HOT SPOTS AND HOT MOMENTS IN RIPARIAN ZONES: POTENTIAL FOR IMPROVED WATER QUALITY MANAGEMENT[1]

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ABSTRACT: Biogeochemical and hydrological processes in riparian zones regulate contaminant movement to receiving waters and often mitigate the impact of upland sources of contaminants on water quality. These heterogeneous processes have recently been conceptualized as "hot spots and moments" of retention, degradation, or production. Nevertheless, studies investigating the importance of hot phenomena (spots and moments) in riparian zones have thus far largely focused on nitrogen (N) despite compelling evidence that a variety of elements, chemicals, and particulate contaminant cycles are subject to the influence of both biogeochemical and transport hot spots and moments. In addition to N, this review summarizes current knowledge for phosphorus, organic matter, pesticides, and mercury across riparian zones, identifies variables controlling the occurrence and magnitude of hot phenomena in riparian zones for these contaminants, and discusses the implications for riparian zone management of recognizing the importance of hot phenomena in annual solute budgets at the watershed scale. Examples are presented to show that biogeochemical process-driven hot spots and moments occur along the stream/riparian zone/upland interface for a wide variety of constituents. A basic understanding of the possible co-occurrence of hot spots and moments for a variety of contaminants in riparian systems will increase our understanding of the influence of riparian zones on water quality and guide management strategies to enhance nutrient or pollutant removal at the landscape scale.

(KEY TERMS: riparian zones; hot spots; hot moments; nitrate; phosphorus; carbon; pesticides; mercury; transport and fate; watershed management; contaminant removal.)

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INTRODUCTION

Riparian zones can be broadly defined as semiterrestrial areas lying at the interface of the terrestrial and aquatic environment. They are often influenced by overbank flooding events and connect upland and aquatic environments through surface and subsurface hydrologic flow paths (Naiman *et al.*, 2005). Although typically a small area within a watershed, riparian zones often have a disproportionate influence on water and solute fluxes to streams. Past studies that encompass a variety of climatic and physiographic regions have identified some critical and complex functions of riparian zones (Correll, 2000; Hill, 2000; Dosskey, 2001). Riparian ecosystems shade streams, stabilize streambanks, and provide habitat for a diverse number of terrestrial and aquatic organisms (Naiman *et al.*, 2005). Riparian zones are now well recognized for removal of nutrients like nitrogen (N) and phosphorus (P) from upland sources (Lowrance *et al.*, 1997a; Dosskey, 2001; Mayer *et al.*, 2007). For this reason, their characterization as "filters" or "buffers" is apt and riparian zones are key elements in watershed management schemes (Burt, 1997; Lowrance *et al.*, 1997a).

Riparian zones occur at the interface of upland and aquatic ecosystems where intersecting hydrologic flow paths produce dynamic moisture and biogeochemical conditions (Figure 1). Variability in space and time of soil moisture conditions, redox potentials, vegetation, and temperature has a substantial impact on the fate and transport of solutes through riparian zones (Korom, 1992; Hedin *et al.*, 1998; Hill *et al.*, 2004; Vidon and Hill, 2004a). This variability in biogeochemical conditions in riparian ecosystems has important implications for the speciation and availability of N (Gold *et al.*, 1998; Jacinthe *et al.*, 1998), P (Reddy and Delaune, 2008), mercury (Hg) (Branfi-reun and Roulet, 2002; Mitchell *et al.*, 2008a), sulfur (S) (Urban *et al.*, 1989; Devito and Hill, 1997; Eimers *et al.*, 2004), organic matter (OM) (Jacinthe *et al.*, 2003; Gurwick *et al.*, 2008), and pesticides and their metabolites (Benoît *et al.*, 1999; Krutz *et al.*, 2006).

Due to temporal heterogeneity of solute fluxes through riparian zones, large fractions of annual solute loadings often occur during brief portions of the year such as during rainfall and snowmelt events (Boyer *et al.*, 1997; Royer *et al.*, 2006; Shipitalo and Owens, 2006; Dalzell *et al.*, 2007). Many studies also show that processes within the stream, hyporheic zone, and riparian zone mutually influence each other and that riparian processes should be investigated within the context of the stream, riparian zone, and upland continuum (Fisher *et al.*, 1998; Meyer *et al.*, 1998; Steinhart *et al.*, 2000; Kasahara and Hill, 2007). A thorough understanding of groundwater flow paths in the riparian zone is also critical to understand riparian function because contaminated groundwater flowing toward the stream may bypass the reactive root zone of riparian systems and negatively impact stream water quality (Bohlke and Denver, 1995; Bohlke *et al.*, 2002; Puckett, 2004; Puckett and Hughes, 2005).

Recently, McClain *et al.* (2003) explored the importance of spatial and temporal variability in biogeochemical transformations at the terrestrial-aquatic interface. Their paper characterized this variability in terms of "hot spots" and "hot moments" and was focused on N and C. Hot spots were defined as regions that exhibited disproportionately high reaction rates relative to the surrounding area (or matrix). Hot moments were defined as short periods of time that displayed disproportionately high reaction rates relative to longer intervening time periods. McClain *et al.* (2003) proposed that these phenomena, which were localized in space and time, had a disproportionately large impact on the fluxes of solutes and thus
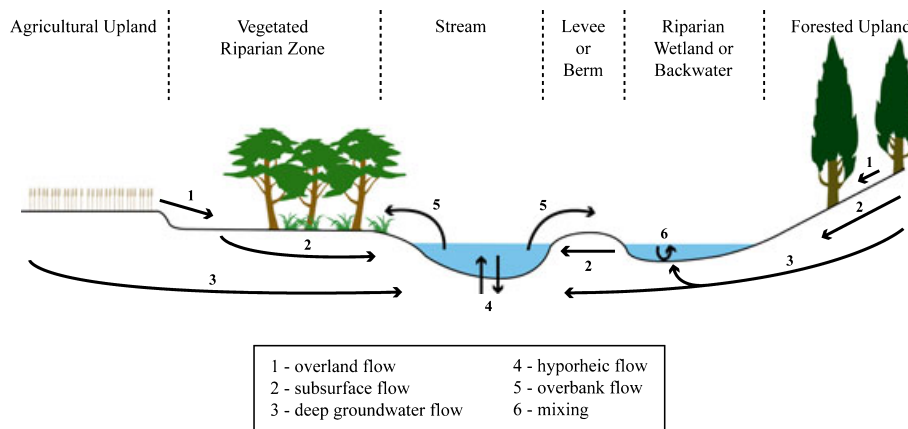

FIGURE 1. Dominant Flow Path Across the Upland-Riparian-Stream Continuum in Both Agricultural and Forested Landscapes.

were critical to furthering our understanding of nutrient cycling. The McClain *et al.* (2003) paper helped to further the concept of hot spots and moments. Subsequently, Groffman *et al.* (2009) explored how hot spots and hot moments may be incorporated into denitrification models.

Beyond N and C, the hot spot and moment concepts may also apply to other chemical constituents including P, Hg, S, OM, and pesticides, among others. Nevertheless, a comprehensive evaluation of the role of hot spots and moments for a broad suite of nutrients, trace metals, and contaminants is lacking. Interactions between elements in hot spots and during hot moments are well documented (Grimm *et al.*, 2003; Ollinger *et al.*, 2003). However, the diversity of effects and responses for a wide variety of chemical constituents because of these hot phenomena in riparian zones is less recognized. For example, a hot moment for one solute may not necessarily be a hot moment for another, and one element may be retained in the riparian zone at the same time that another solute is generated or passed through the riparian zone without reaction. This constituent-specific behavior becomes especially relevant in riparian zones used to implement best management practices (BMPs) to mitigate the impact of various pollutants on water quality. Underlying these hot spot and hot moment patterns and differences in behavior are the rates and heterogeneity of hydrologic processes that transport contaminants through riparian zones to adjacent surface waters. Hydrologic processes that control the location, timing, and duration of solute contact with riparian soils where transformation processes occur are often the primary determinant of riparian hot spots and hot moments.

DEFINITION OF TERMS

In this paper, we adopt the definition proposed by McClain *et al.* (2003) for hot spots and hot moments. However, we distinguish between transport-driven and biogeochemical process-driven hot spots and moments, with the understanding that these terms are not mutually exclusive. Biogeochemical hot spots are areas or patches that show disproportionately high reaction rates (greater than one order of magnitude higher) relative to the surrounding area (or matrix). Biogeochemical hot moments are short periods of time (<20% of the time) that show disproportionately high reaction rates relative to longer intervening time periods. Similarly, transport hot spots are areas or patches where solute fluxes are disproportionately higher (greater than one order of

magnitude higher) than in surrounding areas. Transport hot moments are short periods (<20% of the time) during which solute fluxes are significantly greater than during the intervening time. In that sense, intense hydrologic events such as precipitation events or snowmelt periods can represent hot moments of transport for many solutes.

Although OM is not a pollutant, riparian OM export to streams affects ecosystem metabolism and the rates of most biologically mediated reactions which regulates the fate of contaminants such as N, P, Hg, and pesticides in riparian systems. In this paper, we therefore include organic carbon and frequently refer to OM. We recognize that the term represents an oversimplification of a complex mixture of often unknown molecular structure of which carbon is often the dominant chemical element (along with hydrogen and oxygen), but that also contains N, sulfur, P, and/or small amounts of many other chemical elements. We will use the term OM when referring to the whole of the solid form and dissolved organic matter (DOM) when referring to the dissolved fraction of the organic material. We will use the term organic carbon (OC), or dissolved organic carbon (DOC) for the dissolved fraction of OC, primarily when referring to specific measurements of the carbon contained within a sample of OM or to the role of the carbon contained within the OM in question.

OBJECTIVES

The objectives of this paper are to: (1) summarize current knowledge related to the occurrence of hot phenomena (spots and moments) for a variety of chemical constituents across the stream, riparian zone, and upland continuum; (2) identify variables that control the occurrence and magnitude of hot phenomena in riparian zones for a wide array of contaminants/solutes; and (3) discuss the implications of hot phenomena for multi-pollutant riparian zone management and recognize that the effects of hot phenomena are important at the watershed scale. We also briefly discuss the importance of the interaction between hot spots and hot moments in determining solute and contaminant fluxes at the landscape scale. This review first focuses on biogeochemical process-driven phenomena and then on transport-driven hot spots and moments. We then discuss situations when the co-occurrence of hot phenomena is either possible or incompatible for multiple elements and constituents (i.e., certain hot phenomena may occur simultaneously or be mutually exclusive). Finally, we discuss

the implications for riparian zone management. In this study, we deliberately focus on reactions affecting water quality only and not greenhouse gas production (e.g., methane, carbon dioxide, and nitrous oxide) which is beyond the scope of this review.

BIOGEOCHEMICALLY DRIVEN HOT SPOTS AND MOMENTS

Nitrogen

Plant uptake and microbial transformations of dissolved N in riparian forests can retain large fractions of mobile N that would otherwise flow to streams via subsurface flow paths (Lowrance *et al.*, 1984; Peterjohn and Correll, 1984). Riparian forests are often effective at removing >50% of the N loading where surface and shallow subsurface waters transport ammonium (NH_4^+) and NO_3^- through the rhizosphere (Lowrance *et al.*, 1997a; Kaushal and Lewis, 2005). Assimilative uptake produces organic N that may later be mineralized. The decomposition of biomass after litterfall reintroduces stored N to the soils, which may later create a hot moment of terrestrial and aquatic N availability (Webster *et al.*, 1999). Microbial N transformations include assimilative uptake, assimilatory nitrate reduction to ammonium, and dissimilatory nitrate reduction to NH_4^+ (DNRA) or N gases such as dinitrogen (N_2), nitric oxide, and nitrous oxide gases via denitrification. The riparian literature predominantly focuses on denitrification because this microbial process is common in riparian areas and the production of unreactive N_2 during denitrification represents a permanent removal of N from the terrestrial reactive pool.

Several recent publications on N cycling in riparian zones focus directly or indirectly on biogeochemical process-driven hot spots and hot moments (Gold *et al.*, 2001; McClain *et al.*, 2003; Vidon and Hill, 2004a; Groffman *et al.*, 2009). Parkin (1987) found that more than 90% of denitrification activity in an upland soil core occurred in less than 1% of the core volume, at a microsite where a decomposing leaf was a source of labile OC that sustained denitrification. More recently, Jacinthe *et al.* (1998) found anoxic hotspots of denitrification within otherwise oxic riparian soils. Gold *et al.* (1998) and Jacinthe *et al.* (1998) also found that denitrification occurred within small patches of OC in the C horizon of riparian soils. These and other examples in the literature document denitrification hot spots in riparian soils owing to the development of locally anoxic conditions and/or the presence of OC buried at depth.

For these denitrification hot spots to have an effect on N removal at the riparian zone scale, they must: (1) be relatively abundant or have a large spatial extent and (2) have a large volume of NO_3^--rich water (i.e., a flow path must allow the interaction between NO_3^--rich water and hot spots of denitrification in the soil). These conditions commonly occur at the interface between coarse, permeable materials, and fine organic-rich materials in the subsurface as demonstrated in the examples below from diverse riparian settings. For instance, Devito *et al.* (2000) and Hill *et al.* (2000) found that sand/peat interfaces in southern Ontario were hot spots for NO_3^- removal at the riparian zone scale. In this setting, large fluxes of NO_3^--rich groundwater (300 l/day/meter stream length) flowed through a sandy aquifer and interacted with anoxic and OC-rich groundwater within a few meters of this sand and peat interface, generating a denitrification hot spot in the subsurface. At the Speed River site in southern Ontario, Vidon and Hill (2004b) found that most NO_3^- removal occurred at the interface of a gravel and coarse sand aquifer with a loamy soil. In Rhode Island, Gold *et al.* (2001) showed that outwash and organic or alluvial deposits were hot spots for denitrification owing to the high potential for interaction between NO_3^--rich groundwater and biologically active soil zones. Conversely, seeps at the till interface often limited the interaction of NO_3^--rich groundwater with microbially active soil sites. Therefore, those zones did not substantially contribute to NO_3^- removal at the landscape scale despite locally high denitrification rates. Correll *et al.* (1997) also found negligible NO_3^- removal at the landscape scale in a Maryland riparian zone where low soil OC content within a sandy riparian zone limited NO_3^- removal by denitrification. Although many studies find denitrification at depth, others measure the highest denitrification potential in the surface soils (0-20 cm) of riparian zones (Ambus and Lowrance, 1991; Burt *et al.*, 2002). These high potentials are attributed to high OM levels in surface soils and to the presence of denitrifiers that are periodically active, often when water tables are highest.

Stream channels are also hot spots for N transformations (Groffman *et al.*, 2005; Mulholland *et al.*, 2008). Debris dams increase the contact time between NO_3^--rich water and OM and are potential hot spots of N retention in forested streams (Steinhart *et al.*, 2000; Webster *et al.*, 2000; Ensign and Doyle, 2005; Roberts *et al.*, 2007). Nitrate may also be consumed or produced along hyporheic flow paths. Mineralization and nitrification along hyporheic flow paths are documented sources of stream N in arid streams of Arizona (Holmes *et al.*, 1994; Jones *et al.*, 1995) and coastal forest streams in northern California (Triska

et al., 1990). In contrast, uptake and denitrification along hyporheic flow paths was found to consume N in Catskill mountain streams of New York (Burns, 1998; Sobczak et al., 2003) and N-rich agricultural streams of southern Ontario (Kasahara and Hill, 2007; Duff et al., 2008).

The exchange of water between streams and riparian areas also affects riparian N transformations. For example, Hultine et al. (2008) added inorganic N to artificial stream ecosystems and measured increased primary productivity of riparian vegetation indicating that surface water exchange into riparian soils may create a hot spot of N removal via plant uptake. Similarly riparian hot spots of N uptake were found in Alaska, where trees and shrubs were found to tap into N moving into riparian soils along hyporheic flow paths (Helfield and Naiman, 2002; Compton et al., 2006). The source of this hyporheic N was identified as the decaying carcasses of anadromous salmon. Hot moment releases of N and other nutrients were a widespread occurrence in streams throughout the Pacific Northwest of North America and northeastern Asia prior to overfishing and loss of spawning habitat (Cederholm et al., 1999). These pulsed inputs of marine-derived nutrients, which still occur during various spawning runs during the summer and fall, are transformed instream and are a N source to stream food webs and riparian vegetation (Helfield and Naiman, 2001; Chaloner et al., 2002; Naiman et al., 2002).

Sustained streambank seepage into the riparian zones of low-gradient agricultural streams can also create a hot spot of NO_3^- removal at the stream-riparian interface (Duval and Hill, 2007). Increased stream stage and flooding due to beaver dam creation can increase the spatial extent of NO_3^- removal, suggesting that hot spots are not constant in size, and that beaver dam construction creates biogeochemically driven hot moments of N transformation (Naiman et al., 1994; Hill and Duval, 2009). Similarly, inundation of riparian forest soils may create hot spots and moments of N transformation. N mineralization was higher in riparian soils along the Rio Grande River in New Mexico, that were inundated for 7 to 45 days per year than in riparian soils that had not been inundated in more than 25 years (Follstad Shah and Dahm, 2008). Hot spots of N transformation also occur in riparian areas at and behind natural river levees. Soil water concentrations of NH_4^+ were lowest and NO_3^- were highest in well-aerated levees where nitrification appeared to be the N source (Johnston et al., 2001). Denitrification at these sites was limited by the NO_3^- supply.

At a larger scale, Seitzinger et al. (2006) showed that 50 to 80% of reactive N inputs "disappear" in terrestrial ecosystems before reaching the sea, suggesting that the cumulative effects of hot spot and moment transformations in riparian and instream settings are important at the large watershed scale.

Phosphorus

Phosphorus mobilization and immobilization in riparian areas is a function of the juxtaposition of P sources, hydrological transport, and biogeochemical transformations. For instance, riparian soils may be P sources to streams when soils are anoxic or when mineral dissolution releases mobile P (Baldwin and Mitchell, 2000; Chacón et al., 2008). In subsurface oxic soils, P is often immobile. For example, Carlyle and Hill (2001) measured high dissolved oxygen (DO) concentrations (>3 mg/l), low soluble reactive phosphorus (SRP) concentrations (<2 μg/l), and low ferrous iron (Fe^{2+}) concentrations (<0.2 mg/l) in a sandy riparian zone of southern Ontario. In contrast, in buried channel deposits with more reduced conditions, as evidenced by low DO (<3 mg/l) and high reduced iron (Fe^{2+}) concentrations in excess of 1 mg/l, SRP concentrations were high (50-950 μg/l) (Carlyle and Hill, 2001). This balance between oxidized and reduced conditions is a primary control on when riparian zones are hot spots of SRP production. We expect that riparian zones with large groundwater fluxes, high concentrations of sediment-bound P, and reducing conditions where ferric iron (Fe^{3+}) is reduced to Fe^{2+} are likely hotspots of P release to streams. The sensitivity of P to soil redox conditions suggests that hot moments of P release to streams (as SRP) may respond to hydrological controls on soil biogeochemistry. For instance, Mulholland (1992) found that a deciduous riparian forest in Tennessee was a source of SRP to the stream in summer when DO in soil water was low, but retained P during other seasons when DO was high.

Hot spots for P transformations may also occur at upland edges of riparian zones where sediment from agricultural runoff is deposited (Dillaha and Inamdar, 1997). These deposits (or berms), which often contain abundant coarse and fine-grained sediment, are P sources if P is desorbed and then leached from sediment deposits during subsequent runoff episodes. In contrast, the deposited sediment may be a sink and adsorb dissolved P from surface runoff if sediment P concentrations are low (Sharpley and Rekolainen, 1997). In other cases, upland surface runoff may lose P through adsorption to sediment as upland flow is routed through channels to the riparian zone and where P associated with fine-grained sediment may be deposited overbank onto the riparian zone (Dillaha and Inamdar, 1997). If this sediment is later saturated with water (especially near the riparian-stream

interface) and Fe and Mn are reductively dissolved during anoxic conditions, such deposits may desorb and release P (Reddy and Delaune, 2008). Thus, riparian channels or gullies may be hot spots that alternate as sinks and sources of P depending on transient redox conditions.

Instream processes may also significantly affect P sorption/desorption and therefore create hot spots of P cycling. For instance, P uptake by microbial communities associated with coarse woody debris is an important, although heterogeneous, P sink in forested streams during low flow periods. Mulholland et al. (1985) observed that stream transport distance of P (i.e., the spiraling length) varied inversely with the abundance of coarse particulate OM in the stream channel.

Organic Carbon and Organic Matter

Transformation hot spots for many contaminants in riparian zones occur primarily where anoxia, reactive OM, and electron acceptors are present (McClain et al., 2003). For example, Hedin et al. (1998) documented biogeochemical hot spots at dynamic interfaces that formed where groundwater with high concentrations of electron acceptor species (O_2, NO_3^-, SO_4^{2-}) intersected a groundwater flow path that had high concentrations of DOC. However, these hot spots also often include zones of production as well as consumption of both organic and inorganic carbon, which ultimately affect soil biology and DOC export to streams. Hot spots and moments of OM mineralization or export are important in regulating many biogeochemical cycles in riparian zones.

OM is commonly concentrated in the upper horizons of the soils and also occurs as discreet patches in the soil profile (Parkin, 1987; Hill et al., 2000; Blazejewski et al., 2005), patches that are found in moist spots throughout the landscape (Creed et al., 2002), or as extensive accumulations along riparian corridors (Thompson and Kolka, 2005). OM may be buried deeply in riparian soils and these deeply buried patches may be biogeochemically active hot spots. For example, Gurwick et al. (2008) found a significant positive correlation between soil OC content and microbial biomass in a Rhode Island riparian zone that was independent of burial depth (up to 2 m) and showed that deeply buried horizons and lenses in riparian soils may be hot spots for microbial activity owing to their high OC content. In riparian areas where reducing conditions dominate, microbes generally oxidize OC and reduce available electron acceptors, which releases carbon dioxide (CO_2) and generates alkalinity. Consequently, chemical gradients generally develop as electron acceptor concentra-

tions decrease and alkalinity increases along subsurface hydrological flow paths, as observed in riparian wetlands (fens) in New York state (Bailey Boomer and Bedford, 2008) and beaver ponds in the Adirondack Mountains of New York state (Burns, 1996; Cirmo et al., 2000).

Because riparian zones are commonly in low land areas and generally among the flattest parts of the landscape, they tend to have low subsurface flow velocities conducive to anoxia, shallow water tables, slow decomposition rates of OM, and large accumulations of solid OM as evidenced by riparian wetlands. This in large part explains why riparian zones are often hot spots of biogeochemical transformations. Riparian zones also serve as direct sources of OM to adjacent lakes, streams, and wetlands via inputs from vegetation, erosion of organic soils from streambanks, and hydrological inputs of DOM (Wetzel, 1992). Inputs of woody debris, leaves, and partially decomposed plant parts (coarse and fine particulate OM) from riparian vegetation to streams have been hypothesized to form biogeochemical hot spots that regulate the export of DOC (Meyer et al., 1998) and other nutrients from watersheds (Wetzel and Manny, 1972; Bilby, 1981). When litter inputs from a riparian forest were excluded from an upland stream in North Carolina, food web structure changed (Wallace et al., 1997) and stream DOC concentrations and loadings decreased (Meyer et al., 1998).

OM inputs to streams also influence organic C and N release to stream waters (Wetzel and Manny, 1972; Mulholland and Hill, 1997). In some streams, the availability of reactive DOC may limit microbial transformations. For example, stream NO_3^- concentrations and nitrification rates decreased during experimental DOC additions to forest streams at the Hubbard Brook Experimental Forest in New Hampshire. In this study, Bernhardt and Likens (2002) hypothesized that inputs of reactive OC, such as occurs during autumn leaf fall, stimulated heterotrophic uptake of N, which limited N availability to nitrifying bacteria. As would be expected during leaf fall when reactive OM availability no longer limits N uptake in streams, NH_4^+ spiraling lengths decreased during autumn in the forested Upper Ball Creek at the Coweeta Hydrological Laboratory in North Carolina (Tank et al., 2000).

Although other DOM species are not measured as frequently as DOC, riparian hot spots and moments have effects on other dissolved organic species such as dissolved organic nitrogen (DON). Microbially degraded DOM tends to have lower DOC:DON whereas higher DOC:DON is more typical of DOM that is freshly leached from leaves (Hood et al., 2003). When inputs of deciduous leaf litter increase during autumn leaf fall, stream DON concentrations may

temporarily increase during a hot moment of in-stream OM decomposition (Wetzel and Manny, 1972). The composition of DOM also changes at this time. In an upland forest stream in Vermont, DOC:DON at base flow increased by an order of magnitude during a hot moment of biogeochemical transformation after autumn leaf fall (Sebestyen, 2008). Leaf inputs to the stream from riparian deciduous vegetation during autumn leaf fall affect both stream DOM composition and quantity as leaf litter decomposes during this biogeochemical hot moment. Studies of other dissolved organic species such as P (DOP) and S (DOS) are needed to understand how sources and transformations of these biologically active DOM species are affected by riparian hot spots and moments of OM transformations.

Pesticides

To date, little information is available on the fate or transport of pesticides in riparian systems. Most degradation and adsorption/desorption studies have been carried out in agricultural soils or wetlands (Benoît *et al.*, 1999; Krutz *et al.*, 2006) and new research is necessary to understand processes that regulate pesticide transport to and removal from riparian zones and streams. For instance, the root zone in riparian soils may be a hot spot for the removal of many pesticides. The accumulation of labile OM and organic residues near the root zone may increase microbial biomass and activity. In riparian zones with high surface area contact between roots and pesticides as well as those with sufficient contact time, pesticides and pesticide metabolites may be mineralized and adsorbed (Krutz *et al.*, 2006). Isoproturon was degraded in surficial soils (0-2 cm depth) of a grassed buffer strip that had a high proportion of nondecomposed plant residues (Benoît *et al.*, 1999). Staddon *et al.* (2001) found enhanced degradation and shorter half-life (10 days) of metolachlor in a vegetated buffer strip (VBS) compared to that of an adjacent bare field (23 days). The differences in metolachlor degradation rates were attributed to higher OM content and microbial activity in VBS soils. Mudd *et al.* (1995) found similar results for atrazine in a riparian forest buffer in Georgia. Further, the abundance of microbial populations capable of degrading specific compounds tends to increase after repeated chemical applications (Gonod *et al.*, 2006). Consequently, riparian areas that receive chemicals in runoff or subsurface flow may have microbial populations that degrade pesticides that are applied to and transported from upslope source areas.

Although the examples mentioned here show potential degradation of several pesticides in riparian zones, the degradation potential and processes are expected to depend on individual pesticide formulations, of which there are hundreds. For example, some pesticides are more labile and more hydrophilic than others and more specific studies are needed to generalize hot spot and hot moments of pesticide degradation. Considering the high affinity of many pesticides for OM and the microbial populations that mediate pesticide degradation, debris dams, coarse woody debris and riparian OM sources in streams may be important sites of pesticide retention and degradation in streams and agricultural landscapes in general.

Mercury

Mercury bioaccumulation is the most common cause of fish consumption advisories in the U.S. and was responsible for 80% of all state advisories in 2006 (USEPA, 2007). Several studies have investigated details of Hg cycling in watersheds and in particular, hot spots of Hg cycling across the stream, riparian zone, and upland continuum. Researchers have known since the early 1990s that riparian soils and wetlands are hot spots of Hg mobilization (Mierle and Ingram, 1991; Driscoll *et al.*, 1995) and methylmercury (MeHg) production. Hg methylation in wetlands and riparian zones is associated with saturated soils rich in OM, widespread anoxia, a supply of Hg from atmospheric deposition or Hg that is stored in soils, and the presence of adequate sulfate (SO_4^{2-}) levels and microbes that methylate Hg (i.e., sulfate reducers) (St. Louis *et al.*, 1996).

Fluctuating redox conditions driven by a dynamic water table are hypothesized to be a primary control on the timing, magnitude, and location of Hg methylation (Heyes *et al.*, 2000; Branfireun and Roulet, 2002; Branfireun, 2004). The highest MeHg concentrations typically are found just below the saturated/unsaturated interface where soils are anoxic and electron acceptors and donors are abundant. Branfireun (2004) measured higher rates of Hg methylation in shallow hollows of wetlands than in deep hollows, hummocks, and lawns because shallow hollows likely have reducing conditions and direct inputs of SO_4^{2-} and Hg from atmospheric deposition. Hg methylation hot spots are especially likely where groundwater discharges from mineral soil upward through peat (Branfireun and Roulet, 2002) or where abundant supplies of dissolved Hg and SO_4^{2-} are hydrologically transported across redox gradients that occur where uplands transition into peatlands (Mitchell *et al.*, 2008a). A wetland in a Canadian boreal forest had higher MeHg concentrations where groundwater vertically discharged from a mineral soil
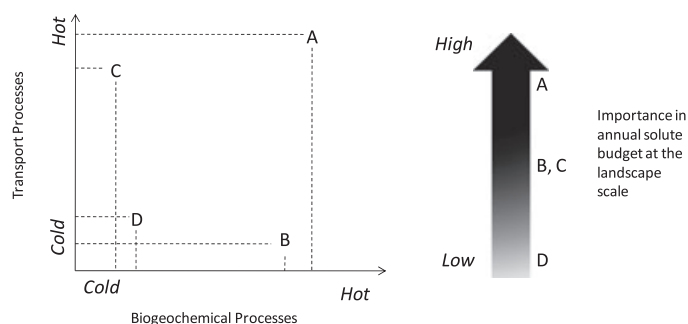
FIGURE 2. Relationship Between Transport and Biogeochemical Processes in Regulating Riparian Zone Function at the Landscape Scale.

through peat and where the rate of groundwater discharge was higher than in nearby wetland soils where flow was largely horizontal and restricted to a shallow peat layer (St. Louis *et al.*, 1996). Because SO_4^{2-} and OC availability may co-limit methylation, hot spots of MeHg are especially likely in riparian areas where hydrologic flow paths deliver reactive OC to anoxic sites (Mitchell *et al.*, 2008b). Given the heterogeneity of Hg transformations, more research is needed in a variety of riparian landscapes to better understand the complex interacting processes that regulate Hg methylation (Benoit *et al.*, 2003; Evers *et al.*, 2007).

Overall, biogeochemical process-driven hot spots and moments occur along the stream, riparian zone, and upland continuum for a variety of constituents including N, P, OM, pesticides, and Hg. Hot spots or hot moments of degradation or production occur because of unique combinations of electron donors and acceptors, redox conditions, and hydrological conditions. However, biogeochemical process-driven hot spots do not necessarily translate into high mass processing rates or fluxes at the landscape scale, because in many settings, the overall net processing of various chemical constituents is transport limited. High net nutrient or contaminant processing only occurs when biogeochemical hot spots are co-located and synchronous with transport driven hot spots and moments (Figure 2).

TRANSPORT-DRIVEN HOT SPOTS AND HOT MOMENTS

Nitrogen Transport

In addition to the importance of OC and redox controls on the occurrence of hot spots or moments of N

processing in riparian zones, the rate of transport of water through riparian zones affects the retention of NO_3^- and other chemical constituents in landscapes. For instance, a riparian zone that has high NO_3^- removal efficiency (biogeochemical hot spot) may have negligible solute fluxes to receiving waters. In this instance, the site would not be considered a hot spot for NO_3^- removal in the landscape despite a high NO_3^- removal rate. Conversely, some riparian zones that have high NO_3^- loading will be large net NO_3^- sinks at the watershed scale in spite of a lower nominal NO_3^- removal efficiency (Vidon and Hill, 2004b). Sites in this category are hot spots for N removal in the landscape owing to large amounts of annual NO_3^- removal. In other situations, nitrate-rich groundwater flowing in OC poor sand aquifers may bypass the riparian zone at depth and discharge directly to the stream, therefore creating a hot spot for NO_3^- transport to the stream (Bohlke and Denver, 1995; Puckett, 2004).

Some riparian zones are source areas of NO_3^- during short-lived hot moments of transport during or immediately following precipitation events. For instance, Vidon and Hill (2004b) report that NO_3^- removal in a riparian zone in southern Ontario dropped from >90 to 60% as the water table rose and groundwater fluxes exponentially increased for several days after a storm. Similarly, NO_3^--rich overland flow during a storm bypassed a riparian zone underlain with clay soil in an agricultural landscape of the Willamette Valley of Oregon, (Wigington *et al.*, 2003). In this case, although denitrification rates were potentially high in this riparian zone, runoff episodes during precipitation events were hot moments for NO_3^- transport. While vegetation uptake may be negligible during winter, mineralization and nitrification may continue in surficial riparian soils in many riparian zones where a snowpack develops, such as in montaine regions (Brooks *et al.*, 1998). Accumulated NO_3^- in these regions may then be flushed during snowmelt resulting in large NO_3^- exports from the riparian zone during this transport hot moment (Creed *et al.*, 1996). In an upland forested catchment of Vermont where stream NO_3^- concentrations are typically low, high stream NO_3^- concentrations during snowmelt occurred during a hot moment of hydrological transport when unaltered atmospherically deposited NO_3^- was transported over saturated riparian soils to the stream (Sebestyen *et al.*, 2008). As streamflow increased during a winter flood in Mattawoman Creek in Maryland, Noe and Hupp (2007) measured higher stream NO_3^- concentrations downstream relative to headwaters in this mixed land use watershed (forested, agriculture, and some urbanization). This hot transport moment was attributed to cold water temperatures (1°C), frozen soils that

reduced infiltration rates, and little biogeochemical processing of NO_3^- that was flushed to streams from the lower reaches of the catchment.

Riparian areas in urban landscapes often have large fractions of impervious surface area, rapidly route water to drainage streams during storm flow, have little woody debris, and have soils that are disconnected from streams due to channel incision (Paul and Meyer, 2001). For these reasons, urban biogeochemical cycles evolve through time as riparian soils become hydrologically disconnected from subsurface flow paths and less water is exchanged with streams. In the Baltimore Ecosystem Study, urban and suburban riparian zones had larger NO_3^- pools, higher nitrification rates, and lower denitrification potentials than rural sites (Groffman et al., 2003). Due to the altered riparian N cycle, hot spots and moments of transport in urban riparian areas have pronounced effects on sources, forms, concentrations, and loadings of stream N. For example, Burns et al. (2009) found that a suburban stream near Albany, New York transported a greater proportion of direct atmospherically deposited NO_3^- to the stream than occurred in nearby streams in agricultural or forested watersheds. Silva et al. (2002) found a similar pattern of large inputs of unprocessed atmospheric nitrate transported directly to urban streams in Austin, Texas during storm flow. In both cases, these direct inputs of atmospheric NO_3^- were flushed from impervious surfaces and rapidly routed to the urban stream.

Phosphorus Transport

Transport hot moments and hot spots are critical to P dynamics in riparian zones. For instance, P (both dissolved and particulate) transport via overland flow occurs during storm flow (hot moments of P transport) that cumulatively account for a majority of annual or seasonal P exports in agricultural settings (Peterjohn and Correll, 1984; Cooke, 1988; Heathwaite and Johnes, 1996; McDowell et al., 2001; Ulén, 2003; Biggs et al., 2006; Väänänen et al., 2006). Overland flow can also be the primary vector for nutrient (including P) transport through riparian zones in many arid and semiarid environments (Jacobs et al., 2007). Concentrated overland flow can pass through riparian buffers with minimal attenuation of nutrient and sediment concentrations, and these pulses represent a hot moment of P transport (Ritter and Shirmohammadi, 2000).

Phosphorus leaching via subsurface flow is generally considered to be lower in magnitude than fluxes from overland flow. However, event-driven dissolved P fluxes in the subsurface can be significant and may even dominate seasonal and annual fluxes of P to surface waters in some agricultural settings (Grant et al., 1996; Krovang et al., 1997; McDowell et al., 2001; Chapman et al., 2005; Scanlon et al., 2005; McKergow et al., 2006; Brazier et al., 2007). These settings typically correspond to sites where coarse-grained soils and shallow confining layers are present, where soils are artificially drained, or where preferential flow through fractures and macropores occurs.

Instream processes can also contribute to hot moments of downstream P transport during episodic high flow conditions (Svendsen et al., 1995; Krovang et al., 1997). The high P fluxes during these hot moments can include terrestrial runoff; however, P exchanges in stream channels may be locally important (Svendsen et al., 1995; Bowes and House, 2001). A net increase in particulate P concentrations in fluvial systems during high flow events, in part caused by the mobilization and export of P-rich bed material, has also been reported in several studies (Dorioz et al., 1998; Bowes and House, 2001; Stutter et al., 2008). Additionally, bank erosion may contribute significantly to suspended P load. Eroded materials may scavenge or release P into solution depending upon P content and mineralogy (Svendsen et al., 1995; Krovang et al., 1997; Russell et al., 1998; Laubel et al., 2003; Stutter et al., 2008).

Carbon and Organic Matter Transport

Storm events are hot moments of transport for DOM. In some upland catchments, stream DOM concentrations increase during storm flow when DOM is hydrologically flushed from forest soils (Boyer et al., 1997). Inamdar et al. (2006) reported that 36% of the annual DOC export from a forested watershed in western New York occurred during storm flow (24% of annual streamflow). Alternating wetting and drying cycles that stimulate OM mineralization and intense summer rainfall events may generate the highest concentrations of stream DOM during hot moments of transport (Inamdar et al., 2006). Leaf litter input during the fall also contributes to high autumnal DOM concentrations during base flow (Meyer et al., 1998) and storm flow (Sebestyen et al., 2009). Hinton et al. (1998) found that 41 to 57% of the total autumn DOC loading was exported from Precambrian shield catchments (Ontario) during transport hot moments, in this instance defined as the highest 10% of the stream discharge. The largest loadings of stream DOM in seasonally snow-covered catchments typically occur during spring snowmelt when catchment wetness is highest and DOM is leached from leaf litter and soluble OM (Inamdar et al., 2006). Between 1992 and 2003, 9 to 48% of the annual stream DOC loading occurred

during the largest single storm flow event (typically snowmelt) at the Sleepers River Research watershed in Vermont (Sebestyen *et al.*, 2009). However, storm events are not always hot moments of DOM transport through riparian zones. For instance, the opposite response (i.e., dilution) has been observed in wetland-dominated catchments where stream DOM concentrations decrease during storm flow when DOM-rich waters from wetlands mix with more dilute waters from other sources such as precipitation and groundwater (Bishop and Pettersson, 1996; Ågren *et al.*, 2007).

Variations in stream DOM concentrations are often directly related to hydrological flow path routing through riparian soils (Bishop *et al.*, 1995; Katsuyama and Ohte, 2002; Sebestyen *et al.*, 2008). Several studies have identified riparian sources of DOM that contribute to peak inputs of DOM during storm flow (McGlynn and McDonnell, 2003; Inamdar *et al.*, 2004; Sebestyen *et al.*, 2008). Streams draining riparian soils may episodically acidify when organic acids are flushed during hot moments of transport (Bishop *et al.*, 1990; Buffam *et al.*, 2007).

Changes in stream DOM composition may also occur during hot moments of transport. During long-duration snowmelt events at a forested watershed in northeastern Vermont, the low observed DOC:DON ratio early in the melt suggested that riparian sources contributed most DOM to the stream from leaching of soil OM during the initial pulse of the melt (Sebestyen *et al.*, 2008). As surface saturation increased later during the melt and surficial soils on hillslopes became hydrologically connected to the stream, DOC:DON increased, suggesting that stream DOM during late snowmelt was leached from leaf litter on hillslopes (Sebestyen *et al.*, 2008).

Pesticides

Because pesticides are applied to the surface of soils, most pesticide losses to streams via runoff occur with overland flow during precipitation events, and these losses can be periodic and related to the timing of application. For instance, Shipitalo and Owens (2006) showed that herbicide transport for seven small watersheds (0.45-0.79 ha) in Ohio was dominated by hot moments of pesticide transport in precipitation driven overland flow. Out of a total of 1,800 storm events monitored, 60 to 99% of herbicide loss was due to the five largest transport events during the nine-year study period. The impact of such intense export events on riparian zone function and on the ability of riparian zones to retain and degrade herbicides in overland flow is unknown, but herbicides may simply bypass riparian zones during

such intense events. Many studies also suggest that pesticide mobility often quickly decreases with time (Benoît *et al.*, 1999, 2000) and that most pesticide transport generally occurs in the days or weeks following application (Field *et al.*, 2003; Shipitalo and Owens, 2006). For instance, most herbicide (atrazine and alachlor) transport in a Georgia riparian zone occurred during storm flow within the two months following herbicide application (Lowrance *et al.*, 1997b). Although input concentrations averaged over 30 μg⁄l, outputs to the stream were less than 1 μg⁄l during these events (Lowrance *et al.*, 1997b). Transport of pesticides during storms soon after initial application may therefore be considered as a hot moment. The extent to which overland flow episodes constitute hot moments of pesticide transport in riparian zones depends on the ability of the riparian zone to reduce overland flow through infiltration. Other important factors to consider include the ability of pesticides to adsorb to organic soils and the type of surface vegetation present in the riparian zone. Although overland flow is often the primary transport pathway to streams for pesticides, areas of groundwater seepage to streams may constitute a hot spot for pesticide transport to streams in some riparian settings (Puckett and Hughes, 2005). Beyond the few studies mentioned above, little detailed information (especially when compared with N and P) is available on pesticide transport in riparian zones. We suggest that further research to identify differences in pesticide transport based on hydrophilic or hydrophobic composition and compound-specific degradation pathways (labile *vs.* refractory) is needed.

Mercury

The hydrological connectivity of wetland and riparian hotspots affects stream loadings of total Hg and MeHg (Bishop *et al.*, 1995; Shanley *et al.*, 2008). The transport of dissolved Hg to surface waters is closely associated with DOC transport, and hot spots and moments of Hg transport through riparian zones and wetlands are important in the annual watershed Hg budgets (Shanley *et al.*, 2008). A general tendency for Hg concentrations to increase during storm flow has been noted in several studies (Allan and Heyes, 1998; Allan *et al.*, 2001; Shanley *et al.*, 2005, 2008). Where dissolved forms of Hg are more prevalent, these increases seem to be largely controlled by the transport of DOC in waters (Kolka *et al.*, 1999). Elsewhere, high Hg concentrations and stream loadings occur during storm flow when particulate OM and suspended sediment concentrations are high (Shanley *et al.*, 2008). The relationship to flow is usually stronger for total Hg than for MeHg in part because total

Hg concentration and flux increases are disproportionately high relative to those of MeHg (Shanley *et al.*, 2005). In some cases, researchers have reported inverse relationships between streamflow and MeHg concentrations because high concentration waters from wetlands were diluted with storm flow inputs from upland source areas that have lower MeHg concentrations (Bishop *et al.*, 1995; Branfireun and Roulet, 2002).

Although MeHg concentrations often increase with flow as dissolved and particulate OC concentrations increase, there is typically a strong seasonal component to MeHg production and availability. In particular, a supply limitation is often present during the cold season when soil and sediment methylation rates are low. Consequently, MeHg concentrations often decrease during high flow periods such as snowmelt. In contrast, MeHg concentrations often increase with discharge during warm weather storms when methylation rates are high (Babiarz *et al.*, 1998). As a result of greater seasonality of MeHg fluxes relative to total Hg fluxes, hot moments of Hg transport generally reflect a greater dominance by nonmethyl forms in the nongrowing season (Selvendiran *et al.*, 2008).

Data therefore suggest that most Hg transport through riparian systems happens during hydrologic events. However, most studies have focused on Hg concentration patterns in stream water, and not directly on Hg transport in riparian zones or wetlands. Consequently, little is known about the internal processes that regulate Hg transport through riparian zones and wetlands during hot moments of Hg transport and their cumulative effects at the watershed scale.

Importance of Biogeochemical and Transport Hot Spots/Moments in Riparian Zones

Overall, research findings indicate that the hot spot and hot moment concepts are relevant for both biogeochemical process-driven and transport-driven hot spots and moments which occur at many locations and times across the stream, riparian zone, and upland continuum (Figure 3). However, the occurrence of transport hot moments is better documented than the occurrence of transport hot spots, as few studies have focused on identifying points of
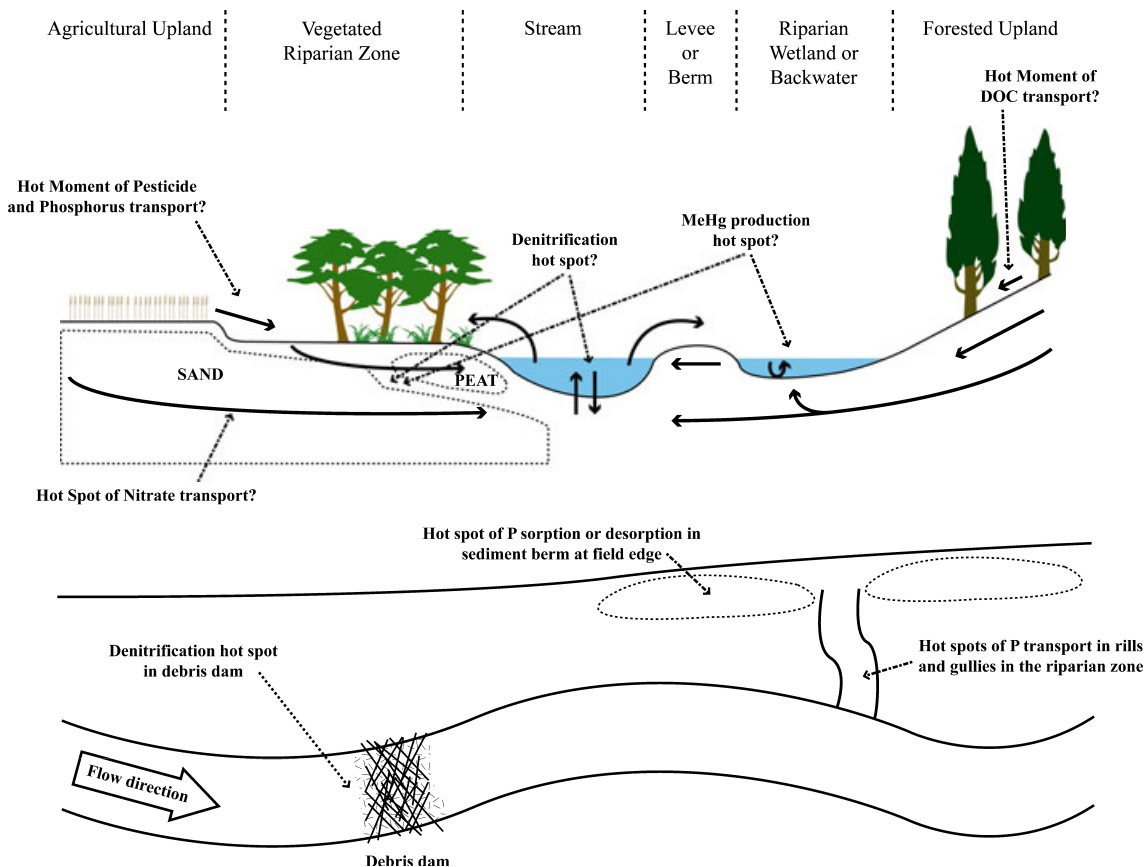

FIGURE 3. Example of Possible Hot and Cold Phenomena Across the Upland-Riparian-Stream Continuum in Both Agricultural and Forested Landscapes.

particularly high contaminant discharge to streams across riparian zones (Bohlke and Denver, 1995; Puckett, 2004). During transport-driven hot moments (e.g., some snowmelt and some storm events), large fluxes of solutes and particulates are transported to, through, and from riparian zones. Large fractions, commonly exceeding 50%, of annual stream loadings occur during hot moments of transport. Inundation frequency, antecedent moisture conditions, and physical factors such as soil hydraulic conductivity and slope must be considered in tandem with the rates of biogeochemical processes to determine whether a given part of the landscape or a certain time of the year will be a hot spot or hot moment for the transformation or transport of chemical constituents such as N, P, Hg, and pesticides.

Riparian areas with fine soil texture and low soil infiltration capacity are more likely to be hot spots for transport of contaminants that tend to be concentrated in overland flow during runoff events (e.g., pesticides, particulate P, and particulate OM). Riparian sites in this category may be biogeochemical hot spots for the transformation of some contaminants such as N (high OM) commonly found in subsurface flow. However, they may not be hot spots of N removal at the landscape scale owing to limited subsurface fluxes. Conversely, riparian soils with high hydraulic conductivity compared to the surrounding landscape and large solute inputs from upland source areas often are transport hot spots for subsurface contaminants such as NO_3^- and SRP.

INTERACTIONS AMONG MULTIPLE SOLUTES AND CONTAMINANTS

The occurrence of biogeochemical hot spots or moments is largely controlled by the relative abundance of electron donors and acceptors, soil redox conditions, hydrology, and the specific degradation/transformation of each potential contaminant. Consequently, an area in a riparian zone may be a hot spot for one chemical and not for another. To date, few researchers have simultaneously studied hot spots and moments for multiple chemical constituents in riparian or wetland environments. However, we feel that a better understanding of which suites of hot spots/hot moments are complementary or mutually exclusive in riparian zones would facilitate riparian zone management. Although not always the case (Alewell et al., 2008), riparian zones are sometimes dominated by a particular redox reaction (e.g., denitrification vs. sulfate reduction vs. methanogenesis).

For instance, Hedin et al. (1998) discussed thermodynamics constraints on redox-sensitive reactions and the theoretical sequence in which redox sensitive species are reduced. There are also many examples of Hg cycling coupled to other element cycles, especially OM and S. Hg transformations occur in anoxic riparian and wetland settings where abundant OM fuels microbial transformations. Because OM binds Hg (Grigal, 2002), total and methyl Hg fluxes are highly associated with both dissolved and particulate OM fluxes (Kolka et al., 1999). Sulfate availability and Hg cycling are also linked in many watersheds because SO_4^{2-}-reducing bacteria are the principal methylators of Hg (Morel et al., 1998). For instance, MeHg concentrations in groundwater and adjacent surface waters have increased after experimental SO_4^{2-} additions to wetlands (Branfireun et al., 1999; Jeremiason et al., 2006). Studies suggest that any alteration to a riparian area that causes either flooding (Hrabik and Watras, 2002) or even just a rise in the water table (Porvari et al., 2003) has the potential to create a hot moment of MeHg production by stimulating SO_4^{2-} reduction. Interestingly, an oversupply of SO_4^{2-} may limit methylation when excess sulfide accumulates and Hg shifts from neutral to less available charged complexes which decreases Hg diffusion and limits Hg that is available for methylating bacteria (Gilmour et al., 1998; Benoit et al., 2001).

Wet conditions that are typical of riparian and wetland areas may also support high rates of nitrification in surface soils if those remain well oxygenated (Ross, 2007). In such soils, nitrification may occur along surficial flow paths and denitrification at depth. The depths of these processes may vary seasonally with water table depth. Paradoxically, riparian soils may be both a source and sink of NO_3^- depending on flow path routing, the amount of flow along particular flow paths, and the depth of the water table. The amount of flow along different hydrologic pathways can significantly alter stream N loadings during storm flow depending on the amount of water that originates from either NO_3^--rich or NO_3^--poor source areas. Although conducive to the development of conditions favorable to denitrification, wet riparian areas may also be hot spots of P release and MeHg production. Many pesticides degrade most rapidly under aerobic conditions, in which case anoxic hot spots for NO_3^- removal may be areas where little pesticide removal occurs in the landscape. This is consistent with results reported by Pavel et al. (1999) who found that dicamba and metribuzin were not degraded rapidly in laboratory incubations of riparian soils under anaerobic conditions with NO_3^- added to stimulate denitrification.

Optimum conditions for the development of a biogeochemical hot spot/moment depend on the particular solute of interest, and there are many situations where a location in a riparian zone could be a hot spot for one chemical and a "cold spot" for another, such as in the previously mentioned denitrification and pesticide degradation example. At this time, our discussion is mostly speculative because researchers typically do not simultaneously study hot spots and moments for multiple chemical species in riparian or wetland environments. However, our literature review suggests that knowledge of the possible co-occurrence, if any, of hot spots and moments for a variety of contaminants in riparian systems may facilitate riparian zone management.

CHALLENGES FOR RIPARIAN ZONE MANAGEMENT

Management Practices

Recognition of the importance of biogeochemical and transport hot spots provides an opportunity to better manage riparian systems. To minimize contaminant inputs to receiving waters, efforts could be made to identify and manage hot spots for contaminant removal or riparian areas that are especially sensitive to change over both space and time. For instance, many studies indicate that NO_3^- removal typically occurs quickly within 20 m of the field and riparian zone margin (Hill, 1996; Dosskey, 2001; Vidon and Hill, 2006), suggesting that more surface area may be available for NO_3^- removal where riparian zones are wider than 20 m. Conversely, some riparian zones do not have the capacity to remove the high NO_3^- loads that occur during storms (Wigington et al., 2003; Vidon and Hill, 2004b). Other riparian zones are N sources following drought periods during which NO_3^- has accumulated near the soil surface owing to water table drawdown and the absence of hydrological flushing (Cirmo and McDonnell, 1997; Mitchell et al., 2006). The recognition of such hot spots of NO_3^- removal and hot moments of transport presents an opportunity to better inform management strategies for riparian zones. Targeting riparian zones with high or low potential for contaminant removal (e.g., NO_3^-) would also help to maintain or restore riparian zones that most effectively remove contaminants in watersheds where water quality is an issue.

While we do not advocate the manipulation of natural or near-pristine settings, riparian conditions in already managed or highly disturbed landscapes could be modified to create hot spots for pollutant removal or minimize hot moments of hydrological transport. Forms of riparian management include: (1) "denitrifying walls" which are strategically placed trenches that are filled with OM such as sawdust to intersect and treat NO_3^--rich groundwater (Schipper et al., 2005); (2) permeable reactive barriers to remove contaminants such as NO_3^- and trace metals from tile drains and subsurface flows (Blowes et al., 1994, 2000); and (3) vegetation buffers that take up NO_3^- and lower riparian water tables to minimize overland bypass flow (Lowrance, 1998; Yamada et al., 2007). Other riparian zone management techniques also have the potential to impact the development of hot spots for a variety of contaminants by manipulating either redox conditions or assimilation capacity. Biogeochemical processes in riparian zones may be managed by altering the availability of reactive OM through brush management, biomass harvesting, and wood chip application (Homyak et al., 2008). Soil grading either adds or removes OM to riparian soils and has the potential to affect the removal of a variety of contaminants in riparian hot spots. Similarly, the hydrological reconnection of stream channels to riparian soils may promote NO_3^- removal (Kaushal et al., 2008a), especially when riparian vegetation and hydrologic regimes are restored so that soils remain in place (Pinay et al., 1993). The introduction of small organic debris dams across streams may increase bank flooding and riparian soil saturation to create hot spots for nutrient transformations. In contrast, it may be beneficial to remove sediment berms that form at the upland edges of riparian zones, channelize flow, and allow a pulse (hot moment) of nutrients in concentrated surface runoff to bypass the riparian buffer. Drainage management or controlled drainage also has the potential to alter riparian zone hydrology in artificially drained landscapes and therefore to favor the development of hot spots for nutrient transformations (Dukes et al., 2003). Manipulation of water levels in regulated rivers and streams also has the potential to generate or alternatively reduce hot spot formation. Surface flow could be directed toward those riparian zones that have untapped potential for contaminant removal with level spreaders or grading. Riparian zones could be widened in human-dominated ecosystems where land is more available to manipulate, especially in agricultural and exurban areas, to accommodate high hydrologic loadings during storms. Vegetation planting also creates structure that detains sediments, promotes infiltration, and increases surface area and contact times. Stream fencing, along with tree planting, can also sometimes be an important strategy at the watershed scale to restore riparian zones in damaged landscapes. Identifying the location of riparian zones

susceptible to provide the most benefits to water quality per mile of stream restored could significantly help guide watershed management activities of this nature at the watershed scale. Developing innovative management practices that mimic the behavior of hot spots and/or take into account hot spot behavior for a variety of contaminants may increase the buffering or filtering potential of riparian zones to improve downstream water quality. Fully understanding the implications of stream and riparian zone management techniques for the development of hot spots of contaminant removal will be a critical area for future research.

Similarly, the recognition of the importance of hot moments for transport of N, P, Hg, and other contaminants offers a unique opportunity to focus watershed management efforts on the development of BMPs to mitigate contaminant pulses during storm flow. Riparian locations that are vulnerable to hot moments of contaminant transport need to be identified and better managed. A better understanding of the variables that control hot spots and moments of removal or transport for a wide variety of solutes in riparian systems will improve our ability to fully assess the risks and benefits associated with various riparian zone management strategies. Examples of strategies that have potential risks as well as benefits include the potential release of SRP and MeHg, potential increases in DOM to drinking water supplies, or potential increases in the production of CH_4 and nitrous oxide gases after implementing man-made strategies to enhance anoxic conditions aimed at increasing NO_3^- removal via denitrification in managed riparian zones.

A better understanding of the interaction of multiple contaminants and of the possible co-occurrence of hot phenomena for various contaminants is critical for the optimization of riparian management strategies to reduce contaminant concentrations, manage stream solute loadings, and prevent mobilization of contaminants. Table 1 is a summary of the phenomena and conditions necessary for the development of transport and biogeochemically driven hot spots and moments at the riparian zone scale for NO_3^-, P, OC, pesticides, and Hg. Although certainly not exhaustive, we provide this summary as a guide for identifying riparian zones likely to have the greatest effects on the fate and transport of specific contaminants (i.e., NO_3^-, P, pesticides, Hg) at the watershed scale.

Monitoring and Modeling

Watershed scale modelers are confronted with many challenges. Better monitoring strategies are needed to capture ephemeral hot moments and to accurately quantify the removal of contaminants in riparian zones. Hot moments of transport are temporally discreet and often occur during rare or occasional events such as drought, floods, or snowmelt that significantly affect stream solute loadings (Kaushal *et al.*, 2008b). Both transport-driven and process-driven hot phenomena should be considered simultaneously to develop accurate watershed-scale models and budgets. The inclusion of hot moments into watershed models requires the development of algorithms that better integrate a wide variety of fine spatial and temporal resolution data. Recent advances in the use of Light Detection and Ranging and other remotely sensed data will likely facilitate the development of improved models that more adequately represent the watershed scale effects of riparian hot phenomena.

Nevertheless, developing monitoring techniques to map the distribution of biogeochemical hot spots in riparian zones is likely to remain a particular concern in the future because other relevant fine-scale data that reflect physical and biological soil heterogeneity are not yet readily available (Groffman *et al.*, 2006). For example, data on locally high OM concentrations and sites where multiple reactants converge are not likely to become as widely available as remotely sensed weather and topographic data. Statistical approaches that quantify the probability of occurrence of hot spots in a given landscape based on a few detailed studies may provide a way to incorporate the effects of riparian hot spots into watershed scale models.

CONCLUSION

This review summarizes a growing number of studies that have investigated biogeochemical and transport hot spots or moments in riparian zones for a variety of water quality constituents (N, P, organic carbon, Hg, pesticides). Research indicates that the development of biogeochemical hot spots and/or moments in riparian systems is generally governed by subtle changes in electron acceptor and donor availability, redox conditions, and hydrological conditions. Although limited in space and duration, biogeochemical hot spots and moments have the ability to alter annual contaminant budgets at the scale of the riparian zone or even the whole watershed. Furthermore, we explicitly identify transport hot phenomena that may or may not co-occur with biogeochemical hot phenomena. Transport hot phenomena are also critical to developing accurate annual contaminant

TABLE 1. Phenomena (a) and Conditions (b) Favorable for the Development of Common Biogeochemical and Transport Process-Driven Hot Spots and Moments for Nitrogen (N), Phosphorus (P), Organic Matter (OM), Pesticides, and Mercury (Hg). These processes occur at the riparian zone scale and affect solute concentrations and fluxes at the spatial scale of streams or watersheds.

Constituent	Biogeochemical Process-Driven Hot Spot	Biogeochemical Process-Driven Hot Moment	Transport-Driven Hot Spot	Transport-Driven Hot Moment
N in the form of nitrate	(a) Denitrification (b) Continuous anaerobic conditions, high OM, high nitrate concentration, medium to large continuous water fluxes[1] (e.g., alluvium outwash interface)	(a) Denitrification (b) Ephemeral soil saturation, high OM, high nitrate concentration, ephemeral medium to large water fluxes (e.g., inundated riparian floodplain)	(a) Transport (b) High nitrate concentration and flux, low water residence time and high soil hydraulic conductivity relative to rest of riparian areas in watershed	(a) Transport (b) Ephemeral high nitrate concentration and high nitrate flux (overland flow or subsurface) owing to extreme event (storm, snowmelt)
P	(a) Desorption (b) High soil P content, reducing conditions ($E_h < -250$ mv), medium to large continuous water fluxes (e.g., some buried channel deposit)	(a) Desorption (b) High soil P content and ephemeral reducing conditions, medium to temporary high water table, and large water fluxes	(a) Transport (b) Upland P source and continuous overland flow (seeps) or preferential subsurface flow (e.g., toe slope seeps)	(a) Transport (b) Ephemeral P transport through riparian zone during extreme event (storm, snowmelt) via overland flow or preferential subsurface flow
OM	(a) Mineralization (b) Large soluble or decomposable OM pool, continuous moist conditions, aerobic conditions	(a) Mineralization (b) Ephemeral large OM input (e.g., leaf fall) and ephemeral moist and aerobic conditions (freeze/thaw cycle, wetting/drying cycle)	(a) Transport (b) High flux of water and reactive solutes through a large OM pool or high flux of POM/DOM from an area and high soil hydraulic conductivity relative to rest of riparian areas in watershed	(a) Transport (b) Ephemeral POM/DOM transport through riparian zone during extreme event (storm, snowmelt) via overland flow or preferential subsurface flow
Pesticides	(a) Degradation (b) Large OM pool, continuous moist conditions, aerobic conditions (e.g., root zones in unsaturated soils)	(a) Degradation (b) High OM, ephemeral pesticide input and ephemeral moist and aerobic conditions	(a) Transport (b) Continuous pesticide source and high soil hydraulic conductivity relative to rest of riparian areas in watershed	(a) Transport (b) Ephemeral pesticide input to riparian zone during extreme event (storm, snowmelt) via overland flow or preferential subsurface flow
Hg	(a) Methylation (b) High soil Hg, high OM, sulfate reducing bacteria, anoxic conditions, medium to large continuous water fluxes (e.g., groundwater discharge through peat)	(a) Methylation (b) High soil Hg, ephemeral soil saturated condition and anoxic conditions, and ephemeral medium to large water fluxes	(a) Transport (b) High soil Hg, high soil hydraulic conductivity and continuous large water fluxes relative to rest of riparian areas in watershed. Often associated with OM transport	(a) Transport (b) High soil Hg and ephemeral OC transport through riparian zone during extreme event (storm, snowmelt) via overland flow or preferential subsurface flow

Notes: DOM, dissolved organic matter; POM, particulate organic matter.
[1]As defined in Vidon, P. and A.R. Hill, 2004. Landscape Controls on the Hydrology of Stream Riparian Zones. Journal of Hydrology 292:210-228. Large: >300 l/day/m stream length; medium: 50-299 l/day/m stream length; small: <50 l/day/stream length.

budgets across the stream, riparian zone, and upland continuum. Often, transport hot moments are associated with episodic hydrological events that occur in response to rainfall or snowmelt. Transport hot spots generally occur in riparian zones where the water table is closer to the surface and/or where groundwater fluxes can be much higher and of longer seasonal duration than in the surrounding uplands.

The recognition of the importance of hot phenomena in annual watershed contaminant budgets is likely to lead to the development of a new generation of water quality models where spatial and temporal heterogeneity is better characterized. Recognizing the importance of biogeochemical and transport hot spots and moments also presents an opportunity to better manage riparian systems at the landscape scale

despite a unique set of challenges that include (1) the development of measurement techniques capable of capturing the ephemeral nature and unique locations of hot moments and spots and (2) the incorporation of hot phenomena into watershed scale solute export models. A critical research need for the future lies with deciphering and managing the co-occurrence of hot phenomena in riparian systems for a wide array of chemical compounds important to water quality.

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