

# TRACE METAL VARIATION IN ATLANTA REGION STREAM WATER AND STREET RUNOFF

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**Abstract.** Trace metal (Zn, V, Cr, Co, Ni, and Pb) and major ion concentrations were measured at 15 stream and three urban/suburban street locations within the Atlanta metropolitan region (AMR) and surrounding region. The primary focus of the study was Peachtree Creek, draining a populated area of Atlanta, and samples were acquired under a wide range of hydrological conditions (e.g. baseflow, stormflow and recession). Zinc was the most concentrated of all the metals within most of the 172 samples collected during the study. This is likely the result of automotive (tire) pollution and extensive use of zinc alloys. The other metals approached "background" concentrations (i.e. < 10 ppb) in most of the stream samples.

Zinc concentrations within street runoff (median = 905 ppb) were significantly greater than within storm runoff (median = 60 ppb) which were in turn greater than non-storm runoff (median = 14 ppb). Metal and major ion concentration variability indicates "hysteresis" is occurring, where concentrations at a given discharge are not equivalent with respect to the rising and falling limb of the storm hydrograph. A simple endmember mixing calculation suggests that a large portion of the zinc washed into Peachtree Creek from street runoff is likely sorbed by the highly turbid runoff at near neutral storm water pH values.

## INTRODUCTION

Trace metal influx to urban streams from diffuse (non-point) sources is an ongoing concern in terms of both water and sediment pollution. However, there have been relatively few studies of heavy metals in AMR streamflow. Leigh and Gamble (1997) observed that non-point source trace metal inputs to Lake Lanier are relatively low. Buell (1997) found that antimony, chromium and cadmium concentrations decreased while lead increased in flood discharge downstream of Atlanta.

The purpose of this study was to analyze and to statistically compare trace metal concentrations between urban watersheds and non-urbanized watersheds within the AMR and to determine how these concentrations compare with street runoff. A related objective was to compare trace metal variation in storm discharge with discharge between storms (or baseflow).

## SAMPLING LOCATIONS AND METHODS

A total of 172 water samples were collected during the period between May, 1998 and October, 1999 from eight urban streams in the AMR, eight relatively undeveloped basins (generally within 100 km of Atlanta), and three urban/suburban street locations. The principal urban/suburban streams were Peachtree Creek, Nancy Creek, Burnt Fork Creek, Yellow River, and South Peachtree Creek which varied in watershed area from 7 to 347 km<sup>2</sup>.

Grab samples of street runoff were acquired from a heavily trafficked downtown Atlanta thoroughfare (Peachtree Center Avenue at Georgia State University), a suburban shopping center parking lot, and a residential street near Decatur, Ga. Stream and street runoff samples were collected in high-density polyethylene sample bottles pre-washed in 18  $\Omega$ ohm DI water, acidified with trace metal grade nitric acid, pre-rinsed with DI water and then rinsed with sample. Sixty milliliters of sample (when possible) were filtered through an acid washed, DI-rinsed plastic syringe filter fitted with a 0.45  $\mu$ m filter membrane.

Sample pH and alkalinity were typically determined within 24 hours of sample collection on unfiltered samples. Major cation concentrations (K, Na, Ca, Mg) were determined on filtered, acidified samples using conventional flame atomic absorption spectroscopy. Alkalinity (HCO<sub>3</sub>) concentrations were determined by gran titration. Major anion concentrations

(SO<sub>4</sub>, Cl, and NO<sub>3</sub>) were determined on filtered, non-acidified samples using ion chromatography. Trace metal concentrations were determined at the ppb level on the acidified samples by inductively coupled mass spectrometry (ICPMS). Relative standard deviations associated with these methods varied between 6% for cobalt and 15% for zinc. Filter blanks were analyzed periodically as a quality control measure.

Runoff samples were grouped into four "populations": "street", non-urban/non-storm, "urban non-storm" and "urban storm/recession". Trace metal concentration variation between these groups were analyzed for statistically significant differences using the non-parametric Wilcoxon-Mann-Whitney test at the 95% confidence interval ( $\alpha=0.05$ ). Non-parametric tests were used because various data sets were skewed by a few relatively high values which also necessitated using the median, rather than the mean, as the descriptive statistic.

## RESULTS AND DISCUSSION

### Overview of Metal Concentrations

Zinc was the only metal that was consistently concentrated at levels far greater than "background" (i.e. ~10 ppb). Zinc variation, both within a specified group and between groups, was much greater than the variation associated with all the other metals. Lead concentrations were only problematic in a few street runoff samples which were ~5-10 times greater than stream runoff. Metal concentrations, including zinc, were in all cases lower than drinking water maximum concentration limit standards (zinc MCL = 5,000 ppb).

The highest metal concentrations were observed within the runoff collected from the heavily trafficked street in downtown Atlanta. Here zinc concentrations exceeded 4,000 ppb in one sample and the median for this location was 905 ppb (n = 16). In contrast, the median zinc concentration associated with the non-urban non-storm runoff was 8.4 ppb (n=19).

### Comparison of Zinc Concentrations in Peachtree Creek Runoff with Other Waters

Zinc concentrations within Peachtree Creek non-storm waters were low (median=14 ppb; n=9) as was the case for the other urban streams (median = 19 ppb; n=40). Zinc was not significantly more concentrated in Peachtree Creek non-storm water than in non-urban, stream water (median=8.4 ppb; n=19) and most of the Peachtree Creek non-storm samples approached "background" environmental levels.

These data strongly suggest that rock and soil weathering within the Piedmont Province only produces low trace concentrations of metals within stream water. These results also imply that the watersheds that store and release ground water as baseflow to Peachtree Creek and the other basins within this study area are not presently contaminated with zinc or other metals.

### Storm Water Chemical Dynamics

It can be inferred from the major ion dynamics that the influx of street runoff has a major influence on the chemistry of storm water. The mean TDS with the urban non-storm runoff was 95.4 mg/L (n=27) compared to 64 mg/L (n=53) in storm and recession flows. Mean alkalinity concentrations were 35% lower in urban storm/recession runoff than in baseflow. An important aspect of urban hydrology is that there is an adequate contribution of soil water alkalinity to buffer the pH of stream runoff during a storm cycle. The mean pH of urban non-storm runoff was 6.77 (n=30) while the mean pH of urban storm and recession runoff was similarly 6.49 (n=55).

In contrast to major ion concentrations, metal concentrations in urban storm runoff were generally greater than in urban non-storm runoff. The maximum and median zinc concentration in Peachtree Creek storm runoff were 157 and 60 ppb respectively (n=15). The median zinc concentration for the urban streams was 37 ppb (n=58) in contrast to 19 ppb (n=40) for urban non-storm runoff. The most obvious source of contamination is street runoff as evidenced by the high zinc concentrations in street and parking lot runoff (median

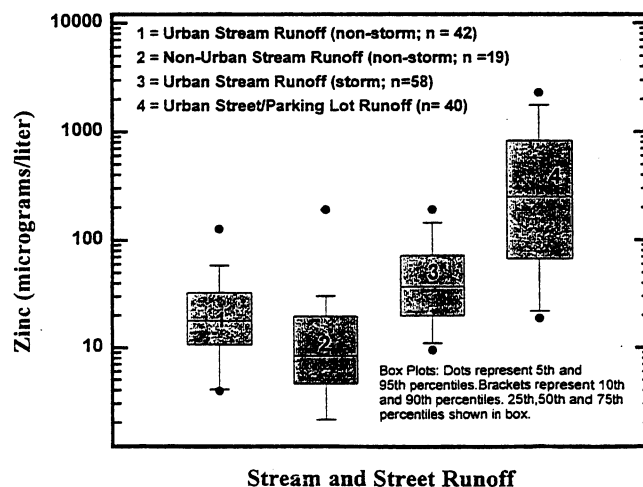


Figure 1. Box plot comparison of zinc concentrations

zinc = 254 ppb; n=40). Figure 1 provides a box plot comparison of zinc concentrations and shows an approximate order of magnitude difference between street runoff and all the other populations.

An analysis of zinc and alkalinity concentrations during a 2,250 cfs Peachtree Creek storm event revealed a pronounced difference with respect to their hydrochemical dynamics (Figure 2). Alkalinity concentrations decreased by more than a factor of two during the rising limb of the storm hydrograph, a good indicator of dilution by street and storm drain runoff. The minimum alkalinity occurred at peak discharge. In contrast, zinc concentrations increased from below 40 to over 100 ppb on the rising limb of the hydrograph and reached their maximum prior to peak discharge. This may indicate a "first flush" phenomenon where zinc was washed off the streets during the initial rainfall associated with this storm. Zinc concentrations then decreased with stream recession when soil and ground water become principal contributors to discharge.

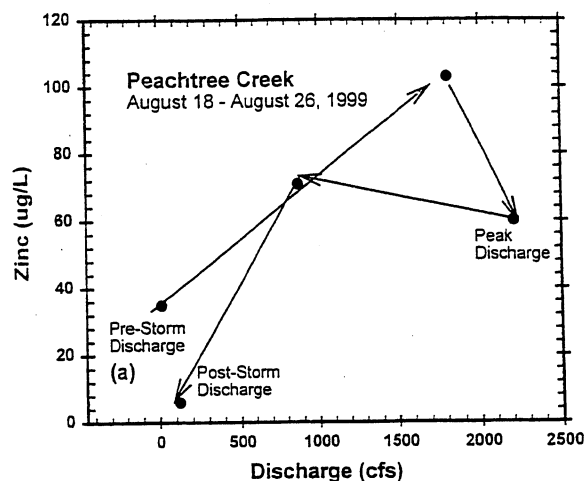
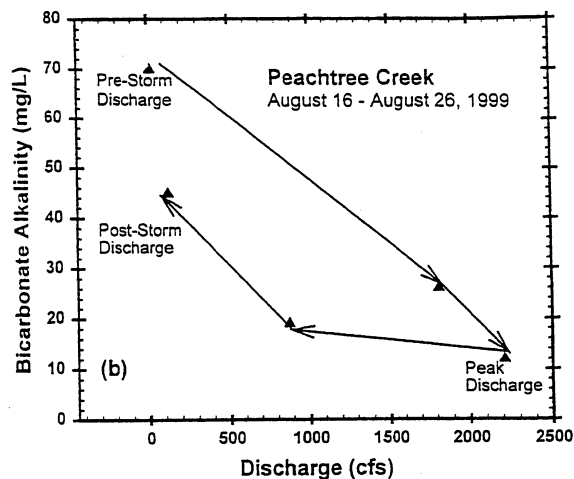
### Mass Balance Analysis of Storm Runoff in Peachtree Creek

Alkalinity concentrations were measured in 13 street runoff samples which facilitated the following two-endmember mixing analysis. The average alkalinity concentration within the street runoff (7.1 ppm) was used to represent the "new water" endmember. Most of this alkalinity likely evolved from contact with cement and other solids present on or near street surfaces. An alkalinity of 69.5 ppm (the highest summer baseflow) was used to represent the ground water component within the mixture. Assuming that a simple mixing process (ground water + street runoff = total stream discharge) can reasonably account for streamflow, the following equation can be used to calculate the percentage of street runoff or "new water" within the mixture:

$$X(7.1 \text{ ppm}) + (1-X) 69.5 \text{ ppm} = \text{Alk}_{\text{obs}}$$

where X = the percentage of new water, (1-X) = the percentage of ground water, and  $\text{Alk}_{\text{obs}}$  = the measured alkalinity within Peachtree Creek storm water. The percentage of new water was calculated within 14 storm and recession samples and these values ranged between 21-86%.

An "expected" zinc concentration ( $\text{Zn}_{\text{exp}}$ ) within runoff can be calculated as follows from the percentage of new water (X):



**Figure 2: Alkalinity and Zinc Concentration Hysteresis in Peachtree Creek Storm Discharge**

$$(X) 592 \text{ ppb} + (1-X) 24 \text{ ppb} = \text{Zn}_{\text{exp}}$$

where X and 1-X are the same as previously defined; 592 ppb = zinc concentration of the new water (mean concentration of the parking lot and street runoff) and 24 ppb = zinc concentration within Peachtree Creek basin ground water (assumed to be equivalent to the average baseflow concentration). The  $\text{Zn}_{\text{exp}}$  calculated in this manner varied between 143 and 512 ppb while the observed concentrations in the 14 storm and recession samples were much lower and varied between 9.2 and 112 ppb.

This analysis strongly suggests that much of the zinc (i.e. on average 75%) that is "expected" to appear in stream runoff during storm events as the result of conservative mixing is not present. It is of course possible that this model is too simplistic and that a three endmember model (ground water + soil water + new water = total discharge) is more realistic. It is also

possible that the zinc and alkalinity concentrations used to represent the endmembers are in need of modification. Nonetheless, it is reasonable to conclude from these calculations that a high percentage of the zinc influx from street runoff is removed from solution in the final mixture comprising storm runoff. The most likely explanation involves adsorption of zinc (and likely many other trace metals) upon the suspended sediment transported by storm discharge. The two factors which support this hypothesis are the very high turbidity and near neutral pH of urban stormflow in the Piedmont Province. Much of the zinc within the storm water can be absorbed upon clay minerals and iron oxyhydroxide coatings of the suspended sediment at the near neutral pH of the storm runoff (Benjamin and Leckie, 1981).

### CONCLUSIONS

- 1) Trace metal (V, Cr, Co, Ni, and Pb) concentrations within stream runoff in the densely populated Atlanta metropolitan region are relatively low and approach "background" levels (i.e. in the low ppb range).
- 2) Zinc is the most concentrated and widely variable trace metal and ranged between 3.0 and 397 ppb in urban streamflow (well below the MCL of 5,000 ppb).
- 3) Metal concentrations were not notably greater than background concentrations in urban non-stormflow. This indicates that rock weathering does not yield high concentrations of zinc or other metals and the soils which comprise the water storage "reservoirs" for urban basins in the AMR are not at this time contaminated with heavy metals.
- 4) The highest metal concentrations were observed in street runoff. Zinc concentrations within street runoff in downtown Atlanta ranged between 88 and 4,019 ppb. The most likely source of most of this metal pollution is automotive tire erosion.
- 5) Urban stream metal concentrations in the AMR were significantly higher in storm runoff than in baseflow, obviously the result of the large influx of street runoff. Zinc concentrations peaked in Peachtree Creek runoff during the early part of the storm cycle and declined during the recession portion of the hydrograph. Therefore, the hysteresis pattern (different concentrations at the same discharge value) for alkalinity (and most other dissolved ions evolved from rock weathering) and zinc are generally opposite from one another.
- 6) A simple mass balance calculation (two-endmember mixing) suggests that most of the zinc (and other metals)

may be absorbed onto particulate matter present within the storm discharge. A key mitigating factor is the near neutral pH of storm discharge which favors the absorption of metals upon clay mineral and iron oxyhydroxide surfaces.

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