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Making 'Chemical Cocktails' – Evolution of Urban Geochemical Processes across the Periodic Table of Elements

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Abstract

Urbanization contributes to the formation of novel elemental combinations and signatures in terrestrial and aquatic watersheds, also known as 'chemical cocktails.' The composition of chemical cocktails evolves across space and time due to: (1) elevated concentrations from anthropogenic sources, (2) accelerated weathering and corrosion of the built environment, (3) increased drainage density and intensification of urban water conveyance systems, and (4) enhanced rates of geochemical transformations due to changes in temperature, ionic strength, pH, and redox potentials. Characterizing chemical cocktails and underlying geochemical processes is necessary for: (1) tracking pollution sources using complex chemical mixtures instead of

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individual elements or compounds; (2) developing new strategies for co-managing groups of contaminants; (3) identifying proxies for predicting transport of chemical mixtures using continuous sensor data; and (4) determining whether interactive effects of chemical cocktails produce ecosystem-scale impacts greater than the sum of individual chemical stressors. First, we discuss some unique urban geochemical processes which form chemical cocktails, such as urban soil formation, human-accelerated weathering, urban acidification-alkalinization, and freshwater salinization syndrome. Second, we review and synthesize global patterns in concentrations of major ions, carbon and nutrients, and trace elements in urban streams across different world regions and make comparisons with reference conditions. In addition to our global analysis, we highlight examples from some watersheds in the Baltimore-Washington DC region, which show increased transport of major ions, trace metals, and nutrients across streams draining a well-defined land-use gradient. Urbanization increased the concentrations of multiple major and trace elements in streams draining human-dominated watersheds compared to reference conditions. Chemical cocktails of major and trace elements were formed over diurnal cycles coinciding with changes in streamflow, dissolved oxygen, pH, and other variables measured by high-frequency sensors. Some chemical cocktails of major and trace elements were also significantly related to specific conductance ($p<0.05$), which can be measured by sensors. Concentrations of major and trace elements increased, peaked, or decreased longitudinally along streams as watershed urbanization increased, which is consistent with distinct shifts in chemical mixtures upstream and downstream of other major cities in the world. Our global analysis of urban streams shows that concentrations of multiple elements along the Periodic Table significantly increase when compared with reference conditions. Furthermore, similar biogeochemical patterns and processes can be grouped among distinct mixtures of elements of major ions, dissolved organic matter, nutrients, and trace elements as chemical cocktails. Chemical cocktails form in urban waters over diurnal cycles, decades, and throughout drainage basins. We conclude our global review and synthesis by proposing strategies for monitoring and managing chemical cocktails using source control, ecosystem restoration, and green infrastructure. We discuss future research directions applying the watershed chemical cocktail approach to diagnose and manage environmental problems. Ultimately, a chemical cocktail approach targeting sources, transport, and transformations of different and distinct elemental combinations is necessary to more holistically monitor and manage the emerging impacts of chemical mixtures in the world’s fresh waters.

Keywords

urban evolution; urban karst; urban watershed continuum; freshwater salinization syndrome; human-accelerated weathering

Introduction

Most of the world’s human population lives in urban areas and relies on the structure, function, and services provided by urban ecosystems for survival (Grimm et al. 2008). The built environment and its structure, ecosystem functions, and ecosystem services evolve over time based on human selective pressures and adaptations (Kaushal et al. 2014; Kaushal et al. 2015). Although less considered, urbanization can modify abundances, distributions, and ratios of elements in terrestrial and aquatic environments (Kaye et al. 2006; Lyons and

Harmon 2012; Chambers et al. 2016; Kaushal et al. 2019). We recently proposed that atmospheric deposition, land use, geology, and climate enhance the formation and transport of novel combinations or mixtures of elements in watersheds, hereafter referred to as 'chemical cocktails' (Kaushal et al. 2018a, 2018b). Chemical cocktails of elements are formed when there is increased probability of biogeochemical interactions, converging transport pathways, and/or novel anthropogenic sources (Kaushal et al. 2018a, 2018b). Watershed chemical cocktails provide distinct signatures of shifting human activities associated with environmental degradation and ecosystem restoration during Earth's latest geological epoch, the Anthropocene. Distinct and diverse watershed chemical cocktails originate from sources such as sewage, automobiles, weathering of impervious surfaces, synthetic chemicals, and widespread proliferation of mineral resources used in human settlements (Bernhardt, Rosi, and Gessner 2017; Long et al. 2017; Kaushal, Gold, et al. 2018; Kaushal, Likens, et al. 2018; Blaszczak et al. 2019). An understanding of the formation of chemical cocktails in watersheds over time and space is important because it can facilitate approaches to co-manage groups of pollutants with similar fate and transport. A watershed chemical cocktail approach can also enable identification and development of continuous sensor proxies for predicting the simultaneous behavior of multiple urban contaminants and chemical mixtures over time. In addition, a watershed chemical cocktail approach allows characterization of emergent effects of chemical mixtures and quantification of ecosystem impacts beyond a simple sum of effects of individual chemicals.

In this paper, we explore how chemical cocktails are made in urban watersheds over space and time. We also illustrate some novel processes contributing to geochemical and biogeochemical patterns in urban infrastructure, soils, and waters. First, we explore novel processes in urban watersheds that influence elemental cycles including urban soil formation, human-accelerated weathering, urban acidification-alkalinization processes, and freshwater salinization syndrome. Second, we review origins and concentrations of distinct chemical cocktails of major ions, carbon, nutrients, and trace metals in different urban waters. We make comparisons between the chemistry of urban waters with minimally disturbed reference watersheds where possible. Thirdly, we conclude with some management implications of chemical cocktails for urban water quality. The watershed chemical cocktail approach allows us to identify and characterize how distinct and diverse chemical mixtures evolve in urban ecosystems (Figure 1).

Part 1. Examples of Urban Processes that Make Chemical Cocktails

Urban Soil Formation: Novel Parent Materials Create Diverse Chemical Cocktails of Major and Trace Elements

Soils remove, transform, and release elements into the hydrosphere and play a major role in influencing many elemental cycles to form chemical cocktails in Anthropocene waters (Lehmann and Stahr 2007). Human activities changing the built environment lead to an "urban evolution" of the structure, function, and ecosystem services of urban areas over time (Kaushal, McDowell, and Wollheim 2014; Kaushal et al. 2015; Hale 2016; Parr et al. 2015; McPhillips and Matsler 2018). It is evident that urbanization influences every state factor of soil formation as humans contaminate, deplete, erode, and move soils around landscapes,

which influences the diversity, distribution, and abundance of elements. Urban evolution creates novel parent materials from human-made materials with distinct elemental combinations from which soils are formed. Human-made materials from which soils form, also known as artifacts or technogenic materials, include bricks, crushed stone, concrete, plastic, mine waste, industrial waste, and metal objects (Effland and Pouyat 1997) (Figure 2). The soil classification 'technosol' defines a soil containing more than 20% artifacts. It is common for urban soils to contain many artifacts. Technogenic materials in urban soils are spatially heterogeneous due to excavation, transport and deposition (Huot et al. 2015). Urban soils are commonly alkaline due to construction materials but can be acidic due to coal and sulfuric acids (Lehmann and Stahr 2007). Urban soils can be high in organic matter and nutrients due to ongoing organic additions, including refractory combustion byproducts and residues; other areas of urban soils can be very low in organic matter and available nutrients, particularly when they originated as clean fill and have been swept or otherwise cleaned of organic matter over time (Lehmann and Stahr 2007). Artifacts can lead to the formation of soil characteristics not native to the climate in which they form. For example, the accumulation of gypsum ($CaSO_4$-H_2O) in lower soil layers, which is usually seen in dry climates, can occur in temperate humid climates due to the presence of gypsum construction materials such as drywall (Zikeli et al. 2005). Urban soils are also characterized by missing B horizons, which is the result of grading, excavation, and filling that can mix soil layers (destroying pedogenic features) or bury them far enough below other mixed materials to substantially influence the vertical distribution of chemical mixtures in these soils, altering their function, morphology, and classification (Herrmann et al. 2018). Leaching of soluble compounds and oxidation of sulfides leads to formation of secondary minerals such as sulfates and Fe (hydr)oxides, which occur in both technogenic materials and natural materials, though rapid initial weathering may occur as some anthropogenic materials are not at equilibrium in the environment in which we place them (Huot et al. 2015). Minerals of unnatural composition and minerals not often found in natural soils can be found in soils created from technogenic materials. Calcite and gypsum are added by concrete. Some industries made clinker, which is common in urban soils and consists of a few minerals including alite, belite, tricalcium aluminate, and brownmillerite. There are many novel minerals and chemical mixtures caused by human activity that have never been found naturally occurring in Earth's crust (Hazen et al. 2017). Urbanization has accelerated the time in which soil forming processes occur, and as a result urban soils are often young due to frequent anthropedoturbation by construction and other human activities (*e.g.*, mixing brings deeper soil horizons in contact with surficial processes) (Effland and Pouyat 1997). Furthermore, legacy artifacts found in urban soils such as underground storage tanks of petrochemicals and hazardous materials in old construction materials such as asbestos tiles (DeKimpe and Morel 2000) can also contribute to formation of unique elemental combinations during urban soil formation. By adding technogenic materials to urban ecosystems, humans accelerate erosion, chemical weathering and formation of distinct chemical cocktails in urban soils. Removal, transportation, and deposition of technogenic materials can break up soils, breaking apart organizational units like clods and fragmenting solids like bedrock and rock fragments. This can result in increased surface area of the material and exposes reactive surfaces that have yet to be weathered to water, oxygen, and other solutes. All of these processes could result in increased weathering rates similar to

some mining sites as analogs (weathering is discussed in more detail below) (Daniels et al. 2016).

Weathering of the 'Urban Karst' Makes Diverse Chemical Cocktails of Major Elements

Chemical weathering from acid precipitation is often distinct in urban areas due to their unique, carbonate-rich lithologies, sometimes referred to as "urban karst." Urban karst refers to the built environment of buildings, bridges, engineered river banks, and impervious surfaces which comprise upward of 75 to 85% of the land surface in industrial, commercial, and densely populated residential environments (Chester Jr and Gibbons 1996; C. Wu and Murray 2003). Accelerated chemical weathering rates occur because many of the minerals found in urban karst are thermodynamically unstable at the temperatures and pressures present at the Earth's surface (Camuffo 2015). Carbonate minerals, such as calcite and dolomite, are the most soluble minerals commonly found in the built environment. Feldspars, clay minerals, and quartz are also vulnerable to acid rain, though with decreasing solubilities (Camuffo 2015). In general, the solubility of a mineral increases as calcium and magnesium content increases and silica content decreases (Camuffo 2015). Cations (such as Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) are released when acidic compounds react with minerals commonly found in building materials such as calcite, dolomite, feldspar biotite and chlorite (Wright et al. 2011; Camuffo 2015; Kaushal et al. 2017) (Figure 3). Calcareous concrete pipes weather at a significant rate, first through a reaction between carbon dioxide and concrete hydrates like calcium hydroxide ($Ca(OH)_2$ or portlandite) and calcium silicate hydrates (CSH) (Davies et al. 2010), producing calcium carbonate ($CaCO_3$) and water (Figure 3). Low pH water from acid precipitation reacts with these alkaline hydration products of cement creating calcium salts and distinct and diverse chemical cocktails rich in base cations and carbonates (Figure 3).

Urban Acidification-Alkalinization Processes Make Iron and Sulfur-Rich Chemical Cocktails

Disturbance of hypersulfidic soil materials during construction contributes to sulfuricization, the process by which sulfidic materials oxidize. Sulfuric acid weathers existing minerals and new mineral phases are formed (Fanning et al. 2017), which can produce acidic soils with pH values less than 2.0–3.5. In response, local waters can become rich in chemical cocktails enriched in dissolved iron and iron oxide flocculate, and the soil surface can become crusted with hydrated sulfate minerals including halotrychite and copiapite group minerals. These elevated levels of iron, aluminum, and acidity also lead to iron and sulfur-rich chemical cocktails (Daniels and Orndorff 2003; Fanning et al. 2004). Sulfuricization can also occur when acid sulfate soils are used as a source for imported fill materials (*e.g.*, to "cap" landfills). In addition to direct disturbance of soil materials, sulfuricization can also be triggered in urban areas by manipulation of the water table. Groundwater levels are altered by drainage, either by ditches, pipes, or uncontrolled incision of urban headwater streams, contributing to urban hydrologic drought and oxic conditions (Groffman et al. 2003). While sulfuricization can cause a decrease in pH and the formation of acidic soils, most urban streams still have a higher pH and are alkaline due to weathering of urban karst and high acid neutralization capacity (Ometo et al. 2000; Zampella 1994). For example, cement has a high acid neutralizing capacity of 955 mg $CaCO_3$ eq./g (Sephton and Webb 2017), which

neutralizes sulfuric acid produced by sulfuricization and makes many urban waters alkaline (Lehmann and Stahr 2007) (Figure 3). Because both limestone and concrete are common building materials (coupled with alkaline soils present in urban environments), many acidic waters originating in acid sulfate soils will eventually still become alkaline and result in higher pH (Kaushal et al. 2017).

Sulfuricization is not generally detectable in urban streams due to the vast amount of acid neutralization that occurs. However, sulfuricization still contributes to the localized weathering of “urban karst” and subsurface infrastructure, such as sewer pipes (Figure 3). A major problem in sewer systems is the corrosion of the metal and concrete pipes (Boon 1995; Mori et al. 1991; Haaning Nielsen et al. 2005; Nielsen and Hvitved-Jacobsen 1988; Pomeroy and Bowlus 1946). The primary causes of corrosion are due to the production of hydrogen sulfide (H_2S) and the oxidation of H_2S to form sulfuric acid (Pomeroy and Bowlus 1946), wherein both processes may be microbially mediated. The production of H_2S is initiated by the reduction of sulfate in wastewater when sulfate interacts with microbes living in biofilms on the walls of sewer pipes and in the sediments in sewer pipes (Liu et al. 2015; Nielsen and Hvitved-Jacobsen 1988). This reduction is dependent on anaerobic bacteria and chemical oxygen demand, as well as sulfate and organic matter availability (Nielsen and Hvitved-Jacobsen 1988). Although H_2S is corrosive and results in the corrosion of metal pipes (Boon 1995), the oxidation of sulfide into sulfate (sulfuric acid) also contributes to the corrosion of concrete pipes (Nielsen et al. 2005). The corrosion of the concrete pipes occurs along an acid front where the cement is broken down into gypsum and ettringite by the following reactions (Jiang et al. 2014).

$$H_2SO_4 + Ca(OH)_2\,(portlandite\ cement) \rightarrow CaSO_4 \cdot 2H_2O\,(gypsum)$$
$$3(CaSO_4 \cdot 2H_2O) + 3CaO \cdot Al_2O_3\,(cement\ component) + 26H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O\,(ettringite)$$

The products of these reactions have larger volumes than uncorroded cement, and thus cause expansion and microcracking of the concrete. The weathering of concrete and corrosion of pipes contributes to the release of chemical cocktails enriched in weathering products such as Ca^{2+}, Mg^{2+}, HCO_3^-, SO_4^{2-} and/or metals, such as iron, into surface and groundwater (*e.g.* see equations below) (Figure 3).

$$CaSO_4 \cdot 2H_2O_{(s)} \leftrightarrow Ca^{2+}_{(aq)} + SO^{-}_{4(aq)} + 2H_2O_{(aq)}$$
$$CaCO_{3(s)} \leftrightarrow Ca^{2+}_{(aq)} + CO^{-}_{3(aq)}$$

Freshwater Salinization Syndrome Makes Diverse Chemical Cocktails

Chronic salinization of surface waters has occurred regionally (Kaushal et al. 2005) and on continental and global scales (Kaushal et al. 2018a, 2018b, 2018c) due to increasing coverage by impervious surfaces and associated salt sources such as road deicers. This phenomenon, known as the Freshwater Salinization Syndrome (FSS); Kaushal et al. 2018a, 2018b, 2018c) influences the transport and transformation of base cations, carbon, nutrients, and trace metals from watersheds to streams. FSS enhances mobilization of various organic

carbon compounds, nutrients, metals, and cations due to coupled biotic and abiotic processes such as ion exchange, rapid nitrification, pH changes, increased ionic strength, organic matter dispersal, and chloride complexation. Unanticipated geochemical relationships associated with FSS impact the efficacy of stream restoration strategies, urban water quality, and safe drinking water. At slightly elevated salinity, the linkage may be due to abiotic mechanisms such as cation exchange on the sediment surface or organic-metal ligand dispersal. At significantly elevated salinity (or prolonged salinity), the cation exchange sites could saturate, and the coupling may be due to biotic mechanisms such as a rapid reduction in nutrient processing, a loss of structure and function of lotic ecosystems, and/or microbial lysis. Chemical cocktails made by FSS can be categorized into distinct mixtures (Table 1). Because relatively little is still known regarding the synergistic effects of FSS in the environment, we propose the following categorization of chemical cocktails:

FSS Organic Matter Complexed Chemical Cocktails: elements/compounds with affinities to complex with natural organic matter. Salinization increases the chloride concentration, which could increase the solubility of metals associated with colloids. Salinization increases the ionic strength of water, which could disperse colloids from the sediment surface into suspension. Through dissolution reactions, elements on colloids could enter the dissolved phase, and the concentration of these elements be influenced by natural organic matter solubility.

FSS Ion Exchangeable Chemical Cocktails: elements/compounds with outer-sphere electrostatic affinities to sorb onto sediment particles. Through increases in chloride concentrations, salinization increases the ionic strength of water, which could affect sorption properties. More importantly, through increases in sodium concentrations (*e.g.* road salt), salinization could increase the competition for cation exchange sites on sediment surfaces. Within an isovalent series, the response of these elements is dominated by their ionic radii as larger cations have a greater sorption affinity due to lower ionic potentials than smaller cations. Across oxidation states, the response of these elements to FSS is a function of their location/exposure on the sediment surface, and the concentration of these elements can typically increase after salinization.

FSS Redox-Sensitive Chemical Cocktails: these are redox-sensitive elements/compounds. Due to ion-exchange with hydrogen, salinization could induce abrupt shifts in pH, which could affect the reduction potential at the sediment-water interface. Increases in ionic strength can cause organic matter dispersal off the sediment surface and shifts in microbial processing, or cellular lysis, both of which could expose the deeper sediment to oxygen and affect the reduction potential. The response of these types of cocktails can be strongly coupled with DOC concentrations, which is also highly redox-sensitive.

FSS Synthetic Chemical Cocktails: the types of chemical cocktails that we mainly discuss are anions, cations, organic matter, metals, nutrients, *etc.*, which are not synthetic (Kaushal et al. 2018 a, b, c). However, there has been widespread proliferation of synthetic chemicals in the environment (Bernhardt et al. 2017) that may also be influenced by FSS such as endocrine disrupting chemicals (EDCs), polycyclic aromatic hydrocarbons (PAHs), and others (Brunk et al. 1997; Borrirukwisitsak et al. 2012). Investigating FSS impacts on

mobilization and cycling of synthetic chemical cocktails can improve our characterization of urban geochemistry into the future research.

Part 2. Examples of Distinct Chemical Cocktails in Urban Waters

Urbanization Makes Chemical Cocktails of Major Ions

Major ions appear regularly in surface waters at concentrations greater than 1 mg L^{-1}, and some examples are Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, and CO_3^{2-} (Figure 4). Major ion concentrations are consistently elevated in urban streams *vs.* minimally disturbed reference conditions, but there is regional variability (Figure 4). Chemical cocktails of major ions form due to inputs from wastewater, infrastructure dissolution, evaporative concentration, atmospheric dust, road salt application, and soil acidification (Table 2). Typically, sewage has high concentrations of Na^{+}, Cl^{-}, SO_4^{2-}, and K^{+} relative to background concentrations. Ca^{2+}, Mg^{2+}, and HCO_3^{-} are also present in high concentrations in sewage and can also reflect weathering sources (Kaushal et al. 2017). K^{+}, which is a limiting nutrient for many plants occurs in relatively low concentrations in natural streams, and is attributed almost solely to human urine in urban streams. Rose (2007) found a strong correlation between Na^{+}, K^{+}, and Cl^{-} concentrations within 50 study basins, which was interpreted to reflect the electrolytes present in the human body. Boron and silica, which are not major ions, are also robust tracers for human activity (Neal et al. 2000; Takagi et al. 2017), as they are not highly concentrated in natural waters, but are concentrated in sewage due to detergents (silica can also be found in some processed foods as clay minerals, where Si can be solubilized). In fact, boron concentrations increase with watershed urbanization along with sodium concentrations from road salt and sewage; strontium concentrations from concrete and weathering sources also increase with Ca^{2+} and most major ions (Purdy and Wright 2019) (Figure 5). Ba^{2+} is another trace element that can increase with major ions in response to watershed urbanization due to inputs from sewage, paint, bricks, ceramics, glass, rubber, automobiles, and medical and industrial wastes (Monaci and Bargagli 1997; Purdy and Wright 2019) (Figure 5). Finally, manganese is one more example of a trace element that can increase with major ions in response to watershed urbanization, and this is likely due to stormdrain and groundwater inputs, batteries, pipes, automobiles and other sources (Paul and Meyer 2001; Joselow et al. 1978) (Figure 5). Thus, chemical cocktails of major ions and trace elements can mix, interact, and co-occur together in urban waters.

Infrastructure dissolution through urban karst in watersheds can create an anthropogenic signal that overrides natural factors and other land use changes. Impervious surface cover in a watershed is linked to increased base cation loads across a variety of settings because chemical weathering of building material is a steady source of cations (*e.g.*, Ca^{2+}, Mg^{2+}, and HCO_3^{-}). Studies investigating the influence of concrete weathering in urban watersheds show that the artificial lithology of concrete is able to overwhelm the natural lithology in determining major ion chemistry. Barnes and Raymond (2009) found that in 19 small watersheds with minimal lithologic differences ion loads in urban streams were significantly higher than in forested or agricultural streams and that human activities contributed 54% to 79% of the dissolved inorganic carbon in streams. Tippler et al. (2014) found an 18-fold increase in HCO_3^{-}, a 14-fold increase in Ca^{2+}, and a 6-fold increase in salinity in urbanized

watersheds versus reference conditions. Fitzpatrick et al. (2007) evaluated baseflow from 31 streams across a land use gradient and observed that Na^+, K^+, Cl^-, and SO_4^{2-} concentrations in streams increased with urbanization. Similarly, Kaushal et al. (2017) found statistically significant positive linear relationships between impervious surface cover and cations (Ca^{2+}, Na^+, K^+) as well as DIC, pH, and silica for streams at the Baltimore LTER site. Other studies in Baltimore streams have shown similar increases in major ions in response to urbanization (*e.g.*, Moore et al. 2017).

Weathering of urban karst also influences sulfate, an abundant major ion in urban waters, which is contained in many building materials (*e.g.* gypsum, concrete, and roofing tiles) (Cevik et al. 2011). The chemical weathering of these materials contributes to sulfate inputs to urban streams. In urban ecosystems, sulfate-rich chemical cocktails typically increase in surface and groundwaters. Pikaar et al. (2014) identified three major sources of sulfate in sewer systems: source waters, addition of aluminum or iron sulfates during water treatment, and human waste. In South East Queensland, Australia, Pikaar et al. (2014) found that 52% of the sulfate in the sewage system was from aluminum sulfate added during water treatment, 10% from source water, and 38% from human waste; totaling ~ 17 mg SO_4-S L^{-1}. Appleyard (1995) concluded that groundwater in non-urban environments had an average of 8 mg/L of SO_4^{2-} and groundwater in older, urban environments increased to an average of 69 mg/L of SO_4^{2-} due to the oxidation of sulfide containing soils and use of fertilizers. The influence of anthropogenic sulfur has also been noted in Paris, France, where during major urbanization in the late 1800s, the sulfur content of groundwater doubled in a historical underground aqueduct (an older form of urban karst) (Pons-Branchu et al. 2017). SO_4^{2-} also contaminates groundwater in China due to air pollution, use of household detergents, industrial runoff, and agricultural inputs (Li et al. 2006).

Evaporation and atmospheric deposition can also enhance formation of watershed chemical cocktails of major ions. In downtown and light industrial locations, evapotranspiration rates can exceed precipitation and require piped water supply (Grimmond and Oke 1986). This results in an evaporative concentration of all major ions in the urban environment. Other direct anthropogenic inputs include atmospheric dust and by atmospheric deposition from road salt applications (Blomqvist and Johansson 1999). Atmospheric dust inputs can represent the underlying lithology, if anthropogenic land denudation exposes minerals to aeolian transport mechanisms. Major ions that are released as dust particles can chemically weather. Sulfate and chloride aerosols may be contributed by through proximity to coal mining and marine air masses (Griffith 2014). Aerosol salt additions also have the potential to increase nitrate leaching and reduce mobility of dissolved organic carbon (Compton and Church 2011), which could form chemical cocktails. In turn, anions like nitrate can also be deposited from the atmosphere and contribute to accelerated concrete weathering through acidification, a phenomenon that is exacerbated by watershed impervious cover (Riha et al. 2014).

Globally, streams draining other cities can show these patterns of increased major ions compared with streams draining less urbanized land use further upstream. For example, along the Ravi River inside and outside of Lahore, Pakistan concentrations of Na^+, Ca^{2+}, Cl^-, and SO_4^2 are significantly higher in the city than in the river upstream of the city over 3

decades from 1978 to 2002 with changes over time. Likewise, Na^+, Ca^{2+}, Cl^-, and SO_4^2 are significantly higher in the Han River downstream *vs.* upstream of Seoul, South Korea from 2010 to 2016 (Figure 6). Interestingly, Cl^- concentrations increase over time in these locations indicating potential impacts of the freshwater salinization syndrome in Asia (Figure 6). Additionally, synoptic data collected along the Anacostia River in Maryland, USA showed increasing concentrations of major ions downstream (Figure 7). Concentrations of major ions increased along the drainage basin of the Anacostia River (as cumulative percent impervious surface area increased downstream from the first sampling point), which either suggests increasing anthropogenic sources with urbanization and/or accumulating inputs from chronic groundwater contamination in urban areas (Figure 7). Conversely, nitrogen and carbon showed an opposite pattern with distance downstream, which was potentially due to dilution and/or biogeochemical transformation. Elevated concentrations of major ions in response to urbanization are related to a variety of processes such as urban soil formation from novel urban parent materials, human-accelerated weathering of urban karst, urban acidification-alkanization processes, and the FSS.

Urbanization Makes Chemical Cocktails of Dissolved Organic Matter

Urbanization makes chemical cocktails of natural organic matter from road runoff, grass clippings, fertilized lawns and fields, and storm drains (Li et al. 2006; Helmreich et al. 2010; Newcomer et al. 2012). Urbanization shifts dissolved organic matter (DOM) away from humic and protein-like DOM, which is often more common in natural environments. Other studies have suggested that urbanization may increase protein-like DOM, but are in agreement that humic-like DOM decreases and fulvic acid-like DOM increases with urbanization (Hosen et al. 2014; Williams et al. 2016). Urban DOM concentrations vary seasonally due to differences in anthropogenic sources, leaf fall, and/or algal blooms (Pons-Branchu et al. 2017). Principal components analysis shows a clear difference in DOM signatures between forested and urban sites; photolabile and recalcitrant components (linked to terrestrial DOM sources) and percent fluorescence of both components are positively related to watershed impervious cover (Hosen et al. 2014). Aromaticity of DOM can be negatively correlated with impervious cover and can be influenced by microbial activity (Hosen et al. 2014). In general, urban streams appear to be enriched with DOM signatures that have a low molecular weight and aromaticity, similarly to other anthropogenically impaired waterways like those affected by agriculture or wastewater (Hosen et al. 2014).

In addition to natural organic matter, a range of anthropogenic carbon signatures are present in urban waters at trace level concentrations (<1μg/l) such as sterols, pesticides petrochemicals, polycyclic aromatic hydrocarbons (PAHs) and antibiotics (Glassmeyer and Shoemaker 2005, Rosi et al. 2018). Anthropogenic sources of organic matter found in urban waters also encompass: agricultural pesticides such as atrazine, steroidal hormones commonly like 17β-estradiol, antibiotics including tetracycline, and chemicals found in personal care products such as triclosan (Kolpin et al. 2013). Other legacy organic contaminants include polychlorinated biphenyls (PCBs) (Rodenburg and Ralston 2017) and polybrominated diphenyl ethers (PBDEs), a common flame retardant (Rodenburg et al. 2014). While most new production of these chemicals has been phased out in industrialized countries, legacy sources are persistent and continue to contaminate urban waters

(Rodenburg et al. 2014; 2010; Praipipat et al. 2017). A survey of chemical and microbial compounds originating from wastewater discharges found that flame retardants common in furniture and bedding are the most common chemical class, being found in ~75% of surveyed rivers (Glassmeyer and Shoemaker 2005). This was followed by plant and animal sterols and non-prescription pharmaceuticals at ~60% and ~ 40% respectively. Wastewater leaks also contribute high levels of estrone, nonylphenol, propylparaben, bisphenol A, triclosan, methyparaben, herbicides, 2-phenylphenol, and other organic contaminants (Peng et al. 2008). Many other organic matter sources can make chemical cocktails such as petrochemicals from leaking underground storage tanks and per-and polyfluoroalkyl substances (PFAS), which have been used in making carpets, plastics, cookware, *etc.*, which we do not review here.

Streamflow, stormwater management, and seasonality all influence chemical cocktails of organic matter in urban waters. For example, chemical cocktails are mixed hydrologically across time and space through transport through altered surface flowpaths (impervious surfaces, construction materials, altered geomorphology *etc.*) and subsurface flowpaths (stream burial, urban karst, pipes, soil compaction *etc.*) Firstly, streamflow conditions (*e.g.*, stormflow *vs.* baseflow) can influence the quantity and quality of organic matter chemical cocktails particularly during the first flush of storm events (Peng et al. 2008; Hook and Yeakley 2005; Kaushal et al. 2014). During the first flush, pulses in DOC concentrations and fluxes are amplified by impervious surfaces and combined sewer system overflows (Sickman et al. 2007); this can occur due to the accumulation of leaves and organic matter on impervious surfaces during dry weather conditions and flushing of organic matter into stormdrains during wet weather conditions contributing to a ‘gutter subsidy’ of organic matter to urban streams (Kaushal and Belt 2012). Secondly, stormwater management influences retention of anthropogenic carbon sources including particulates, polyaromatic cyclic hydrocarbons (PAHs), oil, and grease (Hsieh and Davis 2005; Badin et al. 2008). Sorption to organic matter and filtration of particulate-bound pollutants are the primary removal mechanisms for a range of other compounds associated with organic matter chemical cocktails including phosphorus, oil and grease, PAHs, and pesticides (Badin et al. 2008; Davis et al. 2010). Thirdly, seasonality plays an important role in the quantity, quality, and diversity of organic matter chemical cocktails. During leaf fall, organic C, N, and P chemical cocktails are linked to leaf litter and other organic matter which accumulates on pavement and in pipes and culverts (Duan et al. 2014; Hobbie et al. 2014; Selbig 2016; Smith and Kaushal 2015). During spring and summer months, there can also be increases in concentrations and lability of organic matter chemical cocktails in urban waters due to contributions from algae and bacteria in streams (Kaushal et al. 2014; Arango et al. 2017). Ultimately, watershed chemical cocktails of organic matter vary over space and time based on hydrology, management, and seasonality.

Urbanization Makes Chemical Cocktails of Nutrients

Nitrogen-Rich Chemical Cocktails—Urbanization forms nitrogen-rich chemical cocktails transported in septic systems and sewers. Aging sanitary infrastructure can leak into urban groundwater and transport significant amounts of nitrogen-rich runoff into streams during rainstorms and baseflow. Cities can have increased N inputs to ground water

and streams from leaky pipes and sanitary infrastructure (Kaushal et al. 2011; Pennino et al. 2016; Gabor et al. 2017). For example, sewage contributions of dissolved inorganic nitrogen (DIN) ranged from 6 to 14 kg ha-1 yr-1 in an urban watershed in Pittsburgh, Pennsylvania, USA, and significant DIN loading can occur during both stormflow and baseflow conditions (Divers et al. 2013). Septic systems across different regions can also discharge nutrients below the rooting zone and by-pass plant uptake, which also contributes to nitrogen-rich chemical cocktails in urban ground and surface waters (Steffy and Kilham 2004; Kaushal et al. 2006).

Urbanization makes nitrogen-rich chemical cocktails from atmospheric deposition and lawn fertilizers. For example, atmospheric deposition of nitrogen is 47% and 22% higher in urban and suburban areas, respectively, compared to nonurban areas (Bettez and Groffman 2013). In particular, roads are hotspots for nitrogen deposition, and failing to account for the deposition of nitrogen from fossil fuel combustion on roadways underestimates total nitrogen inputs by 13%−25% (Bettez and Groffman 2013). In addition, nitrogen fertilizers applied to lawns can be transported to urban waters *via* volatilization and atmospheric deposition, surface runoff, or groundwater inputs (Puckett 1994). The application of nitrogen fertilizer to residential lawns can be comparable to the amount applied to agricultural fields and golf courses. For example, homeowners applied 97.6 +/− 88.3 kg N/ha to their lawns in Baltimore, Maryland, USA (Law et al 2004). Higher fertilizer applications were correlated with newer developments, accounting for up to 53% of the total nitrogen inputs to watersheds (Law et al. 2004). For lawns established over a decade, nitrate leaching ranged from 5 mg/l to as high as 20 mg/l in (Frank et al. 2006). Inorganic nitrogen leaching was as high as 30% in areas that used turfgrass (Wang et al. 2014), although urban lawns can have a higher capacity to retain nitrogen than urban forests (Raciti et al. 2008). Ultimately, the amount of nitrogen retained in lawns is dependent on the age of the lawn, the frequency of fertilizer additions, and socioeconomic factors (Raciti et al. 2008).

Finally, nitrogen transformations in urban watersheds influence chemical cocktails in urban waters. In some cases, engineered hydrologic flowpaths and compacted urban soils reduce N transformations; in other cases, N is significantly retained and transformed during baseflow conditions (Groffman et al. 2004; Kaushal and Belt 2012). For example, nitrate can be reduced to N_2 in “hot spots” by microbial denitrification where conditions are anoxic, dissolved organic carbon concentrations are sufficient, and flow rate is low enough to allow for adequate mixing of the necessary constituents such as in urban riparian groundwater ecosystems (Kaushal et al. 2008; Mayer et al. 2010). In addition, urban environments create new hotspots for enhanced denitrification in stormwater detention basins, ditches, gutters, lawns and other places where water, nitrate and organic matter accumulate with sufficient hydrologic residence times (Kaye et al. 2006). Finally, organic nitrogen transformations in urban watersheds contribute to chemical cocktails of humic substances, amino acids, amino sugars and tannins, which influence primary production, trigger harmful algal blooms, and alter the solubility and mobility of metals and pesticides (Aitkenhead-Peterson et al. 2009; Kaushal and Lewis 2003; Petrone et al. 2010; Tufford et al. 2003).

Phosphorus-Rich Chemical Cocktails—Urbanization makes phosphorus-rich chemical cocktails from mixing sewage, fertilizers, and runoff from impervious surfaces.

The most common forms of P in urban waters are phosphates which can be either organic (bound to plant or animal tissue) or inorganic (ortho-/poly-phosphates). In a study of 54 UK rivers, the main source of soluble reactive phosphorus was urban wastewater effluent, which was most concentrated during the peak growing season, thereby posing a greater risk for eutrophication (Jarvie et al. 2006). Runoff from impervious surfaces also contains P, and lawns and streets were the two largest sources of P found in some waters of the Midwestern U.S. (Waschbusch, 2000). Distribution of P pools have been attributed to human density, developed land use, impervious surface cover, and asphalt (Russell et al. 2008, Duan et al. 2012, Metson et al. 2012). The amount of P loading to streams may not be simply related to impervious surface cover, but also drainage simplification and increased hydraulic efficiency of storm water drainage to urban streams (Walsh et al. 2005). Drainage intensification creates shorter and quicker hydrologic flow paths from the landscape, which can funnel significant amounts of P-rich chemical cocktails from nonpoint sources to urban streams.

Biogeochemical transformation of phosphorus-rich chemical cocktails differs from that of nitrogen-rich chemical cocktails. Unlike nitrogen, P cannot be permanently removed through processes like microbial denitrification. P can only be retained by biological uptake, sorption onto particles that are then buried, or mineral precipitation. For example, a major chemical interaction between sediment and P is the coprecipitation of P with calcite, a process driven by the reduction of CO_2 or HCO_3^- during photosynthesis (House 2003). Phosphate can also bind to iron hydroxides creating a Fe(II) phosphate, and in solutions of high SRP, this is precipitated as the mineral vivianite (House 2003). Because P is not permanently removed, it can be remobilized and released back into the water column of urban aquatic ecosystems (Jarvie et al. 2005). Whether sediments in urban waters act as sinks or sources of P varies spatially and temporally (Duan et al. 2016). For example, sorption of P to sediments is controlled by oxygen levels and temperature. The oxic zone is important in controlling the exchange of P between urban sediments and the water column, and in this zone the equilibrium phosphate concentration depends on temperature (House 2003). Urbanization can influence solubility of mineral P by increasing water temperatures through riparian tree removal, wastewater and industrial discharges, and runoff from impervious surfaces (Barrow 1979). The release of P from urban sediments also depends on pH, the most P being released under alkaline conditions and the least under neutral pH (Wu et al. 2014). Phosphorus release from sediments may increase as some urban waters become more alkaline due to freshwater salinization syndrome and human-accelerated weathering (Kaushal et al. 2013, Kaushal et al. 2017).

Silica-Rich Chemical Cocktails—Relatively little is known regarding how urbanization alters Si-rich chemical cocktails compared to nitrogen and phosphorus. However, urbanization can increase dissolved Si transport in watersheds in multiple ways. Rivers draining areas with higher population density have higher Si concentrations (Takagi et al. 2017). Urbanization leads to the replacement of forests and grasslands with buildings and urban infrastructure, which also result in reduced dissolved Si uptake by vegetation (*sensu* Fulweiler and Nixon 2005; Carey and Fulweiler 2012; 2013, Takagi et al. 2017). Impervious surfaces prevent infiltration and increase runoff, which increases river discharge and can increase Si transport from landscapes and anthropogenic sources to streams and rivers

(Fulweiler and Nixon 2005; Carey and Fulweiler 2012; 2013). Approximately 9% of dissolved Si in some river basins can originate from anthropogenic inputs (Zhang et al. 2016). Sewage and wastewater flow systems also alter the flow paths of groundwater and runoff and influence Si in urban watersheds (Maguire and Fulweiler 2016); for example, there is the potential for groundwater to infiltrate into wastewater pipes (Kaushal and Belt 2012). Finally, urban infrastructure acts as exposed bedrock, which leads to an increase in dissolved Si when chemically weathered (Sferratore et al. 2006; Maguire and Fulweiler 2016). Weathering of impervious surfaces can increase the pH of urban waters, and the solubility of Si appears to increase in waters with pH > 8, due to the additional presence of H_3SiO_4 (Alexander et al. 1954). A combination of freshwater salinization syndrome, human-accelerated weathering, increased photosynthesis by algal blooms, and increased use of road salts can synergistically increase the pH of some urban waters to pH levels > 8 over time (Kaushal et al. 2018). Ultimately, an increase in Si loading and a decrease in removal processes can result in greater Si transport downstream in urban watersheds. Compared with N and P, more work is necessary to elucidate the effects of urbanization on Si-rich chemical cocktails, however.

Urbanization Makes Chemical Cocktails of Trace Elements

Trace elements in the built environment differ widely from their expected natural concentrations (Figure 8). Here, we define trace elements as those < 1 mg/L in concentration in surface and ground waters. Trace elements are typically significantly elevated in urban streams across land use and as compared to concentrations in major world rivers on a global scale (Figures 5, 8). Zinc, copper, cadmium, and lead are the four major trace element pollutants in rivers worldwide, and lead is regularly used as an indicator species to assess the level of pollution by urban run-off in a water body (Mohiuddin et al. 2010). Trace elements are ubiquitous in fossil fuels and metal ores which form the basis for many pollutants found in urban landscapes (Pacyna and Pacyna 2001) (Table 3). For example, arsenic, lead, selenium, antimony, vanadium, and cobalt all are found in higher concentrations in many urban watersheds at levels exceeding the World Health Organization's drinking water standards (S. Li and Zhang 2010). Sources of trace elements in urban systems include the combustion of gasoline for automobiles, the combustion of coal and oil in power plant settings, refuse incineration, municipal wastewater treatment, sewage sludge, vehicular and industrial discharge, leakage from decaying service pipes, corrosion of metal objects, and atmospheric deposition from industrial regions adjacent to urban centers (Pacyna and Pacyna 2001; Cereceda-Balic et al. 2012; Mohiuddin et al. 2010; Leung and Jiao 2006; Senesil et al. 1999; Argyraki and Kelepertzis 2014) (Table 3). In some cases, trace elements can increase downstream with watershed urbanization, but in other cases their longitudinal patterns may be more complex due to local hot spots of pollution sources (Figure 9). However, concentrations of trace elements can still show similar patterns with distance downstream suggesting the formation of chemical cocktails (Figure 9).

Urban rivers can have higher amounts of bioreactive dissolved organic carbon (DOC) when compared to their natural counterparts (Kaushal et al. 2014). Trace metals in rivers and streams are mainly found adsorbed onto the surface of particulate clay sediments and associated DOC. Both inorganic and organic colloids are important modifiers of trace

element mobility and chemical cocktails of metals in urban waters (Kaushal et al. 2018a). As clay and/or organic carbon content in stream sediments increase, the concentration of trace elements in streams increases. Concentrations of rare earth elements (REEs) and other associated trace elements such as iron, aluminum, manganese, and zinc have been demonstrated to correlate to certain pH and DOC concentrations in aquatic environments (Gaillardet et al. 2003). For example, most rare earth elements are not coupled with concentrations of major solutes in rivers, and instead are controlled by pH and dissolved organic carbon concentration in river waters.

In addition to organic matter and inorganic colloids, other chemical factors in rivers influence mobility of trace metals such as alkalinity and redox conditions, presence of other trace elements, and major elements. There are relationships between trace and major elements and chemical factors, which we now discuss with a few subsequent examples. For example, alkali and alkaline earth trace elements in rivers show a strong correlation with sodium and calcium concentrations. Concentrations of trace elements such as molybdenum, zinc, cadmium, rubidium, strontium, boron, and barium also correlate strongly to major element concentrations; for example molybdenum correlates with sulfate in global rivers (Gardner et al. 2017). Vanadium, copper, arsenic, barium, and uranium concentrations strongly correlate to the pH of water, while copper correlates with silica concentrations, and selenium with sulfate (Gaillardet et al. 2003). Interestingly, concentrations of some trace and major elements show diurnal cycles also tracking changes in pH, dissolved oxygen, streamflow and other environmental variables (Kaushal et al. 2018a) (Figure 10). More research is necessary to go beyond routine grab sampling to better understand underlying patterns and processes related to correlations between diurnal changes in major and trace elements and chemical factors in urban streams, however.

From a global perspective, there are deviations in urban chemical cocktails of trace elements when compared to chemical cocktails of trace elements found in rivers under mostly natural conditions. Concentrations of trace elements in urban streams are typically much higher than natural conditions, and there can be unique chemical cocktails that are formed across different sites and regions (Figure 8). Our analysis of chemical cocktails of trace elements in urban streams and rivers around the world suggest that the chemical cocktail approach can be used to track and distinguish distinct sources of pollution and contaminant mixtures across urban watersheds. Furthermore, watershed management efforts should consider differences in the composition of chemical cocktails across regions and their unique interactive effects on organisms as multiple stressors to protect aquatic life and human health.

Part 3. Managing Urban Chemical Cocktails

Managing water pollution needs to move beyond monitoring individual chemicals in the environment towards identifying and characterizing complex chemical mixtures in order to better understand the toxicological and synergistic effects of multiple chemicals on human and environmental health (Escher et al. 2020). A more holistic approach will require a better understanding of the sources, composition, and behaviors of different and distinct chemical cocktails over time and space. Currently, water quality is typically managed using an

individual contaminant approach in most regions of the world. Resource management agencies do not manage complex chemical mixtures but establish regulations for individual stressors rather than multiple stressors (National Research Council et al. 2001). An understanding of the complex interactions between diverse chemical mixtures and stressors and their ecological, toxicological, and human health effects are just now gaining more appreciation (Monosson 2005).

In some cases, managing contaminants one at a time can be more expensive and less effective than managing sources and impacts of chemical cocktails holistically. For example, chemical mixtures impact: drinking water taste problems and harmful trihalomethane formation during drinking water treatment (different organic chemical mixtures interacting with chlorination); eutrophication and hypoxia problems leading to fish kills, harmful algal blooms, and reduced water clarity (nutrient-rich chemical cocktails with N, P, and Si alleviating nutrient limitation); increased toxicity to aquatic life in urban waters containing cocktails of heavy metals and organic contaminants from tires and vehicle emissions (Feist et al. 2017; Peter et al. 2018). By classifying similar and/or shared sources, transport, and/or transformations, the watershed chemical cocktail concept can foster the development of co-management strategies to holistically manage multiple chemicals when those chemicals behave similarly (Kaushal et al. 2018, Kaushal et al. 2019). Below, we discuss potential strategies for managing urban chemical cocktails.

Managing Chemical Cocktails by Reducing Shared Pollutant Sources and Impervious Cover

Managing shared sources, transport, and transformation of chemical cocktails (*e.g.*, air pollution, sewage, weathering of impervious surfaces, stormwater inputs and other sources mentioned throughout this paper) is critical for reducing urban contaminants. For example, source reductions through regulatory mandates (*e.g.* Total Maximum Daily Loads or TMDL's) are critical for source control. However, reducing pollutant loads often involves complex land use decisions, human behavioral changes, and timely identification of emerging contaminants of concern. For example, microplastics are now recognized as a ubiquitous ingredient in many organic chemical cocktails (Rochman 2018) and may interact with metals, salt ions, and nutrients as multiple stressors to aquatic life. Reducing sources of microplastics is dependent upon reducing consumption of plastics and disposing of plastics before they are released to the environment. In addition, other activities contribute to microplastic sources and transport such as impervious surface cover and tire wear from vehicles. Rarely is the source of a particular contaminant consolidated, which makes removal difficult. A notable exception is the successful removal of diffuse legacy sediments along streams; removal of legacy sediments has been estimated to be an effective, economical means of reducing chemical cocktails characterized by agricultural nutrients (Fleming et al. 2019). Although there are many challenges, identification of similar sources is critical for reducing chemical cocktails.

Another approach for reducing transport of chemical cocktails is to reduce impervious surface cover and subsurface urban karst (Kaushal and Belt 2012), which both increase transport sediments and solutes (Ca^{2+}, Mg^{2+}, HCO_3^-, *etc.*) in drainage waters. Options to

reduce impervious surfaces and enhance greenspace include various green infrastructure approaches, which can be incorporated into a comprehensive low impact development (LID) designs including green roofs, bioretention systems, and permeable pavement (Martin-Mikle et al. 2015; Passeport et al. 2013). Vacant lots also represent large infiltration areas in an otherwise impervious landscape that can be collectively managed to improve ecosystem services including stormwater management (Shuster et al. 2017; Green et al. 2016). More work is necessary to characterize transport of chemical cocktails into urban ground water as a result of enhancing infiltration. The greening of cities can represent an 'urban evolution' towards a more sustainable form, function, and transformation of chemical cocktails in urban watersheds (*e.g.*, Kaushal et al. 2014; Kaushal et al. 2015; Kelleher et al. 2020; Hobbie and Grimm 2020).

Managing Chemical Cocktails by Microbiomes and Phytoremediation

Plants, biofilms, and microbes in wetlands assimilate contaminants and/or transform contaminants through metabolic breakdown. Thus, phytoaccumulation of metals in the organic matter of plants can also be used to manage and transform chemical cocktails. For example, the common wetland plant *Lemna minor* accumulates and transforms Cd, Cr, Cu, and Se in its tissues, removing these elements from urban soils (Zayed et al. 1998). Microbial uptake can further retain and transform trace elements in the built environment, especially alkalinity- and metal-tolerant species in microbiomes (Mora et al. 2005). Thus, integrating soil microbiomes and metal-tolerant plant species is another potential remediation strategy for managing chemical cocktails of trace metals. For biotic remediation to be most effective at reducing trace metals, however, it must be combined with significant reductions in sources, including vehicular and electrical emissions, refuse incineration, and corrosion of aging infrastructure (as discussed earlier). This is because microbiomes and phytoremediation can have thresholds for the amounts and forms of contaminants that can be assimilated and transformed.

Managing Chemical Cocktails by Riparian Buffers and Wetlands

Most sources of chemical cocktails are difficult to identify and/or are diffuse in the environment. Therefore, managing biogeochemical transformations in watersheds in wetlands and riparian buffers is also key. Natural systems and those restored or designed to mimic natural systems like wetlands and riparian buffers have the capacity to transform and reduce chemical cocktails (Jefferson et al. 2017; Costello et al. 2020). Much work has shown that natural and engineered wetlands can be effective at attenuating transport of multiple contaminants. For example, constructed wetlands have frequently been used for wastewater treatment and are highly effective at remediating pesticides (Lv et al. 2017), mixtures of pharmaceuticals (He et al. 2018), and metals (Gill et al. 2017). In addition, planting vegetation in riparian buffers can reduce exposure of soils, erosion, and weathering, which can mobilize chemical cocktails from soils and urban infrastructure. Riparian buffers are also effective at retaining multiple contaminants and sediments by capturing sediments and multiple chemicals bound to those sediments (*e.g.*, phosphorus bound to clay particles) and by enhancing denitrification (Hoffmann et al. 2009). Riparian buffer width and hydrologic flow paths can enhance the effectiveness of nutrient removal and transformation (Mayer et

al. 2007). Ultimately, physical, biological, and hydrologic factors influence the efficacy of riparian buffers in reducing transport of chemical cocktails to streams and rivers.

Managing Chemical Cocktails by Green Infrastructure

Green infrastructure shows varying efficacy at retaining and transforming nutrients, metals, and organic contaminants based on approaches such as swales, green roofs, bioretention ponds, rain gardens (Shuster et al. 2017), and rain barrels (Thurston et al. 2010). Treatment of stormwater by filtering through soils to simulate green infrastructure can reduce toxicity of complex chemical mixtures from roadside runoff and prevent salmon mortality (Spromberg et al. 2016). The key to effective functioning of green infrastructure is enhancing the ability to capture and retain water and particles for extended periods and to create and sustain conditions conducive for biogeochemical transformations to occur. This may involve: 1) dilution, 2) increasing microbial activity and plant uptake, 3) providing mineral or organic substrates for adsorption, and/or 4) activating or catalyzing chemo-transformation. For example, salt-rich chemical cocktails may be diluted by precipitation events and/or hydrologic flushing (Cooper et al. 2014) or releases of less salty reservoir water where dams exist (Knowles 2002). However, soils and shallow groundwater can also be a reservoir of salt ions (Kaushal et al. 2005, Cooper et al. 2014) and salt ions can be retained in green infrastructure (Mullins et al. 2020). Finally, enhancing microbial activity in green infrastructure can retain and transform nutrient-rich chemical cocktails, especially those containing nitrogen, where denitrifiers can be enhanced by adding organic carbon and/or inducing optimal dissolved oxygen and redox conditions as is done in wastewater treatment (Oakley et al. 2010).

Managing Chemical Cocktails by Permeable Reactive Barriers and Reactive Beds

Permeable reactive barriers (PRB's) are engineered subsurface systems that are designed to intersect groundwater plumes before they reach receiving waters or move into drinking water supplies (Passeport et al. 2013). PRB's are filled with materials such as organic matter or zero valent iron that form substrates for growth of microbes to treat contaminants such as arsenic (He et al. 2008; Ludwig et al. 2009; Wilkin et al. 2009) or process nitrogen (Schipper and Vojvodić-Vuković 2001). For example, chemical cocktails of heavy metals in acid mine drainage can be retained in pervious concrete barriers by raising the pH of drainage water (Shabalala et al. 2017). Construction of such barriers varies by reactive fill material, installation, incorporation into the substrate, and are meant to treat shallow plumes 4–5 m deep (Schipper et al. 2010). Reactive beds function similarly to PRB's by providing an organic substrate for microbial activity (*e.g.* denitrification) but are designed along a horizontal plane using containers a few meters deep filled with organic matter that receive discharge from wastewater or agricultural drainage. Conversely, reactive layers of organic material can be mechanically mixed into deeper soils to treat deeper plumes (Passeport et al. 2013). PRB's and reactive beds are generally small and designed to address point sources of contaminants such as those derived from a spill or in waste water treatment.

Managing Chemical Cocktails by Stream Restoration

Stream restoration is also increasingly being used to manage sediments and transform nutrients in urban watersheds (Newcomer-Johnson et al. 2014; Newcomer Johnson et al.

2016), although less work has investigated the potential for stream restoration to retain and transform chemical cocktails of metals, organic contaminants, and emerging contaminants. In cities with high levels of impervious surface cover, many streams have been buried and contained in pipes or conduits (Elmore and Kaushal 2008), increasing the transport of chemical cocktails. Conversely, certain forms of stream restoration have the potential to transform chemical cocktails derived from multiple sources or diffuse sources in a watershed (Newcomer Johnson et al. 2016; Passeport et al. 2013). Buried streams and those streams in ditches, canals, or encased in concrete, allow rapid transport of chemical cocktails through subsurface hydrologic flowpaths (Elmore and Kaushal 2008). Where encasement can be removed, increased percolation and groundwater-surface water exchange can increase the likelihood of subsurface microbial transformation and/or biological uptake of nutrient-rich chemical cocktails in plants and biofilms. Where buried streams can be daylighted, not only is groundwater-surface water exchange increased thereby increasing microbial transformations of nutrient cocktails (Beaulieu et al. 2014; Pennino et al. 2014), but also, water is exposed to daylight where photolysis can break down chemical cocktails containing pharmaceuticals such as morphine, codeine, and methamphetamine (Lin et al. 2013; Lin et al. 2014; Wang et al. 2014). In agricultural areas with nutrient-rich chemical cocktails, two-stage ditches have also been shown to be effective at enhancing conditions for removal of nitrogen and phosphorus by altering hydrologic flowpaths and retention within streambanks (Hanrahan et al. 2018). However, watershed scale implementation of both nutrient source reductions and stream restoration would be necessary to significantly reduce nutrients (Christopher et al. 2017), which has also been shown for urban drainage networks (Beaulieu et al. 2015).

Managing Chemical Cocktails by Activated Carbon, Zeolites, Nanoparticles, and Mixed Media

As discussed previously, various infiltration systems including basins, chambers, and gutters have been designed to intercept, remove, and transform metals, hydrocarbons, nutrients, PAHs, *etc.* (Fronczyk et al. 2020). Typically, these systems are designed to treat runoff in small, contained catchments like parking lots or street gutters *via* percolation through soils and sands. Other mixed media may also be added such as perlite, vermiculite, activated carbon, zero valent iron, wood mulch, limestone, zeolites, peat, *etc.* Peat-containing, permeable wall treatment systems can be effective at removing PAHs, Zn, Pb, and Cu (Fronczyk et al. 2020), while systems with gravel, vermiculite, and zeolites can significantly reduce chemical cocktails with mineral oil, ammonia, Cu, Zn, and PAHs (Fuerhacker et al. 2011). In addition, gutter systems filled with activated carbon have demonstrated near complete removal of suspended solids, TOC, Cu, and Pb, but have been ineffective at removing salts from road deicers (Hilliges et al. 2013). Infiltration systems and reactive beds with wood mulch or other carbon substrates can be effective at removing nitrogen oxides and ammonium ions *via* denitrification (Schipper et al. 2010). Mineral media such as zeolite, vermiculite, perlite, spongolite, limestone, sand, silt, and clays have been used to treat road runoff and heavy metals (Fronczyk et al. 2020; Fuerhacker et al. 2011; Reddy and Kumar 2017). Organic media such as peat, compost, wood mulch, and other carbon containing media (*e.g.* lignite coke, biochar, activated carbon) have been used to retain contaminants including petrochemicals and organic compounds (Fronczyk et al. 2020). Zero valent iron is

often added to permeable barriers and infiltration systems to retain organic contaminants, heavy metals, radionuclides, and nitrates (Henderson and Demond 2007; Liu and Wang 2019). In addition, zeolites (positively charged, hydrated aluminosilicate minerals containing alkaline-earth metals) are active ion exchange substrates for removing charged particles like ammonium ions (Fronczyk et al. 2020). Soil media may be simultaneously optimized for retaining water from precipitation and enhancing plant growth (Bollman et al. 2019), while these media matrixes may also be enhanced with additives such as biochar created by pyrolysis of various organic matter stocks at high temperatures (Novak et al. 2014). This creates highly adsorptive material that can be tailored to remove chemical cocktails containing heavy metals (Niazi et al. 2018) and/or antibiotic mixtures (Lu et al. 2018). Finally, engineered nanoparticles (ENP's), while themselves potential ingredients for chemical cocktails (Hartmann and Baun 2010), can also be engineered to reduce toxicity of chemical cocktails of pesticides and heavy metals through adsorption to the nanoparticles (Hartmann et al. 2010; Knauer et al. 2007).

Managing Chemical Cocktails by Continuous Monitoring Using Water Quality Sensors

Over recent decades, there has been a widespread proliferation of environmental sensor data related to monitoring and managing water quality in streams (*e.g.*, Spencer et al. 2007; Pellerin et al. 2012; Wollheim et al. 2017; Vaughan et al. 2017). This has been largely driven by agencies such as the U.S. Geological Survey and other monitoring entities. Although multi-parameter sensors can initially be expensive to install and maintain, they offer the potential to obtain high-frequency continuous water quality data for streams and rivers over years. Given that chemical concentrations and loads change rapidly in urban watersheds, continuous monitoring can reveal the presence of chemical cocktails and peaks, persistence, and lag times of multiple contaminants (Haq et al. 2018, Kaushal et al. 2019). For example, specific conductance can be related to concentrations of some base cations and trace metals in urban streams (Figure 11) (Kaushal et al. 2018), and that there can varying relationships between chemical cocktails of trace metals and specific conductance during winter months *vs.* other seasons (Kaushal et al. 2019). In some streams, seasonal changes in concentrations of base cations and trace metal ions are primarily due to inputs of road salts during winter months and enhanced ion exchange in soils and mobilization of base cations and metals (Kaushal et al. 2019). Stream temperature, dissolved oxygen, pH and other parameters can also be related to elemental concentrations within chemical cocktails (Kaushal et al. 2018), which suggests data from sensors as potential proxies for different elements across the Periodic Table. The ability to more accurately predict peaks and persistence of distinct chemical cocktails allows us to understand the timing, magnitude, and duration of exceedances of different thresholds which: impair aquatic life in streams, increase corrosion potential of source waters, degrade drinking water quality, and pose recreation and public health risks.

Managing Chemical Cocktails by Predictive Modeling

Comprehensive data on the spatial and temporal variability of chemical cocktails in the environment is necessary for managing water pollution. However, this level of information is often lacking in addition to a complete understanding of the toxicological effects of different chemical cocktails. Therefore, developing a risk management approach is key to evaluating

potential impacts to humans and the environment (Bopp et al. 2019; Posthuma et al. 2018). Methods for estimating toxicity of chemical cocktails have recently been evaluated in Europe (Kienzler et al. 2016; Scientific Committee on Health and Environmental Risks 2012) based on the concepts of response additivity, probability of responses to individual components of a cocktail, concentration additivity, and/or an aggregated toxicity based on the sum of toxicity of individual chemicals (de Zwart et al. 2018). Modeling and forecasting are necessary to predict scenarios of impacts, especially where uncertainty exists due to lack of information on toxicity and/or incomplete or low-resolution empirical survey data (Abdelnour et al. 2013; Barnhart et al. 2018; Beaulieu et al. 2015). Previous researchers have developed a tiered approach to assessing exposure risks based on chemical concentrations in runoff, runoff volume from impervious surfaces in the watershed, and the associated chemical exposure mixture profiles for respective scenarios in urban environments (de Zwart et al. 2018). Such modeling must be done in concert with field level monitoring to provide realistic model outputs. Future work can characterize risks based on land-use scenarios, pollution sources, dilution effects, climate change, and predict ecosystem effects on species losses and other parameters based on chemical compositions of cocktails, concentrations, and temporal variability (*sensu* Posthuma et al. 2018). Such efforts will require coordination with multiple resource agencies, NGO's, and researchers to plan, prioritize, and implement watershed-scale management strategies.

Challenges to Managing Chemical Cocktails and Avoiding Unintended Consequences

Seemingly subtle variations in management approaches can have disproportionate effects on ecosystem outcomes and/or unintended consequences. For example, the lability of organic carbon source (*e.g.* grass vs algae vs leaves) dictates denitrification activity and phosphorous mobilization (Arango et al. 2017; Duan et al. 2019; Newcomer et al. 2012). Unintended mobilization of phosphorous and precipitation of iron from imported rock substrates can also occur in stream restoration and stormwater management features (regenerative stormwater conveyance) when impounded streamwater creates unique anoxic and redox conditions (Duan et al. 2019). It is also important to recognize that some chemical cocktails may be difficult to remove using standard management practices. Common stormwater management has been ineffective for addressing chemical cocktails stemming from road salt contamination (Snodgrass et al. 2017). Other chemical cocktails can be chronically persistent and may not be significantly transformed or assimilated in the urban environment (*e.g.* plastics, PFAS, dioxins, PCP's, *etc.*). Where these chemical cocktails exist, management efforts may need to focus on isolating and containing the chemical cocktails to avoid human exposure, such as at an USEPA Superfund sites (where public access is restricted and consumption of drinking water or food and fish is prohibited or discouraged). Sometimes, extreme and expensive measures such as dredging river sediments (Wasserman et al. 2016), pumping and treating contaminated groundwater (Truex et al. 2017), or capping the sources of chemical cocktails (Taneez et al. 2018) may be the management options of last resort.

Future Research Directions for Monitoring and Managing Chemical Cocktails

Throughout this paper, we have emphasized that research and environmental management communities can potentially infer many processes related to elemental sources, transport, and transformation along hydrologic flowpaths and chemical evolution of major and trace elements. Future research can use data on chemical cocktails to make inferences and new discoveries about urban groundwater systems and groundwater-surface water interactions. For example, information about chemical cocktails can contribute to a better understanding of gaps in our knowledge of the urban hydrologic cycle, if we had more major and trace element data from both shallow groundwater systems and streams. In addition, more research is necessary to identify how the different processes that define each chemical cocktail affect surface and groundwater differently and how groundwater-surface water interactions (and presumably infiltration and inflow of groundwater and storm water into wastewater pipes and sewage overflow from infrastructure) impact the mixtures of different cocktails.

In addition, geochemical mixing model approaches can be developed using chemical cocktails to track pollution sources in watersheds. Different hydrologic flowpaths along urban ecosystems are characterized by mixtures of distinct chemical cocktails we describe throughout this paper. Along hydrologic flowpaths, surface waters in particular acquire a chemical composition that is the result of the mixing of two or more chemical cocktails. More research is necessary to understand how receiving waters are impacted by the aggregation of distinct and different urban chemical cocktails. Future work can develop statistical methods to perform “unmixing” exercises in geochemically complex waters to determine whether we can reconstitute the complex mixture of chemical compositions from distinct ‘endmembers’ of different chemical cocktails associated with sources. Chemical source tracking approaches could be developed, which are analogous to what is done in many modern sediment and nutrient source-tracking studies. Multiple lines of evidence, including laboratory experiments, empirical data collection, and statistical modeling could all be used in attempts to perform chemical cocktail ‘unmixing’ exercises and improve pollution source tracking in urban waters.

More research is also necessary to delineate how the spatial distributions of various chemical cocktails we discuss throughout this paper are related to the spatial distribution of human activities and land uses across broader spatial scales and hydrologic flowpaths along watersheds (including the exurban, suburban, and agricultural areas that are in the headwaters and the more densely urban areas downstream). The spatial distribution of different chemical cocktails is also due to the evolution of chemical cocktails along the rainfall-runoff pathway (some primarily in urban soils, and others in the shallow groundwater system). In addition, some chemical cocktails evolve within sewage infrastructure and leak into both groundwater and surface water. Along the broader urban watershed continuum (Kaushal and Belt 2012), the cumulative and interactive effects of these different chemical cocktails on water quality may be particularly important in receiving waters.

Conclusions

Urban environments make distinct chemical cocktails, and the watershed chemical cocktail approach can be used to trace pollution sources, better inform co-management strategies for multiple contaminants, track multiple chemicals using proxies from continuous sensors, and understand more holistic impacts on ecosystems from an ecotoxicological perspective. Grouping of elements has already been useful in chemistry through the organization of groups and families of elements along the Periodic Table. In addition, geochemists widely use classification of similarities in chemical behavior of elements in the Earth based on their affinities for reactivity with other elements (siderophillic or affinity for Fe, chalcophillic or affinity for S, Se, Te *etc.*). Our review and synthesis show that chemical cocktails form and evolve in urban waters over diurnal cycles, decades, and throughout drainage basins (Figures 4–10). Contaminant transport and transformation do not occur one element at time in urban watersheds. Multiple approaches may need to be implemented to retain and transform chemical cocktails in watersheds either simultaneously or sequentially along hydrologic flowpaths (Newcomer Johnson et al. 2016) to capture a significant portion of urban runoff (inputs). Ultimately, a watershed chemical cocktail approach targeting sources, transport, and transformations of distinct elemental combinations and contaminants is necessary to more holistically monitor and manage the emerging impacts of chemical mixtures in the world's fresh waters.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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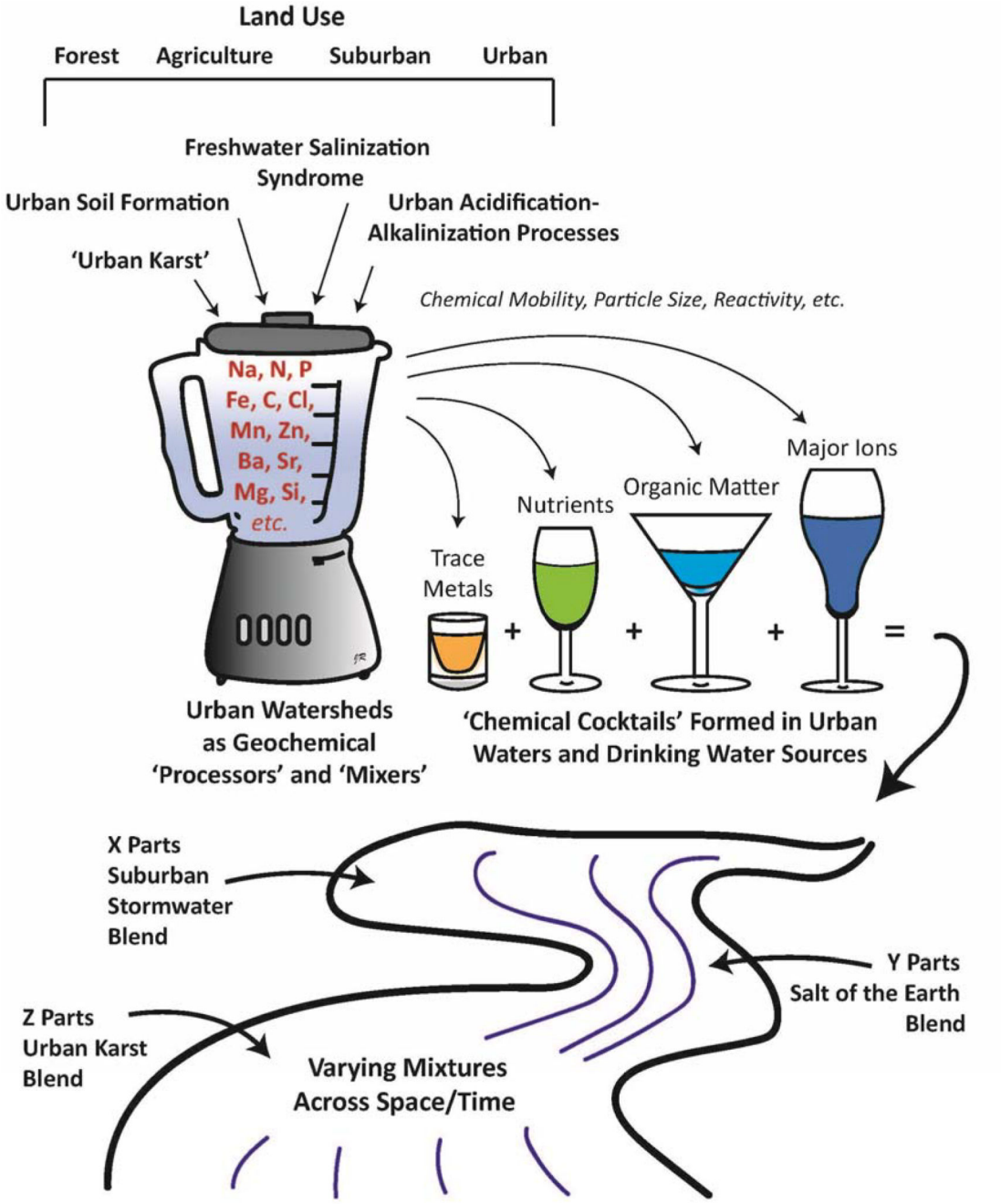

Figure 1.

Conceptual model illustrating how groups of elements can be grouped as 'chemical cocktails' and transported in urban waters. Elemental inputs to the watershed originate from different urban geochemical sources and processes. Chemical cocktails are mixed hydrologically across time and space in watersheds through surface flowpaths (impervious surfaces, construction materials, altered geomorphology, *etc.*) and subsurface flowpaths (stream burial, urban karst, pipes, soil compaction, *etc.*). Urban geochemical processes form distinct elemental combinations of nutrients, metals, salt ions, and organics that are

transported and transformed along hydrologic flowpaths based on factors such as chemical mobility, particle size, and reactivity. These different chemical cocktails can become mixed together along hydrologic flowpaths and their sources may be traced using diverse analytical approaches.

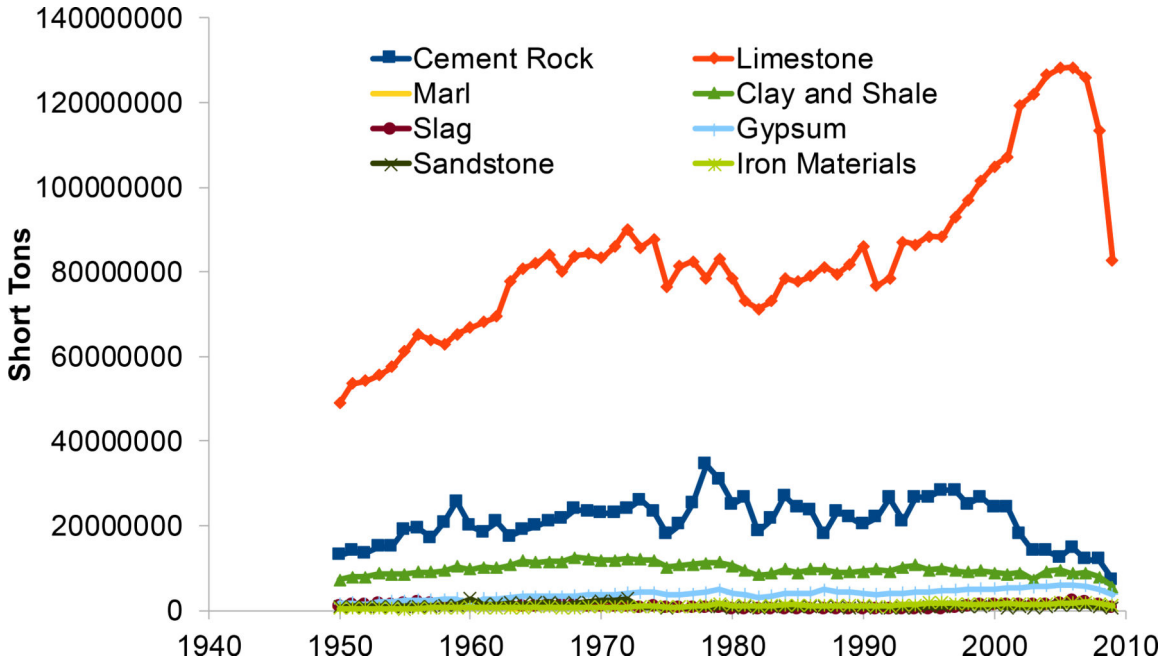

Figure 2.

Long-term changes in geologic materials used to make concrete in the United States. This widespread proliferation of geologic materials used to make concrete can degrade over time through accelerated weathering of impervious surfaces contributing to transport of chemical cocktails of major ions to urban waters. Data are from U.S. Geological Survey Minerals Yearbook.

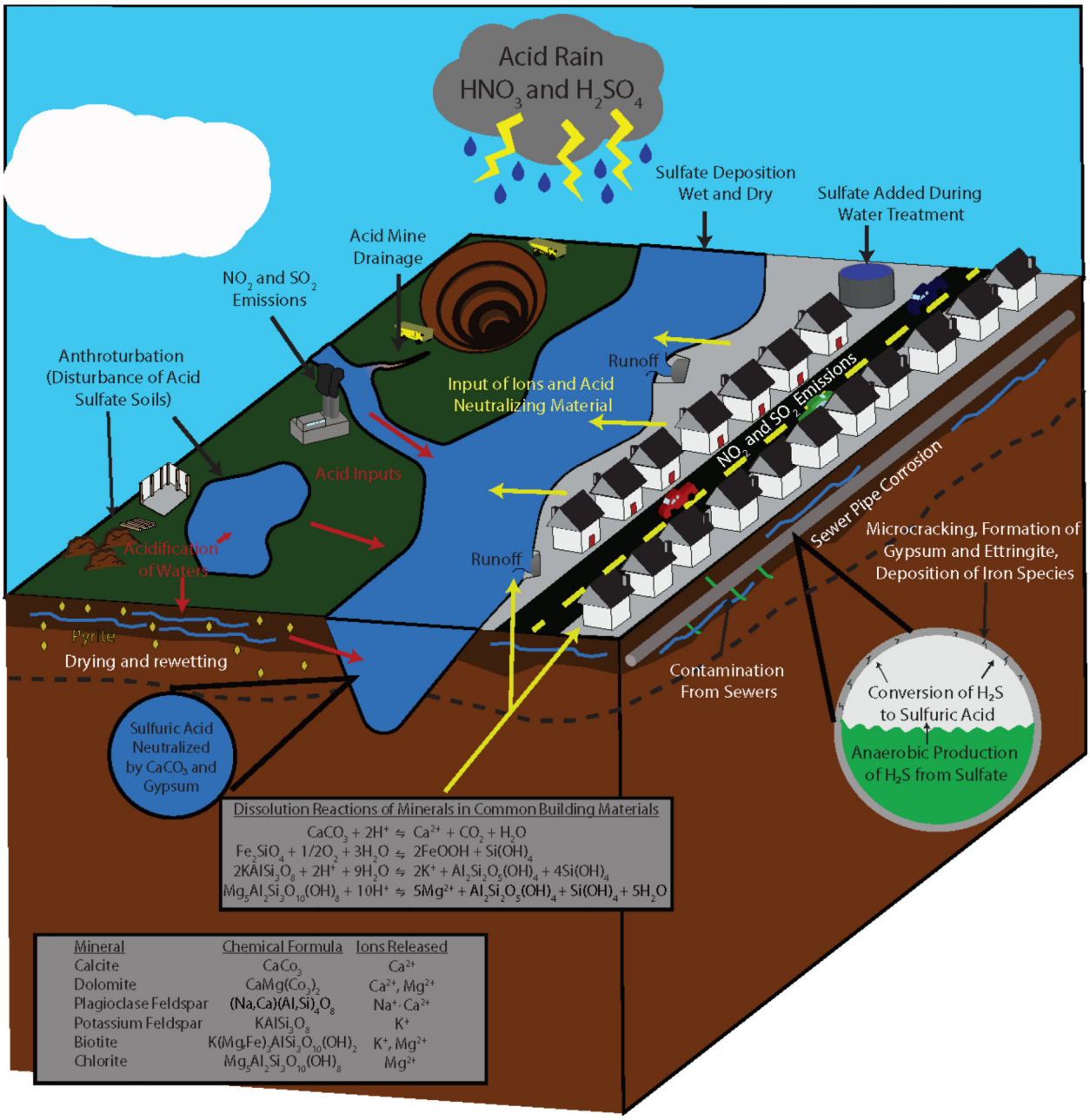

Figure 3.

Conceptual diagram of human-accelerated weathering of impervious surfaces and corrosion of pipes illustrating how human activities contribute major ions and metals to distinct chemical cocktails in urban waters. Human-accelerated weathering and corrosion of infrastructure can be associated with acidic precipitation and anaerobic processes in sewer pipes.

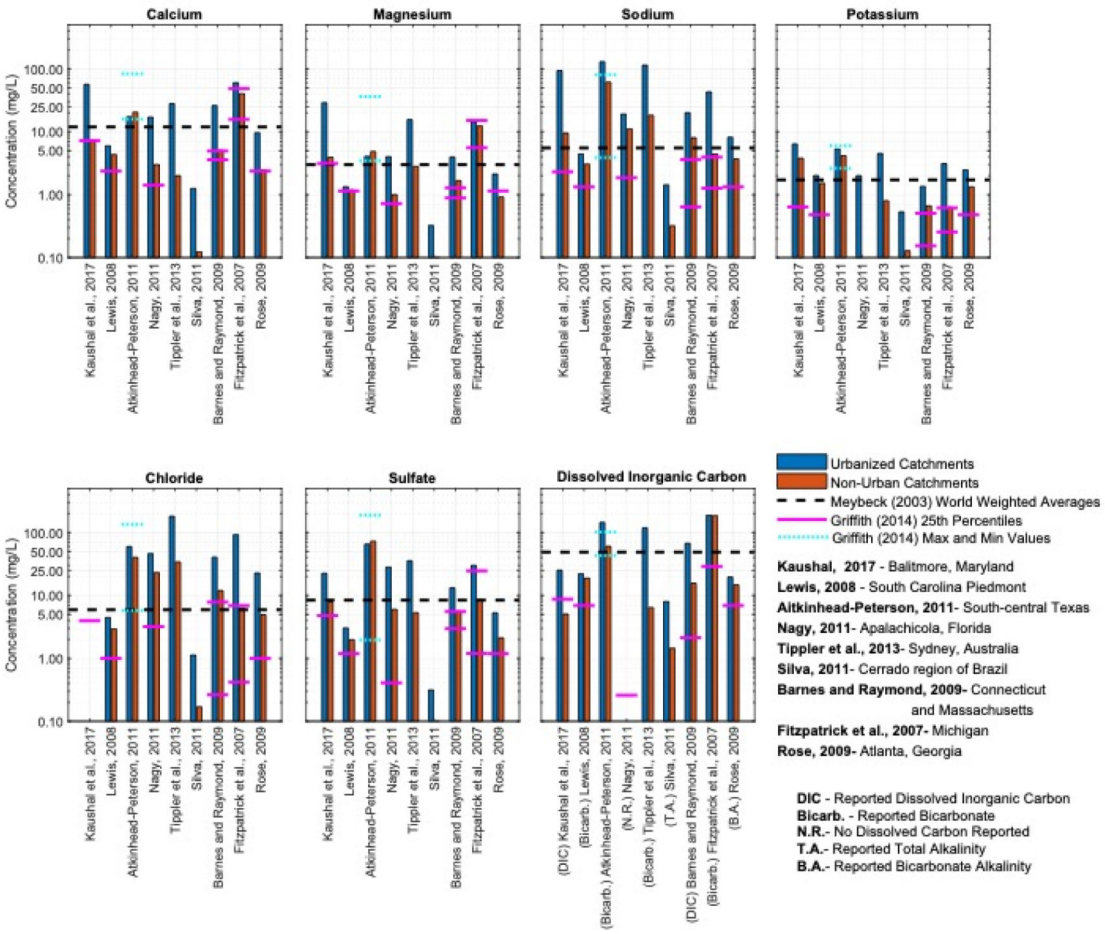

Figure 4.

Mean major ion concentrations in streams for urbanized watersheds and reference watersheds for nine selected studies spanning a range of study areas. Mean dissolved concentrations of major ions are consistently higher within urban watersheds when compared to reference watersheds, despite variability in absolute concentrations among the nine studies. This result is evidence of the ‘overprint’ of urban geochemical processes influencing major ions, which are superimposed onto natural geochemical processes influencing major ion concentrations. Where applicable, the 25th percentile concentration reported by Griffith (2014) is indicated using pink lines for the corresponding US EPA Level III Ecoregion encompassing each study area. Where study areas span Ecoregions, both are indicated. Griffith (2014) only reported maximum and minimum values in some Ecoregions due to limited data availability. These are shown using blue lines for studies without a 25th percentile concentration. Two studies are outside the United States; the world weighted average river concentrations provided by Meybeck (2003) are shown as a dashed horizontal line for reference. The nine studies reported dissolved inorganic carbon (DIC) species in different ways; these ways are listed in the bottom right plot within the figure. Supporting Information includes further details.

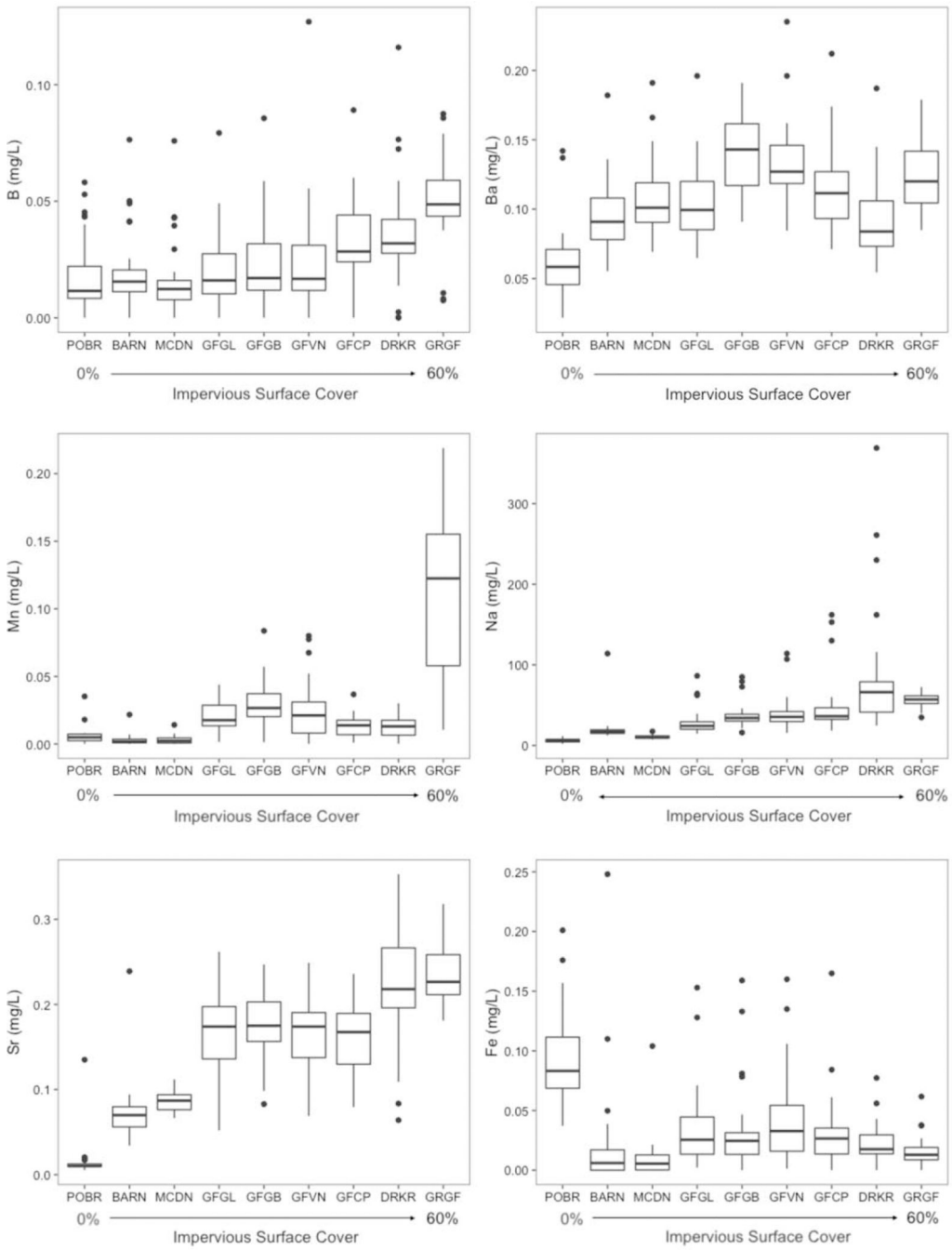

Figure 5.

Concentrations of major and trace elements in streams draining a land use gradient at the Baltimore Long-Term Ecological Research (LTER) site over almost 2 years of bi-weekly sampling. Center vertical lines of the box and whiskers indicate medians. Lengths of each whisker show ranges within which the central 50% of the values lie. Edges of the boxes indicate the first and third quartiles. Dark circles represent outside values.

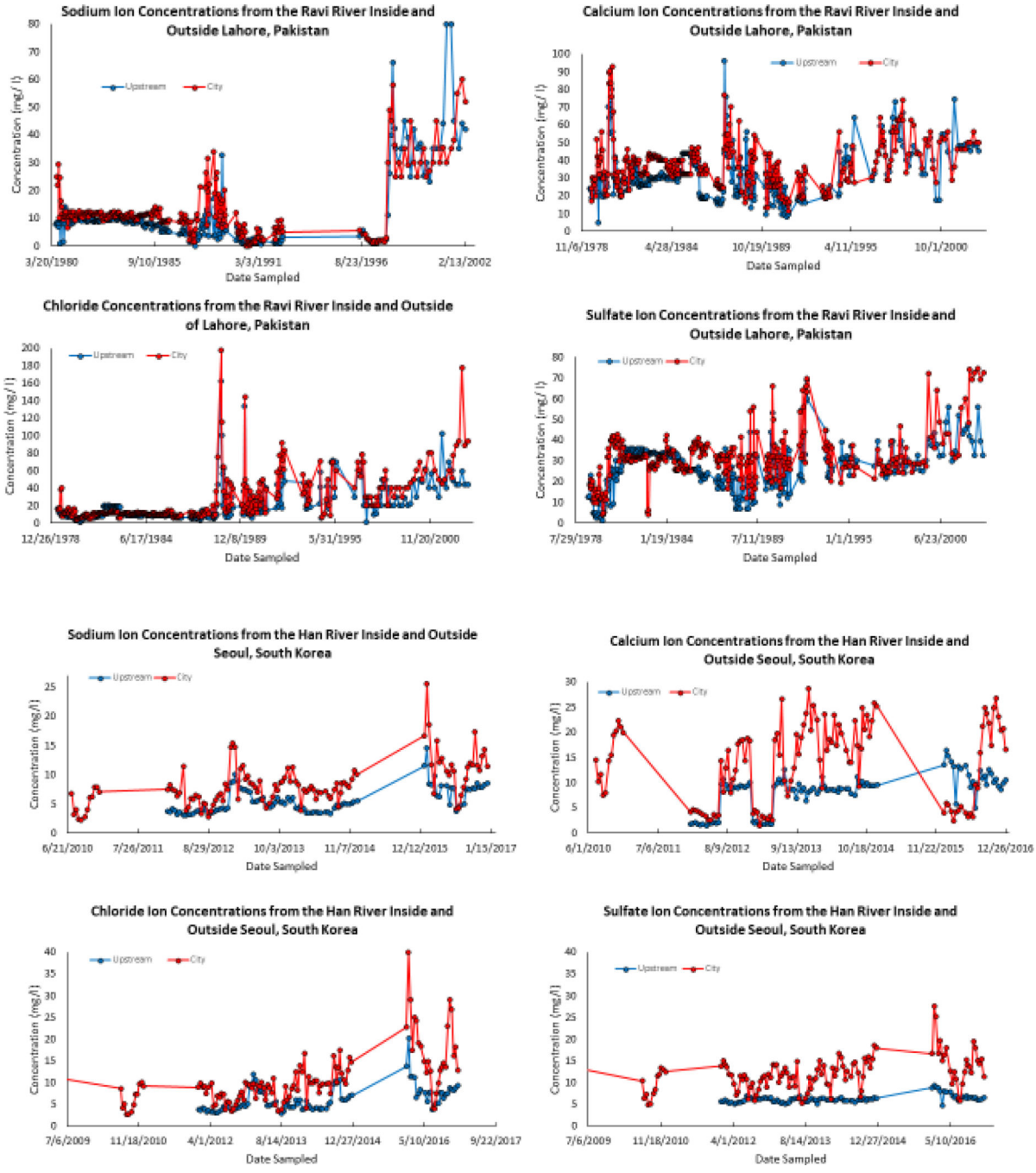

Figure 6.

Major ions can increase in rivers downstream of cities. For example, along the Ravi River inside and outside of Lahore, Pakistan concentrations of Na^+, Ca^{2+}, Cl^-, and SO_4^2 are significantly higher in the city than in the river upstream of the city over 3 decades from 1978 to 2002. Likewise, Na^+, Ca^{2+}, Cl^-, and SO_4^2 are significantly higher in the Han River downstream versus upstream of Seoul, South Korea from 2010 to 2016. Data are from GEMStat.

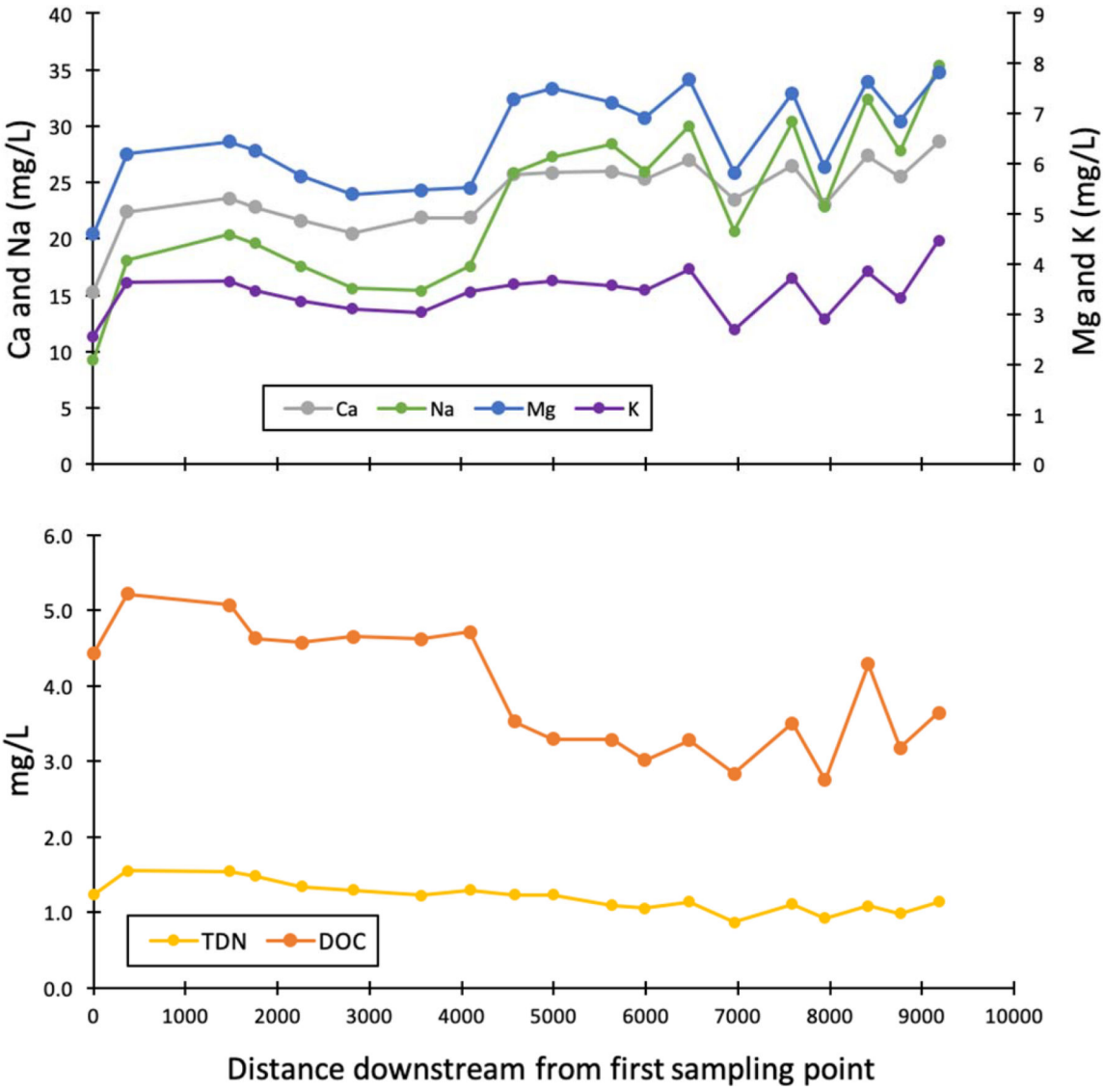

Figure 7.

Concentrations of major ions simultaneously increase with increasing distance downstream (meters) from a fixed sampling point along the Anacostia River near College Park, Maryland. Conversely, concentrations of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) decrease with increasing distance downstream. The simultaneous changes in concentrations suggest similar hydrogeochemical processes and sources contributing to the formation of different chemical cocktails along urbanized drainage networks.

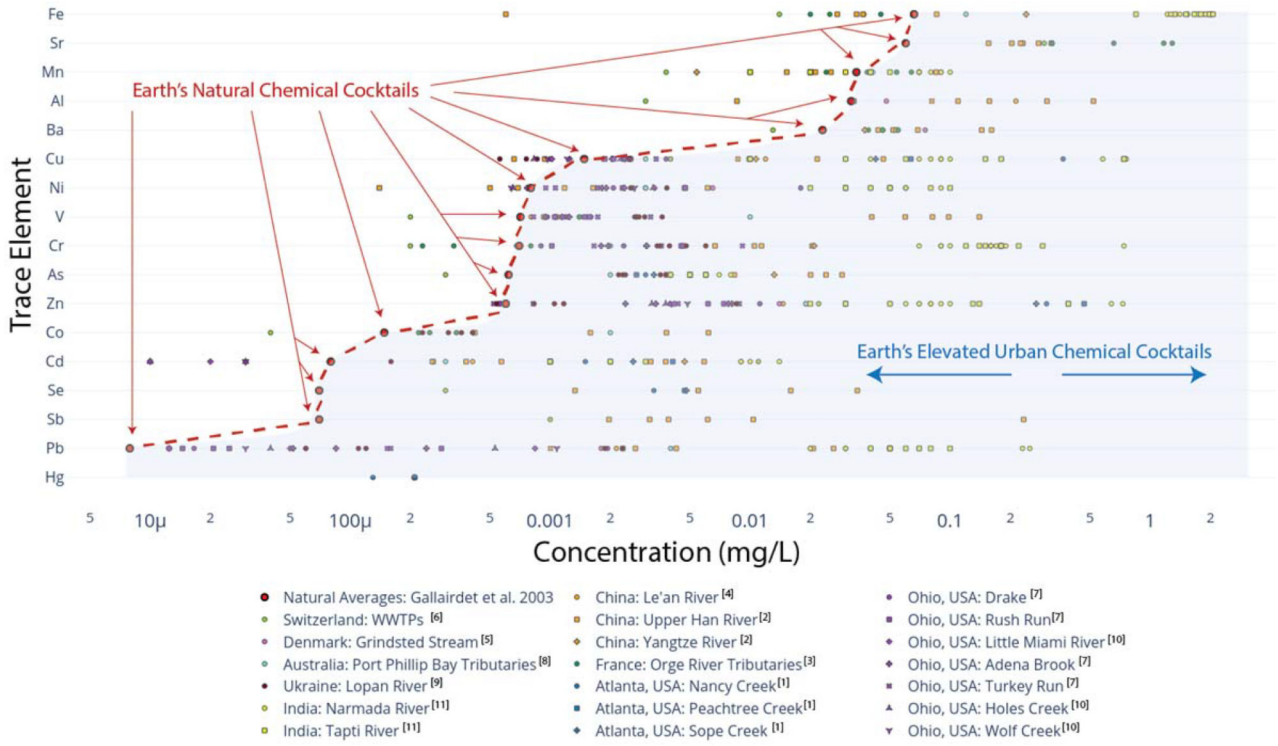

Figure 8.

Global averages of natural concentrations of trace elements in streams and rivers (shown as red dots) are in order from greatest concentration on the bottom to the least concentration on the top. Examples of elemental concentrations in some different urban streams and rivers are typically higher than the natural global averages (shown as black dots). Further information regarding numbers corresponding to specific data sets from literature references are provided in the Supporting Information.

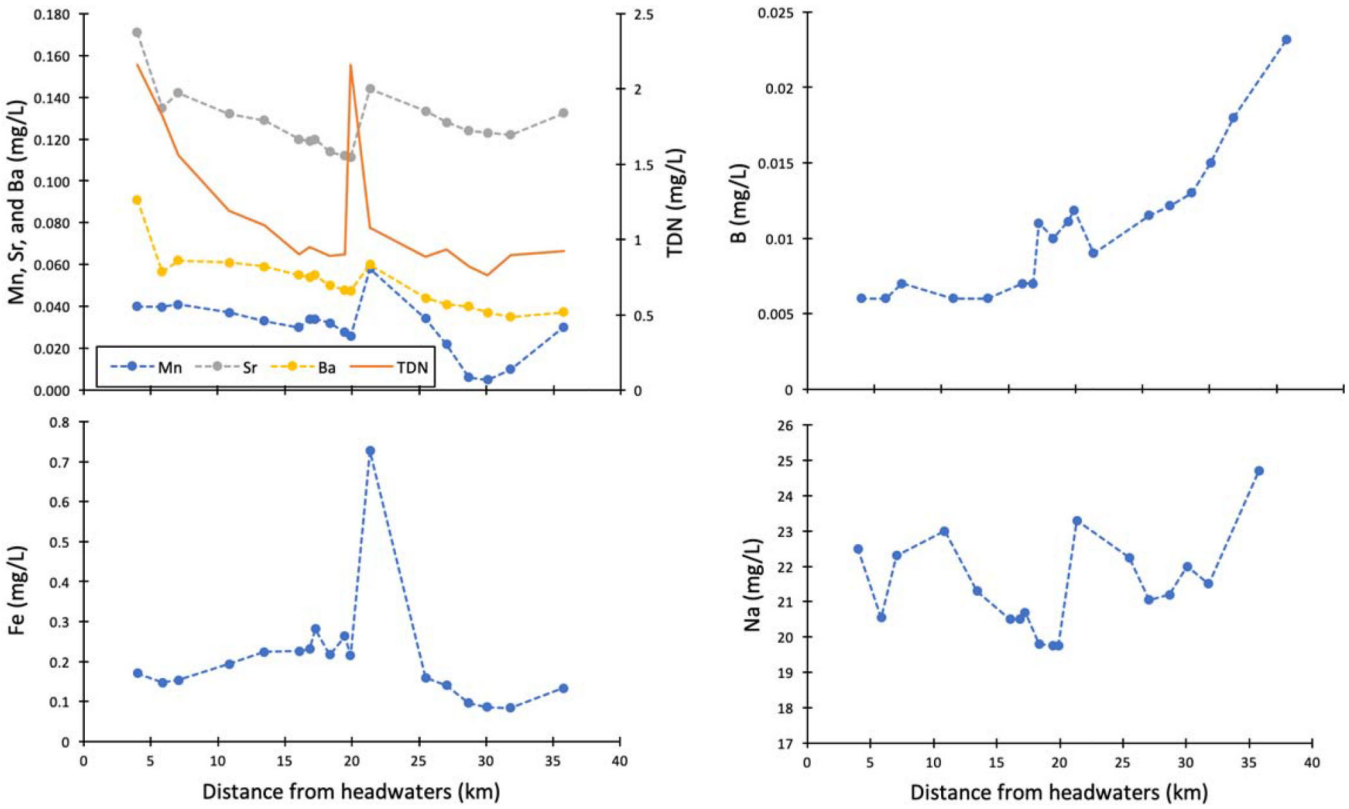

Figure 9.

An example of synoptic patterns in elemental concentrations along the Gwynns Falls watershed of the Baltimore Long-Term Ecological Research site. Concentrations of major and trace elements increase, peak, or show pulsed patterns with increasing distance downstream based on sources, transport, and transformations. Some elemental mixtures show very similar longitudinal patterns suggesting that they can be transported and transformed as watershed chemical cocktails.

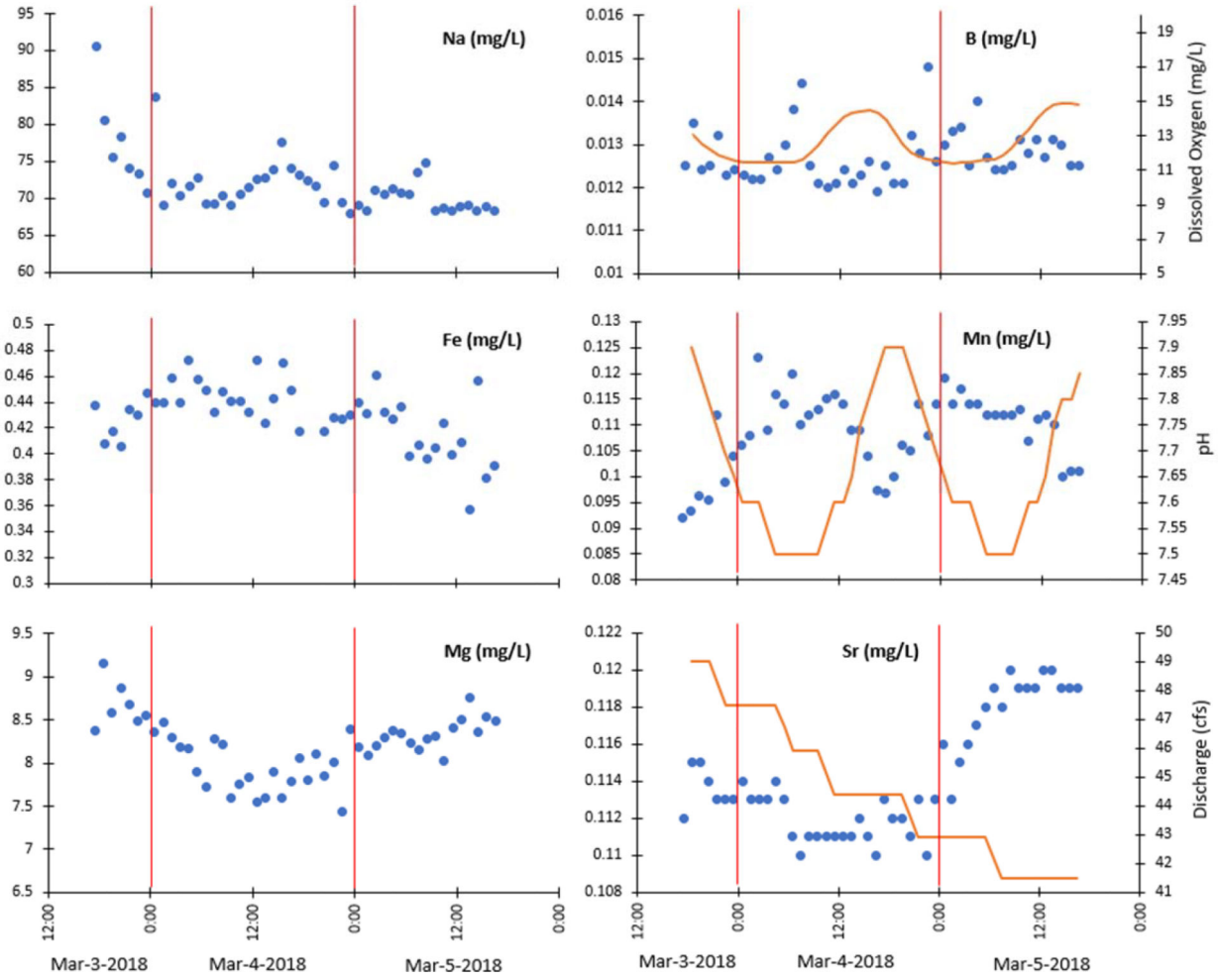

Figure 10.

Chemical cocktails of major and trace elements are formed over diurnal cycles in the Anacostia River near College Park, MD coinciding with changes in streamflow, dissolved oxygen, and pH from *in situ* sensor data in streams. Orange bars indicate the start of each new day. Elemental concentrations from laboratory measurements are plotted as blue circles on the left axes, while data measured by high-frequency sensors is plotted as orange lines on the right axis. Red vertical bars indicate the start of each new day.

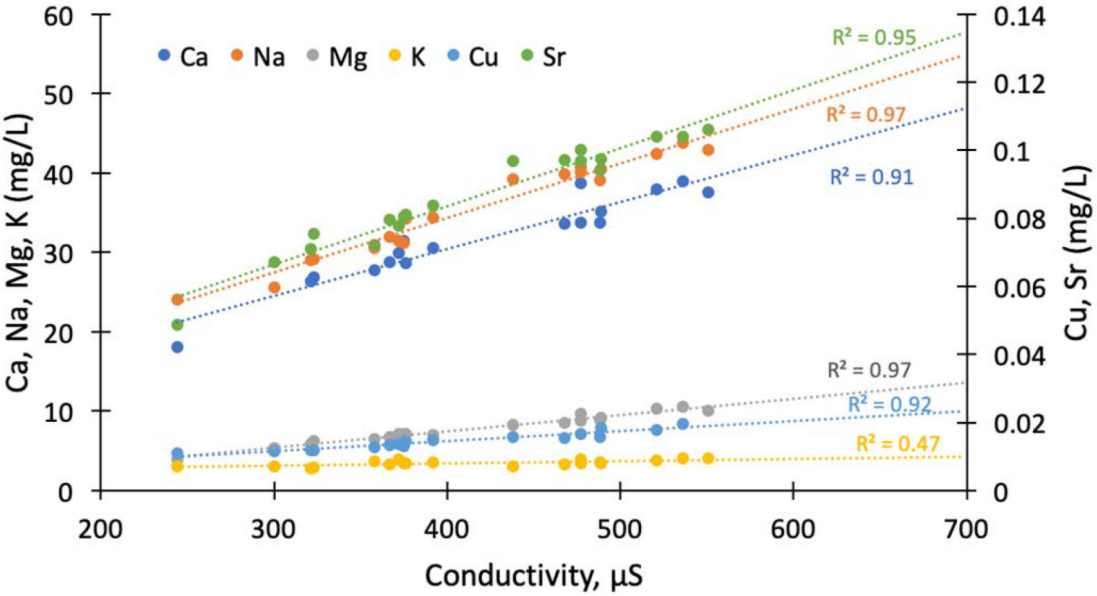

Figure 11.

There are significant relationships between specific conductance and some major and trace elements in Paint Branch, an urban stream near Washington D.C.

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Table 1:

A broad summary of the geochemical affinities of species of nitrogen, phosphorus, carbon, base cations, and trace metals. A major point of this table is to not only list the geochemical affinities, but to give a prediction on how Freshwater Salinization Syndrome can influence the cycling of chemical constituents in urban streams. Based on their affinities, the elements/compounds were demarcated into 1 or more of the 4 categories mentioned in the text (1=organic matter complexes, 2=ion exchangeable, 3=redox sensitive, 4=transition metals), and a directional hypothesis for change in concentration in response to FSS was postulated.

Elemental Compound	Geochemical Affinities	Major Process affected by salinization	Unknown in geochemical behavior	FSS Cocktail Group and Directional Hypothesis	Response Variable	Other studies
NH_4^+	Production in sediments during organic matter decomposition, Strong adsorption onto sediment particles in freshwater (especially clay)	Increase in Na, competition for exchange sites, inhibition of nitrification microbes	Temperature dependency of adsorption, desorption contribution to N mineralization	2,3, Increase	TDN	Weston et al, 2010, Seitzinger et al, 1991
NO_3^-	Relatively mobile form on N, Product of nitrification in shallow sediments	Increase in NH_4 leading to increases in nitrification, inhibition of microbes	Hydrologic flowpath sources in human-dominated watersheds	2, Increase		
DON	Protein and amino acids, largely refractory, Intermediate reduced products during N cycle by microbes or humification reactions, Redox sensitive, coupled with DOC	Increases in ionic strength inducing organic matter colloid dispersion, inhibition of ammonification microbes	Measurement and classification of DON is difficult.	3, Decrease		Burdige and Zheng, 1998
SiO_4	Sediment surface reactions with alkali complexes to form sodium complexes, Ionic composition increases reactivity and hydrolysis reactions, Stable behavior in soils	Increased ionic strength can increase the dissolution kinetics of Silica from quartz or oxide sediments, Increase Na concentrations	Microscopic role of Na at the oxide mineral-solution interface, stoichiometric relationship with aluminum	1, Increase	Si	Dove and Elston, 1992
Ortho PO_4^{3-}	Complexation reactions with metals (Fe, Al, Mn) and base cations to insoluble forms, Flocculation/settling of insoluble forms, Redox reactions, Behavior coupled with S	Increased ionic inducing competing processes of flocculation and colloid dispersal, Changes in pH increasing reduction potential, dissolution desorption, Presence of anions (Cl^-, NO_3^-) increase PO_4^{3-} sorption due to keeping Fe oxidized	Microbial cycling pathways and buffer system, exchange-able phosphorous content on sediment and soils, anaerobic-aerobic transition in stream sediments	1,3, Increase or net effects of competing processes	SRP	Baldwin et al, 2006, Duan and Kaushal 2015, House, 2003
Poly/Organic PO_4^{3-}	Amino and fatty acids bound within organic matter colloids,	Changing ionic composition inhibiting microbial cycling			N/A	
CO_2	Solubility of CO_2 decreases with salinity, microbial metabolism and chemical weathering byproducts	Inhibition of microbial respiration and mineralization, pH induced dissolution of carbonate minerals	Temperature kinetics in sediments and rivers	1, Increase	DIC	Weiss, 1974
HCO_3^-	Solubility increases with salinity, chemical weathering byproducts			1, Increase		Meybeck, 2003

Elemental Compound	Geochemical Affinities	Major Process affected by salinization	Unknown in geochemical behavior	FSS Cocktail Group and Directional Hypothesis	Response Variable	Other studies
Humic/Fulvic Acids	Protein-like, Redox sensitive, Generally coupled with polyphosphates and DON, potentially hydrophobic, binds to colloidal, tendency to flocculate, complexation reaction with base and metal cations	Na dispersal could increase solubility of protein-like material, inhibition of microbial process	Lability of specific compounds and influence of hydrologic flowpaths	1,3, Increase with greater solubility at higher pH or no change	DOC	Green et al, 2009, Duan and Kaushal 2015
Ca	Outer-sphere surface Reactions (hydrated), High Ionic Potential, Sorption affinity controlled by oxidation state, then ionic radius, Potential redox reactions	Increased Na concentrations increases competition for sediment exchange site	Effect of changing ionic composition on sediment and reduction potential	1,2,3, Increase	Ca	Stumm and Morgan 1996, Honeyman and Santschi, 1988, Vengosh, 2003
Mg				1,2, Increase	Mg	
K				1, 2, Increase or Constant *	K	
Zn	Redox Reactions, Surface Protolysis Reactions, Electrolyte Surface Reactions, Cation Inner-sphere Surface Reactions, Low Ionic Potential, Sorption affinity controlled by oxidation state, then ionic radius	Increased Na concentrations increases competition for sediment exchange site	Effect of changing ionic composition on sediment and reduction potential	2,3, Increase	Zn	Stumm and Morgan 1996, Honeyman and Santschi, 1988, Vengosh, 2003, Kaushal et al. (2018 a, b)
Sr				2,3, Increase	Sr	
Cu	Redox Reactions, Complexation Reactions, Chelation-ligand formation, Surface Protolysis Reactions, Electrolyte Surface Reactions, Cation Inner-sphere Surface Reactions, Low Ionic Potential, Transition metal: sorption affinity depends on electron configuration	Shift in pH affects reduction potential, changes in ionic strength causing colloid dispersal from sediment layer to suspension, increased chloride concentration enabling formation of chloro-organic matter complexes, inhibition of microbial metabolisms	Electrostatic thresholds for sorption affinity, anaerobic-aerobic transition in stream sediments, effect of changing ionic competition on reduction potential	3,4, Increase	Cu	
Mn				3,4, Increase	Mn	

*Although we hypothesize the concentrations of elements in FSS cocktail group 1 and 2 to increase and we place K within these groups by behavior, K has a larger ionic radius than Na and is more biologically reactive, which can affect its concentrations.

Table 2.

Examples of urban geochemical processes and the major ions affected by each process.

Urban Geochemical Process	Chemical Cocktails of Major Ions	Some Literature Examples
Wastewater Inputs	K^+, Na^+, Cl^-, SO_4^{2-}	Verbanck et al. (1989) Rose (2007)
Infrastructure Dissolution	Ca^{2+}, Mg^{2+}, HCO_3^-, CO_3^{2-}	Tippler et al. (2014) Davies et al. (2010)
Evaporative Concentration	All Major Ions	Grimmond and Oke (1999)
Atmospheric Particulates	SO_4^{2-}, Cl^-	(Stumm and Morgan; Honeyman and Santschi 1988; Vengosh 2003)
Road Salt Applications	Na^+, Ca^{2+}, Mg^{2+}, Cl^-	Steele, McDowell, and Aitkenhead-Peterson (2010)
Soil Acidification and Weathering	Na^+, Mg^{2+}, Ca^{2+}, K^+, and HCO_3^-	Aquilina et al. (2012)
Urban storm sewer	F^-, Cl^-, SO_4^{2-}, Li^+, Na^+, NH_4^+, and K^+.	Gardner and Carey (2004)

Table 3:

Selected sources of trace elements ubiquitous in the built environment. Data are from Pacyna & Pacyna, 2001; Leung & Jiao, 2006; Nriagu & Pacyna, 1988; Gardner and Carey 2004; Hjortenkrans 2007.

Anthropogenic Source	**Chemical Cocktails of Trace Elements**
Gasoline combustion	Pb, Mn
Coal * and oil combustion (power plants)	V, Ni, Cr, Pb, Mn, Zn, Cu, As, Mo, Sb, Ti, Hg *, Cd, Se *, Mo *
Refuse incineration **	Pb, Zn, Cr, Mn, Cu, As, Ni, Hg, Sb, Sn, V, Se, Cd
Municipal wastewater treatment	Mn, Ni, Zn, Cr, Cu, As, Pb, Cd
Sewage sludge	B, Cr, Pb, As, Zn, Sb, Sn
Motor oil	V, Zn, Cr, Cu, Pb, Ni, and Mo
Vehicular and industrial discharge	Zn, Pb, As, Cr, Cu
Vehicle brake and tire wear	Cd, Cu, Zn, Pb, Sb, Ni, Zn
Leakage from pipes	Sr, Se
Corrosion of metal objects	Mn, V, Co, Mo
Atmospheric deposition	Pb, Zn, Cu, Ni, As, Mn, Cr, V

* denote trace elements produced by coal combustion, not in significant quantities *via* oil combustion.

** denote refuse incineration is highly variable and dependent on the composition of the original refuse (listed elements are those seen on average).