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LAND USE AND CLIMATE VARIABILITY AMPLIFY CARBON, NUTRIENT, AND CONTAMINANT PULSES: A REVIEW WITH MANAGEMENT IMPLICATIONS

Sujay S. Kaushal
University of Maryland, skaushal@umd.edu

Paul M. Mayer
U.S. Environmental Protection Agency

Philippe G. Vidon
Department of Forest and Natural Resources Management

Rose M. Smith
University of Maryland

Michael J. Pennino
University of Maryland

See next page for additional authors

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LAND USE AND CLIMATE VARIABILITY AMPLIFY CARBON, NUTRIENT, AND CONTAMINANT PULSES: A REVIEW WITH MANAGEMENT IMPLICATIONS[1]

Sujay S. Kaushal, Paul M. Mayer, Philippe G. Vidon, Rose M. Smith, Michael J. Pennino, Tamara A. Newcomer, Shuiwang Duan, Claire Welty, and Kenneth T. Belt[2]

ABSTRACT: Nonpoint source pollution from agriculture and urbanization is increasing globally at the same time climate extremes have increased in frequency and intensity. We review >200 studies of hydrologic and gaseous fluxes and show how the interaction between land use and climate variability alters magnitude and frequency of carbon, nutrient, and greenhouse gas pulses in watersheds. Agricultural and urban watersheds respond similarly to climate variability due to headwater alteration and loss of ecosystem services to buffer runoff and temperature changes. Organic carbon concentrations/exports increase and organic carbon quality changes with runoff. Nitrogen and phosphorus exports increase during floods (sometimes by an order of magnitude) and decrease during droughts. Relationships between annual runoff and nitrogen and phosphorus exports differ across land use. CH_4 and N_2O pulses in riparian zones/floodplains predominantly increase with: flooding, warming, low oxygen, nutrient enrichment, and organic carbon. CH_4, N_2O, and CO_2 pulses in streams/rivers increase due to similar factors but effects of floods are less known compared to base flow/droughts. Emerging questions include: (1) What factors influence lag times of contaminant pulses in response to extreme events? (2) What drives resistance/resilience to hydrologic and gaseous pulses? We conclude with eight recommendations for managing watershed pulses in response to interactive effects of land use and climate change.

(KEY TERMS: eutrophication; water quality; hypoxia; nonpoint source pollution; methane; nitrous oxide; carbon dioxide; restoration; wetlands; best management practices.)

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INTRODUCTION

Agricultural and urban watersheds provide key ecosystem services such as food production, drinking water, climate regulation, and recreational opportunities (Foley *et al.*, 2005). However, agricultural and urban land use has also increased carbon, nutrient, and other contaminant loads in many streams and rivers (Cooke and Prepas, 1998; David and Gentry,

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[2]Associate Professor (Kaushal), Graduate Student (Smith, Newcomer), and Research Associate (Duan), Department of Geology and Earth Systems Science Interdisciplinary Center, University of Maryland, College Park, Maryland 20740; Chief (Mayer), Ecological Effects Branch, National Health and Environmental Effects Research Lab, U.S. Environmental Protection Agency, Corvallis, Oregon 97333; Associate Professor (Vidon), Department of Forest and Natural Resources Management, SUNY-ESF, Syracuse, New York 13210; Graduate Student (Pennino), Marine Estuarine Environmental Science Graduate Program; Director (Welty), Center for Urban Environmental Research and Education and Professor (Welty), Department of Chemical Biochemical, and Environmental Engineering, University of Maryland Baltimore County, Baltimore, Maryland 21250; and Hydrologist (Belt), Northern Research Station, USDA Forest Service, Baltimore, Maryland 21228 (E-Mail/Kaushal: skaushal@umd.edu).

2000; McIsaac *et al.*, 2002; Wagner *et al.*, 2008). Simultaneously, increased climate variability in the past few decades has altered regional runoff regimes and water temperatures (IPCC, 2007). As agriculture intensifies to feed the growing human population, urban centers have grown to where over 60% of the world's population now lives in urban areas and relies on urban water resources (Foley *et al.*, 2005; Grimm *et al.*, 2008). We therefore need to better understand how land use and climate interact in agricultural and urban watersheds to predict how key ecosystems services in these landscapes will change in the future.

Previous work has shown that land use and climate variability has contributed to significant degradation of regional and global water quality (Vitousek *et al.*, 1997; Foley *et al.*, 2005; Grimm *et al.*, 2008; Suddick *et al.*, 2012). The interaction between land use and climate variability can increase the amplitude and frequency of contaminant "pulses," or large changes in concentrations or fluxes of materials over relatively short time periods (Kaushal *et al.*, 2008; Vidon *et al.*, 2009; Kaushal *et al.*, 2010a, b). Pulses are important because large fluctuations in concentrations can exceed thresholds for sensitive organisms and water quality regulations, and pulses can deliver large contaminant loads to receiving waters (e.g., drinking water supplies, estuaries, etc.). Although many studies in the literature address the impact of land use or storms on water quality, few (if any) investigate the interactive impacts of land use and climate variability on contaminant pulses at the watershed scale. This hinders our ability to develop adaptation and mitigation strategies for managing water quality in response to future climate extremes. Here, we define climate variability as deviations from a long-term average condition and increased frequency of extreme events due to human activities and global change.

First, we review how the interaction between land use and climate variability amplifies pulses of carbon, nutrients, and contaminants in agricultural and urban watersheds. In some cases, we explore the effects of extreme events and weather patterns to gain insights about potential impacts, in addition to examining longer term patterns. Second, we discuss emerging research questions regarding increasingly pulsed watersheds, and discuss monitoring implications. Third, we discuss how the interactive impacts of land use and climate must be considered in developing management strategies for drinking water supplies and coastal zones. Ultimately, we show that although there may be differences in the absolute levels of response across watersheds, agricultural and urban watersheds often respond surprisingly similarly to climate variability due to: (1) extensive headwater alteration, (2) increased carbon, nutrient, and contaminant inputs, and (3) degradation of watershed nutrient sinks (e.g., riparian zones and wetlands).

RUNOFF AND TEMPERATURE: MASTER VARIABLES

Globally, precipitation and runoff are master variables for regulating transport and transformation of carbon, nutrients, and contaminants within agricultural and urban watersheds (e.g., Dosskey *et al.*, 2010; Vidon *et al.*, 2010). Changes in precipitation and runoff during storms contribute to flushing of carbon, nutrients, and contaminants from agricultural and urban landscapes. Previous work has shown that there have been large changes in exports of nitrogen in urbanizing watersheds of the Chesapeake Bay and agricultural watersheds of the Gulf of Mexico in response to record drought and extreme wet years (Rabalais *et al.*, 2001; Justic *et al.*, 2003; Royer *et al.*, 2006; Kaushal *et al.*, 2008). There are also pulses in organic carbon export during storms in agricultural and urban watersheds across different regions of the United States (U.S.) and Europe (Hook and Yeakley, 2005; Royer and David, 2005; Dalzell *et al.*, 2007; Wagner *et al.*, 2008; Ledesma *et al.*, 2012). There is also evidence that variability in precipitation and runoff can stimulate production of greenhouse gases (GHGs) in watershed soils and riparian zones (Harms and Grimm, 2012; Jacinthe *et al.*, 2012; Vidon *et al.*, 2014).

In addition to extremes in runoff, temperature is a fundamental regulator of carbon, nutrient, and contaminant transformation in watersheds. Amplified stream temperature extremes are caused by extensive riparian zone alteration in agricultural and urban watersheds and drainage modification. Clearing of riparian zones results in decreased shading, which can lead to elevated stream temperatures. For example, water temperatures can be increased by approximately 4-5°C in stream reaches following riparian deforestation compared to shaded stream reaches (e.g., Burton and Likens, 1973; Beschta, 1997; references in Poole and Berman, 2001). Agriculture also produces significant effects on soil and stream temperature extremes by removing vegetation which can shade streams or by altering land cover in ways that reveal bare soil, thus changing soil albedo and contributing to radiative forcing (Quinn, 2000). Urbanization can also increase temperature in streams due to urban heat island effects, and large increases in runoff temperatures in urban watersheds in response to storms draining heated paved surfaces (e.g., Nelson and Palmer, 2007).

LAND USE INCREASES HEADWATER ALTERATION AND HYDROLOGIC CONNECTIVITY

In agricultural watersheds, hydrologic connectivity is often greatly enhanced by tile drains and ditches (Figure 1). In small agricultural watersheds of the U.S. Midwest, where approximately 30% of cropland is tile drained, solute transport to tile drains has been shown to occur quickly (less than one hour) following the beginning of precipitation (Zucker and Brown, 1998; Kung *et al.*, 2000). Baker *et al.* (2006) observed that tile-drain flow contributed between 56 and 99% of streamflow depending on storm characteristics, demonstrating that tile drains effectively move both water and solutes at the watershed scale. In small watersheds where up to 50% of cropland is tile drained, water can move from uplands to tile drains and to streams in as little as 15 min to a few hours during storms (Vidon and Cuadra, 2010). Therefore, dense networks of tile drains (Figure 1) facilitate the transfer of infiltrated precipitation to streams, quickly contributing to more efficient delivery of runoff and contaminants to receiving waters.

In urban watersheds, headwater alteration (e.g., storm drains) have replaced more than 90% of headwater streams (Elmore and Kaushal, 2008) (Figure 1). Storm drains have expanded drainage density and have increased concentrations of carbon, nutrients, and contaminants from several-fold to hundreds of times greater than forest headwater streams (Kaushal and Belt, 2012). Headwater alteration and amplified runoff variability contribute to downstream degradation of urban riparian zones and loss of floodplain wetlands (Walsh *et al.*, 2005). Furthermore, the presence of buried sanitary sewers, potable water pipes, and storm drains alters the groundwater flow field and provides the potential for preferential flow conduits within riparian zones, which further increases efficiency of carbon, nutrient, and contaminant transport (Sharp *et al.*, 2003). All these hydrologic changes can decrease nutrient retention capacity, increase streambank erosion, and further contribute to pulses of multiple contaminants downstream (Paul and Meyer, 2001; Walsh *et al.*, 2005; Allan *et al.*, 2008).

LAND USE AND CLIMATE AMPLIFY CARBON AND NUTRIENT PULSES

Many global climate change models predict an increase in the intensity and frequency of large storm events (Karl and Knight, 1998; Milly *et al.*, 2005). In some regions, weather patterns have already become more variable across time. For example, there have been long-term increases in streamflow variability for

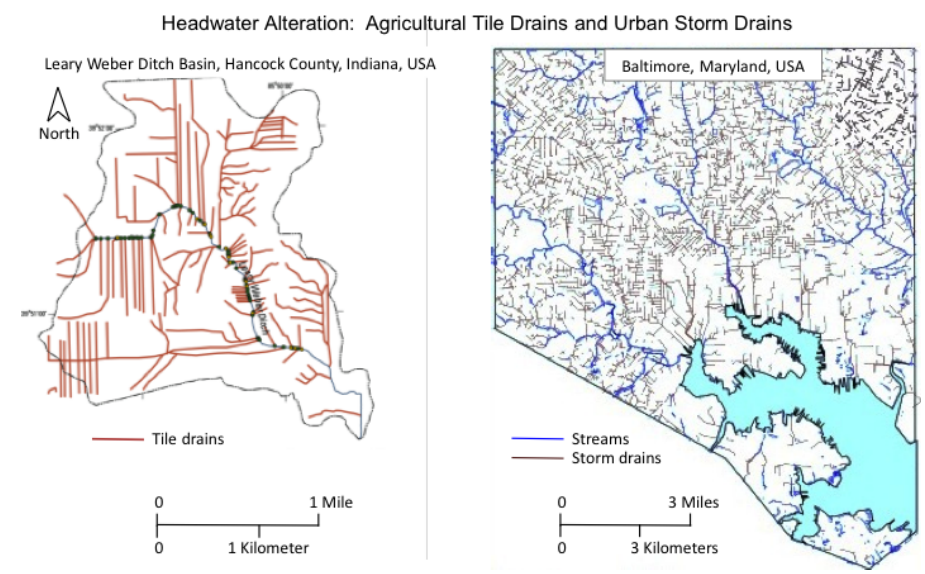


FIGURE 1. Tile Drains Are Pervasive in Agricultural Watersheds Such as Those in Indiana (Source Baker *et al.*, 2006) (left panel). Similarly, many natural streams (blue lines) have been placed underground and there has been a vast expansion of storm drain networks in urban areas such as Baltimore, Maryland (brown lines) (right panel) (see color figure in online version). (Data Courtesy of Bill Stack and Baltimore City Department of Public Works.)

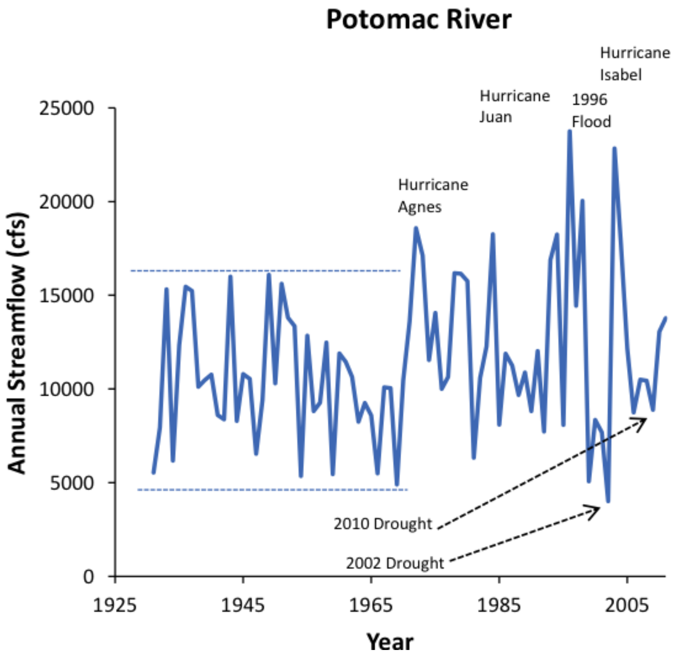


FIGURE 2. An Example of Long-Term Variability in Streamflow for the Potomac River near Washington, D.C. Streamflow data obtained from the U.S. Geological Survey River Input Monitoring Program and modified from Kaushal *et al.* (2010a, b).

some major rivers due to changes in regional climate variability (Figure 2). There is also evidence that agricultural and urban watersheds generate flashier hydrographs than forested watersheds across storm sizes (Shields *et al.*, 2008). Most carbon, nutrient, and contaminant exports occur during high-flow events (Royer *et al.*, 2006; Shipitalo and Owens, 2006; Dalzell *et al.*, 2007; Vidon *et al.*, 2008, 2009). Accordingly, a growing number of studies in streams and rivers demonstrate that the interaction between land use and climate variability can alter the magnitude and frequency of watershed carbon and nutrient pulses globally (Table 1).

Dissolved Organic Carbon Pulses

Dissolved organic carbon (DOC) can contribute to the production of disinfection by-products in drinking water supplies, biological oxygen demand, and adsorb metals and organic contaminants in streams and rivers (e.g., Royer and David, 2005; Stanley *et al.*, 2012). DOC can also influence denitrification, yielding implications for managing nitrogen in some streams (e.g., Newcomer *et al.*, 2012). Given its potential significance for water quality, there is interest in monitoring and managing organic carbon in agricultural and urban watersheds (Royer and David, 2005; Stanley *et al.*, 2012). Storms increase concentrations and fluxes of DOC in agricultural watersheds (Table 1). For example, Dalzell *et al.* (2007) showed that 71-85% of the annual DOC load occurred at high flow in agricultural watersheds in Indiana. DOC concentrations in tile drains can be greater than streams (Warrner *et al.*, 2009), and annual DOC exports from tile drains of 1.78 to 8.61 kg/ha were positively correlated with drain flow (Ruark *et al.*, 2009). Conversely, drought conditions can cause a decline in DOC fluxes from watersheds by three orders of magnitude, indicating hydrologic controls on agricultural DOC export (Vidon *et al.*, 2009). In other agricultural watersheds in Illinois, DOC concentrations (ranging from 1 to 16 mg/l) increased rapidly during floods and droughts (Royer and David, 2005). DOC export from these agricultural watersheds ranged from 3 to 23 kg/ha/yr and was strongly related to runoff (Royer and David, 2005). Similar work has shown that agricultural fields designed for drainage efficiency can export 55 $\pm$ 22% more DOC per year than conventional drainage due to higher concentrations and water yield (Dalzell *et al.*, 2011). DOC may originate from crop detritus and organic-rich upper soils during floods, whereas algal sources may dominate during base flow and drought periods (Royer and David, 2005). Changes in the sources of DOC to streams influence metabolism, oxygen demand, and alter aquatic foodwebs (based on frequency, amplitude, and timing of pulses).

Similar to agricultural watersheds, urban watersheds show strong pulses of DOC concentrations and export during storms (Table 1). DOC increased sharply during storms in urban watersheds of the Chesapeake Bay and reached concentrations greater than 20 mg/l in storm drains (Kaushal and Belt, 2012). DOC export increased as a power function with increasing runoff in urban watersheds (reaching approximately 600 g/ha/day) (Newcomer *et al.*, 2012). In urban watersheds of the U.S. Pacific Northwest, DOC concentrations increased during storm flow where riparian areas were thought to contribute almost 75% of the DOC (Hook and Yeakley, 2005). Sources of DOC can also change with increasing urbanization, reflecting natural sources such as upper soil horizons and leaf debris to anthropogenic sources (Newcomer *et al.*, 2012). This is similar to forest catchments, which are influenced by riparian zones and wetlands, and show increased DOC mobilization during storm events and highest DOC concentrations during the most intense rain events (Inamdar and Mitchell, 2006).

Furthermore, the chemical composition and lability of DOC can change in response to climate variability. For example, the structural complexity of dissolved organic matter decreased as the ratio of continuous agricultural croplands to wetlands increased across 34 watersheds in Europe (Wilson and Xenopoulos, 2009). Specifically, the amount of microbially derived dissolved organic matter increased with greater agricultural land use, and drought periods were associ-

TABLE 1. Examples of the Interactive Effects of Land Use and Climate Variability on Watershed Pulses of Carbon and Nutrients Globally.

Parameter	Land Use	Frequency, Timing, and Magnitude of Pulses	Location	Literature Reference
Carbon	Forest and agriculture	Total organic carbon (TOC) export generally increased with discharge	Europe: Sweden	Ledesma *et al.* (2012)
Carbon	Agriculture	Export of agriculturally derived organic carbon increased with increased streamflow. 71-85% of the total annual organic carbon was exported during high-flow events that occurred during less than 20% of the time	North America: Indiana, USA	Dalzell *et al.* (2007)
Carbon	Agriculture	Export of dissolved organic carbon (DOC) from agricultural streams increased during floods	North America: Illinois, USA	Royer and David (2005)
Carbon	Agriculture	A significant positive relationship was found between tile drain flow and DOC loss in agricultural watersheds	North America: Indiana, USA	Ruark *et al.* (2009)
Carbon	Mixed land use and agriculture	Agriculture and urbanization increased TOC loads. TOC concentrations were positively correlated with temperature and negatively correlated with dissolved oxygen (DO) levels	North America: Coastal plain Georgia, USA	Joyce *et al.* (1985)
Carbon	Mixed land use and agriculture	Precipitation had the strongest correlation with the export of all carbon pools. DOC and particulate organic carbon generally increased with increasing discharge	North America: Ohio River, Upper Mississippi, and Missouri River Basins, USA	Raymond and Oh (2007)
Carbon (and carbon quality)	Agriculture	After a >100 year flood, herbicide concentrations were elevated in soil samples from flooded cornfields	North America: Mississippi River, Illinois, USA	Chong *et al.* (1998)
Carbon (and carbon quality)	Agriculture	After a 500-year flood event, concentrations of organic contaminants were higher than during earlier preflood sampling. For example, dieldrin concentrations increased by an order of magnitude	North America: Lower Missouri River, USA	Petty *et al.* (1998)
Carbon (and carbon quality)	Agriculture	Agricultural fields designed for intensive drainage exported 55 $\pm$ 22% more DOC per year than conventional drainage, due to higher concentrations and water yield. DOC exports were strongly correlated with precipitation	North America: Le Sueur River Basin in south central Minnesota, USA	Dalzell *et al.* (2011)
Carbon (and carbon quality)	Mixed land use and agriculture	DOC concentration increased, and carbon sources and quality shifted from originating from mineral soil layers at base flow to originating from the topsoil layers richer in aromatic substances and lignin during storms	North America: Indiana, USA	Vidon *et al.* (2008, 2009)
Carbon (and carbon quality)	Mixed land use and agriculture	A >100-year flood influenced the spatial distribution of organic contaminants in bed sediments of the Upper Mississippi River. Bed sediments stored in pools along the river were diluted or buried by sediments with different organic compound compositions washed in from urban and agricultural portions of the watershed	North America: Upper Mississippi River, USA	Barber and Writer (1998)
Carbon and nitrogen	Forests, peatlands, and agriculture	TOC export increased with increasing percentage peatland. In contrast, total organic nitrogen export increased with increasing percentage of agricultural land use and was correlated with annual mean air temperature	Europe: The Finnish main rivers flowing to the Baltic Sea and their subcatchments	Mattsson *et al.* (2005)
Carbon and nitrogen	Agriculture and mixed land use	During storms DOC concentrations increased, and DOC was transported via a combination of overland flow and macropore flow. Nitrate concentrations increased during storms and nitrate was exported with groundwater	North America: Indiana, USA	Wagner *et al.* (2008)

(continued)

TABLE 1. Continued.

Parameter	Land Use	Frequency, Timing, and Magnitude of Pulses	Location	Literature Reference
Carbon and nitrogen	Multiple land uses	There was a general pulse in C and N mineralization and export following rain events after dry periods	Multiple global locations	Borken and Matzner (2009)
Carbon and nitrogen	Urban	Storms caused a significant increase in DOC concentration and a significant decrease in total dissolved nitrogen (TDN) concentration	North America: Portland, Oregon, USA	Hook and Yeakley (2005)
Carbon, nitrogen, and phosphorus	Agriculture	There was a significant positive relationship between precipitation and annual ammonium, phosphate, and organic matter loads, with increased loading and concentrations during wet years	Europe: Lake Vortsjarv, Estonia	Noges *et al.* (2007)
Carbon, nitrogen, and phosphorus	Agriculture and urban gradient	Areal C, N, and P export was correlated with runoff and was significantly higher in the urban catchment, which had greater runoff from impervious surfaces, and was significantly lower in the catchment with inland drainage	Australia: Perth, Western Australia	Petrone (2010)
Carbon, nitrogen, and phosphorus	Forest, agriculture, and urban	Discharge controlled the magnitude and chemical form of nutrients in streams. There was a negative relationship between N concentrations and stream discharge in agricultural watersheds, but a positive relationship in urban and forested watersheds. DOC and phosphorus were also controlled by land use and season, with a positive relationship with discharge in agricultural and urban watersheds, but a negative relationship in forested watersheds	North America: 3 watersheds of Mobile Bay, Alabama, USA	Lehrter (2006)
Carbon, nitrogen, phosphorus, and sulfur	Forest, agriculture, and urban	Incubation experiments showed that warming waters generally increased fluxes of DOC, nitrate, soluble reactive phosphorus (SRP), and sulfate from sediments to overlying waters for most land uses	North America: Baltimore, Maryland, USA	Duan and Kaushal (2013)
Carbon, nitrogen, phosphorus, and sediment	Forest, grassland, developed, and agriculture	Concentrations generally increased during wet years. Concentrations also generally increased as the proportion of developed land or cropland increased. During dry years, point sources dominated, but during wet years nonpoint sources dominated	North America: Maryland, USA	Jordan *et al.* (2003)
Carbon, nitrogen, phosphorus, and metals	Forest and agriculture	Floods increased concentrations of nitrate and DOC, and they increased concentrations of filterable reactive phosphorus and ammonium at a station downstream from hog farm wastes. Concentrations of particulate P (PP), Si, and most metals increased during the rising limb of the hydrograph, peaked prior to peak storm flow, and decreased thereafter	North America: Coastal plain North Carolina, USA	Mulholland *et al.* (1981)
Carbon, nitrogen, and chloride	Agriculture and urban	DOC, nitrate, and chloride concentrations increased during storms. The urbanized watershed had higher export during storms, but lower concentrations of nitrate and chloride than the agriculture watershed. While nitrate concentration increased with discharge in the mixed land-use watershed, there were no clear patterns with discharge in the agricultural watershed	North America: Indiana, USA	Vidon *et al.* (2009)
Carbon and multiple contaminants	Multiple land uses	Climate warming and altered hydrology in lakes, rivers, and streams are expected to impact contaminant flux. For example, reduced water inputs may cause increased contaminant concentrations, and increased hydrologic residence times may increase biological processing of contaminants	North America: Canada	Schindler (2001)

(continued)

TABLE 1. Continued.

Parameter	Land Use	Frequency, Timing, and Magnitude of Pulses	Location	Literature Reference
Nitrogen	Forest	The coldest and driest winter of a 52-year record led to freezing and thawing of soils, which contributed substantially to soil nitrate and subsequent record nitrate fluxes from the watershed	North America: Northeastern USA	Mitchell *et al.* (1996)
Nitrogen	Forest, agriculture, and urban	Urban and agricultural watersheds showed a strong increase in concentration during storm-flow conditions. In contrast, there was minimal change in nitrate concentration in the forested watershed during storm flow conditions	North America: Oregon, USA	Poor and McDonnell (2007)
Nitrogen	Forest, agriculture, and urban	The magnitude and timing of watershed N export has been altered by anthropogenic activities. 80% of N inputs were from agriculture, and N exports correlated with climate, precipitation, N inputs, and reservoir releases	North America: California, USA	Sobota *et al.* (2009)
Nitrogen	Forest, agriculture, and urban	Following the 2002 drought, N retention declined significantly during the 2003 wet year in suburban, forest, and agricultural watersheds. The smallest decrease in retention was in the forested watershed and the greatest drop in N retention was in a suburban watershed	North America: Baltimore, Maryland, USA	Kaushal *et al.* (2008)
Nitrogen	Forest, agriculture, and urban	There were pulses in atmospheric nitrate-N source contributions in urban watersheds during storms. In addition, nitrate-N concentrations decreased during storms	North America: Baltimore, Maryland, USA	Kaushal *et al.* (2011)
Nitrogen	Forest and urban	It was estimated that urbanization increased N loading by 45% and reduced N retention by 8-32%. Watershed N retention decreased with increasing runoff	North America: Massachusetts, USA	Wollheim *et al.* (2005)
Nitrogen	Agriculture	Regression modeling indicated that a 10% increase in annual discharge due to climate and heavier fertilizer use for expanded corn production could increase riverine N export by as much as 24%	North America: Lake Michigan watersheds, USA	Han *et al.* (2009)
Nitrogen	Agriculture	Most of the nitrate-N exports occurred during the fallow season, when most of the drainage occurred	North America: Indiana, USA	Kladivko *et al.* (2004)
Nitrogen	Agriculture	Higher nitrate concentrations were associated with higher flow volumes and no dilution occurred even with prolonged flushing events	North America: Indiana, USA	Hofmann *et al.* (2004)
Nitrogen	Agriculture	There was a positive relationship between precipitation amount and nitrate and ammonia export rates, but not with dissolved organic nitrogen (DON) export rates	North America: Indiana, USA	Cuadra and Vidon (2011)
Nitrogen	Agriculture	Large storms (peak flow = 5 times mean base flow) led to significant drops in nitrification rates, probably as a result of scouring and sloughing of nitrifiers. The recovery period for return to prestorm nitrification rates (for one storm) was greater than 14 days	Australia and Oceania: New Zealand	Williamson and Cooke (1985)
Nitrogen	Urban	There was almost a 100-fold variation in watershed N export in response to storms, with N build up during dry periods and flushing during wet periods	North America: Southwestern USA	Lewis and Grimm (2007)
Nitrogen	Multiple land uses	N fluxes may increase by 3-17% by 2030 and 16-65% by 2095, with the increase in net	North America: 16 watersheds from Maine to Virginia	Howarth *et al.* (2006)

(continued)

TABLE 1. Continued.

Parameter	Land Use	Frequency, Timing, and Magnitude of Pulses	Location	Literature Reference
		anthropogenic nitrogen inputs as precipitation and discharge		
Nitrogen	Mixed land use	Changing land cover and stream discharge caused significant shifts in nitrogen concentrations. Average concentrations increased with greater urban and agriculture land use	North America: Patuxent River Watershed, Maryland, USA	Weller *et al.* (2003)
Nitrogen and phosphorus	Forest and agriculture	Particulate organic nitrogen and phosphorus, and inorganic phosphorus concentrations increased up to three orders of magnitude during storm events and ammonia increased up to five times, but dissolved organic nitrogen and phosphorus and nitrate did not change significantly	North America: Atlantic Coastal Plain in Maryland, USA	Correll *et al.* (1999)
Nitrogen and phosphorus	Forest and agriculture	Data from 76 storms showed that concentrations of particulate N and P increased up to three orders of magnitude during storms and usually peaked prior to the peak water discharge, whereas concentrations of dissolved forms did not change significantly. Ammonium had up to a 5-fold increase during storms, but remained low compared to other N forms. The N:P ratios declined during peak flows	North America: Maryland, USA	Correll *et al.* (1999)
Nitrogen and phosphorus	Forest, agriculture, and urban	Model results estimated that mean annual N and P loads will increase due to climate change. In addition, N loads are expected to increase 50% further when climate change and urbanization occur concurrently	North America: Conestoga River Basin and its five subbasins in southeastern Pennsylvania, USA	Chang (2004)
Nitrogen and phosphorus	Agriculture	More than 50% of the annual nitrate export and 80% of phosphorus export from agricultural watersheds occurred during pulses at high flow in less than 10% of the time	North America: Illinois, USA	Royer *et al.* (2006)
Nitrogen and phosphorus	Formerly agriculture	Hourly monitoring of seven summer thunderstorms (12.5-25 mm of precipitation) showed that nitrate and phosphate concentrations increased during the rising limb of storms and decreased during the falling limbs, which suggests surface runoff as their origin	North America: Pennsylvania, USA	McDiffett *et al.* (1989)
Nitrogen and phosphorus	Formerly agriculture	During a wet year nitrate export was 40% higher than during an average year	North America: Northern Mississippi, USA	Schreiber *et al.* (1976)
Nitrogen and phosphorus	Mixed land use	During the wet season there were greater proportions of inorganic nitrogen and phosphorus than the dry season, with higher concentrations associated with higher discharge	Australia: Richmond River catchment	McKee *et al.* (2001)
Nitrogen and phosphorus	Mixed land use	Hurricane Katrina caused a 5.2-fold increase in nitrate and a 2-fold increase in SRP, in Biscayne Bay, Florida	North America: Florida, USA	Zhang *et al.* (2009a, b)
Nitrogen, phosphorus, and sediment	Urban	The first flush of a storm event had the strongest increase on total suspended solids, followed by ammonia, total Kjeldahl nitrogen, nitrate, total phosphorus (TP), and then orthophosphate	North America: Raleigh, North Carolina, USA	Hathaway *et al.* (2012)
Nitrogen, phosphorus, sediment, and bacteria	Agriculture, urban, and undeveloped	Coastal watersheds deliver water and contaminants in discrete pulses. During El Niño years, one in five events produced temporary near-shore nitrate and phosphate concentrations that are approximately 5-10 times above ambient conditions	North America: Southern California, USA	Beighley *et al.* (2008)

(continued)

TABLE 1. Continued.

Parameter	Land Use	Frequency, Timing, and Magnitude of Pulses	Location	Literature Reference
Phosphorus	Forested and agriculture	Near-stream surface runoff during storms and the amount of soil P, controls P exports from the watershed	North America: Pennsylvania, USA	Sharpley *et al.* (1999)
Phosphorus	Forest, agriculture, and urban	P export increased with high-flow conditions and with increased urbanization. In addition, a temperature dependence of SRP release from sediments was found, with SRP concentrations being highest during summer and lowest during winter	North America: Baltimore, Maryland Long Term Ecological Research (LTER) site, USA	Duan *et al.* (2012)
Phosphorus	Multiple land uses	SRP concentrations were positively correlated with water temperature and this correlation increased further downriver in the Mississippi River	North America: Mississippi River and Northern Gulf of Mexico	Duan *et al.* (2011)
Phosphorus	Agriculture	A significant positive relationship was found between SRP and TP with discharge. Phosphorus was transported during storms primarily through macropores	North America: Indiana, USA	Vidon and Cuadra (2011)
Phosphorus	Agriculture	Dissolved reactive phosphorus (DRP) and PP concentrations in both streams and agricultural tile drains increased with streamflow. PP concentrations dominated during overland runoff events. The highest DRP concentrations in the streams were associated with rain events occurring directly after phosphorus fertilizer applications on frozen soils	North America: 3 streams in east-central Illinois, USA	Gentry *et al.* (2007)

ated with a decrease in the structural complexity of dissolved organic matter (Wilson and Xenopoulos, 2009). Wilson and Xenopoulos (2009) suggested that interactive effects of land use and climate variability could have important implications for the chemical composition of DOC, microbial carbon processing, and carbon dioxide (CO_2) production in agricultural streams. Similarly, more labile and redox-active dissolved organic matter was found in streams draining anthropogenic land use including agriculture (Williams *et al.*, 2010). Overall, headwater alteration and modified drainage in agricultural watersheds can impact DOC quality and sources (e.g., Dalzell *et al.*, 2011). An increase in the frequency and intensity of storm events may further shift stream DOC toward more aromatic DOC fractions in some cases (Vidon *et al.*, 2008). An increase in aromatic DOC (less labile) could potentially impact whole-stream metabolism, denitrification, and decrease stream productivity across multiple trophic levels directly following storms (e.g., Warren *et al.*, 1964; Royer and David, 2005; Newcomer *et al.*, 2012).

Nitrogen and Phosphorus Pulses

The interaction between agriculture and climate variability also amplifies nitrogen and phosphorus export from watersheds (Table 1). However, the impacts of storms and floods have various effects on stream solute concentrations depending on agricultural management practices (Sharpley *et al.*, 1999). For example, the concentrations of particulate phosphorus and particulate nitrogen increased significantly with peak water discharge among storms, whereas concentrations of dissolved forms of phosphorus and nitrate were not correlated with peak discharge in agricultural watersheds of Maryland (Correll *et al.*, 1999). In contrast, nitrate and soluble reactive phosphorus concentrations increased 7- and 10-fold, respectively, in an agricultural watershed of Florida during Hurricane Katrina (Zhang *et al.*, 2009a, b). In Illinois, highest concentrations of soluble reactive phosphorus in agricultural streams were associated with rain events and phosphorus fertilizer applications (Gentry *et al.*, 2007). Overall, nutrient concentrations can increase or decrease in agricultural watersheds during storms depending on when sampling occurs along the hydrograph (rising limb, peak, or descending limb), the types of agricultural best management practices (BMPs) employed in the watershed, and/or antecedent conditions.

Typically, storms increase export of nutrients (mass transport) from agricultural watersheds, however (Table 1). Based on almost 20 years of data, riverine N exports increased as an exponential function of agriculture fertilizer inputs (and a power function of annual water runoff) in 18 watersheds of the Lake Michigan Basin (Han *et al.*, 2009). Similarly, N export was a function of fertilizer inputs and runoff in agricultural California watersheds (Sobota *et al.*, 2009). In Illinois, Royer *et al.* (2006) showed that more than 50% of the annual nitrate export from agricultural watersheds occurred during high-flow events during less than 10% of the study period over 8-12 years. In Maryland, there was a 20-fold increase in the annual N export pulse in response to record drought and wet years in an agricultural watershed of the Chesapeake Bay (mechanism discussed in detail further below in the section on lag times and ecosystem resilience and Figure 3); a peak in export of up to 40 kg nitrate-N/ha/yr in an agricultural watershed of the Chesapeake Bay (Kaushal *et al.*, 2008) was comparable to peaks of ~57 kg nitrate-N/ha/yr in agricultural watersheds of Illinois (Royer *et al.*, 2006). Peaks in annual export of soluble reactive phosphorus can approach 1 kg/ha/yr in agricultural watersheds of Illinois depending on runoff conditions (Royer *et al.*, 2006).

Although some studies address the impact of droughts on nutrient pulses in agricultural watersheds, there is much less information than for floods (Table 1). For a late summer storm (stream base flow = 1.3 l/s) following a drought period, nitrate fluxes (kg/ha/storm) were three orders of magnitude lower than in spring for a similar size storm (stream base flow = 40.3 l/s), suggesting that drought conditions in the month preceding the storm (along with increased crop water demand) had a diminishing effect on nitrate exports at the watershed scale (Vidon *et al.*, 2009). During droughts, seasonal changes in antecedent moisture conditions and crop development stage can also have a significant impact of stream-landscape connectivity and reduce nutrient export from agricultural watersheds (Wigington *et al.*, 2005; Poor and McDonnell, 2007; Vidon *et al.*, 2009). Wigington *et al.* (2005) showed that agricultural stream drainage density could vary spatially by nearly two orders of magnitude in response to changes in stream network expansion/contractions associated with the dry season, when riparian forests can play a significant role in reducing high inputs of nitrate (Davis *et al.*, 2011). Regardless, runoff extremes (storms and droughts) are associated with strong responses in nutrient export from agricultural watersheds.

Like agricultural watersheds, the interactive impacts of land use and climate variability on stream nutrient concentrations in urbanized watersheds depend on individual watershed characteristics (Table 1). Precipitation amount and the proportion of impervious surface cover in watersheds can influence the "first flush" of nutrient concentrations during storms (Hathaway *et al.*, 2012). N exhibited a greater "first flush" than P across 36 storm events in two urban watersheds in the Southeastern U.S. and Mid-Atlantic U.S. (Hathaway *et al.*, 2012). The relationship between streamflow and nitrogen concentrations can also show variable concentration-discharge relationships in urban watersheds during record drought and wet years (Shields *et al.*, 2008).

Storms also clearly increase the watershed export of nutrients (mass transport) from urban watersheds (Table 1). There are statistical relationships between runoff and N exports in urban watersheds regionally across the U.S. (Wollheim *et al.*, 2005; Lewis and Grimm, 2007). On an annual basis, there can be more total nitrogen exported per unit runoff in agricultural and urban watersheds of the Baltimore Ecosystem

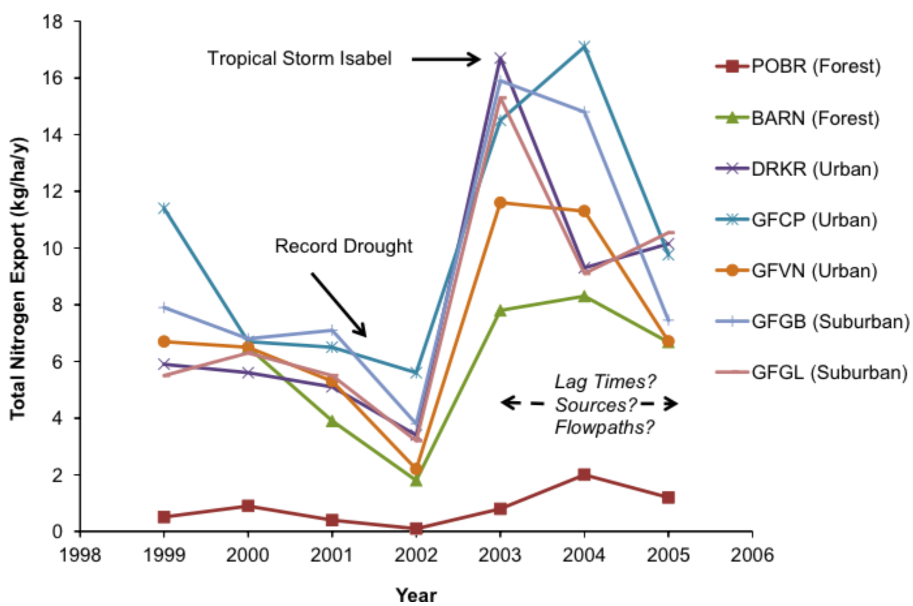


FIGURE 3. Example of an Interannual Pulse and a Lag Time in N Export during a Record Drought and Wet Year in Watersheds of the Baltimore Ecosystem Study Long-Term Ecological Research Site (modified from Kaushal *et al.*, 2008, 2011).

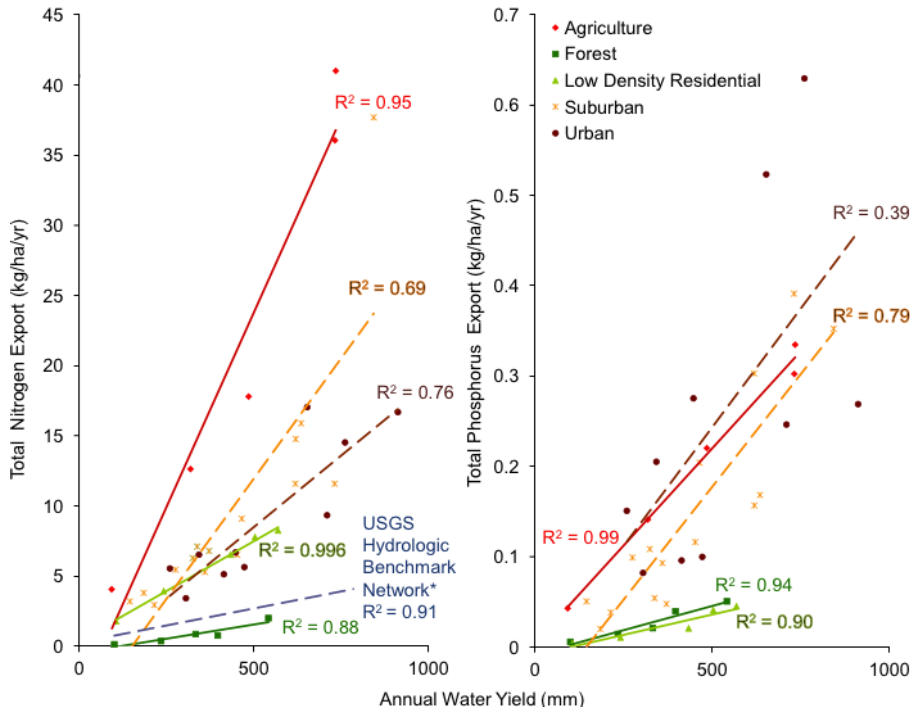


FIGURE 4. Relationships between Annual Runoff and Total Nitrogen Export and Total Phosphorus Exports during 2000-2004 for the Baltimore Ecosystem Study Long Term Ecological Research Site; Export Data Based on Groffman *et al.* (2004), Kaushal *et al.* (2008), and Duan *et al.* (2012). *Relationships between runoff and total nitrogen export are compared to minimally disturbed watersheds of the U.S. Geological Survey (USGS) Hydrologic Benchmark Network (Lewis, 2002).

Study Long Term Ecological Research (LTER) site than minimally disturbed reference watersheds in the U.S. (Lewis, 2002) (Figure 4). In urbanized watersheds, climate variability can produce substantially different levels of amplification of nitrate exports based on the nature and degree of land development. For example, there were 4- to 5-fold increases in nitrate exports in urban watersheds during record drought and wet years in watersheds of the Baltimore Ecosystem Study LTER (Kaushal *et al.*, 2008); nitrate pulses increased during a wet year following a drought, and pulses remained high even as runoff declined suggesting a hydrologic flushing of watershed nitrate (Figure 3). Similarly, there was an almost 100-fold variation in watershed N export in response to storms in an urbanized watershed in the arid Southwestern U.S. (Lewis and Grimm, 2007). The high variability in watershed N export was explained by watershed size and impervious surface cover, and the investigators suggested a "build and flush" hypothesis where N accumulates on the land surfaces and is rapidly flushed to streams during storms (Lewis and Grimm, 2007). Other work has also shown that dry and wet years impact N fluxes from urban watersheds in the Northeastern U.S. in a similar way than for other regions (Jordan *et al.*, 2003; Wollheim *et al.*, 2005; Lewis and Grimm, 2007).

Although less studied, phosphorus exports show pulsed exports in urban watersheds in response to drought and wet conditions, but the degree of amplification of phosphorus in response to climate variability was lower than nitrogen (Duan *et al.*, 2012). Peak export of total phosphorus from urban watersheds during wet years can approach 1 kg/ha/yr (Duan *et al.*, 2012). There are also strong relationships between annual runoff and total phosphorus export in agricultural and urban watersheds, varying significantly across land use (similar to nitrogen) (Figure 4). However, more work is necessary to characterize the impacts of climate variability on phosphorus pulses in urban streams (Table 1), particularly during droughts and warm periods when phosphorus release from sediments may also be high due to abiotic and biotic factors.

LAND USE AND CLIMATE VARIABILITY AMPLIFY WATERSHED GREENHOUSE GAS PULSES

Greenhouse Gas Pulses in Agricultural and Urban Riparian Zones, Wetlands, and Streams

Land use and climate variability can also amplify pulses of GHG (CO_2, CH_4, and N_2O) from watersheds due to shifting patterns in runoff and temperature. An abundance of work regarding the effects of land use and climate on GHG pulses has been conducted in upland soils and agricultural fields, highlighting the influence of water availability, temperature, soil properties, and management practices on the timing and magnitude of GHG pulses (e.g., Jacinthe and Dick, 1997; Mosier *et al.*, 2004; Vilain *et al.*, 2010). Therefore, we do not focus on upland soils for the present review. Instead, we focus on the potential effects of land use and climate on GHG pulses in riparian zones, floodplains, wetlands, streams, and rivers.

Riparian Zones, Floodplains, and Wetlands: Nitrous Oxide. Interactive effects of flooding, temperature, and nitrogen fertilization can amplify pulses of nitrous oxide (N_2O) from agricultural and urban riparian zones, floodplains, and wetlands (Table 2). N_2O is produced in these ecosystems most commonly through denitrification, and N_2O pulses can be stimulated in response to increased NO_3^- fertilization (e.g., Hefting *et al.*, 2003; Vilain *et al.*, 2010; Burgin and Groffman, 2012); N_2O emissions in riparian zones can be minimal compared with agricultural fields, however (Kim *et al.*, 2009). Warming may increase N_2O emissions in agricultural riparian zones and wetlands (Maag *et al.*, 1997; Munoz-Leoz *et al.*, 2011; Soosaar *et al.*, 2011). In the United Kingdom (UK), the effects of temperature on N_2O emissions have been studied in flooded and nonflooded agricultural floodplain wetlands, and this work has shown that flooding and warming can synergistically increase N_2O emissions (Bonnett *et al.*, 2013). Increased flooding frequency led to higher emissions of N_2O in an agricultural riparian zone in Indiana (Jacinthe *et al.*, 2012). Similarly, Vidon *et al.* (2013) showed strong responses of N_2O pulses to storms and rewetting events in a restored riparian wetland. Mander *et al.* (2011) found that a fluctuating water table significantly increased N_2O emissions in a constructed wetland. Ambus and Christensen (1995) found highest N_2O in flooded agricultural riparian soils of Denmark. Although there has been less work in urban watersheds, Groffman *et al.* (2002) found that soils in urban riparian zones of Maryland had high potential for denitrification, but were likely limited by infrequent inundation. Sovik *et al.* (2006) found that N_2O flux rates varied from −2.1 to 1,000 mg N_2O-N/m^2/day in an urban wetland depending on flood inundation time, temperature, and water content. In contrast, Merbach *et al.* (1996) reported that flooding did not affect N_2O emissions from an agricultural peatland in Germany. Similarly, Soosaar *et al.* (2011) reported a negative relationship between water-table height and N_2O emissions. These exceptions suggest that, while flooding may consistently increase anaerobic decomposition, the specific response of N_2O can also be complicated and depends strongly on nitrogen availability and other site-specific factors.

Riparian Zones, Floodplains, and Wetlands: Methane. Climate variability and land use also show potential to amplify methane (CH_4) pulses via flooding, temperature, and organic carbon availability (Table 2). CH_4 fluxes from forested and grassy riparian zones in agricultural watersheds are highly responsive to hydrologic pulses in the form of soil moisture, water-table height, and water-filled pore space (Ambus and Christensen, 1995; Soosaar *et al.*, 2011). Ambus and Christensen (1995) reported rates as high as 7,877 mg C/m^2/day during flooding of a riparian zone in Denmark. Soosaar *et al.* (2011) reported CH_4 emissions as high as 1 mg C/m^2/h during high-water-table periods (>20 cm) compared to zero or negative fluxes when groundwater was below 20 cm in a riparian alder forest in Estonia. Additional work in Texas has shown that flooding had a strong effect on CH_4 pulses in an agricultural river floodplain (up to 1,640 mg/m^2/day) where changes in DOC quality appeared to play a major role (Bianchi *et al.*, 1996). Temperature and organic C availability also appear to be important drivers of CH_4 pulses in some agricultural riparian zones (Soosaar *et al.*, 2011) and permanently inundated wetlands (Altor and Mitsch, 2006, 2008; Sha *et al.*, 2011), and temperature can contribute to diurnal pulses of CH_4 in urban wetlands (Verma *et al.*, 1999). Some notable exceptions contradicting the importance of flooding and temperature are also important to consider, however. In contrast, Altor and Mitsch (2008) and Sha *et al.* (2011) studied continually inundated agricultural wetlands in Ohio and found that experimentally pulsed flood flows significantly decreased CH_4 emissions. There may be other abiotic and biotic factors that are drivers of CH_4 emissions (Sovik *et al.*, 2006; Mander *et al.*, 2011; Samaritani *et al.*, 2011; Sha *et al.*, 2011) including inhibition by nitrate and N_2O during floods (Bonnett *et al.*, 2013). Thus, the response of CH_4 to flooding and temperature can also be ecosystem specific (Le Mer and Roger, 2001).

Riparian Zones, Floodplains, and Wetlands: Carbon Dioxide. Carbon dioxide is a major component of the GHG flux from urban and agricultural forests and wetlands (Mander *et al.*, 2008; Soosaar *et al.*, 2011; Morse *et al.*, 2012) (Table 2). CO_2 is removed from the riparian zone via direct exchange between the soil and atmosphere and indirect transport of dissolved CO_2 from groundwater to the stream (discussed below). The greatest temporal variations

TABLE 2. Examples of Greenhouse Gas (GHG) Pulses and Emissions in Riparian Zones and Floodplains across Watershed Land Use.

GHG	Hydrologic and Thermal Conditions	Land Use	Frequency, Timing, and Magnitude of Pulses	Watershed Position	Geographic Location	Citation
CH_4, CO_2, N_2O	Flood pulses and steady flow	Urban	An experimentally pulsed flooding of wastewater treatment wetlands increased N_2O and CH_4 emissions, but may have also been influenced by higher biochemical oxygen demand in the flooded wetlands. CO_2 emissions were negatively related to water-table depth and positively related to temperature	Constructed wetlands	Estonia, Europe	Mander *et al.* (2011)
CH_4, N_2O	Variability in flow conditions	Urban	In a created wetland, N_2O and CH_4 were both correlated positively with dissolved organic carbon (DOC) in the overlying water	Constructed wetland	Norway, Europe	Sovik *et al.* (2006)
N_2O	Base flow	Urban	In a riparian buffer zone receiving wastewater, N_2O emissions from urban runoff were most highly correlated with soil moisture/sediment water content	Riparian buffer	China, Asia	Huang *et al.* (2013)
CH_4	Base flow	Urban	Temperature is a major driver of CH_4 fluxes in two degraded wetlands receiving polluted water. There were diurnal patterns at both sites	Riparian wetlands	India, Asia	Verma *et al.* (1999)
CH_4, CO_2	High and low flows	Agricultural	Continuous inundation may be important for CH_4 production and hydrologic pulsing can decrease flux from normally stagnant wetlands. The effect of pulsing varies depending on landscape position, however (continuously inundated *vs*. edge zones with or without macrophytes). CO_2 remained unaffected by experimental pulsing of water flows through a constructed floodplain wetland	Floodplain wetland	Olentangy River Wetlands, Ohio, USA, North America	Altor and Mitsch (2008)
CH_4	High and low flows	Agricultural	In a constructed floodplain wetland of an agriculturally impacted river, CH_4 emissions were greatest in permanently inundated portions of marsh	Riparian wetland	Olentangy River Wetlands, Ohio, USA, North America	Altor and Mitsch (2006)
N_2O	Flooded and nonflooded conditions	Agricultural	In a study of flooded *vs.* nonflooded agricultural floodplain wetlands, N_2O production increased exponentially with temperature, but CH_4 was not affected by temperature. CH_4 may be unresponsive at the highest temperatures due to substrate limitation. Flooding increased N_2O production, but may have contributed to a reduction in CH_4 production due to inhibition of methanogenesis via increased nitrate or N_2O production; this could favor alternative anaerobic pathways. Overall, flood events and warming may contribute to pulses of GHG production, particularly N_2O	Floodplain wetland	United Kingdom, Europe	Bonnett *et al.* (2013)
N_2O	High and low flows	Agricultural	N_2O production via denitrification in stream sediments and riparian zones doubled during high-flow despite an overall dilution in NO_3^-. Denitrification rates were correlated with organic matter quality and the proportion of surface water entering hyporheic zones	Riparian zone	Garonne River, France, Europe	Baker and Vervier (2004)
N_2O	Variability in groundwater table	Agricultural	Surface N_2O emissions from riparian soil were highly variable spatially and temporally and showed a significant but weak correlation with temperature, soil moisture, and DOC concentrations in shallow groundwater. Groundwater N_2O concentrations declined between hill slope and stream, but were not correlated with soil-atmosphere fluxes	Riparian zone	Ontario, Canada, North America	DeSimone *et al.* (2010)

(continued)

TABLE 2. Continued.

GHG	Hydrologic and Thermal Conditions	Land Use	Frequency, Timing, and Magnitude of Pulses	Watershed Position	Geographic Location	Citation
N_2O	Flood pulses and steady flow	Agricultural	The response of N_2O fluxes to experimental flooding varied spatially according to marsh height. Intermittently flooded high and edge-marsh zones had the highest N_2O flux overall and were also the most responsive to flood pulse events	Riparian wetland	Olentangy River Wetlands, Ohio, USA, North America	Hernandez and Mitsch (2006)
N_2O	Flood pulses and steady flow	Agricultural	Flood pulses significantly increased springtime N_2O fluxes from drier parts of a created agricultural floodplain marsh, but did not affect permanently inundated parts of the wetland. Denitrification was significantly correlated with temperature in all parts of the wetland	Riparian wetland	Olentangy River Wetlands, Ohio, USA, North America	Hernandez and Mitsch (2007)
N_2O	Variability in soil water content	Agricultural	In tropical agricultural soils, N_2O pulses occurred during the early wet season. When N and C were not limiting, water-filled pore space of soil was the dominant controller of N_2O fluxes	Riparian forest	Thailand, Asia	Kachenchart *et al.* (2012)
N_2O	Variability in soil water content	Agricultural	Denitrification was controlled by water-filled pore space along a riparian zone-hill slope transect, with the highest rates occurring between 60 and 80%. N_2O accounted for 10-50% of denitrification, but the N_2:N_2O ratio varied with water-filled pore space and distance from the stream surface	Riparian zone	United Kingdom, Europe	Machefert and Dise (2004)
CO_2	Variability in groundwater table and soil moisture	Agricultural	CO_2 exchange is much greater in riparian areas than in the adjacent grasslands, and land use (tilling and fertilizer applications) appeared to be more important than differences in microclimate between sites	Riparian zone	Ontario, Canada, North America	Petrone *et al.* (2008)
CH_4, CO_2, N_2O	Variability in groundwater table	Agricultural	Experimental water table lowering increased CO_2 and N_2O in otherwise permanently wetted areas, whereas CH_4 remained the same or decreased. The effect of drawdown on more upland parts of the landscape was variable for each GHG	Prairie pothole wetlands	Nebraska, USA, North America	Phillips and Beeri (2008)
CH_4, CO_2	Flood pulses and steady flow	Agricultural	Seasonal sampling at a variety of sites spanning different flooding frequency showed that CO_2 and CH_4 emissions from riparian and hyporheic zones are controlled mainly by organic matter in sediments and soil properties	Floodplain	Thur River, Switzerland, Europe	Samaritani *et al.* (2011)
CH_4	High flow and low flow	Agricultural	CH_4 emissions were strongly correlated with soil temperature and carbon content, and soil inundation in a constructed wetland. An extreme drought led to CH_4 consumption of 0.04 mg CH_4-C/m^2/h on one sampling date. CH_4 was higher in permanently flooded areas than intermittently flooded	Constructed wetland	Olentangy River Wetlands, Ohio, USA, North America	Sha *et al.* (2011)
CO_2, CH_4, N_2O	Variability in soil moisture conditions	Agricultural	Higher groundwater level significantly increased CH_4 emission and decreased CO_2 and N_2O emission. All three GHGs were positively correlated with increased temperature	Riparian zone	Estonia, Europe	Soosaar *et al.* (2011)
CO_2, CH_4, N_2O	Base flow, storm flow (four seasons)	Agricultural	Seasonal pulses were important for CH_4, CO_2, and N_2O. Daily and hourly fluxes in temperature and moisture led to pulses as well, and surface flow design had more extreme pulses than subsurface flow wetlands	Constructed wetlands	Nova Scotia, Canada	VanderZaag *et al.* (2010)
N_2O	Variability in soil moisture conditions	Agricultural	Large magnitude fluxes of N_2O followed fertilizer application and lasted for several months. Smaller pulses coincided with midwinter increases in soil moisture and NO_3^- concentrations	Riparian zone	Seine Basin, France, Europe	Vilain *et al.* (2010)

(continued)

TABLE 2. Continued.

GHG	Hydrologic and Thermal Conditions	Land Use	Frequency, Timing, and Magnitude of Pulses	Watershed Position	Geographic Location	Citation
N_2O, CH_4	Flooded and dry riparian soil	Agriculture and forested	CH_4 fluxes were highest in the most frequently flooded parts of the riparian zone and related to soil organic matter and water-filled pore space. N_2O fluxes from a riparian grassland were unrelated to flooding frequency, soil organic matter, or soil exchangeable inorganic N, however	Riparian zone	Denmark, Europe	Ambus and Christensen (1995)
N_2O	Variability in soil moisture conditions	Agriculture	N_2O fluxes in riparian grasslands with active grazing by cows were not correlated with NO_3^-, temperature, or soil moisture, due to overriding effects of soil compaction, which introduced microsite variability	Riparian zone	Georgia, United States, North America	Walker *et al.* (2002)
N_2O	Variability in soil moisture conditions	Agriculture	N_2O emissions from two N-loaded buffer zones were correlated with groundwater NO_3^- concentration	Riparian zone	Netherlands, Europe	Hefting *et al.* (2003)
CH_4, N_2O	Variability in groundwater table	Agriculture	In a strongly eutrophic agricultural pond in Germany, N_2O was significantly lower when the water table was high and CH_4 was significantly higher. In a weakly eutrophic pond, there was no effect of water table on CH_4 or N_2O	Riparian wetlands	Germany, Europe	Merbach *et al.* (1996)
N_2O	High-, medium-, low-flood frequency	Agriculture (relict) and forest	Measurements of N_2O emissions in a floodplain showed that N_2O was highest in frequently flooded parts of the floodplain. Temporal trends, however, showed that N_2O pulses were greater after short-duration floods than long-duration	Riparian buffer and floodplain	White River, Indiana, USA, North America	Jacinthe *et al.* (2012)
CO_2, N_2O	Experimental temperature manipulation	Agricultural	Results from a laboratory experimental increase in temperature showed an increase in both CO_2 and N_2O from agricultural riparian wetland soils	Riparian wetland	Spain, Europe	Munoz-Leoz *et al.* (2011)
CH_4, N_2O	Drained, natural, and restored water table	Agricultural	Rewetting contributes considerably to mitigating GHG emission (in CO_2 equivalents) from formerly drained agricultural peatlands by decreasing CO_2 and N_2O emissions, compared to an agricultural, drained peatland	Agricultural peatland	Germany, Europe	Beetz *et al.* (2013)
CH_4, N_2O	Variability in soil moisture and groundwater table	Agricultural	Major pulses of CH_4 and N_2O occurred during rapid water-table drop in which water-filled pore space decreased from 80 to <60%. Both GHGs also exhibited seasonal and spatial variability within prairie pothole ponds	Prairie pothole wetlands	Saskatchewan, Canada, North America	Pennock *et al.* (2010)
N_2O	Experimental temperature manipulation	Agricultural	Potential N_2O production via denitrification activity is strongly related to temperature in riparian soils. NO_3^- and organic C availability are also strong drivers of denitrification kinetics	Riparian buffer	Netherlands, Europe	Maag *et al.* (1997)

in soil-atmosphere CO_2 flux are generally predictable based on variations in temperature, nutrients, vegetation production, and soil moisture (Davidson *et al.*, 1998; Phillips and Beeri, 2008). Phillips and Beeri (2008) found that fertilizer addition led to increased CO_2 exchange irrespective of microclimate and vegetation. Paludan and Blicher-Mathiesen (1996) also reported a significant increase in CO_2 production in a nitrate-loaded agricultural wetland. In temperate climates, periodic hydrologic events, such as over-bank flooding and drought tend to either decrease or have no effect on soil and wetland CO_2 emissions, whereas other GHGs might be stimulated (Davidson *et al.*, 1998; Altor and Mitsch, 2008; Pacific *et al.*, 2008). However, arid floodplains have shown evidence of CO_2 pulses following flooding events (Harms and Grimm, 2012), whereas other studies have shown that wetlands often become CO_2 sources during extreme droughts or draining (Beetz *et al.*, 2013). While soil-atmosphere CO_2 exchange in riparian zones/floodplains/wetlands appears to be controlled by many of the same factors as upland soils (where the literature on CO_2 exchange is much richer), there may be important differences in the timing of seasonal highs and lows, and sensitivity to drought conditions (Pacific *et al.*, 2008, 2009). Overall, complex interactions between water, temperature, and seasonality can influence CO_2 pulses (Davidson *et al.*, 1998).

Greenhouse Gases in Streams and Rivers. To date, the effects of land use and climate variability on GHG emissions from running waters have been relatively less studied compared with riparian zones, floodplains, and wetlands (Table 3, Figure 5). For example, fewer studies have measured N_2O, CH_4, or CO_2 concentrations and fluxes in streams and rivers in response to floods. Nonetheless, nutrient enrichment, organic carbon, and hypoxia have been identified as potential controls of GHG emissions from streams, which has implications regarding the interactive effects of land use and climate change on stream GHG emissions (particularly during low-flow periods and droughts).

Nitrous Oxide. Similar to riparian zones and wetlands, the interactive effects of temperature, precipitation, and nitrogen fertilization have the potential to amplify N_2O pulses from streams and rivers in agricultural and urban watersheds (Table 3, Figure 5). Some of the highest reported N_2O emissions in aquatic environments have been reported for agricultural springs in Italy receiving elevated N fertilizer inputs (Laini *et al.*, 2011). Nitrogen fertilization by agriculture has increased the potential for N_2O pulses in rivers of the Baltic Sea (Silvennoinen *et al.*, 2008). Changes in weather and hydrologic variability altered the production of N_2O in an agricultural stream in Spain impacted by N fertilization, with greatest in-stream N_2O production occurring during dry base-flow conditions (Tortosa *et al.*, 2011). Similarly, McMahon and Dennehy (1999) documented that a river in the western U.S. influenced by both agricultural fertilizer and urban wastewater effluent was 2,500% supersaturated with N_2O, and that N_2O concentrations were primarily related to nitrate concentration and water temperature. This is consistent with other work suggesting the importance of temperature and pH for influencing diurnal pulses of N_2O in a river draining a suburban and agricultural watershed (Laursen and Seitzinger, 2004). In fact, a growing body of work is now demonstrating that variability in hourly (-8.9 to 3,236 μg N_2O-N/m^2/h) and daily (-89 to 21,738 μg N_2O-N/m^2/day) fluxes of N_2O from agricultural streams is considerable, which suggests the potential importance of diurnal and/or short-term pulses (Harrison and Matson, 2003; Harrison *et al.*, 2005; Beaulieu *et al.*, 2008, 2009; Wilcock and Sorrell, 2008; Baulch *et al.*, 2011b, 2012). Besides nitrate enrichment, temperature, and precipitation, some additional controls on N_2O pulses include: organic carbon availability, dissolved oxygen, air-water-gas exchange rates, and groundwater upwelling (Jones and Mulholland, 1998; Harrison and Matson, 2003; Baulch *et al.*, 2011b; Beaulieu *et al.*, 2011, 2008; Werner *et al.*, 2012).

Methane. Methane production and emission from streams are primarily affected by organic carbon availability, dissolved oxygen, temperature, and precipitation (Jones and Mulholland, 1998; Harrison *et al.*, 2005; Wilcock and Sorrell, 2008; Werner *et al.*, 2012) (Table 3, Figure 5). Similar to N_2O, CH_4 production requires low-O_2 conditions and organic carbon (Wilcock and Sorrell, 2008; Baulch *et al.*, 2011a). Also similar to N_2O in streams, CH_4 production in streams can be influenced by precipitation and warming with highest rates during dry base-flow conditions (Tortosa *et al.*, 2011). Several studies have found strong correlations between DOC and CH_4 concentrations and/or emissions in streams (Harrison *et al.*, 2005; Werner *et al.*, 2012). For example, there was a 100-fold increase in CH_4 concentration during early spring potentially due to a pulse of organic carbon in agricultural chalk streams in the UK (Sanders *et al.*, 2007). In China, diurnal pulses of CH_4 in rivers downstream of urban wastewater discharges have been reported (Yang *et al.*, 2012). Because low-O_2 conditions inhibit methanotrophy and stimulate methanogenesis, CH_4 pulses may be especially sensitive to organic carbon loading due to eutrophication and hypoxic events (Naqvi *et al.*, 2000, 2010; Harrison *et al.*, 2005), which may be exacerbated in sediments and shallow groundwater during low-flow periods and droughts.

Carbon Dioxide. The interaction between anthropogenically enhanced carbon sources, precipitation, and temperature can influence CO_2 production and emission from agricultural and urban streams and rivers (Table 3, Figure 5). For instance, variations in the partial pressure of CO_2 in water (pCO_2) have been strongly linked to the oxidation of organic carbon, which can be modified in agricultural and urban watersheds as discussed previously (Neal *et al.*, 1998). In that study, there was a marked increase in pCO_2 in major rivers of the North Sea as watershed urbanization increased, and this response to urbanization was primarily due to enhanced oxidation of organic carbon (Jarvie *et al.*, 1997). Supersaturation of pCO_2 has been documented in an urban river due to organic carbon from wastewater inputs in Viet Nam (Duc *et al.*, 2007) and rivers draining urban watersheds of the Chesapeake Bay (Prasad *et al.*, 2013). There were diurnal pulses of CO_2 (10-70 times atmospheric pressure) in response to carbon from urban sewage in a river of the UK (Neal *et al.*, 2000a). In many cases, urban streams and rivers have higher

TABLE 3. Exploration of the Potential for Greenhouse Gas (GHG) Pulses from Streams and Rivers across Agricultural and Urban Land Use.

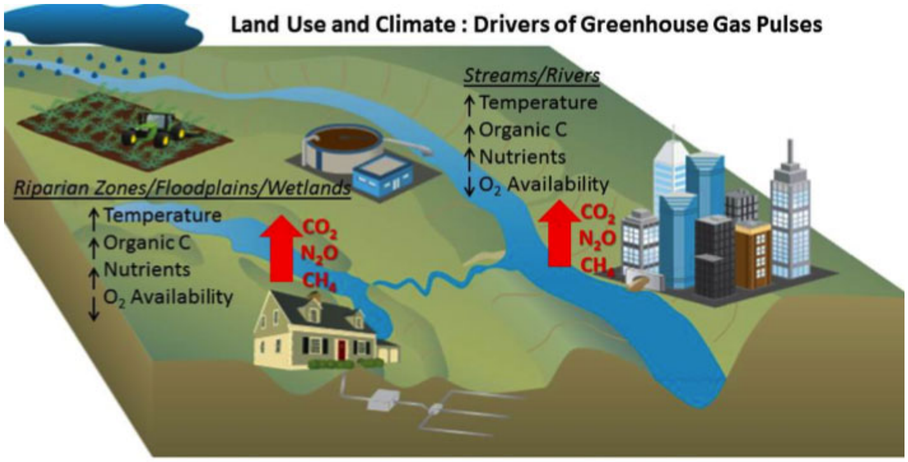
GHG	Land Use	Effect of Land Use and Climate	Geographic Location	Citation
N_2O, CH_4	Agriculture	In five agricultural streams, CH_4 flux to the atmosphere was >10 × higher than N_2O in CO_2 equivalents	Ontario, Canada, North America	Baulch *et al.* (2011a)
N_2O	Agriculture	Nitrogen enrichment was positively correlated with N_2O fluxes from five agricultural stream reaches	Ontario, Canada, North America	Baulch *et al.* (2011b)
N_2O	Agriculture	Study found that daytime measurements overestimate daily N_2O flux; diel measurements are important for accurate fluxes	Ontario, Canada, North America	Baulch *et al.* (2012)
N_2O	Agriculture	N_2O emissions are correlated with NO_3^- concentrations in agricultural streams	Ohio, USA, North America	Beaulieu *et al.* (2008)
N_2O	Agriculture	Extreme N_2O pulses occurred during algal blooms in summer	Yaqui Valley, Mexico, North America	Harrison and Matson (2003)
N_2O	Agriculture	Eutrophication exacerbates diurnal emissions of CH_4 and CO_2. N_2O emissions decrease overnight	Yaqui Valley, Mexico, North America	Harrison *et al.* (2005)
N_2O, CH_4, CO_2	Agriculture	Groundwater is a significant source of CH_4 and N_2O to agricultural streams with anoxic subsurface conditions and high NO_3^-	Wisconsin, USA, North America	Werner *et al.* (2012)
N_2O, CH_4	Agriculture	Streams draining intensively grazed pasture land were net sources of CH_4 and N_2O to the atmosphere	North Island, New Zealand	Wilcock and Sorrell (2008)
N_2O	Agriculture	Agricultural streams had greater N_2O production than forested streams	Kalamazoo River, Michigan, USA, North America	Beaulieu *et al.* (2009)
CH_4	Agricultural	CH_4 production was associated with annual increases in fine sediment deposition during spring and summer months. 90% of CH_4 emissions from the stream were transported through plant stems	England, Europe	Sanders *et al.* (2007)
N_2O	Agricultural	Agricultural drainage channels had higher N_2O fluxes than nearby wetlands during a longitudinal sampling in early spring	England, Europe	Outram and Hiscock (2012)
CO_2, CH_4, N_2O	Agricultural	Flow (especially drought), organic matter, NO_3^- concentration, and seasonal temperature affected production of all three GHGs in an N-loaded stream	Spain, Europe	Tortosa *et al.* (2011)
CO_2	Agricultural	In a river influenced by agriculture in the UK, pCO_2 was supersaturated during most times of year when pH was approximately 7.7, but when pH increased during spring there were declines in pCO_2. The influence of runoff can influence the pH and then pCO_2 dynamics	United Kingdom, Europe	Neal *et al.* (2000b)
N_2O	Urban and agricultural	Diurnal pulses of nitrous oxide in a river draining suburban and agricultural watersheds were related to temperature and pH	Indiana, USA, North America	Laursen and Seitzinger (2004)
CO_2, CH_4, N_2O	Agricultural	Lowland springs in a nitrogen-contaminated agricultural aquifer were hot spots for N_2O, CO_2, and CH_4 emissions, especially during low-oxygen conditions, and the concentrations of all three gases were positively correlated with nitrate concentrations	Northern Italy, Europe	Laini *et al.* (2011)
N_2O	Urban and agricultural	A river in the western U.S., influenced by agricultural fertilizer and urban effluent, showed that water was 2,500% supersaturated with N_2O and concentrations were primarily related to nitrate concentration and water temperature	Colorado, USA, North America	McMahon and Dennehy (1999)
CO_2	Urban	Two rivers, one urbanized and one undeveloped, were sources of CO_2 to the atmosphere. Along with heterotrophic respiration, CO_2 in the urbanized river was additionally supported by dissolution of $CaCO_3$, likely from pedogenic carbonate, crushed limestone/ dolomite, and oyster shells imbedded in old roads in the watershed	Texas, USA, North America	Zeng and Masiello (2010)
CO_2	Urban	Supersaturation of pCO_2 in an urban river was influenced by wastewater inputs, and periods of low dissolved oxygen <1 mg/l	Vietnam, Asia	Duc *et al.* (2007)

(continued)

TABLE 3. Continued.

GHG	Land Use	Effect of Land Use and Climate	Geographic Location	Citation
CO_2	Urban	In a survey of 15 major rivers in Europe, urbanization was correlated with increased pCO_2	Wales, United Kingdom, Europe	Neal *et al.* (1998)
CO_2	Urban	There was elevated pCO_2 in rivers in response to urbanization likely due to enhanced microbial mineralization of organic carbon	Ontario, Canada, North America	Jarvie *et al.* (1997)
CO_2, CH_4, N_2O	Urban and agriculture	A eutrophic river was a major source of CH_4, CO_2, and N_2O to the atmosphere, whereas a downstream estuary was a minor source, or sink for these gases. Downstream, agriculturally influenced reaches of the river had the greatest N_2O emissions, and upland reaches draining peatlands had the greatest CO_2 and CH_4 emissions	Finland, Europe	Silvennoinen *et al.* (2008)
CO_2	Urban	Amplitude of diurnal pulses of CO_2 related to biological activity in streams receiving urban effluent and experiencing diurnal dissolved oxygen variations	United Kingdom, Europe	Neal *et al.* (2000a)
N_2O	Urban	A large urban river reach was a source of N_2O to the atmosphere year round	Ohio, USA, North America	Beaulieu *et al.* (2010)
CO_2	Urban and agriculture	Agricultural and urban streams had higher dissolved inorganic carbon (DIC) and pCO_2 than forested streams	Connecticut, USA, North America	Barnes and Raymond (2009)
N_2O	Urban, agriculture, and forest	Urban streams had the highest N_2O emissions. Agricultural and urban streams were both higher on average than forested reference sites, but no significant effect of land use was reported	Multiple locations, North America	Beaulieu *et al.* (2011)
CH_4	Urban and forested	CH_4 fluxes were substantial from sediments in an urban stream	Baltimore, Maryland, USA, North America	Harrison *et al.* (2012)
CO_2	Urban	Streams draining urban land use had higher mean excess CO_2 than forested streams. In addition, rainfall altered temporal dynamics of dissolved carbon forms, which could also influence pCO_2 dynamics in urban streams	Southeastern Brazil, North America	Andrade *et al.* (2011)
CO_2	Urban, agriculture, and rural	Supersaturation of CO_2 increased with increasing agricultural and urban land use. pCO_2 was greatest during the wet season and correlated with particulate organic carbon	Pearl River, China, Asia	Zhang *et al.* (2009a, b)
CO_2	Urban	Two rivers draining agricultural and urban land use were major sources of CO_2 to the atmosphere. The smaller, more, densely urbanized watershed was a greater source of CO_2 to the atmosphere than a larger, less densely populated watershed	Washington, D.C., USA, North America	Prasad *et al.* (2013)
N_2O	Urban, agricultural	Dissolved oxygen was a major driver of N_2O fluxes from the Grand River in Canada, which was influenced by agricultural fertilizer and wastewater treatment plant effluent. Increased hypoxia is likely to influence future N_2O emissions from rivers	Ontario, Canada, North America	Rosamond *et al.* (2012)
CO_2	Urban, agricultural	The Hudson River was supersaturated with CO_2 on all dates throughout a year. The more urbanized downstream section had greater CO_2 emissions than the upstream section, but only during summer months	New York, USA, North America	Raymond *et al.* (1997)

respiration rates, lower dissolved oxygen, and contribute to increased pCO_2 (Andrade *et al.*, 2011). Precipitation events can also alter temporal dynamics of dissolved carbon forms, which can also alter pCO_2 dynamics in agricultural and urban streams and rivers (Andrade *et al.*, 2011). In a river influenced by agriculture in the UK, pCO_2 was supersaturated during most times of year when pH was approximately 7.7, but pCO_2 declined when pH increased during spring (Neal *et al.*, 2000b). Similarly, there was increased supersaturation of pCO_2 in a river draining a mixed land-use watershed coinciding with increased base flow and oxidation of organic matter (Zhang *et al.*, 2009a, b). Finally, there may also be anthropogenic sources of carbonates in agricultural and urban watersheds that can interact with climate variability and warming and further influence pCO_2 in streams. Work in Texas



	Riparian Zones/Floodplains/Wetlands			Streams/Rivers		
Drivers	N_2O	CH_4	CO_2	N_2O	CH_4	CO_2
↑ Flooding [References A]	+	+	+/-	?	?	+/-
↑ Temperature [References B]	+	+	+	+	+	+
↑ Organic C [References C]	+	+	+	+	+	+
↑ Nutrients [References D]	+	+/-	+	+	+/-	+
↓ O_2 Availability [References E]	+	+	+/-	+	+	+/-

FIGURE 5. A Conceptual Model Exploring Potential Effects of Drivers Related to Land Use and Climate Change on CO_2, CH_4, and N_2O Emissions from Riparian Zones/Floodplains and Streams/Rivers. (+) denotes a general increase, (−) denotes a general decrease, (+/−) indicates a variable response, and (?) denotes too few studies. **References A (Flooding):** Increased N_2O pulses from riparian zones/floodplains/wetlands follow flooding (Baker and Vervier, 2004; Machefert and Dise, 2004; Hernandez and Mitsch, 2006, 2007; Sovik *et al.* 2006; Kachenchart *et al.*, 2012; Huang *et al.*, 2013). CH_4 is controlled more by inundation time than flood pulses (e.g., Zou *et al.*, 2005; Altor and Mitsch, 2008; Pennock *et al.*, 2010; Sha *et al.*, 2011). Flooding can decrease CO_2 emissions temporarily (Mander *et al.*, 2011; Soosaar *et al.*, 2011; Beetz *et al.*, 2013), but the overall CO_2 response can be variable. There are minimal studies examining the effect of flooding on instream N_2O, CH_4, and CO_2 pulses. **References B (Temperature):** Warming can increase N_2O emission riparian zones/floodplains/wetlands and streams/rivers when conditions necessary for denitrification are present (Maag *et al.*, 1997; McMahon and Dennehy, 1999; Laursen and Seitzinger, 2004; Hernandez and Mitsch, 2007; DeSimone *et al.*, 2010; Bonnett *et al.* 2013; Munoz-Leoz *et al.*, 2011; Baulch *et al.*, 2012). CH_4 emissions can also increase in riparian zones/floodplains/wetlands and streams/rivers with warming, but the response is not as strong because CH_4 consumption also increases (Verma *et al.*, 1999; Harrison *et al.*, 2005; Bonnett *et al.* 2013; Sha *et al.*, 2011; Yang *et al.*, 2012). Warming can also increase CO_2 emissions (Davidson *et al.*, 1998; Verma *et al.*, 1999; Mander *et al.*, 2011; Munoz-Leoz *et al.*, 2011). Diurnal studies such as Harrison *et al.* (2005) and Tobias and Böhlke (2011) also suggest that temperature can also play a role in stimulating CO_2 production in streams/rivers. **References C (Organic Carbon):** Several studies have found strong relationships with organic C and N_2O in riparian zones/floodplains/wetlands (Maag *et al.*, 1997; Baker and Vervier, 2004; Sovik *et al.* 2006; DeSimone *et al.*, 2010; Kachenchart *et al.*, 2012) and in streams/rivers (Harrison and Matson, 2003; Tortosa *et al.*, 2011). Similarly, riparian wetlands and streams with increased organic carbon availability tend to have high CH_4 production (Ambus and Christensen, 1995; Bianchi *et al.*, 1996; Silvennoinen *et al.*, 2008; Baulch *et al.*, 2011b; Mander *et al.*, 2011; Samaritani *et al.*, 2011; Sha *et al.*, 2011; Tortosa *et al.*, 2011). Several studies have also found a positive relationship between DOC and DIC/pCO_2 in floodplains, streams, and rivers (Jarvie *et al.*, 1997; Neal *et al.*, 2000a, b; Zhang *et al.*, 2009a, b; Andrade *et al.*, 2011; Samaritani *et al.*, 2011; Tortosa *et al.*, 2011). **References D (Nutrients):** Nutrient enrichment can stimulate N_2O in riparian zones/floodplains/wetlands (Maag *et al.*, 1997; Hefting *et al.*, 2003; Liu and Song, 2010; Vilain *et al.*, 2010; Kachenchart *et al.*, 2012) and streams/rivers (McMahon and Dennehy, 1999; Harrison and Matson, 2003; Beaulieu *et al.*, 2008, 2011; Silvennoinen *et al.*, 2008; Wilcock and Sorrell, 2008; Baulch *et al.*, 2011b; Outram and Hiscock, 2012; Werner *et al.*, 2012). The effect of nutrient enrichment on CH_4 emissions is less studied, but nutrient addition and eutrophic conditions tend to favor CH_4 production in streams/rivers (Wilcock and Sorrell, 2008; Baulch *et al.*, 2011a; Tortosa *et al.*, 2011; Werner *et al.*, 2012); however, some studies have also found inhibition of CH_4 following nitrate fertilization (e.g., Topp and Pattey, 1997). **References E (Oxygen Availability).** O_2 availability is generally linked to flooding frequency, inundation time, and the biological oxygen demand of floodwaters, and N_2O and CH_4 can increase in response to low-O_2 availability. N_2O emissions tend to be highest when O_2 availability is "pulsed" in riparian zones/floodplains/wetlands (e.g., Venterink *et al.*, 2003; Hernandez and Mitsch, 2007; Laini *et al.*, 2011), whereas CH_4 is emitted during hypoxic conditions and consumed during oxic conditions in all ecosystems (e.g., Naqvi *et al.*, 2000, 2010; Harrison *et al.*, 2005; Altor and Mitsch, 2006; Sanders *et al.*, 2007; Yang *et al.*, 2012). CO_2 emissions appear to be generally inhibited by low oxygen (Mander *et al.*, 2011; Soosaar *et al.*, 2011) in soils, but can increase in low-O_2 streams/rivers contributing to a variable response (Neal *et al.*, 1998; Neal *et al.*, 2000a, b; Harrison *et al.*, 2005; Duc *et al.*, 2007; Andrade *et al.*, 2011).

showed that high dissolution of carbonates from impervious surfaces contributed to elevated pCO_2 in an urban stream (Zeng and Masiello, 2010). Similar work has shown that there are anthropogenic carbonate inputs from agricultural liming (Raymond and Oh, 2007; Raymond *et al.*, 2008). Dissolution of carbonates can be temperature dependent and warming and acidic precipitation may accelerate chemical weathering processes thereby altering pCO_2 dynamics (e.g., Kaushal *et al.*, 2013).

EMERGING QUESTIONS

What Factors Influence the Lag Times of Contaminant Pulses and Ecosystem Recovery?

Interestingly, contaminant pulses may follow different lag times in watersheds following extreme events including protracted responses to extreme events or delayed responses (e.g., time lags between peak precipitation and peak streamflow). These lag times can be relevant to both hydrologic and gaseous fluxes. Here, we define time lags based on a return to preevent conditions. For example, some contaminant concentrations and exports can remain elevated for days to decades following extreme events. Lag times of up to decades for nitrogen transport in response to historic agricultural activity have been detected in the Chesapeake Bay watershed due to deep groundwater flow paths with implications for long hydrologic residence times for some contaminants (Phillips *et al.*, 2006). There can also be lag times over interannual time scales. For example, total nitrogen exports declined during record drought in 2002, increased during the wet year of 2003, and surprisingly continued to keep increasing in 2004 as runoff declined (Kaushal *et al.*, 2008). This pattern may have been driven by flushing of nitrate stored during drought or increased N mineralization in soils and stream sediments due to drying and rewetting (Borken and Matzner, 2009) (Figure 3). Similarly, lag times occur over the period of days to weeks for specific conductance in urban streams following winter storms due to groundwater solute storage and changes in hydrologic flow paths (Figure 6). There may also be pulses in GHGs during and after storms, but their duration is also less well known. Anticipating changes in lag times of carbon, nutrients, and GHGs both during and after extreme events is critical. Empirical data on lag times for multiple contaminants following extreme events will be necessary for understanding fate and transport mechanisms in watersheds from days to decades.

How Will Warming Impact Hydrologic and Greenhouse Gas Pulses?

Warming has been shown to affect many aspects of biogeochemical and abiotic reactions that impact C, N, and P biogeochemical cycles and GHG fluxes. Warming increases microbial activity, desorption of phosphorus from sediments, and decomposition and mineralization of organic matter (Conant *et al.*, 2011). Experimental warming increases carbon and nutrient fluxes from sediments in agricultural and urban streams by

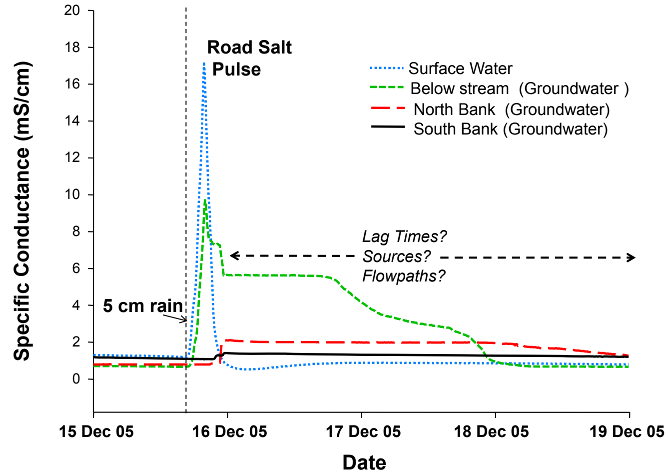


FIGURE 6. Example of a Relatively Short-Term Pulse in Specific Conductance Measured Using Conductivity Loggers (Solinst, Georgetown, Ontario, Canada) Following Road Salt Use during a Winter Storm at Minebank Run Stream, Baltimore, Maryland. Groundwater wells are 1.2 m below the ground and stream bed.

several-fold compared to forest streams and could contribute to decreased water quality in urban streams of the Chesapeake Bay watershed (Duan and Kaushal, 2013). Release of DOC from sediment due to organic carbon decomposition generally increases with warming. Warming may also influence production of some GHG emissions (CO_2, CH_4, and N_2O) in wetlands (Inglett *et al.*, 2012). Because temperature has an effect on reaction kinetics and equilibria in streams, pulses in stream temperature have the potential to impact many instream transformations. Temperature may increase rates of both bacterial mineralization and production of GHGs in streams and rivers, depending on the reactions considered. Considerably more work has focused on impacts of runoff (floods and droughts) on watershed hydrologic exports, but impacts of temperature extremes on instream biogeochemical transformations and hydrologic and GHG emissions warrant attention.

How Can We Improve Predicting Watershed Pulse Dynamics by Coupling Sensor Measurements with Experiments?

Quantifying diurnal variability in pulses can contribute to our understanding of the role of streams and rivers in transporting and transforming contaminants. Sensors show potential for characterizing watershed nitrate and the fluorescent fraction of colored, dissolved organic matter (FDOM) pulses in agricultural watersheds over diurnal time scales (Table 4). Heffernan and Cohen (2010) used nitrate sensors to evaluate fine-scale temporal dynamics in an agricultural spring-fed watershed. They showed

TABLE 4. Sensors Show Potential to Detect Variability in Nitrate and Carbon Quality across Storms and Diurnal Time Scales.

Citation	Land Use	Parameter	Ranges	Source of Temporal Variability
Heffernan and Cohen (2010)	Agriculture	Nitrate	381-456 μg/l (spring); 451-488 μg/l (fall)	Spring water chemistry inputs to river; primary productivity
Pellerin *et al.* (2009)	Agriculture	Nitrate	1.72-2.47 mg/l	Riverine processes; irrigation return flow
Moraetis *et al.* (2010)	Agriculture	Nitrate	1.25-1.75 mg/l (fall); 0.5-2.5 mg/l (summer)	Instream biogeochemical processes
Ferrant *et al.* (2012)	Agriculture	Nitrate	5-35 mg/l	Flood events
Heffernan *et al.* (2010)	Agriculture	Nitrate	0.38-0.46 mg/l (spring); 0.45-0.49 mg/l (fall)	Autotrophic assimilation
de Montety *et al.* (2011)	Agriculture	Nitrate	0.032-0.036 mM	Photosynthesis and respiration of subaquatic vegetation
Saraceno *et al.* (2009)	Agriculture	FDOM (fluorescent fraction of colored, dissolved organic matter)	24-33 ppb QSE (quinine sulfate equivalents) during base flow	Diurnal signals during base flow — possibly a combination of groundwater and algal sources, potentially with microbial grazing and photodegradation processes; storm flow — agricultural soil drainage
Henjum *et al.* (2010a, b)	Urban	Nitrate	100-450 μg/l	Sewage from leaking pipes or septic into shallow groundwater; stormwater ponds
VerHoef *et al.* (2011), VerHoef (2012)	Urban	Nitrate	1-2 mg/l	Groundwater inputs; dilution during storms; diurnal stream processing during base flow

that diurnal variability in nitrate concentration was strongly associated with diurnal changes in primary productivity. de Montety *et al.* (2011) measured high-frequency dissolved oxygen and nitrate over two one-week periods in the same system. Their observations confirmed that photosynthesis and respiration of submersed aquatic vegetation are the dominant processes influencing instream diurnal variation. Saraceno *et al.* (2009) also observed that FDOM showed a strong diurnal signal, which may suggest groundwater and algal sources, potentially with microbial grazing and photodegradation processes.

Besides characterizing the potential for biogeochemical transformations, there are questions regarding how sensors can be used to characterize multiple contaminant pulses during storms and ecosystem recovery following storm disturbances. By characterizing ecosystem recovery, we mean ecosystem retention functions (e.g., denitrification, primary production, P sorption, etc.) related to attenuating concentrations of a contaminant in response to extreme climate events. In urban watersheds, Henjum *et al.* (2010a) investigated the feasibility of using *in situ* turbidity, specific conductance, pH, depth, temperature, dissolved oxygen, and nitrate sensors to predict concentrations of fecal coliforms, herbicides, and caffeine concentrations. Linear correlations among several parameters were observed to be site specific and included: nitrate-caffeine, turbidity-prometon herbicide, and discharge-prometon herbicide at one location, and caffeine-specific conductance at another. The authors concluded that even weak correlations could be beneficial for estimation of pollutant loads (given sensors for the specific contaminants of concern are not available yet). Henjum *et al.* (2010b) used real-time nitrate, specific conductance, and turbidity data to calculate pollutant loads during storms and compare to loads calculated using traditional grab sampling. More than 90% of the pollutant load for nitrate, chloride, and total suspended solids (TSS) was observed to be discharged in 20% of the observation period (i.e., storm events), illustrating that grab sampling would underestimate pollutant loads and pulses. Finally, VerHoef *et al.* (2011) deployed nitrate sensors at six U.S. Geological Survey (USGS) stream gaging stations in nested urban watersheds ranging from 1.3 to 14.3 km^2. These sensors allowed the authors to show that for the watersheds studied, nitrate signals showed a sharp drop in concentration with the onset of storm flow, with minimum values at peak storm flows, and gradual recovery to prestorm conditions as storm flow receded, which can be helpful in refining our understanding of the effect of extreme events on nitrate export at the watershed scale. This is one example of storm dynamics, but we acknowledge that there is a great deal of variation in the response based on antecedent conditions, sources, and spatial distribution of the contaminant (rain, groundwater, streams).

Ultimately, an important area of research will be to integrate sensor data with rates from empirical experiments to inform ecosystem models at the watershed and stream reach scale. Laboratory and *in situ* field experiments are needed to quantify the relationship between sensor parameters (e.g., temperature, dissolved oxygen, nitrate concentrations, FDOM discussed above) and ecosystem-scale biogeochemical processes rates influencing carbon, nutrients, and contaminant pulses at the watershed scale (e.g., denitrification, phosphorus desorption, GHG production). Integration of experimental data can allow us to move beyond correlations to elucidating causal mechanisms at targeted sites, whereas sensor measurements across multiple locations will allow us to gain broader spatial perspectives relevant to watershed management.

WATERSHED MANAGEMENT TO MITIGATE PULSES

Although there are still emerging questions, the impacts of carbon, nutrient, and contaminant pulses in watersheds now require strong management actions. Here, we discuss eight broader recommendations based on our review to manage the impacts of hydrologic and gaseous pulses synergistically. As a caveat, we do not provide an in-depth discussion of specific BMPs, and how BMPs can impact nutrient and carbon flux under changing climate. Given that considerable work has been done in agricultural watersheds in particular, a thorough discussion of BMPs would require a devoted review, and we refer the reader to a recent review by Passeport *et al.* (2013) instead. While some management recommendations would require new or enforced legislation and/or shifts in societal actions/values, the use of these broader approaches based on current scientific understanding could be implemented at local and regional scales.

Reduce Watershed Carbon, Nutrient, and Contaminant Sources

The impacts of carbon, nutrient, and contaminant pulses ultimately increase as a function of watershed inputs and can increase both hydrologic and GHG pulses (e.g., Figure 5). Therefore, reducing point and nonpoint sources is the most critical step to mitigating impacts. Some reductions may be elicited through voluntary curtailments. However, regulatory mechanisms such as policy change, zoning laws, and/or restriction of contaminants are also necessary to effectively achieve source reductions.

Manage Infiltration Rates

In urban areas, impervious surfaces (including roads, bridges, buildings, and other structures) reduce or prevent infiltration and increase hydrologic pulses locally and regionally. Removal of impervious surfaces can be an option, although it may not always be feasible. Replacing paved surfaces with pervious pavement and retrofitting with green infrastructure (Dietz, 2007) may be feasible in some urban areas. Zoning and planning can reduce the need for more impervious surfaces. In agricultural watersheds, row crop agriculture and/or cattle operations can also increase soil compaction, which reduces infiltration rates (McKergow *et al.*, 2003). Reduced tillage, permanent covers, and other approaches to increasing infiltration are important in agricultural watersheds.

Reduce Headwater Alteration and Stream Channelization

Often streams are modified and redirected through drainage structures or ditches to increase the speed and volume of water that can be moved off of the landscape. In urban or agricultural settings, stream restoration can proceed in fashion to reduce stream channel incision, which can allow improved hydrologic connection with the stream and increase groundwater hydrologic residence time (Striz and Mayer, 2008). Removing tile drains that locally redirect water from farm fields is another often used, feasible means of reducing agricultural headwater alteration (Vidon and Smith, 2008). However, subsurface drains are still being installed in many places (Franzmeier and Kladivko, 2001; Franzmeier *et al.*, 2001). An alternative to removing tile drains may be the implementation of artificial headwater wetlands and denitrifying bioreactors to intercept nitrogen, or other contaminants before they reach the stream (Braskerud, 2002; Passeport *et al.*, 2013). For example, there has been extensive work on nitrate removal by wetlands through targeting hydrologic flow paths in agricultural landscapes (e.g., Crumpton, 2001).

Manage Hydrologic Connectivity

Managing hydrologic connectivity can improve the capacity of streams to process contaminants and reduce pulses, for example, by increasing interactions between groundwater and surface water with floodplains, oxbow wetlands, and side channels (Bukaveckas, 2007; Craig *et al.*, 2008; Kaushal *et al.*, 2008; Harrison *et al.*, 2011; Roley *et al.*, 2012). Contaminated water may flow through areas that foster microbial transformation of contaminants and/or adsorption onto soils (Kasahara and Hill, 2006a, b; Mayer *et al.*, 2010). In agricultural watersheds, soil BMPs such as controlled drainage can also enhance overland flow, while reducing N losses in subsurface flow, a tradeoff that could impact watershed pulses.

Restore Riparian Buffers and Their Vegetation

Establishing riparian buffers often is considered a BMP for maintaining water quality (Mayer *et al.*, 2007). The extent to which riparian buffers attenuate nutrients and subsequently mitigate pulses is a function of buffer width, organic matter content, and landscape and hydrogeomorphic characteristics (Vidon and Hill, 2004; Hoffman *et al.*, 2009; Zhang *et al.*, 2010). However, riparian buffers are less effective when agricultural areas are tile drained because tile drains can bypass the buffer and eliminate interaction between nitrate and the riparian soils. Nevertheless, riparian buffers have the potential to significantly decrease nitrogen pulses if there is (1) efficient runoff interception and significant interaction between N-laden subsurface flow and organic-rich soils (Dosskey *et al.*, 2010; Gift *et al.*, 2010; Passeport *et al.*, 2013) and (2) vegetation cover is adequate and diverse to decrease erosion and maintain the soil organic matter content (Dosskey *et al.*, 2010; Passeport *et al.*, 2013).

Reduce Local Stream and River Reach Temperatures

Global temperatures are increasing and temperatures in streams and rivers are also rising locally due to the interactive effects of land use and climate change (Kaushal *et al.*, 2010b). In urban and agricultural watersheds, riparian zones are often removed, thereby eliminating shading effects. Reestablishing riparian zones (see above) can provide shading and reduce summer-time stream temperatures. Reducing impervious surface or thermal pollution sources that transfer heat to streams may be necessary to further reduce potential temperature impacts on GHG pulses and contaminant transformations.

Managing Water Quality to Reduce GHG Pulses

Some of the key factors related to GHG emissions may also be related to successfully managing water quality. For example, targeted reductions in watershed nutrient inputs can reduce pulses of N_2O, CH_4, and CO_2 in aquatic systems (Figure 5). In addition, reducing nonpoint organic carbon loading from crop detritus, algal blooms, sewage leaks, etc. (discussed previously) may also be important. Increasing oxic conditions in streams and rivers may also inhibit anaerobic processes contributing to some GHG emissions.

Preservation and Conservation

While climate and land-use change may be unavoidable globally, ecosystem functions can be enhanced locally. Our review suggests that land development can increase vulnerability to hydrologic and GHG pulses in response to climate variability (Tables 1 and 2). Infiltration and hydrologic residence times can be enhanced by preserving and conserving existing natural ecosystems. Plans should address reducing future development and conversion of natural lands to urban and intensively agricultural systems to buffer extremes in runoff and temperature. Where watersheds have been developed, ecological engineering can sometimes improve a watershed's ability to dampen carbon, nutrient, and contaminant pulses, within limits based on environmental factors such as runoff, temperature, nutrient enrichment, etc., as discussed in this review and elsewhere (e.g., Passeport *et al.*, 2013).

CONCLUSIONS

Our review shows that the interactive effects of land use and climate variability have increased the magnitude and frequency of carbon, nutrient, and GHG pulses globally. Causes include: (1) increased nutrient and organic matter loading, (2) extensive headwater alteration, and (3) loss of ecosystem services to buffer runoff and temperature. Continued research is needed to answer emerging questions such as: What factors influence the lag times of different contaminant pulses and ecosystem recovery? How will rising temperatures influence carbon, nutrient, and greenhouse pulses across watersheds? How can we improve predicting watershed pulse dynamics by coupling sensor measurements with manipulative experiments? Filling in these knowledge gaps will be critical to improve management responses and anticipate the interactive effects of land use and climate change on amplifying watershed pulses.

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