n/a	n/a	n/a	n/a	n/a	n/a
Average	16	n/a	n/a	n/a	n/a	n/a	n/a
COV	0.43	n/a	n/a	n/a	n/a	n/a	n/a

Table B15. Wisconsin Source Area Sheet Flow Concentrations and Particulate Strengths (Pitt, *et al.* 2004) continued.

Source Area	Cu, Total (µg/L)	Cu, Part.* (mg/Kg)	Cu, Dis. (µg/L)	Pb, Total (µg/L)	Pb, Part. * (mg/Kg)	Pb, Dis. (µg/L)
Residential Roofs						
Sample Count	34	28	29	23	21	21
Average	21	160	10.2	43	870	8.47
COV	1.60	1.32	1.37	2.19	0.77	1.52
Commercial Roofs						
Sample Count	18	12	13	13	13	14
Average	19	180	12.9	58	750	27.1
COV	0.81	1.01	1.17	1.06	0.53	1.40
Industrial Roofs						
Sample Count	43	n/a	n/a	4	4	4
Average	9	n/a	n/a	8.25	220	1.50
COV	0.57	n/a	n/a	0.30	1.09	0.0
Commercial Parking Lots						
Sample Count	19	18	19	19	18	19
Average	30	100	14.4	51.1	320	1.72
COV	0.81	0.69	0.89	0.81	0.35	0.35
Industrial Parking Lots						
Sample Count	41	33	34	25	11	11
Average	33	83	11.0	53	180	2.06
COV	0.50	0.48	1.05	0.49	0.46	1.14
Driveways						
Sample Count	19	17	17	19	19	8
Average	37	89	13.0	57	240	3
COV	1.02	1.04	0.74	1.3	0.81	0.55
Small Landscape Areas						
Sample Count	11	10	11	3	3	3
Average	12	14	7.4	54	250	2.83
COV	0.36	0.42	0.51	0.90	1.07	0.64
Commercial Streets						
Sample Count	50	47	48	49	47	37
Average	34	140	12.0	39	210	1.9
COV	0.57	1.26	0.86	0.69	0.47	0.44
Residential Streets						
Sample Count	32	29	29	32	31	23
Average	18	39	7.05	24.4	87	1.55
COV	0.57	0.56	0.72	0.68	0.57	0.49
Industrial Streets						
Sample Count	15	15	15	15	15	15
Average	22	74	21.7	87	100	1.5
COV	0.61	0.43	0.61	0.68	0.33	0
Freeways						
Sample Count	57	21	21	21	8	8
Average	59	300	13	34	230	1.56
COV	0.59	0.54	0.56	1.2	0.38	2.33
Undeveloped Areas						
Sample Count	1	n/a	n/a	1	1	n/a
Average	5	n/a	n/a	1.3	48	n/a
COV	n/a	n/a	n/a	n/a	n/a	n/a

Table B15. Wisconsin Source Area Sheet Flow Concentrations and Particulate Strengths (Pitt, *et al.* 2004) continued.

Source Area	Zn, Total (µg/L)	Zn, Part.* (mg/Kg)	Zn, Dis. (µg/L)
Residential Roofs			
Sample Count	34	5	6
Average	185	2900	278
COV	1.09	0.56	0.80
Commercial Roofs			
Sample Count	15	6	6
Average	322	3500	182
COV	0.54	0.95	0.92
Industrial Roofs			
Sample Count	44	n/a	n/a
Average	319	n/a	n/a
COV	1.49	n/a	n/a
Commercial Parking Lots			
Sample Count	20	7	7
Average	292	802	51
COV	0.91	0.58	0.42
Industrial Parking Lots			
Sample Count	26	17	19
Average	227.7	490	99.5
COV	0.67	0.47	1.25
Driveways			
Sample Count	19	19	15
Average	164	650	166
COV	0.79	0.48	0.48
Small Landscape Areas			
Sample Count	10	2	2
Average	67	160	34.0
COV	0.39	1.28	0.37
Commercial Streets			
Sample Count	50	48	37
Average	302	1150	60.2
COV	0.95	1.23	1.03
Residential Streets			
Sample Count	32	26	11
Average	151	350	45.0
COV	0.71	0.55	0.39
Industrial Streets			
Sample Count	15	15	15
Average	593	540	167
COV	0.48	0.42	0.51
Freeways			
Sample Count	57	21	21
Average	233	1330	22.6
COV	0.78	0.36	0.42
Undeveloped Areas			
Sample Count	n/a	n/a	n/a
Average	n/a	n/a	n/a
COV	n/a	n/a	n/a

B.4.5. Roof Runoff

Förster (1999) and Förster, *et al.* (1999) summarized studies investigating roof runoff as stormwater heavy metal, and other pollutant sources. Runoff samples were taken from an experimental roof system containing five different roofing materials and from house roofs at five different locations in Bayreuth, Germany. It was found that local sources (e.g. PAH from heating systems), dissolution of the roof systems' metal components, and background air pollution were the main sources of the roof-runoff pollution. They found that the first flush from the roofs often was heavily polluted and should be specially treated. They concluded that ***roofs having metal surfaces should not be connected to infiltration facilities as concentrations of Cu and Zn far exceed various toxicity threshold values.*** They also examined a green (vegetated) roof for comparison. These roofs were found to act as a source of heavy metals which were found to be in complexes with dissolved organic material. Leaching from unprotected Zn sheet surfaces on the green roofs resulted in extremely high Zn concentrations in the runoff. In contrast, the green roofs were a trap for PAH.

Zobrist, *et al.* (2000) examined the potential effects of roof runoff on urban stormwater drainage from three different types of roofs: an inclined tile roof, an inclined polyester roof and a flat gravel roof. Runoff from the two inclined roofs showed initially high ("first flush") concentrations of the pollutants with a rapid decline to lower levels. The flat gravel roof showed lower concentrations of most of the pollutants because of the ponding of the water on the roof surface acting like a detention pond. Pollutant loadings was similar to atmospheric deposition, with the exception of Cu from drain corrosion (rate about 5 g/m^2/yr).

Tobiason and Logan (2000) used the whole effluent toxicity test (WET) to characterize stormwater runoff samples from four outfalls at Sea-Tac International Airport. Three of the four outfalls met standards; the source of the toxicity at the fourth outfall was found to be zinc-galvanized metal rooftops. ***Typically, more than 50% of the total Zn in the runoff was in dissolved forms and likely bioavailable.***

Wallinder and Laygraf (2001), Wallinder, *et al.* (2002) and Karlen, *et al.* (2002) studied the seasonal variations in the corrosion and runoff rates from naturally and pre-patinated copper roofs in Singapore and Stockholm. Their experiments lasted for several years, at urban and rural locations. Seasonal variations in corrosion rates were observed at the rural site, likely associated with variations in humidity, while no seasonal variations were observed at the urban site. The corrosion rates continually decreased with time. Measured annual runoff rates from fresh and brown pre-patinated roofs were 1.1-1.6 g/m^2 and 5.5-5.7 g/m^2, in Stockholm and Singapore, respectively. Naturally aged copper sheet (130 years old) and green pre-patinated copper sheet showed slightly higher (1.6-2.3 g/m^2), but comparable runoff rates in Stockholm. In Singapore, runoff rates from green pre-patinated copper sheet were 8.4-8.8 g/m^2. Comparable runoff rates between fresh and brown-patinated copper sheet and between green naturally patinated and green pre-patinated copper sheet at each site were related to similarities in patina morphology and composition. The runoff rates were significantly lower than the measured corrosion rates as long as the adhering copper patina was increasing with exposure time. From 70 to 90% of the Cu in the runoff (collected immediately after leaving the surface) was present in the most bioavailable form, the hydrated cupric ion, $Cu(H_2O)_6^{2+}$. The copper-containing runoff water, sampled directly after release from the roof, caused significant reduction in growth rate of the green alga.

Gromaire, *et al.* (2002) investigated the impact of zinc roofing on urban pollutant loads in Paris. On an annual basis, runoff from Parisian zinc roofs would produce around 34 to 64 metric tons of zinc and 15 to 25 kg of cadmium, which is approximately half the load generated by runoff from all of Paris.

Heijerick, *et al.* (2002) investigated the bioavailability of zinc in runoff from roofing materials in Stockholm, Sweden. Chemical speciation modeling revealed that most zinc (94.3-99.9%) was present as the free Zn ion, the most bioavailable speciation form. These findings were confirmed by the results of the biosensor test (Biomet™), which indicated that all zinc was indeed bioavailable. Analysis of the ecotoxicity data also suggested that the observed toxic effects were due to the presence of Zn^{2+} ions.

Clark, *et al.* (2003) studied the potential pollutant contributions from commonly-used building materials (roofing, siding, wood) using a modified toxicity characteristic leaching procedure (TCLP) test. Results of particular interest included evidence of elevated levels of phosphate, nitrate and ammonia in the leachant following exposure of common roofing and siding materials to simulated acid rain.

Michels, *et al.* (2003) investigated the environmental impact of stormwater runoff from a copper roof. It was shown that the runoff became less toxic as it passed through the drainage system.

Rocher, *et al.* (2004c) investigated the contributions of atmospheric deposition and roof runoff to the hydrocarbon and metal composition of runoff in central Paris (France). Results showed that the roofs (metallic and slate) were not significant contributors of metals to runoff, although Zn-covered roofs released Zn and Ti, while slate roofs mainly released Pb, Ti and Cu. Near chimney stacks, Ni and V concentrations were elevated. Liu, *et al.* (2004) proposed a new coating of Zn-Ca phosphating/acrylic resin-SiO_2 which can stabilize the rusting of steel.

Runoff rates of Cu, Ni, Sn and Zn were investigated in a French industrial area by Jouen, *et al.* (2004). Depending on the solubility of corrosion products, the runoff rates appear to be different for these metals in the following order: zinc > copper > nickel > tin. The results revealed the runoff amount of copper, zinc and nickel released mainly from the dissolution of soluble sulfate compounds present in the corrosion layers.

Clark, *et al.* (2008) presented a summary of the literature on roofing (both surface covers and materials used as subbases such as treated wood); a portion of this summary is presented in Table B16. The older field studies in the table inferred the differences in roofing's pollutant contributions by analyzing runoff from nearby roofs made from different materials, using small areas where atmospheric contributions could be assumed to be similar. Newer studies have directly or indirectly measured atmospheric contributions in order to isolate the materials' contributions. In addition to the research projects that reported runoff concentrations, others have investigated the effects of these materials on receiving waters and biota. In-stream toxicity studies have found that much of the stormwater toxicity may be a result of divalent cations, in particular zinc from galvanized roofs. Other sources of toxicity included tannins and lignins from the woods. As studies have shown, ***wood preservatives released during storms from CCA and other preserved woods used in roofing construction is also sufficiently high to be implicated in stormwater toxicity.*** Wallinder et al. (2007) and Van Assche et al. (2003) modeled worldwide copper and zinc runoff rates, respectively, based on runoff rates and concentrations reported in the literature, in addition to laboratory testing on degradation. These results, in combination with the runoff concentrations reported in Table B16, indicate that roofing has the potential to be a significant pollutant source in the urban environment, where roofing covers a substantial fraction of the landscape.

Table B16. Review of Roof Runoff Analysis (Clark, et al. 2008)

Roof Type	Location	Analytes						Reference
		Cu (µg/L)	Zn (µg/L)	Pb (µg/L)	Cd (µg/L)	As (µg/L)	pH	
Polyester	Duebendorf, Switzerland	6817	2076	510	3.1			Boller (1997)
Tile		1905	360	172	2.1			
Flat Gravel		140	36	22	0.2			
Plywood w/ roof paper/tar	Washington	$166^T/128^D$	$877^T/909^D$	$11^T/<5^D$			4.3	Good (1993)
Rusty galv. metal		$20^T/2^D$	$12{,}200^T/11{,}900^D$	$302^T/35^D$			5.9	
Old metal w/Al paint		$11^T/7^D$	$1980^T/1610^D$	$10^T/<5^D$			4.8	
Flat tar surface w/fibrous reflective Al paint		$25^T/14^D$	$297^T/257^D$	$10^T/5^D$			4.1	
New anodized Al		$16^T/7^D$	$101^T/82^D$	$15^T/<5^D$			5.9	
Zinc-galv. Fe	Dunedin City, New Zealand	560 µg/g	5901 µg/g	670 µg/g				Brown & Peake (2006)
Cu Panels	Munich, Germany	200-11,100					6.7-7.0	Athanasiadis *et al*. (2006)
Galvanized metals (primarily Galvalume®)	Seattle, WA	10 – 1400	420 – 14,700	ND				Tobiason *et al*. (2004)
CCA wood	Florida					1200-1800		Khan *et al*. (2006)
Untreated wood						2-3		

Fraction of Metal: D = Dissolved, T = Total; ND = Not detected.

Roof runoff can therefore be damaging to stormwater quality, mostly associated with the selection of the building and roofing materials. If galvanized metals are used as roofing, zinc concentrations as high as 15 to 20 mg/L have been observed. High copper levels (up to about 10 mg/L) have also been observed in runoff from copper panel roofing. In most cases, lead, zinc and copper concentrations in roof runoff can be several hundred µg/L.

B.4.6. Highway and other Roadway Runoff

Roadway runoff has long been studied as an important stormwater source of heavy metals, with important projects first conducted in the 1960s. Roads are typically directly connected to the drainage system and respond quickly to storm events, plus they are known to have substantial amounts of heavy metal loads. They have therefore been considered a major source of these contaminants to stormwater. Over the years, other sources have also been realized to be important, and the significance of road surface contaminants is less than originally believed in most cases. The following are a selection of some of the more recent research efforts.

Several researchers investigated roadway storm runoff as a nonpoint pollution source and reported their results at the 7th International Conference on Urban Storm Drainage in Hannover (Sieker and Verworn 1996). Wada and Miura (1996) examined storm runoff from a heavily traveled highway in Osaka, Japan. The primary factors affecting storm runoff concentrations of heavy metals were the amount of traffic (and related exhaust emissions and tire wear) and the fraction of the total traffic that was comprised of trucks and buses.

Sansalone and Buchberger (1996) studied metal distributions in stormwater and snowmelt from a major highway in Cincinnati, OH. Zn and Cd were mostly in filterable (dissolved solids) forms in the storm runoff, while lead was mostly associated with particulates.

In the Kerault Region of France, the effects of pollution were studied using solid matter from a section of the A9 motorway. This study analyzed both settled sediments from collecting basin and characteristics of sediments in the water column during and after eight storm events between October 12 1993, and February 6 1994. Settled sediments were used to measure particle sizes, mineral content, and related characteristics, whereas water samples were used to document total suspended solids, mineral content, and heavy metals (Andral, *et al.* 1999).

Barbosa and Hvitved-Jacobsen (1999) examined heavy metals in highway runoff in Portugal. Concentrations of Cd and Cr were usually lower than the detection limit (1 µg/L), Cu levels were between 1 and 54 µg/L, Pb from 1 to 200 µg/L, and Zn from 50 to 1460 µg/L. A lowering of the pH value increased the desorption of previously retained Zn, Cu and Pb from the soil lining the infiltration pond used to treat this water.

The quality of urban road runoff in the Sydney, Australia region was investigated by Ball (2000a), resulting in guidelines for estimating the transportable trace-metal loading from road surfaces. An investigation by Drapper, *et al.* (2000) showed that the pollutant concentrations (heavy metals, hydrocarbons, pesticides, and physical characteristics) in “first flush” road runoff in Brisbane in southeast Queensland, Australia, were within the ranges reported internationally for highways. Traffic volumes were the best indicator of road runoff pollutant concentrations, with interevent duration also being a statistically significant factor. Exit-lane sites were found to have higher concentrations of acid-extractable Cu and Zn, likely due to brake pad and tire wear caused by rapid deceleration, and laser particle sizing showed that a significant proportion of the sediment in runoff was less than 100 um.

The Solids Transport and Deposition Study (STDS) characterized the rates and patterns of solids transfer to, and the collection within, stormwater drain inlets located along Caltrans highway facilities (Quasebarth, *et al.* 2001). The primary objective was to determine if certain distinguishable site characteristics controlled the transport and deposition of sediment, metals, vegetation, litter, and petroleum hydrocarbons to highway drain inlets. The ANOVA results indicated that the four primary factors (erosion control/sediment loading [vegetation factor], litter management [litter factor], toxic pollutant generation potential [adjacent land use factor], and roadway design [design factor]) likely had little overall control on solids accumulation or metals mass accumulation, although roadway design and litter management were possibly important in some cases.

Stenstrom, *et al.* (2001) studied freeway runoff from three sites in the west Los Angeles area. Each site was sampled for 14 storms during the 1999-2000 rainy season. Samples were collected very early in the storm in order to compare water quality from the first runoff to water quality from the middle of the storm. A large range of water quality parameters and metals were analyzed***. The data showed large first flushes in concentration and moderate first flushes in mass emission rates***. Zhou, *et al.* (2001) studied accumulations of heavy metals in roadside soils. Heavy metal accretion in the surficial soils was a function of depth, surface drainage patterns, distance from the pavement edge and soil indices. ***Rapid decreases in heavy metal accumulations were found as the distance from the pavement increased.*** Plasticity and organic matter content were important soil characteristics affecting the observed heavy metal concentrations. Total captured gross pollutants in Southern California highway runoff were monitored by Kim, *et al.* (2004 and 2006b). Approximately 90% of these pollutants were vegetation and 10% litter. Kayhanian and Stenstrom (2005) investigated the mass loading of first flush pollutants from a highway in Los Angeles, California. Mass first flush ratios were developed and used to describe the ability of stormwater treatment practices to treat highway runoff. In a four-year study of highway stormwater runoff in California, Han, *et al.* (2006a) found ***poor correlations between total suspended solids and most other pollutants.*** The strongest correlation between pollutants and storm characteristics was for antecedent dry days. Han, *et al.* (2006b) ***found that for total metals, COD and DOC, a first flush occurred***, indicating that stormwater controls that treat the first-flush mass will be effective for those pollutants. In contrast, the quality of runoff from paved surfaces at two automotive-related industrial sites was investigated by Gnecco, *et al.* (2006). ***First flushes were observed for total suspended solids and hydrocarbons, but not for heavy metals.***

Zinc and other trace metal (V, Cr, Co, Ni, Cu, Cd, and Pb) concentrations were measured in the Atlanta metropolitan region and in relatively undeveloped watersheds within the Georgia Piedmont and Blue Ridge Provinces (Rose, *et al.* 2001). Zinc concentrations in street runoff [median Zn = 905 µg/L] were significantly greater than zinc concentrations in Peachtree Creek storm runoff [median Zn = 60 µg/L], which were, in turn, greater than zinc concentrations contaminants within non-storm baseflow in Peachtree Creek [median Zn = 14 µg/L]. ***A two end***

member mass balance model suggested that a large proportion of the zinc present in the street runoff was adsorbed and transported by the suspended sediment.

Sutherland (2003) investigated the lead in six grain-size fractions of road-deposited sediment from Oahu, HI. Significant Pb concentration was seen in all samples and the median labile Pb concentration was 170 mg/kg (4 to 1750 mg/kg), with the silt plus clay fraction containing 38% of the total sediment in this fraction.

Bridge runoff was found to contribute metals (especially copper and zinc) above background levels to receiving waters in the Seattle area (Colich 2004). During high-volume traffic times, these concentrations were up to three times higher than at the low-traffic-volume times.

Zanders, *et al.* (2005) characterized road sediment and assessed the implications of the results on the performance of vegetated filter strips to treat the sediment-laden runoff. Particles less than 250 µm had the highest metal contents. Smaller particles also were found to have lower densities, which affects their ability to settle out.

Westerlund and Viklander (2006) described the particles and associated metals found in road runoff during snowmelt and rainfall. Important factors influencing the concentrations and loads were the availability of material, the intensity of the lateral flow, and, additionally, the antecedent dry period. During the melt period, particle sizes and TSS were highly correlated with total concentrations of Cd, Cu, Ni, Pb, and Zn. ***During the rain period, the correlations between total metal concentrations and the different particle sizes were not as significant.***

Preciado and Li (2006) evaluated metal loadings and bioavailability in air, water and soil along two British Columbia highways. Metals showed increasing bioavailability with decreasing particle size in all samples. Thus, bioavailability was low in road dust and roadside soils, intermediate in dustfall, and highest in atmospheric suspended particulates and runoff.

Sabin, *et al.* (2006a) examined the dry deposition and resuspension of particle-associated metals near a freeway in Los Angeles, California. Compared with urban background conditions, atmospheric particle size distributions indicated the freeway was a significant source of these metals on large particles >6 µm in diameter.

Walch (2006) monitored contaminants in Delaware street dirt samples. Major contaminants detected were heavy metals, petroleum hydrocarbons, PAHs and phthalates. Bacteria and nutrient levels also were high in some of the street dirt samples.

B.4.7. Treated Wood

There is a growing concern regarding potential toxicant releases from treated woods that are used for utility poles, recreational, commercial, and other wooden structures. Treated woods that have been commonly used in the past include chromated-copper-arsenate (CCA), ammoniacal copper zinc arsenate (ACZA), pentachlorophenol (PCP), and creosote. The volume of treated wood produced in the United States 20 years ago was: CCA/ACZA – 11.9 million cubic meters, PCP – 1.4 million cubic meters, Creosote – 2.8 million cubic meters (Micklewright 1989). It is expected that the production rates of treated woods have increased substantially since then, although there has been a shift in the use of some of the products as regulations have restricted the use of some of these materials. Clark, *et al.* (2001) provided a review of treated wood issues that is summarized below.

The known toxicity of arsenic and chromium to humans has resulted in concern about the possible introduction into the environment of large amounts of these metals in treated wood products (Brooks 1993). Weis and Weis (1996) examined the leaching potential of CCA-treated wood in Chesapeake Bay. Sediment and benthos samples were analyzed for Cu, Cr, and As at varying distances from treated wood bulkheads at test and control sites. In general, sediment metal concentrations decreased with distance from the treated wood bulkheads but not at the control stations. The species diversity and the number of individual species were also less at the treated wood site at the poorly flushed location but not at the control area having similar flushing conditions. Lebow, *et al.* (1999) tested CCA-treated wood in seawater and deionized water. They found that the steady-state release rate of copper was much greater in seawater than in deionized water. In contrast, the steady-state release rate of arsenic was greater in deionized water than in seawater. The rate of chromium release was consistently much less than that of copper and arsenic and was not affected by seawater. Testing of treated and untreated wood panels in freshwater exposure chambers showed that the metals leached from CCA-treated wood, could be taken up by epibiota and trophically transferred. Epibiota on treated panels had more copper and arsenic than epibiota on untreated panels, and amphipods living on the former had elevated copper. There was no evidence of biomagnification in the consumers other than the amphipods (Weis and Weis 1999).

The preparation of CCA-treated wood has been shown to impact the metal leachability (based on TCLP test results). The kiln drying schedule affects the leachability of chromium and arsenic in CCA-treated southern pine, although the drying schedule had no effect on leachability of copper, chromium or arsenic in western hemlock (Boone, *et al.* 1995). In order to improve climbability by electrical linemen, the CCA formulation has been modified with polyethylene glycol to form a preservative called CCA-PEG. Poles treated with this mixture have been reported as acceptable in climbability when compared to poles treated with PCP/oil or creosote (Beauchamp, *et al.* 1997).

PCP is a highly chlorinated, synthetic preservative that also contains 2,3,4,6-tetrachlorophenol; higher chlorophenols; dioxins; and furans (Shields and Stranks 1976). Arsenault (1975) and Stranks (1976) reported the presence of PCP around the base, and in drainage ditches near treated utility poles. Stranks reported drainage ditch waters with 1.8 times the 96-h LC_{50} of chlorophenol for salmonids near PCP treated utility poles. In 1991, the U.S. EPA determined that the use of PCP poses the risk of oncogenicity because of the presence of hexachlorodibenzo-p-dioxin and hexacholorobenzene, both of which have the potential to produce teratogenic/fetotoxic effects) (CALEPA 1996). Creosote is composed of more than 160 different distillates that occur in coal-tar, including aromatic hydrocarbons (such as naphthalene, anthracene, benzene, toluene, xylene, acenaphthene, phenanthrene, and fluorene), tar acids (such as phenols, cresols, xylenols, and naphthols), and tar bases (including pyridines, guinolines, and acridines) many of which are toxicants and carcinogens (Shields and Stranks 1976). The U.S. EPA determined that creosote has the potential for oncogenicity and mutagenicity (CALEPA

1996). Christmann, *et al.* (1989) investigated 16 commercial wood preserving formulations for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF), tri-, tetra-, and PCPs. In 13 samples, they found hepta-CDD/-CDF and octa-CDD/-CDF up to the high ppm range. Other congeners were found in many cases in the ppb range. When compared to the original wood preserving formulations, the level in treated wood is about 1 - 2 and in house dust about 2 - 3 orders of magnitude lower.

The lifespan of wood products is usually determined by their installation location. ***After 30 years in temperate and tropical climates, metal preservative-treated wood was found to fail more often than that treated with the organic preservatives*** (De Groot and Evans 1999). However, when investigating wood preservatives in a tropical/jungle environment, it was seen that the metal-based preservatives showed greater durability (Bratt, *et al.* 1992). According to Edlund and Nilsson (1998), wood decay is mainly caused by brown rot fungi, e.g., the dry rot fungus, Serpula lacrymans, and the cellar fungus, Coniophora puteana. The attack on stakes exposed in the four unsterile soils differed markedly and depended on both the preservative and the soil type. These differences may be caused not only by the preservative's effect against different microorganisms, but also by the pH in the soil and the chemical interaction between soil and preservative. Industrial wood-based construction materials: chipboard, plain and overlaid plywood, phenolic surface film, laminates, and selected synthetic polymers were studied for their biodegradability under aerobic and anaerobic conditions and for the environmental quality of the residue. Plywoods were more readily degraded under both aerobic and anaerobic conditions. The original contents of copper, lead, nickel, and cadmium of the wood-based construction materials were low, < 10 mg/kg, compared to polyvinyl chloride (PVC) and to a typical municipal solid waste. Toxicity and the amount of leachable organic halogen from the wood-based construction materials were low, EC50 of 4 - 8 g/L to V. fischeri and < 12 μg adsorbable organic halogen/g (Peltola, *et al*. 2000).

Lebow, *et al.* (2003) investigated the release of preservatives, primarily arsenic, from CCA-treated wood under simulated rainfall and the ability of wood finishes to prevent/reduce the release. ***Water repellent significantly decreased the amounts of these elements in the runoff, while UV exposure increased the leaching of preservatives from the wood.***

Tests for potential pollutant release from some construction materials were conducted by Pitt, *et al.* (2000) and Clark (2000) as part of a stormwater treatability research project. This project included the construction of pilot-scale treatment devices and there was concern that the selection of the construction materials could affect the test results. Therefore, before the pilot-scale devices were constructed, a series of tests were conducted to examine the pollutant release of different potential construction materials. Samples of the various materials were put in beakers in de-ionized water for set periods of time, and then the water was analyzed for a broad list of constituents of interest. Tables B17 and B18 present the contaminants that were found in the water at the end of the test. The most serious problems occurred with plywood, and included both treated and untreated wood. Other problems were associated with the use of galvanized metals, as expected, where the tests indicated extremely high zinc concentrations. As expected, Teflon did not contribute pollutants to the de-ionized water.

Table B17. Relative Pollutant Releases from Various Construction Materials after Exposure to De-ionized Water (from Pitt et al. 2000; Clark 2000)

Sample	Cu (µg/L)	Cd (µg/L)	Pb (µg/L)	Zn (µg/L)	Fe (µg/L)	Cr (µg/L)	Mg (µg/L)	Ca (µg/L)
Silica caulk	29	<lod[1]	<lod	14	48	8	<lod	0.08
Formica and silica caulk	54	<lod	<lod	26	110	8	<lod	0.38
Metal roof runoff	41	<lod	32	10,200	440	11	0.13	1.2
Treated plywood	1,300	<lod	33	93	110	2,800	0.02	0.67
Untreated plywood	79	<lod	<lod	67	310	12	1.3	3.2
Washed PVC and PVC cement	36	<lod	<lod	32	83	8	<lod	0.60
Washed fiberglass window screen	32	17	<lod	88	47	8	<lod	0.10

[1] <lod: less than the limit of detection.

Table B18. Potential Sample Contamination from Wood (from Pitt et al. 2000; Clark 2000)

Material	Contaminant(s)
Untreated plywood	Toxicity, chloride, sulfate, sodium, potassium, calcium, 2,4-dimethylphenol, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, phenol, N-nitro-so-di-n-propylamine, 4-chloro-3-methylphenol, 2,4-dinitrotoluene, 4-nitrophenol, alpha-BHC, gamma-BHC, 4,4'-DDE, endosulfan II, methoxychlor, endrin ketone
Treated plywood (CCA)	Toxicity, chloride, sulfate, sodium, potassium, hexachloroethane, 2,4-dimethylphenol, bis(2-chlorooethyoxyl) methane, 2,4-dichlorophenol, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, phenol, 4-chloro-3-methylphenol, acenaphthene, 2,4-dinitrotoluene, 4-nitrophenol, alpha-BHC, gamma-BHC, beta-BHC, 4,4'-DDE, 4,4'-DDD, endosulfan II, endosulfan sulfate, methoxychlor, endrin ketone, and likely copper, chromium, and arsenic
Treated plywood (CCA) and Formica	Toxicity, chloride, sulfate, sodium, potassium, bis(2-chloroethyl) ether), diethylphthalate, phenanthrene, anthracene, benzylbutyl phthalate, bis(2-ethylhexyl) phthalate, phenol, N-nitro-so-di-n-propylamine, 4-chloro-3-methylphenol, 4-nitrophenol, pentachlorophenol, alpha-BHC, 4,4'-DDE, endosulfan II, methoxychlor, endrin ketone, and likely chromium, copper, and arsenic
Treated plywood (CCA), Formica and silica caulk	Toxicity, lower pH, bis(2-chloroethyl) ether), diethylphthalate, hexachlorocyclopentadiene, bis(2-ethylhexyl) phthalate, phenol, N-nitro-so-di-n-propylamine, 4-chloro-3-methylphenol, alpha-BHC, heptachlor epoxide, 4,4'-DDE, endosulfan II, and likely chromium, copper, and arsenic

On-going research being conducted at the University of Alabama (Hardin 2009) is investigating leaching problems associated with the ash from burned CCA-treated woods, especially relating to potential runoff and groundwater contamination. ***Agricultural lime and gypsum have been identified as successful soil amendment to demobilize the heavy metals found in the ash-soil mixtures.*** Figure B1 shows that ***the mobility of Cr and As is lowered in the presence of soil while Cu mobility is increased***. During the first leach the soil-ash mixture retarded the leaching of Cr and As by 75% and 74% respectively, but enhanced Cu leaching by 280% compared to CCA-ash alone. Subsequent releaching of the test soil/CCA-ash resulted in a cumulative decrease of 250% in the leached mass of As and 1150% in the leached mass of Cr compared to ash alone. Conversely, an increase of 1550% was recorded in the leached mass of Cu.

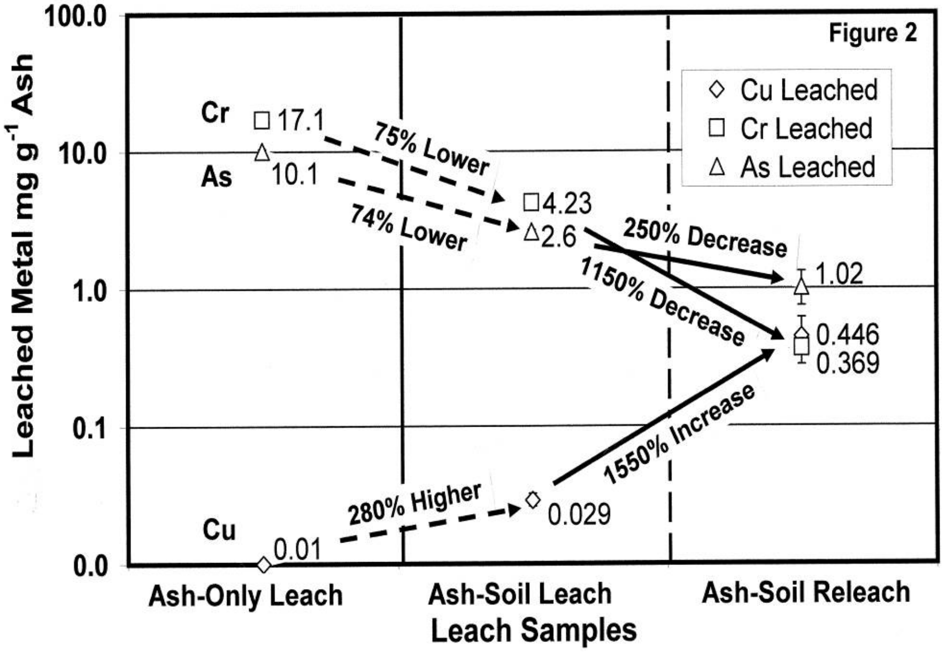


Figure B1. The Impact of Un-Amended Soil on the Rainwater-leaching of CCA Metals (Hardin 2009).

Appendix C: Erosion, Washoff, and Transport of Stormwater Pollutants from Source Areas to Receiving Waters

C.1. Erosion Losses of Watershed Soils

The erosion of soils and contaminated particulates from pervious areas is usually used to estimate the contribution of these materials to runoff during watershed studies. Soil erosion results when soil is exposed to the erosive powers of rainfall energy and flowing water (Barfield, *et al.* 1983). Rain (along with the shearing force of flowing water) acts to detach soil particles, while runoff transports the soil particles downslope. The most significant factor causing sheet erosion is raindrop impact, while the shearing force of flowing water is most important in rill and gully erosion. One common approach to predicting these erosion losses is the Revised Universal Soil Loss Equation (RUSLE) (Renard, *et al.* 1987). Pitt, *et al.* (2006), in their construction site erosion and sediment control book, presents a comprehensive review of RUSLE and how it can be used to calculate expected erosion rates for a variety of watershed conditions.

The Universal Soil Loss Equation (USLE) (Wischmeier and Smith 1965) was based on many years of data from about 10,000 small test plots from throughout the US. Each test plot had about 22 m flow lengths and were all operated in a similar manner, allowing the soil loss measurements to be combined into a predictive tool. The USLE has been extensively used for conservation planning in agricultural operations for many years. Many of the features, and the original database, also allow it to be used to predict erosion losses. The RUSLE only predicts sheet and rill erosion, it does not predict the effects of concentrated runoff.

The Revised Universal Soil Loss Equation (RUSLE) (Renard, *et al.* 1987) was developed to incorporate new research since the earlier USLE publication in 1978 (Wischmeier and Smith 1978). The basic form of the equation has remained the same, but modifications in several of the factors has changed. There are many sources of information for the RUSLE, including the USDA's National Sedimentation Laboratory where extensive information can be obtained.

The underlying assumption in the RUSLE is that detachment and deposition are controlled by the sediment content of the flow. The erosion material is not source limited, but the erosion is limited by the carrying capacity of the flow. When the sediment load reaches the carrying capacity of the flow, detachment can no longer occur. Sedimentation must also occur during the receding portion of the hydrograph as the flow rate decreases (Novotny and Chesters 1981).

The RUSLE relates the rate of erosion from an exposed area (A) in tons per acre per year, to the erosive power of the rain (R), the soil erodibility (K), the land slope and length (LS), the degree of soil cover (C), and conservation practices (P):

$$A = (R)(K)(LS)(C)(P)$$

The important aspect of this equation to note is the linear relationship between the equation parameters. As any parameter is changed, the resulting erosion yield is similarly changed. Also, the basic values for LS, C, and P are all 1.0, and change according to specific site and management conditions change. Many of these factors will change seasonally, especially corresponding to plant growth and according to changes in rain characteristics. A modified version of RUSLE, RUSLE2, is currently being developed that will incorporate many of these seasonal changes. Some of these can be considered in RUSLE. It is also important to note that the predicted erosion rate determined using ***RUSLE does not necessarily relate to the amount of sediment that will actually be discharged from the site during storms. The "delivery" of the eroded material to the outfalls is dependent on many site and drainage system characteristics and can be relatively low for natural sites.***

The RUSLE shows that rain energy is directly related to the annual erosion yield. The annual R is based on long-term rain records for an area and is based on the kinetic energy of the rains and their intensities. For much of the US, R ranges from about 50 to 200, with the area along the SE gulf having the highest values that approach 700. In southern California, R varies from about 50 to 100 in the Los Angeles and Ventura County areas, but can be less than 10 in the deserts. These are long-term averages and can vary greatly from year to year, especially in areas having highly variable rainfall conditions, such as southern California.

The soil texture, and other soil characteristics, affect its susceptibility to erosion. The soil K factors for the USLE were determined experimentally in test plots that were 73-ft (22-m) long and had a uniform slope of 9%. Normally, more than 10 years of runoff plot data was needed to determine these values in order to eliminate any effects from prior organic material and mulch, as well as effects associated with mechanical disturbance from constructing the plots. K values for soils having different textures are simplified below for some common soil types (Dion 2002):

Sandy, fine sand, loamy sand	0.10
Loamy sand, loamy fine sand, sandy loam, loamy, silty loam	0.15
Loamy, silty loam, sandy clay loam, fine sandy loam	0.24
Silty clay loam, silty clay, clay, clay loam, loamy	0.28

There is substantial overlap for the different soil textures, as there are other factors besides texture that are used to determine the K value, but this list does illustrate that K values generally increase as the soil particle sizes decrease. K also directly affects the annual erosion rate. It should be noted that some specific soils may have K values different from these values, depending on site conditions. Site soil surveys are always preferred in order to obtain values appropriate for local conditions.

The erosion of soil from a slope increases as the slope increases and lengthens. RUSLE defines a parameter called the length-slope (LS) factor that is used to calculate the impact of the interaction between these two parameters on erosion losses. The slope length is the horizontal distance from the start of the erosion area (typically a ridge) to the start of the area where deposition of eroded sediment occurs. Selected values for LS are shown on Table C1.

Table C1. Selected LS Factors for RUSLE

LS factors:	15 ft slope length	50 ft	250 ft	1,000 ft
0.2 % slope	0.05	0.05	0.06	0.06
1 %	0.09	0.13	0.19	0.27
5 %	0.23	0.49	1.16	2.55
10 %	0.40	0.91	2.72	7.02
20 %	0.84	2.10	7.16	20.57
50 %	1.91	5.16	19.42	60.84

Obviously, these factors greatly increase as the slope and slope length increase.

The methods used to protect the soil surface will affect the amount of soil erosion that may occur and is reflected in the Cover Management Factor, C. The percentage mulch cover is what generally determines the effectiveness of the mulch. According to Wischmeier and Smith (1978), a simple method of estimating cover is with a line at least 50 ft long that has 100 equally spaced markings. The line is stretched over the surface and the marks that contact a piece of cover are counted and used to determine the percentage cover. The quality of the cover also affects the erosion rate, as thin coverings that are not anchored can easily wash away during rains. Well-established vegetative cover with underlying organic matter make the best cover material. Newly established vegetation is not as effective. During the period of establishment with a crop canopy of about 10 to 50%, the C factor is about 0.6 to 0.75, while for a maturing crop, with a 75 to 95+% canopy, the C factor is significantly reduced to about 0.05 to 0.10. In comparison, the C factor for a woodland with 100 percent duff cover (partly decayed organic matter on the forest floor) would be a low 0.0001 (99.99% erosion control), the lowest reported value. Scrub plants in an arid area would certainly have a larger C factor representing the poorer ground cover and harsh growing conditions.

The method of tillage and crop rotations all affect the soil erosion rate for an agricultural operation and is reflected in the P factor. This factor is mostly applied to agricultural lands and rarely is applicable for natural areas or for urban areas, and is therefore given a value of 1.0.

The use of the RUSLE is therefore straight-forward. Perhaps the most difficult element is in determining the LS factor for a complex site where numerous slopes are present. For a single slope condition, assume the following:

R = 100 (annual value)
K = 0.24 (a loamy soil)
Slope = 20%
Slope length = 250 ft
LS therefore = 7.16 (a relatively extreme condition)
C = 0.5 (poor shrub cover)
P = 1.0

A = (R)(K)(LS)(C)(P) = (100)(0.24)(7.16)(0.5)(1.0) = 86 tons/acre/year

This can be applied to representative slope conditions for the site and weighted based on their individual areas. This is a large erosion loss, corresponding to about 75 cubic yards of soil lost per acre per year, or about 0.55 inches of depth, which is considered excessive in supporting plant growth ("tolerable" losses are usually assumed to be about 3 to 5 tons/acre/year, depending on the soil and agricultural operation). This is the amount of erosion that may be lost from the site, but these calculations do not consider the transport of this material to the receiving waters. Much of this material will be deposited at the base of the slope and other areas when the flowing water slows and losses some of its carrying capacity. RUSLE2, a further expansion of RUSLE, is being developed to more accurately account for site variability and sediment transport issues.

C.2. Erosion Potential and Sediment Transport at Santa Susana Field Laboratory

The erosion potential of the site helps determine the likely movement of natural site soils and associated heavy metals. ***Atmospheric deposition materials that have fallen on the site are also moved as part of this material.*** The erosion calculations using the RUSLE estimate the amount of soils that are eroded from slopes as sheet and rill erosion. These amounts of materials are not necessarily transported through the drainage system to the outfall. It is possible that some of this material will be deposited on downslope areas as the carrying capacity of the flowing water decreases. This commonly occurs when the slope is reduced. Much of the eroded material may also accumulate in the channels themselves in deposition areas. This occurs as the hydrograph changes during an event and the flow subsides. Previously deposited material may in turn be resuspended and transported further to the outfall during subsequent events when the tractive force of the flowing water increases. These processes are all highly dependent on the particle size distribution of the material. Larger particles are more difficult to erode and to keep suspended in the flowing water, and to resuspend from the bed, while small particles are preferentially eroded and are more efficiently transported to the outfalls.

The erosion potentials at the 008 and 009 site watersheds are quite large, mostly due to the steep slopes present. As an example, Geosyntec conducted a detailed erosion potential evaluation of the 008 and 009 site watersheds. The 008 watershed in 62 acres, but about 11% is exposed rock, as indicated in the photographs in Figure C1.

Figure C1. Watershed 008 area showing extensive amounts of exposed rock along with steep slopes (Boeing Co photographs).

The soil K values were obtained from the NRCS's SSURGO (the Soil Survey Geographic Database) for Ventura County. For the 008 watershed, the K soil erodability value was determined to range from 0.08 to 0.55, with an area-averaged mean value of 0.48. Figure C2 shows the distribution on these K values in the 008 watershed. Site LS factors also change dramatically over the site. Figure C3 is a map of the 008 watershed showing how they varied from a low of 0.005 to a high of 48, with an area-averaged value of 7.2.

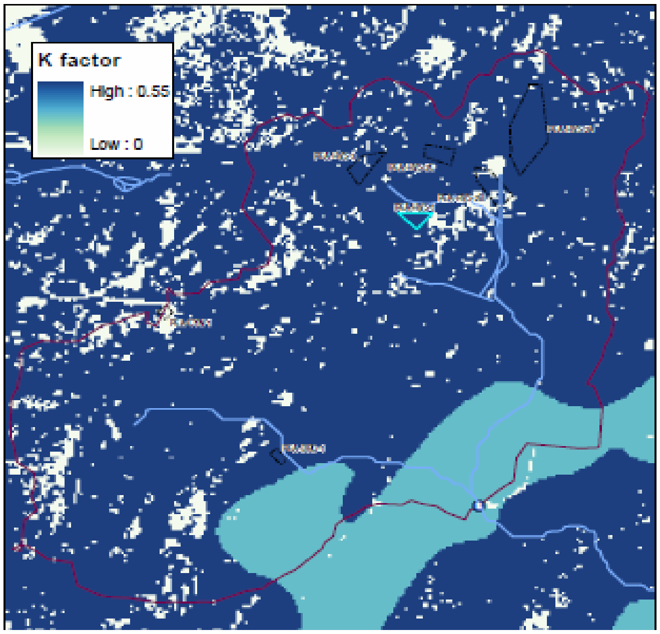


Figure C2. Site variability of soil erodability K values in the 008 watershed (from the NRCS SSURGO database for Ventura County, reported by Geosystec).

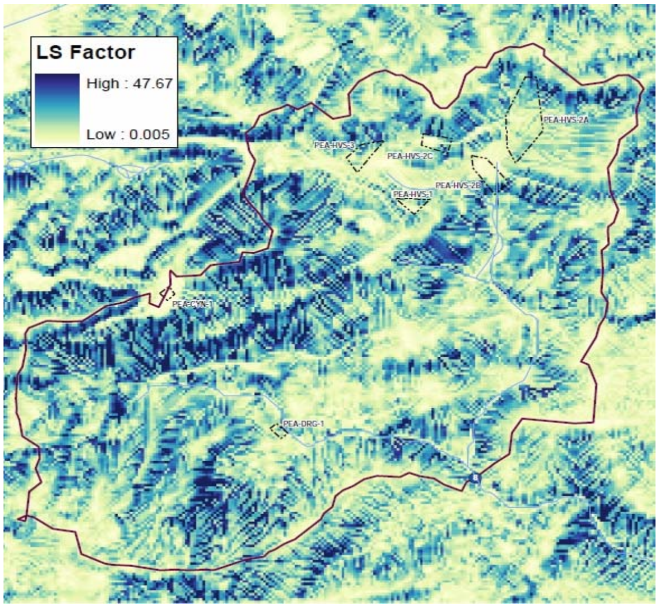


Figure C3. LS factors calculated using Ventura County LIDAR data (reported by Geosyntec)

Figure C4 is a map showing the unit area erosion rates for the 008 watershed. The variability of erosion rates is very similar to the variability in the LS factors shown in Figure C3. The calculated annual erosion rate in this watershed is about 17 tons/acre/year, or about 1,000 tons per year over the total 62 acre watershed.

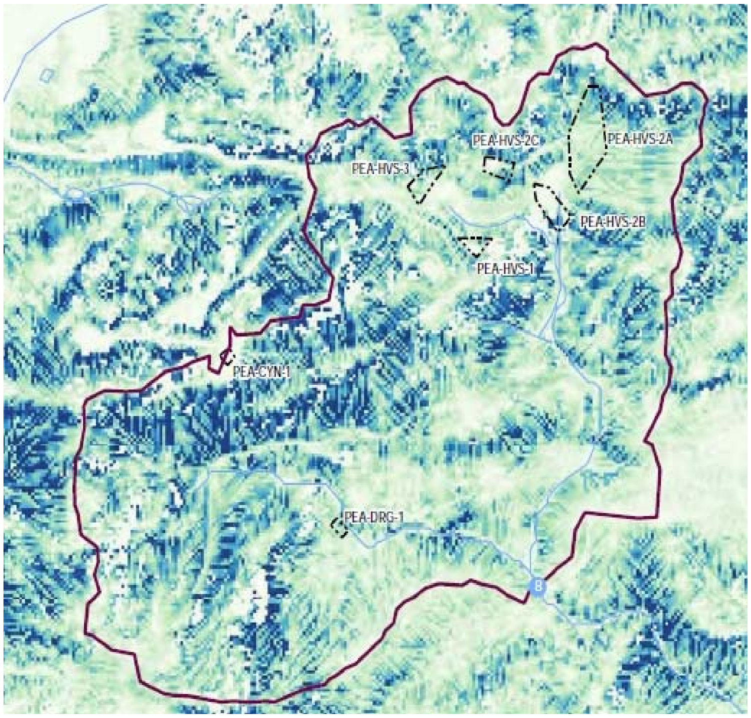


Figure C4. Map showing the relative calculated erosion rates in the 008 watershed (prepared by Geosyntec)

The observed sediment yields from the site watersheds, based on outfall monitoring and calibrated modeling of runoff quantities, are about 4 tons per year for watershed 008 and 30 tons per year for watershed 009. However, these sediment yields are much smaller than the calculated erosion rates for these watersheds using the RUSLE. It is likely that less than 1% of the eroded material actually is discharged to the outfalls, with the remaining material being deposited on lower slopes below the steep areas, and in the channels.

A larger fraction of the finer material would be discharged compared to the larger eroded material. Figure C5 shows particle size distributions from two outfall samples collected at outfalls 008 and 009 on February 3, 2008. These show the preponderance of fine particles in the outfall samples. However, these samples were obtained during later portions of the runoff events when the samples could be safely obtained. They likely do not contain as many larger particles as may occur during peak flow periods. The median particle sizes of the suspended particles in these samples was between about 5 and 15 µm, with no particles observed larger than about 125 µm observed. With only the one sample available that was collected during later periods of the flow, it is not possible to rule out the transport of larger particles during larger events, and during higher flow periods. However, it would require tractive forces of at least 0.2 lb/ft^2 to potentially cause scour of particles larger than 10 mm (0.4 inches) in diameter. In contrast, the necessary tractive force to resuspend and keep 100 µm particles moving varies from about 0.025 to 0.08 lb/ft^2, depending on the silt content of the water.

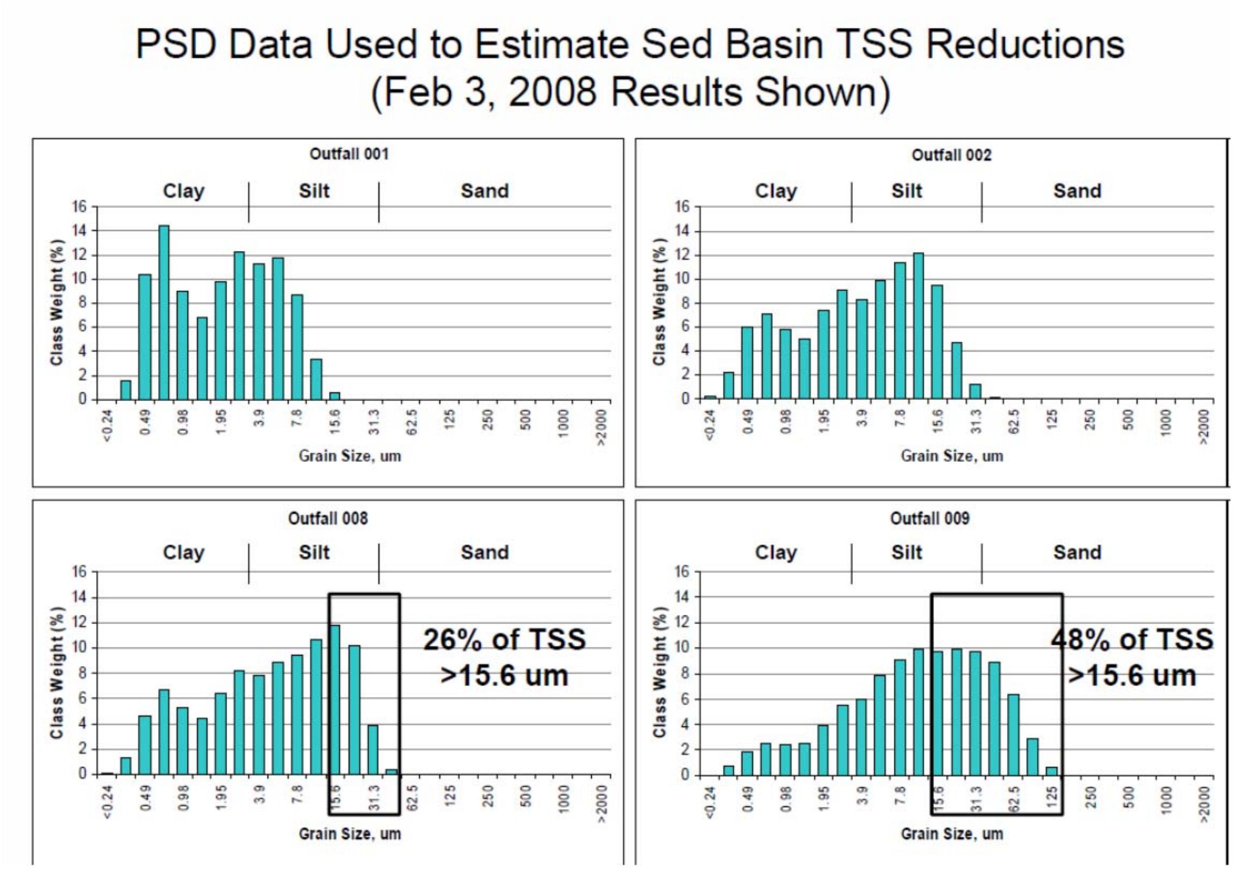


Figure C5. Particle size distributions observed at watershed outfalls.

C.2.1. Sediment Transport

These larger tractive forces can be expected to frequently occur on the site. The main channel slopes on the site vary from about 1.5 to 20% (with typical values of about 6%). Tributary channel slopes are obviously steeper, and the land slopes are steeper still. The tractive force for the water flowing in the main channels can be calculated using:

$$\tau_o = \gamma RS \quad (\text{lb/ft}^2)$$

Where:

γ = specific weight of water (62.4 lbs/ft^3)
R = hydraulic radius (ft) (the cross sectional area divided by the wetted perimeter; approaches the water depth for wide channels)
S = hydraulic slope (ft/ft)

For the slopes present on the site, a tractive force of 0.2 lb/ft^2 may occur with hydraulic radius conditions of only about 0.2 to 0.02 ft if unconsolidated. However, if compacted, the depths needed would be about 10 times these values just to move sandy clays. These higher hydraulic radius conditions could move much coarser material, if loose, as observed in much of the channel deposits.

Visual surveys on the site have shown many areas of sediment deposition in the main channels. Observed material ranged from coarse sandy deposits in channel depressions that were several months old (small plants starting to take root in the deposits) to small boulders that were obviously unstable. The mass of observed material in the channels was quite large, but was not quantified. Much of the loose material in the Northern Drainage channel in watershed 009 is being removed as part of site cleanup efforts.

C.2.2. Slope Protection

Calculations can be made based on the methods presented by Pitt, *et al.* (2006) to determine the likely shear stress associated with exposed slopes and different rain conditions, and the need for slope protection. If the desired failure rate is less than 10% and the service life is 10 years for a protected slope, a storm with a 1% chance of occurring in any one year should be used for the design. In contrast, a storm having a 5% chance of occurring in any one year could result in about a 30% maximum failure rate during a 10 year service life. The 10% desired failure rate corresponds to a rain intensity of about 7.1 inches per hour (and a time of concentration of about 6 minutes, appropriate for small slopes) using the Ventura County IDF relationships. For a 25% slope that has a one acre area (with a slope length of about 200 ft), the resulting depth of runoff would be about 0.16 inches at the bottom of an unvegetated slope. The maximum resulting shear stress would be about 0.20 lb/ft^2. A steeper 50% slope that is also one acre may have a maximum shear stress of about 0.34 lb/ft^2 at the bottom of the slope. These are relatively large and exceed the permissible shear stress for most soils (sandy soils would be exceeded by about tenfold, for example). These slopes obviously need protection to prevent excessive erosion.

Efforts are being made to better stabilize and prevent erosion on the steeper areas at the site. As noted above, there are relatively steep and long slopes in both watershed areas. If exposed due to poor vegetation cover which has been associated with slow recovery from site fires, the erosion rates can be high. On the steeper slopes, current site practice uses multiple rows of closely spaced rolled coir logs staked to the slopes and all covered with a spray-on adhesive and mulch mixture. Mild slopes with smaller areas of exposed ground from cleanup efforts or fire damage are protected with geotextile woven mats and are also covered with a spray-on mixture.

C.3. Transport of Particulates in Drainage Systems

After the eroded particulates start to move towards the drainage system (any natural or constructed conveyance), they will tend to settle as they flow towards the receiving water. If they settle slowly, such as occurs for small particles, they will remain suspended and not become part of the bed load or sediment. However, if they settle to the bottom before reaching the receiving water, they may become part of the bed load which will bounce along the conveyance bottom, or become trapped with other settled debris. When the flow stops, the sediments will tend to dry and become more consolidated. The next runoff event may cause some of this settled material to become resuspended and may move towards the receiving water. Therefore, there are three phases to particulate transport in drainage systems: 1) settling of the particulates in the flowing water, 2) movement as bed load during the event, 3) accumulating as sediment and potentially subsequent scour. The following discussion summarizes these sediment transport phases.

Settling velocities of discrete particles are shown in Figure C6, based on Stoke's and Newton's settling relationships for laminar or turbulent settling conditions, respectively. This figure also illustrates the effects of different specific gravities on the settling rates. In most cases, stormwater particulates have specific gravities in the range of 1.5 to 2.5, depending on the mixture of organic and inert material in the particle. This corresponds to a relatively narrow range of settling rates for a specific particle size on this figure.

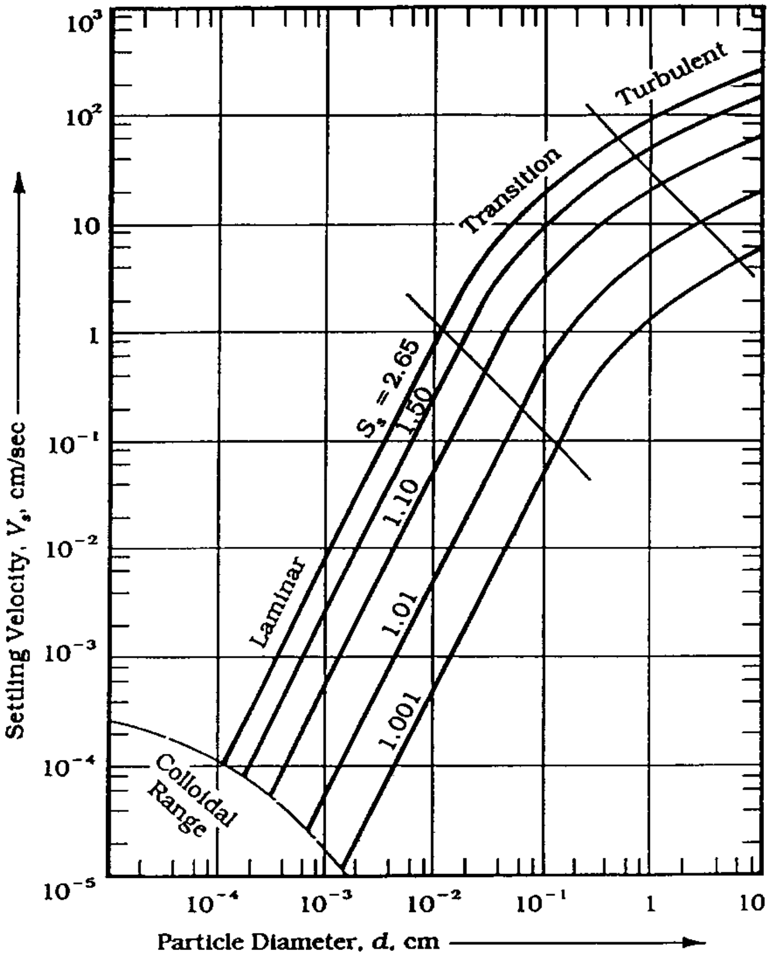


Figure C6. Type 1 (discrete) settling of spheres in water at 10° C (Reynolds and Richards 1996).

C.3.1. Scour of Previously Deposited Materials

Boundary shear stress (sometimes called tractive force) is commonly used as an appropriate criterion for predicting the stability of deposited materials in conveyances. The average boundary shear stress in uniform flow is calculated by:

$$\tau_o = \gamma RS \quad (\text{lb/ft}^2)$$

Where:

γ = specific weight of water (62.4 lbs/ft^3)
R = hydraulic radius (ft)
S = hydraulic slope (ft/ft)

Flow characteristics predicting the initiation of motion of sediment in noncohesive materials are usually presented in nondimensional form in the Shield's diagram. The Corps of Engineers (COE 1994) in their assessment manual states that the use of the Shield's diagram is likely to over-predict the erodibility of the channel bottom material under most conditions. The problem occurs because the Shield's diagram assumes a flat bottom channel and the total roughness is determined by the size of the granular bottom material. The actual Manning's roughness value is likely much larger because it is largely determined by bed forms, channel irregularities, and vegetation, and not grain size. They recommend, as a more realistic assessment, that empirical data based on field observations be used. In the absence of local data, they present Figure C7 (from Chow 1959) for applications for channels in granular materials. This figure shows the permissible unit tractive force (shear stress) as a function of the average particle diameter, and the fine sediment content of the flowing water.

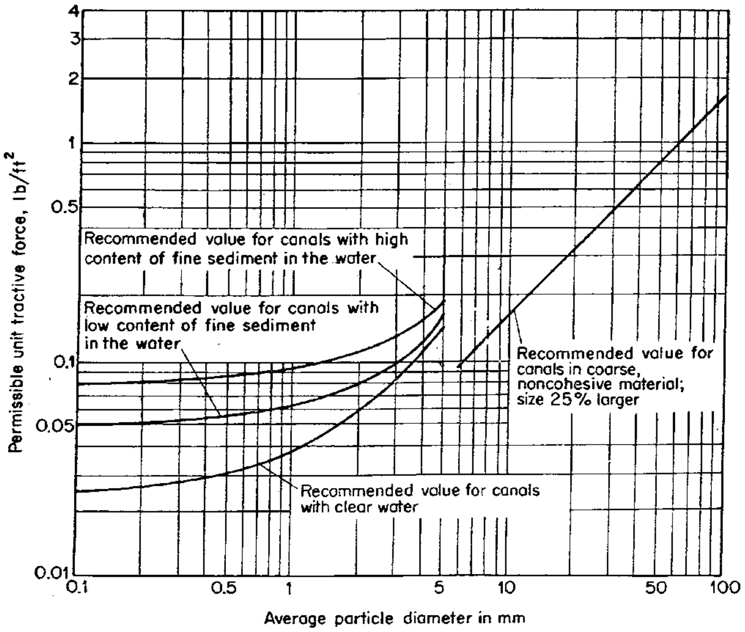


Figure C7. Allowable shear stresses (tractive forces) for canals in granular materials (U.S. Bureau of Reclamation, reprinted in Chow 1959).

C.3.2. Erodibility of Previously Settled Material after Consolidation

Figure C8 is an example of allowable shear stresses for a range of cohesive materials having a range of void ratios corresponding to varying amounts of consolidation. Again, the COE recommends that local field observation or laboratory testing results be given preference. If the void ratio was about 0.4, corresponding to a compact sediment, the shear stress would have to be greater than about 0.3 lb/ft^2 to affect particles larger than clays.

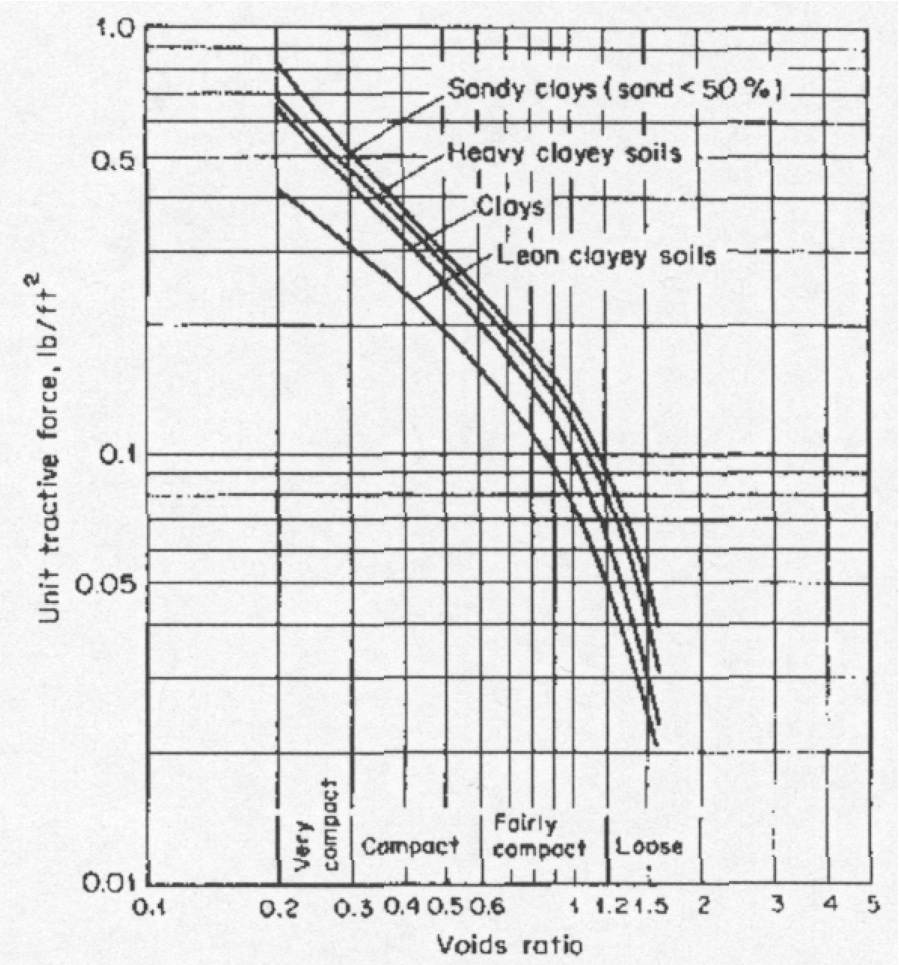


Figure C8.Example of allowable shear stresses (tractive forces) for cohesive materials (COE 1994) (A Leon clayey soil is hardpan. Hardpan is a condition of the soil or subsoil in which the soil grains become cemented together by such bonding agents as iron oxide and calcium carbonate, forming a hard, impervious mass).

SSFL site slopes can vary significantly, from less than 1% in the main drainage channels to approaching 50% on the steep hillsides. The flow depths can be several feet deep in the main channels during large rains, while they would only be a fraction of an inch on the steep slopes. Therefore, the shear stresses would also vary greatly on the site, possibly being in the order of about 0.1 to 1 lb/ft^2 on the steep slopes and about 1 to 5 lb/ft^2 in the main channels during the larger rains. Therefore, much of the eroded material from the steep slopes will tend to accumulate on the lower slopes and channels during most rains, while periodic very large events are quite capable of moving much of the deposited material.