Ecological Indicators 84 (2018) 648–661

Contents lists available at ScienceDirect

Ecological Indicators

journal homepage: www.elsevier.com/locate/ecolind

Original Article

Variation in fish mercury concentrations in streams of the Adirondack region, New York: A simplified screening approach using chemical metrics

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ARTICLE INFO

Keywords:
Mercury
Fish
Adirondack
Stream
Dissolved organic carbon
Brook trout

ABSTRACT

Simple screening approaches for the neurotoxicant methylmercury (MeHg) in aquatic ecosystems may be helpful in risk assessments of natural resources. We explored the development of such an approach in the Adirondack Mountains of New York, USA, a region with high levels of MeHg bioaccumulation. Thirty-six perennial streams broadly representative of 1st and 2nd order streams in the region were sampled during summer low flow and analyzed for several solutes and for Hg concentrations in fish. Several landscape and chemical metrics that are typically strongly related to MeHg concentrations in aquatic biota were explored for strength of association with fish Hg concentrations. Data analyses were based on site mean length-normalized and standardized Hg concentrations (assumed to be dominantly MeHg) in whole juvenile and adult Brook Trout *Salvelinus fontinalis*, Creek Chub *Semotilus atromaculatus*, Blacknose Dace *Rhinichthys atratulus*, and Central Mudminnow *Umbra limi*, as well as on multi-species z-scores. Surprisingly, none of the landscape metrics was related significantly to regional variation in fish Hg concentrations or to z-scores across the study streams. In contrast, several chemical metrics including dissolved organic carbon (DOC) concentrations, sulfate concentrations (SO_4^{2-}), pH, ultra-violet absorbance (UV_{254}), and specific ultra-violet absorbance were significantly related to regional variation in fish Hg concentrations. A cluster analysis based on DOC, SO_4^{2-}, and pH identified three distinct groups of streams: (1) high DOC, acidic streams, (2) moderate DOC, slightly acidic streams, and (3) low DOC circum-neutral streams with relatively high SO_4^{2-}. Preliminary analysis indicated no significant difference in fish Hg z-scores between the moderate and high DOC groups, so these were combined for further analysis. The resulting two groups showed strong differences ($p < 0.001$) in DOC and SO_4^{2-} concentrations as well as in pH and UV_{254} values. Median fish z-scores were significantly higher ($p = 0.002$) in the group of streams with higher DOC and UV_{254} and lower pH and SO_4^{2-}. Screening values of DOC > 6.9 mg/L, SO_4^{2-} < 2.8 mg/L, pH < 6.6, and UV_{254} > 0.31 cm^{-1} were tested as thresholds to identify Adirondack stream sites likely to have higher fish Hg concentrations. By applying a combined threshold of exceedance for either pH or UV_{254}, sites with fish Hg concentrations that exceeded a wildlife guideline of 100 ng/g were correctly identified about 75% of the time among the 36 study streams. An estimate of Hg risk applied to a data set of 391 streams based on DOC concentrations showed that about 28% were likely to pose high risk to wildlife; most of these streams were located in the western Adirondacks.

1. Introduction

Despite recent evidence that mercury (Hg) emissions have declined in North America and globally over the past two to three decades (Zhang et al., 2016), Hg contamination of aquatic ecosystems remains a widespread concern (Wiener, 2013). In landscapes with abundant fresh waters, Hg contamination poses neurological risks to: humans who consume fish (Mergler et al., 2007), piscivorous mammals and birds including the common loon (*Gavia immer*, Lazorchak et al., 2003; Evers et al., 2008), and the fish themselves (Sandheinrich and Wiener, 2011). Methylmercury (MeHg) is a potent neurotoxicant that bioaccumulates and biomagnifies in aquatic food webs, and is therefore, the Hg form that poses the greatest risk to humans and wildlife (Rice et al., 2014).

Geographically widespread Hg contamination of aquatic ecosystems has been described in many studies (Lavoie et al., 2013; Wang et al., 2013; Wathen et al., 2015). This contamination extends globally and results from emissions sources dominated by human activities including coal combustion, mining, and cement manufacturing, but also including

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http://dx.doi.org/10.1016/j.ecolind.2017.09.031
Received 30 March 2017; Received in revised form 15 September 2017; Accepted 17 September 2017
Available online 26 September 2017
1470-160X/ Published by Elsevier Ltd.

emissions from volcanoes and geothermal activity (Streets et al., 2011). Although atmospheric deposition is the dominant Hg source to most ecosystems where a geologic or local contaminant source is not evident, many other factors including landscape methylation potential, food chain length, and food web complexity are important determinants of Hg contamination of aquatic food webs (Chasar et al., 2009; Lavoie et al., 2013).

Models using multivariate statistical approaches have been applied to describe spatial variation in MeHg concentrations in aquatic biota and/or surface waters across scales that range from individual watersheds to entire regions (Roué-LeGall et al., 2005; Burns et al., 2012; Shanley et al., 2012). These models typically use several predictive variables to represent the effects of land cover, geomorphology, climate, and Hg deposition on the spatial variation of total Hg (THg) or MeHg concentrations in biota or surface waters. The effectiveness of these spatial models likely results from the ability of explanatory variables to reflect the factors and processes primarily responsible for spatial variation in methylation, transport, and (or) bioaccumulation of MeHg across landscapes. Similar spatial models based on chemical parameters such as DOC and pH (or acid-neutralizing capacity, ANC) have also proven effective at accounting for spatial variation in MeHg concentrations in surface waters and in aquatic biota in many regions (Håkanson, 1980; Wiener et al., 2006; Shanley et al., 2012). An advantage of spatial Hg models is their ability to provide estimates of the magnitude and extent of Hg contamination across a region including unsampled waters. Because of the extensive human and financial resources necessary to directly assess environmental Hg contamination, spatial predictive models using indirect measures have a long history of application in Hg research, policy, monitoring, and assessment (Håkanson, 1980; Roué-LeGall et al., 2005; Shanley et al., 2012).

The Adirondacks of New York State comprise a large mountainous region in the northeastern U.S. with abundant lakes, streams, and wetlands. The region is extensively forested with predominantly thin soils developed on glacial till that overlies resistant bedrock. These landscape characteristics result in high regional sensitivity to the effects of acidic atmospheric deposition and high risk of Hg bioaccumulation from atmospheric Hg deposition (Sullivan, 2015). As a result, hundreds of Adirondack streams and lakes are impaired by acidification (Lawrence et al., 2008; Sullivan et al., 2012; Fakhraei et al., 2014), and the region is also considered a "hot spot" of Hg bioaccumulation (Evers et al., 2007; Chen et al., 2012). These two sources of impairment are likely related because higher levels of Hg bioaccumulation are observed in surface waters with the lowest pH and ANC values (Yu et al., 2011).

In the U.S., states have the authority to establish guidelines for human exposure to environmental contaminants such as Hg, and issue advisories accordingly. Currently, all 50 U.S. states have advisories for at least one water body that recommend limiting fish consumption due to Hg contamination (US EPA, 2011). The number of these Hg advisories has generally increased with time largely due to the ubiquitous nature of Hg contamination, suggesting that the principal factor limiting these advisories is the number of waters sampled, often limited by a combination of time and available financial resources. Widespread Hg contamination throughout the Adirondacks has resulted in an advisory for women under 50 years of age and children under 15 years of age to refrain from eating 6 common fish species from all waters as well as specific fish consumption advisories for 65 water bodies (https://www.health.ny.gov/publications/2779.pdf, accessed 6/16/17). The effects of dietary Hg on piscivorous wildlife is also a widespread concern, and guidelines have been suggested for fish Hg concentrations above which harmful effects are expected for belted kingfisher (*Megaceryle alcyon*, 30 ng/g, Lazorchak et al., 2003), river otter (*Lontra canadensis*, 100 ng/g, Lazorchak et al., 2003), fish themselves (200 ng/g, Beckvar et al., 2005), and loon (*Gavia immer*, 3000 ng/g, Evers et al., 2008).

All current water body-specific fish consumption advisories in the Adirondacks apply to lakes, reflecting their importance as a natural resource, but also illustrating that streams and rivers are often overlooked in this region and other northern regions with abundant lakes (Scudder et al., 2009). Nevertheless, Hg concentrations in fish and other aquatic biota that feed at the same trophic levels are typically similar among lakes and streams in a given region (Kamman et al., 2005; Scudder et al., 2009), and some species have shown greater tissue concentrations in streams than in nearby lakes (Bank et al., 2005; Pennuto et al., 2005; Eagles-Smith et al., 2016). The strong historical focus on Hg studies (Lorey and Driscoll, 1999; Simonin et al., 2008; Yu et al., 2011), the high Hg levels observed in stream biota (Riva-Murray et al., 2011, 2013a), and the abundance of streams (~48,000 km; http://apa.ny.gov/About_Park/; accessed 7/11/2017) across the region indicate a need for further investigation of the spatial and temporal patterns of Hg in Adirondack streams and rivers. Recent studies of factors that control the spatial variation of Hg in stream water and biota in the upper Hudson River basin in the central Adirondack region have shown that combinations of variables based on land cover, geomorphology, and Hg-associated water chemistry are promising indicators of Hg variation in surface waters (Burns et al., 2012) and biota (Riva-Murray et al., 2011), and may have wider application across the Adirondack region and in other parts of eastern North America.

In the study reported here, we explore the ability of various GIS-derived landscape metrics and inexpensive and readily applied chemical metrics to account for the spatial variation in Hg concentrations in fish of Adirondack streams. Our aim is to help focus the resources of management agencies where higher levels of Hg in fish are expected and to improve understanding of the factors that affect fish Hg concentrations across this region and in other areas with similar climatic and landscape features. Our hope is to develop a screening approach to assist in identification of streams with high Hg sensitivity that can focus monitoring efforts for wildlife and human health and minimize extensive and expensive sampling of waters or biota for MeHg concentrations, as well as to focus fish collection efforts for future Hg monitoring.

2. Study area

The Adirondack region of northern New York State is commonly defined by the "blue line" boundary of the Adirondack State Park, an area of 24,280 km^2 (Fig. 1). The Adirondacks are predominantly forested by a mix of northern hardwoods and spruce – fir reflecting a classification in the Eastern forest – boreal transition ecoregion (Ricketts, 1999). The climate is humid continental with short, cool summers and long, cold winters (Driscoll et al., 1991). There is considerable regional climatic variation with latitude, longitude, and elevation reflected in distinct spatial patterns of precipitation, temperature, snowfall, and vegetation communities (Ollinger et al., 1993). The region includes more than 3000 lakes and 48,000 km of streams and rivers (http://apa.ny.gov/About_Park/, accessed 7/11/2017), and about 14% of the Park area consists of wetlands (LaPoint et al., 2004). The Adirondacks form a circular dome that rises 600–1600 m above adjacent lowland regions (Isachsen, 1975). Bedrock is dominantly Precambrian igneous and metamorphic (Isachsen, 1975) overlain by till and outwash deposits from glaciation that ended about 11,000 years ago (Cadwell and Muller, 2004). Therefore, regional soils are young and vary widely with well-drained acidic soils developed in till and outwash in steep upland areas, and poorly drained organic or mucky soils in riparian and wetland areas (Driscoll et al., 1991). Large parts of the region are wilderness or wild forest with little influence of human development except in towns and villages and along roadways.

3. Methods

3.1. Site selection

Thirty-six stream sites were selected for this study (Fig. 1). Twenty-nine of the 36 sites were selected for sampling from among 391 streams