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Metal concentrations in urban riparian sediments along an urbanization gradient

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Abstract Urbanization impacts fluvial systems via a combination of changes in sediment chemistry and basin hydrology. While chemical changes in urban soils have been well characterized, similar surveys of riparian sediments in urbanized areas are rare. Metal concentrations were measured in sediments collected from riparian areas across the urbanization gradient in Baltimore, MD. Average metal concentrations are similar to those observed in other regional studies. Two important spatial patterns are evident in the data. First, calcium concentrations double across the urbanization gradient, regardless of changes in underlying geochemistry at the boundary between the Eastern US Piedmont and Coastal Plain physiographic provinces. Alkali-earth metal ratios indicate that the additional Ca is very pure and possibly arises from cement common to urban systems. Second, hot spots of trace metals typically associated with urban systems (e.g., Cu, Zn, and Pb) occur in areas that have been artificially filled to create additional real estate in high land value areas. Together, these data indicate that riparian sediments exhibit unexpected patterns of metal contamination. If these sediments are remobilized, during events such as droughts or floods, this contamination may perpetuate legacy impacts to ecosystem health from a history of fluvial contamination.

Keywords Baltimore · Calcium · Trace metal fate and transport · Urban fluvial systems

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Introduction

Urban riparian sediments are influenced by urban environmental processes ranging from metal contamination to changes in urban riparian geomorphology. In particular, urban centers are common areas of metal contamination from the processing, manufacture and use of metal based materials (Pouyat et al. 2007). In fluvial systems, these metals are predominantly transported while sorbed to sediments (Elder 1988). As these sediments are deposited in overbank areas during flooding, riparian sediments receive a substantial portion of metal loadings to fluvial systems. Moreover, once sediments are deposited in overbank systems, they can remain in floodplain areas for considerable lag periods, before remobilizing during processes like channel alluviation.

Therefore, while receiving waters are becoming relatively less metal contaminated in some urban areas (Mahler et al. 2006), upstream areas may retain high levels of contamination. Ultimately, the metal loadings from urban systems may impart riparian sediments with high concentrations of a wide variety of metals.

In addition to metal contamination, urban riparian zones can be adversely affected by the changes in storm flow hydrographs commonly associated with increased impervious surfaces (Walsh et al. 2005). In general, more efficient drainage via shorter flowpaths results in larger peak flows to stream channels. The increased sediment transport capacity resulting from changes in discharge tends to entrench and widen urban stream channels, particularly in the Eastern US Piedmont (Hammer 1972; Wolman 1967). These changes in riparian geomorphology can affect the stored contamination in contrasting ways. On one hand, as stream channels widen, near stream and bank sediments are mobilized and contribute to contamination loadings in receiving waters, impacting regulatory efforts. On the other hand, as stream channels are partially decoupled from the floodplain, thick overbank deposits can remain relatively stable (Jacobson and Coleman 1986), particularly when further stabilized via human engineering. Further, the lowered local water tables resulting from deep channels effectively drain the riparian areas and alter the redox environments throughout riparian soils (Groffman et al. 2002) potentially impacting the speciation and mobility of metals stored in these sediments. The combination of metal contaminated sediments and predictable physical changes make trace metal characterization of urban riparian sediments an area of considerable importance for urban risk management and ecosystem analysis.

While there is an established literature on trace metal contamination in mining impacted areas (e.g., Knox 1987; Marron 1992; Miller 1997) and upland urban soils (e.g., Mielke et al. 2000; Yesilonis et al. 2008), metal contamination in urban floodplain soils has not been characterized despite the intersection of metal inputs and geomorphic change, though some research focuses on trace metals in fresh deposits (e.g., Grosbois et al. 2006; Rogers et al. 2002). This data gap inhibits our understanding of metal fate and transport through urban ecosystems, a question of vital importance in characterizing and predicting the impact to and function of these ecosystems. In particular, many metal species are toxic, stressing ecosystem health and impacting biota in receiving waters. In addition, the proportion of trace metals shed during urban processes retained in floodplain deposits remains poorly quantified. And ultimately, are natural sediment characteristics or human inputs controlling the distribution of metals in urban riparian sediments? Similarly, the characterization of major cationic species in urban systems is limited, though emerging techniques allow insight into over-riding geochemical process (e.g., Bailey et al. 2003; Land et al. 2000). We have only a limited idea of how common urban building materials like calcium (cement) impact system function. Understanding this geochemistry is important to understanding metal cycling through urban ecosystems.

This study examines trace metal concentrations in riparian sediments from a transect of riparian soil cores across an urbanization gradient in Baltimore, MD (USA). The impact of urbanization on geophysical systems is becoming well documented, though geographic patterns of metal concentrations and the processes responsible for these distributions are not well characterized (Yesilonis et al. 2008). For example, though urban centers are associated with increases in trace metal concentrations in soils, particularly near roads, it is not clear how this contamination impacts riparian sediments further away from the road network. In addition, the flux in basic crustal materials increases in urban systems due to the construction and maintenance of the built environment. Inputs to the system arising from byproducts of these processes must impact urban chemistries, though it is unclear how, particularly in riparian sediments. This study analyzes riparian sediment samples collected across an urbanization gradient to characterize the increases in metal concentrations in riparian sediments associated with increased urbanization and understand catchment scale controls on these distributions.

Methods

Study area

The Gwynns Falls watershed (GFW) is located in western Baltimore city and county (Fig. 1) and is the

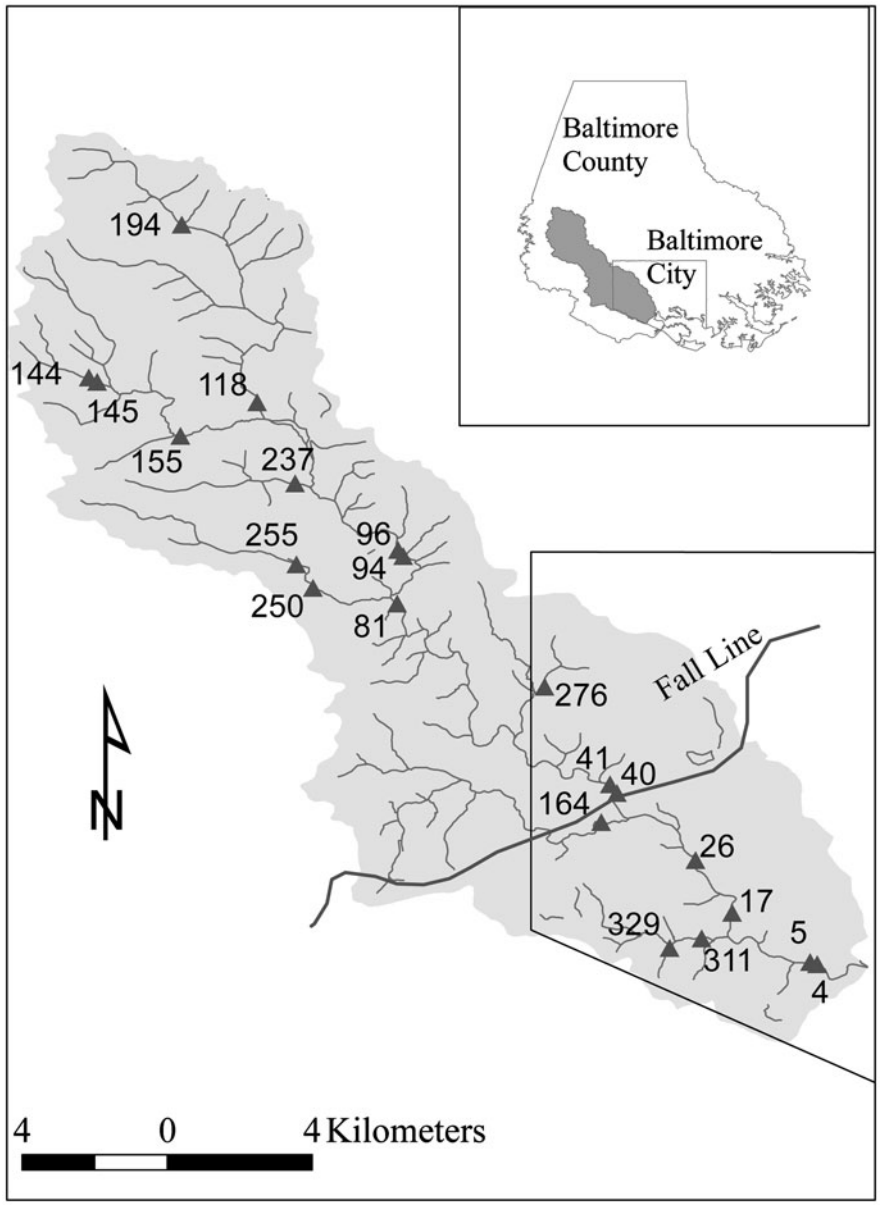

Fig. 1 Map showing location of GFW, core sampling locations, local political boundaries, and the border between the Piedmont and Coastal Plain

focus of the Baltimore ecosystem study, one of two urban long-term ecological research (LTER) sites. The GFW drains 17,100 ha of urban or rapidly suburbanizing areas. It straddles the Fall Line, the boundary between the Coastal Plain and Eastern Piedmont. In the upper portions of the watershed, the Eastern Piedmont is characterized by a variety of metamorphic bedrock including schist, with outcrops of serpentinite, marble, and gneiss. The lower, Coastal plain portions are dominated by sedimentary deposits lying atop metamorphic basement rock (Hunt 1967). The falls occurring along this physiographic boundary spurred much economic development, including extensive milling prior to 1900 (McGrain 1985).

The clearance of the watershed in the 1800s for charcoal production, wheat production, etc. (McGrain 1985) lead to a sequence of erosion and riparian sedimentation that continues to influence the GFW (Bain and Brush 2005; Groffman et al. 2002). The bulk of the rapid accumulation of overbank sediments, likely occurred in the Gwynns Falls before 1900 (Bain and Brush 2005). However, sediments

continue to accumulate in these Piedmont overbank areas, even in very recent periods (Allmendinger et al. 2007; Bain and Brush 2005). Therefore the sediments filling the Gwynns Falls valley have been in place for extended periods and additional sediments contaminated with contemporary urban signatures continue to be deposited by modern fluvial process.

Field sampling & chemical analysis

Sediments were collected from floodplain sediments in first through fourth order streams (drainage areas: 83–16,600 ha) in the GFW during the summer of 1999 (Fig. 1). Twenty-six soil cores (≥1 m deep, 2.54 cm diameter) were collected 10 m from the edge of the channel. Soil profiles were divided into horizons, sediments from each horizon were homogenized, sieved (2 mm), and dried at 105°C until a constant weight was obtained. This process precludes the precise dating of these riparian sediments and therefore limits our ability to understand temporal patterns of sediment contamination. All laboratory procedures were conducted with acid washed labware. Approximately 2 g of each horizon were subsampled and ashed at 475°C for 4 h. 10 ml 7.7 N HNO_3 were added to the ash and the solution brought almost to a boil. The digestions were filtered through #42 Whatman 2.5 μm filter paper and diluted to 50 ml with DI water. A subaliquot of diluted digest was further diluted ($\sim 100\times$) with 2% HNO_3 solution and metal concentrations for a suite of metals (see Table 1 for a complete list) were measured on a Perkin-Elmer ELAN 6,000 ICP-MS (Be, Ge, Tl internal standards). Digestion replicates were run for 93% of all samples, and samples were generally within 10% of each other, though elements with concentrations near the detection limit were less accurate due to the threshold nature of that limit. Sediment concentrations are reported as the measured value or, if applicable, the arithmetic mean of the replicates/duplicates. All elemental ratios are calculated using molar concentrations.

For this study, we are concentrating on sediments collected from the uppermost core horizons, generally 0–15 cm. While deeper horizons are important, this paper will concentrate on spatial variability in shallowest sediments as we expect that the uppermost sediments are the youngest. Therefore these sediments are most impacted by contemporary metal contamination associated with urban systems (Mahler et al. 2006) and are likely the driest and therefore the most oxic sediments in the floodplain. Further, shallow sediments are least impacted by the geochemical signatures imparted by local bedrock, allowing examination of basin trends in sediment chemistry by minimizing local source effects.

Results

Riparian sediment metal concentrations were similar to concentrations measured in upland soils collected throughout Baltimore city and in forest soils of an urban–rural transect in New York City (Table 1). In the Baltimore upland study, while a slightly smaller suite of trace metals were collected, the coefficient of variance for all elements ranged from 0.31 to 1.78, a range almost identical to the variance observed in the riparian sediments. The most obvious, albeit minor, differences are as follows: in upland soils, major elements tend to be depleted and trace elements enriched when compared to riparian sediments. This may result from the fact that riparian sediments are essentially eroded soil and erosion impacts the entire soil profile. It follows that these riparian sediments may be a mixture of base cation depleted, trace metal enriched surface soils and less weathered, less human influenced soils from depth. This sort of mixing could explain the relative enrichment of base cations and dilution of trace metals observed when comparing upland and riparian surface sediments. Differences may also arise from the wider variety of urban conditions sampled in the Baltimore upland study (e.g., more industrial, residential, commercial, and transportation sites) compared to the lower variety of urban conditions sampled in the forest soils under the same soil series in the New York study and this study.

Longitudinal trends

In the GFW, the longitudinal transect from the headwaters to the mouth roughly corresponds with an urbanization gradient. Linear regression of percent cover urban land as a function of distance from the Gwynns Falls mouth explains 50% of the variation in urban land cover in the contributing area (USGS

Table 1 Summary statistics for elemental concentrations measured in GFW riparian sediments

Element	Gwynns falls riparian sediments			Baltimore City Soils			New York Transect	Unit
	Median	Mean	CV	Median	Mean	CV	Mean	
Al	1.9	1.8	0.50	1.4	1.4	0.53	–	%
Ca	0.29	0.46	0.80	0.25	0.43	1.2	–	%
Cu	20	30	0.67	35	45	0.74	32	μg/g
Fe	2.2	2.0	0.37	2.2	2.3	0.49	–	%
Mg	0.39	0.39	0.43	0.22	0.27	0.78	–	%
Mn	450	440	0.54	420	470	0.72	340	μg/g
Pb	35	76	1.1	89	231	2.5	110	μg/g
Sr	13	15	0.30	–	–	–	–	μg/g
Zn	63	120	0.90	81	141	1.2	73	μg/g
As	1.5	1.6	0.52	–	–	–	–	μg/g
Ba	72	68	0.34	–	–	–	–	μg/g
Cd	54	170	0.76	89	106	0.68	–	ng/g
Co	11	12	0.52	12	15	0.78	7	μg/g
Cr	32	31	0.46	38	72	1.3	29	μg/g
Cs	790	890	0.68	–	–	–	–	ng/g
K	0.12	0.14	0.60	0.076	0.090	0.70	–	%
Li	12	13	0.78	–	–	–	–	μg/g
Mo	35	97	0.47	300	500	2.0	–	ng/g
Na	150	150	0.49	96	120	0.65	–	μg/g
Ni	26	40	0.78	18	27	1.3	22	μg/g
P	300	330	0.43	460	530	0.64	–	μg/g
Rb	13	15	0.63	–	–	–	–	μg/g
Ti	110	110	0.50	197	282	0.84	–	μg/g
U	1.1	0.92	0.58	–	–	–	–	μg/g
V	31	33	0.34	31	37	0.66	–	μg/g

Elements discussed in this paper have been promoted to the top. For elements with samples below detection limit (bdl), i.e., Cd and Mo, the reported coefficient of variance reflects only those samples with concentrations above the detection limit. Additional data are included for comparison. The "Baltimore City Soils" data is as reported in (Pouyat et al. 2007) and represents soils samples collected from throughout the city of Baltimore (i.e., it does not include the substantial rural/suburban area sampled in this study, nor is it confined to the Gwynns Falls watershed). The "New York Transect" data is from remnant forest patches and as reported for the "0–20 km Distance Class" in Pouyat and McDonnell (1991)

1999) despite the heterogeneity in land cover and variability of human activity. Moreover, given the history of land use change in the basin, where urbanization has grown toward the headwaters (Bain and Brush 2008), this is also a gradient of accumulative urban land use effects. We use distance from mouth as a proxy for urbanization throughout the remainder of this manuscript, which was found to be an acceptable approximation for the effects of the urban environment on soils in the Baltimore metropolitan region (Pouyat et al. 2008).

As we move downstream through the fluvial system, in general, we expect riparian sediments to be largely composed of a mixture of residual, weathered sediments derived from contributing areas. Therefore while the Piedmont bedrock in the upper basin may have distinct chemistries derived from bedrock like serpentinite (high Cr, Ni, and Mg; low Ca) or marble (high Ca and Mg; low Al), these distinctions will tend to be diminished through mixing with other contributing rock types. Despite this expected mixing, fundamental differences, like

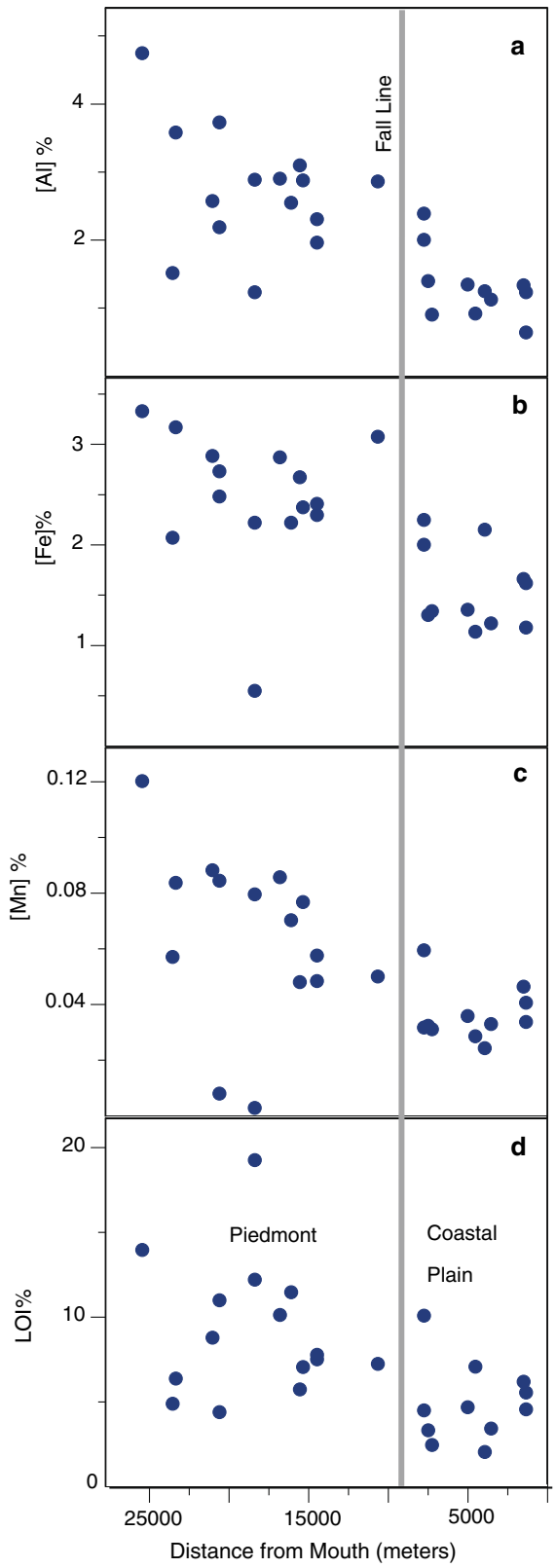

Fig. 2 Riparian surface sediment metal concentrations and content lost on ignition (LOI) along the Gwynns Falls longitudinal transect. The *thick grey* horizontal line indicates the location of the physiographic boundary. Average concentrations for each physiographic province differ significantly for all constituents shown (pooled-variance two-sample *t*-test, $p < 0.01$)

the transition from Piedmont metamorphic bedrock to Coastal Plain residual sediments (e.g., sands) is obvious in sediment chemistry (Fig. 2). Both LOI and mineral matrix element concentrations decrease in the Coastal Plain portion of the GFW (Fig. 2). Sandy Coastal Plain sediments result from millennia of continental weathering and tend to consist of residual minerals depleted of aluminum (Fig. 2a). Soils in these areas, arising from weathered, fluvially worked parent materials, begin depleted in base cations and low in clay content. This characteristic grain size is obvious in surface area dependent materials such as iron and manganese as there is a significant decrease in mean Fe and Mn concentration below the fall line (pooled-variance two-sample *t*-test, $p < 0.01$, Fig. 2b, c). In addition, LOI decreases at the change in physiography are significant (pooled-variance two-sample *t*-test, $p < 0.01$, Fig. 2d), likely due to a combination of sediment surface area and previous weathering of parent material resulting in nutrient depletion/lower fertility affecting organic inputs.

Together, these changes in sediment chemistry should provide a strong control on trace metal chemistry, as organic material, surface area, and Fe/Mn rinds all decrease in the Coastal Plain and all influence metal cation content sorbed to sediments. However, metal inputs from urban sources seem to be overwhelming geochemical controls.

Riparian sediment calcium concentrations

Calcium concentrations increased substantially (500–11,000 μg/g) in riparian sediments as surrounding areas become increasingly urbanized (Fig. 3a). Elevated calcium concentrations have been associated with urban environments in other studies (Lovett et al. 2000; Pouyat et al. 1995), however, the observed Ca concentrations would not be expected for riparian systems, as we expect regular Ca flushing in temperate climates (Burns et al. 1998). Moreover, nitric acid extractions do not breakdown silicate

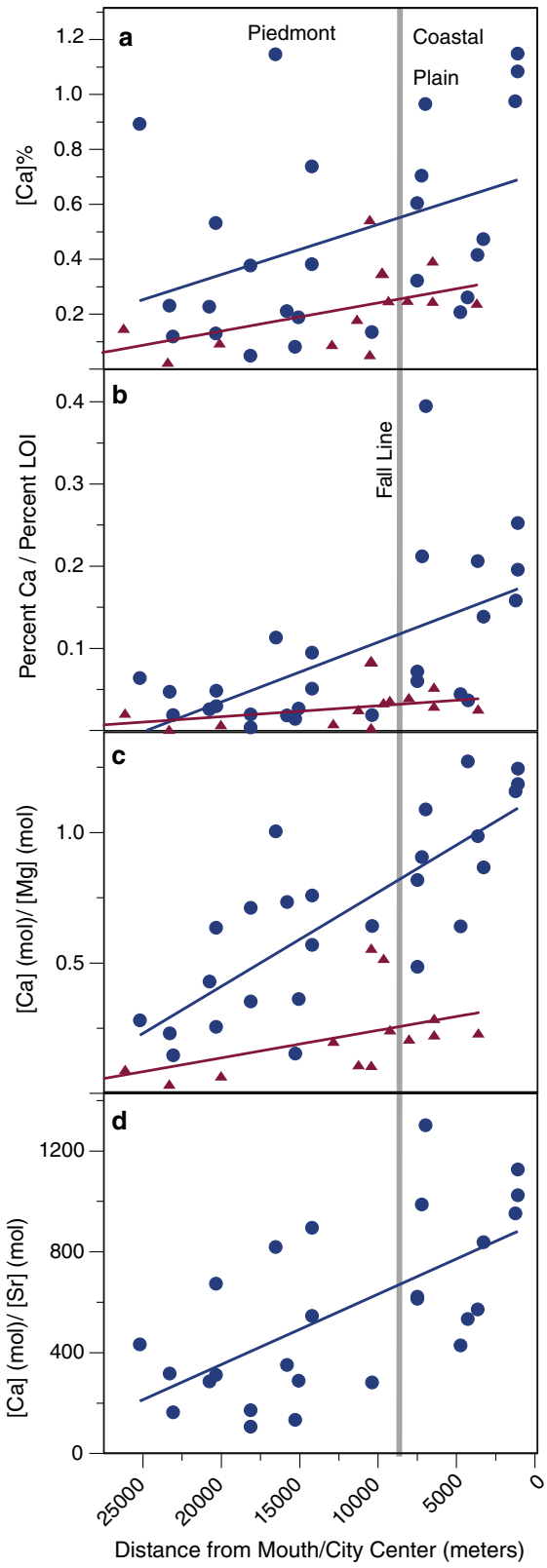

Fig. 3 Plots showing the concentration of Ca along the riparian and forested patch transects through the Gwynns Falls/Baltimore City and County. Results from this study are shown as *circles*. *Triangles* represent data from a transect of soils under forested patches, with distance calculated from the city center as reported here (Pouyat et al. 2008). **a** shows raw Ca concentrations, and the other panels show Ca normalized with material lost on ignition (**b**), magnesium (**c**), and strontium (**d**). Strontium concentrations were not measured in the upland forest plot transect. Linear fits of the data series as a function of distance are as follows: Ca **a** This study ($r^2 = 0.15$, $p < 0.05$), forested patches ($r^2 = 0.32$, $p < 0.05$). Ca/LOI **b** This study ($r^2 = 0.35$, $p < 0.005$), forested patches ($r^2 = 0.21$, $p < 0.05$). Ca/Mg. **c** This study ($r^2 = 0.63$, $p < 0.0001$), forested patches ($r^2 = 0.29$, $p < 0.05$). Ca/Sr **d** This study ($r^2 = 0.41$, $p < 0.0005$)

matrices, so we are not measuring Ca derived from the mineral structure. Calcium concentration trends do not follow geochemical controls at the physiographic boundary, and therefore likely are not a function of biological activity [e.g., Ca storage in soil organics (Fig. 3b) or Ca/Mg ratios set by biotic activity (Fig. 3c)]. Further, Ca concentration does not seem to result from changes in weathering rates (e.g., due to increased acidification), as Ca concentration trends are not diminished when ratioed with strontium (Sr) concentrations (Fig. 3d) which should be present in mineral structures at concentrations proportional to Ca and have limited urban inputs. This evidence indicates a consistent and substantial input of relatively pure Ca to riparian sediments associated with urban areas.

Urban suite (Cu, Pb, Zn) concentration patterns

Metals associated with urban centers (e.g., lead, copper, and zinc) also increase in concentration with urbanization and do not follow concentration trends expected based on changes in sediment characteristics at the fall line (Fig. 4a–c). While this is less surprising for these metals, as they are typically associated with urban biogeochemistry, they are more strongly tied to sediment surface area and organic and Fe/Mn oxide content than calcium. Yet, increases in Pb, Zn, and Cu concentrations are greater than increases in Ca concentrations. At the fall line, once normalized with aluminum and plotted on a log scale, the change in lead concentrations is striking (Fig. 4a) as an inflection occurs near or at the fall line opposite from what would be predicted from sediment geochemistry. This pattern is consistent with patterns in

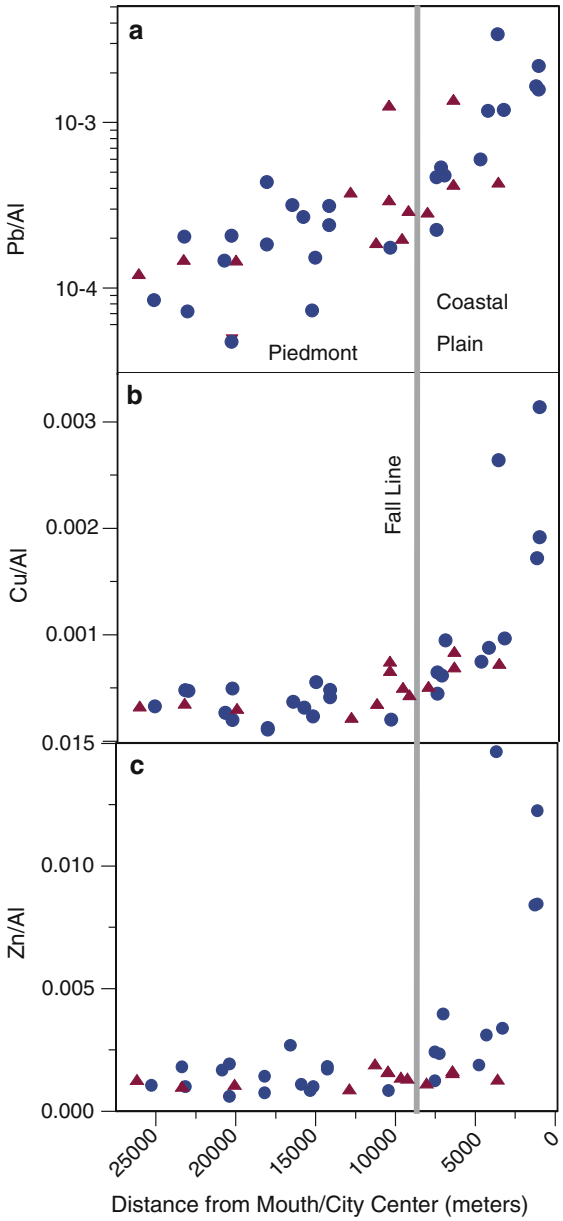

Fig. 4 Concentrations of urban suite trace metals along Gwynns Falls transect. **a–c** Shows lead, copper, and zinc (respectively) concentrations normalized with aluminum concentration (a proxy for clay concentration and therefore surface area). Results from this study are shown as *circles*. *Triangles* represent data from a transect of soils under forested patches, with distance calculated from the city center as reported here (Pouyat et al. 2008)

aluminum normalized zinc and copper concentrations (Fig. 4b, c). Despite decreases in surface area and organic material in the more urban areas, these riparian sediments are enriched with trace metals and these sediments may be stored for considerable periods in urban systems.

Discussion

Processes driving riparian sediment chemistry patterns

The spatial trends in Ca concentration are surprising as Ca is relatively mobile in soil matrices. The observed accumulation of calcium implies a steady and significant input of calcium to the system, particularly in the more urban and low sediment surface area Coastal Plain. This increase is in Ca concentration outpaces similar increases observed in a transect of soil samples (Pouyat et al. 2008) from forested upland plots (triangles on Fig. 3). Several potential sources may explain the observed patterns. First, urban precipitation enriched with dust derived from concrete, wallboard, etc., may supply significant levels of Ca to urban systems (Kuang et al. 2004; Nath et al. 2007). However, existing work suggests that Ca:Mg ratios in wet deposition/throughfall along a rural to urban transect do not exhibit any strong trend (Lovett et al. 2000). To ensure this is not a deposition effect local to Baltimore, long term precipitation data from the National Atmospheric Deposition Program sites closest to the GFW [sites MD03, MD13, MD99 (National Atmospheric Deposition Program (NRSP-3) 2008)] were examined and the event-weighted Ca:Mg ratios were 2.5. While this value could begin to explain values observed in upland plots (triangles, Fig. 3c) this ratio is only moderately higher than values observed in the sediment near the mouth (circles, Fig. 3c), requiring substantial atmospheric deposition to clearly cause the increases in Ca:Mg. And while Sr concentrations are not reported by the NADP, we expect that Ca:Sr ratios should be set by oceanic compositions (Ca:Sr $\sim$ 112) which is below ratios observed in the sediment. However, these NADP locations are relatively distant from Baltimore and urbanization may increase atmospheric deposition of Ca above that observed in these sites. To check the urban influence, we compared Ca and Mg chemistry in pairs of national atmospheric deposition program sites, where each pair contained a relatively urban area and the other an upwind, relatively rural areas (Table 2).

Table 2 Averaged annual event weighted precipitation chemistry from six pairs of National Atmospheric Deposition Program (NADP) sites

State	Urban NADP	Rural NADP	Urban Ca:Mg	Rural Ca:Mg
California	CA42	CA98	1.24	2.53
Illinois	IL19	IL18	2.87	3.45
Massachusetts	MA13	MA08	1.08	1.72
Minnesota	MN01	MN23	4.53	3.93
North Carolina	NC41	NC34	1.40	2.01
New York	NY99	NY68	1.61	2.46

In each pair is an "urban" site and a rural site in the same state, with the rural sites located distant and upwind from the urban system

There are actually relative increases in Mg concentrations in the urban member of every pair except for that in Minnesota, affirming that wet atmospheric deposition is not a promising explanation for the observed Ca concentration patterns in riparian sediments.

Increased Ca concentrations may also result from releases of weathered and exchangeable Ca due to soil acidification. However, soil acidification cannot explain the observed data without a complex combination of processes. The soil acidification must be more intense in the upper basin, as Ca would also be removed from the soil column near the mouth during acidification. In addition, if Ca is mobilized upstream, there are few processes that move mobile base cations from surface waters to riparian sediments. Moreover, other elements in the acidified soils should be mobilized proportionally, particularly chemically similar elements. Therefore, when Ca concentrations are normalized with Sr or Mg concentrations, the Ca:Sr or Ca:Mg ratio should reflect mineral sources. For example, in the GFW, the least weathering resistant bedrock, the Cockeysville Marble has a Ca:Mg ratio of roughly 0.98 (Choquette 1960), which is within the observed Ca:Mg range and therefore not likely an important end member. Further, in GFW riparian sediments, these normalizations do not substantially diminish the observed trend in Ca concentrations, suggesting that increased Ca concentrations are not explained with increases in soil acidification.

The best explanation for high concentrations of Ca observed in the urban lower watershed seems to be the direct shedding of human materials that have been imported to the system. Most cement has a Ca:Mg ratio larger than 10, with many cements well above 25 (Goguel and St John 1993). While Ca:Sr ratios in concrete vary widely, molar Ca:Sr of up to 4,000 have been measured (Goguel and St John 1993; Graham et al. 2000), making cement the most likely high Ca end member. Wallboard (gypsum) is another potential Ca source in urban centers (Oktay et al. 2003). However, literature Ca:Mg ratios in wallboard are not consistently high [11.5 (Carr and Munn 2001) vs. 1.86 (Marvin 2000)] and Ca:Sr ratios seem to fall in the 570–650 range (Oktay et al. 2003), well below observed values in the urban portions of the watershed. The low end member influencing the upper watershed is likely the schist bedrock (Crowley 1977). The ratio of average calcium and magnesium concentrations in similar bedrock (i.e., Wissahickon Schists near Philadelphia, PA) is less than one (Weiss 1949). While measurement of Sr concentrations in local rocks are limited, most rocks and particularly shales in the upper watershed have Ca:Sr ratios below 500 (Hanan and Sinha 1989). Therefore observed patterns in Ca:Sr appear to result from a combination of bedrock derived compositions with increasing Ca additions or accumulations along this transect. Together, this evidence suggests that Ca concentrations along the GFW longitudinal transect are low in the upper watershed due to bedrock geochemistry and are subsequently enriched by human input from building materials, particularly cement, at the lower end of the watershed.

It is difficult to predict the impacts of this Ca enrichment to the local ecosystem as the literature on the ecosystem effects of excess Ca is limited. We know Ca plays an important role in the physiology of trees and therefore terrestrial ecosystems (McLaughlin and Wimmer 1999). The advent of Ca limitation via human accelerated weathering impacts forest health (Bailey et al. 2005). However, natural analogs for systems with excess Ca (e.g., carbonate bedrock dominated systems) have been disproportionately disturbed for agriculture (Helms 2000). This may explain the lack of literature on the impacts of excess Ca. For example, an excess of Ca can allow relatively less efficient Ca assimilators a competitive advantage. This may play a role in deleterious processes, including exacerbating invasions by exotic species of fluvial systems (Whittier et al. 2008). These results

suggest urban systems are an area of opportunity for examining the effects of excess Ca to terrestrial systems.

The role of fill in urban sediment chemistry

Trace metal concentrations also increased going downstream despite the changes in sediment characteristics associated with physiography. However, while Ca increases steadily, four locations have trace metal concentrations two to three times more contaminated than any of the other sites. Further, these concentrations exceed those measured in soils along a similar upland forested soil transect [triangles, Fig. 3. Data from (Pouyat et al. 2008)]. Upon further examination, these metal concentrations seem to be closely related to human filled areas of "made" land. Three of the sites fall in areas mapped as "fill" in bedrock geology mapping (Crowley and Reinhardt 1979). The other site (311) is on a small stream far from estuarine areas (which are typically filled areas) and therefore not necessarily subject to this contamination. Yet, examination of historical photographs (1938) indicates this stream was historically buried under an athletic field and has been daylighted since 1938 (Fig. 5, see marked stars). While the number of cases remains small, the chemistry indicated fill in a site distant from estuarine areas without presumption, reinforcing the anomalous concentrations possible in fill and implies that managers and planners be aware that areas made up of fill could be significant sources of trace metals.

The high concentration in fill suggests these sediments may have received significant loads of contamination at the time of fill, as other areas with similar levels of urbanization in adjacent areas have much lower concentrations of trace metals. The potential association between trace metal contamination and fill is an important consideration for urban environmental managers. While the relationship between transportation corridors and metal contamination has been demonstrated (e.g., Mahler et al. 2006; Mielke et al. 2000), the association of trace metal contamination and made land (often located in or near sensitive receiving waters), is not typically as well established. Further, recent findings on the geochemical role of rubble in urban soil processes (Mekiffer et al. 2010; Nehls et al. 2010), demonstrate that these pools, whether contaminated or not, provide a relatively available source of nutrients (e.g., Ca) and contaminants (e.g., sulfate) to the system.

The patterns of these redox sensitive and surface bound metals present particular challenges to urban managers. Redox status can control metal speciation (Bostick et al. 2001) and therefore metal bio-availability. Further, if changes in dissolved carbon dynamics due to redox status (e.g., Miller et al. 2005) affect metal mobility, riparian sediments in flashy urban systems may be particularly prone to mobilization. Therefore, in the case of the Gwynns Falls, not only is metal contamination associated with low surface area sediments, it also is concentrated in redox environments that potentially enhance mobility. While the catchment scale consequences of this soil wetting/drying may be accentuated by urbanization

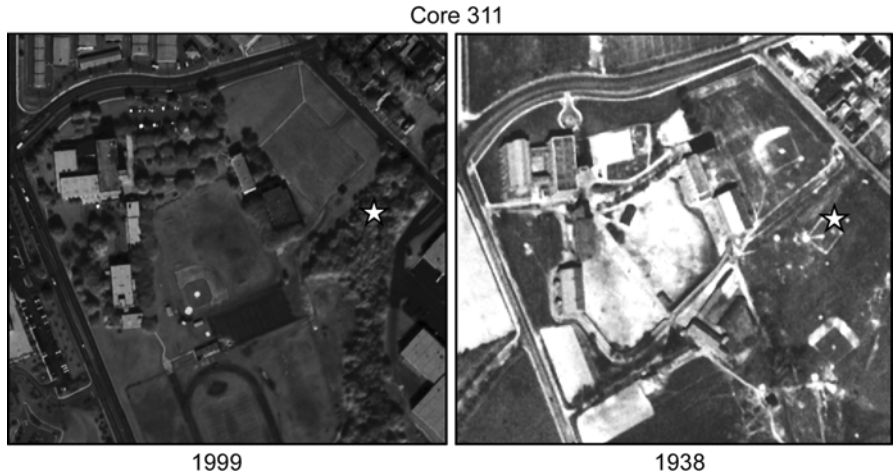

Fig. 5 Aerial photos showing local land uses around transect 311. Note that while contemporary imagery shows a forested riparian zone, this core was taken from an area that was athletic fields as late as 1938, which can explain some of the observed chemistry

(Kaushal et al. 2008), the potential increase of trace metal flux could be substantially larger than that observed for macronutrient fluxes, as these materials accumulate in reducing environments while nutrients can be assimilated or transformed to gaseous phases. Together, these patterns create the possibility for significant legacy inputs of metal contamination to urban surface waters, requiring sophisticated characterization and management, with particular attention to coastal plain and filled areas.

Conclusions

The results of this study indicate an important juxtaposition of three important geochemical and urban processes with the potential for synergistic and negative impacts on water quality. This potential is particularly strong for fluvial systems in urban centers that straddle important geologic changes, such as the Fall Line along the Eastern Seaboard (USA). First, streams impacted by urban land use (Walsh et al. 2005), continue to deposit sediment, potentially contaminated by urban processes, on top of legacy overbank deposits. Second, the unique geochemical environment, e.g., oxic, dry, of urban riparian sediments (Groffman et al. 2002) combined with floodplain processes, e.g., hydrologic flushing (Burns 2005), provide the potential for increased flushing of trace materials or base cations from these fluvial systems. Third, fall line industrial centers along the Eastern Seaboard are centered just below or on the physiographic boundary, similar to the arrangement in Baltimore. As many of these cities have a long history of industrial activity, they also have a long history of primitive sanitation practices. This early lack of sanitation has lead to a significant loading and variety of contamination to and in these areas (Mason et al. 2004; Sinex and Helz 1981, 1982), areas with characteristically low surface area sediments (sand). Additionally, the process of creating land in formerly estuarine areas may have introduced contaminated sediments directly into receiving waters. These riparian and estuarine deposits are poorly characterized and a potentially important source of metals to urban surface waters that deserve additional scrutiny.

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