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Climate Change and Cleaner Emissions Decrease Methylmercury Export from a Headwater Peatland Catchment

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Key Points:

- Lower annual streamwater methylmercury concentrations due to compounding effects of climate change and cleaner air

- Higher mean annual air temperature increases annual streamwater methylmercury

- Lower wet atmospheric mercury deposition and runoff ratio offset higher air temperatures, resulting in lower methylmermcury concentrations

21 **Abstract**

22 Peatlands are sources of the bioaccumulating neurotoxin methylmercury (MeHg) and linked to

23 adverse health outcomes, yet the impact of climate change and reductions in atmospheric

24 pollutants on mercury (Hg) export from peatlands are highly uncertain. Here, we present the

25 response in annual flow-weighted concentrations (FWC) and yields of total-Hg (THg) and MeHg

26 to cleaner air and climate change using an unprecedented hydroclimatic (55-years; streamflow,

27 air temperature, precipitation, regional and peatland water tables), depositional chemistry (21-

28 years; Hg and major ions concentration and total mass), and streamwater chemistry (~17-years;

29 THg, MeHg, major ions, total organic carbon, and pH) datasets from a reference peatland

30 catchment in the north central USA. Over the hydroclimatic record, annual mean air temperature

31 increased by ~1.8 °C, decreasing baseflow and, subsequently, the efficiency that precipitation

32 was converted to streamwater runoff (runoff ratio). Concurrently, precipitation-based deposition

33 of sulfate and Hg declined, where wet Hg deposition rates declined to near pre-industrial levels.

34 Annual MeHg FWC was positively correlated mean annual air temperatures (p=0.03, r=0.51),

35 annual runoff ratio (p<0.0001, r=0.76), and wet Hg deposition concentration (p<0.0001, r=0.79).

36 Over the study period, decreasing wet Hg deposition concentration and annual runoff ratios

37 counterbalanced increased peatland MeHg production due to higher air temperatures, leading to

38 an overall decline in streamwater MeHg FWC. Climate change and cleaner air were responsible

39 for 0.51 and 0.32 of the variability in MeHg FWC, respectively. Streamwater MeHg export may

40 continue to decrease only if declines in runoff ratio and wet Hg deposition concentration

41 persistently outpace increased air temperature.

42 **Plain Language Summary**

43 Climate change and cleaner air are unequivocally altering mercury cycling in a headwater stream

44 fed by a peatland-rich catchment. Using long-term and broad environmental measurements we

45   show that decreasing stream methylmercury is due to lower annual mean wet mercury deposition

46   concentration and annual runoff ratios, which offsets potential increases of methylmercury from

47   elevated mean annual air temperatures. As such, methylmercury export from headwater peatland

48   catchments will continue to decrease over time if climate change continues to accelerate the

49   reduction of runoff ratios and atmospheric wet mercury deposition further decreases. To better

50   adapt to future climate and environmental change, there is a need for more and longer integrated

51   multidisciplinary datasets. Without these long-term and integrated measures these critical

52   insights would not have been possible.

53

1 Introduction

Climate change is altering stream and river water chemistry (Li et al., 2022; Meyer-Jacob et al., 2019). In boreal and hemi-boreal catchments, wetlands, including peatlands, play a critical role in regulating water chemistry (Gorham et al., 1985; Lam et al., 2022; Schelker et al., 2014), particularly the contaminant mercury (Hg) (Kronberg et al., 2018; Lam et al., 2022; Mitchell et al., 2008b; Tjerngren et al., 2012a). Yet, other concurrent environmental disturbances potentially compound or mask changes in water chemistry from climate change (Li et al., 2021). Even in ecosystems that are assumed to be least impacted and that serve as reference sites, decreased atmospheric deposition of pollutants, such as sulfate (SO_4^{2-}) or Hg, with cleaner air legislation (Lee et al., 1998; Pannatier et al., 2011; Sickles II & Shadwick, 2015; Zhang et al., 2019) may mask or enhance effects of climate change on aqueous contaminants like Hg. Untangling relative effects of climate and environmental change in reference ecosystems is critical to inform science, management, and policy.

The bioaccumulating neurotoxin methylmercury (MeHg) is a contaminant of global concern linked to adverse human health conditions (O'Connor et al., 2019). Mercury mobilization, either as MeHg or total-Hg (THg), from uplands and wetlands to downstream water bodies is controlled by interacting hydrological and biogeochemical processes that affect both concentrations and fluxes (Bishop et al., 2020; Branfireun et al., 2020; McCarter et al., 2022b; O'Connor et al., 2019; Woerndle et al., 2018). Peatlands are often sources of MeHg to surface waters (Branfireun et al., 1998; Lam et al., 2022; Skyllberg et al., 2003; Woerndle et al., 2018). The net export of MeHg from peatlands to surface waters is a balance between Hg methylation and demethylation(Kronberg et al., 2018; Tjerngren et al., 2012b), MeHg solubility (Skyllberg, 2008), and the hydrological transport of Hg from a peatland to a stream (McCarter et

79   al., 2022b). In peatlands, wet atmospheric Hg deposition is usually lower than dry Hg deposition

80   but is often more readily available to resident microbial communities (Hsu-Kim et al., 2013),

81   likely resulting in quicker incorporation into the peatland Hg cycle. Elevated atmospheric SO_4^{2-}

82   deposition to peatlands has been linked to increased MeHg concentrations in receiving

83   streamwater (Jeremiason et al., 2006; McCarter et al., 2022b) but the effect is rapidly reversible

84   once SO_4^{2-} additions decline (Coleman Wasik et al., 2012; McCarter et al., 2017; McCarter et al.,

85   2022b). While both SO_4^{2-} and Hg deposition have decreased in response to clean air legislation,

86   climate change likely affects the ecohydrological and biogeochemical process that underpin Hg

87   cycling and export (Bishop et al., 2020; Yang et al., 2016). Model simulations of the effect of

88   climate change on Hg cycling are unclear due to large uncertainties associated with both climate

89   change and Hg biogeochemical processes (Golden et al., 2013), while *in-situ* experimental

90   warming of boreal peatlands have shown increases in both inorganic Hg and MeHg porewater

91   concentrations (Sun et al., 2023). However, few long-term empirical datasets exist to document

92   contemporary responses and trends, particularly at catchment scales. Correspondingly, the

93   response in Hg export from peatlands due to the long-term and interacting effects of climate

94   change and cleaner air is uncertain (Sonke et al., 2023), largely due to only a few select places

95   with sustained, routine Hg monitoring in streamwater in conjunction with relevant environmental

96   data collection.

97

98   We present an unprecedented 17-year record of annual flow-weighted concentrations

99   (FWC) of THg and MeHg and frame that record within longer 55-year hydroclimatic and ~30-

100   year atmospheric deposition records for Hg and basic chemistry. Combined, we used these

101   datasets to quantify directionality and magnitude of responses and to discern mechanisms that

102   govern Hg concentrations and yields in a headwater hemi-boreal stream. Data were collected

103   within the long-term ecosystem research program of the USDA Forest Service at the S2

104   catchment on the Marcell Experimental Forest (MEF) in Minnesota. As far as we are aware, the

105   dataset is the only multi-decadal, uninterrupted record for boreal or hemi-boreal streamwater

106   MeHg and THg. The hydroclimatic record consists of the annual mean, minimum, and maximum

107   air temperature, total precipitation, catchment runoff, baseflow/event flow contributions, and the

108   fraction of precipitation that occurs as streamflow (runoff ratio) (Sebestyen et al., 2021).

109   Atmospheric deposition records include the Hg concentration, total mass of wet Hg deposition,

110   and total wet-deposited mass of nitrate, SO_4^{2-}, hydrogen ion, sodium, and chloride (National

111   Atmospheric Deposition Program (MN16), 2020, 2021). Streamwater chemistry samples were

112   taken 8 to 24 times a year, when water was flowing, and analyzed for THg, MeHg, total organic

113   carbon (TOC) and major anions and cations (Sebestyen et al., 2022). Our findings are the first

114   catchment-scale observations that show how both THg and MeHg export from peatland-

115   dominated catchments change with interacting effects of cleaner air and climate change.

116

117   **2 Study Site**

118   The S2 catchment has served as a minimally disturbed reference catchment at the MEF

119   since the 1960s (Sebestyen et al., 2011). The MEF is located in north-central Minnesota with a

120   continental climate and average daily temperature of 3.5 °C and annual precipitation of ~787 mm

121   (Sebestyen et al., 2021). The 9.7 ha catchment is comprised of a 6.5 ha upland that surrounds a

122   centrally located 3.2 ha forested ombrotrophic bog peatland (Sebestyen et al., 2021). The bog

123   peatland has an overstory of chiefly *Picea mariana* and an understory of *Sphagnum* mosses,

124   graminoids, and ericaceous shrubs (Verry & Janssens, 2011). The upper ~30 cm of peat is

125 derived from the current forested bog vegetation and transitions from poor fen to rich fen peat

126 deeper through the peat profile (Verry & Janssens, 2011). The peat depth is from 10s of cm to ~7

127 m (Verry & Janssens, 2011). The uplands are dominated by a mixed deciduous forest of *Populus*

128 *tremuloides* with other coniferous and deciduous tree (Verry & Janssens, 2011).

129   The peatland and upland both hydrologically feed a lagg that surrounds the peatland,

130 which ultimately drains into a small stream (Sebestyen et al., 2011; Verry et al., 2011). The

131 ombrotrophic bog peatland and surrounding uplands are perched above the regional aquifer,

132 isolating deep groundwater contributions from both the uplands and peatland (Verry et al., 2011).

133 Consequently, the uplands provide local groundwater to the lagg and peatland through relatively

134 shallow permeable loess sandy loam horizon overlying a low-permeability Koochiching clay

135 loam till (Mitchell et al., 2009; Verry et al., 2011). The water flow at the catchment stream outlet

136 is monitored at a v-notch weir (Verry et al., 2018).

137 **3 Methods**

138   All the data and associated QA/QC used in this study are from freely accessible data

139 publications and aggregated to annual and/or seasonal values for analysis (Table 1), as well as

140 additional QA/QC analysis is presented McCarter et al. (2022b) and the associated supplemental

141 information. The collated dataset included water chemistry (including major ions, TOC, and Hg

142 measured at least every 1 to 2 weeks when there was streamflow), atmospheric deposition (SO_4^{2-},

143 pH, ions, and Hg), total daily precipitation amount, mean (and min/max) daily air temperature,

144 daily streamflow, daily peatland water table elevation, and monthly water table elevation in the

145 aquifer adjacent to the peatland catchment, and calculated runoff ratios (*RR*), daily

146 baseflow/event flow, proportion event flow, potential evapotranspiration (PET), and the 10-year

147 average PET (Table 1).

148 **Table 1.** Data sources for the different measured parameters, with measurement frequency and
149 the calculations used for each parameter.

150

Data Source	Parameters	Measurement Frequency	Calculations
Sebestyen et al. (2021)	Streamflow, air temperature, precipitation, regional and peatland water tables	Daily (1962-2017)	All Parameters: Annual and seasonal means, standard deviations, and deviations from long-term mean (1962-1972); event flow and baseflow, proportion of baseflow/event flow; annual and seasonal total precipitation (P); Annual and seasonal runoff ratio, standard deviation of annual runoff ratio (calculated using monthly data); Annual mean potential evapotranspiration (PET), Annual and 10-year mean potential evapotranspiration P-PET
Sebestyen et al. (2022)	THg, MeHg, K^+, Na^+, Ca^{2+}, Mg^{2+}, $Fe^{2/3+}$, Cl^-, SO_4^{2-}, PO_4^{3-}, pH, TOC	~bi-weekly (1998-2017, 9-24 samples per year)	MeHg/THg: annual and seasonal FWC and yields, standard error of FWC and yields; Cations/anions/pH/TOC: annual FWC and yields
National Atmospheric Deposition Program (MN16) (2021)	Total wet Hg deposition, precipitation wet Hg deposition concentration	Monthly (1996-2017)	Seasonal and annual totals, means, and standard deviation
National Atmospheric Deposition Program (MN16) (2020)	Precipitation concentration of: SO_4^{2-}, Cl^-, NH_4^+, NO_3^-, Br^-, K^+, Na^+, Ca^{2+}, Mg^{2+}, pH	Monthly (1978-2017)	Annual and seasonal means

151

3.1 Data Calculations

152

153 Solute yields were calculated following Sebestyen and Kyllander (2017), whereby

154 concentrations were linearly interpolated between water chemistry samples. Daily yield was

155 calculated by multiplying the sample concentration or interpolated concentration by daily

156 streamflow. Daily yields were either seasonally or annually summed (Sebestyen & Kyllander,

157 2017). The seasonal or annual yields were then divided by catchment area (9.7 ha) and the total

158 volumetric streamflow to determine the annual FWC (Sebestyen & Kyllander, 2017). Seasons

159 were defined as: Spring: March-May, Summer: June-August, Fall: September-November,

160 Winter: December-February.

161

162   The 95% confidence intervals for annual MeHg FWC and yields were determined

163   following Hope et al. (1997). The 95% confidence interval of the monthly FWC, *var(C$_F$)*, were

164   determined using,

$$var(C_F) = \left[\sum (C_i - C_F)^2 \cdot \frac{Q_i}{Q_n}\right] \sum \frac{Q_i^2}{Q_n^2}$$

Eq. 1

165   where, C_F is the monthly FWC for a given solute, C_i is the instantaneous concentration for a

166   given sample, Q_i is the instantaneous discharge, and Q_n is the sum of Q_i. The 95% confidence

167   interval of the yields were then determined by,

$$std.\,error(Y) = F \cdot \sqrt{var(C_F)}$$

Eq. 2

168   where, F is the total monthly discharge.

169

170   Wet deposition of most solutes and total deposition of Hg were measured as part of the

171   National Atmospheric Deposition Program (NADP). The NADP site is in the Marcell

172   Experimental Forest about 2 km from the S2 catchment.

173

174   Streamflow was separated into base and event flow following Nathan and McMahon (1990),

175   with a recession coefficient of 0.8. Runoff ratios were calculated by,

$$RR = \frac{Q_s}{P}$$

Eq. 3

176   where, Q_s is the annual total streamflow (mm), and P is the annual total precipitation (mm) for a

177   given time period.

178

179   Calculated daily potential evapotranspiration (mm) was determined following Hargreaves and

180   Samani (1985),

$$PET = 0.0023 \cdot 0.408 \cdot R_a (T_{avg} + 17.8)(T_{max} - T_{min})^{0.5} \qquad \text{Eq. 4}$$

181   where, R_a is the extra-terrestrial solar radiation (mm H_2O m^{-2} day^{-1}), T_{avg} is the average daily

182   temperature (°C), T_{max} is the maximum daily temperature (°C), and T_{min} is the minimum daily

183   temperature (°C).

184

185   *3.2 Statistical Analysis*

186   Unless otherwise stated, all statistical analysis was performed in R Statistical Software (R

187   Development Core Team, 2021). All daily values were then averaged to seasonal or annual

188   scales for comparison to the annual MeHg or THg FWC and yields. The annual Hg FWCs and

189   annual Hg yields were first compared to all 118 variables using a Pearson correlation matrix with

190   hierarchical clustering (Wei & Simko, 2017) to identify potential controls on either THg or

191   MeHg. Variables with significant moderate correlations ($R^2 > 0.5$, $p > 0.05$) were identified and

192   the initial 118 variables were reduced by removing temporal co-variates (*i.e.*, annual and

193   seasonal measures) and choosing annual values over seasonal values. However, in some

194   instances it was not immediately clear which co-variate should be removed and, in those cases,

195   both were kept for further analysis (*i.e.*, annual and summer average air temperature). This

196   procedure resulted in a total of seven, eight, three, and six variables for annual MeHg FWC,

197   annual MeHg yield, annual THg FWC, and annual THg yield, respectively.

198

199   Despite reducing the number of potential governing variables, these variables were likely

200   correlated to each other and necessitate further reduction before error in variable linear

201   regression. Hierarchical partitioning of R^2 with the *hier.part* package (Walsh & Mac Nally,

202   2020) was used to assess the relative importance of these independent variables on annual Hg

203   FWC and yield. The independent variables (potential drivers) were scaled to the mean and unit

204   variance equal to 0, and the proportion of variance that could be explained by a given

205   independent variable was determined from 999 randomized data matrix using the *rand.hp*

206   function in *heir.part*. Significance ($p < 0.05$) was assessed by the upper confidence 95%

207   confidence interval (Z-score ≥ 1.65) (Mac Nally, 2002; Walsh & Mac Nally, 2020). Hierarchical

208   partitioning determines the proportion of independent and joint variances explained by each

209   variable, allowing for the identification of variables with strong independent correlation with the

210   dependent variable (Chevan & Sutherland, 1991; Mac Nally, 2000), in this case either annual Hg

211   FWC or yield. As such, variables with high correlations but with little independent effect due to

212   joint correlations with other variables would not be significant and were excluded from further

213   analysis.

214

215   The remaining significant variables from the hierarchical partitioning analysis were used

216   as the independent variables in individual bivariate linear regressions. However, since both

217   independent and dependent variables vary throughout each year, Deming regression was

218   calculated in SigmaPlot 12.0$^{©}$. Deming regression is a form of error in variable orthogonal

219   regression that accounts for the standard deviation of the dependent and independent variables at

220   each data point (Deming, 1943). Following York (1966) and Wu and Yu (2018), Deming

221   regression minimizes the sum of squares (*SS*) residuals in both independent and dependent

222   variable by,

$$SS = \sum_{i=1}^{N} [\omega(X_i)(x_i - X_i)^2 + \omega(Y_i)(y_i - Y_i)^2] \qquad \text{Eq. 5}$$

223   where, X_i is the measured driving variable (*e.g.*, mean annual temperature), Y_i is the measured Hg

224   FWC or yields, x_i is the regressed driving variable, and y_i is the regressed Hg FWC or yields. The

225   individual Hg FWC or yields and driving variable were weighted based on annual variability in

226   X_i and Y_i, respectively, following,

$$\omega(X_i) = \frac{1}{\sigma_{X_i}^2}, \omega(Y_i) = \frac{1}{\sigma_{Y_i}^2} \qquad \text{Eq. 6}$$

227   where, σ_{Xi} and σ_{Yi} are the annual standard deviation of X_i and Y_i, respectively. See Wu and Yu

228   (2018) for a detailed comparison of Deming regression to other error in variable linear regression

229   techniques. The error of the independent variables was taken as the standard deviation around the

230   annual mean of a given driver. By using Demming regression rather than other linear regression

231   techniques, we are better able to account for the natural variability in annual measures, which

232   provides a clearer picture of the critical factors controlling Hg dynamics under changing

233   atmospheric conditions.

234

235   **4 Results and Discussion**

236   There was considerable inter-annual variability in THg FWC but no trend (τ = -0.07, p

237   =0.71, Figure 1, Table S1). Without considering the intra-annual variability in THg FWC, spring

238   runoff ratio was suggested to correlate with THg FWC (Table S2). However, when considering

239   the intra-annual viability in spring runoff ratio and THg FWC, the correlation breaks down at

240   higher THg FWC (Figure 2). As such, none of our measured hydroclimatic variables strongly

241   drive THg FWC, while THg yields (Figure 3, Table S1) were correlated with THg FWC (Figure

242   2, Table S3). Despite no apparent effect of climate change on THg at annual time-scales, changes

243   in other unmeasured or time-lagged mechanisms will likely induce shifts in THg fluxes

244   (McCarter et al., 2022a; McCarter et al., 2021a), such as experimental evidence that warmer

245   temperatures increase peatland inorganic Hg pore water concentrations from enhanced microbial

246   activity (Sun et al., 2023). As such, there is an urgent need for more careful consideration and

247   study of the interacting processes that influence THg mobilization to aquatic ecosystems.

248
249   Throughout the study period, MeHg FWC varied independently of THg FWC, suggesting

250   disconnects between THg and MeHg transport and cycling processes (Figure 1). Methylmercury

251   FWC decreased ($\tau = -0.356$, p = 0.07) over the 17-year streamwater Hg record from the highest

252   annual MeHg FWC in 2001 and 2002 to the lowest annual concentrations in 2009 and 2013

253   (Figure 1, Table S1). The proportion of THg as MeHg (%MeHg) significantly decreased ($\tau = -$

254   0.452, p = 0.02) over the 17-year study, paralleling the decrease in MeHg FWC (Figure 1). The

255   observed decrease in both MeHg FWC and yields (Figure 3) could not be ascribed to a single

256   change in climate, streamwater chemistry, or atmospheric deposition metric. A combination of

257   declines in annual wet Hg deposition concentration (23.8%) and the runoff ratio (20.4%), and an

258   increase in mean annual air temperature (22.8%) explains 67% of the independent variability in

259   annual MeHg FWC (Table S4). In contrast, the decline in annual MeHg FWC (32.2%) and

260   annual runoff ratio (16.2%) were the only significant drivers for MeHg yield, accounting for

261   48.4% of the independent variability but this value increases to 60.5% when including annual

262   streamflow (Table S5). Thus, changes in MeHg FWC, along with climate-controlled streamflow

263   measures (*e.g.*, declines in baseflow or runoff ratios), govern the total mass of MeHg leaving the

264   catchment to downstream aquatic ecosystems. Interestingly, no streamwater chemistry

265   parameters, including TOC and sulfate, were correlated with MeHg FWC or yields. It is

266   important to note that in both cases, THg and MeHg, the yields were strongly dependent on the

267 FWCs, suggesting that monitoring a larger number of streamwater MeHg concentration may be

268 more an impactful action to assess MeHg impacts than fewer streams with both yields and

269 FWCs.

270

271 *4.1 Cleaner Air*

272   Sulfur dioxide emissions and subsequent SO_4^{2-} deposition have decreased following clean

273 air legislation first introduced in the 1970s and amended through the 1990s (O'Meara, 1998;

274 Pannatier et al., 2011; Sickles II & Shadwick, 2015). The decline in SO_4^{2-} deposition primarily

275 occurred from the 1970s-1990s, decreasing from 28 kg ha^{-1} yr^{-1} in 1979 to 10 kg ha^{-1} yr^{-1} in 1999

276 (National Atmospheric Deposition Program (MN16), 2020). During the 2001-2017 streamwater

277 Hg record, annual SO_4^{2-} deposition steadily declined from ~10 to ~4 µg SO_4^{2-} m^{-2} (Figure 3). We

278 expected that atmospheric SO_4^{2-} deposition would be a strong predictor of annual MeHg FWC

279 due to the partial dependence of Hg methylation on microbial SO_4^{2-} reduction in peatlands

280 (Mitchell et al., 2008a; Pierce et al., 2022). However, there was no correlation between SO_4^{2-}

281 deposition and annual MeHg FWC in the outflowing streamwater (Figure S4). Given the large

282 store of sulfur in the surficial peat to buffer these lower SO_4^{2-} inputs (Urban et al., 1989), it is

283 likely that the relative change in SO_4^{2-} deposition during the Hg measurement period was small

284 in relation to the total peat sulfur pool that would allow a detectable change in annual MeHg

285 FWC at the catchment scale from increased Hg methylation (Åkerblom et al., 2013; Mitchell et

286 al., 2008a; Pierce et al., 2022) or solubility (Skyllberg, 2008). As such, current SO_4^{2-} deposition

287 rates are not controlling streamwater MeHg as would have been during past higher SO_4^{2-}

288 deposition rates that stimulate elevated streamwater MeHg (McCarter et al., 2022b) prior to

289 clean air legislation.

290

291   Annual wet Hg deposition at the MEF, first measured during 1996, declined from a peak

292   in 1999 of 10,000 ng Hg m^{-2} to between 6000 to 7000 ng Hg m^{-2} during the 2010s (Figure 4),

293   approaching pre-industrial deposition rates (Li et al., 2020). While wet Hg deposition

294   concentration varied between 9.5 and 14.6 ng L^{-1} (total range 5.1 ng L^{-1}) over the study period

295   (Figure 4). Wet Hg deposition concentration (Figure 4) was positively correlated ($p < 0.0001$, r =

296   0.79) with the annual MeHg FWC (Figure 5). Despite dry Hg deposition (e.g., litter fall) being

297   the largest atmospheric Hg input at the MEF (Woerndle et al., 2018), its mobility and availability

298   is often limited relative to wet Hg deposition as additional decomposition or surface erosion

299   processes are often required before impacting streamwater Hg concentrations or yields (Bishop

300   et al., 2020; Demers et al., 2007). As such, given the annual timescales investigated here, recent

301   wet Hg deposition would likely be more bioavailable to the resident methylating microbiota than

302   both legacy Hg that has been bound to organic matter (Chiasson-Gould et al., 2014; Gorski et al.,

303   2008; Hintelmann et al., 2002; Hsu-Kim et al., 2013) and dry Hg deposition, where availability

304   to methylating bacteria may lag well beyond one year. In this case, the decline in the wet Hg

305   deposition explained the greatest amount of variability in the annual MeHg FWC (Figure S2,

306   Table S4), suggesting that further reduction in global atmospheric Hg emissions and subsequent

307   deposition would have a substantial and rapid impact in reducing MeHg in northern peatland

308   catchments. However, given the current deposition concentrations are approaching pre-industrial

309   levels at the MEF, future decreases in wet Hg deposition concentrations may lessen its

310   importance relative to other drivers in this region.

311

312   *4.2 Climate Change*

313   Climate change is readily apparent at the MEF (Figure 4). From 1962 to 2017, annual

314   mean air temperature significantly increased by ~1.8 °C, with no trend in precipitation amount

315   (Figure 4). Mean annual air temperature was positively correlated (1.8 ± 1.2 nmol L^{-1} °C^{-1}) with

316   annual MeHg FWC (Figure 5). However, over the Hg sampling period, there was no increase in

317   annual mean air temperature ($\tau = -0.26$, $p = 0.12$), unlike the clear increase from 1961 to 2017 (p

318    $= 0.003$, Figure 4). In general, mercury methylation is expected to increase with higher microbial

319   activity at warmer air temperatures (Hsu-Kim et al., 2013; Sun et al., 2023; Yang et al., 2016).

320   Such an increase in microbial activity is thought to be more important in the shoulder seasons

321   (spring and fall) where the average air temperatures are further from optimal microbial activity

322   temperatures (IPCC, 2021). However, at annual scales, neither shoulder season mean, minimum,

323   or maximum air temperatures were strong predictors of annual MeHg FWC. Here, warmer mean

324   summertime air temperatures were positively correlated with annual MeHg FWC (Figure S2,

325   Table S2) suggesting that warmer summers combined with *in situ* increases in SO$_4^{2-}$ and changes

326   in water table (Sun et al., 2023) will likely produce higher MeHg FWC. Importantly, these

327   results suggest that annual MeHg FWC responds to mean annual temperature and that future

328   climate warming may have an immediate impact on MeHg concentrations in peatland-fed

329   streamwaters.

330

331   In peatlands, other microbially mediated processes, such as heterotrophic respiration or

332   methanogenesis, are sensitive to the timing and magnitude of temperature and water table

333   anomalies but may be temporally limited and masked by using annual means (Feng et al., 2020;

334   Helbig et al., 2022). In the S2 peatland, the seasonal peatland water tables have been

335   disproportionally decreasing due to climate change during the drier summer (-0.0021 ± 0.0008 m

336   yr^{-1}, p < 0.0001) and fall (-0.0020 ± 0.0014 m yr^{-1}, p = 0.005) periods relative to the wetter

337   spring (-0.0015 ± 0.0009 m yr^{-1}, p = 0.002). Here, annual MeHg FWC was positively correlated

338   (p < 0.05) with the variability in the annual minimum temperature (defined as one standard

339   deviation of the mean minimum temperature; Figure S1). This increase in temperature variability

340   would likely increase the lower limit of temperature limitations on Hg methylation rates, while

341   lower water tables increase the oxidative production of SO_4^{2-} (Sun et al., 2023). These processes

342   are likely to increase future MeHg concentrations in peatlands (Sun et al., 2023). However,

343   higher soil temperatures can increase gaseous sulfur losses from peatlands that can suppress pore

344   water MeHg concentrations and partially offset the aforementioned increases in MeHg

345   concentrations (Åkerblom et al., 2013). Our results suggest that in isolation further increases in

346   air temperature and variability due to climate change, MeHg concentrations in peatland-fed

347   streams, rivers, and lakes will increase due to this positive feedback.

348

349   In general, higher air temperatures increase evapotranspiration losses (Dymond et al.,

350   2014; Helbig et al., 2020), lowering available soil water in the uplands and decreasing peatland

351   water tables, thus converting less precipitation to stream runoff. Higher evapotranspiration

352   combined with steady precipitation drove a significant decline in baseflow (τ = -0.25, p = 0.008),

353   streamflow (τ = -0.15, p = 0.1), the amount of precipitation that became streamflow (runoff ratio,

354   τ = -0.224, p = 0.02), and an increase in the proportion of event flow (τ = 0.321, p < 0.001),

355   particularly since 2000 (Figure 4 and Figure S1). Seasonally, the decline in annual runoff ratio

356   was driven by a significant decrease in fall (τ = -0.203, p = 0.03), while both the spring (τ = -

357   0.134, p = 0.15) and summer (τ = -0.102, p = 0.28) did not significantly decline during the same

358   period (Figure S2). Such declines in runoff ratio due to decreasing baseflow and increases in air

359   temperature that drove higher evapotranspiration is consistent with observations at MEF

360   (Dymond et al., 2014) and projections of climate change (Reshmidevi et al., 2018; Zhang et al.,

361   2023). Despite potential increases in hydrological connectivity between the stream and the

362   catchment during wet periods such as the spring freshet (Jones et al., 2023; Woerndle et al.,

363   2018), the decline in annual runoff ratio is driven by lower water tables during dry periods that

364   offsets any increases in hydrological connectivity during wet periods at annual time scales,

365   driving an overall decrease in the hydrological connectivity of uplands and the peatland to the

366   stream at annual time scales. Thus, precipitation that falls on the catchment is less likely to be

367   transported to the stream during more frequent drier periods (summer and fall).

368

369   The flow and pathways that water moves through a catchment, in short the hydrology, is

370   key to regulating downstream aquatic Hg concentrations and cycling (Branfireun et al., 2020) but

371   the mechanisms are often confounded by other landscape features such as ecosystem types or

372   disturbances (Lam et al., 2022). At the MEF, there has been a clear climate change induced

373   decrease in runoff ratio that decreased overall catchment hydrological connectivity. As such,

374   climate warming has reduced the annual runoff ratio, significantly decreasing annual MeHg

375   FWC and yields (Figure 5). With a 10% decline in annual runoff ratio, which is the approximate

376   average decline over the hydroclimatic record, annual MeHg FWC declined by 2.1 ± 0.6 nmol L^{-1}

377   and yields by 0.001 ± 0.0003 mg ha^{-1}. While no seasonal change in hydrology, upland or

378   peatland, correlated with annual MeHg FWC, peatland water table (*i.e.*, catchment water storage)

379   plays a critical role in facilitating water and solute transport, where higher water tables increase

380   solute transport rates (McCarter & Price, 2017). With the decline in peatland water tables due to

381   climate change, it takes longer and more precipitation for the catchment to hydrologically

382   reconnect and transport any MeHg produced in the catchment to the streams and increases

383   likelihood of chemical or microbial demethylation (Barkay & Gu, 2022). At the S2 catchment,

384   photodemethylation would likely be limited due to the stream often being dry for extended

385   durations during summer rather than stagnant water, which is also limited in the peatland

386   (Sebestyen et al., 2021). While the increased mean annual air temperature and increased

387   minimum temperature anomalies would increase *in situ* peatland MeHg production, the produced

388   MeHg would be less likely to reach the catchment outlet due to decreased runoff from the

389   peatland to the stream and provides a critical negative feedback limiting MeHg in our aquatic

390   ecosystems under a warming climate.

391

392   *4.3 Future Mercury Export Dynamics*

393   Droughts and subsequent hydrological recovery are commonly linked to increased

394   concentrations of cations, such as Hg, from peatlands (Szkokan-Emilson et al., 2013) and MeHg

395   increases within peatlands (Coleman Wasik et al., 2015). There were several droughts (1967/68,

396   1976/77, 1990/91, and 2006/07) with annual precipitation < 603 mm (< 77% of the 1962-2017

397   mean) during the long-term record. Annual runoff ratios during drought years (0.17 ± 0.05) were

398   significantly lower (p = 0.04, t = 2.23, df = 10) than the long-term mean (1962-2017, $0.22 \pm$

399   0.02), indicating that on average the entire catchment (both uplands and peatlands) was less

400   hydrologically connected to the stream during droughts. During the 2006/07 drought, Coleman

401   Wasik et al. (2015) observed SO_4^{2-} regeneration and subsequent elevated pore water MeHg

402   concentrations of a nearby peatland and an increase in THg pore water concentrations after the

403   drought. Despite increases in pore water MeHg concentrations, there was no detection of

404   elevated annual MeHg FWC in the stream during or following the 2006/07 drought. While

405   droughts may promote elevated THg FWC and yields, potentially covarying with runoff ratios

406   (Figure 2), this was not observed during the Hg record and the response was relatively limited at

407   the annual scale. Regardless of internal Hg cycling during and after droughts, the export of Hg

408   from peatland catchments was more dependent on the efficiency that precipitation is converted to

409   streamwater runoff, which declines during droughts, limiting limit both MeHg and THg export

410   under more frequent climate change induced droughts (IPCC, 2021).

411

412   Under an increasingly warming climate, MeHg production within peatlands will likely

413   increase the pore water MeHg concentrations (Sun et al., 2023; Yang et al., 2016). However,

414   with higher temperatures and water losses to the atmosphere, annual streamflow decreases. A

415   resulting reduction in annual hydrological connectivity between MeHg sources and biological

416   sinks will likely be critical in modulating aquatic MeHg concentrations under future climates.

417   Our results using this unprecedented dataset suggest that MeHg export from headwater peatland

418   catchments will continue to decrease over time if climate change continues to accelerate the

419   reduction of runoff ratios and atmospheric wet Hg deposition further decreases.

420

421   **5 Conclusions**

422   Climate change and cleaner air are unequivocally altering the ecohydrological and

423   biogeochemical processes that underpin Hg cycling and export in peatland-rich catchments. We

424   present a clear linkage between decreasing wet Hg deposition concentration due to reductions in

425   atmospheric Hg over North America (cleaner air) that when coupled with the climate change

426   induced reductions in runoff ratios more than offsets the increase in MeHg production due to

427   warmer air temperatures. Yet, the response of THg to cleaner air and climate change was much

428 less clear. As such, we highlight the clear need for further research into unravelling how future

429 changes in timing and strength of hydrological connectivity within and from catchments will

430 impact Hg export, determine the ubiquity and strength of these relationships across a greater

431 number of catchments, and elucidate how these changes will feedback on Hg cycling in wetland

432 and aquatic ecosystems. These critical insights would not be possible without the long-term and

433 broad environmental measurements at the MEF. To better adapt to future climate and

434 environmental change, there is a need for more and longer integrated multidisciplinary datasets.

435

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443

Author contributions

445 Conceptualization: CPRM; Methodology: CPRM, SDS, JDJ; Investigation: CPRM, SDS, JDJ,

446 RKK, EAN; Visualization: CPRM; Funding acquisition: CPRM, JDJ, SDS; Project

447 administration: SDS, RKK; Writing – original draft: CPRM; Writing – review & editing: CPRM,

448 SDS, JDJ, RKK, EAN

449

Data Availability Statement

451   All data, code, and analysis are available in the main text, the supplementary materials, or

452   referenced in Table 1. The data underlying this study are openly available in Sebestyen et al.

453   (2022), Sebestyen et al. (2021), National Atmospheric Deposition Program (MN16) (2020), and

454   National Atmospheric Deposition Program (MN16) (2021).

455

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673 **Figure Captions**

674

675 Figure 1. Annual THg and MeHg flow-weighted concentrations (FWC) and %MeHg from 2001

676 through 2017 at the S2 catchment in the USDA Forest Service Marcell Experimental Forest.

677 Linear regression (solid lines) and 95% confidence intervals illustrate the average temporal

678 trends. Note the gap in the MeHg record due to a resolved analytical contamination issue

679 (McCarter et al., 2022b).

680

681 Figure 2. Error-in-variable linear regressions using Deming Regression (solid line) between

682 annual flow-weighted MeHg concentration and the annual average air temperature, annual

683 average wet Hg deposition concentration, and annual runoff ratio. Dashed lines represent the

684 95% confidence interval.

685

686 Figure 3. Annual THg (**A**) and MeHg (**B**) yields from 2001 through 2017 at the S2 catchment in

687 the USDA Forest Service Marcell Experimental Forest.

688

689 Figure 4. Annual total and concentration of wet Hg deposition, and the annual average

690 precipitation pH and SO_4^{2-} concentration from 1980 through 2017 (Hg: 1995 – 2017) at the

691 USDA Forest Service Marcell Experimental Forest.

692

693 Figure 5. The change in annual average air temperature (**A**), total precipitation (**B**), streamflow

694 (**C**), and runoff ratio (**D**) from 1962 through 2017 at the USDA Forest Service Marcell

695 Experimental Forest. Solid lines are the LOESS smoothed lines resulting from the Mann-Kendall

696 trend tests.

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