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Gaining insights on urban critical zone processes via intensive sampling of small watersheds

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Critical zones in urban areas are highly disrupted by the addition of quickly weatherable materials such as deicing salt and concrete, by partitioning water into quick flow paths due to impervious surface cover, and by physical disturbance due to construction and infrastructure. These disruptions are apparent in the eastern United States (US) where forested streams are dilute due to a deep critical zone developed in a tectonically quiescent setting. In contrast, urban streams in the same setting have much higher concentrations and altered mixtures of dissolved constituents. To gain insight on the generation and transport of dissolved constituents in urban critical zones, stream geochemistry was intensively sampled in one exurban and two urban small watersheds in the US Mid-Atlantic near Baltimore, Maryland along with a forested watershed. In (ex)urban watersheds, inputs from deicing salt result in elevated chloride and sodium concentrations during both winter and non-winter seasons. Differing winter and non-winter ratios of chloride versus sodium, calcium, and magnesium along with stoichiometric relationships suggest that cation exchange driven by sodium plays a large role in cation behavior in (ex)urban watersheds. Sodium shows moderate dilution at higher discharge in non-winter and enrichment during the winter, while calcium and magnesium consistently exhibit moderate to strong dilution. Bicarbonate concentrations are several times higher in the urban streams than the forested and exurban streams. Bicarbonate is strongly diluted in urban watersheds during stormflow but shows little variation with discharge in the exurban watershed. Bicarbonate is a product of carbonate and/or silicate weathering in forested watersheds and may be a product, at least in part, of concrete weathering in urban watersheds. Dissolved silica concentrations are relatively similar across watersheds and exhibit the most consistent dilution behavior during storm events across the (ex)urban watersheds, suggesting that urbanization minimally affects weathering of silicate minerals. Bicarbonate and dissolved silica are strongly correlated in the urban watersheds, moderately correlated in the forested watershed, but not correlated in the exurban watershed. The disruptions that occur in urban watersheds, including frequent addition of material, likely keep urban critical zones in a state of disequilibrium.