

ATMOSPHERIC DEPOSITION AND RUNOFF OF MERCURY AND TRACE METAL IN AN URBAN WATERSHED

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ABSTRACT

Non-point and diffuse sources can be the most significant sources of pollutants in a watershed. Atmospheric deposition in its three forms (ambient, dry, and wet) has often been neglected and thus was not included in watershed approach for water resources management. Often regulatory frameworks for water resources protection have not taken into account atmospheric deposition because little or no data is available. The project undertaken is new and unique in its scope and approach to monitor and measure pollutants in atmospheric deposition and its impact on storm water quality within a river watershed.

Specialized sampling equipment and ultra-clean analytical methodology were employed to quantify the concentrations or masses in ambient air, precipitation, and runoff for twelve trace metals. These metals include mercury (Hg), cadmium (Cd), antimony (Sb), aluminum (Al), arsenic (As), chromium (Cr), copper (Cu), manganese (Mn), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn). Meteorological parameters including wind speed, wind direction, temperature, and relative humidity were also measured.

This study represents the most complete set of atmospheric concentration and deposition data for trace metals and mercury in an urban watershed at this time. Additionally, this is the first time that mercury together with other trace elements in dry deposition and runoff has been measured in a study of this length. The results of this study provide both the critical information and valuable study approaches to monitor trace metal deposition in urban watersheds.

KEYWORDS

Atmospheric deposition, non-point sources pollution, diffuse pollution sources, mercury, trace metals, watershed, TMDL.

INTRODUCTION

Atmospheric deposition represents an important mechanism for transporting trace metals, mercury, and nutrient to a watershed. Understanding the transport mechanism of pollutants through air deposition, its relationship to surface water runoff and impact on receiving water quality are critical for watershed management. Atmospheric deposition is also an important part of the Total Maximum Daily Loads (TMDL) analysis. However, information on atmospheric deposition of pollutants is not readily available due to the following factors: 1) difficulties in carrying out the sampling tasks, and 2) the mechanism of deposition and interactions are not well understood, and 3) quantifying the trace level chemicals in different media is often difficult.

This paper will summarize the Wayne County (Michigan) atmospheric deposition study on the Rouge River watershed. The study is an element of the Rouge River National Wet Weather Demonstration Project. The 436-square-mile Rouge River watershed, located in the Southeastern part of Michigan (Detroit), has 125 miles of river channel, and is highly urbanized with 1.5 million population residing in 43 communities.

METHODOLOGY

The monitoring network consisted of three sampling sites located in three distinct geographic locations and land-use types within the City of Detroit and the Rouge River watershed. One site was situated in each of industrial area (Livernois Center, or LV), a residential/park area (Rouge River Park, or RRP), and a rural area (Dexter, or DEX). The industrial site was intended to determine a “worst-case” scenario for atmospheric deposition and loading impact, relative to rural site which would be expected to provide background level of atmospheric deposition.

This monitoring plan thus allowed for identification of “background” pollutant concentrations in the atmosphere, as well as the localized urban signal within portions of the City of Detroit where monitoring was performed. Runoff samples were taken from controlled-sites with minimum traffic. Limited monitoring at impacted runoff site with heavy traffic was used to identify the potential significance of the additional component of direct impacted locations.

The methods used for the collection and analysis of samples are summarized in Table 1. Twenty-four hour total particulate mercury and particulate metals samples were collected daily. Total suspended particulate (TSP) concentration was determined by dividing the total particulate mass for the sample period by the volume of air sampled. Twenty-four hour fine fraction (<2.5 µm) particulate mercury and particulate metals samples were collected at the Livernois sampling site. Every third day a 24-hour vapor phase ambient mercury sample was collected at each site. Dry deposition samples were collected during the dry periods between each precipitation event and ranged in duration from 2-5 days. If more than one dry deposition sample was collected during a single, lengthy dry period, samples were composited. Dry deposition samples were analyzed for both metals and mercury. Precipitation samples were collected over the entire rain event, while runoff was composited on a flow-weighted basis during each precipitation event. The protocols for the sampling and analysis are those documented in the DWSD Atmospheric Deposition Study QAPP and reports, as well as earlier publications.

Field sampling and sample concentrating procedures employed meticulous ultra-clean techniques. All analyses were done in ultra clean state-of-the-art laboratory. Air and water samples collected for Hg were analyzed by the University of Michigan Air Quality Laboratory (UMAQL) using cold-vapor atomic fluorescence spectrometry with gold trap that allows detection limits to picogram (parts per quadrillion) levels. Air and water samples collected for Cd and other metals were analyzed by UMAQL using inductively coupled plasma mass spectrometry (ICP-MS) that allows detection limits to 0.002 microgram (parts per billion [ppb]) levels. All field and laboratory activities followed a strict Sampling and Analysis Quality Assurance Project Plan (SAQAPP) prepared for the study.

Over 1000 samples were collected from 3 sites (with 4 sampling stations). Ambient and vapor phase (for mercury), dry deposition, wet deposition, storm runoff samples were collected. Each site had a full meteorological station to monitor the weather conditions (e.g. wind speed and direction, air moisture and temperature). The atmospheric deposition equipment, were mounted on a specially designed wooden deck ten feet above the ground. Storm water runoff flow was monitored using ultrasonic flow measurement devices. Storm water samples were collected using programmable automatic sampling equipment interfaced with the primary flow measurement device. Each site is equipped with telemetering system to download flow and meteorological data. Ambient air monitoring used active PS-1 sampling units. A specially designed ambient monitoring unit was used for the mercury. Wet Deposition utilized a MIC sampler and dry deposition used the EAGLE-III sampler designed by Dr. Thomas Holsen of Clarkson University (Postdam, NY).

RESULTS

The box-and-whisker plot is used to describe the overall picture of the data set distribution. The middle cross-line represents the 50th percentile of the data set (median); the lower and upper edges of the box represent 25th and 75th percentiles. The two whiskers represent the minimum and maximum excluding the outliers. The asterisks and circles represent the outliers and far outliers (in comparison to the rest of the data), which are defined as beyond 1.5 times and 3 times the length of the box (the scattering of the middle 50% data set), respectively. “n” represents the numbers of the data points. The data set was log transformed.

Figure 1 and Figure 2 present the results of dry and wet deposition fluxes for all twelve trace metals. Figure 3 shows the runoff concentrations for the twelve trace metals. The quantitative values can be seen clearly from the graphs.

The dry deposition results have revealed clear spatial differences in dry flux among the three locations. Metal deposition fluxes are high in industrial sites (LV1 or LV2), while low in residential/rural sites (RRP or DEX), except for metal Sb.

Spatial differences are also shown for wet deposition fluxes among different sites for most metals. However, there is no spatial difference of As dry deposition fluxes among three locations (4 sites), while Hg and Sb only show spatial differences at DEX site alone.

Runoff concentrations were only monitored at two locations (LV and RRP). Some metals, such as Mn, Cu, Cd, Pb, and Zn, have higher concentrations in runoff at LV sites than at RRP site. While other metals (As, Cr, and V) have higher runoff concentrations at RRP site. It is suspected that RRP site is actually a traffic-impacted site due to some drivers who seek shortcut and drive on the pavement near the sampling site.

COMPARISON OF METAL DISTRIBUTIONS AT EACH SITE AND MEDIA

Figures 4 and 5 compare the concentrations of twelve metals monitored at the LV site for total and fine ambient particulate, respectively. The nickel level is virtually undetectable at the current detection limit (about 2 ng/m³). The ambient total particulate concentrations range from 0.05 ng/L for Hg to 240 ng/L for Al. The ambient fine particulate concentrations for these metals are from 0.03 ng/L for Hg to 54 ng/L for Zn.

Figure 4

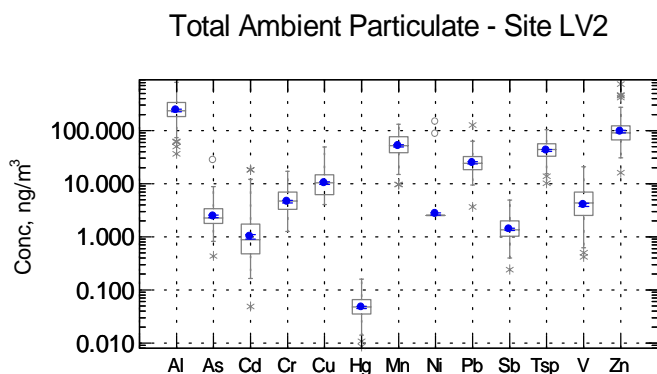
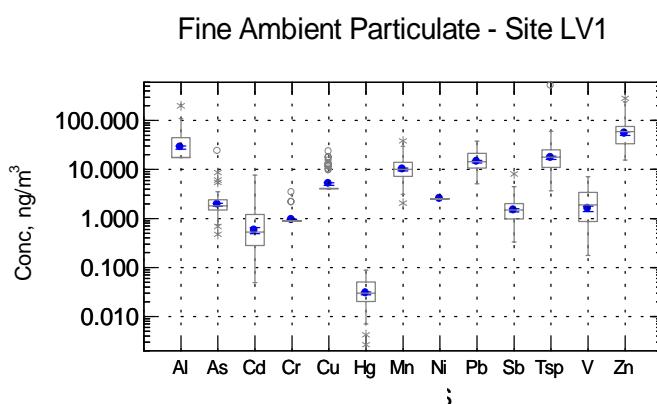


Figure 5



(Note: the total suspended particulates - TSP unit is in µg/L)

The total ambient level ranks, in ascending order, are as following:

Hg < Cd < Sb < Ni < As < V < Cr < Cu < Pb < Mn < Zn < Al
 (0.05) (1.0) (1.5) (<2.0) (2.4) (4.0) (4.6) (10) (25) (51) (96) (240)

While the rank orders for metal level in fine particulate, are slightly different:

Hg < Cd < Cr < Ni < Sb ≈ V < As < Cu < Mn < Pb < Al < Zn
 (0.03) (0.56) (0.9) (<2.0) (1.5) (1.6) (1.9) (5.1) (10) (14) (28) (54)

The metals that have different ranks between the total and fine particulate concentrations are Cr, Mn and Al, all with less than 20% of the mass found in the fine particles. In contrary, Sb and As have over 80% of their mass associated with fine particles.

Figure 6 compares the dry deposition fluxes among the twelve metals at the LV sites. The daily flux ranges from 0.04 ug/m²/day for Hg to 2,100 ug/m²/day for Al. The complete ranking order of the geomean fluxes for the twelve metals are:

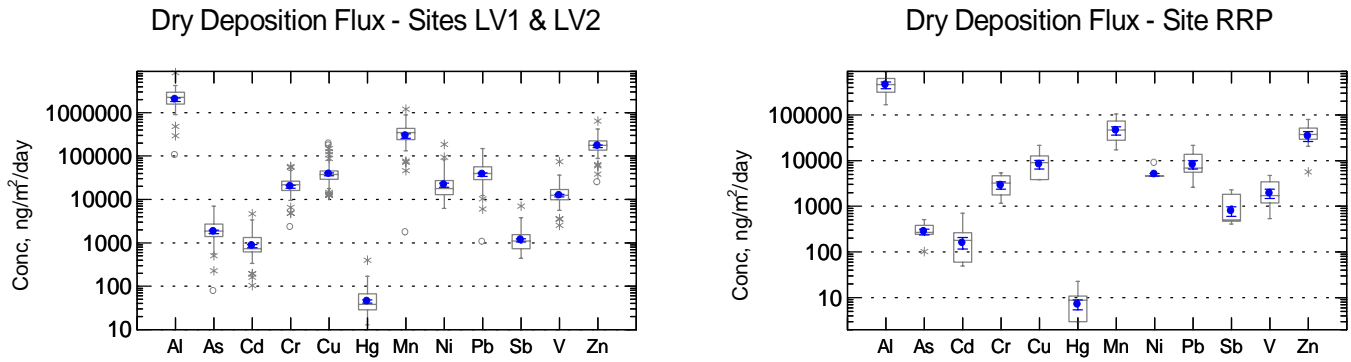
Hg < Cd < Sb < As < V ≈ Ni < Cr < Cu < Pb < Zn < Mn < Al
 (0.04) (0.8) (1.0) (2.0) (12) (13) (20) (34) (40) (150) (300) (2,100)

The ranking orders of geomean daily dry deposition flux are quite similar to that of ambient total particulate metal level. Higher dry deposition flux was found for Mn than Zn, despite lower ambient level of Zn than Mn. This is due to Mn's association with the coarse ambient particulate which can deposit at a faster rate.

The deposition flux ranking orders are similar between the LV sites and RRP site (Figure 7).

Figure 6

Figure 7



The dry deposition velocities from the total particulate for the twelve metals are plotted in Figure 8. The order of the velocities, in ascending order, is as following: Hg < Sb < As < Cd < Pb < Zn < Cu < Cr < V < Ni < Mn < Al.

Figure 8

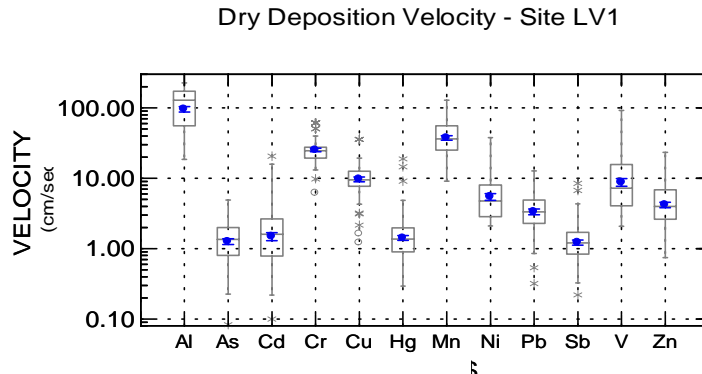


Figure 9 compares the precipitation concentrations among the twelve metals at the LV sites. The precipitation level ranges from 0.02 ug/L for Hg to 67 ug/L for Al.

Figure 9

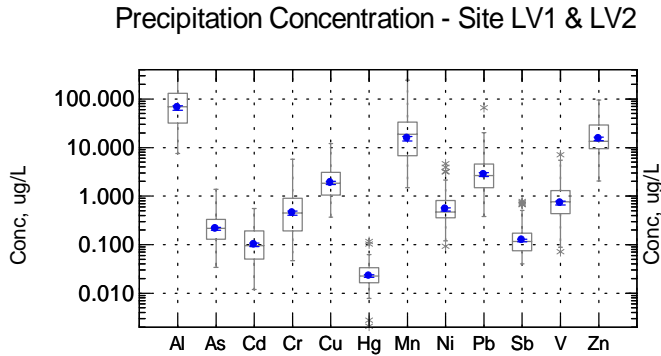
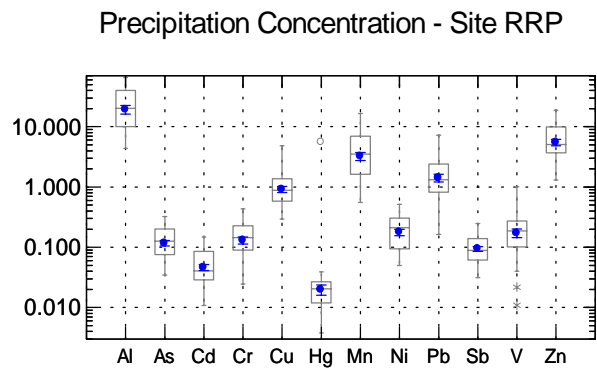


Figure 10



The ranking orders of the geomean fluxes for the twelve metals are:

Hg < Cd ≈ Sb < As < Cr ≈ Ni < V < Cu < Pb < Zn ≈ Mn < Al
 (0.02) (0.1) (0.12) (0.21) (0.45) (0.52) (0.72) (1.9) (2.8) (15) (15.5) (67)

As expected, the above order is almost identical to the one for ambient concentrations, because the ambient metal levels contribute directly to precipitation metal levels. The ranking at RRP site follows the same order, only with lower concentration in general (Figure 10).

Figures 11 through 13 show the wet deposition event fluxes for all measured metals at two LV sites, the RRP site, and the DEX site, respectively.

Figure 11.

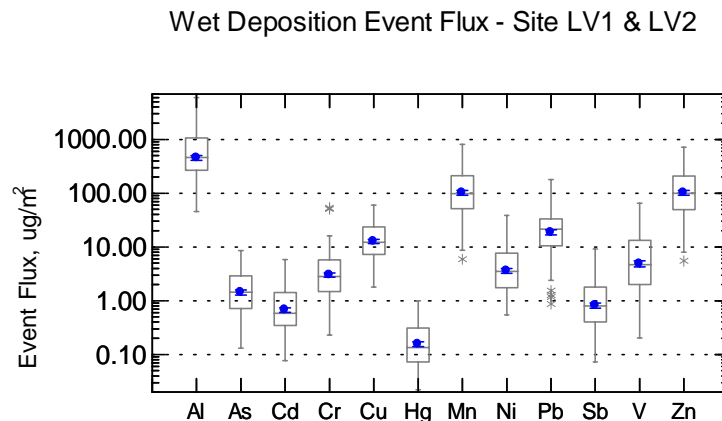


Figure 12

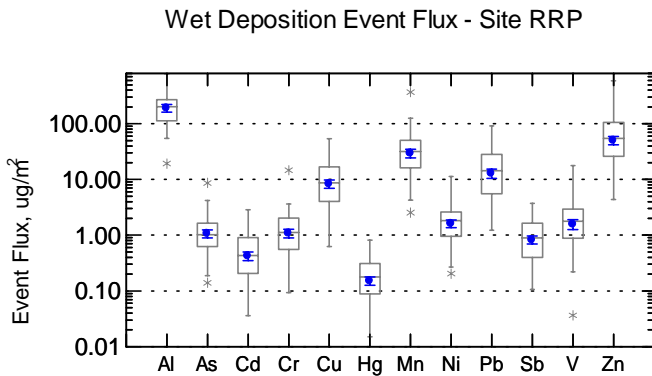
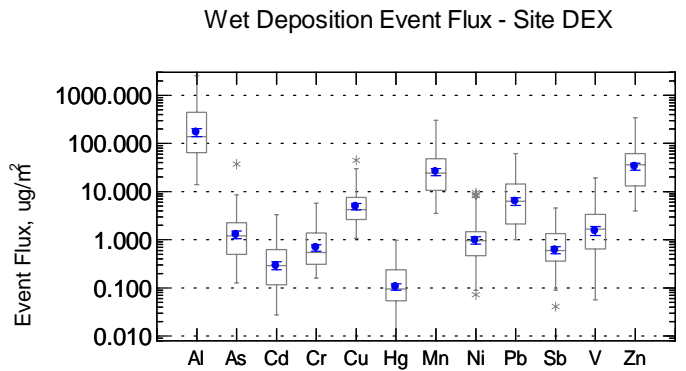


Figure 13



As expected, the ranking orders of the wet deposition flux at the LV sites are similar to the orders observed in ambient and in precipitation samples. RRP and DEX sites have similar ranking order, although with lower values in general.

Hg < Cd ≈ Sb < As < Cr < Ni < V < Cu < Pb < Zn ≈ Mn < Al
 (0.16) (0.7) (0.8) (1.4) (3.0) (3.7) (4.9) (13) (19) (100) (100) (470)

Figures 14 and 15 present the total and dissolved runoff concentrations for all twelve monitored metals, respectively.

Figure 14

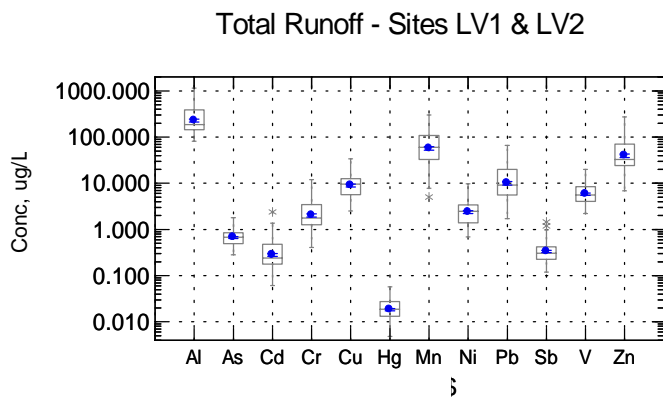
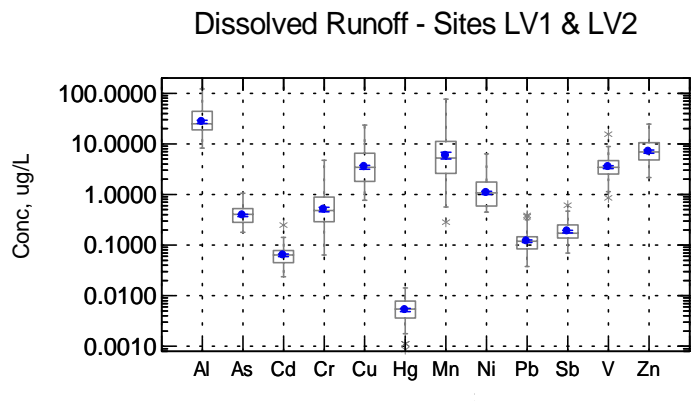


Figure 15



The ranking order of the metal runoff concentration is the same as the ranking order of metal levels in ambient air, precipitation, and wet deposition. After all, they are all from the same air source.

Hg < Cd ≈ Sb < As < Cr < Ni < V < Cu < Pb < Zn < Mn < Al
(0.02) (0.3) (0.3) (0.7) (2.0) (2.3) (5.8) (9.0) (11) (40) (60) (220)

The ranking order for dissolved metals has minor exceptions. Lead (Pb) has a much lower ranking in the dissolved runoff category than in the total runoff category, probably due to its low solubility in water or strong association with the particles in runoff.

Hg < Cd < Pb < Sb < As < Cr < Ni < Cu ≈ V < Mn < Zn < Al
(0.005) (0.06) (0.12) (0.18) (0.40) (0.47) (1.1) (3.6) (3.7) (4.0) (7.0) (30)

CONCLUSIONS

Some of the conclusions of the study are (further data analysis are being performed):

1. Spatial differences in pollutant concentrations were evident among the three sites. Pollutant concentrations at the heavy industrial site (LV) were generally higher than residential (RRP) site and rural site (DEX) for most pollutants.
2. The dry and wet deposition fluxes, as well as runoff concentrations of the twelve trace metals are quantified at three representative sites.
3. Air deposition can be a significant non-point pollution source for trace metals within an urban watershed.

REFERENCES

- Tetra Tech MPS – submitted to Wayne County Department of Environment. Mercury and Trace Metals from Atmospheric Deposition and in Runoff: Data Report and Appendices. May 2000.
- Tetra Tech MPS – submitted to Detroit Water and Sewerage Department. Atmospheric Deposition Study of PCBs, Mercury, and Cadmium, Phase I final report: Project Summary and Recommendations. December 1998.
- Tetra Tech MPS – submitted to Detroit Water and Sewerage Department. Atmospheric Deposition Study of PCBs, Mercury, and Cadmium, Sampling And Quality Assurance Project Plan (SAQAPP). December 1996.
- Atasi, K.Z., C. Hufnagel, T.P. Chen, G. Fujita, L.P. Geoffrey, G. Keeler, and J. Graney (2000) Impact of Atmospheric Deposition on Surface Water Runoff of Toxic Chemicals in Urban Environment. Water Environmental Federation Special Conference: Watershed 2000. Vancouver, British Columbia, Canada. July 9-12.

Atasi, K.Z., G. Fujita, L.P. Geoffrey, C. Hufnagel, G. Keeler, J. Graney, T.P. Chen (2000) Impact of Atmospheric Deposition on The Headworks of Wastewater Treatment Plant – A Case Study. 1st World Congress of the International Water Association. Paris, France. July 3-7.

Atasi, K.Z., G. Fujita, L.P. Geoffrey, C. Hufnagel, G. Keeler, J. Graney, T.P. Chen (1999) Atmospheric Deposition Impact on the Headworks of Wastewater Treatment Plant for Mercury, PCBs, and Cadmium – A Detroit Case Study. 72nd Water Environment Federation Annual Conference. New Orleans. Louisiana. October 9-13.

Atasi, K.Z., G. Fujita, L.P. Geoffrey, C. Hufnagel, G. Keeler, J. Graney, T.P. Chen (1998) Impact of Atmospheric Deposition On Surface Water Runoff of Mercury, Cadmium and PCBs. 71st Water Environment Federation Annual Conference. Orlando, Florida. October 3-7.

Table 1. Sample Collection and Analytical Methods

Parameter	Method of Collection	Collection Medium	Flow rate	Analytical Method	Sample Duration	Sample Frequency
Total Vapor Phase Hg	URG pump	gold amalgamation	0.3 LPM	CVAFS	24 hour	every 3 rd day
Total Particle Phase Hg	“	47 mm glass fiber filter	30 LPM	“	“	daily
Fine Fraction Particle Phase Hg	“	47 mm glass fiber filter	17.5 LPM	“	“	“
Dry Deposition Hg	Eagle III dry-only collector	Apiezon grease on acid-cleaned Duralar	---	“	2-5 days	between rain events
Wet Deposition Hg	MIC-B wet-only collector	acid-cleaned borosilicate glass funnels and bottles	---	“	event	event
Total Runoff Hg	ISCO 3700 flow proportioned composite sampler	acid-cleaned borosilicate glass bottles, teflon lined tubing	---	“	“	“
Dissolved Runoff Hg	“	“	---	“	“	“
Total Particle Phase Metals	URG pump	47 mm Teflon filter	30 LPM	ICP-MS	24 hour	daily
Fine Fraction Particle Phase Metals	“	“	17.5 LPM	“	“	“
Dry Deposition Metals	Eagle III dry-only collector	Apiezon grease on acid cleaned Duralar	---	“	2-5 days	between rain events
Wet Deposition Metals	MIC-B wet-only collector	acid-cleaned polyethylene funnels and bottles	---	“	event	event
Total Runoff Metals	ISCO 3700 flow proportioned composite sampler	acid-cleaned polyethylene bottles and teflon lined tubing	---	“	“	“
Dissolved Runoff Metals	“	“	---	“	“	“
Total Suspended Particulate	URG pump	47 mm Teflon filters	---	Micro-balance	24 hour	daily

Figure 1. Dry Deposition Flux for All Trace Metals

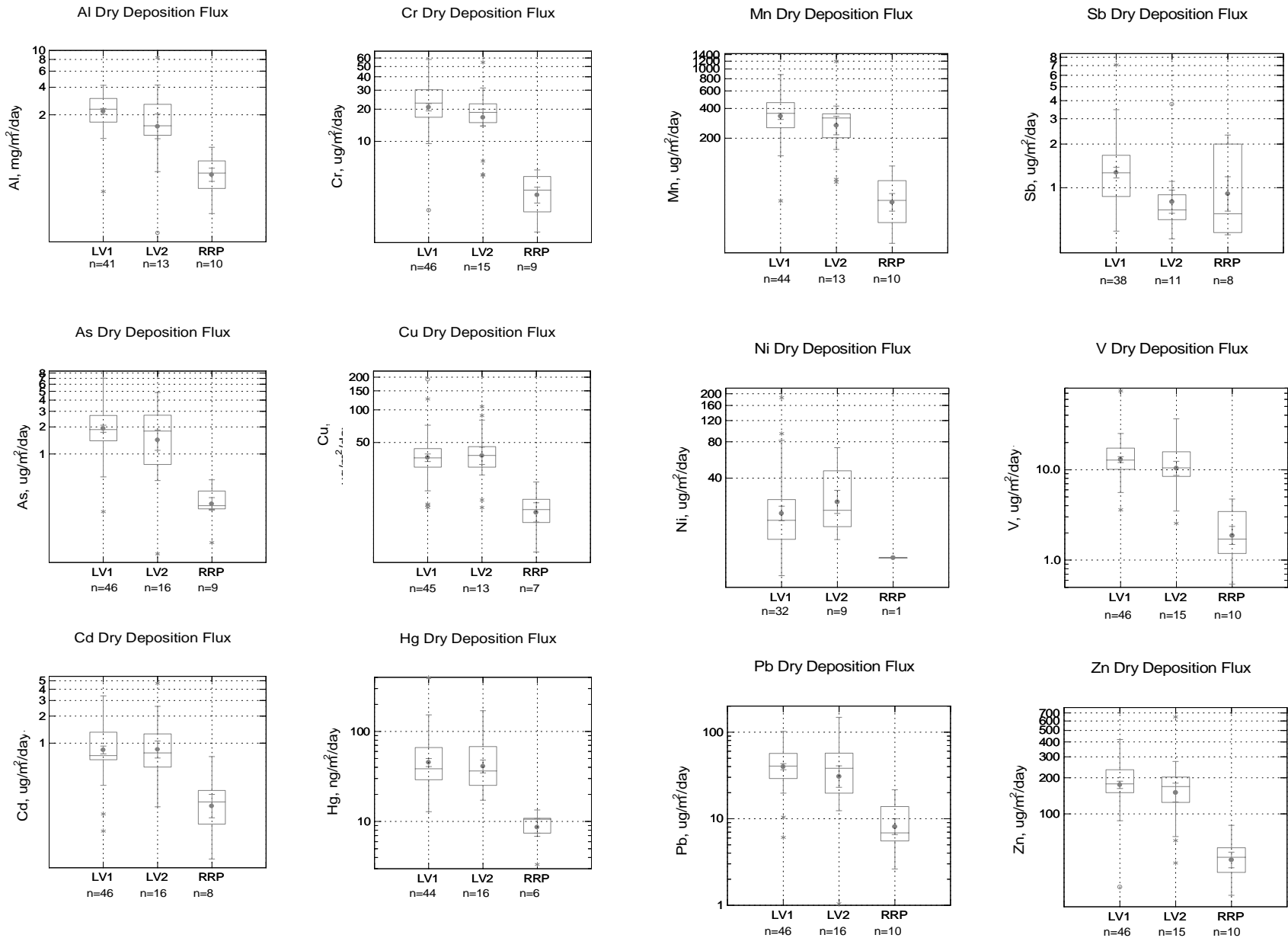


Figure 2. Wet Deposition Flux for All Trace Metals

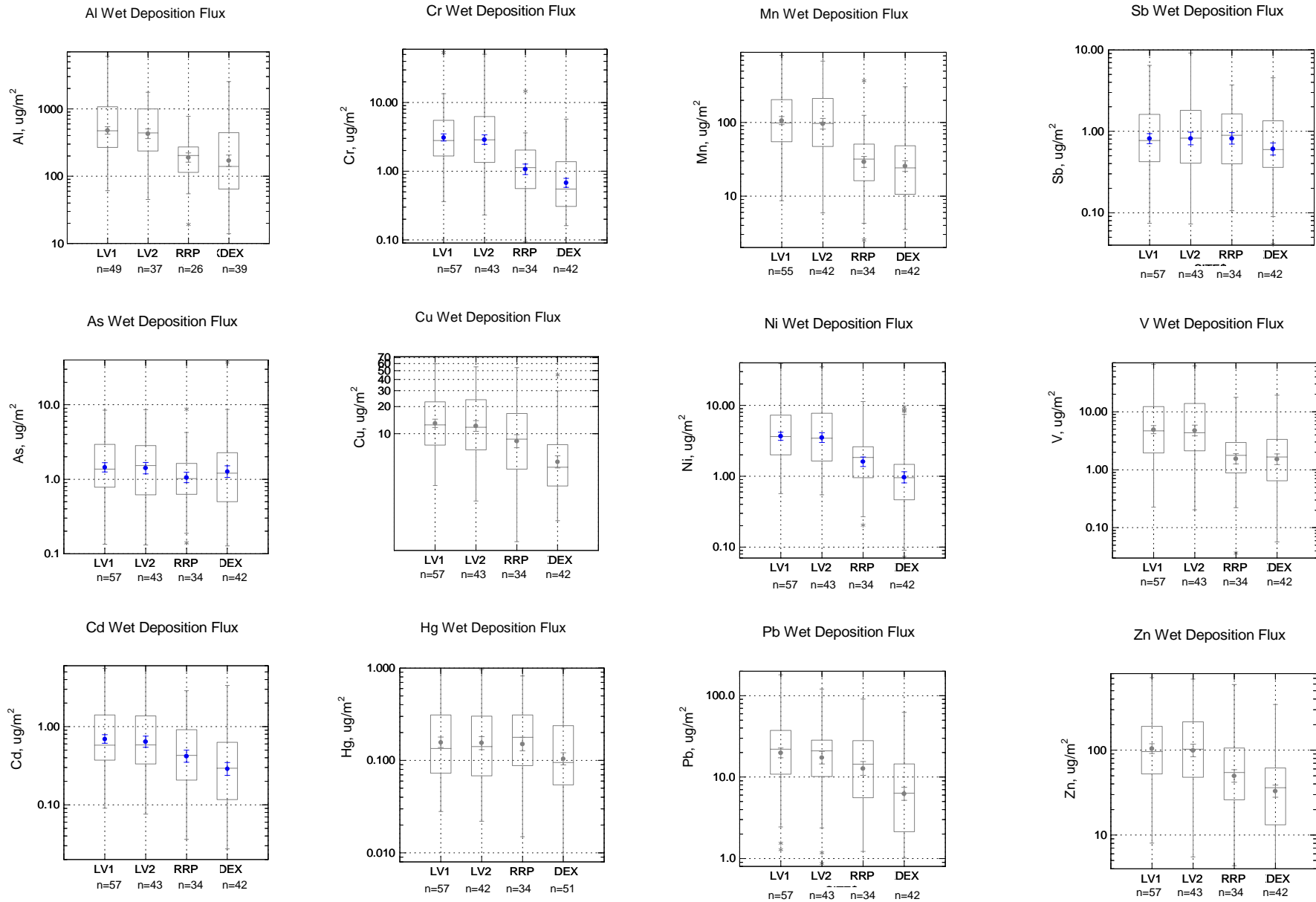


Figure 3. Runoff Concentrations for All Trace Metals

