

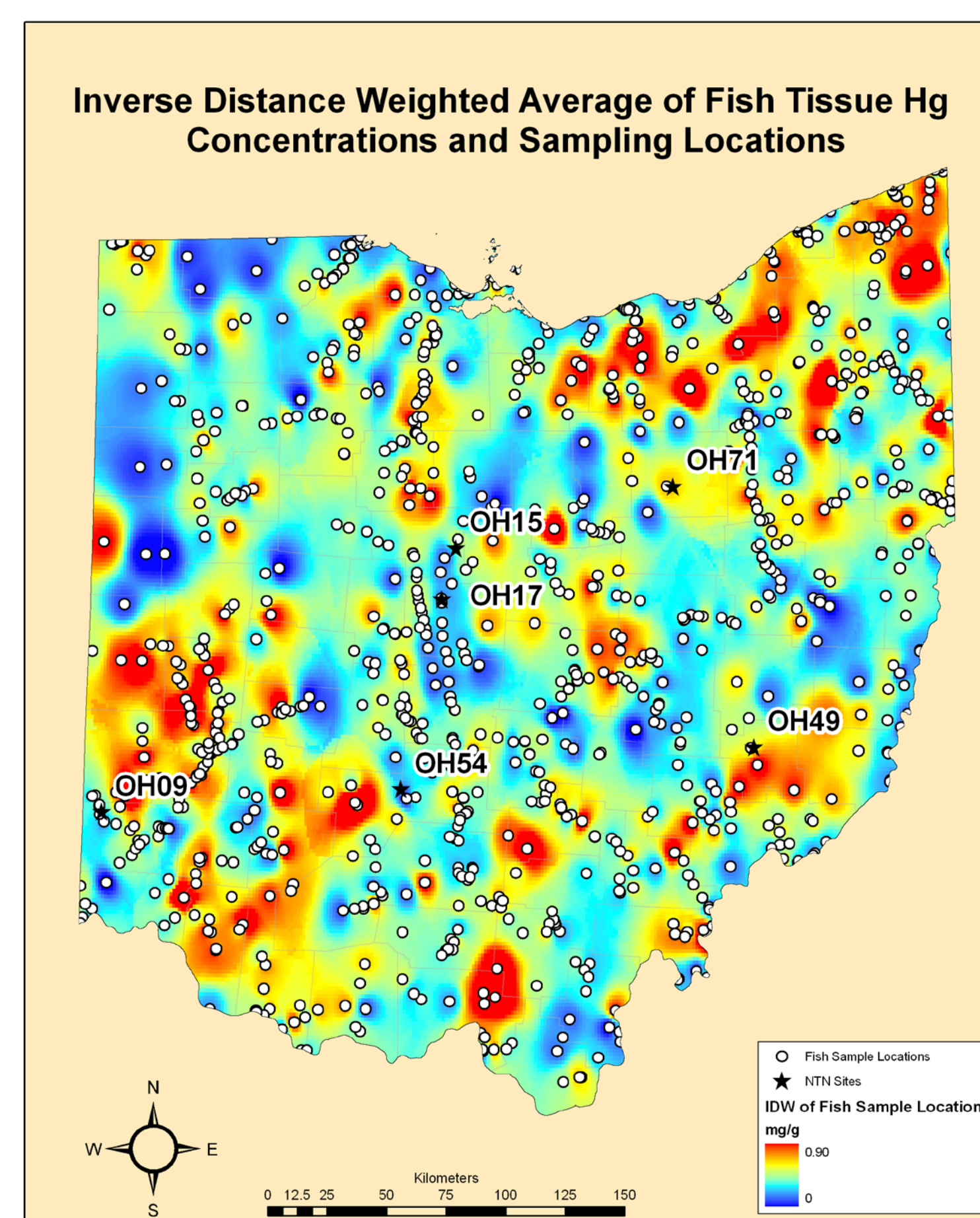
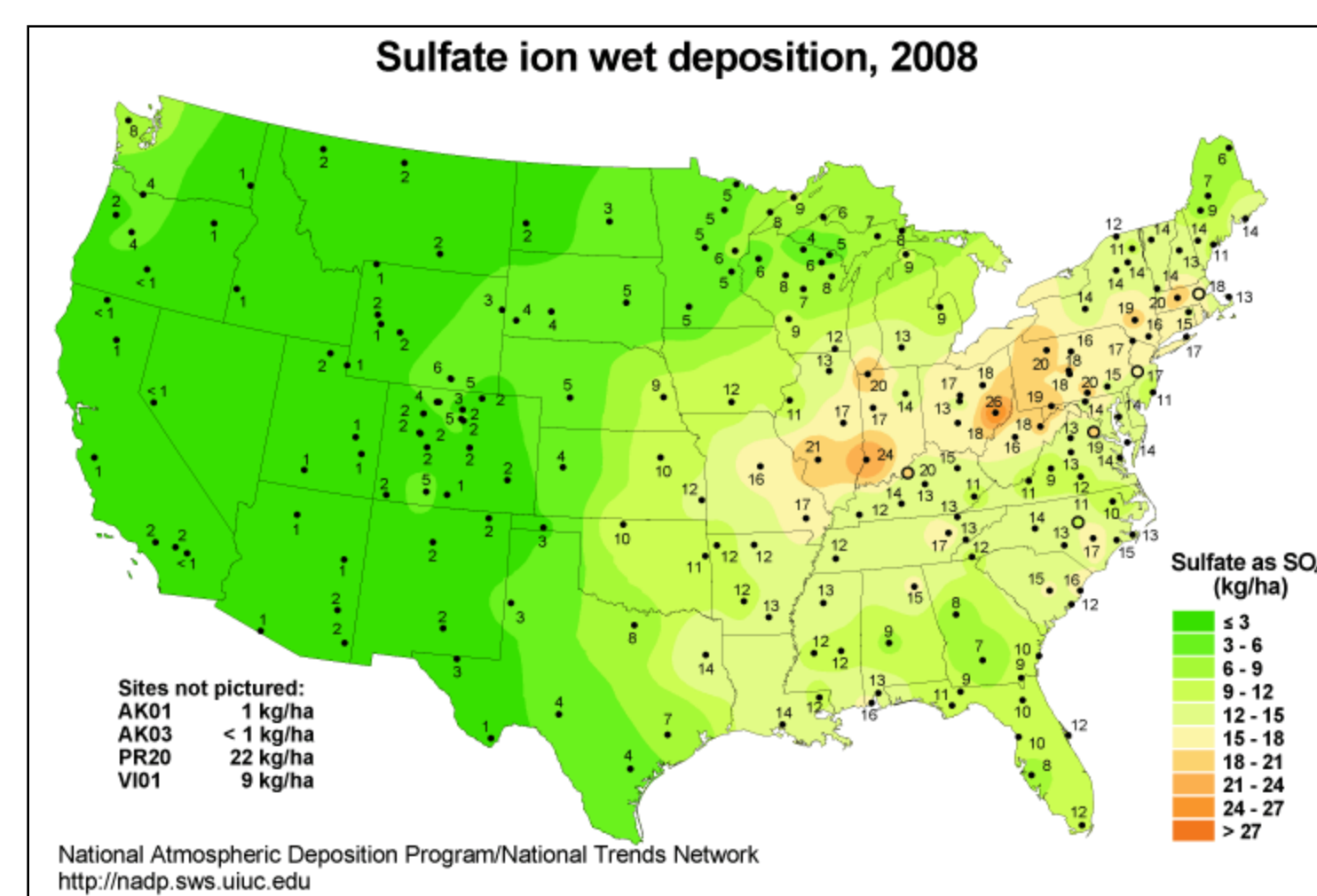
Introduction

Researchers have recently begun using spatial datasets to explore the distribution of environmental mercury and its relationship to atmospheric deposition and ecosystem processes. While spatial analysis presents numerous problems when comparing varying types of data, diverse approaches have been employed. Recent efforts have involved mapping large amounts of tissue data from both fish and loons (Evers and Clair, 2005; Kamman et al., 2005; Driscoll et al., 2007). In this meso-scale approach, tissue data were aggregated into raster cells of 50km and hot spots were identified. One recent macro-scale approach by Hammerschmidt and Fitzgerald (2006) fish tissue data, mercury deposition records, acid rainfall records, and climate data were aggregated by state political boundaries. While somewhat linear relationships were discovered to exist from state to state, some variables have only one sample within a state. Drevnick (2007) demonstrated a significant correlation between reductions in sulfate deposition and reductions in methylmercury concentrations in lake across Isle Royale NP.

This study began by addressing the underlying question inherent in all spatial analysis techniques: What is the appropriate scale? Statistical distance or inverse-distance weighted techniques depend upon an exponent to determine how much weight nearby points receive over others. In spatial aggregation, whether it is to grids, a lattice, or another physical or political units, there lies a concern that aggregating will result in the loss of variance. We decided to explore relationships that have previously been revealed concerning acid rainfall and mercury bioaccumulation, not to discover if a relationship exists, but to see how these relationships change at over varying scales. It was expected that the strength of association would increase with decreasing scale until some point that too few samples are within range.

Study Area

We decided to use the State of Ohio as our study area primarily due to the variation in sulfate deposition across the state, ample NADP data, and an extensive fish tissue dataset. Consistently, the highest deposition of sulfate and hydrogen ions of any NTN site in North America is sampled in southeast Ohio at OH49. There are six NTN sites active in Ohio that exhibit a similar spatial pattern to fish tissue collection locations. Fish tissue data were provided by the OEPA from streams and lakes across Ohio. Fish sampled between the years 1990 and 2006, inclusive, and the average annual deposition for each pollutant collected at the Ohio NTN sites during the same time period were used in this study. All fish tissue records were included that had valid lab results and were not sampled in Lake Erie, home of the top piscivores and the most significant industrial influence.



Methodology

In order to view the effect of increasing radius on the association between fish tissue and NTN records the following set of steps was followed by utilizing a python script and ESRI ArcGIS 9.3. The steps were performed on increasing radii at an interval of 5km until an upper-bound of 140 km was reached.

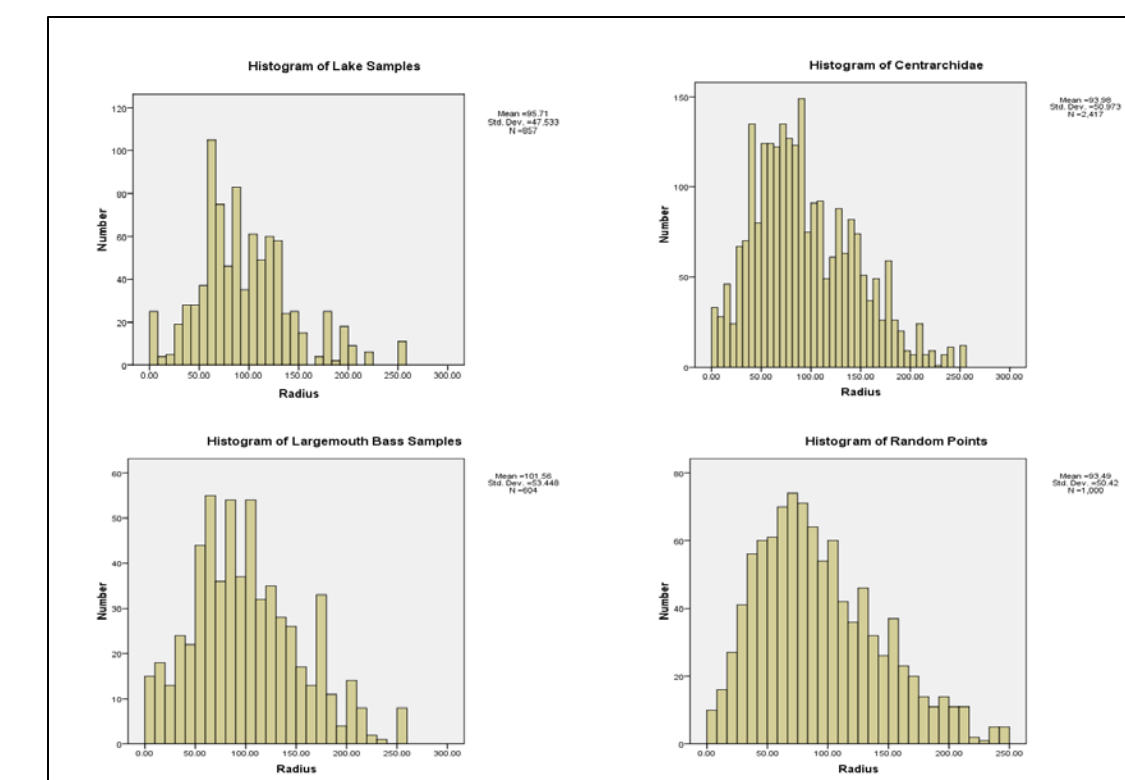


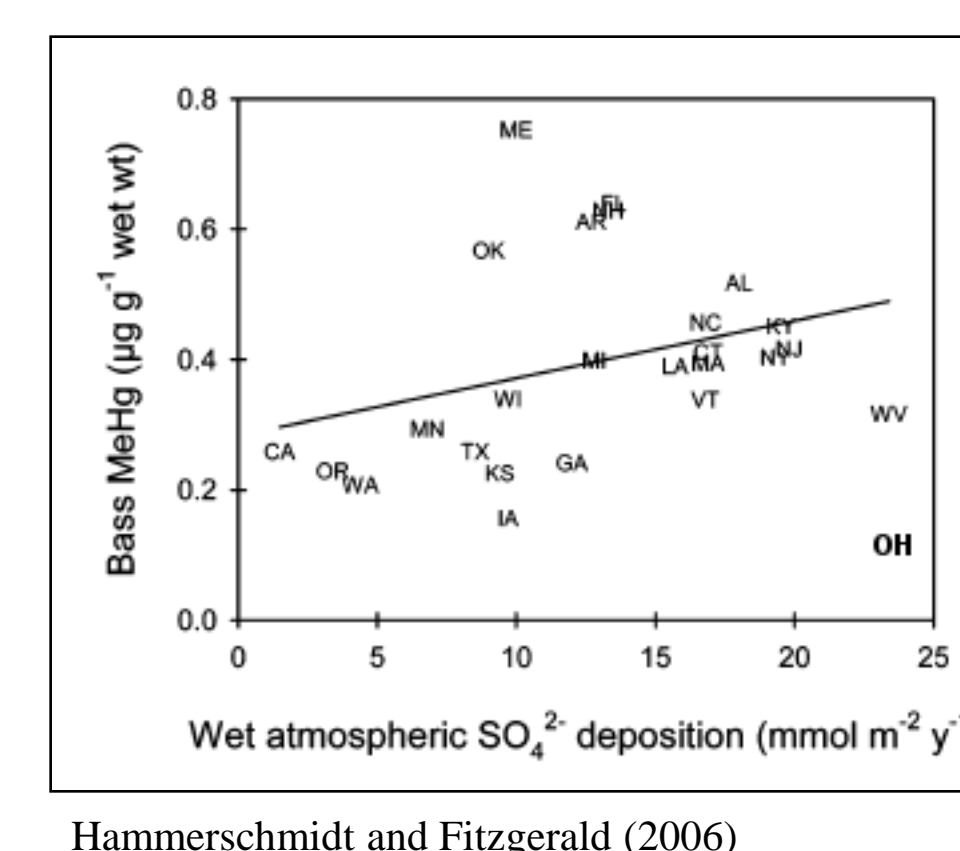
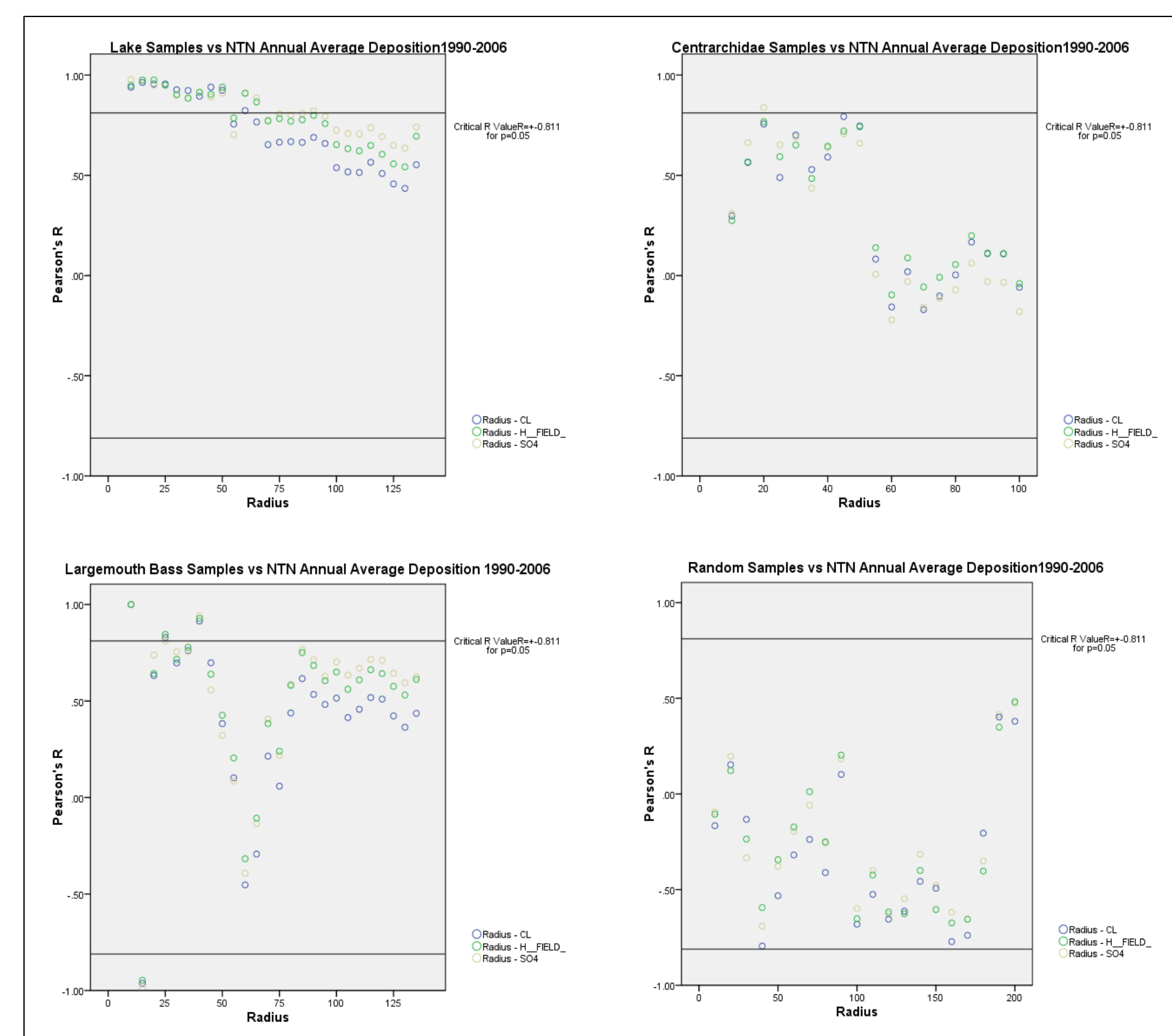
Fig 1: Number of fish samples at each radius interval from nearest NTN Site in each sub-study.

1. A random selection of fish records was made consisting of half the samples, or three fourths in the case of the lake test.
2. A buffer was drawn around each NTN site with the current radius.
3. The selected fish tissue records were spatially joined to the buffer polygons and aggregated by taking a mean value.
4. This process was repeated 100 times and a final average for each polygon was computed and recorded.
5. The process was repeated again at the next radius interval.

Following the procedure, the fish tissue concentrations were compared with NTN annual deposition averages. This was done by calculating Pearson's R for each variable at each tested radius. The results were then graphed for a visual comparison to each other. The procedure was performed using several different subsets of fish tissue concentrations. The ones included in this report are lakes only, the *Centrarchidae* family, largemouth bass, and random fish samples. The random samples were intended as a control and a test against the statistical methodology and spatial pattern of sampling.

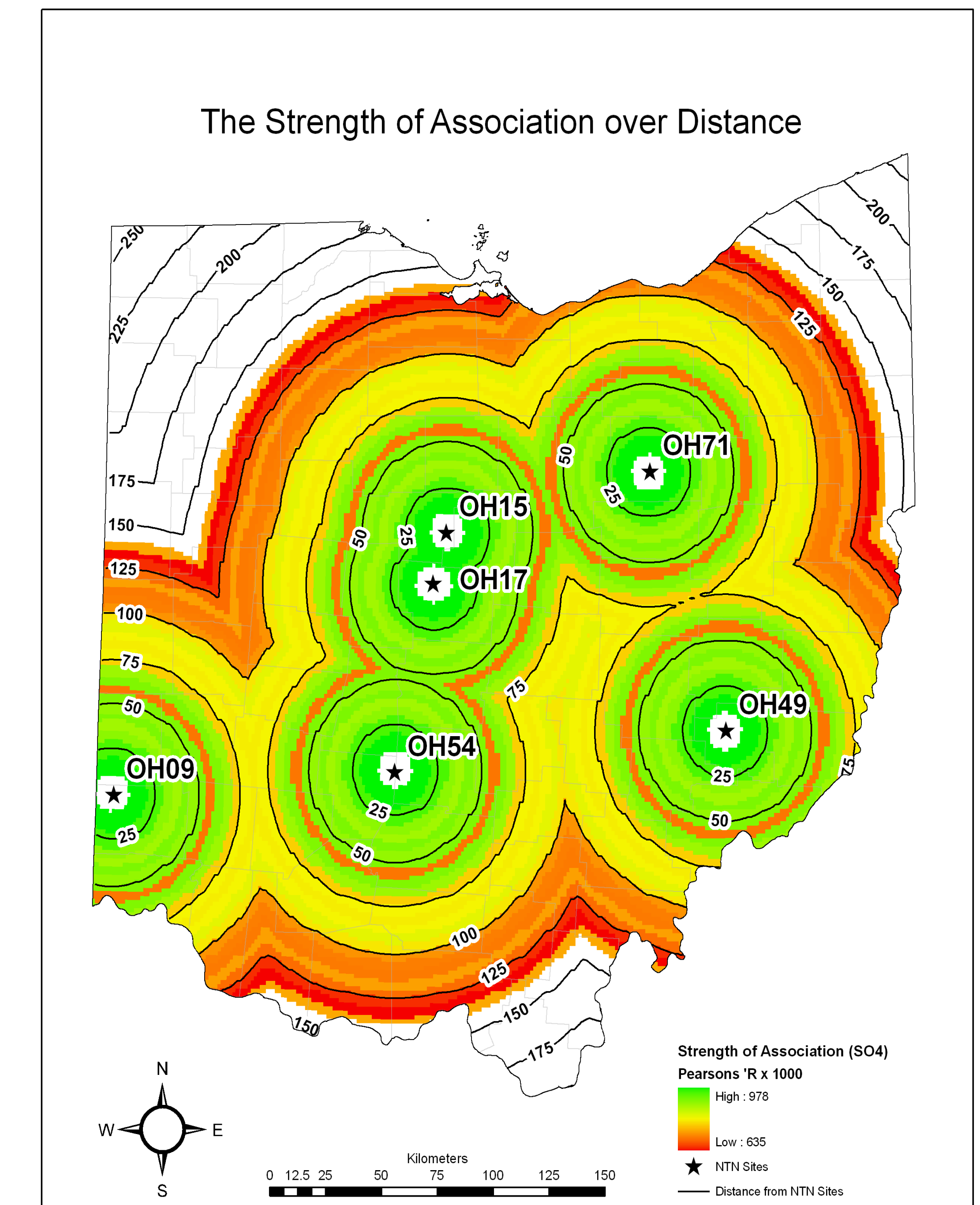
Results

Upon first glance, there is a trend in each graph with the exception of the random test. Near a radius of 50-70km the relationships suddenly diminish, observable as a drop in Pearson's R. Likewise, this is also the range where each distribution has the highest frequency of values. Most of the fish samples tend to lie at a distance of 50-70km from the nearest NTN site. Pearson's R also seems to be inversely related to radius. This is to be expected. In the case of the lake only run, results become statistically significant at 60 km and less (See map). This would imply that it is better to use distances less than 60 km when performing a similar spatial analysis technique. In comparing Ohio data to previously published relationships of this nature, Ohio falls well below the linear function of wet sulfate deposition and methylmercury concentrations in fish tissue. Hammerschmidt and Fitzgerald (2006) found no significant correlation when comparing states to one another and suggested "that wet atmospheric fluxes of sulfate may not be a major control on the net production and bioaccumulation of MeHg". These results however suggest that the scale of their approach may have been inappropriate to observe this variable relationship and that wet deposition of sulfate, hydrogen, and/or chloride ions may be a factor in MeHg bioaccumulation.



Hammerschmidt and Fitzgerald (2006)

The Strength of Association over Distance



The strength of the association at varying distances in this map was determined by calculating Pearson's R for fish at different distance to the respective NTN site. Distance was incremented by 5 km from 10 to 140 km. Fish tissue used in the creation of this map came from Lake samples from the year 1990 to 2006 and provided on behalf of the State of Ohio Fish Tissue

Conclusions

- This approach clearly demonstrates a correlation between wet deposition of SO_4^{2-} , H^+ , and Cl^- when compared to methylmercury concentrations found in Ohio sport fish
- When comparing Ohio NTN and fish MeHg data, the association remains fairly strong to about 60km and then diminishes rapidly for all datasets examined, except the random sample which showed none to begin with
- This could be a good approach, or guide to estimating fish concentrations at the meso-scale elsewhere.
- These relationships could likely be enhanced by normalizing output to Landuse/Landcover and/or watershed dynamics
- Reductions in acid rain deposition may result in a decrease in fish tissue mercury concentrations, as well as many other levels of the ecological system and decrease human risk
- These results may not be representative of other locations or ecotones

References

C. T. Driscoll, Y.-J. Han, C. Y. Chen, D. C. Evers, K. F. Lambert, T. M. Holsen, N. C. Kamman, and R. K. Munson. Mercury contamination in forest and freshwater ecosystems in the northeastern United States. *Bioscience*, 57(1), January 2007.

Paul E. Drevnick, Aaron P. Roberts, Ryan R. Otter, Chad R. Hammerschmidt, Rebecca Klaper, James T. Oris. Mercury toxicity in livers of northern pike (*Esox lucius*) from Isle Royale, USA. *Comparative Biochemistry and Physiology Part C: Toxicology & Pharmacology*, Volume 147, Issue 3, April 2008, Pages 331-338, ISSN 1532-0456, DOI: 10.1016/j.cbpc.2007.12.003.

D. C. Evers and T. A. Clair. Mercury in northeastern north America: A synthesis of existing databases. *Ecotoxicology*, 14:7-14, 2005.

C. R. Hammerschmidt and W. F. Fitzgerald. Methylmercury in freshwater fish linked to atmospheric mercury deposition. *Environmental Science and Technology*, 40(24):7764-7770, 2006.

N. C. Kamman, N. M. Burgess, C. T. Driscoll, H. A. Simonin, W. Goodale, J. Linehan, R. Estabrook, M. Hutcheson, A. Major, A. M. Scheuhammer, and D. A. Scruton. Mercury in freshwater fish of northeastern North America - a geographic perspective based on fish tissue monitoring databases. *Ecotoxicology*, 14(1-2):163-180, 2005