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Watershed 'chemical cocktails': forming novel elemental combinations in Anthropocene fresh waters

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Abstract In the Anthropocene, watershed chemical transport is increasingly dominated by novel combinations of elements, which are hydrologically linked together as 'chemical cocktails.' Chemical cocktails are novel because human activities greatly enhance elemental concentrations and their probability for biogeochemical interactions and shared transport along hydrologic flowpaths. A new chemical cocktail approach advances our ability to: trace contaminant mixtures in watersheds, develop chemical proxies with high-resolution sensor data, and manage multiple water quality problems. We explore the following questions: (1) Can we classify elemental transport in watersheds as chemical cocktails using a new approach? (2) What is the role of climate and land use in enhancing the formation and transport of chemical cocktails in watersheds? To address these questions, we first analyze trends in concentrations of carbon, nutrients, metals, and salts in fresh waters over 100 years. Next, we explore how climate and land use enhance the probability of formation of chemical cocktails of carbon, nutrients, metals, and salts.

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Ultimately, we classify transport of chemical cocktails based on solubility, mobility, reactivity, and dominant phases: (1) sieved chemical cocktails (e.g., particulate forms of nutrients, metals and organic matter); (2) filtered chemical cocktails (e.g., dissolved organic matter and associated metal complexes); (3) chromatographic chemical cocktails (e.g., ions eluted from soil exchange sites); and (4) reactive chemical cocktails (e.g., limiting nutrients and redox sensitive elements). Typically, contaminants are regulated and managed one element at a time, even though combinations of elements interact to influence many water quality problems such as toxicity to life, eutrophication, infrastructure corrosion, and water treatment. A chemical cocktail approach significantly expands evaluations of water quality signatures and impacts beyond single elements to mixtures. High-frequency sensor data (pH, specific conductance, turbidity, etc.) can serve as proxies for chemical cocktails and improve real-time analyses of water quality violations, identify regulatory needs, and track water quality recovery following storms and extreme climate events. Ultimately, a watershed chemical cocktail approach is necessary for effectively co-managing groups of contaminants and provides a more holistic approach for studying, monitoring, and managing water quality in the Anthropocene.

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Introduction

The Anthropocene has typically been characterized by an acceleration of climatic, biological, and geochemical signatures of human activity preserved in the geologic record beginning in the mid 20th century (Waters et al. 2016). While the term Anthropocene is widely used, it is still being debated in the scientific community as to whether it is a distinct geological epoch and exactly when it begins. The Anthropocene can be characterized by an increase in the transport of novel combinations of inorganic and organic chemicals (i.e., chemical cocktails) in fresh waters over time (Bernhardt et al. 2017a; Kaushal et al. 2018). For example, nonpoint source pollution in human-impacted watersheds has increased in recent decades resulting in trends in concentrations of carbon, nutrients, salts, and metals (Foley et al. 2005; Kaushal et al. 2005; Raymond et al. 2008; Sinha et al. 2017; Seitzinger and Phillips 2017; Dugan et al. 2017; Kaushal et al. 2017). In addition to increased nonpoint source pollution, the frequency of floods and droughts has increased (Mallakpour and Villarini 2015;

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Archfield et al. 2016). The interaction between nonpoint source pollution and climate variability (Milly et al. 2008) amplifies watershed storage and release of most inorganic and organic chemicals, which can be observed in water quality records (e.g., Kaushal et al. 2014a, b; Loecke et al. 2017). Yet, the transport behaviors of distinct chemical mixtures within watersheds is controlled by a complex suite of hydrologic interactions between atmospheric deposition, geology, landscape modification, and water management (e.g., Bernal et al. 2012; Kaushal and Belt 2012; Likens 2013). Human interactions simplify drainage networks, amplify stormwater pulses, accelerate chemical weathering, and magnify fluctuations in redox potentials across soil/sediment-water interfaces. All of these interactions enhance the formation of novel elemental combinations in watersheds, which we herein define as 'chemical cocktails'. These chemical cocktails are novel because human activities significantly: (1) enhance elemental concentrations above natural background conditions and (2) increase the probability for biogeochemical interactions and/or shared transport of elements along hydrologic flowpaths.

A watershed chemical cocktail approach accounts for converging sources, flowpaths, and reactivity of novel combinations of elements in the Anthropocene. Most studies in watershed science have focused on the dynamics of one or only a few elements in isolation rather than the synergistic behavior of combinations of elements (e.g., Burns et al. 1998; Kaushal et al. 2008, and many other biogeochemical studies). Here, we propose that interactions between landscape modifications and climate enhance formation of novel combinations of elements, or chemical cocktails, depending upon their physical and biogeochemical properties (e.g., particle size, solubility, charge, and reactivity) across both short and long-term temporal scales. There is a need to move beyond the 'black box' approach of watershed mass balances for individual elements to simultaneous examination of multiple element cycles. A watershed chemical cocktail approach allows for the characterization of distinct water quality signatures and sources for multiple elements across land use, underlying geology, atmospheric deposition, and climate, which has not been fully considered in watershed science. A watershed chemical cocktail approach can also be applied to high-frequency sensor data to develop surrogates and proxies (e.g., turbidity, specific conductance, pH, nitrate, etc.) for characterizing complex chemical mixtures transported in watersheds. Chemical cocktails can also be used to diagnose interactive effects of emerging contaminants on ecosystem functions and services and comprehensively evaluate unintended consequences or multiple benefits of watershed restoration. Elemental transport and transformations don't function in isolation in nature, and we demonstrate that this is particularly the case for chemical cocktails throughout this paper.

Climate and land use change mobilize different chemical cocktails during hydrologic events due to increasingly pulsed mixing of water and chemical reactants in soils and aquatic ecosystems (Kaushal et al. 2014a, b; Loecke et al. 2017). Drainage simplification, increasingly pulsed hydrology, and an increased probability of biogeochemical interactions warrant a reconceptualization of watershed transport and transformation processes based on natural conditions (e.g., Vannote et al. 1980). Widespread drainage of wetlands and stream channelization decreases hydrologic storage and groundwater—surface water interactions, which exacerbates drying of soils and oxidation of chemical species during droughts. As a result, multiple oxidation by-products (sulfate, nitrate, Fe oxides, Mn oxides) accumulate during oxic events, and are then flushed together either as dissolved, colloidal or sediment bound chemical cocktails during storms (Burgin et al. 2011; Jenne 1968; Lupon et al. 2016; Hartland et al. 2015). Engineered drainage networks designed to efficiently move water downstream accelerate combined transport of dissolved carbon, nutrients, and sediment-bound chemical cocktails of metals (Helsel et al. 1979). In contrast, wetlands and stormwater management slow runoff, reduce dissolved O_2 during inundation, enhance microbial reduction events, dissolution, and mobilization of iron, manganese, phosphorus, and arsenic cocktails (Jenne 1968; Hartland et al. 2015). Human-accelerated weathering (such as carbonate dissolution from impervious surfaces) enhances formation of novel combinations of major ions (Kaushal et al. 2013, 2017; Haq et al. this issue). Finally, atmospheric deposition interacts with climate and land use to affect sorption and formation of organic carbon cocktails transported to streams and rivers (Monteith et al. 2007; Duan and Kaushal 2013).

In this paper, we propose a new watershed chemical cocktail approach based on a review and analysis of evidence from previously published case studies that trace mechanisms of shared sources, hydrologic flowpaths, formation, and reactivity of elements along the terrestrial-aquatic continuum. We explore the following two questions: (1) can we classify elemental transport in watersheds as chemical cocktails using a new conceptual approach? (2) what is the role of climate and land use in enhancing the formation and transport of watershed chemical cocktails in the Anthropocene? We also explore the potential impacts of an increase in frequency, magnitude, and speed of drying-rewetting cycles on the short-term and long-term evolution of chemical cocktails.

Reconceptualizing watersheds as sieves, filters, chromatographic columns, and reactors

We propose an approach that classifies both the formation and transport behaviors of novel combinations of elements into distinct chemical cocktails based on their solubility, reactivity, binding capacity, and dominant phases during hydrologic events. These physical and biogeochemical properties influence the formation and transport mobility of groups of elements within watersheds, and thus, the timing of the chemical pulse in streams and rivers during storms (vertical axis in Fig. 1) and their chemical transport distance downstream (horizontal axis in Fig. 1). Note that the same element can show multiple transport and transformation behaviors depending upon redox conditions, biological demand, solubility and other environmental factors (Fig. 2). All of these factors fluctuate significantly during drying-wetting cycles (Fig. 2). For example, nitrate and sulfate can show chromatographic transport behavior or reactive transport behavior depending upon the degree of ion exchange, biological demand, and redox conditions. Similarly, metals can show chromatographic transport behavior when mobilized from ion exchange sites or they can show sieved and filtered transport behavior when they form organometallic complexes or are present in mineral colloid and particulate forms. Thus, examples of chemical cocktails described below only represent a typology or spectrum of potential transport behaviors of different elemental combinations and mixtures.

Watersheds as sieves: particulate organic matter, mineral solids, and sorption of metal oxyhydroxides

Particulate bound or 'sieved' chemical cocktail transport behavior describes when particulate organic matter (POM), nitrogen, and phosphorus of biogenic origin, iron, aluminum, and manganese oxyhydroxides and elements associated with aluminosilicate species (as aggregates and coatings, and various other organometallic complexes) are rapidly flushed during storms. These particulate chemical cocktails settle out in response to changes in flow velocities or are 'sieved' out as water flows through soils and sediments (largely physical and mechanical separation based on size and density). Therefore, suspended solids and particulate bound elements are mobilized in an initial chemical pulse during storms in streams and rivers (e.g., Mulholland et al. 1990), typically showing a rapid increase during the ascending limb of the hydrograph and rapid decrease on the falling limb, although there can be exceptions in timing and hysteresis based on locations of sediment sources (Hamshaw et al. 2018). Sediment mobilization is also represented by an increase in turbidity, which can serve as a proxy or surrogate for suspended sediment concentrations, on the ascending limb of the storm hydrograph (Fig. 3). The magnitude of this particulate-bound cocktail pulse and its transport downstream is influenced by sedimentation and adsorption rates, while insoluble elements become adsorbed onto clay particles and other organic, mineral, and sediment surfaces (Chiarenzelli et al. 2012). Overall, the location of watershed sediment sources (stream channel, riparian zone, floodplains, vs. uplands) impacts the composition, timing, duration, and travel distance of downstream particulate-bound pulses before they are sieved by soils and sediments, through mechanical and physical separation based on size, density, and changing particle velocities (e.g., Hamshaw et al. 2018) (Fig. 1).

Watersheds as filters: colloidal and dissolved organometallic complexes

Transport of sieved and filtered chemical cocktails varies primarily based on particle size (particulate vs. dissolved), and the smaller sized colloids and dissolved organic matter are further 'filtered'
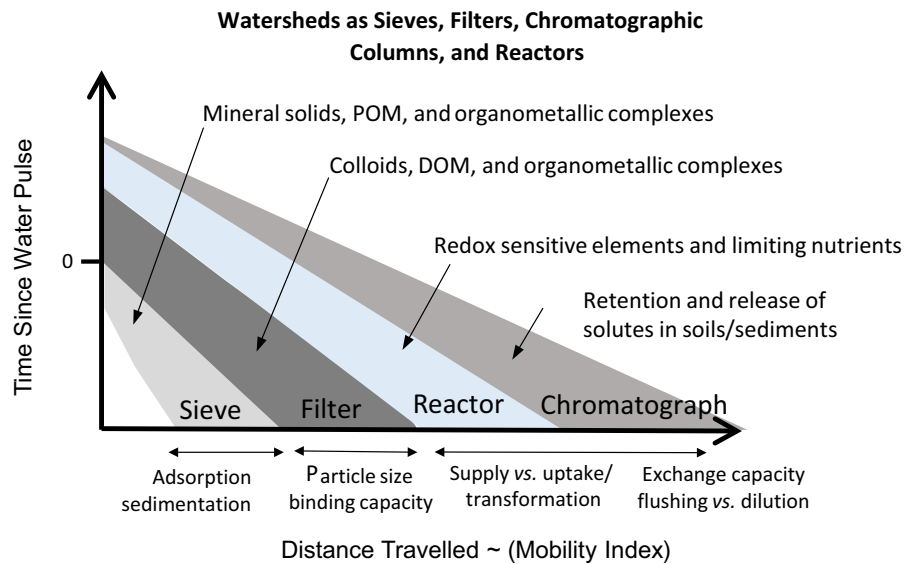
Fig. 1 Conceptual model illustrating how groups of elements can be hydrologically linked as 'chemical cocktails' and transported along fluvial networks of the Anthropocene depending on the timing of the peak (before or after the hydrograph peak), and the distance travelled along the fluvial network. Chemicals showing 'sieved' behavior such as mineral solids, particulate organic matter (POM) and organometallic complexes usually lead to primary pulses because sources are in surficial soil layers; they travel short distances due to sedimentation and adsorption or 'sieving' through soils and sediments. Secondary pulses correspond to elements showing 'filtered' transport behavior such as colloids, dissolved organic matter (DOM) and bound metals. These have a smaller particle size as dissolved chemicals compared to sieved transport. Consequently, they are more persistent, and can travel longer

distances than sieved transport before eventually being filtered through soils and sediments based on size, hydrophobicity, and sorption. Chemicals showing chromatographic transport behavior such as cations and anions can have the highest mobility as they are either eluted or diluted from different catchment pools. The timing of transport from these pulses will depend on the size and location of sources within watersheds and on the soil ion-exchange capacity. The pulse and mobility of reactive chemical cocktails, mostly biologically essential and limiting nutrients and redox sensitive elements, further depend on biogeochemical transformations and biological assimilation within watersheds and fluvial networks. Thus, reactive chemical cocktails can exhibit shorter travel distances than pure chromatographic transport behaviors of elements

mechanically and chemically based on size, density, hydrophobicity, and charge as water flows through soils and sediments. Dissolved organic matter (DOM) and associated elements bound to DOM molecules represent a secondary pulse of chemical cocktails mobilized during floods following coarser particulates. Typically, the pulse in DOM is initiated later in a hydrologic event than the pulse in sediment bound chemicals, which can be represented by turbidity as a surrogate or proxy. However, the proportional relationships between total suspended solids and turbidity and DOC and turbidity can be different (Fig. 3). Similar to coarser particulate matter, finer colloidal and dissolved organic matter form complexes with metals (iron, copper, lead, zinc, mercury), and their binding capacity depends on different size fractions, hydrophobic versus hydrophilic chemical fractions of DOM, and sorption potential (Kaushal and Lewis

2005). In response to storms, the DOM pulse (and associated elements) is more persistent than the POM pulse over time (Fig. 3). Firstly, this is because POM typically originates from near stream sources while DOM can be flushed through the catchment from sources further away. Secondly, this is because during the recession limb of the hydrograph, coarser particles settle out rapidly while the finer size fractions of DOM can still be mobilized and travel further downstream, until they are filtered through smaller pores in soils and sediments.

Watersheds as chromatographic columns: ions are eluted from soil and sediment exchange sites

Ions represented by 'chromatographic' transport behaviors include H^+, Ca^{2+}, Mg^{2+}, Na^+, and Cl^-. These ions can be rapidly flushed in a primary pulse, or

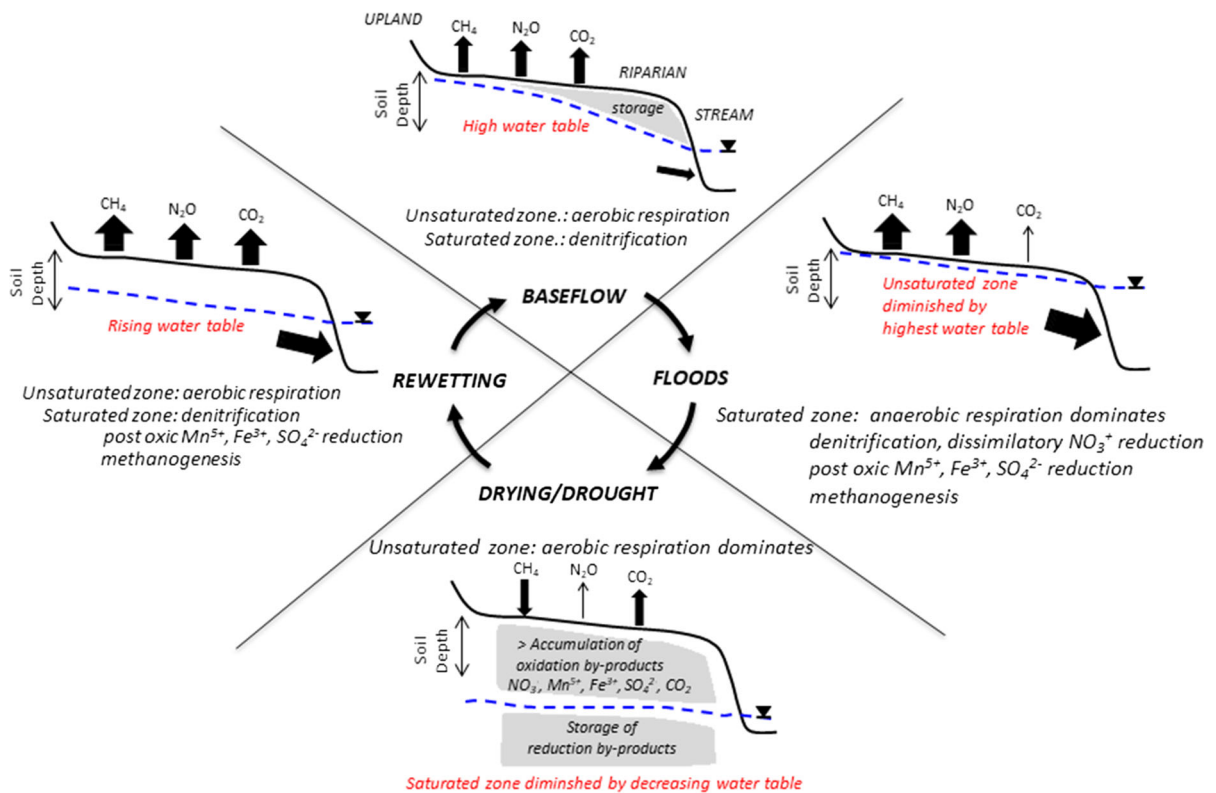## Formation of Reactive 'Chemical Cocktails' during Drying-Rewetting Cycles

Fig. 2 Conceptual model illustrating how reactive chemical cocktails vary in formation and transport along the drying-rewetting cycle with water table, pre versus post precipitation conditions, and soil redox conditions. Sources and sinks of reactive chemical cocktails are stratified vertically along the soil profile and longitudinally along the drainage network as water moves along elevation gradients (Grimm et al. 2003). During floods, peaks in greenhouse gas production may occur due to inundation and decreases in redox potential. During hydrologic contractions, the riparian groundwater table can become vertically disconnected from superficial soil layers. As the groundwater table lowers, previously reducing zones become oxidized and rates of mineralization increase, which produces an abundance of oxidized products such as nitrate, sulfate, iron and manganese oxides, and others. As soils rewet, anaerobic greenhouse gas production increases again and oxidized products and DOM can be quickly mobilized (DOC, NO_3^-, SO_4^{2-}, PO_4^{2-}, Fe and Mn oxides, etc.). During rewetting periods, old water enriched with reduced forms of elements (e.g., Fe, Mn), weathering products (e.g., Ca, Mg, K, Na), and solutes concentrated by evapotranspiration are also pushed out laterally in ground water. Thus, elements are sequentially reduced or oxidized while moving from uplands to streams, starting the drying-rewetting cycle over and over again

'first flush', if they have accumulated in near surface environments (e.g., acid rain, urban road salts, agricultural liming). However, significant pools of these ions are also typically located deeper in soil profiles due to chemical weathering of bedrock or mobile ion effects leading to rapid transport through the soil profile and eventual accumulation in ground water (Fig. 1). Therefore, many of these ions show differences in their chromatographic transport behaviors based on shallower versus deeper hydrologic flowpaths. Along deeper hydrologic flowpaths, chemical cocktails exhibiting chromatographic transport are diluted on the ascending limb of the hydrograph, and there is increased transport during the recession limb from groundwater recharge forming a tertiary pulse during storm hydrographs that follows the pulses of particulates (sieved) and dissolved organic matter (filtered) chemical cocktails. Specific conductance can serve as a proxy or surrogate for most major ions and tends to peak on the receding limb of the hydrograph along with nitrate, following pulses in sediment-bound chemicals (represented by turbidity) and DOM (Fig. 3). As an example, chloride and base cations typically peak on the recession limb of hydrographs
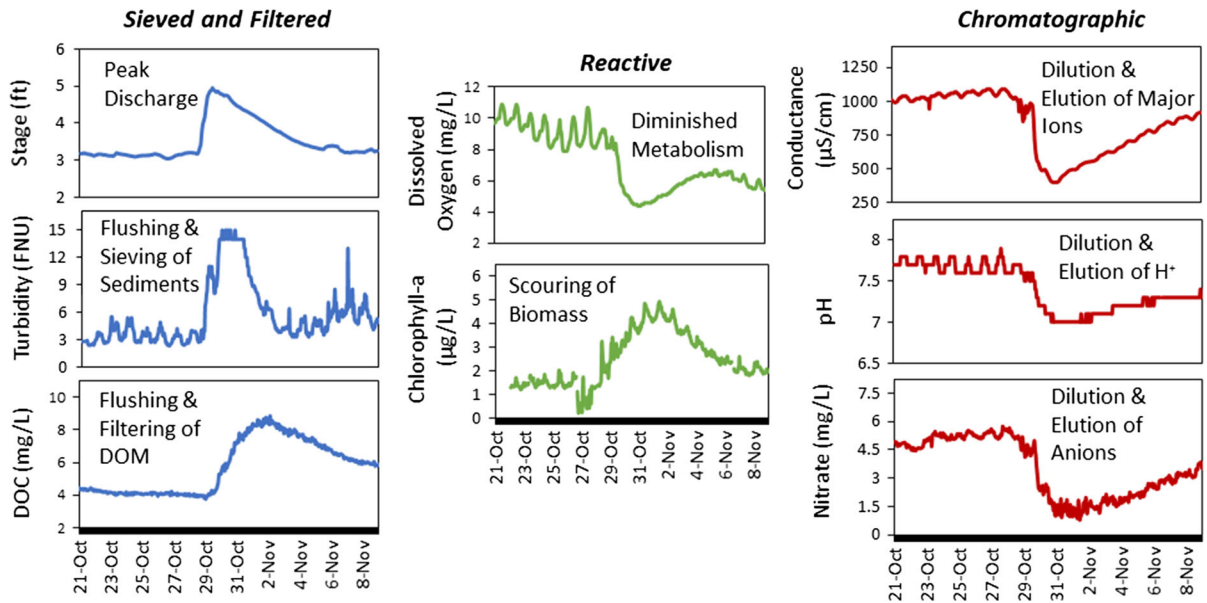
Fig. 3 Changes in water quality during Hurricane Patricia in the Passaic River, New Jersey, USA. The responses in water quality are typical of urban streams and rivers in the Mid-Atlantic U.S. region. Sediment bound chemicals and dissolved organic matter form a primary pulse before they are retained by being 'sieved' and 'filtered' as they pass through soils and sediments. Reactive chemical cocktails are highly influenced by stream metabolism and redox conditions. Microbial biofilms are scoured during floods and then gradually recover afterwards contributing to increasing amplitudes in diurnal cycles of oxygen and nitrate. Chromatographic chemical cocktails are typically diluted during the peak in the hydrograph and then increase on the receding limb as groundwater recharge increases in importance. An exception can be H^+ ion, which can be rapidly flushed from soil exchange sites and contribute to episodic acidification and a decrease in pH during storms. Data are courtesy of USGS gauge 1389005

due to accumulation and recharge from deeper groundwater flowpaths. In contrast, hydrogen ions accumulate in upper surficial soil horizons from acid rain and peak on the ascending limb of the hydrograph due to ion exchange and rapid flushing, which causes a rapid decline in pH resulting in episodic acidification (Fig. 3). The potential for flushing versus dilution of chromatographic chemical cocktails is based on pool sizes, storage during preceding drying periods, and deeper versus shallower hydrologic flow paths. When dominant pools are mobilized along deeper hydrologic flowpaths, chromatographic chemical cocktails produce longer sustained pulses downstream than sieved and filtered chemical cocktails before undergoing ion exchange in soils and sediments.

Watersheds as reactors: redox sensitive elements and limiting nutrients

Reactive transport behavior of chemical cocktails such as ammonium, nitrate, phosphate and sulfate is strongly influenced by biogeochemical processes occurring throughout drying/rewetting cycles (Fig. 1). Biological demand and redox conditions within the watershed and along the drainage network influence pulse magnitude as well as the transport distance of these bioreactive ions (Lupon et al. 2016). The importance of ecosystem metabolism as a regulator of chemical transport during baseflow conditions in human-impacted watersheds can be lost transitorily after storms. For example, there is initial scouring of stream microbial biofilms during extreme storms, but photoautotrophic biofilms and chlorophyll *a* can exhibit a rapid recovery (Fig. 3). However, stream metabolism and diurnal fluctuations of oxygen, nitrate, and other chemicals can recover over weeks

following disturbances (Smith and Kaushal 2015; Reisinger et al. 2017) (Fig. 3). Biological activity contributes to remove essential and limiting nutrients that support life from soil water and ground water, and to dynamically transform chemical phases from dissolved to particulate to gas. For example, elements such as C, N, and S can be "lost" from watersheds as gases due to aerobic respiration, methanogenesis, hydrogen sulfide formation, and denitrification (Fig. 2). Moreover, they can be retained and stored in biomass or in soils as particulate organic matter due to biological assimilation and microbial decomposition. This organic matter can then be decomposed and mineralized into soluble C, N, P, and S ions.

As mentioned previously, elements can show multiple transport behaviors as chemical cocktails depending upon environmental conditions. For example, iron and manganese can show reactive transport behavior depending on redox conditions and their presence as dissolved versus particulate forms (Fig. 2). Ultimately, reactive transformations such as organic matter mineralization, biological uptake, and abiotic/biotic oxidation-reduction reactions (in the context of metals, sulfur, and other elements) form pools of elements that are sieved, filtered, diluted, or eluted before being transformed again in response to drying-rewetting cycles (Fig. 2). There have been synergistic increases in nutrients such as nitrate and dissolved organic carbon in many fresh waters over the long-term, which suggests a potential increase in the global significance of biologically reactive chemical cocktails (Fig. 4). In succession, an increase in long-term total and dissolved organic carbon concentrations can also influence transport of complexed metals in fresh waters (sieved and filtered chemical cocktails). Below, we discuss examples of formation and different transport behaviors of chemical cocktails in watersheds. We use chemical abbreviations for brevity in some cases, particularly for ions.

Chemical cocktails illustrating sieved and filtered transport behavior: organic C, N, and P and organometallic complexes

Organic matter represents a diversity of chemical mixtures, which transport organic nutrients and complexed metals (Buffam et al. 2001; Inamdar and Mitchell 2007; Raymond and Saiers 2010; Wilson

et al. 2013) that are both sieved and filtered through soils and sediments. Changes in DOM cocktails [e.g., dissolved organic carbon (DOC), nitrogen (DON), phosphorus (DOP)] and their chemical composition occur with increasing discharge and are associated with a shift to shallower flow paths through near surface soils, riparian soils, and wetlands with high organic matter content (Boyer et al. 1996; Mei et al. 2014; Wilson et al. 2016; McGlynn and McDonnell 2003; Inamdar et al. 2011). Under flushing conditions characterized by high flow and high concentration, a shift toward the export of more carbon rich DOM (higher C:N), higher molecular weight, and more aromatic material has frequently been observed in headwater systems (Hood et al. 2006; Vidon et al. 2008; Wilson and Xenopoulos 2009; Wilson et al. 2016). Accompanying these compositional changes, amounts and proportions of labile DOM cocktails can also increase because recently flushed aromatic compounds have been identified as more bioreactive and photoreactive (greater %DOC reactive to biodegradation and photodegradation) than those exported during baseflow (Kaushal and Lewis 2005; Fellman et al. 2010; Fasching and Battin 2012; Lu et al. 2013; McLaughlin and Kaplan 2013; Coble et al. 2016; Wilson et al. 2016). The magnitude, persistence, and transport distance of aromatic compounds increases with storm magnitude (Raymond and Spencer 2015; Creed et al. 2015), which has implications for associated organic nutrients and complexed metals.

Many trace metals share similar modes of transport and transformation associated with chemical cocktails of DOM and colloids, inorganic clays, or particulates as ligands or metal oxides and hydroxides. The close association between organic and inorganic particulates and colloids, and metals fosters the formation of chemical cocktails of organometallic complexes in watersheds (Fig. 1). For example, there are significant positive relationships between iron and DOC concentrations during storms in urban watersheds (Fig. 5). Rapid pulses in total iron and aluminum concentrations during storms in urban watersheds suggest chemical transport as oxyhydroxide particulates from surface soils and near stream environments more similar to POM and DOM responses rather than deeper flowpaths typical of nitrate and calcium ions (Fig. 5). Concentrations of dissolved trace elements such as iron, aluminum, manganese, and zinc all show correlations with pH and DOC concentrations in aquatic
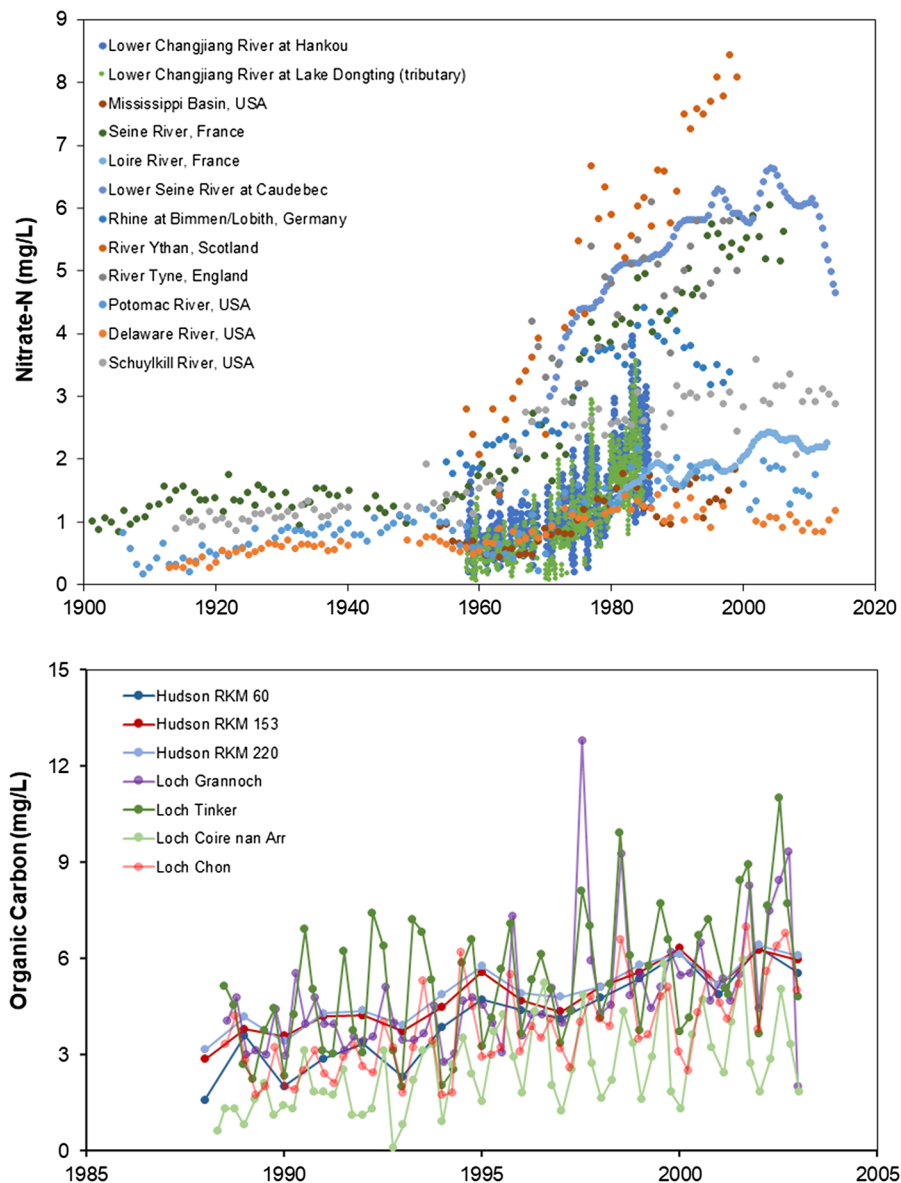
Fig. 4 There has been an increase in chemical cocktails of nutrients and organic carbon in global fresh waters during the Anthropocene. (Top panel) Nitrate concentrations ($N-NO_3^-$ in mg/L) from rivers around the world from 1902 to 2014. Before the 1950s these records show concentrations below 2 mg/L. After 1950, nitrate concentrations increased coinciding with events such as the production of chemical fertilizers for modern agricultural practices (US EPA 2015). North American datasets include the Potomac River, USA, Delaware River, USA, Schuylkill River, USA (Jaworski, unpublished data), and the Mississippi River, USA (Goolsby and Battaglin 2001). European datasets include the Loire River, France (Minaudo et al. 2015), Seine River, France (Meybeck et al. 2016; Romero et al. 2016), Rhine at Bimmen/Lobith, Germany (European Environment Agency 2012), River Ythan, Scotland (European Environment Agency 2012), and River Tyne, England (European Environment Agency 2012). Asian datasets include the Lower Changjiang River at Hankou and at Lake Dongting, China (Duan et al. 2007). (Bottom Panel) Monthly and seasonal organic carbon concentrations (in mg/L) from surface waters in the northeastern United States and United Kingdom from 1988 to 2003. United Kingdom datasets of upland catchments show significant upward trends potentially resulting from changes in discharge, increased temperatures, and changes in land management (Worrall et al. 2004). Hudson River data also demonstrate upward DOC and DOM teens (Findlay 2005), potentially linked to changes in temperature, rainfall, land-use, nitrogen, and CO_2 enrichment (Evans et al. 2005). WebPlotDigitizer was used to extract data from graphs when it was not available in text form (Rohatgi 2017)

Fig. 5 (Top panel) Relationships between total iron concentrations (particulate plus dissolved) and dissolved organic carbon (DOC) following Superstorm Sandy in urbanized streams of the Baltimore Long-Term Ecological Research site. (Middle panel) Relationships between total dissolved nitrogen and dissolved organic carbon (DOC) following Superstorm Sandy in urbanized streams of the Baltimore Long-Term Ecological Research site. GFGL and GFGB are suburban watersheds and GFVN and GFCP are urban watersheds. (Bottom panel) Changes in elemental exports in the Gwynns Falls watershed at the Baltimore Long-Term Ecological Research site following Superstorm Sandy. Fe and Al fluxes are attenuated more rapidly than base cations likely due to settling and 'sieving' of particulate Fe and Al oxyhydroxides as water passes through soils and sediments
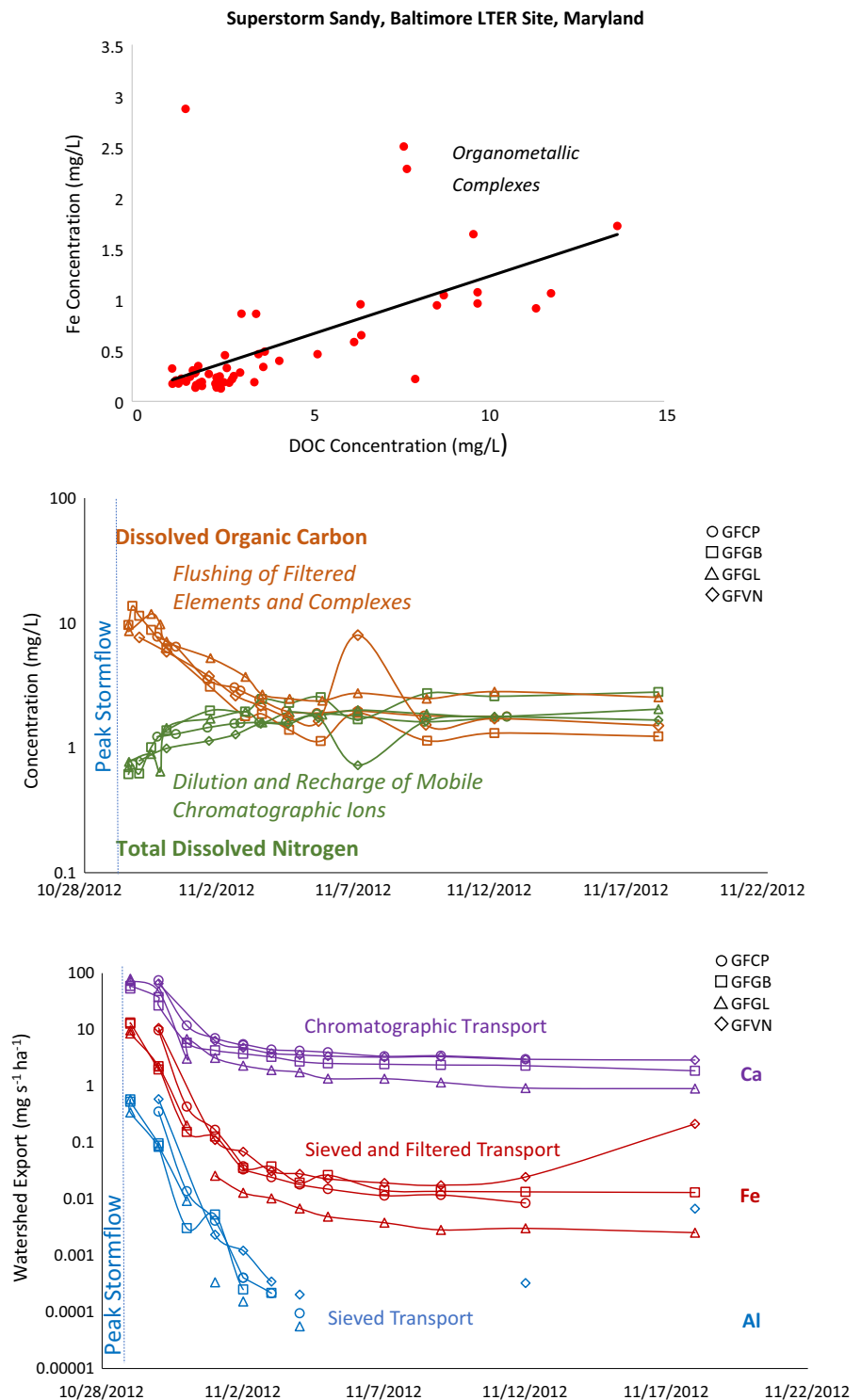
environments, which affects solubility and potential for watershed sieving and filtering (Gaillardet et al. 2003). In particular, trace metal ions complex with the negatively-charged surfaces of organic colloids within the pH range of natural waters, at 4–8 (Dupre et al. 1999). As such, organic colloids are important carriers

of a variety of low-mobility trace metals (beyond just iron) in riverine waters and therefore influence coupled geochemical transport and transformation (Gaillardet et al. 2003). Because clay and/or DOC content can increase during high-flow events, the concentrations of trace elements in the stream water also increase during floods (Mohiuddin et al. 2010), and copper, cobalt, manganese, chromium, and vanadium all exhibit positive linear relationships with the proportion of colloidal DOC in fresh waters.

Inorganic colloids are also important in the formation of chemical cocktails with trace metals, which are sieved and filtered through soils and sediments. Inorganic colloids can be enhanced during extreme climate events by: (1) reduction and dissolution of iron oxides during wetting; (2) precipitation of iron and other metal oxides (manganese) at the oxic riparian stream interface; and (3) sorption of DOM by hydrous iron and aluminum oxides in oxic stream water (McKnight and Bencala 1990). Metallic oxyhydroxides—especially those composed of iron, aluminum, and manganese—are the most common mineral colloids in streams and rivers (Gaillardet et al. 2003). Inorganic colloids often occur in close association with organic colloids, and also with clay particles in the water column. As such, DOC is a useful index of both inorganic and organic colloidal chemical cocktails as suggested by the positive relationships between trace element contamination and colloid concentrations in streams worldwide (e.g., Dupre et al. 1999; Viers et al. 1997). However, it is important to note that mineral colloids can track sediment pulses in some cases. Ultimately, the transport behavior of inorganic colloids as sieved or filtered chemical cocktails depends largely on their provenance and surface chemistry.

How do land use and climate alter elemental responses and give rise to novel combinations?

DOM exported from agricultural and urban watersheds exhibits a greater prevalence of microbially derived and protein- like DOM (Baker and Spencer 2004; Wilson and Xenopoulos 2008, 2009; Petrone et al. 2011; Hosen et al. 2014; Kaushal et al. 2014a, b, c; Lu et al. 2014; Williams et al. 2016). These chemical fractions of organic matter are important for transport of DOC, DON, and DOP in sieved chemical cocktails, which can eventually contribute to eutrophication and hypoxia in receiving waters. These changes in DOM quality have been attributed to reduction of the relative input of more aromatic DOM from terrestrial sources and increased in-stream DOM production and processing due to increased loading of N and P primarily during baseflow (Wilson and Xenopoulos 2009; Hosen et al. 2014; Lu et al. 2013, 2014; Kaushal et al. 2014a, b; Butman et al. 2015; Williams et al. 2016). Pulses of aromatic DOM with high binding capacity for metals are amplified in urban and agricultural watersheds during storm events (Kaushal et al. 2014a, b, c; Smith and Kaushal 2015), and this affects chemical cocktails of DOM, organic N and P, and complexed metals (Frost et al. 2015). There are also pulses of aromatic DOM and POM from human sources (e.g., polycyclic aromatic hydrocarbons), which are rapidly flushed during storms across land use (Fig. 6).

Changes in the chemical cocktails of POM, DOM, and inorganic particulates associated with urbanization and agriculture alter timing, duration, and transport distance of metals during storms (copper, zinc, iron, etc.) (Characklis and Wiesner 1997). Both urban and agricultural lands experience elevated levels of POM and labile DOM from nonpoint sources (Kaushal et al. 2014a, b, c), which are associated with a significant fraction of metals loads in streams. Riparian zones, streambeds, stormwater ponds, and wetlands can also be important sources or sinks of particulate matter and associated copper, zinc, lead, and cadmium chemical cocktails depending on streamflow; thus, hydrological and structural alterations of these landscape components influence the formation and transport of different organometallic chemical cocktails (Bain et al. 2012; Kuusisto-Hjort and Hjort 2013; Frost et al. 2015).

Chemical cocktails illustrating reactive transport behavior: Fe and S compounds

Iron behaves as a transport vector or agent of sequestration for sieved and filtered chemical cocktails (as described above), but it can also contribute to formation and transport of reactive chemical cocktails (Rosenberg and Schroth 2017). While the majority of iron exported to coastal zones from rivers is in the particulate or suspended sediment form (Martin and Meybeck 1979; Poulton and Raiswell 2002; Schroth
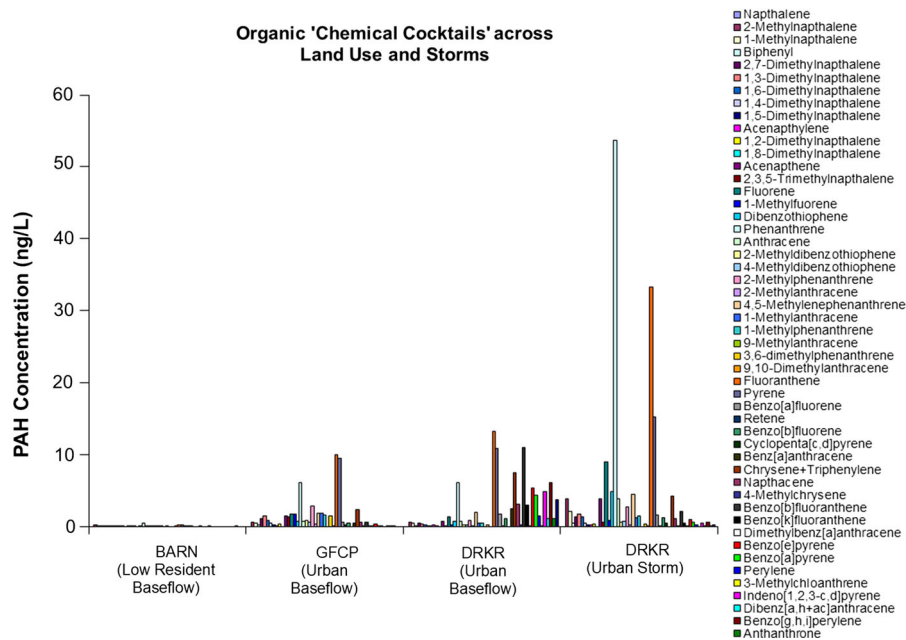
Fig. 6 Anthropogenic sources can also contribute to chemical cocktails of organic matter. Polycyclic aromatic hydrocarbons (PAHs) vary in streams across a land use gradient at the Baltimore Long-Term Ecological Research site. BARN is forest dominated with low residential development, and sites are described in Kaushal et al. (2008). Automated samplers were used to capture the first flush of organic contaminants during storms and to also characterize baseflow concentrations. Concentrations of PAHs increased in streams with increasing watershed urbanization, and they also increased rapidly during the first flush of storms

et al. 2011), the speciation and reactivity of iron in the suspended sediment load is driven by iron mineralogy (Poulton and Raiswell 2002; Raiswell and Canfield 2012). Changes in chemical speciation of Fe(III)(oxy)hydroxides and organics regulate the chemical and biological reactivity of chemical cocktails coupled with iron, which influence nitrogen, phosphorus, arsenic, carbon, and trace metal cycles in coastal waters (sensu Tagliabue et al. 2017). Iron and sulfur chemical cocktails are also coupled during drying-rewetting cycles through the formation and oxidation of iron sulfides (Burgin et al. 2011; Schoepfer et al. 2014) (Fig. 2), which sorb other metals and arsenic and co-occur with other metal sulfides such as zinc and copper. These iron sulfides accumulate through 'sulfidization,' a microbially driven process in which sulfate-S is converted to sulfide-S during organic matter decomposition. This produces hydrogen sulfide and bisulfide, which react with iron to precipitate minerals eventually forming FeS_2 (pyrite), creating chemical cocktails associated with mineral sorption (Fanning and Fanning 1989; Leventhal and Taylor 1990).

Drying events contribute to increases in watershed transport of sulfate and acidity to streams during re-wetting due to sulfide oxidation or 'sulfuricization' (Kerr et al. 2012). Sulfuricization produces sulfuric acid while releasing metal chemical cocktails that were previously sequestered as trace components of the soil minerals (Fanning and Fanning 1989). Furthermore, the decrease in pH causes dissolution of aluminum, leading to groundwater and drainage concentrations, which may be high enough to cause toxicity to aquatic organisms (Muhrizal et al. 2003; Demas et al. 2004). The pyrite in exposed soils and sediments can oxidize depending on drying conditions and droughts, and an oxidation front may advance into unoxidized materials along the vertical soil profile (Rabenhorst and Valladares 2005). During droughts, sediments containing iron sulfide can be exposed to air and oxidized to form 'active acid sulfate soils,' which increase acidity to pH < 4 and have the potential to dissolve chemical cocktails of metals (Creeper et al. 2013; Mosley et al. 2017). Thus, the formation and dominant transport modes of reactive chemical cocktails of iron and sulfur are driven by both the amount of

time a soil spends in either saturated or unsaturated conditions and the time-period between drying and rewetting events (Fig. 2).

How do land use and climate alter elemental responses and give rise to novel combinations?

In the Anthropocene, the most biologically reactive iron pool in floods is likely associated with colloidal/nano-colloidal size fractions (Raiswell 2011), much of which is complexed to various components of the DOM pool including phosphorus, arsenic, and trace metals (Hassellov and von der Kammer 2008; Warren and Haack 2001). Altered hydrology in human-impacted watersheds can also amplify redox extremes and tighten the coupling of iron and sulfur cycles and formation and transformation of reactive chemical cocktails during baseflow. For example, agricultural and urban drainage promote the oxidation of reduced species including iron-sulfides (Boman et al. 2008). Groundwater levels are altered by ditches or channel incision in agricultural and urban watersheds, causing hydrologic drought and sulfuricization or production of sulfuric acid in soils (Boman et al. 2008). In addition, production of sulfuric acid can also occur when marine soils (high in sulfate) are diked and drained for agricultural production and development (Pons and Vandermo 1973). The formation of reactive iron and sulfur chemical cocktails (and associated metals and arsenic) eventually becomes increasingly coupled during floods in agricultural and urban watersheds as water tables rise and reducing conditions dominate. As agricultural and urban waterways become eutrophic, organic matter increases, O_2 is depleted by microbial metabolism, and sulfide minerals accumulate (Valdemarsen et al. 2010). These iron sulfides are then vulnerable to another repeated cycle of oxidation during drying in soils and oxic conditions. An increase in iron and associated chemical cocktails transported in watersheds can have implications for increased nutrient and contaminant loads to coastal receiving waters (sensu Schroth et al. 2014).

Chemical cocktails illustrating chromatographic transport behavior: cations and anions

Cations and anions are paired in fresh waters to maintain electroneutrality and form distinct watershed chemical cocktails based on underlying geology, land use, and atmospheric deposition. During storms, chemical cocktails of major ions observed within streams and rivers change with respect to baseflow composition either through dilution or concentration of multiple paired ions to maintain electroneutrality and charge balance. The major ion composition of ground water is controlled by the ion exchange capacity of the soil (shallower) and mineral dissolution (deeper). In general, overland and shallow subsurface flow during storm events dilute concentrations of major ions in stream (Burns et al. 1998), with the exception of chromatographic chemical cocktails vulnerable to flushing (e.g., nitrate and sulfate and base cations are mobilized by road salts and ion exchange). For example, nitrate and phosphate concentrations can peak on the descending limb of the hydrograph during storms in agricultural watersheds in the Northeastern U.S. due to increased groundwater contributions, except where artificial tile drainage enhances rapid runoff (Fig. 7). Nitrate dilution and hysteresis also occurs across urban streamflow due to high groundwater nitrate sources (e.g., Kaushal et al. 2008; Koenig et al. 2017; Vaughan et al. 2017; Wollheim et al. 2017). However, hysteresis patterns can also be quite variable across hydrologic events based on the advent of continuous high-frequency measurements of solutes (Vaughan et al. 2017), and such data could be useful in further calibrating the chemical cocktail approach for different watersheds in the future. On the other hand, concentrations of base cations show strong relationships to specific conductance as a proxy (Fig. 8). Multiple base cations can also rapidly increase during snowmelt events in urban watersheds of the Northeastern U.S. (Kaushal et al. 2017); Na^+ increases from road salt and Ca^{2+} and Mg^{2+} can increase from deicer inputs and/or rapid ion exchange in urban soils (Kaushal et al. 2017, Haq et al. this issue). In addition, concentrations of some metal cations also peak and are also mobilized during snowmelt due to ion exchange induced by Na^+ in road salts (Fig. 8).

Although exceptions do exist, concentrations of H^+ increase during rain storms in human-impacted watersheds whereas concentrations of NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, DIC, Cl^- are typically diluted as chromatographic chemical cocktails. However, differential responses to rain storms are due to the magnitude and duration of the storm, antecedent precipitation

Fig. 7 Changes in water quality during storms in the Maidford River, which drains an agricultural watershed in Rhode Island, USA. High frequency data were obtained from a combination of sensor data and grab samples for streamwater chemistry analyses throughout the duration of the storm. Mobile anions were flushed after the peak in discharge as groundwater contributions increased in importance
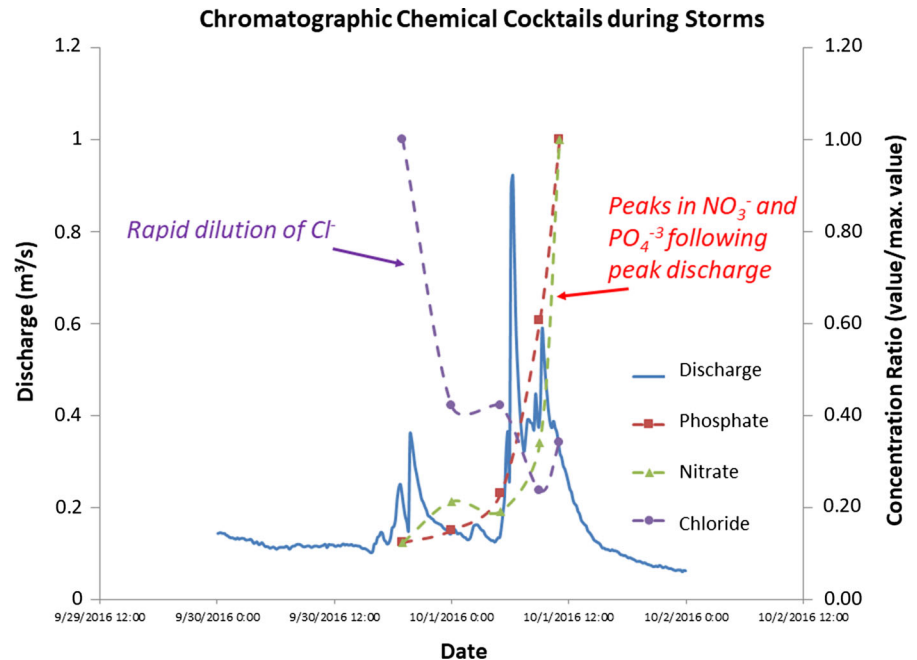
patterns, and relative contributions of different hydrologic pathways. In contrast to the other base cations, concentrations of K^+ can peak along with DOM during storms, even though K^+ is under biotic control (Tripler et al. 2006; Hood et al. 2006; Vidon et al. 2008). Therefore, base cations increase or decrease as discharge increases depending on geology and supply versus biotic demand in watersheds draining natural land cover.

How do land use and climate alter elemental responses and give rise to novel combinations?

Human activities have significantly altered the composition of chemical cocktails of major ions on a global scale. Freshwater salinization syndrome due to acid rain, land-use change, and climate change has altered chromatographic chemical cocktails of Na^+, Ca^{2+}, Mg^{2+}, K^+, Cl^-, HCO_3^- and H^+ across North America, particularly in the Eastern U.S. (e.g., Kaushal et al. 2013, 2018; Dugan et al. 2017). Widespread deforestation has resulted in increased ion exports to streams including NO_3^-, Cl^- and K^+ salts (Likens et al. 1994; Jayawickreme et al. 2011). Interestingly, SO_4^{2-} leaching has decreased in response to deforestation because the associated decrease in soil pH increases SO_4^{2-} retention by soils

(Nodvin et al. 1986; Welsch et al. 2004). Thus, increased NO_3^- from nitric acid in precipitation and microbial nitrification in soils is the primary driver of acidification and can mobilize Al to toxic levels (Burns and Murdoch 2005; Baldigo et al. 2005).

Human activities synergistically enhance formation of chromatographic chemical cocktails and transport of major ions in streams and rivers (Aquilina et al. 2012; Kaushal et al. 2017). Soil acidification from increased soil respiration, fertilizer application and ammonia oxidation, and evaporative concentration of irrigation waters are all mechanisms that contribute to formation of chemical cocktails of base cations in agricultural lands. Agriculture has led to a 50-year increase in chemical cocktails of base cations in rivers in France due to accelerated silicate weathering from fertilizer use (Aquilina et al. 2012). Similarly, salinization from human-accelerated weathering of geologic materials and impervious surfaces and salt pollution has synergistically increased chromatographic chemical cocktails of major ions over almost a century in rivers in the U.S. (Fig. 9) (Kaushal et al. 2005, 2017). Mobile anions from acid rain and salt pollution (SO_4^{2-}, NO_3^-, and Cl^-) further contribute to increased mobilization of base cations via maintenance of charge balance through ion pairing and electroneutrality (Mitchell et al. 2006; Kaushal et al.
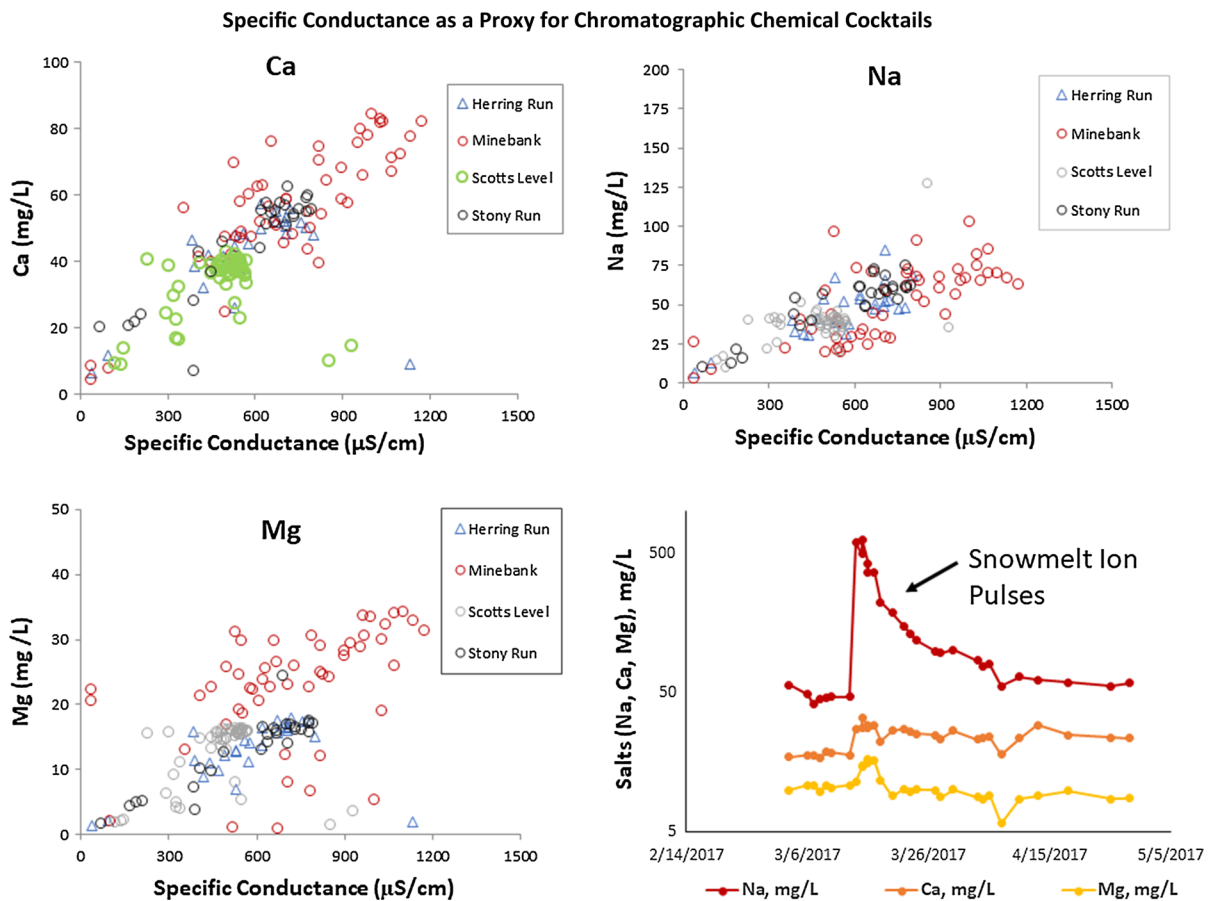
Specific Conductance as a Proxy for Chromatographic Chemical Cocktails

Fig. 8 (Top panels and bottom left panel) Mobilization of chromatographic chemical cocktails from soil exchange sites and relationships between specific conductance and base cations. Specific conductance can serve as as a proxy and surrogate for chromatographic chemical cocktails in watersheds of the Baltimore Long-Term Ecological Research (LTER) site. (Bottom right panel) Pulses in cation concentrations following road salt applications suggest the importance of ion exchange in response to sodium chloride inputs in urban watersheds and streams of the Baltimore-Washington DC metropolitan region
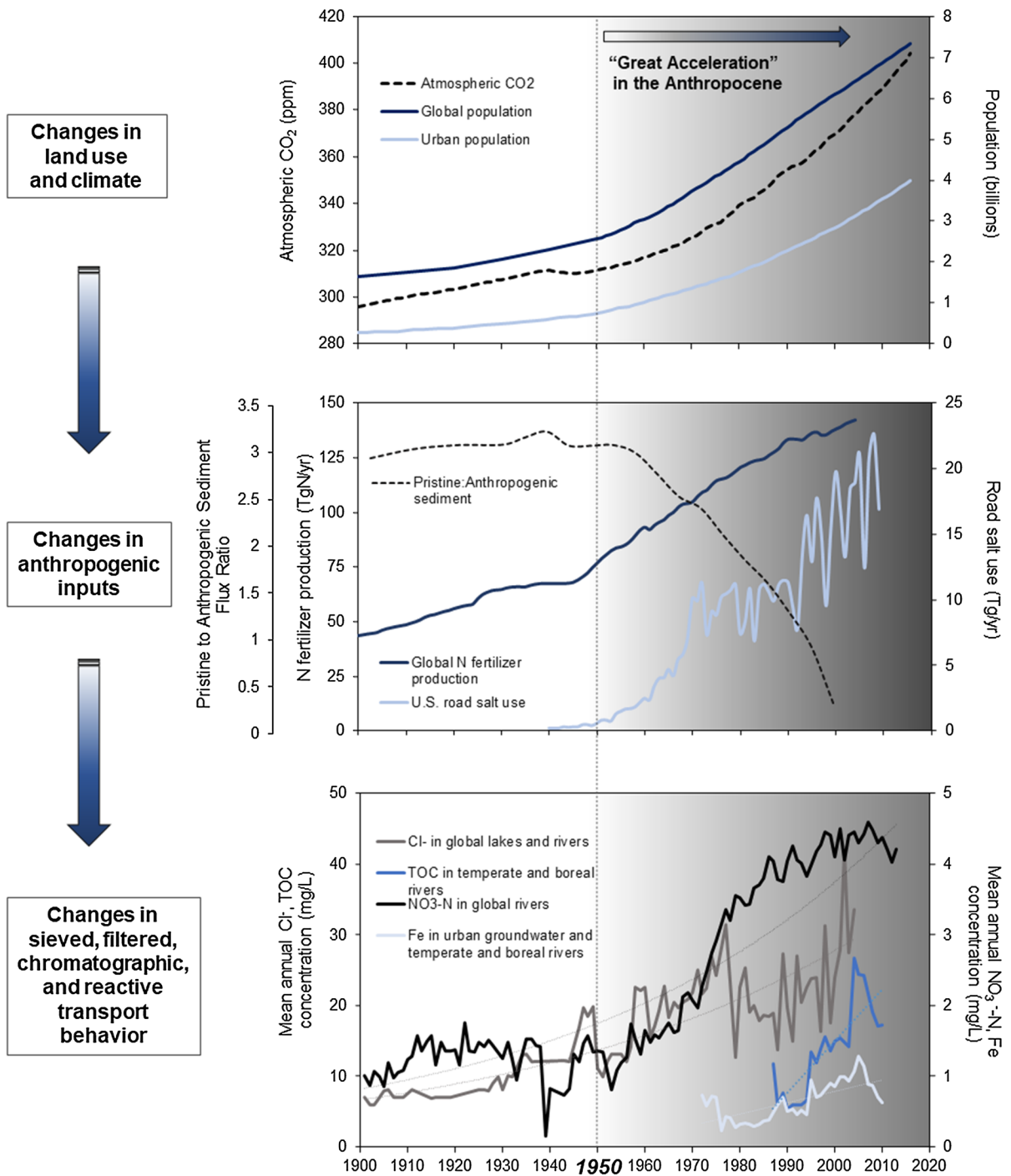
2017). Long-term changes in pH can also influence ion exchange capacity of soils, hence mobilizing different chemical cocktails of ions (Duan and Kaushal 2015; Kaushal et al. 2018; Haq et al. this issue). Ultimately, formation and transport of chromatographic cocktails are enhanced by cation-anion pairing in waters, ion exchange in soils, salt pollution, and accelerated chemical weathering (Kaushal et al. 2013, 2018).

Chemical cocktails illustrating reactive transport behavior: C, N, and greenhouse gases

Production and transport of greenhouse gases (GHG) and reactive chemical cocktails during hydrologic events in human-impacted watersheds are related to temperature, organic matter availability, nutrient status, oxygen availability, and redox status (Kaushal et al. 2014a, b). The consumption and production of GHG (GHG: CO_2, N_2O, CH_4) is fundamentally linked to C and nutrient cycles and dominant heterotrophic processes in soils (Hedin et al. 1998). For instance, aerobic respiration produces CO_2, while nitrification can lead to N_2O production (Naiman et al. 2005). Denitrification, or the reduction of NO_3^- to N_2 gas, can also lead to the production of N_2O gas when denitrification is incomplete due to low pH, fluctuating water tables, and limited pools of labile soil organic C (Reddy and DeLaune 2008). Under aerobic conditions, methane oxidation can consume CH_4 in soils, while under anoxic conditions methanogenesis produces CH_4 (Castro et al. 1995; Morse et al. 2012).

Changes in land use and climate

Changes in anthropogenic inputs

Changes in sieved, filtered, chromatographic, and reactive transport behavior

Redox conditions, electron acceptors' and donors' availability, temperature, and moisture also impact water quality and reactive chemical cocktails by influencing NO_3^- removal by denitrification, PO_4^{3-} release when iron oxides become unstable under anoxic conditions, and methylmercury production when sulfate reduction actively occurs.

◄ **Fig. 9** There have been significant changes in sieved, filtered, reactive, and chromatographic transport behaviors of chemical cocktails due to climate and land use change over the past century. (Top Panel) In the mid-20th century, the "Great Acceleration" of the Anthropocene was marked by significant increases in rates of change in global population, urban population (World Bank data, Steffen et al. 2015), and atmospheric CO_2 (NASA.gov data). (Middle Panel) In the mid-20th century, global population, agriculture, and industrialization increased watershed inputs of highly reactive elements and chromatographic elements such as salts (World Bank data, US EPA data, Steffen et al. 2015; Anning and Flynn 2014; USGS Mineral Resources). Land development Querydecreased the amount of pristine sediment and increased anthropogenic sediment loads overwhelming watershed sieves (Syvitski and Kettner 2011). (Bottom panel) During the Anthropocene, there has been an increase in: (1) highly reactive chemical cocktails containing nitrate-N (annual mean concentrations in global rivers are estimated from Bührer and Ambühl 2001; Goolsby and Battaglin 2001; Duan et al. 2007; Friedrich and Pohlmann 2009; Bouraoui and Grizzetti 2011; EEA 2012; Kelly et al. 2015; Minaudo et al. 2015; Jaworski, unpublished data; Meybeck et al. 2016; Romero et al. 2016). (2) Sieved and filtered chemical cocktails containing organic carbon (annual mean concentrations are estimated from temperate and boreal rivers analyzed in Worrall et al. 2004; Evans et al. 2005; Kritzberg and Ekstrom 2012; Sarkkola et al. 2013); (3) sieved and filtered chemical cocktails containing iron (annual mean concentrations are estimated from rivers and groundwater wells in forested and urban areas in the United States and Europe analyzed in Sloto 2003; Kritzberg and Ekstrom 2012; Sarkkola et al. 2013; Kritzberg et al. 2014); (4) chromatographic chemical cocktails containing Cl^- (annual mean concentrations are estimated from global rivers and lakes in studies reviewed previously by Kaushal et al. (2014a, b) and Kaushal (2016)

Environmental conditions also influence the diffusion of N_2O, CO_2, and CH_4 through the soil surface. Under dry conditions, large pores tend to be aerated, which facilitates not only the diffusion of oxygen from the atmosphere into the soil, but also the release of GHG produced at depth in the saturated zone out to the atmosphere. High CO_2, CH_4, and N_2O fluxes can be observed at the soil-atmosphere interface of riparian zones when the water table drops due to a combination of O_2 diffusion and stimulation of aerobic microbial respiration in upper soils and anoxic conditions occurring in deeper soils (Vidon et al. 2014a, b, 2017). This illustrates the formation of different GHG cocktails across soil depths and their transport through soil pores to the atmosphere (Groffman et al. 2009; Vidon et al. 2010; Bernhardt et al. 2017b) (Fig. 2).

How do land use and climate alter elemental responses and give rise to novel combinations?

GHG cocktails are shifting towards more pulsed transport in the Anthropocene. In human modified landscapes, organic matter reactivity, redox extremes, temperature, and nutrient availability all increase synergistically (Kaushal et al. 2014a, b). Precipitation events stimulate N_2O and CH_4 pulses in riparian zones, streams, and rivers affected by both agricultural and urban land uses (Kim et al. 2010, 2012; Jacinthe et al. 2012; 2015; Sieczko et al. 2016). Engineered and artificial drainage lead to more rapid (and less seasonal) water table fluctuations and associated solute flushes and pulses (Kaushal et al. 2017b). These hydrologic changes alter GHGs production and their subsequent flushing to streams (Kaushal et al. 2017b). Pulsed transport of GHG cocktails through stream and river channels may be significant unrecognized components of watershed N and C mass balances (Beaulieu et al. 2011; Butman and Raymond 2011; Smith et al. 2017). The role of stream channels as 'vents' from the soil critical zone to the atmosphere warrants further research (Smith et al. 2017; Gardner et al. 2016). Further, we hypothesize that headwater areas may be more sensitive to GHG fluxes in the Anthropocene because of increased potential for drying-rewetting cycles compared to the mainstem of rivers where perennial flow predominates. Given that headwaters drain a large area of landmass that aggregates over space, their role in regulating GHG fluxes could become more prevalent on a continental scale.

The chemical cocktail approach as a tool for advancing watershed science

Developing a unified concept for chemical transport in catchments in response to hydrological events

Analyzing how chemical cocktails respond similarly or differently over time can allow us to formulate a unified concept for catchment chemical transport in response to hydrologic events (e.g., based on common modes of transport, mobility, and reactivity for carbon, nutrients, redox sensitive metals, and ionic salts). For example, NO_3^-, DOC, and turbidity dynamics all

change simultaneously during storms and are linked to hydrologic flowpaths and watershed source areas, but chemical species can have different response times (Fovet et al. 2018). A unified conceptual model (like the one proposed here) can allow us to include novel combinations of elements and how they are formed, transformed, and transported across the hydrograph through shallow ground water, deep ground water, riparian corridors, and uplands. Testable hypotheses can investigate the relative importance of hydrologic versus biological drivers on formation, transport, and transformation of different chemical cocktails across gradients of land use, climate, geology, and atmospheric deposition.

Developing sensor data as proxies
for characterizing pulses of chemical cocktails

There has been growing research on applications of in situ water quality sensors, but not all chemicals of interest can be measured continuously. Proxies can be developed based on statistical relationships between continuous sensor data in the field and water quality measurements in the laboratory at a less expensive cost and higher resolution than more intensive sampling. For example, specific ultra violet absorbance at 254 nm (SUVA) can be measured in the field with a spectrophotometer at higher frequency, and may be a robust surrogate or proxy for Hg and methylmercury in some watersheds along with fluorescent dissolved organic matter (FDOM) (Burns et al. 2013, Vidon et al. 2014b). Specific conductance data can be a robust proxy for chromatographic chemical cocktails such as Cl^-, Ca^{2+}, Mg^{2+}, Na^+, etc. (Fig. 8), while turbidity can be a proxy for heavy metals in organometallic complexes and organic contaminants. All surrogates and proxies need to be individually calibrated based on changes in relationships across streamflow and watershed state factors such as climate, underlying geology, topography, human activities, and time. High frequency characterization of elemental peaks, times of concentration, recession curves, and fluxes for different chemical cocktails can reveal changes in sources, transport, and transformation within watersheds. The magnitude, frequency, and persistence of different chemical cocktail pulses are still unknown for many watersheds at finer temporal scales. This information is critical for identifying water quality violations, characterizing

ecosystem resilience and recovery from extreme events, and evaluating the success of watershed management and restoration outcomes.

How do watershed chemical cocktails interact
to influence ecosystems and water quality
problems?

Interactions between chemical cocktails often produce environmental effects greater than the sum of individual elements, and watershed chemical cocktails can be linked to the most pressing problems in modern water quality. However, the causes and consequences of water quality problems often focus on one or a few elements, and they are considered in isolation of potential interactions with other groups of elements. For example, chemical cocktails showing sieved and filtered transport behaviors (such as POM and DOM) can be linked to brownification and transport of heavy metals and organic contaminants (sensu Kritzberg and Ekstrom 2012; Sarkkola et al. 2013; Kritzberg et al. 2014). Chemical cocktails showing chromatographic transport behavior can be linked to salinization and influence acid-base status of fresh waters (acidification vs. alkalinization) based on different ion mixtures (Kaushal et al. 2013, 2018). Finally, reactive chemical cocktails can be linked to eutrophication, hypoxia, and increased solubility of mineral oxyhydroxides and mobilization of associated contaminants. By recognizing novel combinations of elements holistically as chemical cocktails, we gain an understanding of how water quality problems relate to each other and how increases in one chemical cocktail (e.g. combinations of elements influenced by salinization) can affect mobilization of another (e.g. combinations of elements influenced by brownification or eutrophication) (Duan and Kaushal 2013; Haq et al. this issue).

Managing multiple chemical cocktails
and contaminants in a changing environment

Managing multiple water quality problems presents trade-offs because no single best management practice is a panacea in the Anthropocene. In fact, one form of water quality management can exacerbate management of another due to differences in fate and transformation. For example, anoxic conditions and organic matter are needed to foster denitrification and nitrate removal in riparian zones, but anoxic

conditions and low redox potential enhance desorption of P from Fe and Mn oxyhydroxides (sensu Duan et al. 2016). Similarly, wetlands are effective at denitrification, but they are also hot spots of methylmercury production (St. Louis et al. 1994). Finally, imbalances in pollution management strategies targeting only one element can influence changes in elemental ratios of N:P:Si:Fe and harmful algal blooms (Paerl 1997). The watershed chemical cocktail concept implies managing novel combinations of elements based on their potential for transport and transformation in relationship to environmental conditions. Water quality management can be optimized for chemical cocktails instead of individual compounds based on knowledge of shared sources, outcomes, and trade-offs. Models of contaminant toxicity can explicitly consider chemical cocktails and their interactive effects. Finally, ecosystem restoration strategies can consider managing chemical cocktails instead of individual elements, and anticipate effects of contrasting watershed management on transport and transformation of chemical cocktails.

Formation, transport, and transformation of watershed chemical cocktails in the Anthropocene

Overall, a watershed chemical cocktail approach suggests that novel combinations of elements have transformed the chemistry of fresh waters in the Anthropocene. Over the past 100 years, there have been trends in novel combinations of elements showing different transport behaviors in fresh waters (Fig. 9). Long-term increases in organic carbon and metals concentrations (e.g., sieved and filtered transport) provide information about the effects of changing atmospheric deposition, climate change, and/or changing ecosystem retention functions of floodplains and riparian zones. In headwaters, watershed retention processes such as sieving and filtering can be overwhelmed during storm flow when there is a high degree of hydrologic connectivity between landscapes and aquatic systems, and chemicals pass through watersheds faster than they can react. Further downstream, sediment fluxes from land to aquatic networks have increased, but much of this sediment is often held on the continents behind dams shifting sieving and filtering functions downstream along fluvial networks

and establishing new reactive surfaces (effects of dams on sediment transport have been discussed extensively in other publications). As impoundments fill with sediment, mobilization may occur during large storms, representing a shift in behavior of sediment-associated elements and sieved chemical cocktail transport behavior along river networks (Zhang et al. 2013). Furthermore, a shift towards more reactive DOM in human-impacted streams alters their role as bioreactors, and stimulates microbial metabolism and formation of reactive GHG chemical cocktails. Finally, increased chromatographic transport behavior occurs due to freshwater salinization syndrome and human-accelerated weathering (Kaushal et al. 2018) (Fig. 9). These coupled transport and transformation dynamics help advance and redefine our understanding beyond minimally disturbed river networks (Vannote et al. 1980).

Many questions still remain regarding how land use and climate change will modify the formation, transport, transformation, and ecological stoichiometry of different chemical cocktails and ecosystem impacts. Chemical cocktails in fresh waters are likely reflecting a warming climate over large geographic scales and temperature influences biological and weathering reaction rates. Increasing water temperatures, increasing solutes, increasing dissolved inorganic carbon, and increasing pH can shift the role of inland waters as sources and sinks of CO_2 and other greenhouse gases (Kaushal et al. 2010, 2018). Characterizing concentrations, compositions, and consequences of varying chemical cocktails across local, regional, and global scales allows us to develop more coordinated research, management, and monitoring approaches. A reconceptualization of watershed transport and transformation processes as chemical cocktails is critical to holistically managing freshwater ecosystems in the Anthropocene.

suggestions. The research has been subjected to U.S. Environmental Protection Agency review, but does not necessarily reflect the views of the agency, and no official endorsement should be inferred. Anthropocene is a term used by scientists and nonscientists to highlight the concept that we are living in a time when human activities have significant effects on the global environment. The Anthropocene currently has no formal status and is not recognized by the USGS. If international agreement is reached, it could become a series/epoch above the Holocene. This is accordance with: U.S. Geological Survey Geologic Names Committee, 2018, Divisions of geologic time-major chronostratigraphic and geochronologic units: U.S. Geological Survey Fact Sheet 2018-3054, 2p., https://doi.org/10.3133/fs20183054.

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