Journal of Environmental Monitoring

Cite this: *J. Environ. Monit.*, 2012, **14**, 2327

www.rsc.org/jem

PAPER

Long-term changes in fish mercury levels in the historically impacted English-Wabigoon River system (Canada)†

Margaret R. Neff,[a] Satyendra P. Bhavsar,*[bc] George B. Arhonditsis,[d] Rachael Fletcher[c] and Donald A. Jackson[ab]

Received 3rd January 2012, Accepted 1st June 2012
DOI: 10.1039/c2em30324h

The English-Wabigoon River system in Northwestern Ontario, Canada, was one of the most heavily mercury-contaminated waterways in the world due to historical discharges in the 1960s from a chlor-alkali plant. This study examines long-term (1970–2010) monitoring data to assess temporal trends in mercury contamination in Walleye, Northern Pike and Lake Whitefish, three species important for sport and subsistence fishing in this region, using dynamic linear modeling and piecewise regression. For all lakes and species, there is a significant decline (36–94%) in mercury concentrations through time; however, there is evidence that this decline is either slowing down or levelling off. Concentrations in the English-Wabigoon fish are elevated, and may still present a potential health risk to humans consuming fish from this system. Various biotic and abiotic factors are examined as possible explanations to slowing rates of decline in mercury concentrations observed in the mid-1980s.

Introduction

The English-Wabigoon River system in northwestern Ontario, Canada had been described as one of the most severely mercury-contaminated waterways in the world.[1] Armstrong and Hamilton[1] reported that from 1963 to 1970, approximately 9–11 metric tonnes of mercury from a chlor-alkali plant in Dryden, Ontario were released into the Wabigoon River. In 1970, this release was reduced by 99%, and by 1975 the chlor-alkali plant had converted to a process that did not use mercury. Investigations in the 1970s and early 1980s suggested that many fish species throughout this river system had mercury concentrations well over 0.5 μg g^{-1}, which is generally considered to be the upper limit for safe human consumption, with fish consumption advisories more restrictive for locations closer to downstream of Dryden.[2,3] Mercury contamination of fish is an important issue in this region, particularly for the Grassy Narrows and Wabaseemoong First Nations communities that rely on these species for subsistence fishing and tourism. While commercial fishing was banned in 1971, sport fishing is still permitted. Observational studies in the 1970s and in 2005 examined the high prevalence of symptoms of mercury poisoning in the human population along the English-Wabigoon River system, and it was suggested that ingestion of mercury-contaminated fish was the likely cause.[4–6] However, a comprehensive epidemiological study has yet to be carried out in these populations.

In the 1970s and 80s, a number of studies were conducted in this area to examine the spatial patterns in sediment mercury concentrations and the associated effects on local biotic communities. Bligh[7] identified the English-Wabigoon River system as potentially contaminated due to the activities of the

[a]*Department of Ecology and Evolutionary Biology, University of Toronto, 25 Willcocks Street, Toronto, Ontario, Canada M5S 3B2*
[b]*Centre for the Environment, University of Toronto, 33 Willcocks Street, Suite 1016V, Toronto, Ontario, Canada M5S 3E8*
[c]*Ontario Ministry of the Environment, Sport Fish Contaminant Monitoring Program, Environmental Monitoring and Reporting Branch, 125 Resources Road, Toronto, Ontario, Canada M9P 3V6. Tel: 416-327-5863. Fax: 416-327-6519. E-mail: satyendra.bhavsar@ontario.ca; s.bhavsar@utoronto.ca*
[d]*Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, Canada M1C 1A4*

† Electronic supplementary information (ESI) available: Supplementary figures (*e.g.*, Fig. S1–S3) and tables (*e.g.*, Tables S1 and S2). See DOI: 10.1039/c2em30324h

Environmental impact

The English-Wabigoon River was among the most heavily mercury-contaminated waterways in the world. In this study, long-term fish mercury trends were examined using multiple statistical methods to show that mercury levels in three sport fish species have significantly declined over time in this system. However, the rate of decline appears to have slowed, and current mercury levels are mostly higher than those in other regional water bodies.

Dryden chlor-alkali plant, and reported mercury concentrations in fish from the Wabigoon River system that were as high as 16.65 μg g^{-1} in Burbot (*Lota lota*). Armstrong and Scott[8] noted that once contaminated discharges were reduced, there were rapid declines of mercury concentrations in the biota, but the rate of decline was showing signs of slowing down. Studies summarized by the Canada – Ontario Steering Committee[3] suggested that there had been rapid initial declines in mercury contamination throughout the English-Wabigoon River system, but the rates were slowing down in crayfish, Northern Pike (*Esox lucius*) and Walleye (*Sander vitreus*). The report also concluded that mercury concentrations in the sediments declined rapidly moving downstream from Wabigoon Lake, but there was increasing bioavailability of mercury with increasing distance downstream.[3] While various remediation techniques, such as dredging to remove the most contaminated sediment, were suggested,[13] there is no evidence that significant efforts at remediation were conducted.

Subsequent studies have further explored the relationships between contaminated sediments, mercury concentrations in the water column, and the movement of mercury into biota in the English-Wabigoon River system.[9–11] However, a long-term examination of the trends of mercury concentrations in biota has been largely neglected. Kinghorn *et al.*[12] investigated current levels of mercury in Walleye, Northern Pike, Largemouth Bass (*Micropterus salmoides*) and Lake Whitefish (*Coregonus clupeaformis*) in thirteen lakes and rivers downstream of Dryden in order to assess contamination of lakes close to local First Nations reserves. They found that fish from lakes closest to Dryden had the highest mercury concentrations compared to lakes downstream, and that mercury concentrations in some fish species appear to have declined over the last 25 years. In addition several lakes are still above Health Canada guidelines established for frequent consumption of fish (*i.e.*, 0.2 μg per g total Hg). However, Kinghorn *et al.*[12] made only a very limited comparison between historical *vs.* current levels, as long-term temporal data were not available.

A number of biotic and abiotic factors can influence mercury concentrations in fish, including lake size,[13,14] watershed characteristics,[15] season,[14,16] organic content of lake sediments,[17] water chemistry,[15] productivity,[16,18] climate and warming/cooling cycles,[19,20] trophic position,[13,16,21] fish condition,[15,16,20] fish length, weight and age,[14,22,23] growth rate,[24] and gender.[14,23] Observed patterns in mercury concentrations over time could thus be confounded if one or more of these factors were to also show temporal trends. For example, temporal patterns in fish mercury concentrations may be linked to temporal changes in fish condition (k, the relative weight of a fish compared to its length), as fish of lower condition tend to have elevated mercury burdens due to the higher concentration of mercury within the available tissue.[16,20] If long-term declines in mercury concentrations are observed in this system, it is important to rule out that these changes are not simply an artifact of changes in fish condition over time, which may be linked to a number of different factors, such as food availability, population density, and predator–prey interactions.[15]

This study investigated the long-term temporal trends (1970s–2010) in mercury concentrations in three important fish species – Walleye, Northern Pike, and Lake Whitefish – within four lakes of the English-Wabigoon River system based on comprehensive fish mercury monitoring data collected by the Ontario Ministry of the Environment (OMOE), in partnership with the Ontario Ministry of Natural Resources (OMNR). These species are important commercially and recreationally, as well as for subsistence fishing activities. Several statistical methods were used to thoroughly assess patterns in fish mercury concentrations across this time period, as well as the relationship between fish condition and mercury concentrations. Observed patterns were related to known changes in the trophic structure (*via* the introduction of Rainbow Smelt) and regional climate. Current mercury levels in these lakes were then compared to other water bodies in Northwestern Ontario to provide context with regional mercury levels, and present-day concentrations in additional fish species were evaluated in reference to current consumption guidelines.

Materials and methods

Study area

The English-Wabigoon River is a lotic–lentic system which flows northwest from Wabigoon Lake near Dryden, Ontario, to Tetu Lake, where it joins the Winnipeg River flowing to Lake Winnipeg, Manitoba. Since the early 1970s, around the time it was discovered that the river was heavily contaminated with mercury due to the chlor-alkali plant in Dryden, OMOE, in partnership with OMNR, has consistently analyzed samples of a variety of fish species from lakes within the river system for mercury content. From the 1970s to the late 1980s, fish were sampled on an annual basis, and then either every two, three or five years until the most recent sampling event in 2010. Samples were most consistently taken from four representative lakes: Clay, Ball, Separation and Tetu (Fig. 1). Clay Lake, the closest to the historical point-source of mercury, is approximately 87 km downstream of Dryden, followed by Ball Lake (∼50 km downstream from Clay), then Separation (∼50 km from Ball) and Tetu (∼65 km from Separation). Walleye, Northern Pike and Lake Whitefish were sampled from 1970 to 2010 in Clay Lake, and from 1974 to 2010 for Ball, Separation and Tetu Lakes. These three species were extensively sampled over this time period, and are among the most commonly consumed species in this region.

Sample collection and processing

Data for this analysis were collected as part of the Sport Fish Contaminant Monitoring Program of OMOE, which provides fish consumption advisories based on a wide variety of environmental contaminants known to occur in Ontario waters. Individual fish samples of varying numbers and fish sizes were collected by OMNR field crews during late summer or early fall using gill or trap nets. After collection, fish were measured for total length and weight, their sex determined, filleted (with skin removed) and stored at −20 °C until chemical analysis at the OMOE laboratory in Toronto, Ontario. Mercury was analyzed using protocols as in the OMOE method HGBIO-E3057 (as described in Bhavsar *et al.*[25]). Fish tissue was first digested with 4 : 1 concentrated sulphuric acid to nitric acid (v/v). To determine total mercury content, samples were diluted, mixed and placed in a Gilson autosampler for cold vapour-flameless atomic

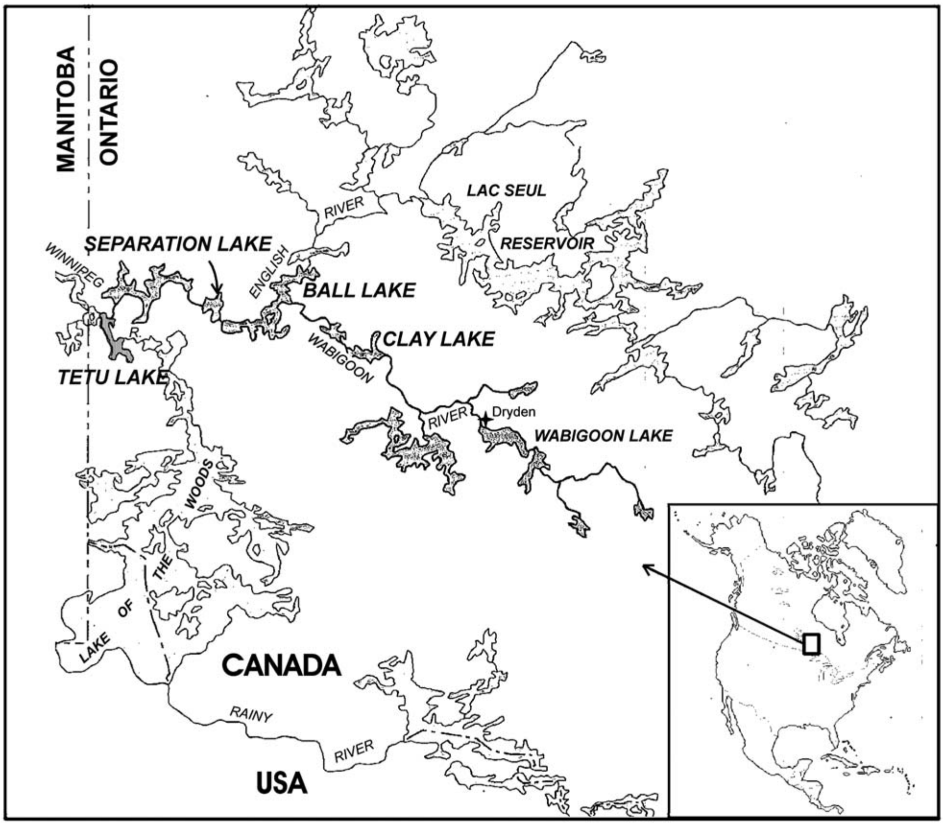

Fig. 1 Map of the English-Wabigoon River system showing the location of the four sampled lakes (Clay, Ball, Separation and Tetu).

absorption spectroscopy (method detection limit (MDL) = 0.01 μg g^{-1} w/w). Five concentrations, covering the range of tissue concentrations, were used to develop calibration curves, and were accepted if correlation coefficients were ≥0.99. One sample and one in-house reference material were analyzed in duplicates. Recoveries were monitored by spiking both the sample and reference material. Samples were not pooled, and were treated as individual samples in the following data analysis.

Statistical analysis

Temporal trends in fish mercury concentrations. Traditional regression methods on temporal data are static, such that values early in the time series have equal weight and influence as values later in the time series. Recently, DLMs have been utilized in the ecological literature to describe changes in some environmental variables such as contaminant concentrations over time.[26–29] With DLMs, the level of the response variable (*e.g.*, mercury concentration) at each time step (*e.g.*, year) is related to levels of the response variable at earlier time steps in the time series. Hence, the parameter estimates of the model at any one time step are only influenced only by prior values, not by subsequent values in the time series. DLMs are based on the thought that newer information is the most relevant and informative in summarizing current conditions, and so progressively discounts posterior information by adding a stochastic uncertainty term to the model, representing the aging of the information over time. In this analysis, DLMs were used to show the trend in mercury concentrations over time, using individual fish samples within each year (*i.e.*, there were multiple data points for each year of data for a species/lake.

DLM equations for this analysis were structured as follows:

Observation equation:

$$\ln[\mathrm{THg}]_{ti} = \mathrm{level}_t + \beta_t \ln[\mathrm{length}]_{ti} + \psi_{ti},\ \psi_{ti} \sim N[0,\Psi_t]$$

System equations:

$$\mathrm{level}_t = \mathrm{level}_{t-1} + \mathrm{rate}_t + \omega_{t1},\ \omega_{t1} \sim N[0,\Omega_{t1}]$$

$$\mathrm{rate}_t = \mathrm{rate}_{t-1} + \omega_{t2},\ \omega_{t2} \sim N[0,\Omega_{t2}]$$

$$\beta_t = \beta_{t-1} + \omega_{t3},\ \omega_{t3} \sim N[0,\Omega_{t3}]$$

$$1/\Omega_{tj}^{\,2} = \zeta^{t-1}\cdot 1/\Omega_{1j}^{\,2},\ 1/\Psi_t^{\,2} = \zeta^{t-1}\cdot 1/\Psi_1^{\,2},\ t > 1 \text{ and } j = 1 \text{ to } 3$$

$$\mathrm{level}_1,\ \mathrm{rate}_1,\ \beta_1 \sim N(0,10\,000),\ t = 1$$

$$1/\Omega_{1j}^{\,2},\ 1/\Psi_1^{\,2} \sim \mathrm{gamma}(0.001,0.001)$$

where $\ln[\mathrm{THg}]_{ti}$ is the observed natural logarithm transformed total mercury concentration at time t in the individual sample i, level_i is the mean mercury concentration at time t when accounting for the covariance in fish length, $\ln[\mathrm{length}]_{ti}$ is the observed standardized fish length at time t in the individual sample i, rate_t is the rate of change of the level variable, and β_t is a length (regression) coefficient. ψ_t, ω_{t1}, $\omega_{t2,}$ and ω_{t3} are normal, zero mean error terms with respective variances of Ψ_t, Ω_1, Ω_2, and Ω_3. The discount factor ζ represents the aging of information with the passage of time; $N(0, 10\,000)$ is the normal distribution with mean 0 and variance 10 000; and gamma(0.001, 0.001) is the gamma distribution with shape and scale parameters of 0.001. Prior distributions for the parameters of the initial year, level$_1$, rate$_1$, β_1, $1/\Omega_{1j}^2$, and $1/\Psi_1^2$ are considered "non-informative."

In the previous model, fish length is included as a covariate, as it is well-established that mercury concentrations often vary with fish size.[23,30,31] To test the validity of this approach, DLMs were also developed with either no covariate with mercury concentration (random walk model), or with fish weight as a covariate instead of length. The performance of each model was assessed using the Deviance Information Criterion (DIC), a Bayesian equivalent of Akaike's Information Criterion (AIC), and is interpreted in the same manner,[32] where models with the lowest DIC score are interpreted to be of the best fit. This analysis was conducted using the WinBUGS software (WinBUGS, version 1.4.3, 2007); model run details and the WinBUGS code used for these analyses can be found in Table S1†.

In previous studies in other lake systems in the region, it has been noted that declines in contaminant concentrations appear to be slowing down in recent years[25,33–36] which may or may not be also the case in lakes of the English-Wabigoon River system. To examine this potential decline, we used piecewise regression to identify a year or a range of years where the slope of a trend may have changed. This analysis also serves a second purpose, in that it is a static, linear model which we use here to corroborate results from the Bayesian DLM method.

The following piecewise regression model was used in this analysis:[37]

$$B_l(x) = \begin{matrix} c - x, & \text{if } x < c \\ 0, & \text{otherwise} \end{matrix}$$
$$B_r(x) = \begin{matrix} x - c, & \text{if } x > c \\ 0, & \text{otherwise} \end{matrix}$$

$$y = \beta_0 + \beta_1 B_l(x) + \beta_2 B_r(x) + \varepsilon$$

where c indicates the division between the two time periods (*i.e.*, breakpoint), and β_0, β_1, and β_2 represent coefficients in a standard regression model where two linear parts meet at c.[37] To determine which year or years represent the breakpoint – *i.e.*, where the trend in the data changes – for each species in each lake, individual models with the breakpoint year varying annually were built. For example, for data ranging from 1970 to 2010, individual piecewise regression models were built where the first model had a breakpoint in 1971, the second model in 1972, the third in 1973, and so on up to 2010. The fit of each individual model plus the full linear regression model to the data were compared using Akaike's Information Criterion (AIC). AIC is a measure of the goodness of fit of a statistical model, and provides a means for comparing statistical models to determine which best represent the data.[38,39] The model with the lowest AIC value was retained as the best-fit model, but all models with ΔAIC < 2 were considered (ΔAIC = AIC value − AIC value of best-fit model).[39] If ΔAIC for the simple linear regression model (*i.e.*, a piecewise regression model with no breakpoint) is >2, then we conclude that a piecewise regression model is a better fit to the data, and that there was a change in the overall trend of the data at the breakpoint in the time series. This approach has been used previously in the literature for examining long-term temporal trends in fish contaminants.[40]

Incorporating fish length or weight as a covariate, as was done with DLM, assumes that the relationship between fish size and mercury concentrations is the same among all years in a species/lake combination. For piecewise regression analysis, we employed two additional methods which do not make this assumption in order to control for the effect of fish size on mercury concentrations.

First, the size range of fish samples in each year of data for a species and lake was limited to a 10 cm interval, such that within that interval, there is no relationship between fish length and mercury concentration. Size intervals were selected based on those used in the published literature,[25] or the grand mean length for each species and lake, and were 45–55 cm for Walleye, 55–65 cm for Northern Pike and 38–48 cm for Lake Whitefish. All fish samples for particular year in each species/lake combination which did not fall in this size range were discarded, and the remaining data were averaged to obtain the mean mercury concentration for that year. Data for a particular year were retained as long as there were at least three samples within the size range for that year, in order to both obtain a meaningful mean value and to retain as many years of data as possible. ANOVA and rank-based ANOVA with Tukey's test were used to check for significant differences in length among years for each species and lake. In all cases, there were no significant pairwise differences in length among years for each species/lake.

While the limited size-range approach should reduce the influence of fish length on patterns in mercury concentrations, it had two main drawbacks. First, data outside of the limited size range are discarded, and as a result, only a small portion of the original dataset was included in the analysis. Second, some time intervals are completely excluded, often in the most recent years when fewer measurements were collected. To address these concerns, standardized mercury concentrations for three fish lengths for each species were calculated using power series regression using the equation $Y = aX^b$,[35,41] where Y is the predicted contaminant concentration in the sport fish (*i.e.*, standardized concentration) and X is the fish length. Constants a and b were estimated using an iterative process to solve for the best fit regression (SPSS, 2001), and this was done for each species/lake combination. The three lengths were chosen for each species prior to the analysis to represent small, medium and large size classes for each species: 30, 45 and 60 cm for Walleye; 40, 50 and 70 cm for Northern Pike; and 30, 40 and 55 cm for Lake Whitefish. These lengths provide mercury values for fish lengths outside of the limited size range previously used for each species, but are within the range of fish lengths available in the dataset. This approach of using a power series regression is identical to the method used by the Ontario Ministry of Environment for the development of consumption advisories of Ontario sport fish.[42]

This resulted in four datasets for each species/lake combination – limited size-range mercury values, and standardized mercury values at small, medium and large fish lengths. Henceforth, each dataset will be referred to by the species and fish length, such that each lake has four Walleye datasets ($WE_{45\text{–}55cm}$, WE_{30cm}, WE_{45cm} and WE_{60cm}), four Northern Pike datasets

($NP_{55–65cm}$, NP_{40cm}, NP_{50cm}, and NP_{70cm}), and four Lake Whitefish datasets ($WH_{38–48cm}$, WH_{30cm}, WH_{40cm} and WH_{55cm}). These four types of data allow for analysis of mercury concentrations in these species over a range of sizes that may be consumed by humans.

Trends in fish condition and mercury concentration

To determine whether fish condition was a factor related to changes in fish mercury concentrations over time, the relationship between lake- and species-specific fish condition and mercury concentrations was assessed. As many traditional measures of condition can be problematic,[43] we first used linear regression on the log-transformed length and weight of all lake- and species-specific samples within a year, for all years. The residual values for each sample in the regression were considered an estimate of that condition of the fish sample, where a positive value indicates that the sample had a greater weight than would be predicted by length (*i.e.*, greater condition), and a negative value indicates the sample was underweight (*i.e.*, lower condition). Within each species/lake combination, average condition estimates for each year were calculated using the mean residual value of the samples for that year. Thus, fish condition was estimated for each year of data for a species/lake combination, and then matched with the corresponding mean mercury concentration for each year. Linear regression was then used to examine the relationship of mercury concentration as a function of fish condition, as well as trends in fish condition over time.

Comparisons to regional water bodies and analysis of additional species

Data from the period 2000–2010 were examined to assess current levels of mercury concentrations in relation to other regional water bodies. Standardized mercury concentrations at three fish lengths were calculated from combined 2000–2010 data for Walleye, Northern Pike and Lake Whitefish from a larger dataset of other locations in Northwestern Ontario (*i.e.*, Ontario water bodies north of 48° N and west of 85° W, generally corresponding to the northwestern region of the OMNR). All available data for each species were screened according to three criteria prior to calculation of standardized mercury values: (1) the sample size was $\geq$5 for a sample year for each water body, (2) the minimum fish length was no more than 10 cm greater than the smallest selected length (*i.e.*, WE_{30cm}, NP_{40cm}, or WH_{30cm}), and (3) the maximum fish length was no more than 10 cm below the largest selected length (*i.e.*, WE_{60cm}, NP_{70cm}, or WH_{55cm}). If 2000–2010 data for a particular location failed to meet any of these criteria, the water body was not included. The final dataset included 143 locations for Walleye ($n = 3043$ fish samples), 123 locations for Northern Pike ($n = 1759$ fish samples) and 38 locations for Lake Whitefish ($n = 854$ fish samples), which was used to calculate standardized mercury values at three fish lengths for each water body. The spread of these values were then compared to mean values of annual (2000–2010) standardized mercury concentrations for each of the four English-Wabigoon lakes. In addition, combined 2000–2010 mercury concentrations in four additional fish species from the English-Wabigoon River lakes – Yellow Perch (*Perca flavescens*), Sauger (*Sander canadensis*), White Sucker (*Catostomus commersonii*) and Mooneye (*Hiodon tergisus*) – were compared to current fish consumption guidelines used by OMOE as well as the Canadian Food Inspection Agency (CFIA) using a power series regression on fish length *versus* mercury concentration data.

Results

Long-term temporal trends

Initial concentrations in each species and lake are described in Table 1, and were in agreement with values reported by Fimreite and Reynolds.[2] Over the sampling period, mercury concentrations in Walleye fell by 83–89% in Clay Lake, 66–73% in Ball Lake, 55–77% in Separation Lake and 36–78% in Tetu Lake, depending on the size class. Northern Pike mercury concentrations fell by 57–71%, 51–54%, 60–73% and 67–70%, while Lake Whitefish concentrations fell by 72–76%, 72–83%, 50–58% and 73–94% for Clay, Ball, Separation and Tetu Lakes, respectively. In general, initial concentrations in the early 1970s for Walleye were higher than Northern Pike (6–14%) and Lake Whitefish (63–94%) in all four lakes. The raw data for each size class showed either immediate declines or slight initial increases in mercury concentrations, followed by overall declines to 2010, with annual or biannual variability (Fig. S1†).

DLMs were first used in the analysis of long-term temporal trends in fish mercury concentrations in these four lakes. The analysis was conducted using three different versions of the DLM model – one with fish length as a covariate, another with fish weight as a covariate, and the last a model with no covariate (*i.e.*, random walk). In all species/lake combinations, models with a length covariate outperformed random walk and fish weight models, with the exception of Ball Lake Lake Whitefish, in which weight and length both performed equally well (Table S2†). In the cases where two models could not be distinguished from each other (*i.e.*, DIC < 2), the resulting DLM plots of mercury concentrations across time were nearly identical, and hence we include only the model with the lowest DIC score. It should also be noted that the width of the posterior predictive intervals tends to increase across the time series for most species/lake combinations (Fig. 2). As we did not observe any increase in the within-year variability of mercury concentrations for any lake/species, this is likely due to a decrease in the frequency of sampling from the 1990s to 2010. Generally, each lake was sampled every 1–2 years until 1991, and thereafter was sampled every 3–5 years. Interpretations concerning recent trends in mercury concentration should be made with some caution.

Overall, all four lakes showed declines in fish mercury concentrations from the start of sampling to 2010, for each of the three species considered in this study. However, the pattern of decline varied slightly with the species and lake. Mercury levels for Walleye and Northern Pike in Clay and Ball Lakes initially decreased rapidly until early 1980s (Fig. 2a and b). Concentrations then remained mostly constant until a small spike in 2005, followed by declines to 2010. The lowest mercury concentrations over the sampling period for Clay Lake Walleye were observed in 2010. Clay Lake Whitefish followed a similar pattern, but remained mostly constant following a small decline around 1995 (Fig. 2a). In Ball Lake, Lake Whitefish mercury levels declined

Table 1 Summary of (a) initial mercury concentrations in English-Wabigoon lakes included in this study, with (b) historical mercury concentrations in various impacted water bodies in Canada, the United States, Japan and Sweden

Location	Taxa	Year	Hg (μg g^{-1})
(a) Initial mercury concentrations in English-Wabigoon lakes			
Clay Lake	Lake Whitefish	1976	0.75–2.6
	Northern Pike	1976	3.6–13
	Walleye	1970	1.2–24
Ball Lake	Lake Whitefish	1974	0.13–3.25
	Northern Pike	1974	0.54–7.98
	Walleye	1974	0.94–4.42
Separation Lake	Lake Whitefish	1974	0.13–0.65
	Northern Pike	1974	0.81–6.52
	Walleye	1974	0.76–4.51
Tetu Lake	Lake Whitefish	1974	0.11–2.52
	Northern Pike	1974	0.22–6.51
	Walleye	1974	0.4–2.7
(b) Comparison of mercury concentrations from other contaminated water bodies worldwide			
Minamata Bay, Japan[44]	Various marine species	Unknown	5.61–35.7
Pinchi Lake, British Columbia, Canada[45]	Lake Trout	1968–1969	10.5
St Clair River, Ontario, Canada[45]	Pumpkinseed	1968–1969	7.09
Lake St Clair, Ontario, Canada[45]	Walleye	1968–1969	5.01
Onondaga Lake, NY, USA[46]	Smallmouth Bass	1970	1.5–2.5
Lake Vanem, Sweden[47]	Northern Pike	1977	1.39
Ottawa River, Ontario, Canada[48]	Various piscivores	1976	0.15–0.4

over the entire sampling period, with steep declines from 1974 to 1985/6, followed by a period of relatively constant concentrations until the early 1990s. Concentrations then very slowly decreased to 2010. Ball Lake Mercury concentrations across time for Lake Whitefish were considerably less variable from year-to-year compared to Walleye and Northern Pike (Fig. 2b).

Mercury concentrations in Walleye and Northern Pike from Separation Lake showed initial increases followed by strong declines from 1974 to the early 1980s, another strong decline from 1990 to 1997, then slowly increasing concentrations to 2010 (Fig. 2c). Lake Whitefish concentrations also declined to the mid-1980s, then continued to decline at a slower rate to 2010 (Fig. 2c). In Tetu Lake, concentrations over time for Walleye and Northern Pike are somewhat more variable on a year-to-year basis compared to Clay, Ball and Separation Lakes, but overall show similar patterns to those of species in the other three lakes (Fig. 2d). Walleye mercury concentrations have since declined from the local maximum in 2005, while Northern Pike concentrations have remained constant. Tetu Lake Whitefish trends are consistent with trends for this species in the other three lakes (Fig. 2d).

Piecewise regression analyses further highlight patterns for each species/size class/lake combination, where the majority of breakpoint years were estimated in the mid-1980s, corresponding to a shift from initial rapid declines to slower declines (Table 2). However, piecewise regression analysis for all three species in Separation Lake indicates breakpoints in the early or mid-1990s (Table 2c).

The majority of pre-breakpoint mercury trends were statistically significant ($p < 0.05$, we have not adjusted for multiple comparisons throughout), indicating that natural log-transformed fish mercury concentrations followed a significant linear decline from the start of sampling to the predicted breakpoint year (Table 2). However, the majority of post-breakpoint trends, with the exception of Ball Lake populations (Table 2b), were insignificant ($p > 0.05$), indicating that the trend could not be distinguished from a line of slope 0. One population, $NP_{55\text{–}65cm}$ from Separation Lake, exhibited a significantly ($p < 0.05$) increasing post-breakpoint trend (Table 2c). In nearly all cases, the piecewise regression model better explained the data than the simple linear regression (*i.e.*, ΔAIC of piecewise model compared to simple regression model > 2), with the exception of Clay Lake WH_{30cm}, Ball Lake $WE_{45\text{–}55cm}$ and WE_{60cm}, and Tetu Lake WH_{30cm} (Table 2). In these populations, the data are best explained by a simple linear regression model with a constant slope over the time period. These linear trends were all statistically significant ($p < 0.05$), with the exception of Tetu Lake WH_{30cm}, which had statistically insignificant declines.

Overall, for Walleye and Northern Pike, initial rapid declines were evident from the start of sampling to approximately 1985, which were then followed by slightly elevated but constant mercury concentrations to ∼1995. Following 1995, mercury concentrations dipped and then slowly increased to a peak around 2005. Trends from 2005–2010 were variable among lakes and species, exhibiting increasing, constant or decreasing trends. In contrast, patterns for Lake Whitefish were less variable among years, and either show steadily declining concentrations (Separation Lake) or steep declines to ∼1985 and then relatively constant concentrations to 2010.

Analysis of fish condition (as residuals of a log-length, log-weight linear regression) over time revealed no significant temporal trends in fish condition (linear regression, $p > 0.05$). In addition, significant, positive linear relationships between fish condition and mercury concentration were observed for Walleye in Clay and Tetu Lakes ($p < 0.001$ and $p = 0.005$, respectively), and Lake Whitefish in Clay and Ball Lakes ($p = 0.009$ and $p < 0.001$, respectively).

Comparisons to regional water bodies and analysis of additional species

Means of annual (2000–2010) mercury concentrations for Walleye, Northern Pike and Lake Whitefish in Clay Lake were

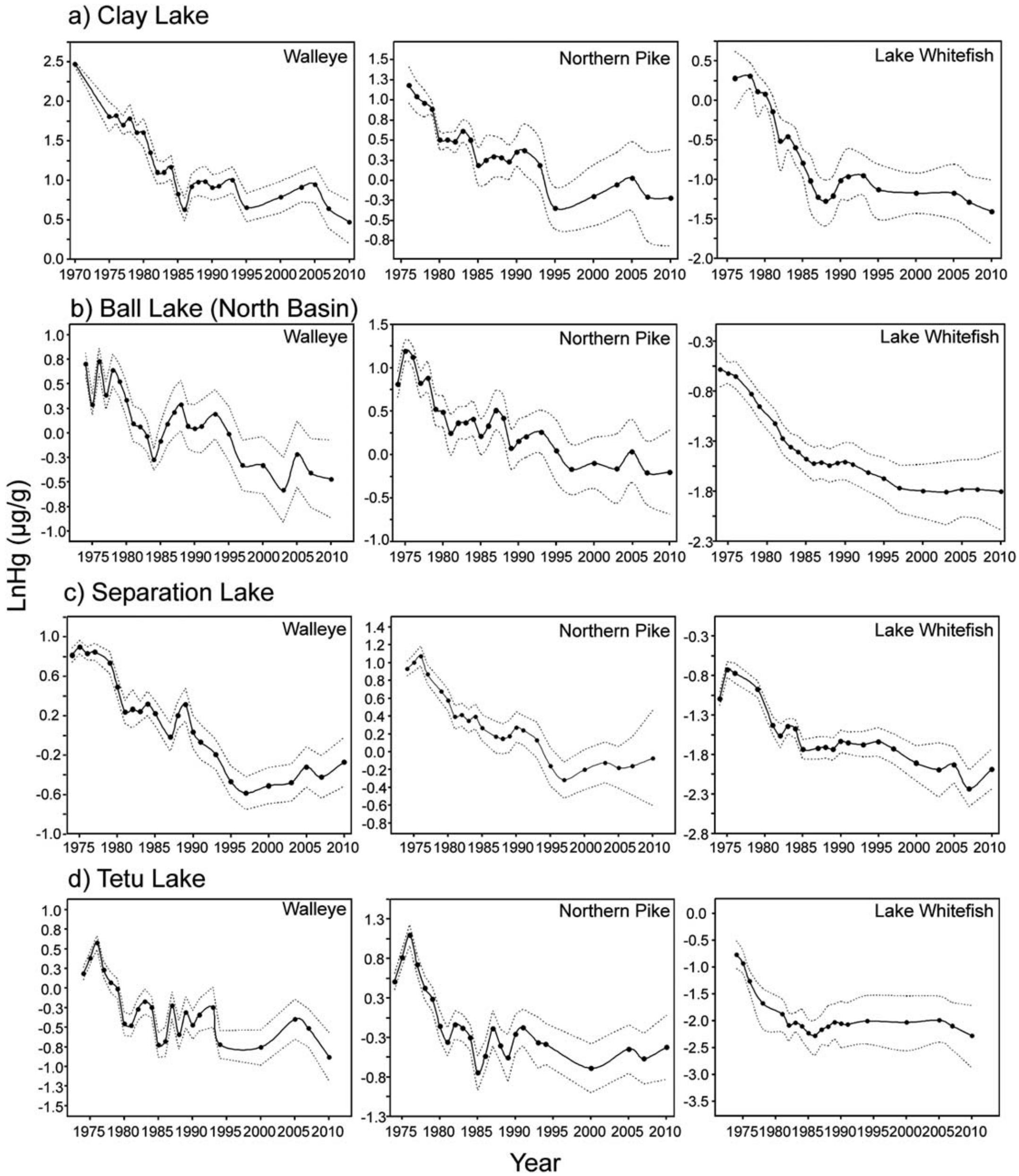

Fig. 2 Dynamic Linear Model (DLM) plots of ln-transformed mercury concentrations over time for Walleye, Northern Pike and Lake Whitefish for (a) Clay Lake, (b) Ball Lake (North Basin), (c) Separation Lake and (d) Tetu Lake. DLMs presented in these plots are the best predicted model for each lake/species combination. The solid and dashed lines correspond to the median and the 95% posterior predictive intervals, respectively.

well above mercury concentrations for similar sized fish found in other Northwestern Ontario water bodies (Fig. 3). As noted previously, Clay Lake is the closest lake examined in this study to the original source of mercury contamination in Dryden, Ontario, and while there have been statistically significant declines over time since the 1970s, mercury concentrations were well above the 75th percentile of other regional water bodies. Mercury concentrations in species from Ball and Separation Lakes were also above the 75th percentile for all three species, except for WE60 cm (Fig. 3). Tetu Lake fish were generally within the quartile range of mercury concentrations in regional water bodies, suggesting that mercury levels in fish from this lake are closer to natural background levels. However, concentrations in the smallest size classes for Walleye and Northern Pike were slightly above the 75th percentile.

Recent data from 2000 to 2010 were also available for Yellow Perch and Sauger for all four lakes, as well as White Sucker for Clay, Separation and Tetu Lakes, and Mooneye for Ball, Separation and Tetu Lakes. Power series regression models for each species are plotted with the upper limit of consumption guidelines for both the general population as well as the sensitive population (*i.e.*, children and women of child-bearing age) (Fig. S2†). Due to the paucity of data for these species, these results should be regarded as a coarse overview, but indicate that Clay Lake populations of medium- and large-sized Yellow Perch, and Sauger should be avoided by the sensitive population

Table 2 Summary of piecewise regression results for (a) Clay Lake, (b) Ball Lake, (c) Separation Lake, and (d) Tetu Lake[a,b]

Species	Break	Pre-trend	Post-trend	Full model ΔAIC	Species	Break	Pre-trend	Post-trend	Full model ΔAIC
(a) Clay Lake					*(b) Ball Lake (North Basin)*				
$WE_{45-55cm}$	1985–1987	↓*	↓	14.5	$WE_{45-55cm}$	n/a	n/a	n/a	0.69
WE_{30cm}	1981–1982	↓*	↓	19.1	WE_{30cm}	1980–1985	↓*	↓*	3.7
WE_{45cm}	1983–1985	↓*	↓*	34.2	WE_{45cm}	1981–1985	↓*	↓*	5.9
WE_{60cm}	1985–1986	↓*	↓	29.4	WE_{60cm}	n/a	n/a	n/a	1.3
$NP_{55-65cm}$	1981–1984	↓*	↓	8.3	$NP_{55-65cm}$	1978–1983	↓*	↓*	3.5
NP_{40cm}	1978–1989, 1994–1999	↓*	↓*	3.6	NP_{40cm}	1979–1983	↓*	↓	2.2
NP_{50cm}	1980–1986	↓*	↓	7.3	NP_{50cm}	1979–1982	↓*	↓*	6.3
NP_{70cm}	1981–1986	↓*	↓	7.2	NP_{70cm}	1980–1985	↓*	↓*	8.6
$WH_{38-48cm}$	1985–1988	↓*	↓	7.7	$WH_{38-48cm}$	1981–1983	↓*	↓*	25.5
WH_{30cm}	*n/a*	n/a	n/a	−0.2	WH_{30cm}	1982–1983	↓*	None	31.8
WH_{40cm}	1985–1988	↓*	↓	11.9	WH_{40cm}	1983	↓*	↓*	53.2
WH_{55cm}	1986–1989	↓*	None	13	WH_{55cm}	1995–2003	↓*	↑	6.6
(c) Separation Lake					*(d) Tetu Lake*				
$WE_{45-55cm}$	1992–1998	↓*	↑	14.6	$WE_{45-55cm}$	1984–1987	↓*	None	13.5
WE_{30cm}	1996–2003	↓*	↑	8.7	WE_{30cm}	1979–1987	↓*	None	3.5
WE_{45cm}	1995–1999	↓*	↑	21.9	WE_{45cm}	1980–1985	↓*	↓	12.4
WE_{60cm}	1990–1996	↓*	None	12.9	WE_{60cm}	1980–1986	↓*	↓*	10.5
$NP_{55-65cm}$	1995–1999	↓*	↑*	16.5	$NP_{55-65cm}$	1981–1986	↓*	None	17.9
NP_{40cm}	1983–1999	↓*	↑	6.4	NP_{40cm}	1981–1989	↓*	↓	2.2
NP_{50cm}	1985–1988, 1994–1998	↓*	↑	10.9	NP_{50cm}	1983–1986	↓*	↓	12.3
NP_{70cm}	1995–2000	↓*	↑	14	NP_{70cm}	1981–1985	↓*	None	22.2
$WH_{38-48cm}$	1982–1988	↓*	↓	10.3	$WH_{38-48cm}$	1978–1987	↓*	None	7.3
WH_{30cm}	1980–1986, 2007–2009	↓*	↓	2.7	WH_{30cm}	*n/a*	*n/a*	*n/a*	0.24
WH_{40cm}	1981–1985	↓*	↓*	8.7	WH_{40cm}	1977–1978	↓*	None	11.3
WH_{55cm}	1982–1988	↓*	↓*	7.3	WH_{55cm}	1977–1978	↓*	None	25.2

[a] Arrows indicate the direction of the slope pre- and post-breakpoint. [b] Asterisks (*) denote those trends which were statistically significant ($p < 0.05$).

(Fig. S2a†). In addition, the sensitive population should also avoid consumption of large Sauger from Ball, Separation and Tetu Lakes (Fig. S2b†). In contrast, Mooneye populations in all four lakes appear to be generally safe for consumption by the general population, but with larger individuals posing a potential risk for the sensitive population (Fig. S2d†).

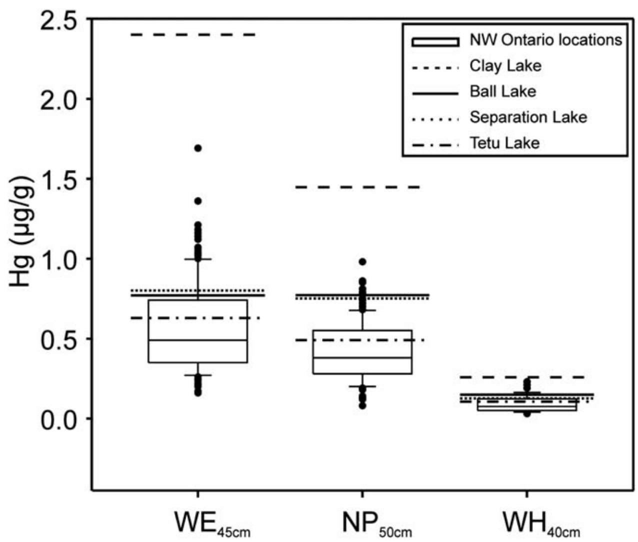

Fig. 3 Box plots of recent (2000–2010) mercury levels in Northwestern Ontario locations (north of 48° N and west of 85° W) compared to study lakes at three standardized mercury concentrations for (a) Walleye (n = 143 locations), (b) Northern Pike (n = 123 locations) and (c) Lake Whitefish (n = 38 locations). Lines in each box represent the median concentration, boxes indicate the 25th and 75th quartile values, and whiskers indicate the upper and lower values not classified as statistical outliers or extremes. Horizontal lines indicated mean mercury concentrations for Clay, Ball, Separation and Tetu Lakes for 2000–2010, for each respective fish length.

Discussion

The adverse effects of mercury contamination of aquatic ecosystems on both the associated biota and human populations was first documented in the 1950s in Minamata Bay, Japan, where mercury-contaminated waste had been discharged for several decades.[44] Comparisons of initial fish mercury concentrations in the English-Wabigoon lakes to concentrations in various fish species from other contaminated water bodies worldwide show that English-Wabigoon mercury concentrations were comparable to values measured in these other water bodies – particularly those of one of the most famous sites for mercury contamination, Minamata Bay (Japan) (Table 1).

Despite highly elevated initial fish mercury concentrations in the English-Wabigoon River system, our analysis shows that concentrations have substantially declined in three fish species in the last 35 years. This finding is in agreement with the only other recent examination of fish mercury concentrations in this region, which indicated that concentrations in Clay Lake declined between 1974 and 2003.[12] In general, for each species and lake, initial rapid declines transitioned in the mid-1980s to slower declines to 2010, with very similar patterns of decline for Walleye and Northern Pike in all four lakes. However, there are some notable differences in temporal mercury concentration patterns among lakes. Walleye and Northern Pike from Ball Lake show nearly constant rates of decline over the entire sampling period, whereas rates of decline showed more variability in the other three lakes for these species (Fig. S3†). In addition, mercury concentrations in Walleye and Northern Pike from Separation Lake do not level off from 1985–1995 to the same degree as the other lakes, and instead show stronger changes to the overall trend in the mid-1990s, as evidenced by the estimated breakpoint years for those trends (Table 2). These two populations also exhibit the strongest upward trend in recent years, with a statistically significant increasing linear trend observed in $NP_{55-65cm}$ (Table 2).

Abiotic and biotic factors influencing pattern of decline

Recent studies in North America have noted that despite overall long-term declines in contaminant (*e.g.*, PCBs, mercury) concentrations, recent concentrations in some systems suggest that rates of decline are slowing down, or, in some cases, reversing to increasing trends[4,19,25,29,33–36,49] Bhavsar *et al.*[25] showed that although overall mercury concentrations in the Great Lakes fish species had declined over a period from the 1970s to 2007, Walleye from Lake Erie showed increasing mercury concentrations in recent years. Sadraddini *et al.*[29] described trends in mercury concentrations in a number of fish species in Lake Erie with a wide variety of behavioural and dietary habits, and found that most populations have either stabilized or increased mercury concentrations in recent years. Monson[49] found that initial declines in mercury concentrations in piscivorous fish species in Minnesota appeared to reverse to upward trends in the mid-1990s. Monson *et al.*[36] similarly showed recent increasing trends in fish mercury concentrations within the Great Lakes region. Several hypotheses have been proposed to explain these recent trends, including temporal trends in fish condition,[16] the introduction of invasive species[25] and regional climate warming.[19,20]

Fish of lower condition tend to have elevated mercury burdens due to a concentration of mercury within the available tissue.[16,20] While we did observe significant relationships between condition and mercury concentrations in four cases (Walleye in Clay and Tetu Lakes, and Lake Whitefish in Clay and Ball Lakes), the positive slopes of these trend were opposite to what we would expect, given the hypothesis that fish of lower condition will have higher mercury levels due to a concentration effect within the available tissue. In addition, we did not observe any changes in fish condition over time, and thus it seems unlikely that fish condition and its potential effects on mercury concentrations is influencing the temporal patterns observed in this system.

As the dominant pathway of mercury uptake in fish is from food,[50] any changes to the within-lake trophic structure could have significant impacts on mercury burdens in fish, it has been hypothesized that the spread of invasive species may influence contaminant (*e.g.*, mercury, PCBs) concentrations by lengthening pre-existing food chains leading to top predators. Studies have shown that lakes with invasive fish species often show higher mercury concentrations in top piscivores,[51–53] and other studies have hypothesized that benthic aquatic invasives such as Dreissenid mussels and Round Gobies (*Neogobius melastomus*), disrupt food webs by releasing contaminants previously concentrated in benthic food webs to top predators.[25,40,54] French *et al.*[40] supported this hypothesis indirectly, by reporting that changes in the rate of decline in contaminant concentrations coincided with the introduction of invasive species. In the English-Wabigoon system, 1989–1990 surveys revealed the presence of Rainbow Smelt (*Osmerus mordax*), an invasive fish species in this region.[55] It is possible that Rainbow Smelt may have been present several years prior to their discovery, which coincides with many of the estimated breakpoints (~1985) in the observed trends in mercury concentrations, particularly for top predators such as Northern Pike and Walleye. However, an earlier study in Northwestern Ontario found no such changes in mercury concentrations in forage fish species and adult Walleye in lakes recently invaded by Rainbow Smelt, despite evidence of food chain lengthening in lakes where Rainbow Smelt was present.[56] In addition, Rennie *et al.*[20] observed no relationship between changes to fish mercury concentrations after the establishment of another invasive species, the Spiny Water Flea (*Bythotrephes longimanus*). Despite the apparent coincidence between the invasion of Rainbow Smelt and changes in the rate of decline in mercury concentrations in this system, it is still unclear whether the two events are related. It should be noted, however, that the studies which specifically examine the relationship between invasive species and/or food chain length and mercury concentrations[20,56,57] were not conducted in systems with a history of point-source contamination, which adds another level of complexity to a system like the English-Wabigoon River.

The relationship between warmer water temperatures and higher mercury methylation rates has been observed in several systems,[11,13] and climate cycles and warming have been linked to changes in fish mercury concentrations in several studies.[19,20] Bodaly *et al.*[13] observed higher methylation rates with warmer epilimnetic temperatures, and observed a positive relationship between fish mercury concentration and epilimnetic water temperature. However, studies which have examined changes in temperature over time in conjunction with fish mercury concentrations suggest that warming temperatures are instead associated with decreasing fish mercury concentrations.[19,20] French *et al.*[19] tied this observation to fluctuations in the prey population of predatory fish, whereas Rennie *et al.*[20] proposed that the declines in precipitation and reduction of transport of atmospheric and terrestrial inputs to lakes in regions associated with climate warming may explain the reduction in fish mercury concentration. In this study, there were no obvious connections between changes to mean annual air temperature or mean annual precipitation in relation to patterns in mercury decline in the English-Wabigoon fish populations, even in the most recent two decades (*i.e.*, 1990 onwards), despite significantly increasing mean annual air temperatures for this region, as reported by Rennie *et al.*[20] However, Schneider *et al.*[58] recently showed that lake temperatures warm faster than air temperatures in the face of climate change, and provides the possibility that there may be greater impacts of climate change than air temperature data might suggest. This is especially true in consideration that most studies have examined systems that were not subjected to the same degree of point-source mercury pollution as the English-Wabigoon system, and hence may experience different overall responses to climate warming.

Lastly, atmospheric deposition has been identified as a major source of mercury to aquatic food webs, the importance of which depends on the system being studied.[59] While there has been evidence of declining mercury concentrations in precipitation following the enactment of legislation on emissions in North America,[60,61] global increases in mercury emissions were observed from 1990 to 1995.[62,63] It is possible that despite efforts to control mercury inputs to aquatic systems in the United States and Canada, global emissions still contribute significant inputs to watersheds, and hence may explain recent slowing in decline rates.

Patterns among study lakes and species within the English-Wabigoon River system

It appears, then, that potential factors such as the introduction of invasive species, changes to fish condition and climate change do not individually provide adequate explanations for the patterns in mercury decline observed in this system. It is possible that instead, dynamics in mercury concentrations are more related to changes in rates of methylation and demethylation. While we did find expected differences in initial mercury concentrations depending on the distance of the water body to the original source of mercury discharges at Dryden, we also saw that Separation Lake – the third most downstream of the lakes studied – had weakly increasing trends in the most recent years. One possibility is that the transport of contaminated sediments downstream over time is influencing recent trends in this lake, or that morphological or physicochemical differences among the lakes are influencing methylation rates, and thus mercury concentrations in their fish populations. Studies conducted in the English-Wabigoon system during the 1980s indicated that methylating activity was likely responsible for the continuing high mercury concentrations in aquatic biota.[17] Further, Parks *et al.*[11] showed that MeHg concentrations could respond rapidly to changing environmental conditions, suggesting a degree of local control on overall MeHg concentrations in lakes and rivers. While an examination of the physical and chemical differences between these four study lakes was not within the scope of this study, it is possible that local dynamics in factors known to influence methylation rates, such as water chemistry,[22] watershed characteristics[59] or land use[64] may account for differences seen among lakes.

In general, we observed that Walleye and Northern Pike populations in the four lakes had similar trends in mercury concentrations over the course of this study, and had higher initial mercury concentrations than Lake Whitefish. Walleye and Northern Pike are often considered top predators in aquatic food webs, and as it is generally known that mercury concentrations increase with the trophic position,[16] these results coincide with established patterns in the literature. In addition, Bodaly *et al.*[13] suggested that because species such as Lake Whitefish prefer cool-water benthic habitats, they may be subjected to lower methylation rates and hence have slower uptake of mercury from both food and water.

Comparison of statistical methods

This study utilized two statistical treatments of the data, with three different ways of accounting for the influence of fish size on mercury concentrations. It is worth noting the relative merits of each method, given that they are all used to some degree in the fish contaminant literature. First, we used Dynamic Linear Models (DLMs) to show the relationship between time and mercury concentrations, including fish length as a covariate in the model. Then, we used piecewise regression on annual means of mercury concentrations calculated from a subset of data within a restricted range of fish lengths. In addition, we used the same statistical analysis on a second treatment of the data, where we used standardized mercury values for three fish lengths, based on a length–concentration relationship predicted by a power series regression. Within this analysis, individual piecewise regression models with varying breakpoint years were compared against each other as well as a simple linear regression model with no breakpoint. All these statistical methods have a common goal in this study of representing the trend of mercury concentrations over time, but ultimately highlight different aspects of the data. Simple linear and piecewise regression employ static models, where early events and later events have equal weight and influence on the predicted values, whereas the premise of DLMs is that the predicted value in any single year is only influenced by previous years, not those that come after. In addition, the choice of data treatment with respect to the influence of fish length on mercury concentrations also requires slightly different interpretations of the results. For instance, both the restricted size range and the standardized mercury value approaches initially reduce the amount of variability in the dataset before being applied to simple linear or piecewise regression. This inherently leads to a better fit of the data around a regression line, and a greater R^2 value.

However, it is clear from the results of this study that regardless of the approach, each statistical method and data treatment tells the same story in regards to the temporal trends of mercury concentrations in sport fishes of the English-Wabigoon River system. In this case, the utilization of multiple statistical methods and data treatment approaches lends further support to the conclusion that there is a very strong signal in the data. Selection of the appropriate statistical approach for similar work in other systems will depend on the structure of the data and the objectives of the study. Impact of logging activities in this area might also have influenced mercury dynamics and fish mercury levels, and needs to be investigated further.

Conclusions

In this study, multiple methods of statistical analysis were used to thoroughly assess long-term temporal trends in mercury concentrations of the English-Wabigoon River system in Northwestern Ontario, Canada. Accurate assessment of contaminant data over time often presents statistical challenges, and the use of traditional methods (*e.g.*, linear regression) coupled with more recent developments such as DLMs, allows for a comparison of results and further confidence in the conclusions. This study clearly shows that mercury concentrations in three sport fish species in four study lakes of the English-Wabigoon River system have substantially declined since the stoppage of mercury discharges in the early 1970s. Patterns of decline follow trends seen in other long-term studies in the Great Lakes region, with rapid initial declines followed by slowing declines. Finally, data from the most recent decade indicate that mercury concentrations in sport fish may still pose a risk to human consumers, despite an overall dramatic reduction in mercury burdens.

Acknowledgements

We thank Ram Prashad and Rusty Moody (OMOE) for sample analysis, the Ontario Ministry of Natural Resources for sample collection and the Ontario Ministry of Aboriginal Affairs. Somayeh Sadraddini (University of Toronto Scarborough) provided support on the implementation of the WinBUGS software and DLM development.

Notes and references

1 F. A. J. Armstrong and A. L. Hamilton, in *Trace Metals and Metal-Organic Interactions in Natural Waters*, ed. P. C. Singer, Ann Arbor Science Publishers, Ann Arbor, 1973, pp. 131–156.
2 N. Fimreite and L. M. Reynolds, *J. Wildl. Manage.*, 1973, **37**, 62.
3 Canada-Ontario Steering Committee, *Mercury Pollution in the Wabigoon-English River System of Northwestern Ontario, and Possible Remedial Measures*, Government of Ontario and Government of Canada Technical Report Summary, 1983.
4 M. Harada, T. Fujino, T. Akagi and S. Nishigaki, *Bull. Inst. Const. Med.*, 1976, **26**, 169.
5 M. Harada, T. Fujino, T. Akagi and S. Nishigaki, *Kumamoto Med. J.*, 1977, **30**, 64.
6 M. Harada, M. T. Fujino, T. Oorui, S. Nakachi, T. Nou, T. Kizaki, Y. Hitomi, N. Nakano and H. Ohno, *Bull. Environ. Contam. Toxicol.*, 2005, **74**, 689.
7 E. G. Bligh, *Mercury and the Contamination of Freshwater Fish*. Fisheries Research Board of Canada Manuscript Report 1088, 1970.
8 F. A. J. Armstrong and D. P. Scott, *J. Fish. Res. Board Can.*, 1979, **36**, 670.
9 J. W. Parks, J. A. Sutton and A. Lutz, *Can. J. Fish. Aquat. Sci.*, 1986, **43**, 1426.
10 J. W. Parks, *Water, Air, Soil Pollut.*, 1988, **42**, 267.
11 J. W. Parks, A. Lutz and J. A. Sutton, *Can. J. Fish. Aquat. Sci.*, 1989, **46**, 2184.
12 A. Kinghorn, P. Solomon and H. M. Chan, *Sci. Total Environ.*, 2007, **372**, 615.
13 R. A. Bodaly, J. W. M. Rudd, R. J. P. Fudge and C. A. Kelly, *Can. J. Fish. Aquat. Sci.*, 1993, **50**, 980.
14 P. W. Rasmussen, C. S. Schrank and P. A. Campfield, *Ecotoxicology*, 2007, **16**, 541.
15 K. Suns and G. Hitchen, *Water, Air, Soil Pollut.*, 1990, **650**, 255.
16 J. V. Cizdziel, T. A. Hinners, J. E. Pollard, E. M. Heithmar and C. L. Cross, *Arch. Environ. Contam. Toxicol.*, 2002, **43**, 307.
17 J. W. M. Rudd, M. A. Turner, A. Furutani, A. L. Swick and B. E. Townsend, *Can. J. Fish. Aquat. Sci.*, 1983, **40**, 2206.
18 P. C. Pickhardt, C. L. Folt, C. Y. Chen, B. Klaue and J. D. Blum, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 4419.
19 T. D. French, L. M. Campbell, D. A. Jackson, J. M. Casselman, W. A. Scheider and A. Hayton, *Limnol. Oceanogr.*, 2006, **51**, 2794.
20 M. D. Rennie, W. G. Sprules and A. Vaillancourt, *Ecography*, 2010, **33**, 471.
21 H. K. Swanson, T. A. Johnston, D. W. Schindler, R. A. Bodaly and D. M. Whittle, *Environ. Sci. Technol.*, 2006, **40**, 1439.
22 C. T. Driscoll, V. Blette, C. Yan, C. L. Schofield, R. Munson and J. Holsapple, *Water, Air, Soil Pollut.*, 1995, **80**, 499.
23 S. B. Gewurtz, S. P. Bhavsar and R. Fletcher, *Environ. Int.*, 2011, **37**, 425.
24 M. Simoneau, M. Lucotte, S. Garceau and D. Laliberté, *Environ. Res.*, 2005, **98**, 73.
25 S. P. Bhavsar, S. B. Gewurtz, D. J. McGoldrick, M. J. Keir and S. M. Backus, *Environ. Sci. Technol.*, 2010, **44**, 3273.
26 E. C. Lamon, S. R. Carpenter and C. A. Stow, *Ecol. Appl.*, 1998, **8**, 659.
27 C. A. Stow, E. C. Lamon, S. S. Qian and C. S. Schrank, *Environ. Sci. Technol.*, 2004, **38**, 359.
28 S. Sadraddini, M. E. Azim, Y. Shimoda, S. P. Bhavsar, K. G. Drouillard, S. M. Backus and G. B. Arhonditsis, *J. Great Lakes Res.*, 2011, **37**, 507.
29 S. Sadraddini, M. Ekram Azim, Y. Shimoda, M. Mahmood, S. P. Bhavsar, S. M. Backus and G. B. Arhonditsis, *Ecotoxicol. Environ. Saf.*, 2011, **74**, 2203.
30 K. M. Somers and D. A. Jackson, *Can. J. Fish. Aquat. Sci.*, 1993, **50**, 2388.
31 M. A. Miller, *Arch. Environ. Contam. Toxicol.*, 1994, **27**, 367.
32 D. J. Spiegelhalter, N. G. Best, B. P. Carlin and A. van der Linde, *J. Roy. Stat. Soc. B*, 2002, **64**, 583.
33 M. E. Azim, A. Kumarappah., S. P. Bhavsar, S. M. Backus and G. Arhonditsis, *Environ. Sci. Technol.*, 2011, **45**, 2217.
34 S. B. Gewurtz, S. P. Bhavsar, D. A. Jackson, R. Fletcher, E. Awad, R. Moody and E. J. Reiner, *J. Great Lakes Res.*, 2010, **36**, 100.
35 S. B. Gewurtz, S. P. Bhavsar, D. A. Jackson, E. Awad, J. G. Winter, T. M. Kolic, E. J. Reiner, R. Moody and R. Fletcher, *J. Great Lakes Res.*, 2011, **37**, 148.
36 B. A. Monson, D. F. Staples, S. P. Bhavsar, T. M. Holsen, C. S. Schrank, S. K. Moses, D. J. McGoldrick, S. M. Backhus and K. A. Williams, *Ecotoxicology*, 2011, **20**, 1555.
37 J. T. Faraway, Practical Regression and ANOVA using R, www.stat.lsa.umich.edu/~faraway/book, 2002.
38 H. Akaike, in *Second International Symposium on Information Theory*, ed. B. N. Petrov and F. Csaki, Budapest, Akaemiai Kiado, 1973, pp. 267–281.
39 K. P. Burnham and D. R. Anderson, in *Model Selection and Multimodel Inference*, Springer, New York, 2nd edn, 2002.
40 T. D. French, S. Petro, E. J. Reiner, S. P. Bhavsar and D. A. Jackson, *Ecosystems*, 2011, **14**, 415.
41 W. A. Scheider, C. Cox, A. Hayton, G. Hitchin and A. Vaillancourt, *Environ. Monit. Assess.*, 1998, **53**, 57.
42 S. P. Bhavsar, E. Awad, C. G. Mahon and S. Petro, *Ecotoxicology*, 2011, 1588–1598.
43 S. G. Sutton, T. P. Bult and R. L. Haedrich, *Trans. Am. Fish. Soc.*, 2000, **129**, 527.
44 M. Harada, *Crit. Rev. Toxicol.*, 1995, **25**, 1.
45 S. Effler, *Water, Air, Soil Pollut.*, 1987, **33**, 85.
46 N. Fimreite, W. N. Holsworth, J. A. Keith, P. A. Pearce and I. M. Gruchy, *Can. Field Nat.*, 1971, **85**, 211.
47 L. Lindestrom, *Ambio*, 2001, **30**, 538.
48 D. R. Miller, D.R., H. Akagi, M. Brownstein, A. S. W. DeFreitas, A. Kudo, D. C. Mortimer, R. Norstrom, D. Peter, J. S. Hart, Q. N. LaHam, M. Dickman, D. J. Kushner, S. U. Qadri, S. Ramamoorthy, D. R. Townsend, R. G. Warnock and B. R. Rust, *Environ. Res.*, 1979, **243**, 231.
49 B. A. Monson, *Environ. Sci. Technol.*, 2009, **43**, 1750.
50 B. D. Hall, R. A. Bodaly, R. J. P. Fudge, J. W. M. Rudd and D. M. Rosenberg, *Water, Air, Soil Pollut.*, 1997, **100**, 13.
51 H. R. MacCrimmon, C. D. Wren and B. L. Gots, *Can. J. Fish. Aquat. Sci.*, 1983, **40**, 114.
52 D. O. Evans and D. H. Loftus, *Can. J. Fish. Aquat. Sci.*, 1987, **44**, 249.
53 M. J. Vander Zanden and J. B. Rasmussen, *Ecol. Monogr.*, 1996, **66**, 451.
54 L. S. Hogan, E. Marschall, C. Folt and R. A. Stein, *J. Great Lakes Res.*, 2007, **33**, 46.
55 W. G. Franzin, B. A. Barton, R. A. Remnant, D. B. Wain and S. J. Pagel, *N. Am. J. Fish. Manag.*, 1994, **14**, 65.
56 H. K. Swanson, T. A. Johnston, W. C. Leggett, R. A. Bodaly, R. R. Doucett and R. A. Cunjak, *Ecosystems*, 2003, **6**, 289.
57 G. Cabana, A. Tremblay, J. Kalff and J. B. Rasmussen, *Can. J. Fish. Aquat. Sci.*, 1994, **51**, 381.
58 P. Schneider, S. J. Hook, R. G. Radocinski, G. K. Corlett, G. C. Hulley, S. G. Schladow and T. E. Steissberg, *Geophys. Res. Lett.*, 2009, **36**, 1–6.
59 J. M. W. Rudd, *Water, Air, Soil Pollut.*, 1995, **80**, 697.
60 D. S. Jeffries, T. G. Brydges, P. J. Dillon and W. Keller, *Environ. Monit. Assess.*, 2003, **88**, 3.
61 C. J. Watras and K. A. Morrison, *Can. J. Fish. Aquat. Sci.*, 2008, **65**, 100.
62 E. G. Pacyna and J. M. Pacyna, *Water, Air, Soil Pollut.*, 2002, **137**, 149.
63 E. G. Pacyna, E. J. M. Pacyna, F. Steenhuisen and S. Wilson, *Atmos. Environ.*, 2006, **40**, 4048.
64 J. Munthe, R. A. Bodaly, B. A. Branfireun, C. T. Driscoll, C. C. Gilmour, R. Harris, M. Horvat, M. Lucotte and O. Malm, *Ambio*, 2007, **36**, 33.