Available online at www.sciencedirect.com
SCIENCE DIRECT®

Science of the Total Environment 368 (2006) 138–148

Science of the Total Environment
An International Journal for Scientific Research into the Environment and its Relationship with Humankind

www.elsevier.com/locate/scitotenv

Elevated methylmercury concentrations and loadings during flooding in Minnesota rivers

Steven J. Balogh [a,*], Edward B. Swain [b], Yabing H. Nollet [a]

[a] Metropolitan Council Environmental Services, 2400 Childs Road, St. Paul, MN 55106-6724, USA
[b] Minnesota Pollution Control Agency, 520 Lafayette Road, St. Paul, MN 55155-4194, USA

Received 29 October 2004; received in revised form 10 August 2005; accepted 12 September 2005
Available online 27 October 2005

Abstract

Previous studies have identified flooded landscapes (e.g., wetlands, impoundments) as sites of elevated methylmercury (MeHg) production. Here we report MeHg and total Hg (THg) concentrations and mass loadings in rivers in Minnesota during major flooding episodes in the summer of 2002. Frequent intense precipitation events throughout the summer resulted in extraordinarily wet conditions in east-central and northwestern Minnesota. Streamflow remained at record-setting high levels in many rivers and streams in these regions for several weeks. We observed high concentrations of MeHg (>1.4 ng/L) accompanied by high MeHg/THg ratios (0.39 to 0.50) in the Roseau River in northwestern Minnesota and in the Elk and Rum Rivers in east-central Minnesota. Very high MeHg mass loadings were observed in the Mississippi River just upstream of Minneapolis on July 17 (51 g MeHg/day) and July 23 (42 g MeHg/day), when MeHg concentrations at this site were 0.89 and 0.99 ng/L, respectively. The elevated MeHg concentrations in the Roseau River were associated with low dissolved oxygen and high dissolved reactive phosphorus concentrations, both of which are characteristic of anoxic waters. These rivers drain landscapes containing varying amounts of wetlands, and some of the MeHg discharged is thought to have been flushed from anoxic wetland soils. In addition, the flooding of vast areas of normally dry land surfaces probably also resulted in increased MeHg production, adding to the quantities of MeHg exported from these watersheds. Changing climate patterns are expected to result in more frequent heavy precipitation and flooding events in Minnesota. Our results suggest that as flooding and wet conditions in this region increase, the production of MeHg and its export from terrestrial areas to surface waters will increase also.

Keywords: Methylmercury; Mississippi; River; Flood; Minnesota

1. Introduction

Methylmercury (MeHg) bioaccumulates with increasing trophic level in aquatic food webs, presenting potential health effects for both larger fish and their predators. Atmospheric deposition and in-situ production may contribute some of the MeHg found in surface waters (Rudd, 1995), but source areas in the watershed are often more important. The flooding of terrestrial surfaces and the inundation of vegetation appear to be important facilitating processes in the production of MeHg in natural settings. Several studies have shown that natural wetlands are major sites of MeHg production (St. Louis et al., 1994; Hurley et al., 1995; Krabbenhoft et al., 1995; St. Louis et al., 1996; Branfireun et al., 1996; Babiarz et al., 1998; Galloway and Branfireun, 2004). Differing hydrological characteristics among a variety of wetland types were thought to

* Corresponding author. Tel.: +1 651 602 8367; fax: +1 651 602 8215.
E-mail address: steve.balogh@metc.state.mn.us (S.J. Balogh).

0048-9697/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.scitotenv.2005.09.045

explain differences in the amounts of MeHg exported from those wetlands (St. Louis et al., 1996), with higher MeHg production at sites of groundwater discharge (Krabbenhoft et al., 1995; Branfireun et al., 1996). Boreal wetlands appear to contain a large store of MeHg, and higher water yield from these areas yields higher MeHg mass export (St. Louis et al., 1996). Higher MeHg concentrations in the porewater of an experimentally impounded boreal peatland were attributed to higher net MeHg production associated with the decomposition of the flooded vegetation (Heyes et al., 2000). Increased MeHg production was also observed in the seasonally flooded soils of a tropical river floodplain (Roulet et al., 2001). Methylmercury concentrations in the litter and organic horizon of the flooded forest soils increased following inundation, and MeHg production was enhanced by the decomposition of fresh forest litter. Overall, watershed export of MeHg increases with increasing wetland area as a percentage of total watershed area (Grigal, 2002).

Most studies of flooded terrestrial systems have indicated that enhanced MeHg production is established relatively quickly following inundation. Water column MeHg concentrations increased in an experimentally flooded boreal wetland two weeks after impoundment (Kelly et al., 1997), while MeHg concentrations in zooplankton increased 10-fold within six weeks (Paterson et al., 1998). Elevated water column MeHg concentrations were observed in temporary flood-control impoundments in Minnesota within 10–15 days following inundation (Brigham et al., 2002).

The production of MeHg in wetland systems is biologically mediated. Sulfate reducing bacteria (SRB) are known to methylate Hg in aquatic systems (Compeau and Bartha, 1985; Gilmour and Henry, 1991; Gilmour et al., 1992), and SRB in anoxic zones of flooded areas may be responsible for increases in MeHg production. Heyes et al. (2000) found that sulfate addition to flooded peat samples in the laboratory resulted in higher MeHg concentrations in the porewater, and Porvari and Verta (1995) observed increased Hg methylation in inundated humus and peat samples under anoxic conditions. Experimental sulfate additions to a poor fen in Ontario resulted in increased MeHg concentrations in pore waters (Branfireun et al., 1999). Bacterial methylation of Hg in anoxic zones of flooded soils may be a major source of MeHg in the overlying waters.

Here we report MeHg and total Hg (THg) concentrations and loads in flooded river systems in Minnesota. Frequent and often intense precipitation throughout much of the summer of 2002 resulted in record discharge levels in several rivers in east-central and northwestern Minnesota. Wetlands constitute significant portions of the landscape in the affected watersheds, and the extreme amounts of precipitation resulted in sustained flooding of many lowland areas. We sought to characterize the effect of these extraordinary flooding and discharge events on MeHg concentrations and loads in these rivers.

2. Methods

2.1. Environmental setting

The Mississippi River above its confluence with the Minnesota River drains 51,500 km^2 in the central and north central portions of Minnesota, USA (Fig. 1). Land use in the southwestern portion of this “headwater Mississippi River” watershed is largely given over to agriculture, but much of the northern and eastern sections of the basin are covered in pine forest or wetlands (Balogh et al., 1998). The prevailing climate across the watershed is subhumid continental, characterized by dry, cold winters and wet, warm summers. Unstable atmospheric conditions result in frequent and sometimes severe thunderstorms during the summer months. Mean annual precipitation ranges from 62 to 81 cm with wetter conditions in the eastern portion of the basin (1971–2000; Minnesota State Climatology Office, 2003). We sampled the headwater Mississippi River at Anoka at river kilometer 1402, above the confluence of the Rum River, and above the Minneapolis/St. Paul (Twin Cities) metropolitan area (Fig. 1). The drainage area above this site is 49,475 km^2.

The Rum and Elk Rivers are tributaries of the headwater Mississippi River, draining areas just to the northwest of the Twin Cities metropolitan area (Fig. 1). The Rum River has a total drainage area of 4035 km^2 characterized by substantial areas of forest, wetlands, and open water (Table 1). Land use characteristics in the Elk River watershed (total area = 1588 km^2) show a greater percentage of land under cultivation and lower percentages of open water and wetland area relative to the Rum River basin (Table 1). Mean annual precipitation ranges from 69 cm in the western portion of the Elk River basin to 78 cm in the southeastern portion of the Rum River basin (1971–2000; Minnesota State Climatology Office, 2003). Our sampling sites on these rivers were located at USGS streamflow monitoring stations 05286000 (Rum River near St. Francis) and 05275000 (Elk River near Big Lake; Fig. 1). These sites are approximately 25 and 14 km, respectively, above the mouths of these two rivers. The drainage areas above these sites are 3522 and 1448 km^2, respectively.