Transport and fate of mercury and other metals in Tucson's urban metropolitan area: Role of watershed sources versus atmospheric deposition

Basic Information

Title:	Transport and fate of mercury and other metals in Tucson's urban metropolitan area: Role of watershed sources versus atmospheric deposition
Project Number:	2009AZ312B
Start Date:	3/1/2009
End Date:	2/28/2010
Funding Source:	104B
Congressional District:	8
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Surface Water, Sediments
Descriptors:	fate and transport, mercury, urban watershed, atmospheric deposition
Principal Investigators:	Kathleen Ann Lohse, Paul David Brooks, Jennifer McIntosh

Publications

1. Lohse, K.A., E. L. Gallo, and J. R. Kennedy, 2010, Possible tradeoffs from urbanization on groundwater recharge and water quality, Southwest Hydrology, 9 (1), 18- 19; 32.
2. Lohse, K.A., E. L. Gallo, P. D. Brooks, J.E.T. McLain, J. McIntosh, and T. Meixner, Influence of channel substrate type on storage and transport of urban storm runoff in a semi-arid environment, In preparation for Journal of Environmental Quality
3. Gallo, E.L. P.D. Brooks, K. A. Lohse, and J.E.T. McLain, Patterns and controls of storm runoff quality in semi-arid urban catchments, In preparation for Hydrologic Processes
4. Gallo, E.L. K.A. Lohse, and P.D. Brooks, Temporal variation in urban storm runoff and water quality, In preparation for Hydrologic Processes.
5. Carlson, M, 2010, Impacts of urbanization on groundwater quality and recharge rates in a semi-arid alluvial basin. "MS Thesis" School of Natural Resources and the Environment, University of Arizona, Tucson, AZ, p. 65.
6. Carlson, M., K.A. Lohse, J.C. McIntosh, Impacts of urbanization on groundwater quality and recharge rates in a semi-arid alluvial basin, In preparation for Journal of Hydrology.
7. Lohse, K.A. and A.M. Merenlender. 2009. Impacts of exurban development on water quality In G. McPherson and A. Esparza, editors. The Planner's Guide to Natural Resource Conservation: The Science of Land Development Beyond the Metropolitan Fringe. New York: Springer-Verlag, pp. 159-180.

TRANSPORT AND FATE OF MERCURY AND OTHER METALS IN TUCSON'S URBAN METROPOLITAN
AREA: ROLE OF WATERSHED SOURCES VERSUS ATMOSPHERIC DEPOSITION

PROBLEM AND RESEARCH OBJECTIVES

Numerous studies have documented that urbanization increases runoff and the occurrence and loads of nutrients, metals and organic pollutants to surface and ground water that have negative consequences for aquatic life and drinking water (*Kolpin et al. 2002, Barber et al. 2006*). Despite this trend, water managers lack information on how the process of urbanization alters localized hydrologic processes and the subsequent transport and fate of different pollutants. In arid to semi-arid environments, such as Arizona, runoff from urban areas is often actively managed as a part of storm water management but also as active and/or focused recharge to groundwater. These activities result in a modified hydrologic template in which to understand water quality issues and raise concerns and questions about the tradeoffs between urban storm-recharge and water quality.

In particular, there is growing concern about the adverse effects of mercury and other metals in the environment. Human activities have dramatically accelerated the release of mercury and other metals into the environment via coal-fire combustion and mining of metals for industry. Due to specific concerns related to mercury, the Mercury Deposition Network was initiated in 1996 to monitor inputs of mercury in wet deposition; it currently has 100 sites in the United States. The network remains limited in the Southwest with only one site in Arizona despite the fact that relatively high concentrations have been observed at the sole monitoring site in Phoenix (25.8 ng/L).

An alternative means to evaluate potential human and wildlife exposure to atmospherically deposited mercury is to monitor concentrations of mercury in storm runoff. Preliminary data from a study initially funded by the Water Sustainability Program (WSP) (partial match for this grant) showed high concentrations of mercury (Hg) in the urban runoff across the sites. Average Hg concentrations were 6.47 ± 0.43 ug/L, exceeding ephemeral wash standards of 5.0 ug/L as dissolved Hg. These concentrations are 1000 times higher than concentrations observed in rainwater at the Phoenix site. High concentrations of Hg across all sites compared to other metals and pollutants suggested that atmospheric deposition was the dominant pathway. However, these averages only represented a small subset of the urban runoff samples from 2007 (37 out of 400). As such, questions remained about whether these samples are representative of different storm events and seasonal loads and/or whether they are biased towards peak concentrations.

In this study, we expanded our analysis of mercury and other metals in surface, ground waters and soils in the Tucson Basin, Arizona, a semi-arid urban environment. We addressed the following objectives posed here as questions: **How does urban land use influence storm transport and delivery of metals to surface and groundwater? What roles do soils in ephemeral washes play in retaining or removing these pollutants and controlling the rate at which pollutants are transported to regional groundwater?**

We hypothesized that metals derived from different land uses would vary with watershed characteristics. Alternatively, atmospheric derived metals would be similar across all watersheds. We predicted mercury concentrations would be high across watersheds whereas watersheds with higher impervious surface area such as commercial and high urban density

(HDH) would have higher concentrations of metals (Zn, Cu, Cd) in surface waters relative to lower urban density watersheds (LDH). We also hypothesized that naturally surfaced washes would act as a sink for metals compared to concrete line washes with the prediction that vegetated lined washes would retaining more metals than soil lined washes.

To address these objectives, we trained and supported two graduate students in field and laboratory procedures and analyzed runoff and soil samples from 2007 and 2008 campaigns for metals on an ICP MS to evaluate how metals and mercury (Hg) vary with land use. Lateral ephemeral washes contrasting in housing age and density along the Rillito River (a proposed site for artificial recharge) afforded us the opportunity to evaluate the relative importance of these controls on water quality. In addition, we sampled groundwater samples in 2008 and 2009 across the Tucson Basin and analyzed these samples for metals.

Approach, methods, procedures, and facilities -

Study Site   The study was conducted in the Tucson Basin in southeastern Arizona, USA (Figure 1). Tucson metropolitan area (population 1,000,000) occupies the alluvium-filled valley and foothills. The basin is bounded by the Santa Catalina, Rincon, and Tucson Mountains, and the Santa Cruz River and its major tributaries, the Canada del Oro, the Rillito River, and the Pantano Wash flow intermittently toward the northwest. Tucson experiences hot summers and mild winters with two distinct rain seasons (total ~28 cm/yr): intense and localized summer-monsoon storms (accounting for 2/3 of the annual precipitation) and protracted, widespread winter rains.
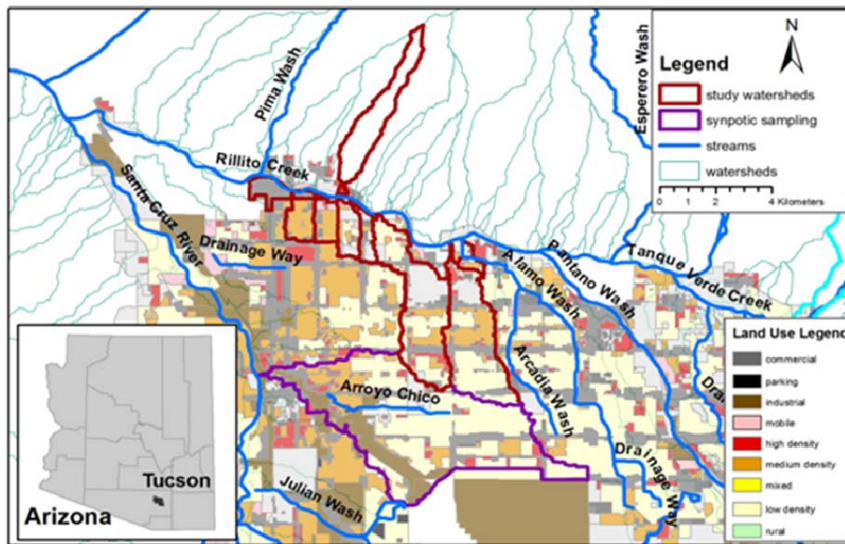

Figure 1: Tucson Basin showing study watersheds draining into the Rillito Creek and synoptic sampling watershed (Arroyo Chico) draining into the Santa Cruz.

We focused our study on urbanizing watersheds draining laterally into the Rillito River because water managers have identified sections of the Rillito as potential area of recharge, and recent studies indicate the transient flow conditions during summer monsoon flooding result in more infiltration that predicted from steady state conditions (Blasch et al. 2006). Moreover, the Rillito and lateral drainages are not impacted by any wastewater treatment plants (WWTP).

Surface Storm Runoff Procedures and Methods   For this study, we used 5 previously established sites in the Tucson basin representing a range of urban land use watersheds (5 sites, commercial, high density housing, mixed density housing, highly engineered mixed density housing, low density housing). In June 2007, we installed 10 rain gauges within the study

watersheds and 5 automated storm water collectors with pressure transducers each in a culvert at the outlet of lateral sub-watershed draining into the Rillito Creek that vary in land use (Figure 1). We collected storm events over the course of the summer 2007 monsoon season to characterize the summer hydrograph and quantify nutrients, metals, organic pollutants, and bacteria. In addition, we installed 2 automated storm water samplers with pressure transducers along the Arroyo Chico in upstream and downstream positions. We then performed synoptic grab sampling of water from 12-15 sites along the Arroyo Chico over several storm events along with collections from the automated water collectors to evaluate possible sources and transformations in space and time, respectively. In total, we collected over 400 samples. In the summer of 2008, we collected a smaller set of runoff samples to evaluate year to year variability and fill gaps in data (~200 samples).

Groundwater sampling   To examine the impacts of urbanization on groundwater quality and recharge rates, 40 groundwater samples were collected from water supply and monitoring wells operated by Tucson Water and the Winterhaven Living Community along the Rillito Wash in May 2008 and June 2009 (Figure 2). Groundwater wells were selected for access, proximity to the Rillito Creek and a shallow static water depth, as areas of focused channel infiltration and recent recharge tend to be closer to the surface (ranging from 10 to 50 m). Fifteen of the 40 groundwater wells were also sampled for CFCs, ^{3}H and noble gases to estimate recharge rates along the Rillito Creek. These wells were selected partially as they had been previously sampled by Eastoe et al. (2004) for ^{3}H in the 1990s. This study collected unfiltered aliquots for ^{3}H in sample-rinsed 1 L HDPE plastic bottles; care was taken to collect samples without any headspace. CFC samples were collected in 125 mL clear glass bottles with aluminum foil-lined plastic caps. In order to avoid atmospheric contamination, bottles were filled and capped in a bucket under water through copper tubing connected to the wellhead. The bottles were sealed with electrical tape and stored and shipped upside down. Duplicate CFC samples were collected at each site. Additional protocol details are available from the USGS CFC collection website (http://water.usgs.gov/lab/chloroflu orocarbons/sampling/bottles/).
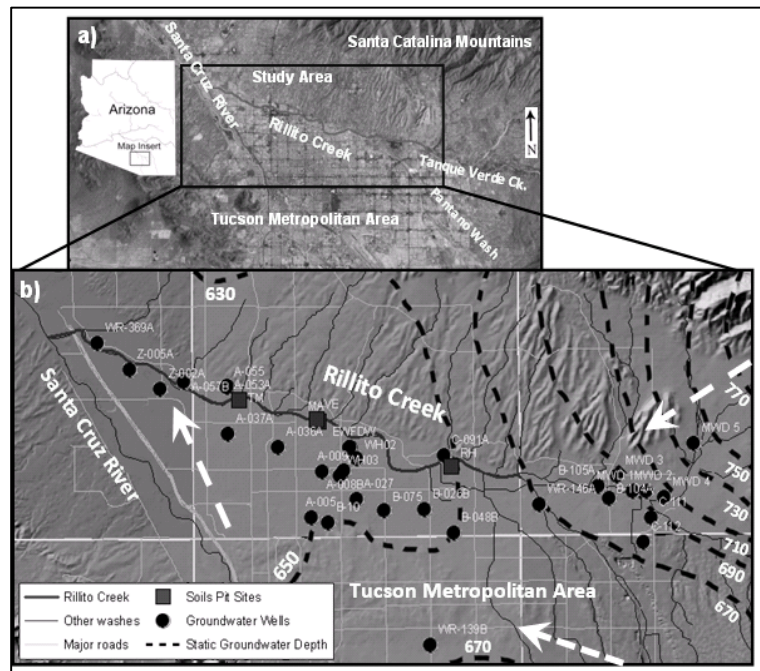

Figure 2. a) Location of study area and urban development in the Southern Arizona. b) Within the study area, location of the Rillito Creek and its tributaries, groundwater wells, soil pits and static groundwater depth contours (measured in meters above sea level). White arrows represent the direction of groundwater flow.

Soil Sampling Procedure and Methods   In addition to sampling storm runoff in 2008, we also sampled soils in ephemeral washes and Rillito to evaluate the transport and fate of nutrient, organic pollutants and metals in soils. We collected tributary sediments to the Rillito before and after the monsoon for solute concentrations, organic matter content, and soil moisture status. In addition, we collected soils in Rillito Creek itself. The purpose of this approach is to be able to assess the reaction and transport of the metals and organic matter rich runoff as it propagates through the surface and subsurface hydrologic system. Due to the alluvial nature of the Tucson basin and the sandy texture of sediments, we collected surface soil cores (0-5 cm) at the outlet of the washes and at grab sampling points (defined by surface water sampling above) within the watershed before and after each monsoon season for the duration of this project (150 samples + blanks). We also collected sediment cores before and after each monsoon season from Rillito Creek at the outlets wj ere we had established surface water sampling sites (Figure1). Two to three soil cores were collected in the Rillito to approximately 1 m depth (2-3 per site, 4 sites, 12 cores, 120 samples + blanks). We extracted soils in artificial rainfall water to evaluate those nutrients, pollutant and metals that could be readily exchanged and transported in runoff.

Metal analyses
Samples for analysis of metals in runoff and groundwater were collected in sterile amber glass vials and filtered them through 0.7 and 0.1 μm glass fiber filters. We preserved dissolved metals in amber glass vials with concentrated ultrapure nitric acid so that sample pH was below 2 and analyzed these samples on an ICP MS in the ALEC lab at the University of Arizona.

PRINCIPLE FINDINGS AND SIGNIFICANCE
Preservation and methodology challenges
        Methodology for preservation of mercury (Hg) is inherently challenging. Debate exists as to how to preserve mercury, particularly mercury compounds in aqueous matrices. Factors affecting mercury stability include the form of mercury, the container material, the matrix, and the preservation techniques (EPA 2003). The currently accepted method for preservation of

mercury samples is a 2% HNO_3 as preservative, with an allowed holding time of 26 days prior to instrumental analysis. However, studies have shown significantly low recoveries with 2% HNO_3 as a preservative. Other studies suggest that mercury ions bind to the high density polyethylene (HDPE) water sample containers. Finally, mercury vapor may be lost when the bottles are uncapped.

        We analyzed 2007 samples preserved with HNO_3 in glass that had been shown to have high mercury (>5 ug/L Hg) and found that mercury concentrations were below detection limit. We hypothesized that low mercury
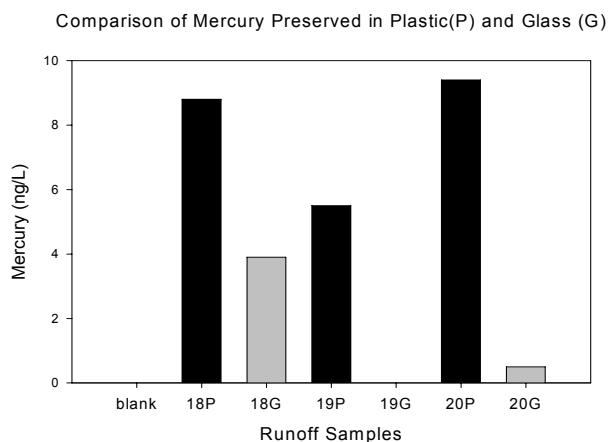

Figure 3: Comparison of mercury concentrations in water contained in plastic (#P) or glass (#G)

recoveries might be due to loss on glass or plastic containment, time of containment, or analytical problems on the ICP MS. We ran additional 2008 samples that had been contained for the same amount of time as those observed with high concentrations but also found that these at lower concentrations (ng/L) suggesting containment issues or analytical errors.

<u>Plastic versus Glass Bottles for Containment</u> We tested the effects of differences in containment (plastic versus glass) on 3 sets of samples contained in plastic or glass and analyzed them for mercury. We found higher recoveries of Hg in plastic compared to glass suggesting loss of Hg to binding on the glass or vaporization (Figure 3). However, concentrations in plastic were still an order or magnitude lower than expected (ng versus ug/L) suggesting loss of Hg or analytical errors. Other studies suggest that a 1 ppm solution of $AuCl_3$ in HNO_3 is sufficient to preserve Hg but will not affect any other analytes or analytical techniques (EPA 2003). Prior collections of runoff for the 2007 and 2008 season were not solely oriented at measuring Hg so that a 2009 sampling campaign was organized to test whether observations of high Hg in runoff could be reproduced if the samples were preserved with $AuCl_3$ and then run immediately for Hg on the ICP MS.
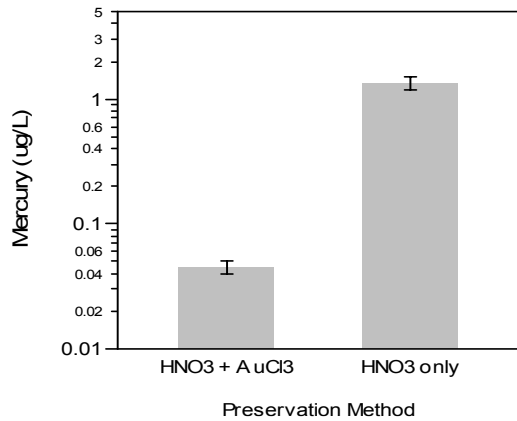

Figure 4: Comparison of preservation treatment

<u>Comparison of Preservation with Gold Chloride ($AuCl_3$)</u>   Eight samples were collected during the 2009 monsoon runoff season, preserved with $AuCl_3$, and analyzed immediately for Hg analysis to eliminate preservation and containment issues. If runoff samples were high in runoff as observed across all sites in the 2007 season, we expected to observe high Hg in runoff samples. If the problem was analytical in nature (i.e. ICP MS not calibrated correctly or dilutions incorrect), we expected to observe low levels of Hg. Indeed, we found low levels of Hg in runoff samples preserved with gold chloride relative to preliminary analyses suggesting possible analytical mis-calibration contamination or other spurious error (Figure 4). Interestingly, concentrations in runoff samples preserved with nitric acid alone were higher (1 ug Hg/L) relative to those preserved with nitric acid and gold
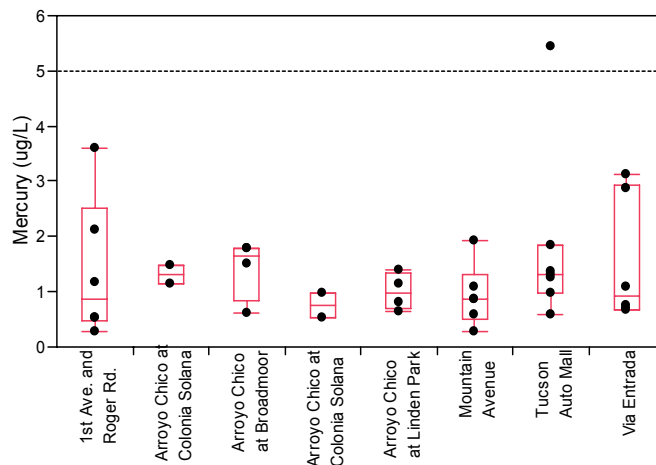

Figure 5: Concentrations of mercury in storm runoff across the Tucson Basin (n=37 samples) and ephemeral wash standard of 5 μg/L m (dashed line).

chloride. Hg concentrations were also much higher than those observed in Phoenix rainfall concentrations (25. 8 ng/L) suggesting that high concentrations in runoff may be real but extreme precaution and a study solely devoted to tracking Hg may be warranted.

Reanalysis of ICP MS data   To attempt to address possible analytical issues, we requested re-analysis and recalibration of our samples on the ICP MS. Post-analysis showed that the average Hg concentrations declined relative to preliminary analyses. Average concentrations were 1.35 ± 0.17 ug/L, still 530% greater than those observed at the Phoenix monitoring site, and one sample exceeded the ephemeral wash standards of 5.0 ug/L as dissolved Hg (Figure 5). From this study we concluded that we could not reproduce high Hg concentrations observed in preliminary analyses and suspect that calibration issues affected our analyses as well containment issues. We also concluded that Hg concentrations appear to be high relative to the Phoenix monitoring site and that further research should be devoted solely to Hg analyses. For the remaining samples that we ran on the ICP MS, we analyzed samples for other metals and not Hg.

Data set enhancement with metal analysis for 2008 monsoon
An additional objective of metal analysis for a second monsoon season was to complement our 2007 runoff quality data set.
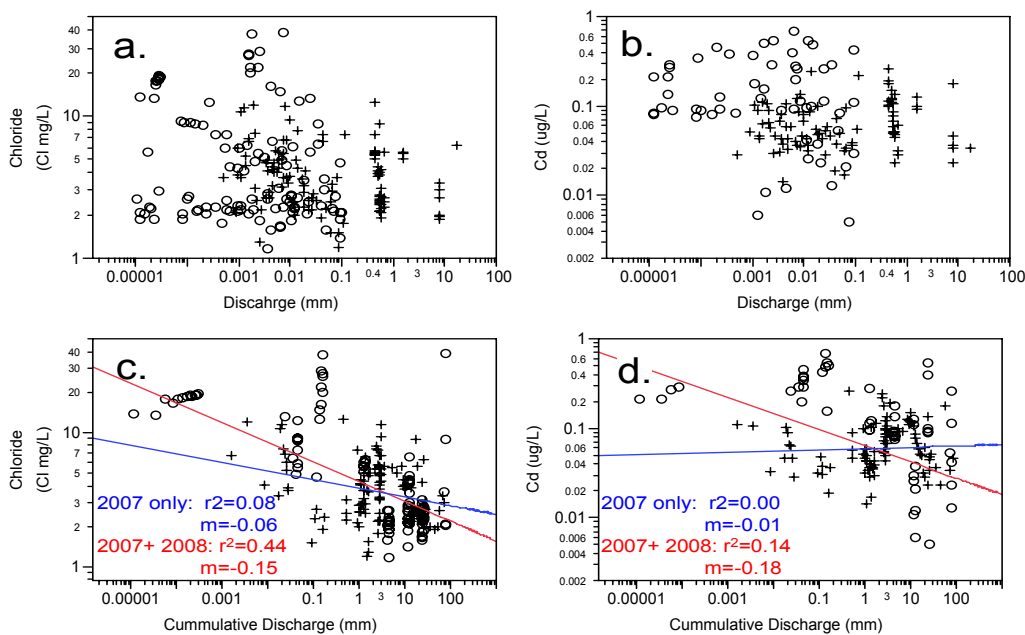

Figure 6 – Chloride and cadmium concentrations for the 2007 (crosses) and 2008 (open circles) monsoon against discharge magnitude (panels a and b) and cumulative discharge (panels c and d). Solute concentrations for 2008 plot along a wider range of discharge and cumulative discharge values, and enhance temporal trends thus illustrating the importance of additional analysis to complementing our data set.

We enhanced our existing data by analyzing metal concentrations of 2008 monsoonal runoff samples that were collected over a wider range of discharge magnitudes, and which were more evenly distributed throughout the monsoon. For example, panels a and b in Figure 6 show chloride

and cadmium concentrations, respectively, against discharge for the 2007 (crosses) and 2008 monsoons (open circles). The 2008 chloride (Cl) and cadmium (Cd) data plot along smaller discharge events and show that chloride concentrations are highly variable at small discharges whereas cadmium concentrations are higher during smaller runoff magnitudes. Panels c and d in Figure 6 show chloride and cadmium concentrations, respectively, for both monsoons plotted against cumulative discharge. Given that cumulative discharge increases as the monsoon season progresses, we can use cumulative discharge as a time variable that can help us identify temporal trends in runoff quality. Panel c and d show that for the 2007 season, chloride concentrations significantly decreased as the season progressed ($r^2 = 0.08$, $p = 0.001$); whereas cadmium concentrations did not ($r^2 = 0.00$, $p = 0.61$).   However, a clearer image emerges when the 2007 and 2008 data are combined and concentrations across a wider range of cumulative discharge values are added. The combined data set shows that chloride and cadmium concentrations decrease as the season progresses and cumulative discharge increases ($r^2=0.44$, $p < 0.001$ for chloride, $r^2=0.14$, $p <0.001$ for cadmium), however, the weaker correlation of cadmium with cumulative discharge suggests that the mechanisms impacting runoff quality vary among solutes. Specifically, the impact of time since the onset of monsoonal runoff is greater for chloride than cadmium. The seasonally distributed chemistry data enhances our ability to identify dominant runoff quality trends over space and time. The impact of runoff vs. the impact of land cover can therefore be better addressed by a data set containing 2 years of data (Gallo et al, manuscript in revision, Gallo et al. in preparation).

How does urban land use influence storm transport and delivery of metals to surface water?

Land use and discharge alone were not good predictors of metal concentrations across all of our sites. Surprisingly, metals including aluminum, arsenic, iron, nickel, lead and zinc; and the cations calcium, sodium and potassium exhibit chemostasis where concentrations vary independently of discharge, rather than inversely with discharge, suggesting that these solutes are constantly sourced during runoff events. This may occur due to a very large reservoir of solute stored in the watershed, or to a constant input of solute into our study sites via weathering of geologic
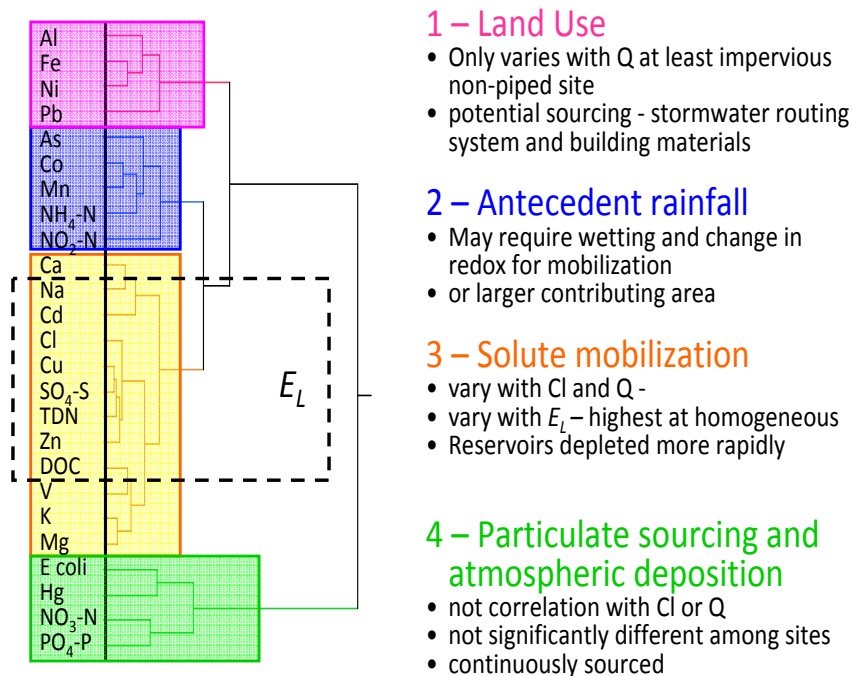

1 – Land Use
- Only varies with Q at least impervious non-piped site
- potential sourcing - stormwater routing system and building materials

2 – Antecedent rainfall
- May require wetting and change in redox for mobilization
- or larger contributing area

3 – Solute mobilization
- vary with Cl and Q -
- vary with E_L – highest at homogeneous
- Reservoirs depleted more rapidly

4 – Particulate sourcing and atmospheric deposition
- not correlation with Cl or Q
- not significantly different among sites
- continuously sourced

Figure 7 – Cluster analyses showing dominant sources of metals and other solutes

and urban construction materials, or atmospheric deposition.

A cluster analysis of mean solute correlations identified factors that appear to largely impact concentrations of different metals in urban runoff (Figure 7). We identified 4 major controls on the runoff quality of urban runoff: 1) land cover characteristics, 2) antecedent rainfall conditions and catchment wetting 3) hydrologic transport of solutes with finite sourcing and reservoirs and 4) constant particulate sourcing and atmospheric deposition. Cluster 1 (pink) included aluminum, iron, nickel and lead. Regressions against land cover attributes, including road density, stormwater routing piping density and land cover types (e.g. percent low density residential), suggest that these solutes are mainly sourced from weathering of land cover components such as pipes and roofing materials. Cluster 2 includes arsenic, copper, manganese, nitrate-nitrogen and nitrite-nitrogen, the mobility of which is closely associated with a change in redox conditions. The high correlation of concentrations of these solutes with antecedent rainfall conditions suggests that these solutes are likely sourced from stream channels. Cluster 3 is the largest of the clusters and includes the hydrologic tracer chloride and solutes that were highly correlated with rainfall frequency, duration and discharge magnitude, suggesting that as the amount of catchment wetting increases, these solutes are mobilized and flush out of our study sites. Finally, cluster 4 included nitrate-N, phosphate-p, mercury and *E. coli* and is indicative of solutes that are constantly sourced to the catchment either via atmospheric deposition or through land use practices. These solutes do not correlate with discharge, but do correlate with the amount of parks, open land and low density residential housing at our study sites, suggesting that a coupling of land use practices and atmospheric sources control their concentrations in runoff.

How does urban land use influence storm transport and delivery of metals to groundwater? All measured trace metal concentrations were below U.S. EPA standards (Carlson 2010). However, groundwaters located near commercial land use (well A-037), the western landfill site (Z-002) and agricultural plots (DW-001) had relatively high concentrations of Ni, Zn, Cu, and Fe indicating possible point source contamination. Although unrelated to any known point source of anthropogenic contamination, some groundwaters also showed high variability among wells. Measured groundwaters furthest from the Santa Cruz River along the eastern edge of the study site (well C-112), for example, had some of the highest concentrations of Ni (4.6 μg/L), Pb (>0.8 μg/L), As (2.5 μg/L) and Cu (>1.5 μg/L).

In contrast to our expectations of using chlorofluorocarbons (CFC) for groundwater dating, we found that CFC concentrations were anomalously high across the basin. Non-point source pollution in runoff and/or leaky infrastructure was identified as the most plausible source of this contamination (Carlson 2010). Interestingly, CFCs were strongly and positively correlated to nitrate (r^2=0.77) and mobile trace metal, nickel (r^2=0.71) suggesting that that solutes were sourced from a similar source. This statistical analysis was based on non-point source contamination, excluding effluent dominated wells, known to have high CFCs. Groundwater concentrations of Cu and Fe showed similar spatial variation to Ni, however the correlations

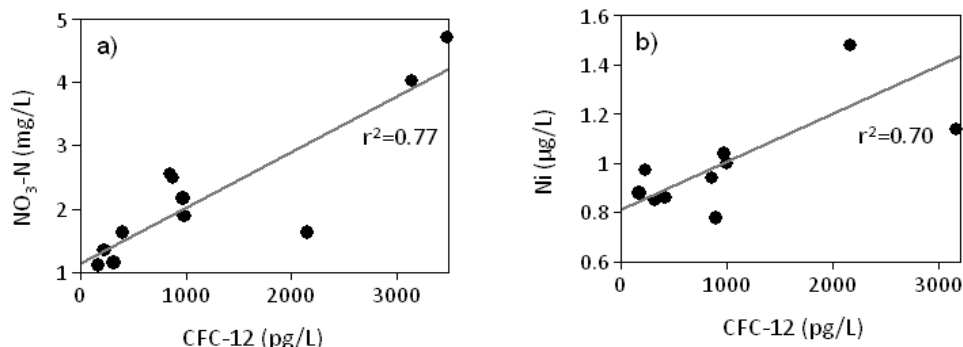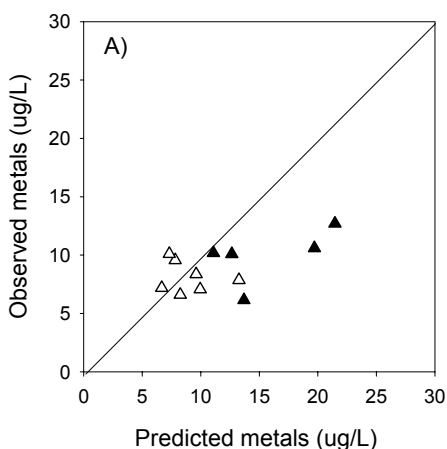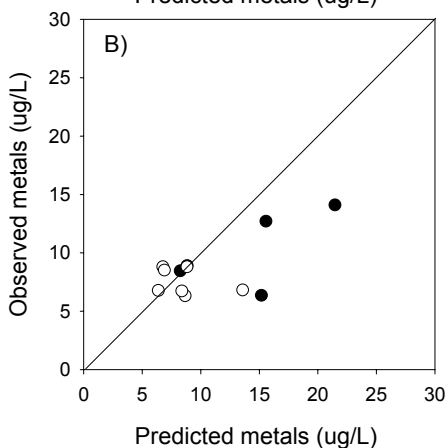were relatively weak for Ni and Fe (r^2=0.24, p=0.13) and Ni and Cu (r^2=0.18, p=0.19).

Figure 8. Groundwater concentration of a) NO3-N and b) Ni versus dissolved groundwater concentration of CFC-12.

What roles do soils in ephemeral washes play in retaining or removing these pollutants and controlling the rate at which pollutants are transported to regional groundwater? We measured upstream-downstream concentrations of solutes and metals to evaluate the role of soils in retaining or removing metals. We used chloride as an inert hydrologic tracer and compared observed to predicted downstream solute concentrations, based on the product of upstream solute concentrations and the ratio of the downstream to upstream Cl concentrations during flow recession. We found that observed concentrations of metals such as Cu and Zn in runoff were much lower than predicted concentrations in most of the grass-lined reaches compared to gravel-lined reaches suggesting that grass-lined channels are retaining more metals than gravel-lined reaches during transport (Figure 9). Little modification or retention of solutes and metals appears to be occurring in gravel lined washes. Our findings suggest that urban waterways that are lined with grass may provide ecosystem function services of removing metals and possibly other nutrients and pollutants, similar to those observed in constructed basins. Higher amounts of soil organic matter and cation exchange capacity in grass-lined systems are likely factors explaining the enhanced retention of metals and other constituents in these reaches. Additionally the finer texture of stream bed composition in the grass-lined reaches indicated increased surface area availability for adsorption of metals such as Cu and Zn.

Figure 9: Observed versus predicted metals in runoff

Training and Education: Funding provided matching support for training and research support through Peace Corp Fellowship work study program for 1 MS graduate student (Mark Carlson) and research funding for 1 PhD student student (Erika Gallo) and 1 undergraduate (Shane Clark). This research has been integrated into several courses by Lohse (UNVR 195a: Water Quality and the Environment, WSM 468/568:Wildland Water Quality [guest lecture]). Graduate student (Erika Gallo) attended several local and national conferences in December 2009, and PI's and graduate students are preparing manuscripts for peer-reviewed articles. Some of these findings have recently been published in *Southwest Hydrology* and resulted disseminated to the public, stakeholders at City of Tucson Transportation and Water Departments, and science community. In addition, a layman discussion of the impacts of urbanization and exurban development on water quality has been published in Lohse and Merelender (2009).

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Table 1 – Solute concentrations (Mean (SE), [minimum – maximum]) at our Tucson Basin study sites. S
superscript are not significanlty distinct from each other (p≤0.05)

Solute (units)	Solute Type	Low Density	Medium Density	High Density	Mixed
Cl (mg L^{-1})	Hydrologic Tracer	7.0 (3.7), [1.2 - 19.2]^b	4.0 (2.7), [1.4 - 12.5]^c	2.6 (0.1), [1.3 - 5.7]^c	3.4 (0.2), [1.
Ca (mg L^{-1})	Major Cation	14.5 (1.4), [8.0 - 38.8]^{ab}	14.6 (13.1), [7.7 - 30.4]^{ab}	13.8 (0.6), [10.6 - 17.8]^{ab}	12.7 (0.5), [7.
Mg (mg L^{-1})	Major Cation	1.4 (0.2), [0.6 - 3.9]^{ab}	1.6 (1.3), [0.8 - 3]^a	1.2 (0.1), [0.8 - 1.7]^{ab}	1.1 (<0.1), [(
K (mg L^{-1})	Major Cation	4.1 (0.5), [1.6 - 12.6]^a	4.7 (3.5), [2 - 12.1]^a	2.7 (0.1), [2 - 3.9]^a	3.7 (0.3), [1.
Na (mg L^{-1})	Major Cation	5.7 (0.9), [2.5 - 20.9]^b	4.0 (3.6), [2.3 - 8.3]^b	3.6 (0.2), [2.4 - 4.9]^b	3.7 (0.2), [2
Al (ug L^{-1})	Metal	441 (370), [192 - 1100]^{ab}	567 (421), [172 - 1739]^a	419 (69), [160 - 942]^{ab}	497 (39), [156
As (ug L^{-1})	Metal	1.4 (1.3), [0.2 - 2.9]^a	1.7 (1.6), [0.9 - 3.6]^a	1.9 (0.1), [1 - 2.7]^a	1.9 (0.2), [0.
Cd (ug L^{-1})	Metal	0.1 (0.1), [nd - 0.3]^{bc}	0.1 (0.1), [nd - 0.5]^{ab}	<0.1 (<0.1), [nd - 0.1]^c	<0.1 (<0.1), [
Co (ug L^{-1})	Metal	1.0 (0.7), [0.1 - 3.1]^{ab}	1.6 (1.2), [0.1 - 4.6]^a	0.9 (0.1), [0.6 - 1.4]^{ab}	0.9 (0.1), [0.
Cu (ug L^{-1})	Metal	20.3 (17.7), [3.7 - 61.3]^b	16.2 (14.1), [3.9 - 48.7]^{bc}	7 (0.6), [4.5 - 15.5]^c	9.9 (1.2), [3.
Fe (ug L^{-1})	Metal	692 (446), [193 - 7725]^a	571 (576), [305 - 1090]^a	504 (20), [374 - 633]^a	471 (28), [211
Pb (ug L^{-1})	Metal	1.2 (0.8), [0.1 - 3.4]^a	2.9 (1.2), [0.2 - 39.2]^a	0.7 (0.3), [0.2 - 5.2]^a	1.1 (0.1), [0.
Mn (ug L^{-1})	Metal	108 (18), [2 - 440]^a	106 (24), [3 - 423]^a	8 (3), [2 - 58]^b	25 (5), [2 -
Hg (ug L^{-1})	Metal	1.5 (0.9), [0.7 - 3.1]^a	1.4 (0.9), [0.3 - 3.6]^a	n.a.	0.9 (0.2), [0.
Ni (ug L^{-1})	Metal	5.6 (3.7), [1.1 - 16.7]^a	8.3 (5.8), [1.3 - 50.7]^a	6.9 (2.4), [1.6 - 41.6]^a	6.1 (0.9), [0.
V (ug L^{-1})	Metal	5.6 (3.9), [2.1 - 15.7]^{abc}	6.5 (6.1), [2.3 - 17.4]^{ab}	3.3 (0.1), [2.5 - 4.4]^c	4.5 (0.3), [2.2
Zn (ug L^{-1})	Metal	57.3 (25.6), [5.0 - 248.5]^b	51 (30.7), [6.3 - 370.1]^{bc}	9.4 (0.9), [3.8 - 19.1]^{bc}	14.5 (2.3), [4.