

Final integrated report: Establishing paired gauged watersheds at Acadia National Park for long-term research on acidic deposition, nitrogen saturation, forest health, and mercury biogeochemistry (1998-2002)

All or portions of abstract written or compiled by ACAD staff.

The following manuscripts are included in this report:

Summary: Establishing paired gauged watersheds at Acadia National Park for long-term research on acidic deposition, nitrogen saturation, forest health, and mercury biogeochemistry (1998-2002);

The following is taken from portions of the executive summary:

"This report covers the inception of long-term ecological research using two forested, gauged watersheds at Acadia National Park (Acadia NP), with initial funding from the US Environmental Protection Agency, US Geological Survey, and the National Park Service. The goal is to create a baseline of watershed data upon which to build future research. Several other research projects have already built their contributions on the infrastructure of the gauged watersheds. The major environmental stressors at Acadia NP are generally regional rather than local, in part because the park occupies the uplands of Mount Desert Island. This topographic position means that regional, and even global issues are focal issues of concern for ecosystems at Acadia NP, including long-range transport of pollutants and climate change. The focus of this research is atmospheric deposition of acids, nitrogen (N), and mercury (Hg), and their ecological consequences."

"Justification. There are many scientific and management uncertainties that led agencies to be interested in this research. At the start of this research, we lacked an explanation of the high accumulation rates of Hg in sediment and peat cores compared to wet-only deposition, and had not explained why Acadia has some of the highest Hg concentrations in biota in the world. We did not understand the changes in watershed response to the changes in atmospheric deposition in recent decades. We were not sure if N saturation was an issue for the forests, freshwaters, or estuaries of Acadia NP. Because of the regional scale of these issues, results of this research will be applicable well beyond the borders of Acadia NP. The forest types encompassed by this research are common throughout New England, and the fire history of Acadia NP (fire being 'typical' of the historical New England landscape), combine to offer unique research opportunities that apply to Acadia NP management concerns but have relevance to the region and beyond. Project design. The experimental design for this study is a paired watershed study with a reference watershed and a 'treatment' watershed that resulted from severe wildfire in 1947. Much of the Cadillac Brook Watershed burned in 1947; the Hadlock Brook watershed did not burn, and our investigations suggest that it has not experienced a major fire for hundreds of years. Although this research program is new, its design and site selection were based on watershed evaluations and modern water chemistry data from collections that began in 1982. The objectives of this research were to determine if N and Hg pools were substantively reduced in the treated watershed by the fire of 1947 and subsequent vegetation changes, such that total N and Hg biogeochemistry has been altered. By studying these hypothesized contrasts between the treated and reference watersheds, we believed we could learn about ecosystem mechanisms governing the cycling of N and Hg, ultimately leading to better predictions of future exposure to biota and overall ecosystem health. N loading to estuaries was addressed by periodic sampling of estuary tributaries as 'satellite' locations, whose N-loading will be extrapolated from occasional sampling by using the more intensively monitored main watersheds as index sites."

Summary continues from here with the following sections: general approach; the companion watersheds at Bear Brook Watershed in Maine (BBWM); Current status of watershed forests;

Paleoecological reconstructions; characteristics of soils; precipitation inputs; mercury input; watershed mass balances; nutrient loading to estuaries; mercury in soils; ongoing and upcoming research; and Management implications.

Chapter 1. Introduction: Inferring regional patterns and responses in N and Hg biogeochemistry using two sets of gauged paired-watersheds, J.S. Kahl, I. Fernandez, S. Norton, B. Wiersma, G. Jacobson, D. Manski, T. Haines, L. Rustad, C. Roman, R. Lent;

"Abstract. This project was part of long-term ecological research using two gauged-watersheds implemented at Acadia National Park through collaborative funding by the U.S. Geological Survey (USGS) and the U.S. Environmental Protection Agency. The focus of this project was atmospheric deposition of N and Hg, and their ecological consequences. Both elements are of major concern, both regionally and to the Park Service at Acadia. This location offered the advantages of a) co-funding for cost-effectiveness; b) a natural experimental design for the two watersheds because of a major forest fire in part of the Park in 1947; c) parallel design with the acidic deposition experiment on paired-watersheds at the nearby Bear Brook Watershed, Maine (BBWM); and d) prior research at Acadia and BBWM that supplied background data, and provided the basis for ecosystem indicators applied at Acadia. Our *objectives* addressed N cycling and saturation, and Hg input and bioavailability, in paired watersheds with different forest types. We used the natural landscape contrasts provided by fire to compare patterns and processes in N and Hg sequestration and mobility. N loading to estuaries was addressed by periodic sampling, implemented by USGS, of estuary tributaries as 'satellite' locations, whose N-loading was extrapolated from occasional sampling by using the more intensively monitored main watersheds as index sites. Our *approach* involved using input/output measurements at the watershed scale to define the unknowns of Hg inputs to landscapes, determine locations and processes of Hg speciation, resolve the status of N retention, and estimate N-loading to selected estuaries that have prior background data. We determined the relative input of Hg and methyl-Hg from wet deposition, throughfall and litterfall. The *results* provide new information for Acadia and for the New England region on the ecological consequences of high N deposition at Acadia, and the loading of N to estuaries in the region. We lack an explanation of the high accumulation rates of Hg in sediment and peat cores compared to wet-only deposition, and have not explained why Acadia has some of the highest Hg concentrations in biota in the world. The general representativeness of Acadia forests for the New England region, combined with the fire history to be included in our experimental design (fire also being 'typical' of the historical New England landscape), offers the opportunity to understand some key issues for Acadia, while providing insight into these issues at the regional scale."

Chapter 2. Paleoecological assessment of forest-disturbance in upper Hadlock Brook and upper Cadillac Brook watersheds. M. Schauffler, S.J. Nelson, K.B. Johnson, J.S. Kahl, G.L. Jacobson Jr.;

"Abstract. Paleoecological reconstructions of forest stand histories for two upland watersheds at Acadia National Park in Maine (in conjunction with related watershed chemistry studies) support the hypothesis that forest type and fire history influence long-term cycling and storage of atmospheric mercury and nitrogen within watersheds. The reconstructions document major vegetation and disturbance differences in upper Hadlock Brook and upper Cadillac Brook watershed forests during the last several centuries, and allow investigators to compare the processing of these elements in the two different settings. Pollen and charcoal stratigraphies from organic sediment accumulations from forested wet depressions in the two watersheds indicate that the two watersheds have contrasting histories of vegetation and disturbance during recent centuries. Hadlock Brook watershed has been dominated by spruce (*Picea rubens*) and fir (*Abies balsamea*) for 500 years or more and has not recently burned or been substantially cleared. Cadillac Brook watershed is dominated by a heterogeneous forest of patchy hardwood, mixed wood, and softwood stands. A large portion of the Cadillac Brook watershed

burned severely in 1947 and possibly in the 1800s, and has supported heterogeneous successional forests for two hundred years or longer."

Chapter 3. Baseline Forest Vegetation Monitoring in Acadia National Park. J.D. Eckhoff, G.B. Wiersma, J.A. Elvir;

"Abstract. This report provides baseline information for long-term forest vegetation monitoring in the deciduous and coniferous forests in Cadillac Brook and Hadlock Brook watersheds. USDA Forest Service Forest Health Monitoring (FHM) program indicators were used at Acadia, including forest mensuration, crown condition classification, and damage and mortality indicators. Foliar chemical analyses were also performed, to determine if there were significant differences in foliar chemistry between the two watersheds for either of two indicator tree species. This report also presents a comparison of the results of the foliar chemical analyses from Acadia with reported foliar chemical analyses results from BBWM."

Chapter 4. Determining atmospheric deposition inputs with partial record data, Acadia National Park, Maine, USA. S J. Nelson, J. S. Kahl, I.J. Fernandez, C.S. Cronan, A. White, K.C. Weathers;

"Abstract. Two small upland watersheds, Cadillac Brook and Hadlock Brook, have been gauged and monitored at Acadia National Park since 1998. Cadillac Brook watershed burned in a wildfire in 1947. Hadlock Brook watershed has been undisturbed for several centuries, and serves as the reference site. Precipitation and throughfall volume and chemistry data have been collected using wet-only and continuously open collectors. Hydrologic and chemical inputs to the sites have been determined for each site. Differences in watershed and vegetation characteristics control the input of water and major ions to these watersheds. Vegetation type was the dominant control on enhancement of precipitation across the heterogeneous watersheds. Relative annual enhancement of throughfall over wet-only deposition for coniferous stands at Hadlock was 2.0 for NH_4 and NO_3 ; 2.7 for SO_4 ; 7.1 and 7.3 for Cl and Na, respectively; 6.8 for Ca; 92 for Mg; and 58 for K. Enhancement was similar for mixed coniferous and deciduous stands, intermediate for deciduous stands, and lowest (except Cl and Na) at scrub and open sites. At Cadillac, enhancement was slightly lower for each ion, but the same pattern, coniferous > mixed > deciduous > scrub/open, was observed. Seasonal differences were important, with highest throughfall deposition in fall and summer; however, wet deposition inputs of Cl and Na were highest in winter. Because we were unable to collect winter throughfall, relationships between NADP and throughfall data in the non-freezing seasons were used to scale up NADP concentrations when throughfall data were not available."

Chapter 5. Fire and its effects on Mercury and Methylmercury inputs for two watersheds in Acadia National Park, Maine. K.B. Johnson, T.A. Haines, J.S. Kahl, S.A. Norton, A. Amirbahman;

"Abstract. Precipitation and litterfall samples were collected for two gauged watersheds at Acadia National Park, Maine, during the period between 17 November 1999 and 16 November 2000, to determine which landscape factors affected mercury (Hg) deposition and export. One of the watersheds, Cadillac Brook, burned in 1947, providing a natural experimental design to study the effects of fire on metal deposition to, cycling within, and export from forested catchments. Hg and methylmercury (MeHg) deposition and export were quantified in order to develop budgets for each watershed. Site aspect and differing vegetation type were the most influential factors affecting Hg deposition to these watersheds. Sites that face south to southwest received the highest Hg deposition, which may be due to the interception of cross-continental movement of contaminated air masses and prevailing wind direction. Sites covered with softwood vegetation also received higher Hg deposition than other vegetation types because of the higher scavenging efficiency of the canopy structure. MeHg deposition was not affected by these factors. Hg deposition was lower in Cadillac Brook watershed (burned) than in Hadlock Brook watershed (unburned) because regeneration after the fire was

dominated by mixed hardwood, whereas softwoods dominate the landscape in Hadlock Brook watershed. The lower deposition could also be a result of the watershed aspect; Cadillac Brook watershed faces southeast to east and Hadlock Brook watershed faces south to southwest. The 1947 fire that burned Cadillac Brook watershed likely removed organic material from the soil through combustion and subsequent erosion. Much of the Hg in the remaining organic material would have been volatilized by the elevated temperature caused by the fire, breaking the chemical bonds between Hg and DOC releasing the Hg, possibly enhancing the soil's ability to sequester Hg more efficiently. As a result, Cadillac Brook exports less Hg from its watershed than Hadlock Brook, which has unburned soils containing more organic material. Hadlock Brook exports more MeHg, but export cannot be explained by inputs and may be controlled by production in peat and other organic-rich materials in the riparian zone. Hg and MeHg inputs were weighted by season and vegetation type for budget determination because these two factors had the most influence on deposition. Hg volatilization from soils, water, and vegetation surfaces was ignored because of the difficulties associated with analyzing gaseous Hg. Litter contributed two to five times the Hg to the forest floor as precipitation. Cadillac Brook watershed received 57.1 $\mu\text{g}/\text{m}^2/\text{year}$ of Hg from litter while Hadlock received 29.0 $\mu\text{g}/\text{m}^2/\text{year}$ of Hg, demonstrating that litterfall is a major Hg pathway to the forest floor. The residence time of the Hg from litter and the ultimate fate of the litter itself are unknown."

Chapter 6. Mercury and major ion streamwater chemistry at Acadia National Park. K.B.

Johnson, S.J. Nelson, J.S. Kahl, T.A. Haines, J. Peckenham;

"Abstract. Streamwater samples were collected at the outlet of each of two gauged watersheds at Acadia National Park, Maine, during the period between 17 November 1999 and 16 November 2000, to determine the relative patterns of export for mercury (Hg), methylmercury (MeHg), and nitrogen (N) in streamwater. Cadillac Brook watershed burned in 1947, providing a natural experimental design to study the effects of fire on metal and nutrient deposition, cycling, and export for these forested catchments. We hypothesized that Hg and N export would be lower from Cadillac Brook watershed because: 1) the soil pool of Hg was depleted by the fire allowing the remaining soil to retain more Hg, and 2) regenerating vegetation in the burned watersheds would consume more N than the unburned, more mature watershed. Cadillac Brook streamwater concentrations of Hg and N were consistently lower than in Hadlock Brook. Cadillac Brook (burned) Hg concentrations averaged 0.6 ng/L while Hadlock averaged 1.5 ng/L. Hg and DOC correlated well with stream discharge. As discharge increased, Hg and DOC increased and were well correlated with each other (linear regression: Cadillac $R^2 = 0.53$, $p < 0.05$, Hadlock $R^2 = 0.71$, $p < 0.01$). The relationship between Hg and DOC is supported by other research in the northeast (Scherbatskoy *et al.*, 1998). The strong correlation may signify that mercury moves as part of an organo-metallic complex and its transport warrants further investigation. MeHg concentrations in streamwater were not correlated with precipitation volume, corresponding DOC concentrations, or stream discharge. Higher concentrations of MeHg were observed in Hadlock Brook during spring, which agrees with observations by Lee *et al.* (2000). NO_3 concentration in Cadillac Brook averaged $0.5 \mu\text{eq}/\text{L}$ while Hadlock averaged $6.5 \mu\text{eq}/\text{L}$. These average NO_3 concentrations support the hypothesis that Acadia data and Bear Brook (BBWM) data constitute a gradient of NO_3 concentrations, with East Bear brook NO_3 concentration averaging $1.3 \mu\text{eq}/\text{L}$ and West Bear brook (added ammonium sulfate) averaging $38.6 \mu\text{eq}/\text{L}$. BBWM has the advantage of ongoing experimental manipulations that cannot be done at Acadia."

Chapter 7. Mercury and nitrogen dynamics in paired watersheds at Acadia National Park, Maine, USA. J.S. Kahl, S.J. Nelson, T.A. Haines, K.B. Johnson;

"Abstract. Elemental stream flux was calculated using discharge data from the U. S. Geological Survey, combined with periodic water chemistry data, for paired watersheds at Acadia National Park. The chemical mass balance in the watersheds was determined from wet plus dry inputs minus stream

outputs, where negative values indicate retention within the watershed. At Cadillac and Hadlock, H₂, Mg, K, NH₄, NO₃, and Hg are retained; Ca and SO₄ are lost. Retention of DIN (NO₃ plus NH₄) was 96% at Cadillac (burned watershed) and 72% at Hadlock (undisturbed watershed), indicating that differences related to vegetation and/or soils controlling the relative patterns of retention and release. The Hg budget for Cadillac Brook watershed was 9.4 g/m²/year (input) – 0.4 g/m²/year (export) = 9.0 g/m²/year, or 95% of the total Hg deposited on Cadillac Brook watershed was retained by the watershed. The Hg budget for Hadlock Brook watershed was 10.2 g/m²/year (input) – 1.3 g/m²/year (output) = 8.9 g/m²/year, or 87% of the total Hg deposited on Hadlock Brook watershed was retained by the watershed. The MeHg budget for Cadillac Brook watershed was 0.05 g/m²/year (input) – 0.04 g/m²/year (output) = 0.01 g/m²/year, or 25% of the MeHg deposited was retained by the watershed. The MeHg budget for Hadlock Brook watershed was 0.10 g/m²/year (in) – 0.06 g/m²/year (out) = 0.04 g/m²/year, 39% of MeHg deposited was retained by the watershed. MeHg export appears to be controlled by soil processes in the riparian zone rendering a “MeHg budget” an inaccurate portrayal of MeHg dynamics in these watersheds. We do not believe that there is any relationship between MeHg deposited from the atmosphere and MeHg in streamwater due to the transformations of Hg in soils and wetlands.”

Chapter 8. Twenty years of surface water chemistry: how does Acadia fit into the regional response? J.S. Kahl, S. Nelson, J. Stoddard, S. Norton, T. Haines, B. Breen, B. Gawley;

"Abstract. Surface water chemistry in the northeastern U.S. has changed significantly as a result of changes in atmospheric deposition during the past 20 years. During 1990-2000, sulfate concentrations in deposition declined significantly at a rate between -0.75 and -1.5 $\mu\text{eq/L/year}$. Nitrogen concentrations (nitrate + ammonium) declined slightly. Base cations in deposition have not changed significantly. These changes in deposition are a continuation of trends occurring for more than 20 years. In response to the changes in deposition, sulfate concentrations in sensitive Maine lakes have declined by 10 to 25% since 1982, in part due to the 1995 implementation of Phase I controls of the Clean Air Act Amendments and in part to other long-term pollution reduction efforts. Sulfate in surface waters of Acadia NP declined 10%, the low end of the range in the region, perhaps because of the input of sulfate from marine aerosols. The expectation for reductions in sulfate was a parallel reduction in lake acidity. However, the slight trend toward decreased lake acidity seen in the 1980s in Maine has slowed or reversed in the 1990s. As a group, lakes at Acadia show a slight decrease in acidity. The reason for the lack of recovery in the region is the simultaneous decline in base cation concentrations that are a by-product of alkalinity generation, e.g. calcium (Ca), magnesium (Mg). At Acadia, the decline in the sum of Ca + Mg was 14%. The decline in base cations appears to be related to several interacting factors: continued high atmospheric deposition of nitrogen, a lag time in response, or the inter-related influence of climate and acidic deposition on watershed response. Freshwaters at Acadia National Park may hold a key to understanding the regional response in base cations, because deposition of base cations from the atmosphere is very high in this island environment, compared to other regions with long-term water chemistry data."

Chapter 9. Hydrologic, chemical, and landscape controls on Mercury in streams on Mount Desert Island. J.M. Peckenham, S.J. Nelson, K.B. Johnson, J.S. Kahl, M.S. Bank, C.S. Loftin;

"Abstract. Fall and spring streamwater samples were collected at 52 locations on Mount Desert Island in Maine. Samples were collected in zones that were burned in wildfire in 1947 and in zones that were not burned. Samples were analyzed for total mercury (Hg) and major ions. We hypothesized that Hg concentrations would be higher in unburned sites than burned sites. Although results were not statistically significant, the mean concentration in streamwater collected at burned sites (1.48 ng/L) was lower than at unburned sites (1.69 ng/L). Two-lined salamanders (*Eurycea bislineata*) collected in streams throughout Acadia contained higher levels of total Hg in samples from streams in unburned

regions of the park than in watersheds within the fire perimeter. Cadillac and Hadlock Brooks, intensively monitored streams that are part of PRIMENet research, were sampled for this study and supported the pattern of lower Hg in burned sites. An evaluation of alternate sampling sites on the two PRIMENet streams showed that: 1) Hg was higher in the unburned, mature upper section of Cadillac Brook watershed (Summit), and 2) Hg was higher in upper portions of Hadlock Brook watershed, where the stream is fed by wetlands. Further research is necessary to determine the contribution of sub-catchment landscape features to export of Hg further downstream."

Appendix A. Papers published and submitted;

Appendix B. Project funding report;

Appendix C. Presentations and abstracts;

Appendix D. Graduate theses;

Appendix E. News Stories, Press Releases, and Public Interest Articles;

Appendix F. Project Data, Calculated Fluxes, and Site Data;

Appendix G. Quality Assurance Project Plan;