

CLOUD WATER CHEMISTRY AND MERCURY DEPOSITION IN A HIGH ELEVATION SPRUCE FIR FOREST

In Partial Fulfillment of the Requirements
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During 1997 and 1998, Sean Lawson carried out much of his research for his Masters degree in Forestry. Tim Scherbatskoy (UVM School of Natural Resources) served as his thesis advisor. This research was carried out in cooperation with the Vermont Monitoring Cooperative (VMC) within the VMC study area on the western slope of Mt. Mansfield, specifically in the summit area to the west of the radio and television transmitter facilities. What follows are the abstract of this thesis and relevant figures that show some of the key findings of this research. A copy of his entire thesis can be obtained from the UVM Libraries or from the VMC data library .

Cloud Water Deposition and Throughfall Chemistry in a High Elevation Spruce-Fir Forest at Mt. Mansfield, Vermont.

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As part of the Lake Champlain Basin watershed study of mercury (Hg) and pollutant deposition, cloud water and cloud throughfall collections were conducted at the south summit (1204m) of Mt. Mansfield, Vermont between August 10 and October 16, 1998, for multi-element chemical analysis. A passive strand-type Teflon collector was deployed during non-precipitating events to sample cloud/fog water at timberline, while three sets of paired funnels collected cloud throughfall under the red spruce-balsam fir canopy. Samples were analyzed for pH, conductivity, and concentrations of Hg, major ions (Ca^{2+} , K^+ , Mg^{2+} , Na^+ , Cl^- , NO_3^- , SO_4^- , NH_4^+), and 28 trace elements. Ultra-clean sampling and analysis techniques were utilized throughout the study.

Six events were sampled for cloud water alone and four events were sampled for both cloud water and cloud throughfall. Cloud water pH values were highly acidic, with a volume-weighted mean of 3.0 and a range of 2.1 to 4.4. Cloud throughfall chemistry showed substantial modification with a mean increase in pH

of 1.2 units. Much higher concentrations of Hg (2.3x), base cations (Ca²⁺, K⁺, Mg²⁺; 3-18x) and certain trace metals (Al, Ni, Cu, Mn, Rb, Sr; 2-34x) were observed in throughfall than in cloud water. These results suggest that despite recent reductions in S inputs to the atmosphere, cloud water remains highly acidic and can leach important nutrients from tree foliage. Cloud water deposited an average of 0.42 ± 0.12 mm H₂O hr⁻¹ and a total of 279 ng m⁻² Hg to the forest floor during three non-precipitating cloud events. Estimated cloud water deposition of Hg was 7.4 mg m⁻² for the period August 1 - October 31. Cloud events likely deposit significant annual amounts of water, mercury, and other pollutants to the high elevation ecosystem at Mt. Mansfield.

Table 1 - Estimated annual cloud water deposition at mountain locations in the northeastern United States.

Site	Elevation (meters)	Year	Cloud H ₂ O (cm yr ⁻¹)	Cloud (%) frequency	Reference
Mt. Mansfield, V	1204	1998	92 p 26 ^a	25 ^b	Lawson et al. (1999)
Whiteface Mt., NY	1225	1986-90	81.1	23	Miller et al. (1993a)
Mt. Moosilauke, NH	1220	1990	40.5		Schaefer and Reiners (1990)
Mt. Moosilauke, NH	1220	1980-81	84.0	40	Lovett et al. (1982)
Madonna Mt., VT	1110	1980-81	154.0	--	Scherbatskoy and Bliss (1984)
Camels Hump, VT	1110	1970	76.0		Leedy (1972)
Whiteface Mt., NY	1050	1986-89	28.4	10	Miller et al. (1993b)
Whiteface Mt., NY	1350	1986-89	153.5	36	Miner et al. (1993a)
Whiteface Mt., NY	1483	1987	127.0	42	Mohnen (1988)

- a. Annual cloud water deposition estimated in this study from three non-precipitating cloud events, where mean cloud water input was measured at 0.42 ± 0.12 mm hr⁻¹ and extrapolated to annual basis using cloud frequency.
- b. Cloud frequency estimate based on lower limit of visual and meteorological observations at Mt. Mansfield summit station (NCDC, 1999).

Table 2 - Mean concentrations (volume-weighted) of trace metals in four paired cloud water and throughfall collections at Mt. Mansfield, Vermont.

<u>Element ($\mu\text{g L}^{-1}$)</u>	<u>Al</u>	<u>Cr</u>	<u>Mn</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>	<u>As</u>	<u>Rb</u>	<u>Sr</u>	<u>Cd</u>	<u>Pb</u>
<u>Cloudwater (n=9)</u>											
Mean	7.92	0.09	1.73	0.24	0.51	5.52	0.13	0.07	0.30	0.03	0.58
Std. dev.	31.60	0.19	5.33	0.58		12.08	6.82	0.34	1.42	0.16	2.56
Median	6.82	0.10	1.52	0.24	0.56	4.06	0.18	0.13	0.51	0.03	0.93
Maximum	101.31	0.63	7.30	1.90	3.64	30.27	2.12	1.08	4.61	0.52	8.17
Minimum	2.01	0.01	0.29	0.05	0.12	0.68	0.04	0.03	0.04	0.01	0.11
<u>Throughfall (n=10)</u>											
Mean	17.32	0.11	40.93	0.64	0.99	6.91	0.18	2.53	1.18	0.07	0.76
Std. dev.	13.79	0.08	52.30	0.57	0.36	6.76	0.12	3.14	1.73	0.09	0.49
Median	15.94	0.13	50.66	0.64	1.03	3.74	0.13	2.06	0.53	0.04	0.62
Maximum	55.58	0.23	172.14	2.11	1.61	23.94	0.39	10.26	4.62	0.27	1.54
Minimum	7.10	0.00	4.98	0.26	0.54	2.94	0.07	0.52	0.17	0.01	0.27
Net throughfall	9.40	0.02	39.20	0.40	0.48	.39	0.05	2.46	0.88	0.05	0.18
Enrichment factor ^a	2.2	1.2	23.7	2.7	1.9	1.3	1.4	38.3	4.0	3.0	1.3

a. Enrichment factor calculated as mean throughfall divided by mean cloud water

Table 3 - Mean (volume-weighted) mercury concentrations in three paired cloud water (CW) and throughfall (TF) collections at Mt. Mansfield, Vermont.

<u>Hg (ng L^{-1})</u>	<u>Paired collections</u>	
	<u>Cloud water (n=7)</u>	<u>Throughfall (n=9)</u>
Mean	7.51	17.49
Std. Dev	2.73	6.62
Median	6.18	16.47
Maximum	11.81	33.30
Minimum	3.74	9.95
Net Throughfall (TF-CW)		9.97
Enrichment factor (TF/CW)		2.3

Table 4 - Mean Hg concentrations and estimated deposition in four paired cloud water and cloud throughfall (TF) collections at Mt. Mansfield, Vermont.

	Date	8/18	8/26	9/10	10/1*	Total	Units
Hg Concentration	Throughfall	15.02	*	13.47	19.58		
	Cloud	7.52	33.9	*	4.83		ng L ⁻¹
	Net Throughfall	7.50	*	1.66	14.75		
Hg Deposition	Cloud ^b	37.12	31.67	19.32	37.21	125.32	
	Net throughfall ^c	37.03	*	2.71	113.79	153.53	ng m ⁻²
	Total	74.15	31.67	22.03	151.00	278.85	
Cloud Deposition Rates	Hg	3.91	9.74	3.86	6.47		ng m ⁻² hr ⁻¹
	Water	0.52	0.29	0.33	1.34 ^a		mm h ⁻¹

Cloud event on 10:1 contained some precipitation in brief showers which could not be excluded from collection. All data for 10/1 reflects cloud + precipitation.

Hg deposition calculated as mean cloud Hg concentration x mean TF volume and does not account for evaporation or retention of water in the canopy, and thus underestimates total deposition.

- c. Net throughfall deposition calculated as difference of cloud and total throughfall deposition,
- * Volume obtained in 8/26 throughfall sample (17ml) too small for Hg analysis.

Table 5 - Cloud water and throughfall deposition of trace metals to the forest floor during four cloud events and estimated deposition of cloud water for the three month period (August 1 - October 31, 1998) at Mt. Mansfield, Vermont.

	Al	Cr	Mn	Ni	Cu	Zn	As	Rh	Sr	Cd	Pb
Cloud water	107.26	1.49	30.58	2.95	8.24	90.50	4.42	1.55	6.49	0.54	9.89
Net throughfall	181.12	0.35	662.93	7.49	7.12	4.18	-1.65	40.34	12.55	0.60	1.77
Total throughfall	288.38	1.84	693.51	10.44	15.36	94.68	2.77	41.89	19.04	1.14	11.66
Estimated cloudwater deposition (mg m ⁻¹) (August 1 - October 31, 1998)	4.18	0.05	1.04	0.20	0.55	5.49	0.19	0.07	0.27	0.05	0.82