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Hydrology and Methylmercury Availability in Coastal Plain Streams

Paul Bradley and Celeste Journey
U.S. Geological Survey,
USA

1. Introduction

The primary matrix of occurrence strongly influences the impacts of contaminants on environmental and human health. In groundwater and surface-water settings, water 1) dominates environmental transport and distribution, 2) influences contaminant reactivity, transformation and, by extension, toxicity, and 3) mediates direct and indirect exposure pathways. The role of hydrology in determining contaminant risk in groundwater and surface-water environments varies with contaminant type. Consequently, this chapter focuses on mercury (Hg), a widely distributed environmental pollutant, in order to illustrate the critical role that hydrology plays in determining contaminant risk. A comprehensive review of all of the mechanisms by which hydrology affects Hg risk is beyond the scope of this chapter. Rather, this chapter will discuss a few specific mechanisms that illustrate the critical link between hydrology and Hg risk in the environment.

1.1 Hg in the environment

Mercury occurs naturally in the environment, primarily in subsurface mineral deposits (Grigal, 2002, 2003; Pacyna et al., 2006; Selin, 2009; Swain et al., 2007). Although volcanic activity and volatilization from mineral outcrops can mobilize Hg to the surface atmosphere, the importance of Hg as an environmental contaminant increasingly is attributed to mining activities and subsequent anthropogenic releases to the surface biosphere. Historically, mercury has been mined from mercuriferous (cinnabar) belts in western North America, central Europe, and southern China. A notable example is the Almadén mine, in operation since Roman times (Selin, 2009). Annual releases of Hg to the surface atmosphere are estimated to be 5000-6600 Mg y^{-1} (Driscoll et al., 2007; Pacyna et al., 2006; Selin, 2009; Swain et al., 2007).

Direct use in a variety of applications, as a liquid metal or chemical constituent, has resulted in widespread environmental releases and, in some cases, heavily contaminated sites resulting from Hg point sources (Selin, 2009; Swain et al., 2007). Until recently, Hg was a common constituent of commercial products throughout the world. Recognition of the environmental and human health risks of Hg has prompted regulation and a shift toward Hg-free substitutes in many industrialized countries. However, even today, the extent of regulation and enforcement varies considerably "across jurisdictions and industrial sectors" (Selin, 2009; Swain et al., 2007). Countervailing environmental concerns over energy

conservation combined with a lack of cost-effective alternatives has continued the use of energy efficient Hg-vapour, fluorescent lighting. Thus, domestic exposures to harmful levels of Hg vapour resulting from breakage and/or improper disposal of fluorescent lamps remain significant concerns in industrialized countries, as does continued use of legacy, Hg thermometers. Direct exposure to high concentrations of Hg vapour is a particular concern in less industrialized areas where small-scale (artisanal) mining practice typically involves amalgamation of gold with Hg followed by heating to release Hg vapour and concentrate the gold (Selin, 2009; Swain et al., 2007).

Hg also is present in low concentrations in many natural materials, most notably in coal, oil, and minerals. The mining and use of low-Hg materials in large quantities, particularly combustion of fossil fuels, are primary pathways of Hg release and non-point source, environmental Hg contamination. Approximately 60% of the estimated annual global anthropogenic Hg release to the atmosphere is attributed to combustion of coal and other fossil fuels (Swain et al., 2007). Coal-fired power plants, waste incinerators (municipal and medical), chlor-alkalai facilities, and industrial boilers, contribute about 80% of anthropogenic emissions in the USA (Driscoll et al., 2007; Driscoll et al., 1998; EPRI, 1994; Seigneur et al., 2004). These on-going Hg emissions have resulted in regional and global atmospheric Hg reservoirs and widespread deposition to terrestrial and aquatic environments, albeit at generally low environmental concentrations (Selin, 2009; Swain et al., 2007).

1.2 Hg bioaccumulation and environmental risk

Atmospheric Hg deposition represents a substantial environmental threat even at low concentrations, due to the potential transformation to neurotoxic and highly bioaccumulative methylmercury (MeHg)(Bloom, 1992; Brumbaugh et al., 2001; Hall et al., 1997) by microorganisms indigenous to wetlands, lake sediments, and other saturated environments. MeHg bioconcentration factors in the order of 10^4 to 10^7 have been reported in aquatic food webs (Grigal, 2003; Rudd, 1995; Ullrich et al., 2001). Thus, in the USA, Canada and in many other industrialized nations, the primary risk of mercury (Hg) in the environment, including the risk to human health, is due to accumulation of Hg in aquatic biota (Environment Canada, 2011; Mergler et al., 2007; Selin, 2009; Swain et al., 2007; U.S. Environmental Protection Agency, 2009a).

MeHg contamination in fish is the leading cause of fish consumption advisories in the United States (U.S. Environmental Protection Agency, 2009a). A comparable percentage of the lakes (40% of total area) and streams (36% of total river distance) in the United States are Hg impaired (U.S. Environmental Protection Agency, 2009a). In 2008, the United States Environmental Protection Agency listed 3361 fish consumption advisories, affecting 50 states and covering more than 6.8×10^6 ha of lake and 2.1×10^6 km of river (U.S. Environmental Protection Agency, 2009a). Hg-driven fish consumption advisories, likewise, are common throughout Canada (Environment Canada, 2011). For this reason, identification of surface-water environments that are susceptible to bioaccumulation of Hg above accepted human and wildlife adverse impact thresholds and improved understanding of the key geochemical, hydrological, and biological characteristics that contribute to Hg vulnerability in the environment are global health priorities (Benoit et al., 2003; Mergler et al., 2007).

1.3 Purpose

A number of surface-water settings in North America are characterized by elevated levels of Hg bioaccumulation in fish (Bauch et al., 2009; Krabbenhoft et al., 1999; Scudder et al., 2009). Much of the current understanding of the factors contributing to elevated Hg bioaccumulation in aquatic habitats of North America is based on research conducted in the extensive peatland environments of Canada and in the organic-enriched surface waters of the northeastern USA, where Hg bioaccumulation in top predator fish and piscivorous bird species is well documented (Driscoll et al., 2007). Recent studies have demonstrated that Coastal Plain stream environments also are particularly prone to elevated Hg concentrations in fish and other indigenous aquatic communities (Bauch et al., 2009; Bradley et al., 2011; Bradley et al., 2010; Glover et al., 2010; Guentzel, 2009; Scudder et al., 2009), but considerably less is known about the specific ecological interactions contributing to elevated Hg bioaccumulation in this physiographic setting. However, recent research indicates that the elevated Hg risk associated with Coastal Plain streams is inextricably linked to the hydrologic characteristics of the Coastal Plain physiographic region.

The concentration of MeHg in fish tissues can be attributed to interactions between three conceptual components of the aquatic MeHg biocycle: 1) production and accumulation of MeHg, often in near-stream wetland environments, 2) transport of MeHg from source areas to the stream aquatic habitat, and 3) uptake by and trophic transfer in the aquatic foodweb (Figure 1)(Bradley et al., 2009). In this chapter, the general impact of hydrology on microbial production and in situ persistence of MeHg in saturated sediment environments is discussed with specific emphasis on characteristics relevant to the southeast region of the USA. The role of hydrology in the transport of MeHg from the site and matrix of production to the point of entry into the food web in Coastal Plain stream systems is illustrated by recent research in a paired basin study in South Carolina (Bradley et al., 2010; Bradley et al., 2009). Although water quality and quantity also affect the composition, trophic structure, and trophic transfer efficiency of indigenous communities, the role of hydrology in the uptake and accumulation of Hg in Coastal Plain aquatic food webs is beyond the scope of this chapter.

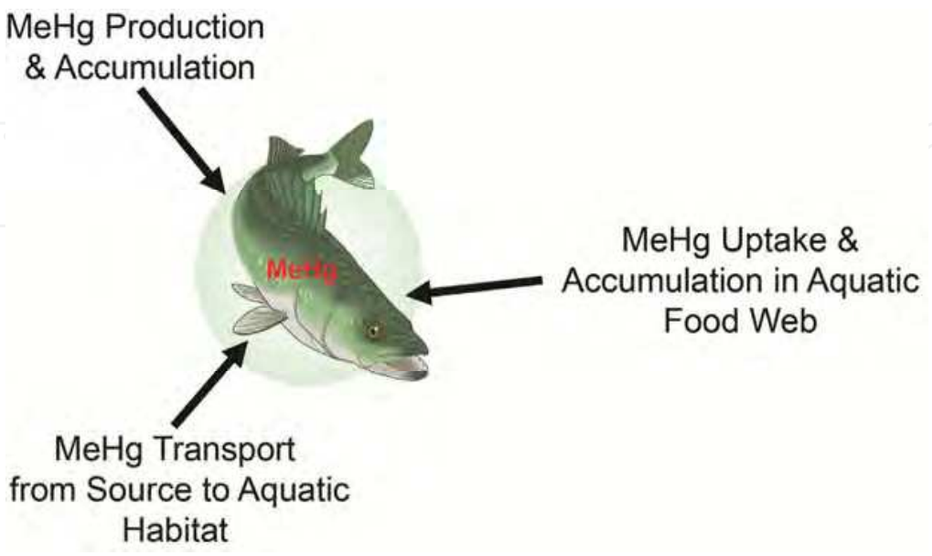

Fig. 1. Conceptual model of factors affecting Hg bioaccumulation in fish.

2. Hydrologic controls on methylmercury production

Hydrologic processes affect the production and accumulation of MeHg in the environment, in general, and in the Coastal Plain region of the USA, in specific, in a number of ways. In this section, two fundamental roles are presented as examples. The supply of Hg, primarily inorganic Hg, is a prerequisite to MeHg production and accumulation in saturated environments and hydrologic transport is critical to Hg supply to the landscape and to sites of active methylation. Likewise, the geochemical characteristics of saturated wetland sediments are conducive to microbial methylation of Hg and wetland environments are among the most important sources of MeHg in the environment.

2.1 Hydrologic controls on Hg supply to riparian wetlands

Wet deposition is a substantial pathway for transfer of atmospheric inorganic Hg to terrestrial and aquatic environments. Hg is emitted from natural sources primarily in elemental form (Hg(0)) and from anthropogenic sources as Hg(0), divalent Hg (Hg^{2+}), or particulate Hg (Hg(P))(Selin, 2009). The dominant form of Hg in the surface atmosphere is Hg(0), with mean concentrations estimated to be 1.6 ng m^{-3} (Selin, 2009). Delivery of Hg to terrestrial and aquatic surfaces occurs year round via wet and dry deposition on open areas and via throughfall (wash off of foliar Hg deposition during rainfall events). Mean concentrations of Hg^{2+} and Hg(P) in the surface atmosphere are estimated in the range of 1-100 pg m^{-3} (Selin, 2009). However, because Hg^{2+} and Hg(P) are more soluble in water, these are the primary forms of Hg deposited in wet and dry deposition and throughfall. Elevated atmospheric concentrations can occur regionally, downwind of major emission sources such as power facilities. Atmospheric Hg deposition can also occur on a more seasonal basis as litterfall following direct deposition (wet and dry) and/or direct uptake of gaseous Hg by plants (Selin, 2009).

The highest wet deposition rates in the USA occur in the southeast, with elevated rates also occurring in the midwest to northeast of the USA downwind of major North American industrial centers. Elevated Hg wet deposition in the midwest and northeast of the USA correspond to a region of high Hg emissions. The cause of elevated Hg wet deposition in the southeast is less clear, but may be related to scavenging of reactive Hg(0) from the higher altitude global pool by convective storm events during the summertime (Selin, 2009). The Mercury Deposition Network (MDN) in the USA routinely monitors wet deposition only. Dry deposition is not currently monitored systematically on a national scale. Thus, while it is clear that wet deposition processes, particularly throughfall (Grigal, 2002), are substantial sources of Hg to the landscape, the relative importance of the various mechanisms of Hg transfer from the atmosphere to the landscape is a matter of considerable uncertainty. In forested systems, substantially more Hg is deposited as throughfall than as dry or wet deposition in open areas (Grigal, 2002). In the southeastern USA, dry Hg deposition generally is estimated to be substantially lower than wet deposition (Brigham et al., 2009).

Terrestrial systems are an important indirect source of atmospheric Hg to aquatic systems via runoff (Lee et al., 1994; Lorey & Driscoll, 1999). On an area basis, terrestrial systems receive more atmospheric Hg from direct deposition, throughfall or litterfall than do freshwater aquatic systems (Grigal, 2002). Terrestrial landscapes are a significant environmental Hg reservoir, estimated to contain a mass of Hg many times greater than

the annual flux from the atmosphere (Gabriel & Williamson, 2004; Grigal, 2002; Mason et al., 1994).

Thus, hydrologic transport from the landscape to down-gradient wetland environments is a long-term control on Hg methylation in the environment (Gabriel & Williamson, 2004). The predominant form of Hg in terrestrial soils is Hg^{2+}. Although Hg^{2+} can bind to OH^-, and Cl^-, it is primarily associated with organic matter, specifically reduced S groups that are present in the environment in sufficient concentration to bind all Hg (Schuster, 1991; Skyllberg, 2008). Wet erosion and overland flow of particulate organic carbon (POC) is considered a major pathway of Hg transport from upslope to wetlands in steep and erosive systems with significant surface runoff (Balogh et al., 2000; Balogh et al., 1997, 1998; Grigal, 2002). This transport pathway appears to predominate in agricultural watersheds and is particularly sensitive to agricultural and land management practices (Balogh et al., 2000; Balogh et al., 1997, 1998). In contrast to agriculture-dominated watersheds, transport in the dissolved phase dominates in forested watersheds (Balogh et al., 1997, 1998; Hurley et al., 1995). Occurrence and down-gradient transport of Hg in groundwater is strongly related to the presence and mobility of dissolved organic carbon (DOC) and is expected to occur primarily in shallow groundwater flow paths (Grigal, 2002). Wet erosion and overland flow of POC are not expected to be primary Hg transport mechanisms in highly permeable low-gradient environments like the Coastal Plain of the USA (Bradley et al., 2010).

2.2 Hydrologic controls on Hg methylation

Most of the attention on environmental Hg pollution is focused on MeHg, a potent neurotoxin with reported bioconcentration factors on the order of 10^4 to 10^7 in aquatic food webs (Rudd, 1995; Ullrich et al., 2001). Previous studies have demonstrated microbial Hg methylation under Fe(III)-reducing and SO_4-reducing conditions, and Fe(III)-reducing and SO_4-reducing microorganisms are widely considered responsible for the bulk of Hg methylation in the environment (Compeau & Bartha, 1985; Gilmour & Henry, 1991; Gilmour et al., 1992; Grigal, 2003; Morel et al., 1998; Ullrich et al., 2001). MeHg production and accumulation are promoted under anaerobic conditions, whereas aerobic conditions support demethylation processes (Ullrich et al., 2001). The quantity and quality of DOC plays an important role in the bioavailability of Hg to methylating microorganisms and in the uptake and bioaccumulation of MeHg in the aquatic food web (Ravichandran, 2004).

Oxygen supply is limited in saturated sediments, because of the low solubility of oxygen in water and limitations on advective resupply in the sediment matrix. Aerobic microbial activity in environments with high bioavailable electron donor (organic carbon) can lead to rapid oxygen depletion and the onset of reducing conditions immediately following saturation. Extended experience in groundwater remediation has demonstrated the onset of substantial anaerobic activity at dissolved oxygen concentrations below 0.5 mg L^{-1} (Barcelona, 1994; Chapelle et al., 1995; Wiedemeier et al., 1998). Such conditions are routinely satisfied in wetland environments, particularly in peatland and organic rich bottomland floodplains, (Grigal, 2002, 2003) and wetlands are recognized areas of Hg methylation and elevated MeHg concentrations (Bradley et al., 2011; Bradley et al., 2010; Brigham et al., 2009; Grigal, 2002, 2003; Hurley et al., 1995; St. Louis et al., 1994a). Positive correlations between fish Hg burdens, dissolved MeHg concentrations, and basin wetland densities (Brigham et al., 2009; Chasar et al., 2009; Glover et al., 2010; Grigal, 2002; Guentzel,

2009; Hurley et al., 1995; St. Louis et al., 1994a) are widely reported, indicating that wetlands are the proximal source of MeHg in stream biota.

3. Hydrology and MeHg availability in Coastal Plain streams

In light of the demonstrated importance of wetlands as areas of substantial MeHg production and accumulation and as primary sources of MeHg to nearby lake and stream aquatic environments, transport of MeHg from wetlands to adjacent lake and stream aquatic habitats is a fundament control on environmental Hg bioaccumulation. Much of the current understanding of the controls on MeHg production, transport to primary aquatic habitats, and subsequent uptake and accumulation in aquatic foodwebs of lakes and streams in North America is based on research conducted in peatland, wetlands, and organic-rich surface-water environments of Canada and the northeastern USA. In contrast, comparatively little is known about the fundamental controls on Hg bioaccumulation in the Coastal Plain region of the southeastern USA, despite the recognized pattern of elevated fish Hg concentrations (Brumbaugh et al., 2001; Glover et al., 2010; Guentzel, 2009; Krabbenhoft et al., 1999; Scudder et al., 2009) in this geographically extensive physiographic region (Fenneman, 1928, 1938; Vigil, 2000). Consequently, the remainder of this chapter will focus on the role of hydrology as a control on MeHg availability in Coastal Plain stream settings. In the following subsections, the pattern of Hg bioaccumulation and the potential contribution of Coastal Plain hydrologic characteristics are discussed.

3.1 Hg bioaccumulation in Coastal Plain streams

In the summer and fall of 1998, the National Water Quality Assessment (NAWQA) and Toxics Substances Hydrology (Toxics) Programs of the U.S. Geological Survey (USGS) conducted a national pilot survey of Hg concentrations in the sediment and water (Krabbenhoft et al., 1999) and in axial muscle tissues of top predator fish (Brumbaugh et al., 2001) from 106 sites in 20 stream basins across the US. Among other findings, the results identified the Edisto River in South Carolina as having among the highest top predator fish Hg concentrations in the nation. Corresponding stream and sediment MeHg and total Hg concentrations also were among the highest reported in the USA, with the MeHg to total Hg ratios in the sediment and water of the Edisto basin being the highest observed in the study (Krabbenhoft et al., 1999). A follow-up assessment by the USGS assessed data from a total of 367 sites. This study included the data from the original 107 sites in the pilot survey, 159 stream sites from a second USGS national survey conducted in 2002 and 2004-5, and 101 stream sites from 4 USGS regional studies (Bauch et al., 2009; Scudder et al., 2009). While the highest Hg concentrations in fish were observed in gold or Hg-mined basins in the western USA, comparable concentrations were observed in unmined basins where atmospheric Hg was considered the primary source of Hg to the aquatic environment. The highest fish Hg concentrations in unmined basins were observed in “black-water” (high DOC) Coastal Plain streams in the eastern and southeastern USA (Bauch et al., 2009; Scudder et al., 2009)(Figure 2). While previous studies had demonstrated that elevated bioaccumulation of Hg is common in the organic-rich surface waters of the industrialized northeastern USA, these results indicated that stream habitats within the Coastal Plain physiographic region of the predominantly forested/agricultural southeastern USA also were among the most Hg vulnerable ecosystems in North America (Bauch et al., 2009; Brumbaugh et al., 2001; Krabbenhoft et al., 1999; Scudder et al., 2009).

Fig. 2. Spatial distribution of Hg (µg/g wet weight) in piscivorus game fish, 1998-2005 (modified from Scudder et al., 2009).

3.2 Coastal Plain geology and hydrologic implications

The Coastal Plain physiographic region of the southeast USA (Fenneman, 1928, 1938; Vigil, 2000) covers more than 1 million km², greater than the combined area of France, Germany, and the UK (Hupp, 2000). The Coastal Plain extends from New Jersey to eastern Texas and is primarily the result of alluvial (from adjacent mountain and Piedmont regions) and marine deposits of Late Cretaceous and Holocene age (Fenneman, 1928, 1938; Hupp, 2000; Vigil, 2000). The geomorphology of the modern Coastal Plain is largely due to fluvial processes during the last sea-level low stand (approximately 15,000 years ago) and to subsequent oceanic transgression (Hupp, 2000). Shallow surface sediments in the Coastal Plain primarily consist of deposits of quartz sand, glauconitic sand, silt, and clay. The predominantly coarse-grained sandy character of the Coastal Plain sediments favor efficient vertical recharge and generally low surface runoff (Atkins et al., 1996; Aucott, 1996).

Coastal Plain rivers of the southeastern USA are characteristically low-gradient meandering streams with generally broad floodplains, which are subject to extended and frequent flooding (Hupp, 2000). Coastal Plain stream systems typically exhibit two distinct hydrological seasons, low-flow season typically from June to October and high-flow season when extensive areas of floodplain may become inundated. Coastal Plain streams are often divided into two major types, according to the location of the stream headwaters and the associated geochemical characteristics of the stream water. Alluvial rivers originate in mountain or Piedmont uplands, often exhibit an abrupt reduction in gradient downstream of the Fall Line, and typically carry significant loads of mineral sediment. Alluvial streams are often further characterized as brown-water and red-water systems according to the coloration of the sediment load, with the latter deriving their characteristic red color from iron-oxide coated Piedmont sediment (Hupp, 2000). In contrast, black-water streams arise entirely or almost entirely on the Coastal Plain and typically have low gradients and low sediment loads. Extended leaching of tannins from organic-rich, riparian bottomlands and wetlands generates the characteristic colour and low pH of black-water Coastal Plain streams (Hupp, 2000).

3.3 Conceptual model of Coastal Plain hydrology and MeHg transport

Low topographic gradients and shallow water tables yield low-gradient stream systems with extensive riparian wetlands (Glover et al., 2010; Guentzel, 2009; Hupp, 2000) throughout the Coastal Plain. Characteristically coarse-grained sandy sediments favor efficient hydrologic transport within the shallow groundwater system and between connected groundwater and surface-water systems (Atkins et al., 1996; Aucott, 1996). Coastal Plain sediments generally exhibit efficient vertical recharge and low surface runoff (Atkins et al., 1996; Aucott, 1996), with discharge from the shallow flow system often representing 72-100% of the total groundwater discharge to Coastal Plain streams (Atkins et al., 1996). These characteristics support a conceptual model of Coastal Plain hydrodynamics, which has important implications for MeHg transport between wetland source areas and adjacent stream habitat under flood conditions.

3.3.1 Flood hydrology and MeHg transport in black-water Coastal Plain streams

In Coastal Plain stream reaches, the gradient and the direction of shallow groundwater flow is generally toward the stream channel, under normal to low-flow conditions (Figure 3A). Under these conditions, wetlands and channel margins are the primary areas of hydrologic exchange between groundwater and surface-water compartments. Surface-water connectivity between wetland areas and stream channel habitats often is restricted to small

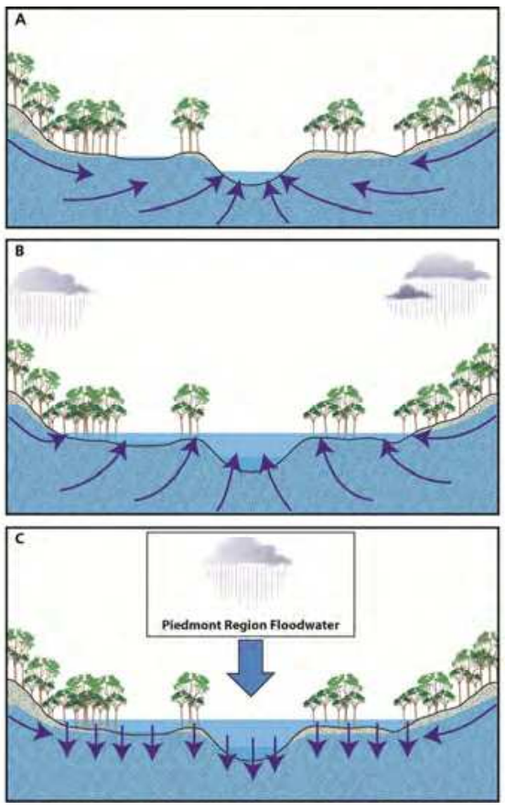

Fig. 3. Conceptual model of flood hydrodynamics in Coastal Plain rivers: (A) low to normal flow conditions, (B) flood conditions driven by Coastal Plain precipitation, and (C) flood conditions caused by downstream transport of Piedmont floodwater.

surface drainages. Rainfall occurring within the Coastal Plain is expected to recharge groundwater with little to no surface runoff, owing to the generally high permeability of the predominantly coarse-grained sandy Coastal Plain sediment. Consequently, high-flow events caused by Coastal Plain rainfall are expected to maintain the general pattern of groundwater flow toward the stream, with flooding predominated by rising groundwater and subsequent discharge across the surface of the riparian floodplain (Figure 3B). Under this scenario, advective transport of pore-water MeHg to the overlying water column and toward the stream channel habitat is enhanced by the increased hydraulic gradient and the expanded surface area for groundwater/surface-water exchange.

3.3.2 Flood hydrology and MeHg transport in alluvial Coastal Plain streams

For alluvial Coastal Plain rivers (i.e. rivers with contributing basins that extend upstream beyond the Coastal Plain), water column MeHg concentrations in Coastal Plain stream reaches are expected to reflect the contribution of upstream mountain and Piedmont drainages, which exhibit comparatively low wetlands coverage (generally less than 2%; (Glover et al., 2010; Guentzel, 2009; NLCD, 2001). The impact of this upstream MeHg signature is expected to be greatest at the upstream margin of the Coastal Plain region and to decrease with distance downstream.

Thus, flood events in Coastal Plain reaches of alluvial stream systems can result from two distinct hydrologic mechanisms, each with important and markedly different implications for MeHg transport to and availability in the adjacent stream aquatic habitat. Flooding events caused by rainfall within the Coastal Plain would be expected to follow the internal groundwater flood mechanism discussed above (Figure 3B) and efficiently transport wetland porewater MeHg toward the stream channel habitat even under flood conditions. In contrast, high-flow events caused by floodwaters from the upstream mountain and Piedmont regions may cause a reversal of the hydraulic gradient and infiltration of mountain and Piedmont floodwater into the shallow subsurface (Figure 3C). Net effects of a flow reversal might include dilution of porewater MeHg concentrations in the shallow subsurface, displacement and downward advection of sediment porewater MeHg, increased MeHg demethylation in the sediment porewater, and decreased transport of wetland sediment MeHg to the stream aquatic habitat. The availability of MeHg in the aquatic habitat of the Coastal Plain portion of such alluvial systems would be expected to reflect the relative importance of these alternative flood mechanisms.

4. Hydrology & MeHg availability: South Carolina Coastal Plain example

The results of the USGS national surveys identified a black-water Coastal Plain stream (Edisto River) in South Carolina as being among the highest in the USA with respect to bioaccumulation of Hg in the tissues of top predator fish. Elevated top predator fish Hg concentrations in South Carolina are not unique to the Edisto, however. Rather, fish Hg concentrations in excess of the criteria for wildlife and human health are common and the substantial variation in Hg bioaccumulation within the state provides an opportunity to better understand the primary controls on Hg bioaccumulation in different environmental settings.

4.1 Hg bioaccumulation in South Carolina Coastal Plain streams

Accumulations of Hg in excess of established guidelines for wildlife and human health are common in game fish as well as in a number of other top-predator and lower trophic level fish species in many streams in South Carolina. The South Carolina Department of Health and Environmental Control (SC DHEC) has established fish consumption advisories for Hg that affect approximately half of the state, primarily within the South Carolina Coastal Plain (DHEC). Figure 4A shows the mean Hg concentrations (µg/g wet weight) observed in *Micropterus salmoides* (largemouth bass) collected by SC DHEC during the period 2001-2007. The orange color indicates 8-digit Hydrologic Unit Code (HUC) basins for which mean largemouth bass Hg concentrations exceeded the 0.3 µg/g wet weight United States Environmental Protection Agency criterion for human health (U.S. Environmental Protection Agency, 2001, 2009b). These data reveal a strong spatial trend of increasing largemouth Hg concentrations along a gradient from Blue Ridge to Piedmont to Coastal Plain physiographic provinces (Bradley et al., 2010; Glover et al., 2010; Guentzel, 2009).

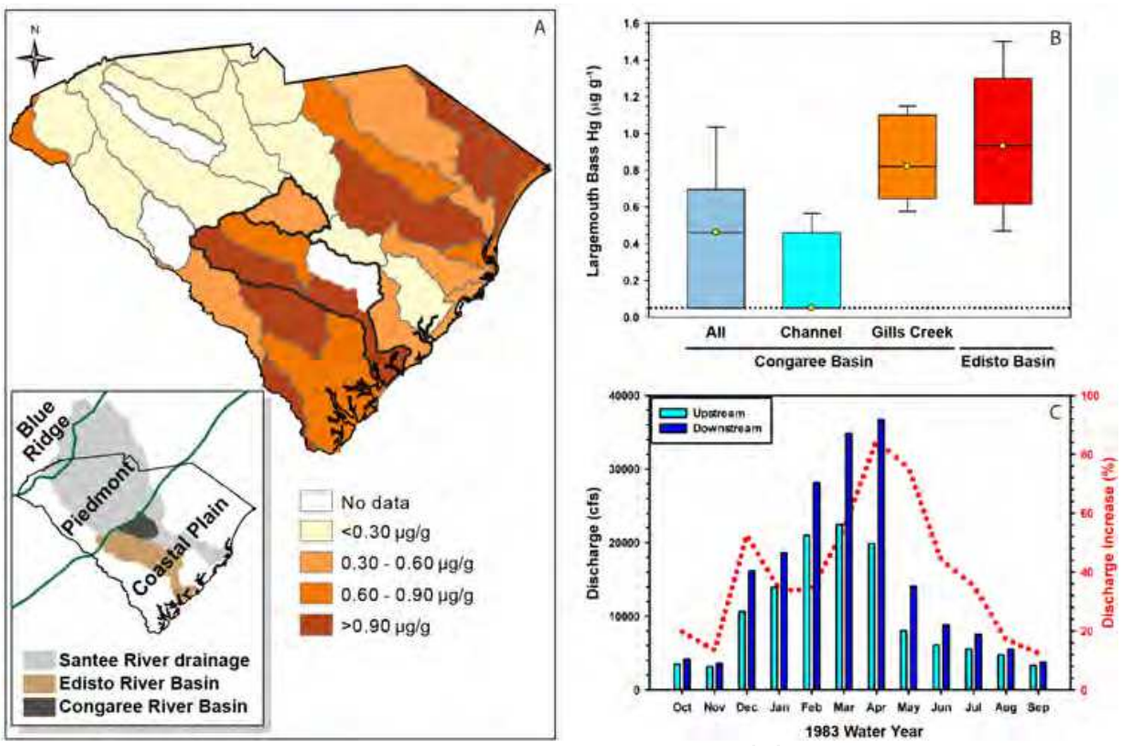

Fig. 4. (A) Mean Micropterus salmoides (largemouth bass) Hg concentrations (µg/g wet weight) in stream basins in South Carolina (SC DHEC). (B) Boxplots (median; interquartile range; 10th and 90th percentiles) of largemouth bass concentrations in Congaree and Edisto (SC DHEC). (C) Increase in discharge between upstream and downstream margin of Congaree in 1983 (USGS).

The pattern of increasing fish Hg burdens from mountains to Coastal Plain in South Carolina corresponds to a pattern of increasing wetland coverages (NLCD, 2001) from Blue Ridge (wetlands coverage: less than 1%) to Piedmont (wetlands coverage: 1-2 %) to Coastal Plain (wetlands coverage: 8-30%) physiographic regions (Guentzel, 2009). Strong

correlations between wetlands coverage, dissolved MeHg concentrations, and fish Hg burdens suggest that wetlands coverage is a useful indicator of MeHg source strength (Chasar et al., 2009; Glover et al., 2010; Guentzel, 2009; Scudder et al., 2009). The close correspondence between basin mean fish Hg concentrations and wetlands coverage observed in South Carolina is consistent with this interpretation and with the importance of the MeHg source term as a driver of Hg bioaccumulation in the Coastal Plain region.

4.2 Significant inter-basin variation in Hg bioaccumulation

Substantial variation in median fish Hg concentrations is observed within the Coastal Plain of South Carolina between adjacent stream basins (Figure 4A). The Edisto River and the adjacent Congaree River basins of South Carolina lie within the Coastal Plain physiographic region (Fenneman, 1928, 1938; Vigil, 2000); Figure 4A), which closely corresponds to the Middle Atlantic Coastal Plain and Southeastern Plains Level III Ecoregions (Griffith, 2002). Fish Hg burdens in the Edisto are systematically higher than in the Congaree basin or in the downstream portion of the Santee Basin (Figure 4B). South Carolina Department of Health and Environmental Control (SC DHEC) data for 2001-2007 (Glover et al., 2010; U.S. Environmental Protection Agency, 2010) indicate median concentrations of Hg are at least two times higher in *M. salmoides* from the Edisto River basin than in those collected throughout the Congaree River basin or from the Santee River basin locations downstream from the Congaree River (Figure 4B).

Because MeHg is the primary form of Hg in fish (Bloom, 1992; Rudd, 1995; Wiener & Spry, 1996), the concentration of Hg in fish tissues can be attributed to interactions between three conceptual components of the MeHg biocycle (Bradley et al., 2010; Bradley et al., 2009; Chasar et al., 2009): (1) microbial production and in situ persistence of MeHg; (2) transport of MeHg from the site and matrix of production to the base of the food web; and (3) efficiency of biotic uptake and trophic transfer of MeHg within the food web (Figure 1). An assessment of sediment throughout both basins revealed no statistically significant difference in concentrations of MeHg or net methylation potential in sediments collected from Edisto and Congaree locations (Bradley et al., 2009). Stream channels in both systems were characterized by coarse sands and net methylation potentials at least an order of magnitude lower than in sediments from adjacent wetland and riparian floodplain areas. Likewise, no difference in wetlands coverage is apparent between the Edisto (wetlands coverage: 20.4%) and the Congaree (wetlands coverage: 19.4 %) basins (Bradley et al., 2010; NLCD, 2001). Comparable riparian wetlands coverages (Table 1) and similar ranges of sediment Hg methylation potentials (Bradley et al., 2009) suggest that differences in Hg bioaccumulation between the two systems are not due to systematic differences in MeHg production in adjacent wetland and floodplain sediments.

4.3 Role of hydrology in inter-basin variation in Hg bioaccumulation

The Edisto is a black-water Coastal Plain stream basin, which falls entirely within the Coastal Plain. In contrast, the Congaree River is part of the Santee River drainage, an alluvial Coastal Plain system extending from the Atlantic Ocean to the Blue Ridge region of the Carolinas (Figure 4A). This fundamental difference in hydrology has important implications for the availability of MeHg for uptake/accumulation by the aquatic food web.

4.3.1 Wetland coverage in contributing basin

The Edisto stems from groundwater discharge and precipitation runoff occurring only within the Coastal Plain region and the mean wetlands coverage for the basin is 20.4% (Bradley et al., 2010; NLCD, 2001). In contrast, the contributing area for the Congaree River includes upstream Blue Ridge and Piedmont drainages. The wetlands coverage for the drainage area upstream of the Congaree is approximately 2% (NLCD, 2001), such that the combined wetlands coverage is about 3.5% for the entire drainage area contributing to flow at the downstream margin of the Congaree River (NLCD, 2001). Thus, the generally lower Hg concentrations in largemouth bass from the Congaree basin may reflect hydrologic and geochemical impacts of the Blue Ridge/Piedmont contribution (Bradley et al., 2010).

This hypothesis is supported by the substantially lower largemouth bass Hg concentrations observed in the Blue Ridge/Piedmont-influenced main channel of the Congaree compared to those concentrations in largemouth bass from the Gills Creek drainage (Figure 4B). During 2001-2007, SC DHEC collected largemouth bass (n = 40) from three locations (near the upstream margin, approximate mid-reach, and downstream margin) in the main channel of the Congaree River and the median Hg concentration was below the 0.05 µg/g (wet weight) detection limit. Largemouth bass also were collected (n = 20) from the headwater region of Gills Creek, a small Congaree tributary, which has a wetlands coverage of approximately 9% (NLCD, 2001) and which, like the Edisto River, lies entirely in the Coastal Plain. The median Hg concentration for these bass was 0.82 µg/g (wet weight), comparable to the median Hg concentration for bass from the Edisto River basin. These results indicate that, for Congaree basin black-water tributaries that lie entirely in the Coastal Plain, the hydrologic transport of MeHg from wetlands to the stream aquatic habitat and the extent of Hg bioaccumulation in the food web are comparable to that of the Edisto. However, the aquatic habitat within the Congaree River main channel primarily reflects the upstream Blue Ridge and Piedmont contributing drainage.

4.3.2 Source of water in Congaree basin

Owing to substantially lower wetlands coverages (generally less than 2 %), dissolved MeHg concentrations and the associated availability of MeHg in the aquatic habitat are expected to be low in the Saluda and Broad Rivers and, by extension, in the upstream reaches of the Congaree River (Chasar et al., 2009; Glover et al., 2010; Guentzel, 2009). Low dissolved MeHg concentrations measured in the Saluda, Broad and Congaree Rivers in 2009 (Bradley et al., 2010) are consistent with this expectation, as are the low largemouth bass Hg concentrations (median = 0.05 µg/g wet weight) observed in the Congaree main channel in 2001-2007 (Figure 4B) (U.S. Environmental Protection Agency, 2010).

However, surface-water discharge increases substantially within the Congaree basin, indicating that Coastal Plain water sources also are an important contributor to discharge at the downstream margin of the basin (Figure 4C). During 1982-1983, the USGS collected discharge data at a short-term gage station near the downstream margin of the Congaree River (station 02169740; (NWIS, 2010)). For this period of record, the increase in monthly mean stream discharge between the most upstream Congaree gage (station 02169500; (NWIS, 2010)) and gage 02169740 ranged from about 20% to more than 85%, with the greatest contribution from the Coastal Plain occurring during the hydroperiod (high-flow

season). The long-term record at the upstream location (02169500) indicates that discharge in the Congaree River in 1982-1983 was in the normal range, falling within the 50th to 75th percentile range for all observations. Based on these observations, a substantial fraction of the water at the downstream margin of the Congaree River originates within the Congaree basin. The consistently low largemouth bass Hg burdens observed in the downstream portions of the basin despite this substantial Coastal Plain contribution, the 20% wetlands coverage within the basin (NLCD, 2001), and the demonstrated potential for elevated Hg burdens in tributaries that fall entirely in the Coastal Plain (Figures 4A and 4B), suggests that the Blue Ridge/Piedmont-derived component of discharge inhibits MeHg transport from the wetland margins of the Congaree River to the stream aquatic habitat.

4.3.3 Fundamental differences in flood hydrology

Hydrologic connectivity between wetland MeHg source areas and adjacent aquatic habitats is recognized as a significant control on Hg bioaccumulation in aquatic and associated terrestrial communities (Krabbenhoft & Babiarz, 1992; Krabbenhoft et al., 1999; Rypel et al., 2008; St. Louis et al., 1994b; Stoor et al., 2006). In stream reaches dominated by riparian wetlands, flood conditions maximize hydrologic connectivity between the wetland margins and the stream aquatic habitat by maximizing the area for groundwater/surface-water exchange (Poff et al., 1997; Schuster et al., 2008; Ward et al., 2010). However, the direction of water and solute transport during flood conditions is dictated by the hydraulic gradient (Krabbenhoft & Babiarz, 1992). Thus, the observations of Krabbenhoft and others (Krabbenhoft & Babiarz, 1992; Stoor et al., 2006) suggest a mechanism by which the floodwater source may contribute fundamentally to the disparity in Hg bioaccumulation between Coastal Plain rivers like the Edisto and Congaree. The crucial hypothesis is that characteristic coarse-grained sediments favor high hydrologic connectivity throughout the Coastal Plain region, but essential differences in flood hydrodynamics determine the direction of water movement and thus the efficiency of dissolved MeHg transport between wetland MeHg source areas and the adjacent stream aquatic habitat. The validity of this hypothesis was assessed with stream channel and shallow groundwater level data from locations in the Edisto River basin and Congaree River basin(Bradley et al., 2010).

Figure 5A presents groundwater level changes in monitoring well transect ELB near the streamgage (02172305) in McTier Creek within the Edisto basin (Bradley et al., 2010). Observation wells 1-4 were located approximately 1, 3, 21 and 45 m, respectively, from the edge of the stream (Figure 5A; inset). Prior to flooding the gradient was approximately 0.3 m from the well nearest to the channel toward McTier Creek. Approximately 4 h after rainfall began, stream and groundwater levels began rising essentially simultaneously, indicating good hydrologic connectivity between the stream and inland groundwater locations. At the onset, peak, and end of flood conditions the groundwater gradient was upward, indicating discharge of groundwater from the sediment to the overlying water column at all well locations. Similar patterns were observed at other McTier Creek locations during multiple events (Bradley et al., 2010).

The Congaree River is periodically flooded by Blue Ridge/Piedmont-derived red-water (color due to iron-oxide coated piedmont sediment load) as shown in Figure 6B. Figure 6C shows Piedmont red-water from the Broad River drainage inundating the floodplain at the Congaree National Park. Water level data collected within the Congaree National Park

illustrate the strong downward hydraulic gradient that characterizes these Piedmont flood events. Prior to flooding, the gradient between well RIC-346 and Cedar Creek at station 02169672 was generally low (Figure 6A). Groundwater levels at RIC-346 were approximately 1.5 m below land surface at the onset of flood conditions and more than 2 m below flood water levels at the peak of flooding, demonstrating a dramatic downward gradient throughout. The rapid rise in groundwater level following the onset of flood conditions indicated vertical infiltration of floodwaters. This pattern was repeated a few days later (Figure 6A). Similar patterns were observed at other Congaree locations during multiple events.

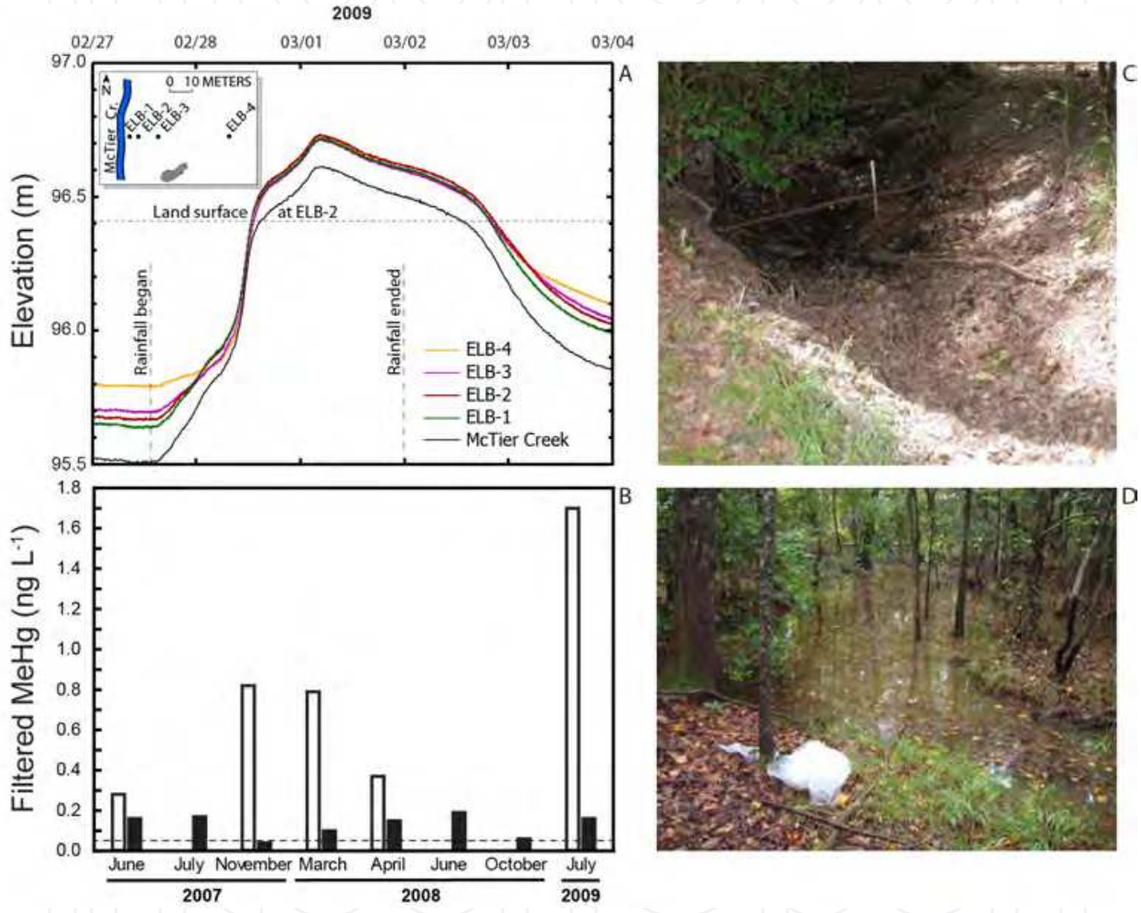

Figure 4. (A) Groundwater and surface-water levels during a flood in McTier Creek. (B) Filtered MeHg concentrations in floodplain depression (white) and in stream (black) at McTier Creek. Floodplain depression; (C) dry and (D) filled by rising groundwater.

4.4 Implications for MeHg availability in South Carolina Coastal Plain streams

The hydrologic pattern observed in the McTier Creek sub-basin of the Edisto River system indicates that in black-water Coastal Plain stream reaches groundwater continues to discharge from the shallow subsurface toward the stream channel aquatic habitat even during flood conditions. This type of hydrologic response favors transport of MeHg from the subsurface source area to the stream channel aquatic habitat. To illustrate, filtered MeHg

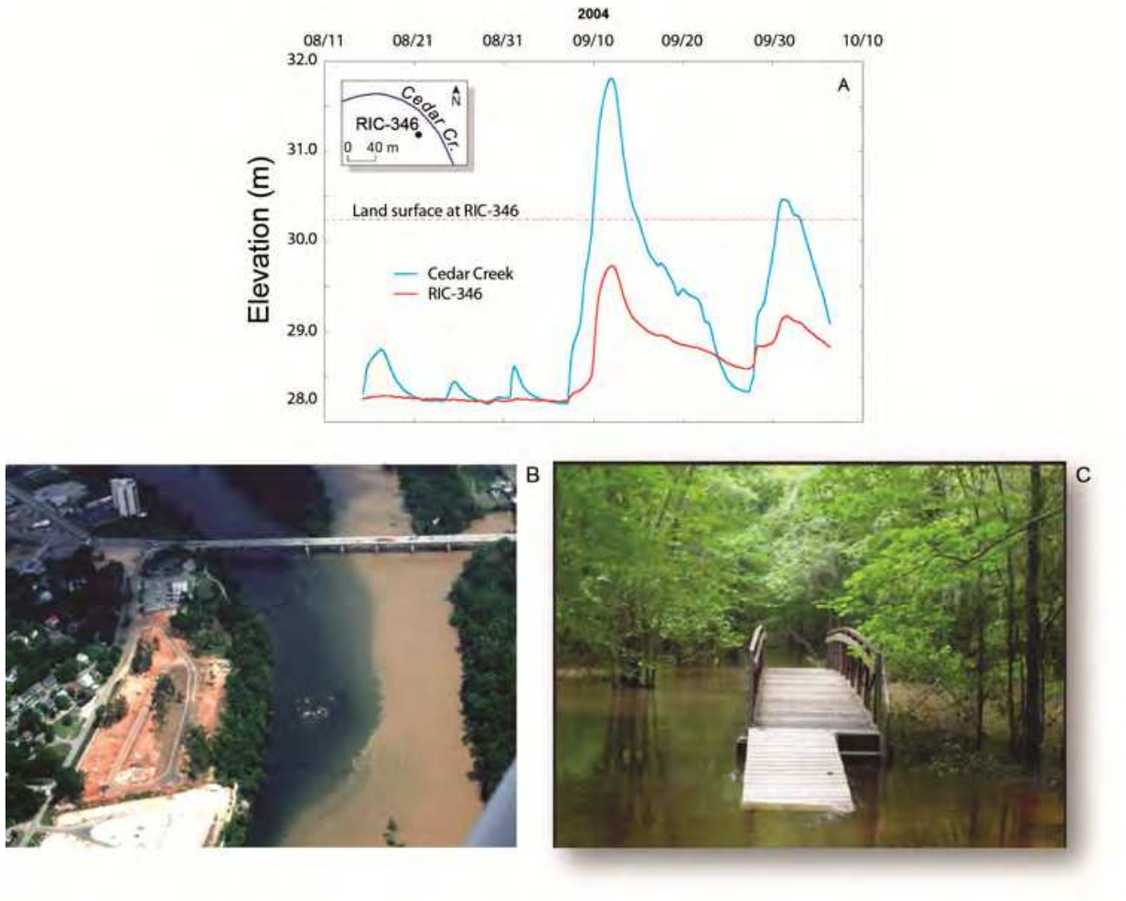

Fig. 5. (A) Groundwater and surface-water levels during a flood in Congaree National Park. (B) Confluence of Saluda River (upper left) and Broad River (upper right) forming the Congaree River. The Broad is shown under flood conditions. (C) Red-water Piedmont flood inundating Congaree National Park.

samples were collected from a shallow depression in the McTier Creek floodplain (Figures 5C and 5D). These floodplain depressions are inundated by rising groundwater before flooding creates an overland connection to the stream and provide an opportunity to assess MeHg in discharging groundwater prior to the mixing with stream-channel surface water that occurs during flood conditions. This floodplain depression was assessed eight times during 2007-2009 (Figure 5B). On the five occasions that standing water was present no overland connection to McTier Creek existed. In every instance the dissolved MeHg concentrations observed in the pool were greater than were measured in the adjacent stream channel, with concentrations ranging from approximately two times higher to greater than 10 times higher than in the stream channel (Bradley et al., 2010).

Samples collected from the floodplain depression in November 2007 provided particular insight into the MeHg signature associated with groundwater discharging through the floodplain land surface (Bradley et al., 2010). A localized rainfall event the day before sample collection resulted in rising groundwater and stream water levels. Discharging groundwater partially filled the previously dry depression but did not overtop the

floodplain. Dissolved oxygen concentrations, measured in the pool during MeHg sample collection in 2007-2009, ranged from 2-5 mg/L, indicating that redox conditions in the standing water did not favor Hg methylation. Thus, because the pool and the surrounding floodplain were dry less than 12 h prior to sample collection; the 0.8 ng L^{-1} dissolved MeHg concentration in the November 2007 riparian depression sample (compared with less than 0.05 ng L^{-1} dissolved MeHg concentrations in the stream) reflects the immediate transport of MeHg into the surface-water compartment. These results demonstrate that groundwater flooding in black-water Coastal Plain streams efficiently transfers MeHg from the floodplain sediment porewater to the surface-water compartment.

In contrast, flooding in alluvial Coastal Plain rivers, like the Congaree, that is caused by Piedmont-derived floodwater can decouple wetland MeHg transport to the stream aquatic habitat, preserving low dissolved MeHg concentrations and, consequently, decreasing MeHg availability for biotic uptake and accumulation in the main channel aquatic habitat. For example, dissolved MeHg concentrations observed in the Congaree flood in November 2009 were low, consistent with the comparatively low wetlands coverage of the upstream Blue Ridge/Piedmont drainages (Saluda and Broad River basin wetlands coverages are 2%; (NLCD, 2001) and indicating lower MeHg availability within the Congaree River channel aquatic habitat (Bradley et al., 2010).

4.5 Implications for MeHg bioaccumulation in Coastal Plain streams

These results illustrate that the coarse-grained sediment that characterizes much of the Coastal Plain physiographic region favors efficient exchange of water between streams, wetlands, and shallow groundwater systems. This hydrologic context suggests that black-water Coastal Plain streams, like the Edisto River, are particularly vulnerable to Hg bioaccumulation, because they lie entirely or largely within the Coastal Plain and are primarily subject to groundwater discharge-driven flooding. In contrast, alluvial Coastal Plain stream reaches, like the Congaree River, which experience groundwater-driven flooding as well as external floodwater events, are expected to exhibit reduced MeHg availability in the stream channel aquatic habitat, depending on the relative frequency of the two mechanisms.

The results of this study have regional-scale implications for Hg bioaccumulation, because the Coastal Plain physiographic region extends along the Atlantic and Gulf Coasts of the USA from New Jersey to Texas. The fundamental hydrologic characteristics of the South Carolina Coastal Plain are common in the Coastal Plain physiographic region and a similar relationship between flood dynamics and Hg bioaccumulation is expected throughout the region. The recent USGS national survey of Hg burdens in high trophic level piscivores (Scudder et al., 2009) indicated an elevated incidence of high Hg concentrations in top predator fish from stream reaches along the Atlantic and Gulf Coasts, which correspond closely to the Coastal Plain physiographic region. Thus, the hydrologic characteristics of the Coastal Plain region appear to contribute to an increased vulnerability to Hg bioaccumulation in Coastal Plain rivers.

5. Conclusions

The primary risk of mercury (Hg) in the environment, including the risk to human health, is due to accumulation of Hg in aquatic biota (Mergler et al., 2007) and is inextricably

linked to hydrology. Water provides habitat for aquatic biota, limits oxygen supply in saturated soil and sediment, and contributes to the onset of iron- and sulfate-reducing conditions, which support microbial production of toxic alkyl-mercury species (Benoit et al., 2003; Compeau & Bartha, 1985; Fleming et al., 2006). MeHg, in particular, is neurotoxic (Clarkson et al., 2003) and readily accumulated in aquatic foodwebs (Bloom, 1992; Brumbaugh et al., 2001; Hall et al., 1997). MeHg is the primary form of Hg in fish (Bloom, 1992) and wetlands are recognized MeHg source areas (Bradley et al., 2011; Bradley et al., 2009; Brigham et al., 2009; Grigal, 2003; Hall et al., 2008; Rypel et al., 2008; St. Louis et al., 1994b). Hydrologic transport of MeHg from sediment sources in riparian wetlands and floodplains to the stream channel is a fundamental control on the availability of MeHg in the stream aquatic habitat and, thus, on Hg bioaccumulation in the stream foodweb (Bradley et al., 2011; Rypel et al., 2008; Ward et al., 2010). The coarse-grained sandy sediment that characterizes much of the Coastal Plain from New Jersey to Texas in the USA favors efficient transport of MeHg from wetlands to the stream habitat (Atkins et al., 1996; Aucott, 1996; Bradley et al., 2010; Hupp, 2000). The hydrologic characteristics of the Coastal Plain region appear to contribute to an increased vulnerability to Hg bioaccumulation in Coastal Plain rivers (Bradley et al., 2011; Bradley et al., 2010).

6. References

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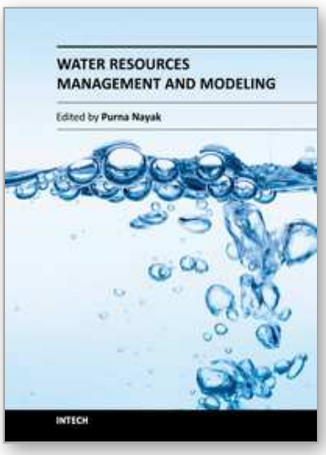

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Hydrology is the science that deals with the processes governing the depletion and replenishment of water resources of the earth's land areas. The purpose of this book is to put together recent developments on hydrology and water resources engineering. First section covers surface water modeling and second section deals with groundwater modeling. The aim of this book is to focus attention on the management of surface water and groundwater resources. Meeting the challenges and the impact of climate change on water resources is also discussed in the book. Most chapters give insights into the interpretation of field information, development of models, the use of computational models based on analytical and numerical techniques, assessment of model performance and the use of these models for predictive purposes. It is written for the practicing professionals and students, mathematical modelers, hydrogeologists and water resources specialists.

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
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Unit 405, Office Block, Hotel Equatorial Shanghai
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中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
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