



EPA Public Access

Author manuscript

Biogeochemistry. Author manuscript; available in PMC 2019 August 19.

About author manuscripts

Submit a manuscript

Published in final edited form as:

Biogeochemistry. 2018 ; 141(3): 281–305. doi:10.1007/s10533-018-0502-6.

Watershed ‘Chemical Cocktails’: Forming Novel Elemental Combinations in Anthropocene Fresh Waters

Sujay S. Kaushal¹, Arthur J. Gold², Susana Bernal³, Tammy A. Newcomer Johnson⁴, Kelly Addy², Amy Burgin⁵, Douglas A. Burns⁶, Ashley A. Coble⁷, Eran Hood⁸, Yuehan Lu⁹, Paul Mayer¹⁰, Elizabeth C. Minor¹¹, Andrew W. Schroth¹², Philippe Vidon¹³, Henry Wilson¹⁴, Marguerite A. Xenopoulos¹⁵, Thomas Doody¹, Joseph Galella¹, Phillip Goodling¹, Katherine Haviland¹⁶, Shahan Haq¹, Barret Wessel¹⁷, Kelsey Wood¹, Norbert Jaworski¹⁸, Kenneth T. Belt¹⁹

¹Department of Geology & Earth System Science Interdisciplinary Center, University of Maryland, College Park, Maryland 20740, USA

²College Park, Maryland 20740, USA department of Natural Resources Science, University of Rhode Island, Kingston, Rhode Island 02881, USA

³Integrative Freshwater Ecology Group, Center for Advanced studies of Blanes (CEAB-CSIC), C/ Acces Cala St. Francesc 14, 17300, Blanes, Girona, Spain

⁴National Exposure Research Lab, Systems Exposure Division, U.S. Environmental Protection Agency, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268, USA

⁵University of Kansas and Kansas Biological Survey, 2101 Constant Ave., Lawrence, Kansas 66047, USA

⁶U.S. Geological Survey, New York Water Science Center, 425 Jordan Rd., Troy, NY 12180, USA

⁷National Council for Air and Stream Improvement, Inc., 227 NW Third Street, Corvallis, Oregon 97330, USA

⁸Environmental Science and Geography Program, University of Alaska Southeast, Juneau, Alaska 99801, USA

⁹Department of Geological Sciences, University of Alabama, Tuscaloosa, Alabama 35487, USA

¹⁰US Environmental Protection Agency, National Health and Environmental Effects Research Lab, Western Ecology Division, 200 SW 35th Street, Corvallis, Oregon 97333, USA

¹¹Large Lakes Observatory and Dept. of Chemistry and Biochemistry, University of Minnesota, Duluth, 109 RLB, 2205 East 5th St, Duluth, Minnesota 55812, USA

¹²University of Vermont, Department of Geology, Burlington, Vermont, USA

¹³Department of Forest and Natural Resources Management, The State University of New York College of Environmental Science and Forestry (SUNY- ESF), Syracuse, New York, USA

¹⁴Brandon Research and Development Centre, Agriculture and Agri-food Canada, Brandon, Manitoba, Canada

¹⁵Department of Biology, Trent University, Peterborough, Ontario, Canada

¹⁶Department of Natural Resources, Cornell University, Ithaca, New York 14853 USA

¹⁷Department of Environmental Science and Technology, University of Maryland, College Park, Maryland 20740, USA

¹⁸US Environmental Protection Agency (Retired), Baltimore Field Station, Baltimore, Maryland 21228, USA

¹⁹US Forest Service, Northern Research Station, Baltimore Field Station, Baltimore, Maryland 21228, USA

Abstract

In the Anthropocene¹, watershed chemical transport is increasingly dominated by novel combinations 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. 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 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 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.

Keywords

storms; floods; droughts; organic contaminants; metals; salts; cations; nutrients; eutrophication; hypoxia; acidification; salinization

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. 2010, 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, 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., 2014, 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, 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. 2014, 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 O₂ 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, Kaushal et al., 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 Figure 1) and their chemical transport distance downstream (horizontal axis in Figure 1). Note that the same element can show multiple transport and transformation behaviors depending upon redox conditions, biological demand, solubility and other environmental factors (Figure 2). All of these factors fluctuate significantly during drying-wetting cycles (Figure 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 (Figure 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) (Figure 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’ 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 (Figure 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 vs. 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 (Figure 3). Firstly, this is because POM typically originates from near--stream sources while DOM can be flushed through the catchment from sources further 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 ‘first flush’, if they have accumulated in nearsurface 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 (Figure 1). Therefore, many of these ions show differences in their chromatographic transport behaviors based on shallower vs. 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 (Figure 3). As an example, chloride and base cations typically peak on the recession limb of hydrographs 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 (Figure 3). The potential for flushing vs. dilution of chromatographic chemical cocktails is based on pool sizes, storage during preceding drying periods, and deeper vs. 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 (Figure 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 transiently 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 (Figure 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) (Figure 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 (Figure 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 vs. particulate forms (Figure 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 (Figure 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 (Figure 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_v 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_v 1996; Mei et al_v 2014; Wilson et al_v 2016; McGlynn and McDonnell, 2003; Inamdar et al_v 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_v 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_v 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 (Figure 1). For example, there are significant positive relationships between iron and DOC concentrations during storms in urban watersheds (Figure 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 (Figure 5). Concentrations of dissolved trace elements such as iron, aluminum, manganese, and zinc all show correlations with pH and DOC concentrations in aquatic 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 et al., 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; Wilson and Xenopoulos, 2009; Petrone *et al.*, 2011; Hosen *et al.*, 2014; Kaushal et al., 2014; Lu et al. 2013 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.*, 2014; Kaushal et al., 2014, 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. 2014, 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 (Figure 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. 2014), 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 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(II)(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) (Figure 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 FeS₂ (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 (Crepper 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 (Figure 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 (Hasselov 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, O₂ 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 (Figure 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 (Vaughn 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 (Figure 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 Ca²⁺ and Mg²⁺ 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 (Figure 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 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 vs. biotic demand in watersheds draining natural land cover (Hill, 1993; O'Brien et al., 1993).

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, Dugan et al. 2017; Kaushal et al., 2018). 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. (Figure 9) (Kaushal et al., 2005, Kaushal et al., 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., 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; Kaushal et al. 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., 2014). The consumption and production of GHG (GHG: CO₂, N₂O, CH₄) is fundamentally linked to C and nutrient cycles and dominant heterotrophic processes in soils (Hedin et al., 1998). For instance, aerobic respiration produces CO₂, while nitrification can lead to N₂O production (Naiman et al., 2005). Denitrification, or the reduction of NO₃ to N₂ gas, can also lead to the production of N₂O 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 CH₄ in soils, while under anoxic conditions methanogenesis produces CH₄ (Castro et al., 1995; Morse et al., 2012). Redox conditions, electron acceptors' and donors' availability, temperature, and moisture also impact water quality and reactive chemical cocktails by influencing NO₃ removal by denitrification, PO₄ release when iron oxides become unstable under anoxic conditions, and methylmercury production when sulfate reduction actively occurs.

Environmental conditions also influence the diffusion of N₂O, CO₂, and CH₄ 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 CO₂, CH₄, and N₂O fluxes can be observed at the soil- atmosphere interface of riparian zones when the water table drops due to a combination of O₂ diffusion and stimulation of aerobic microbial respiration in upper soils and anoxic conditions occurring in deeper soils (Vidon et al. 2014a; Vidon et al. 2017). This illustrates the formation of different GHG across soil depths and their transport through soil pores to the atmosphere (Groffman et al., 2009, Vidon et al., 2010, Bernhardt et al., 2017b) (Figure 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. 2014). Precipitation events stimulate N₂O and CH₄ pulses in riparian zones, streams, and rivers affected by both agricultural and urban land uses (Kim et al., 2010, Kim et al., 2012, Jacinthe et al., 2012, Jacinthe et al., 2015, Sieckzko 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., 2014). These hydrologic changes alter GHGs production and their subsequent flushing to streams (Kaushal et al., 2014). 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, NO₃, 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 vs. 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 nanometers (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⁻, Ca²⁺, Mg²⁺, Na⁺, *etc.* (Figure 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 et al. 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. alkalization) based on different ion mixtures (Kaushal et al. 2013, Kaushal et al. 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 et al. 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 tradeoffs. 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 (Figure 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) (Figure 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 CO₂ and other greenhouse gases (Kaushal et al. 2010, Kaushal et al. 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.

Acknowledgements

This work was funded by USDA (award # 2016-67019-25280) and NSF-EPSCoR (#1641157) for supporting collaborations at the AGU Chapman Conference on Extreme Climate Events. Significant funding for data collection/analyses in this paper was provided by NSF EAR1521224, NSF CBET1058502, NSF Coastal SEES1426844, NSF DEB-0423476 and DEB-1027188, NSF RI EPSCoR NEWRnet Grant No. IIA-1330406, EPA ORD, Chesapeake Bay Trust, and Multi-state Regional Hatch Project S-1063. Gene Likens and Michael Pace

provided helpful discussions and insights. Matthew Miller, Matthew Wright, Neha Patel, and David Tilley provided edits. The research has been subjected to U.S. Geological Survey and U.S. Environmental Protection Agency review, but does not necessarily reflect the views of any of the agencies, 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 in the Divisions of Geologic Time and is not recognized by the USGS. If international agreement is reached, it could become a series/epoch above the Holocene.

References

- Aquilina L, Poszwa A, Walter C, Vergnaud V, Pierson-Wickmann AC, Ruiz L (2012) Long-term effects of high nitrogen loads on cation and carbon riverine export in agricultural catchments. *Environmental Science & Technology* 46(17): 9447–9455 [PubMed: 22839503]
- Archfield SA, Hirsch RM, Viglione A, Bloesch G (2016) Fragmented patterns of flood change across the United States. *Geophysical Research Letters* 43(19): 10232–10239 [PubMed: 27917010]
- Bain DJ, Yesilonis ID, Pouyat RV (2012) Metal concentrations in urban riparian sediments along an urbanization gradient. *Biogeochemistry* 107(1–3): 67–79
- Baker A, Spencer RGM (2004) Characterization of dissolved organic matter from source to sea using fluorescence and absorbance spectroscopy. *Science of the Total Environment* 333(1–3): 217–232 [PubMed: 15364531]
- Baldigo BP, Murdoch PS and Burns DA (2005) Stream acidification and mortality of brook trout (*Salvelinus fontinalis*) in response to timber harvest in Catskill Mountain watersheds, New York, USA. *Canadian Journal of Fisheries and Aquatic Sciences*, 62(5), pp.1168–1183.
- Beaulieu JJ, Tank JL, Hamilton SK, Wollheim WM, Hall RO Jr., Mulholland PJ, Peterson BJ, Ashkenas LR, Cooper LW, Dahm CN, Dodds WK, Grimm NB, Johnson SL, McDowell WH, Poole GC, Valett HM, Arango CP, Bernot MJ, Burgin AJ, Crenshaw CL, Helton AM, Johnson LT, O’Brien JM, Potter JD, Sheibley RW, Sobota DJ, Thomas SM (2011) Nitrous oxide emission from denitrification in stream and river networks. *Proceedings of the National Academy of Sciences of the United States of America* 108(1): 214–219 [PubMed: 21173258]
- Bernal S, Hedin LO, Likens GE, Gerber S, Buso DC. 2012 Complex response of the forest nitrogen cycle to climate change. *Proceedings of the National Academy of Sciences* 109 (2012): 109, 3406–3411.
- Bernhardt ES, Rosi EJ, Gessner MO (2017a) Synthetic chemicals as agents of global change. *Frontiers in Ecology and the Environment* 15(2): 84–90.
- Bernhardt ES, Blaszcak JR, Ficken CD, Fork ML, Kaiser KE, Seybold EC (2017b) Control points in Boman A, Astrom M, Frojdo S (2008) Sulfur dynamics in boreal acid sulfate soils rich in metastable iron sulfide-The role of artificial drainage. *Chemical Geology* 255(1–2): 68–77
- Boyer EW, Hornberger GM, Bencala KE, McKnight D (1996) Overview of a simple model describing variation of dissolved organic carbon in an upland catchment. *Ecological Modelling* 86(2–3): 183–188
- Buffam I, Galloway JN, Blum LK, McGlathery KJ (2001) A stormflow/baseflow comparison of dissolved organic matter concentrations and bioavailability in an Appalachian stream. *Biogeochemistry* 53(3): 269306
- Burgin AJ, Yang WH, Hamilton SK, Silver WL (2011) Beyond carbon and nitrogen: how the microbial energy economy couples elemental cycles in diverse ecosystems. *Frontiers in Ecology and the Environment* 9(1): 44–52
- Burns DA, Murdoch PS, Lawrence GB, Michel RL (1998) Effect of groundwater springs on NO₃ concentrations during summer in Catskill Mountain streams. *Water Resources Research* 34(8): 19871996
- Burns DA, Murdoch PS (2005). Effects of a clearcut on the net rates of nitrification and N mineralization in a northern hardwood forest, Catskill Mountains, New York, USA. *Biogeochemistry*, 72(1), pp.123–146
- Burns DA, Aiken GR, Bradley PM, Journey CA, Schelker J (2013) Specific ultra-violet absorbance as an indicator of mercury sources in an Adirondack River basin. *Biogeochemistry* 113: 451–466

- Butman D, Raymond PA (2011) Significant efflux of carbon dioxide from streams and rivers in the United States. *Nature Geoscience* 4(12): 839–842
- Butman DE, Wilson HF, Barnes RT, Xenopoulos MA, Raymond PA (2015) Increased mobilization of aged carbon to rivers by human disturbance. *Nature Geoscience* 8(2): 112–116
- Castro MS, Steudler PA, Melillo JM, Aber JD, Bowden RD (1995) Factors controlling atmospheric methane consumption by temperate forest soils. *Global Biogeochemical Cycles* 9(1): 1–10
- Characklis GW, Wiesner MR (1997) Particles, metals, and water quality in runoff from large urban watershed. *Journal of Environmental Engineering-Asce* 123(8): 753–759
- Chiarenzelli J, Lock R, Cady C, Bregani A, Whitney B (2012) Variation in river multi-element chemistry related to bedrock buffering: an example from the Adirondack region of northern New York, USA. *Environmental Earth Sciences* 67(1): 189–204
- Coble AA, Marcarelli AM, Kane ES, Toczydlowski D, Stottlemeyer R (2016) Temporal patterns of dissolved organic matter biodegradability are similar across three rivers of varying size. *Journal of Geophysical Research: Biogeosciences* 121.6 (2016): 1617–1631
- Creed IF, McKnight DM, Pellerin BA, Green MB, Bergamaschi BA, Aiken GR, Burns DA, Findlay SEG, Shanley JB, Striegl RG, Aulenbach BT, Clow DW, Laudon H, McGlynn BL, McGuire KJ, Smith RA, Stackpole SM (2015) The river as a chemostat: fresh perspectives on dissolved organic matter flowing down the river continuum. *Canadian Journal of Fisheries and Aquatic Sciences* 72(8): 1272–1285
- Creeper N, Fitzpatrick R, Shand P (2013) The occurrence of inland acid sulphate soils in the floodplain wetlands of the Murray Darling Basin, Australia, identified using a simplified incubation method. *Soil Use and Management* 29(1): 130–139
- Demas SY, Hall AM, Fanning DS, Rabenhorst MC, Dzantor EK (2004) Acid sulfate soils in dredged materials from tidal Pocomoke Sound in Somerset County, MD, USA. *Australian Journal of Soil Research* 42(5–6): 537–545
- Duan SW, Xu F, Wang LJ (2007) Long-term changes in nutrient concentrations of the Changjiang River and principal tributaries. *Biogeochemistry* 85(2): 215–234
- Duan SW, Kaushal SS (2013) Warming increases carbon and nutrient fluxes from sediments in streams across land use. *Biogeosciences* 10: 1193–1207
- Duan S, Kaushal SS (2015) Salinization alters fluxes of bioreactive elements from stream ecosystems across land use. *Biogeosciences* 12: 7331–7347
- Duan S, Newcomer-Johnson T, Mayer P, Kaushal S (2016) Phosphorus retention in stormwater control structures across streamflow in urban and suburban watersheds. *Water* 8, 390
- Dugan HA, Bartlett SL, Burke SM, Doubek JP, Krivak-Tetley FE, Skaff NK, Summers JC, Farrell KJ, McCullough IM, Morales-Williams AM, Roberts DC, Ouyang Z, Scordo F, Hanson PC, Weathers KC (2017) Salting our freshwater lakes. *PNAS* 114(17): 4453–4458 [PubMed: 28396392]
- Dupre B, Viers J, Dandurand JL, Polve M, Benezeth P, Vervier P, Braun JJ (1999) Major and trace elements associated with colloids in organic-rich river waters: ultrafiltration of natural and spiked solutions. *Chemical Geology* 160(1–2): 63–80
- European Environment Agency (2012) Nitrate concentrations since the 1950s in selected European rivers. <https://www.eea.europa.eu/data-and-maps/figures/nitrate-concentrations-since-the-1950s-in-selected-european-rivers>. Accessed 11 Aug 2017
- Evans CD, Monteith DT, Cooper DM (2005) Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environmental pollution* 137(1): 5571
- Fanning DS, Fanning MC (1989) *Soil morphology, genesis and classification*. John Wiley and Sons Inc.
- Fasching C, Battin TJ (2012) Exposure of dissolved organic matter to UV-radiation increases bacterial growth efficiency in a clear-water Alpine stream and its adjacent groundwater. *Aquatic Sciences* 74(1): 143–153
- Fellman JB, Hood E, Spencer RGM (2010) Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. *Limnology and Oceanography* 55(6): 2452–2462

- Findlay SE (2005) Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition? *Frontiers in Ecology and the Environment* 3(3): 133–137
- Foley JA, DeFries R, Asner GP, Barford C, Bonan G, Carpenter SR, Chapin FS, Coe MT, Daily GC, Gibbs HK, Helkowski JH, Holloway T, Howard EA, Kucharik CJ, Monfreda C, Patz JA, Prentice IC, Ramankutty N, Snyder PK (2005) Global consequences of land use. *Science* 309(5734): 570–574 [PubMed: 16040698]
- Fovet O, Humbert G, Dupas R, Gascuel-Oudou C, Gruau G, Jaffrezic A, Thelusma G, Fauchaux M, Gilliet N, Hamon Y, Grimaldi C (2018) Seasonal variability of stream water quality response to storm events captured using high-frequency and multi-parameter data. *Journal of Hydrology* 559(2018): 282–293
- Friedrich G, Pohlmann M (2009) Long-term plankton studies at the lower Rhine/Germany. *Limnologica* 39(1): 14–39
- Frost PC, Song K, Buttle JM, Marsalek J, McDonald A, Xenopoulos MA (2015) Urban biogeochemistry of trace elements: What can the sediments of stormwater ponds tell us? *Urban Ecosystems* 18(3): 763–775
- Gaillardet J, Millot R, Dupre B (2003) Chemical denudation rates of the western Canadian orogenic belt: the Stikine terrane. *Chemical Geology* 201(3–4): 257–279
- Gardner JR, Fisher TR, Jordan TE, Knee KL (2016) Balancing watershed nitrogen budgets: accounting for biogenic gases in streams. *Biogeochemistry* 127(2–3): 231–253
- Grimm NB, Gergel SE, McDowell WH, Boyer EW, Dent CL, Groffman P, Hart SC, Harvey J, Johnston C, Mayorga E, McClain ME, Pinay G (2003) Merging aquatic and terrestrial perspectives of nutrient biogeochemistry. *Oecologia* 137(4): 485–501 [PubMed: 14505024]
- Groffman PM, Butterbach-Bahl K, Fulweiler RW, Gold AJ, Morse JL, Stander EK, Tague C, Tonitto C, Vidon P (2009) Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. *Biogeochemistry* 93(1–2): 49–77
- Goolsby DA, Battaglin WA (2001) Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, USA. *Hydrological Processes* 10.1002/hyp.210
- Hamshaw SD, Dewoolkar M, Schroth AW, Wemple BC, Rizzo DM (2018) A new machine-learning approach for classifying hysteresis in suspended-sediment discharge relationships using high-frequency monitoring data. *Water Resources Research* 10.1029/2017WR022238
- Hartland A, Larsen JR, Andersen MS, Baalousha M, O’Carroll D (2015) Association of Arsenic and Phosphorus with Iron Nanoparticles between Streams and Aquifers: Implications for Arsenic Mobility. *Environmental Science & Technology* 49(24): 14101–14109 [PubMed: 26544638]
- Haq S, Kaushal SS, Duan S Episodic salinization and freshwater salinization syndrome mobilize base cations, carbon, and nutrients to streams across urban regions. *Biogeochemistry* (This Issue)
- Hasselov M, von der Kammer F (2008) Iron oxides as geochemical nanovectors for metal transport in soil-river systems. *Elements* 4(6): 401–406
- Hedin LO, von Fischer JC, Ostrom NE, Kennedy BP, Brown MG, Robertson GP (1998) Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. *Ecology* 79(2): 684–703
- Helsel DR, Kim JI, Grizzard TJ, Randall CW, Hoehn RC (1979) Land-use influences on metals in storm drainage. *Journal Water Pollution Control Federation* 51(4): 709–717
- Hood E, Gooseff MN, Johnson SL (2006) Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, Oregon. *Journal of Geophysical Research-Biogeosciences* 111(G1)
- Hosen JD, McDonough OT, Febria CM, Palmer MA (2014) Dissolved organic matter quality and bioavailability changes across an urbanization gradient in headwater streams. *Environmental Science & Technology* 48(14): 7817–7824 [PubMed: 24919113]
- Inamdar SP, Mitchell MJ (2007) Storm event exports of dissolved organic nitrogen (DON) across multiple catchments in a glaciated forested watershed. *Journal of Geophysical Research-Biogeosciences* 112(G2)
- Inamdar S, Singh S, Dutta S, Levia D, Mitchell M, Scott D, Bais H, McHale P (2011) Fluorescence characteristics and sources of dissolved organic matter for stream water during storm events in a forested mid-Atlantic watershed. *Journal of Geophysical Research-Biogeosciences* 116(G03043)

- Jacinthe PA, Bills JS, Tedesco LP, Barr RC (2012) Nitrous oxide emission from riparian buffers in relation to vegetation and flood frequency. *Journal of Environmental Quality* 41(1): 95–105 [PubMed: 22218178]
- Jacinthe PA, Vidon P, Fisher K, Liu X, Baker ME (2015) Soil methane and carbon dioxide fluxes from cropland and riparian buffers in different hydrogeomorphic settings. *Journal of Environmental Quality* 44(4): 1080–1090 [PubMed: 26437089]
- Jayawickreme DH, Santoni CS, Kim JH, Jobbagy EG, Jackson RB (2011) Changes in hydrology and salinity accompanying a century of agricultural conversion in Argentina. *Ecological Applications* 21(7): 23672379
- Jenne EA (1968) Controls on Mn Fe Co Ni Cu and Zn concentrations in soils and water - significant role of hydrous Mn and Fe oxides. *Advances in Chemistry Series* (73): 337
- Kaushal SS, Groffman PM, Band LE, Shields CA, Morgan RP, Palmer MA, Belt KT, Fisher GT, Swan CM, Findlay SEG (2008) Interaction between urbanization and climate variability amplifies watershed nitrate export in Maryland. *Environmental Science & Technology* 42 5872–5878, 2008. 10.1021/es800264f [PubMed: 18767638]
- Kaushal SS, McDowell WH, Wollheim WM (2014) Tracking evolution of urban biogeochemical cycles: past, present, and future. *Biogeochemistry* 121(1): 1–2
- Kaushal SS, Lewis WM (2005) Fate and transport of organic nitrogen in minimally disturbed montane streams of Colorado, USA. *Biogeochemistry* 74(3): 303–321
- Kaushal SS, Belt KT (2012) The urban watershed continuum: evolving spatial and temporal dimensions. *Urban Ecosystems* 15(2): 409–435
- Kaushal SS, Likens GE, Utz RM, Pace ML, Grese M, Yepsen M (2013) Increased river alkalization in the eastern US. *Environmental Science & Technology* 47(18): 10302–10311 [PubMed: 23883395]
- Kaushal SS, Mayer PM, Vidon PG, Smith RM, Pennino MJ, Newcomer TA, Duan S, Welty C, Belt KT (2014) Land use and climate variability amplify carbon, nutrient, and contaminant pulses: a review with management implications. *Journal of the American Water Resources Association* 50(3): 585–614
- Kaushal SS, Duan S, Doody TR, Haq S, Smith RM, Johnson TAN, Newcomb KD, Gorman J, Bowman N, Mayer PM, Wood KL, Belt KT, Stack WP (2017) Human-accelerated weathering increases salinization, major ions, and alkalization in fresh water across land use. *Applied Geochemistry* 83: 121–135 [PubMed: 30220785]
- Kaushal SS, Likens GE, Pace ML, Utz R, Haq S, Gorman J, Grese M (2018) Freshwater salinization syndrome on a continental scale. *Proceedings of the National Academy of Sciences of the United States of America* DOI 10.1073/pnas.1711234115
- Kelly V, Stets EG, Crawford C (2015) Long-term changes in nitrate conditions over the 20th century in two Midwestern Corn Belt streams. *Journal of Hydrology* 525: 559–571
- Kerr JG, Eimers MC, Creed IF, Adams MB, Beall F, Burns D, Campbell JL, Christopher SF, Clair TA, Courchesne F, Duchesne L, Fernandez I, Houle D, Jeffries DS, Likens GE, Mitchell MJ, Shanley J, Yao H (2012) The effect of seasonal drying on sulphate dynamics in streams across southeastern Canada and the northeastern USA. *Biogeochemistry* 111(1–3): 393–409
- Kim DG, Mishurov M, Kiely G (2010) Effect of increased N use and dry periods on N₂O emission from a fertilized grassland. *Nutrient Cycling in Agroecosystems* 88(3): 397–410
- Kim DG, Vargas R, Bond-Lamberty B, Turetsky MR (2012) Effects of soil rewetting and thawing on soil gas fluxes: a review of current literature and suggestions for future research. *Biogeosciences* 9(7): 24592483
- Koenig LE, Shattuck MD, Snyder LE, Potter JD, McDowell WH (2017) Deconstructing the Effects of Flow on DOC, Nitrate, and Major Ion Interactions Using a High-Frequency Aquatic Sensor Network. 10.1002/2017WR020739
- Kritzberg ES, Ekstrom SM (2012) Increasing iron concentrations in surface waters - a factor behind brownification? *Biogeosciences* 9(4): 1465–1478
- Kritzberg ES, Villanueva AB, Jung M, Reader HE (2014) Importance of boreal rivers in providing iron to marine waters. *Plos One* 9(9): 1–10

- Kuusisto-Hjort P, Hjort J (2013) Land use impacts on trace metal concentrations of suburban stream sediments in the Helsinki region, Finland. *Science of the Total Environment* 456: 222–230 [PubMed: 23602975]
- Leventhal J, Taylor C (1990) Comparison of methods to determine degree of pyritization. *Geochimica et Cosmochimica Acta* 54(9): 2621–2625
- Likens GE, Driscoll CT, Buso DC, Siccama TG, Johnson CE, Lovett GM, Ryan DF, Fahey T, Reiners WA (1994) The biogeochemistry of potassium at Hubbard Brook. *Biogeochemistry* 25(2): 61–125
- Likens GE (2013) *Biogeochemistry of a Forested Ecosystem*, Third Edition. Springer 208.
- Loecke TD, Burgin AJ, Riveros-Iregui DA, Ward AS, Thomas SA, Davis CA, St Clair MA (2017) Weather whiplash in agricultural regions drives deterioration of water quality. *Biogeochemistry* 133(1): 7–15
- Lu YH, Bauer JE, Canuel EA, Yamashita Y, Chambers RM, Jaffe R (2013) Photochemical and microbial alteration of dissolved organic matter in temperate headwater streams associated with different land use. *Journal of Geophysical Research-Biogeosciences* 118(2): 566–580
- Lu YH, Bauer JE, Canuel EA, Chambers RM, Yamashita Y, Jaffe R, Barrett A (2014) Effects of land use on sources and ages of inorganic and organic carbon in temperate headwater streams. *Biogeochemistry* 119(1–3): 275–292
- Lupon A, Sabater F, Minarro A, Bernal S (2016) Contribution of pulses of soil nitrogen mineralization and nitrification to soil nitrogen availability in three Mediterranean forests. *European Journal of Soil Science* 67(3): 303–313
- Mallakpour I, Villarini G (2015) The changing nature of flooding across the central United States. *Nature Climate Change* 5(3): 250–254
- Martin JM, Meybeck M (1979) Elemental mass-balance of material carried by major world rivers. *Marine Chemistry* 7(3): 173–206
- McGlynn BL, McDonnell JJ (2003) Role of discrete landscape units in controlling catchment dissolved organic carbon dynamics. *Water Resources Research* 39(4):
- McKnight DM, Bencala KE (1990) The chemistry of iron, aluminum, and dissolved organic material in 3 acidic, metal-enriched, mountain streams, as controlled by watershed and in-stream processes. *Water Resources Research* 26(12): 3087–3100
- McLaughlin C, Kaplan LA (2013) Biological lability of dissolved organic carbon in stream water and contributing terrestrial sources. *Freshwater Science* 32(4): 1219–1230
- Mei Y, Hornberger GM, Kaplan LA, Newbold JD, Aufdenkampe AK (2014) The delivery of dissolved organic carbon from a forested hillslope to a headwater stream in southeastern Pennsylvania, USA. *Water Resources Research* 50(7): 5774–5796
- Meybeck M, Lestel L, Carré C, et al. (2016) Trajectories of river chemical quality issues over the Longue Durée: the Seine River (1900s-2010). *Environ Sci Pollut Res* 1–17.
- Milly PCD, Betancourt J, Falkenmark M, Hirsch RM, Kundzewicz ZW, Lettenmaier DP, Stouffer RJ (2008) Climate change - Stationarity is dead: Whither water management? *Science* 319(5863): 573–574 [PubMed: 18239110]
- Minaudo C, Meybeck M, Moatar F, Gassama N, Curie F (2015) Eutrophication mitigation in rivers: 30 years of trends in spatial and seasonal patterns of biogeochemistry of the Loire River (1980–2012). *Biogeosciences* 12(8): 2549–2563
- Mitchell AC, Brown GH, Fuge R (2006) Minor and trace elements as indicators of solute provenance and flow routing in a subglacial hydrological system. *Hydrological Processes* 20(4): 877–897
- Mohiuddin KM, Zakir HM, Otomo K, Sharmin S, Shikazono N (2010) Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. *International Journal of Environmental Science and Technology* 7(1): 17–28
- Monteith DT, Stoddard JL, Evans CD, Wit HA, Forsius M, Hogasen T, Wilander A, Skjelkvale BL, Jeffries DS, Vuorenmaa J, Keller B, Kopacek J, Vesely J (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature* 450: 537–541 [PubMed: 18033294]
- Morse JL, Ardon M, Bernhardt ES (2012) Greenhouse gas fluxes in southeastern U.S. coastal plain wetlands under contrasting land uses. *Ecological Applications* 22(1): 264–280 [PubMed: 22471089]

- Mosley LM, Biswas TK, Cook FJ, Marschner P, Palmer D, Shand P, Yuan C, Fitzpatrick RW (2017) Prolonged recovery of acid sulfate soils with sulfuric materials following severe drought: causes and implications. *Geoderma* 308: 312–320
- Muhrizal S, Shamsuddin J, Husni MHA, Fauziah I (2003) Alleviation of aluminum toxicity in an acid sulfate soil in Malaysia using organic materials. *Communications in Soil Science and Plant Analysis* 34(19–20): 2993–3012
- Mulholland PJ, Wilson GV, Jardine PM (1990) Hydrogeochemical response of a forested watershed to storms - effects of preferential flow along shallow and deep pathways. *Water Resources Research* 26(12): 3021–3036
- Naiman RJ, Decamps H, McClain ME (2005) Riparia: ecology, conservation, and management of streamside communities.
- Nodvin SC, Driscoll CT, Likens GE (1986) The effect of pH on sulfate adsorption by a forest soil. *Soil Science*, 142(2): 69–75
- Paerl HW (1997) Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as “new” nitrogen and other nutrient sources. *Limnology and Oceanography* 42: 1154–1165.
- Petrone KC, Fellman JB, Hood E, Donn MJ, Grierson PF (2011) The origin and function of dissolved organic matter in agro-urban coastal streams. *Journal of Geophysical Research-Biogeosciences* 116 (G01028)
- Pons LJ, Vandermo Wh (1973) Soil genesis under dewatering regimes during 1000 years of polder development. *Soil Science* 116(3): 228–235
- Poulton SW, Raiswell R (2002) The low-temperature geochemical cycle of iron: From continental fluxes to marine sediment deposition. *American Journal of Science* 302(9): 774–805
- Rabenhorst MC, Valladares TM (2005) Estimating the depth to sulfide-bearing materials in Upper Cretaceous sediments in landforms of the Maryland coastal plain. *Geoderma* 126(1–2): 101–116
- Raiswell R (2011) Iron Transport from the Continents to the Open Ocean: The Aging-Rejuvenation Cycle. *Elements* 7(2): 101–106
- Raiswell R, Canfield DE (2012) the iron biogeochemical cycle past and present. *Geochemical Perspectives* 1(1): 1–220
- Raymond PA, Saiers JE (2010) Event controlled DOC export from forested watersheds. *Biogeochemistry* 100(1–3): 197–209
- Raymond PA, Spencer RGM (2015) Riverine DOM. *Biogeochemistry of Marine Dissolved Organic Matter*, 2nd Edition: 509–+
- Reddy KR, DeLaune RD (2008) *Biogeochemistry of wetlands: science and applications*. CRC press Boca Raton, FL 774 pages.
- Reisinger AJ, Rosi EJ, Bechtold HA, Doody TR, Kaushal SS, and Groffman PM 2017 Recovery and resilience of urban stream metabolism following Superstorm Sandy and other floods. *Ecosphere* <https://doi.org/10.1002/ecs2.1776>
- Rohatgi A (2017) WebPlotDigitizer, Version 3.12. <http://arohatgi.info/WebPlotDigitizer>. Accessed 11 Aug 2017 and 20 Oct 2017.
- Romero E, Le Gendre R, Garnier J, Billen G, Fisson C, Silvestre M, Riou P (2016) Long-term water quality in the lower Seine: Lessons learned over 4 decades of monitoring. *Environmental Science & Policy* 58: 141–154
- Rosenberg BD, Schroth AW (2017) Coupling of reactive riverine phosphorus and iron species during hot transport moments: impacts of land cover and seasonality. *Biogeochemistry* 132(1–2): 103–122
- Sarkkola S, Nieminen M, Koivusalo H, Lauren A, Kortelainen P, Mattsson T, Palviainen M, Piirainen S, Starr M, Finer L (2013) Iron concentrations are increasing in surface waters from forested headwater catchments in eastern Finland. *Science of the Total Environment* 463: 683–689 [PubMed: 23850658]
- Schoepfer VA, Bernhardt ES, Burgin AJ (2014) Iron clad wetlands: Soil iron-sulfur buffering determines coastal wetland response to salt water incursion. *Journal of Geophysical Research-Biogeosciences* 119(12): 2209–2219

- Schroth AW, Crusius J, Chever F, Bostick BC, Rouxel OJ (2011) Glacial influence on the geochemistry of riverine iron fluxes to the Gulf of Alaska and effects of deglaciation. *Geophysical Research Letters* 38 (L16605)
- Schroth AW, Crusius J, Hoyer I, Campbell R (2014) Estuarine removal of glacial iron and implications for iron fluxes to the ocean. *Geophysical Research Letters* 41(11): 3951–3958
- Seitzinger SP, Phillips L (2017) Nitrogen stewardship in the Anthropocene. *Science* 357(6349): 350–351 [PubMed: 28751593]
- Sinha E, Michalak AM, Balaji V (2017) Eutrophication will increase during the 21st century as a result of precipitation changes. *Science* 357(6349): 405–408 [PubMed: 28751610]
- Sloto RA (2003) Historical ground-water-flow patterns and trends in iron concentrations in the Potomac--Raritan--Magothy aquifer system in parts of Philadelphia, Pennsylvania, and Camden and Gloucester Counties, New Jersey. USGS Report No. 2003-4255
- Smith RM, Kaushal SS (2015) Carbon cycle of an urban watershed: exports, sources, and metabolism. *Biogeochemistry* 126(1–2): 173–195
- Smith RM, Kaushal SS, Beaulieu JJ, Pennino MJ, Welty C (2017) Influence of infrastructure on water quality and greenhouse gas dynamics in urban streams. *Biogeosciences* 14(11): 2831–2849
- St. Louis VL, Rudd JW, Kelly CA, Beaty CA, Beaty KG, Bloom NS, and Flett RJ (1994) Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *Canadian Journal of Fisheries and Aquatic Sciences* 51: 1065–1076
- Steffen W, Broadgate W, Deutsch L, Gaffney O, Ludwig C (2015) The trajectory of the Anthropocene: the great acceleration. *The Anthropocene Review* 2(1):81–98.
- Syvitski JPM, Kettner A (2011) Sediment flux and the Anthropocene. *Philosophical Transactions of the Royal Society a-Mathematical Physical and Engineering Sciences* 369(1938): 957–975
- Tagliabue A, Bowie AR, Boyd PW, Buck KN, Johnson KS, Saito MA (2017) The integral role of iron in ocean biogeochemistry. *Nature* 543(7643): 51–59 [PubMed: 28252066]
- Tripler CE, Kaushal SS, Likens GE, Walter MT (2006) Patterns in potassium dynamics in forest ecosystems. *Ecology Letters* 9(4): 451–466 [PubMed: 16623731]
- US EPA (2015) Fertilizer Applied for Agricultural Purposes; EPA's Report on the Environment. <https://cfpub.epa.gov/roe/indicator.cfm?i=55#2>. Accessed 11 Aug 2017
- Valdemarsen T, Kristensen E, Holmer M (2010) Sulfur, carbon, and nitrogen cycling in faunated marine sediments impacted by repeated organic enrichment. *Marine Ecology Progress Series* 400: 37–53
- Vannote RL, Minshall GW, Cummins KW, Sedell JR, Cushing CE (1980) The River Continuum Concept. *Science* 37: 130–137
- Vaughan MCH, Bowden WB, Shanley JB, Vermilyea A, Sleeper R, Gold AJ, Pradhanang SM, Inamdar SP, Levia DF, Andres AS, Birgand F, Schroth AW (2017) High-frequency dissolved organic carbon and nitrate measurements reveal differences in storm hysteresis and loading in relation to land cover and seasonality. *Water Resources Research* 53(7): 5345–5363
- Vidon P, Wagner LE, Soyeux E (2008) Changes in the character of DOC in streams during storms in two Midwestern watersheds with contrasting land uses. *Biogeochemistry* 88(3): 257–270
- Vidon P, Allan C, Burns D, Duval TP, Gurwick N, Inamdar S, Lowrance R, Okay J, Scott D, Sebestyen S (2010) Hot spots and hot moments in riparian zones: potential for improved water quality management. *Journal of the American Water Resources Association* 46(2): 278–298
- Vidon P, Jacinthe P-A, Liu X, Fisher K, Baker M (2014a) Hydrobiogeochemical controls on riparian nutrient and greenhouse gas dynamics: 10 years post-restoration. *Journal of the American Water Resources*
- Vidon P, Carleton W, Mitchell M (2014b) Mercury proxies and mercury dynamics in a forested watershed
- Vidon P, Marchese S, Rook S (2017) Impact of Hurricane Irene and Tropical Storm Lee on riparian zone hydrology and biogeochemistry. *Hydrological Processes* 31(2): 476–488
- Viers J, Dupre B, Polve M, Schott J, Dandurand JL, Braun JJ (1997) Chemical weathering in the drainage basin of a tropical watershed (Nsimi-Zoetele site, Cameroon): Comparison between organic-poor and organic-rich waters. *Chemical Geology* 140(3–4): 181–206

- Warren LA, Haack EA (2001) Biogeochemical controls on metal behaviour in freshwater environments. *Earth-Science Reviews* 54(4): 261–320
- Waters CN, Zalasiewicz J, Summerhayes C, Barnosky AD, Poirier C, Galuszka A, Cearreta A, Edgeworth M, Ellis EC, Ellis M, Jeandel C, Leinfelder R, McNeill JR, Richter DD, Steffen W, Syvitski J, Vidas D, Wagreich M, Williams M, An ZS, Grinevald J, Odada E, Oreskes N, Wolfe AP (2016) The Anthropocene is functionally and stratigraphically distinct from the Holocene. *Science* 351(6269): 137–+
- Welsch DL, Burns DA, Murdoch PS (2004) Processes affecting the response of sulfate concentrations to clearcutting in a northern hardwood forest, Catskill Mountains, New York, USA. *Biogeochemistry*, 68(3): 337–354
- Williams CJ, Frost PC, Morales-Williams AM, Larson JH, Richardson WB, Chiandetti AS, Xenopoulos MA (2016) Human activities cause distinct dissolved organic matter composition across freshwater ecosystems. *Global Change Biology* 22(2): 613–626 [PubMed: 26390994]
- Wilson HF, Xenopoulos MA (2008) Ecosystem and seasonal control of stream dissolved organic carbon along a gradient of land use. *Ecosystems* 11(4): 555–568
- Wilson HF, Xenopoulos MA (2009) Effects of agricultural land use on the composition of fluvial dissolved organic matter. *Nature Geoscience* 2(1): 37–41
- Wilson HF, Saiers JE, Raymond PA, Sobczak WV (2013) Hydrologic drivers and seasonality of dissolved organic carbon concentration, nitrogen content, bioavailability, and export in a forested New England stream. *Ecosystems* 16(4): 604–616
- Wilson HF, Raymond PA, Saiers JE, Sobczak WV, Xu N (2016) Increases in humic and bioavailable dissolved organic matter in a forested New England headwater stream with increasing discharge. *Marine and Freshwater Research* 67(9): 1279–1292
- Wollheim WM, Mulukutla GK, Cook C, Carey RO (2017) Aquatic nitrate retention at river network scales across flow conditions determined using nested in situ sensors. *Water Resources Research* 10.1002/2017WR020644
- Worrall F, Harriman R, Evans CD, Watts CD, Adamson J, Neal C, Tipping E, Burt T, Grieve I, Monteith D, Naden PS (2004) Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry* 70(3): 369–402
- Zhang Q, Brady DC and Ball WP, 2013 Long-term seasonal trends of nitrogen, phosphorus, and suspended sediment load from the non-tidal Susquehanna River Basin to Chesapeake Bay. *Science of the total environment*, 452, pp.208–221. [PubMed: 23506853]

Watersheds as Sieves, Filters, Chromatographic Columns, and Reactors

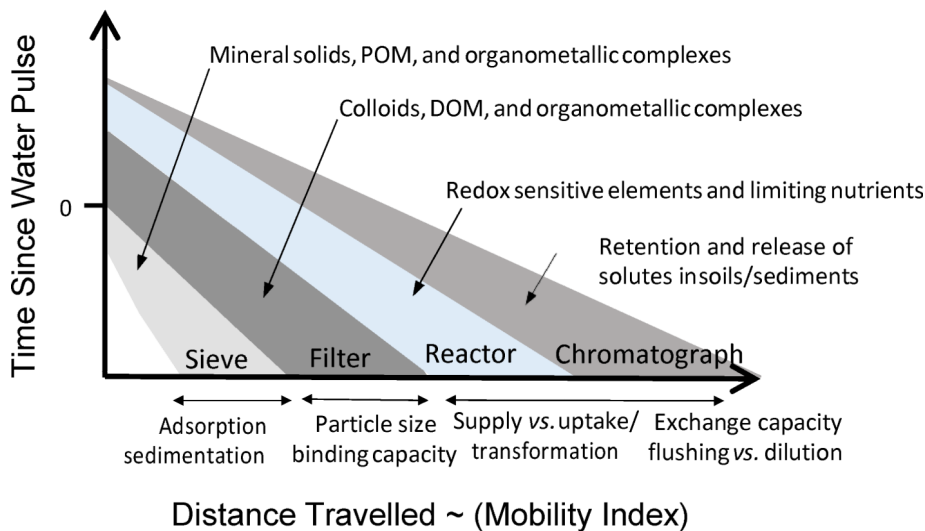
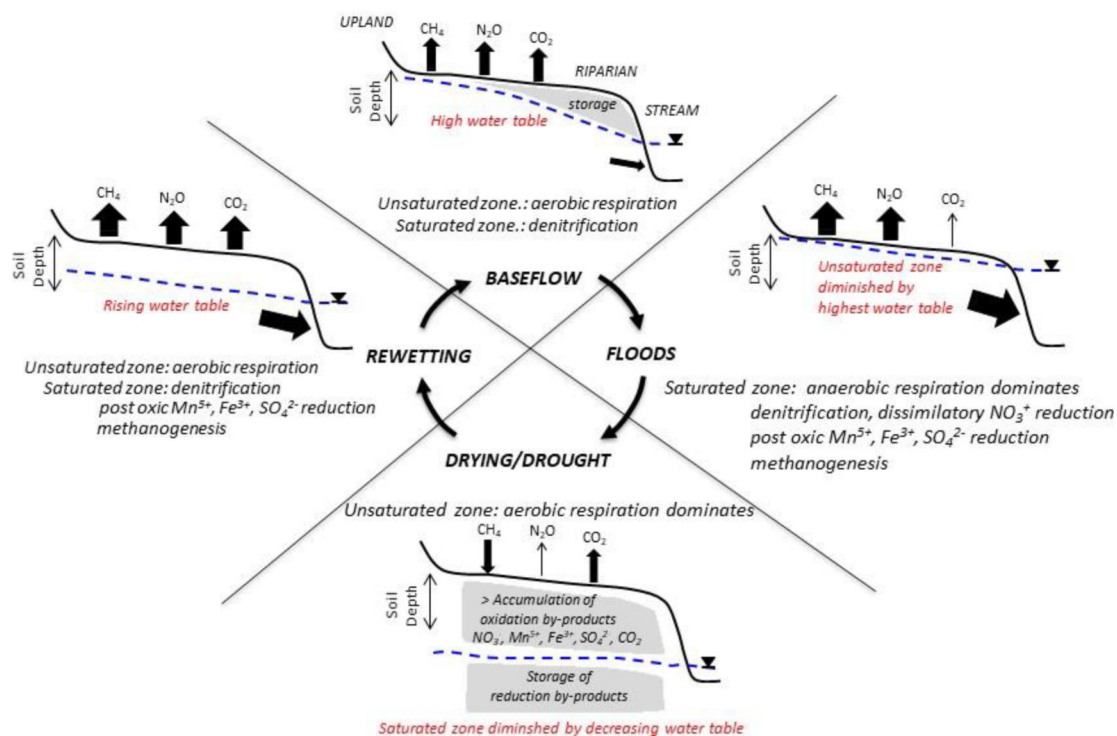


Figure 1. Conceptual model illustrating how groups of elements can be hydrologically linked as ‘chemical cocktails’ and transported along fluvial networks of the Anthropocene depending on the timing of the peak (before or after the hydrograph peak), and the distance travelled along the fluvial network. 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.

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

**Figure 2.**

Conceptual model illustrating how reactive chemical cocktails vary in formation and transport along the drying-rewetting cycle with water table, pre vs. 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, NO₃, SO₄, PO₄, 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.

Urban watershed “chemical cocktail” transport responses during extreme storm events

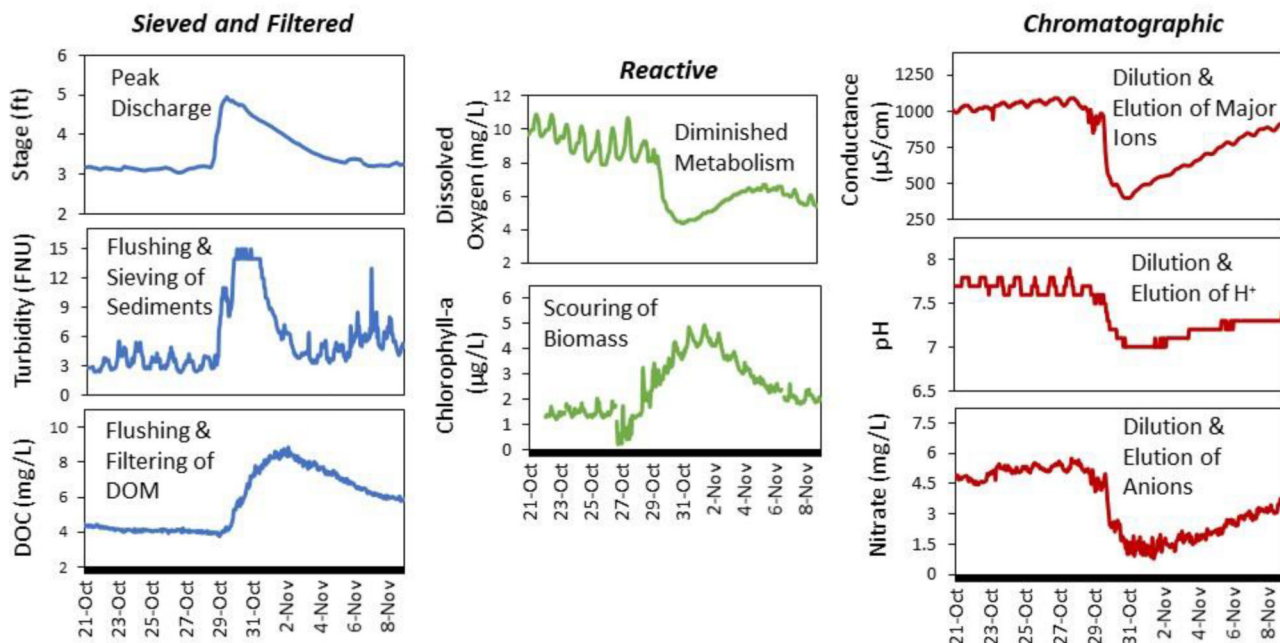


Figure 3.

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.

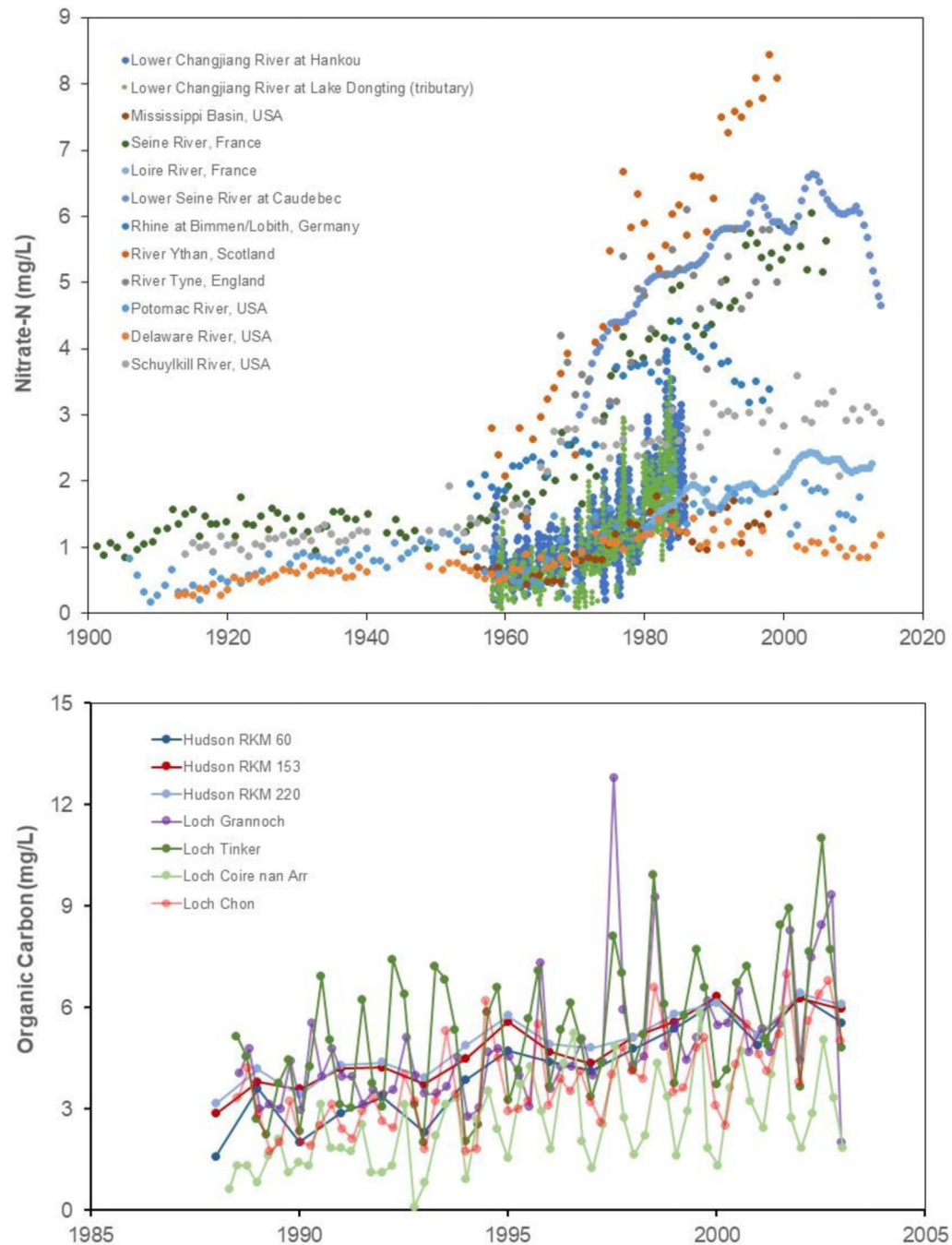


Figure 4.

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-NO₃ 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 1988–2003. 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 trends (Findlay et al. 2005), potentially linked to changes in use, nitrogen, and CO₂ enrichment (Evans et al., 2005). WebPlotDigitizer was used to extract data from graphs when it was not available in text form (Rohatgi 2017).

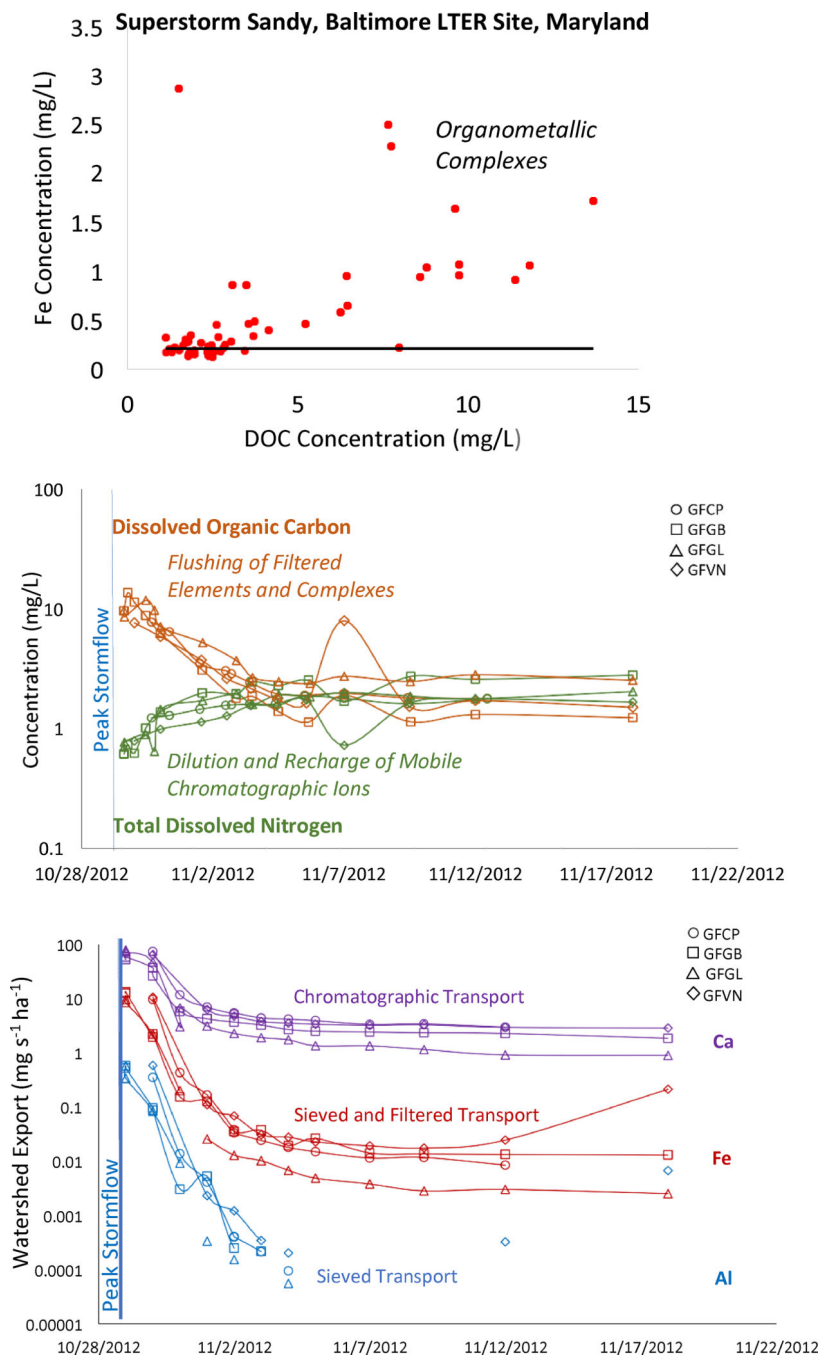


Figure 5. (Top Panel) Relationships between total iron concentrations (particulate plus dissolved) and dissolved organic carbon (DOC) following Superstorm Sandy in urbanized streams of the Baltimore LongTerm Ecological Research site. (Middle Panel) Relationships between total dissolved nitrogen and dissolved organic carbon (DOC) following Superstorm Sandy in urbanized streams of the Baltimore LongTerm 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.

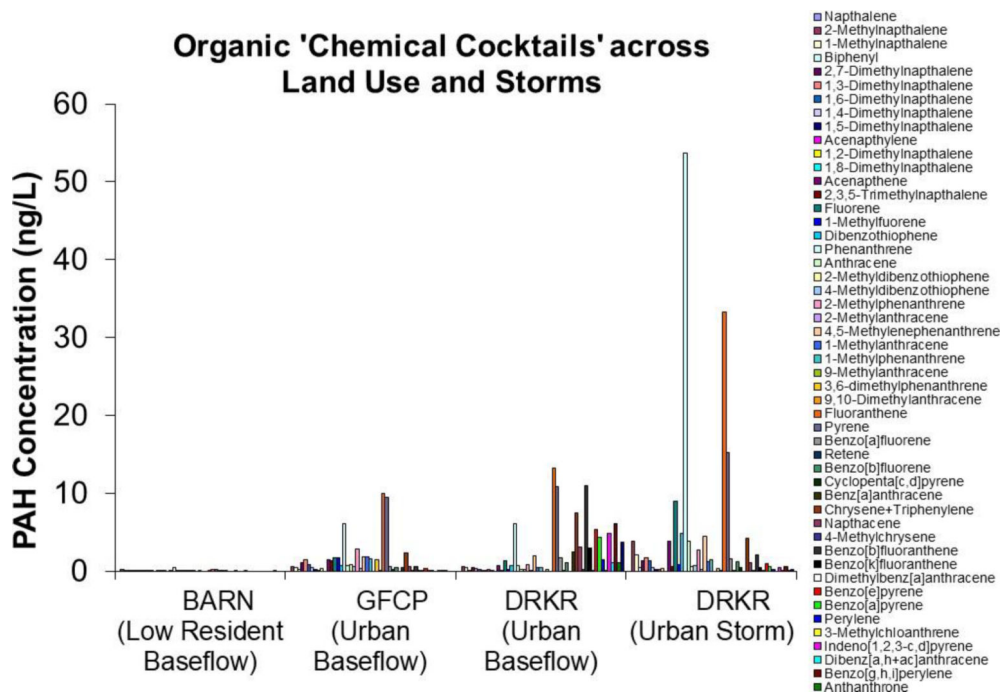


Figure 6. Anthropogenic sources can also contribute to chemical cocktails of organic matter. Polycyclic aromatic hydrocarbons (PAHs) vary in streams across a land use gradient at the Baltimore Long-Term Ecological Research site. BARN is forest dominated with low residential development, and sites are 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.

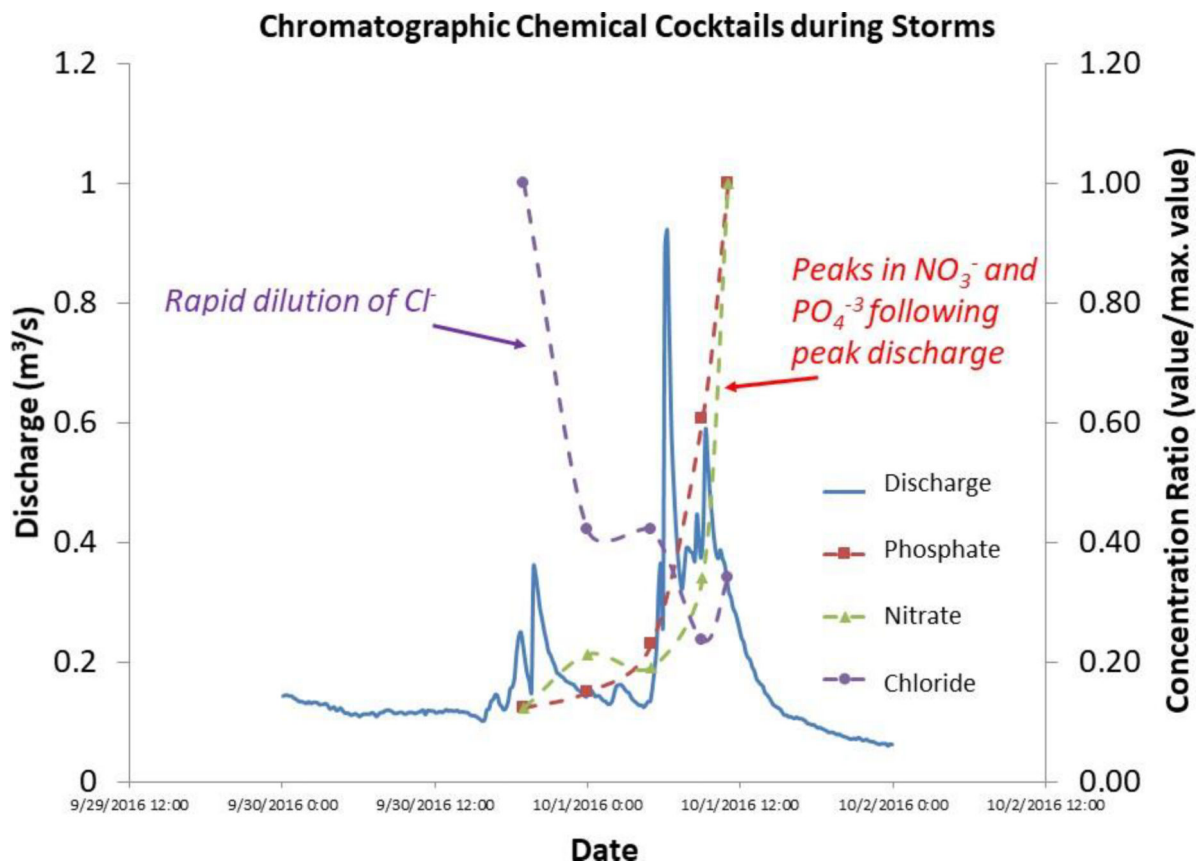


Figure 7.

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.

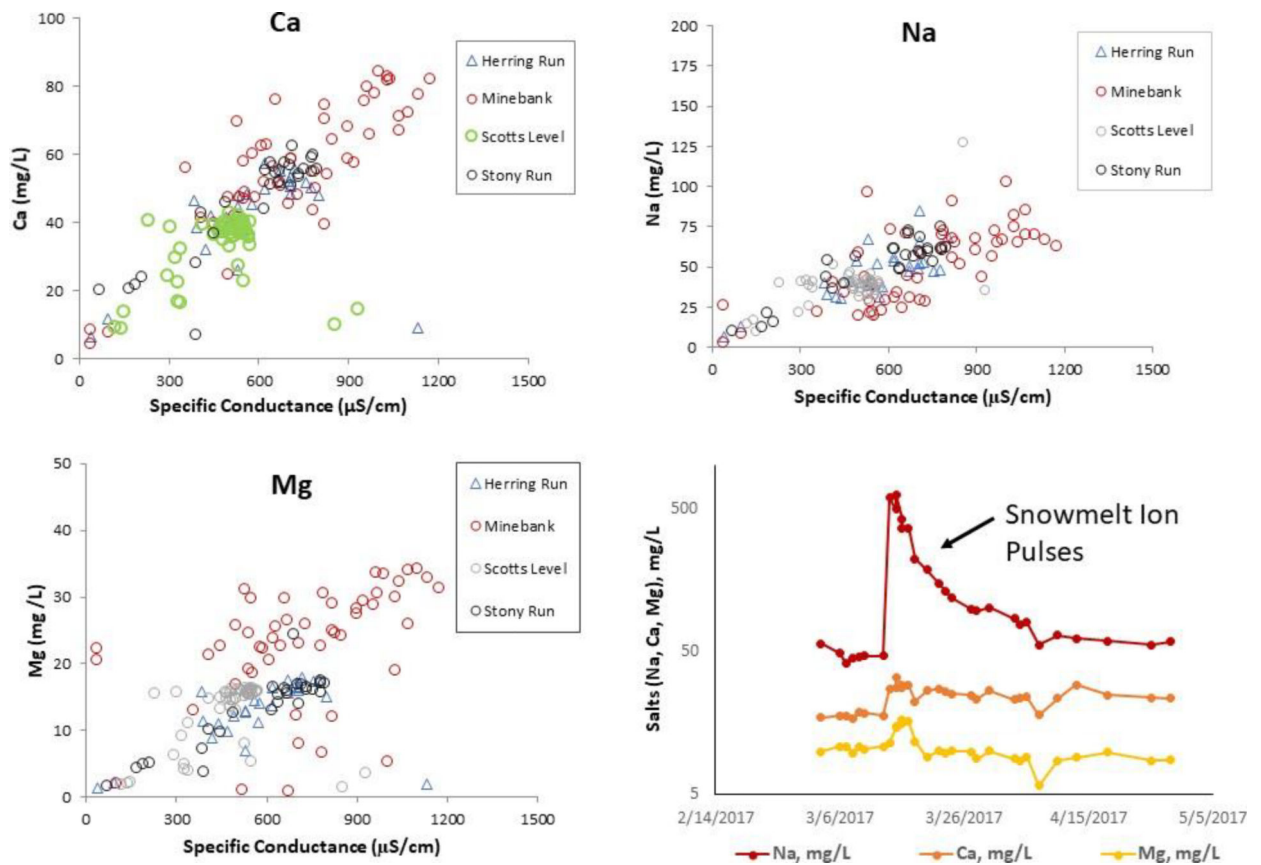


Figure 8.

(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 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.

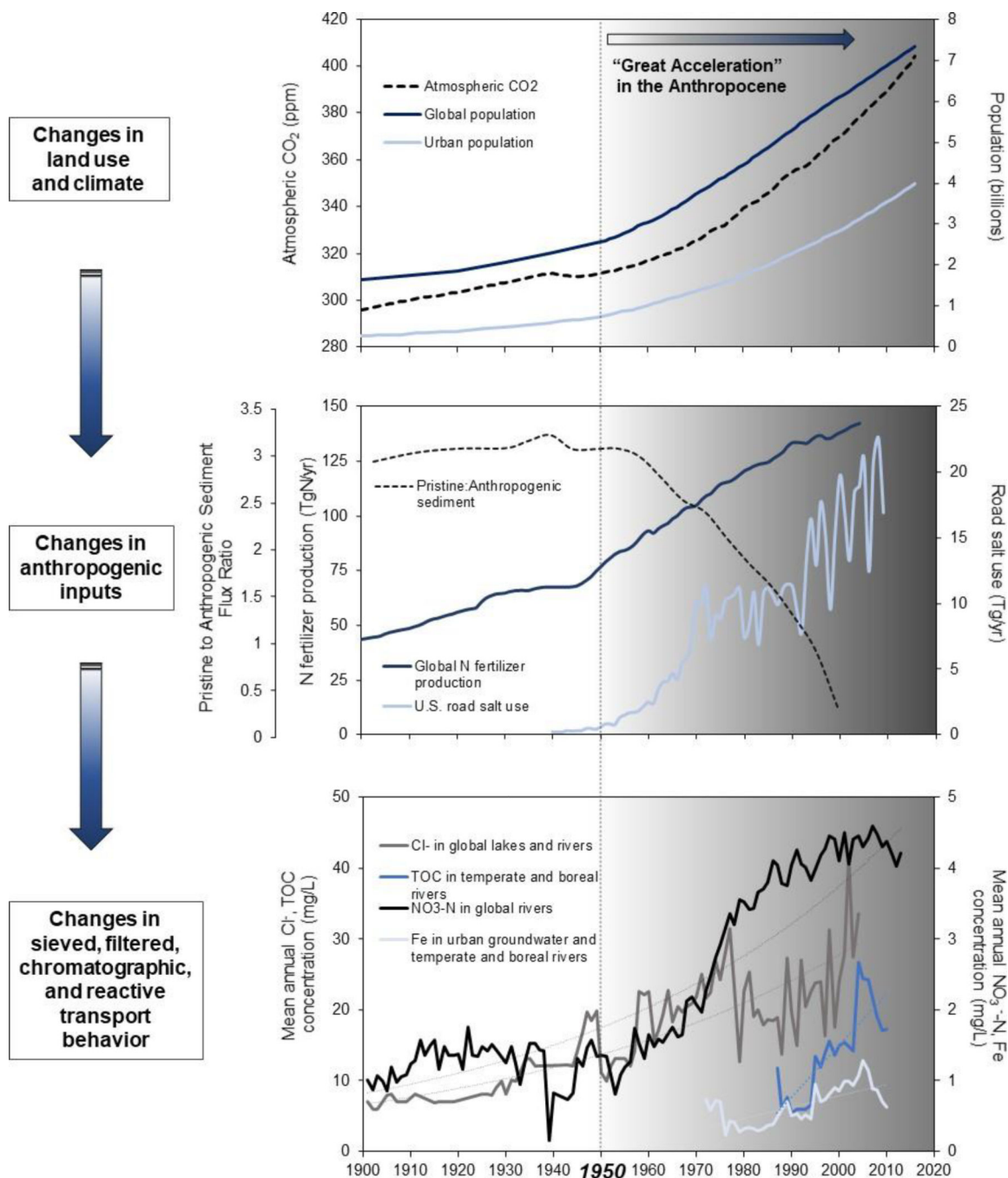


Figure 9.

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 CO₂ (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 et al. 2014, USGS Mineral Resources). Land development decreased 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); (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. 2014, Kaushal 2016).