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Title: Freshwater Fish Tissue Mercury Concentration Changes Associated with Mercury Emissions Reductions

11 pp.

2 figures

3 tables

Supporting Materials – Hutcheson et al., Temporal and Spatial Trends in Freshwater Fish Tissue Mercury Concentrations Associated with Mercury Emissions Reductions

1. WATER QUALITY SAMPLING AND ANALYSIS

Water temperature, pH, dissolved oxygen concentration, conductivity were measured *in situ* at one station at the deepest part of each lake at 1 m depth intervals with multiprobe field instruments. Dependent upon whether or not the water column was stratified at the time of sampling, either mid-epilimnion and hypolimnion water samples were taken or a single mid-depth sample was taken for analysis of major cations and anions (Na, K, Ca, Mg, Fe, Mn, SO_4, Cl), dissolved organic carbon content (DOC), total organic carbon content (TOC), nitrate+nitrite nitrogen, total phosphorus, and ammonia.

Table S- 1. Analytical Methods for Water Quality

Analyte	Method Reporting Limit, mg/L	Method
Na	0.02	US EPA 200.7[1]
K	0.07	US EPA 200.7[1]
Ca	0.01	US EPA 200.7[1]
Mg	0.005	US EPA 200.7[1]
SO_4	0.06	US EPA 300[2]
Cl	0.07	US EPA 300[2]
Fe	0.01	US EPA 200.7[1]
Mn	0.005	US EPA 200.7[1]
TOC	0.2	US EPA 415.1[3]
DOC	0.2	US EPA 415.1[3]
Alkalinity	0.25	US EPA 310.1[4]
NO_2	0.003	US EPA 300.0[2]
NO_3	0.002	US EPA 300.0[2]
NH_3	0.001	Standard Methods. 4500-NH_3 F[5]
Tot. P	0.001	Standard Methods. 4500-P E[6]

Table S- 2. Lake Descriptive Information

Area	Lake	Latitude N, Longitude W	Surface Area (ha)	Watershed Area (ha)	Max. Depth (m)
Northeastern MA	Baldpate Pond	42° 41' 55", -71° 00'06"	24	1037	12
	Chadwicks Pond	42° 44' 31", -71° 04' 49"	70	416	8
	Lake Cochichewick	42° 42' 16", -71°05' 50"	233	1236	14
	Haggetts Pond	42° 38' 54", -71° 11' 55"	85	561	14
	Johnson Pond	42° 43' 58", -71° 03' 06"	78	399	7
	Kenoza Lake	42° 47' 31", -71° 02' 60"	105	341	19
	Lake Attitash	42° 51' 03", -70° 58' 57"	149	997	7
	Lake Pentucket	42° 47' 29", -71° 04' 24"	15	50	8
	Lake Saltonstall	42° 47' 00", -71° 03' 59"	18	5850	9
	Long Pond	42° 41' 49", -71° 22' 08"	67	1912	8
	Lowe Pond	42° 40' 35", -70° 59' 07"	14	1725	2
	Millvale Reservoir	42° 47' 22", -71° 01' 49"	18	509	3
	Pomps Pond	42° 38' 09", -71° 09' 07"	10	691	3
	Rock Pond	42° 43' 47", -71°00' 23"	20	911	6
	Stevens Pond	42° 41' 29", -71° 06' 30"	9	473	3
Rest of State	Bare Hill Pond	42° 29' 24", -71° 35' 54"	126	1976	5.5
	Massapoag Pond - Dunstable	42° 38' 55", -71° 29' 42"	45	2529	10
	Newfield Pond	42° 38' 00", -71° 23' 21"	31	519	7
	North Watuppa Pond	41° 43' 06", -71° 06' 07"	700	2992	8
	Onota Lake	42° 28' 27", -73° 16' 43"	262	899	16
	Upper Reservoir	42° 32' 10", -71° 58' 05"	17	1981	1
	Lake Wampanoag	42° 36' 58" -71° 57' 54"	93	773	4
	Wequaquet Lake	41° 40' 22" -70° 20' 30"	232	54373	9

2. MERCURY METHODS

QA/QC

The accuracy (i.e., percent Hg recovery from Hg-spiked fish samples) and precision (i.e., relative percent difference in Hg among duplicate fish samples) in the analyses of fish samples prior to 2005 by US EPA Method 245.6 were 103 ± 9.1 % and 4.0 ± 3.8 % (means ± 1 s), respectively. The accuracy of analyses of a Hg fish tissue reference standard consisting of freeze-dried tuna tissue (BCR ref. std #463) was 103 ± 4.7 % recovery. Hg in all laboratory reagent blanks was less than the method detection limit (MDL) of 0.02 mg/kg.

Mercury Methods Intercomparison

Samples analyzed through 2004 were analyzed following US EPA Method 245.6[7] with a Perkin Elmer Flow Injection Mercury System (FIMS 100) consisting of a Perkin Elmer FIAS 100 flow injection platform interfaced to a mercury measurement system (i.e., mercury cold vapor generator and atomic absorption spectrometer). Samples analyzed from 2005 on were analyzed following US EPA Method 7473[8] with a Milestone DMA80 mercury analyzer. This method employs sample thermal decomposition, mercury amalgamation, and atomic absorption spectrophotometry. The mercury concentrations determined by each analytical method employed during the course of this study on the same frozen fish tissue samples were compared. Total mercury concentrations in ninety-one tissue samples from largemouth bass and yellow perch stored frozen for 11 months were analyzed with both analytical methods. Initially, 10-25 g samples of dorsal muscle were dissected from fish brought in from the field on ice. These samples were homogenized and frozen. Eleven months later the frozen homogenized tissue samples were analyzed with the FIMS analyzer (samples treated as described in Rose et al. (1999)[9]) and a DMA80 mercury analyzer. We chose to analyze fish representing a spectrum of mercury concentrations as determined shortly after original processing with the FIMS method in order to determine if the degree of correspondence between mercury concentrations determined by the two methods was sensitive to the amount of mercury in the tissues.

The percent differences between mercury concentrations determined with the two methods are plotted against the mercury concentration in the tissues determined with each method (abscissa on Figure S 1). The values determined with the two methods agreed within approximately +/- 15-20% except for cases where the amount of mercury in the tissues was below about 0.2 mg/kg where the disparity between mercury results generated by the two methods becomes greater. DMA80 concentrations were generally greater than FIMS-generated concentrations below concentrations of about 0.2 mg/kg (Figure S2A). Above that concentration, the agreement was excellent (Figure S2B, slope of fitted regression line 0.98 with r^2 of 0.98). The mean % difference between readings when mercury was >0.2 mg/kg was 1.8% (s= 8%, n=68). At concentrations below 0.2 mg/kg, agreement was less with a mean of 20.2% (s = 18%, n=25). The methods did not produce significantly different mercury concentrations above 0.2 mg/kg, but at concentrations below that value, they did produce significantly different concentrations (p= 0.05 determined with paired sample t-tests on $\log_{10}$-transformed mercury concentrations).

Given that the concentrations of most interest in this monitoring program were those which were greater than 0.2 mg/kg, the agreement between the two methods was acceptable. In addition, the high bias exhibited by the DMA80-determined samples at mercury concentrations below about 0.2 mg/kg would lead us to underestimate any temporal changes in mercury concentrations when comparing samples from prior to 2005 with those from 2005 on.

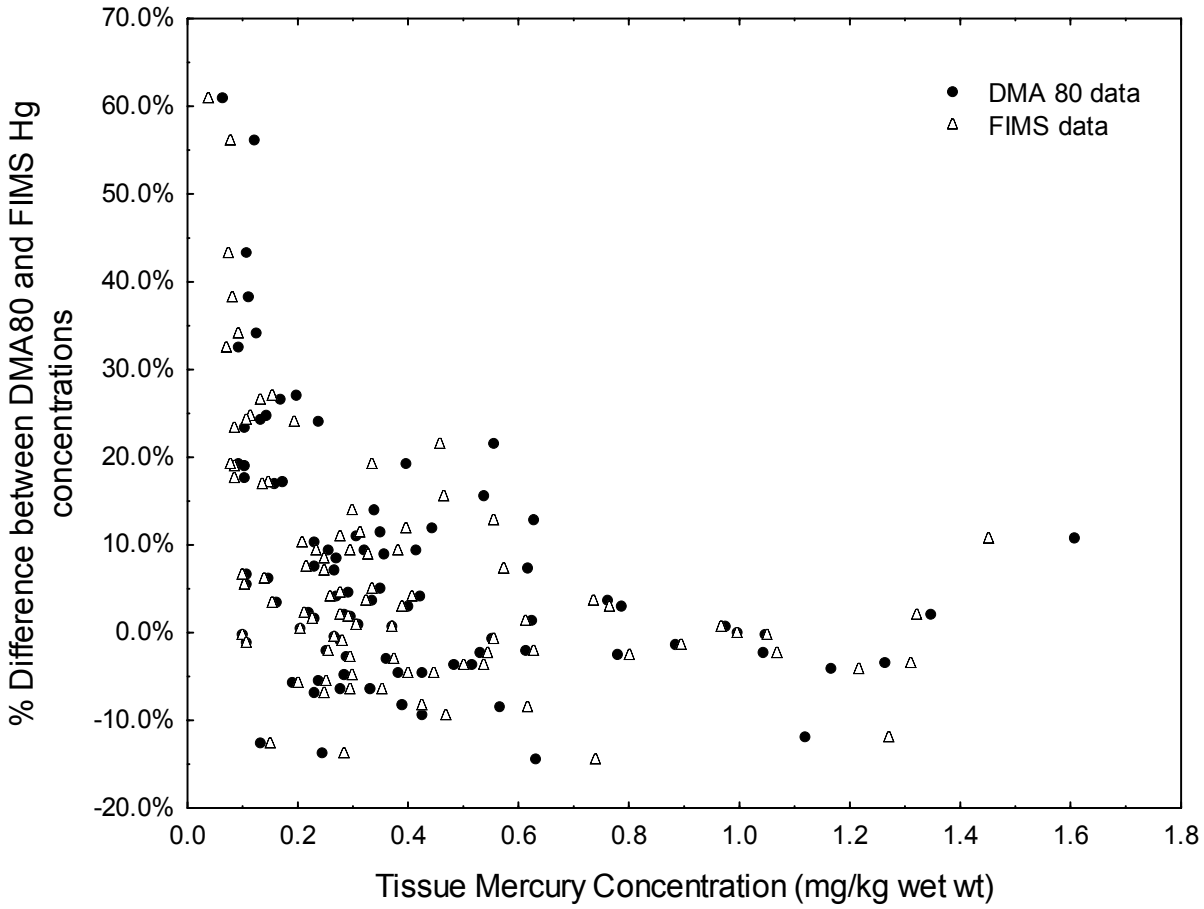

Figure S 1. Percentage difference between mercury concentrations determined with FIMS and DMA80 versus mercury concentration determined with each method, mg/kg.

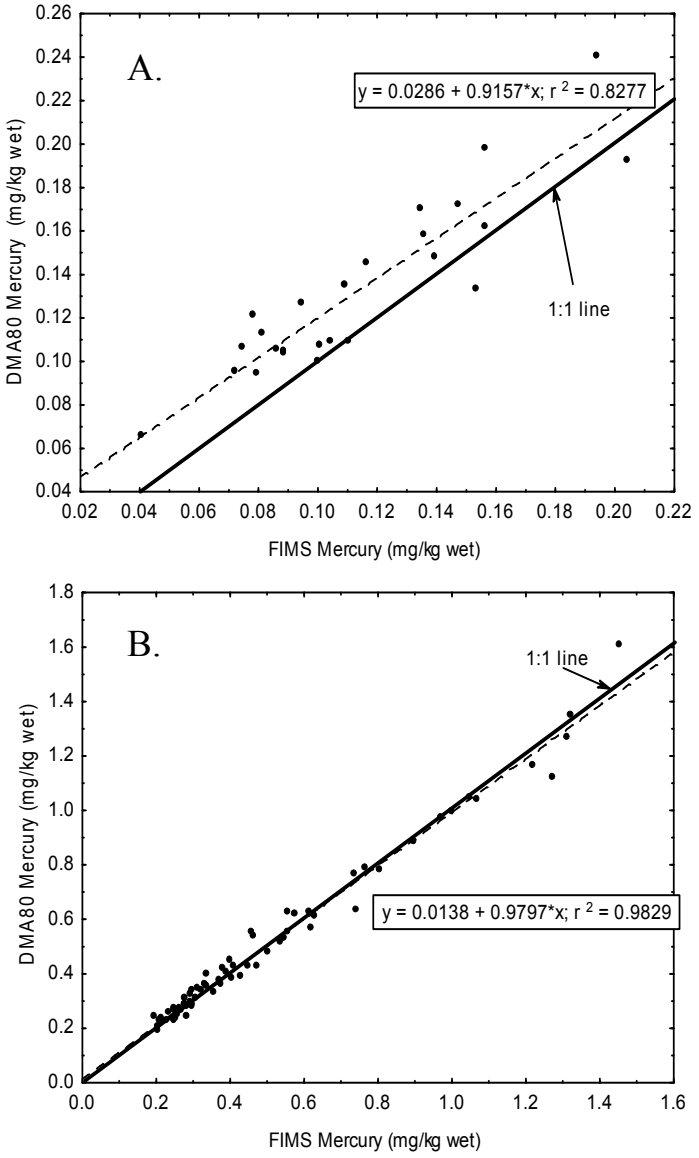

Figure S2**.** DMA80 mercury concentrations versus FIMS mercury concentrations on same samples for samples with mercury concentrations: A. <0.2 mg/kg; B. ≥ 0.2 mg/kg.

3. METEOROLOGICAL DATA REDUCTION PROCEDURES

Precipitation data were available for northeastern Massachusetts from the Lawrence, Massachusetts Airport from the National Oceanic and Atmospheric Agency's National Climatic Data Center.[10] More complete precipitation data sets containing precipitation volumes, sulfate and hydrogen ion concentrations were available (online at http://nadp.sws.uiuc.edu) from two National Atmospheric Deposition Program network stations located to the west of the study area. One was in urban Waltham, Massachusetts (MA13) located 40 km southwest and the other at the rural Quabbin Reservoir (MA09) 100 km west southwest of the northeastern part of the state.[11] Volume-weighted annual mean sulfate and hydrogen ion concentrations were downloaded directly from the website. Rainfall amount data for the northeast region of the state for 1991-2011 were obtained for the Lawrence, MA Airport in the center of that area from NOAA's National Climatic Data Center: http://cdo.ncdc.noaa.gov/pls/plclimprod/poemain.accessrouter?datasetabbv=SOD

The downloaded file consisted of monthly total precipitation amounts in hundredths of inches. These units were converted to centimeters and annual totals calculated. Five of the 21 years had from 1-3 months of data missing. In each of the years, the data values for 2-8 of the months were flagged as missing from 1-9 days of data. No attempt was made to interpolate values for this missing data.

4. EXCEPTION TO SIZE-STANDARDIZATION PROCEDURE

Tissue mercury concentration size standardization methods are described in Hutcheson et al.[12] The data from one lake were treated differently for size-standardization. Yellow perch (YP) from Johnsons Pond in NE MA were predominantly smaller than the YP standardization length of 243 mm. There was therefore no practical basis for extrapolating to larger fish beyond the range of measured lengths. In this case for comparing the temporal differences between years, a different approach was taken than for the rest of the data. All of the fish in the 1999 group except for an outlier were in a narrow length range (210-234 mm total length) with mercury concentrations showing no relationship with length over this narrow interval. Size standardization of the 2004 though 2011 groups were therefore made to the mean length of the 1999 group (221 mm). The 1999 unadjusted mercury concentrations and the size-adjusted 2004-2011 group Hg concentrations were then compared with a t-test and were significantly different (t-test, $p>0.05$), deceasing by 28.9%.

5. MERCURY EMISSIONS CALCULATIONS

MA statewide and "hotspot" emission inventory estimates were derived as described in NESCAUM (2011)[13], MassDEP (1996)[14] and below. Briefly, annual stack emission test data obtained using US EPA standard methods, conducted under MassDEP supervision, were used to generate emissions estimates for municipal solid waste combustors (MSWC), medical waste incinerators (MWI), sewage sludge incinerators (SSI) and coal-fired electricity generating units (EGU). Emissions from other source categories were generated using emission factors as described in NESCAUM (2011)[13] and MassDEP (1996).[14]

MWSC emissions were derived using the average of all available emission stack tests (from 1-4 per facility per year), each comprised of 3 sampling runs, conducted at each MA MSWC facility during the specified year. Facility-specific stack outlet mercury emissions rates determined in kg Hg/hr from

these stack tests were multiplied by either: a) the actual number of hours that the facility operated per year, when available; or b) an operational time scaling factor of 92.5% applied to an assumed 100% operation to derive yearly emission values. The scaling factor was based on the overall facility average from 2002 emission calculations for all Massachusetts MSWC using actual hours of operation for all facilities on a quarterly basis.

Emissions from MWIs were estimated as described using available stack test data stack test emission data.[13, 14]

Emissions from the other less significant classes of emitters (Table S- 3) were apportioned between the northeast and remainder of the state on a population weighted basis based upon the assumption that the mercury emissions from these source categories are generally related to population density. Population figures for towns in the northeastern (NE) part of the state comprising the mercury fish tissue and deposition hotspot and the entire Commonwealth were obtained from the 1990, 2000 and 2010 US Census records. Each census year's NE population was divided by the whole state population for that year to obtain a figure for the percentage of the state's population residing in the NE (1990: 6.8%; 2000: 7.0 %; 2010: 7.0%). These figures can be applied to any of the total source emission figures in Table S- 3 to arrive at emission amounts for the NE and the remainder of the state.

For a few classes of major Hg emitters (MSWC, EGU, and SSI), emissions were apportioned to the hotspot area and the rest of the state based on the locations of individual facilities. None of the SSI or EGU were located in the NE.

Summary data for the MSWC are shown in the paper. Emissions data of the type reported here for Massachusetts are reported to the US EPA and are reflected in the National Emission Inventory database for Criteria and Hazardous Air Pollutants[15] , which has been used in mercury deposition modeling by US EPA and others. Emissions from MSWC were the largest source category, accounting from more than 80% of the total inventory during the baseline period of 1991 – 1994. In 1998, MA adopted stringent mercury emissions regulations for MSWC. These took effect in 2000, required quarterly stack tests and established a stringent mercury emission limit of 0.028 mg Hg per dry standard cubic meter (dscm); a limit approximately 3 times lower than the federal emission limit at that time. In response to these regulations, the MSWC in Lawrence MA, located in the "hotspot" area, ceased operations in 1998 and, in 1999, the MSWC in Fall River also closed. Over 2000 - 2001, upgraded air pollution control devices (APCD) were installed (i.e. activated carbon injection) and optimized at the remaining MA MSWCs. Mandatory mercury material source separation plans were also developed and implemented in the facilities waste sheds. Due to federal and pending state regulations targeting dioxin and mercury emissions from these facilities, many MWIs ceased operation in the mid to late 1990s and by 2002 no MWI were in operation in MA.

Table S- 3. All Source Mercury Emissions (kg/yr) Estimates for Massachusetts (adapted from NESCAUM, 2011)[13]

SOURCES	1991-1994	% of total emissions	2002	% of total emissions	2008	% of total emissions
POINT SOURCES:						
COMBUSTION SOURCES						
Municipal Waste Combustors	**3223**	82%	**230**	47%	**133**	40%
Sewage Sludge Incinerators	**73.2**	2%	**78.4**	16%	**78.6**	24%
Medical Waste Incinerators	**326.2**	8%	**0**	0%	**0**	0%
ICI Boilers Total	**20.1**	1%	**8.28**	2%	**3.82**	1%
Coal-fired	3.2	0%	3.18	1%	3.2	1%
Oil-fired	16.8	0%	4.97		0.46	0%
Wood-fired	0.16	0%	0.13	0%	0.16	0%
Electric Utility Boilers Total	**86.1**	2%	**80.4**	16%	**45.3**	14%
Coal-fired	83.9	2%	75.5	15%	42.8	13%
Oil-fired	2.17	0%	3.71	1%	1.17	0%
Wood-fired		0%	1.19	0%	1.35	0%
Total Combustion Sources	**3728.4**	**95%**	**397.1**	**82%**	**260.7**	78%
MANUFACTURING SOURCES						
Limestone manufacturing	15.4	0%	1.23	0%	0.45	0%
Total Manufacturing Sources	**15.4**	**0%**	**1.23**	**0%**	**0.45**	**0%**
TOTAL POINT SOURCES	**3743.8**	**96%**	**398.2**	**81%**	**261.2**	**78%**
AREA SOURCES:						
Residential Heating	**5.1**	0%	**5.33**	1%	**4.1**	1%
Coal			0.09	0%	0.1	0%
Distillate oil			5.24	1%	4.0	0%
Industrial Processes	**160.3**	4%	**89**	18%	**68.3**	21%
Paint Use	96.5	3%	0	0%	0	0%
Electronic Lamp Breakage	27.3	1%	35.8	7%	18.8	6%
General Lab Use	10.9	0%	18.2	4%	18.5	6%
Dental Preparation & Use	13.7	0%	14.2	3%	7.66	2%
Crematoria	11.9	0%	20.8	4%	23.3	7%
TOTAL AREA SOURCES	**165.4**	4%	**94.33**	19%	**72.4**	22%
TOTAL AREA + POINT SOURCES	**3909.2**	**100%**	**492.6**	**100%**	**333.6**	100%

Totals and percentages may not add exactly due to rounding

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