Fog Studies In The Bay Of Fundy Over A Span Of 60 Years

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Abstract: This paper reviews various studies made of fog water samples collected on Bowdoin College's Kent Island Scientific Station, noting the changing reasons for making these collections. The first study might be labeled as supporting a basic cloud physics goal: what are the important cloud condensation nuclei? In 1938 and 1939 twenty-three samples were collected which showed the important presence of the SO_4 ion even in these apparently marine fogs. In 1983 & 1984 the same nickel screen used 47 years before was reinstalled. Fifty-one samples were collected and analyzed for six ions. This time the driving interest was an applied one, the interest in detecting a change in sulfate ion content (and pH) from, presumably, anthropogenic sources. The average non-maritime SO_4 content in '38 & '39 was 128 μeq/l increasing to 307μeq/l in '83 & '84. The scatter of the values and results from later summers through 1996 are discussed. Most of the trajectories for the samples with the highest non-marine SO_4 passed over or near to urban centers. Generally, those with the lowest values had a maritime track. In recent years, 1987 to the present, our fog studies have been in support of problems of interest to the forestry research community. Beginning in 1993, these fog studies shifted from looking at long term average conditions (3 to 6 hours) to a pH sample every 10 minutes taken from a 15 ml volume. Some interesting acid fog plumes have been detected, one reaching a minimum pH of 2.9. It may be that highly acid fogs are of short duration, a possibility that should be included in both the design of a collecting program and in considering effects on vegetation.

1. INTRODUCTION

While most summer research activities at the Bowdoin Kent Island Scientific Station have been related to the large bird populations, the author has taken advantage of the high frequency of fog occurrence. The large bird populations are, in fact, no help. Dense fog occurs in July, on average, some 19 days. This narrow Canadian island, 3km long by 300 meters wide at the fog collection site, lies in the middle of the entrance to the Bay of Fundy, halfway between Eastport, Maine and the Nova Scotia coast. Its location on most of the foggy days is downwind either from the open ocean to the SE - SW or from the highly industrialized northeastern United States 300 to 400 km. to the W - SW. There are a few fogs that pass Kent Island in a SW flow and then, after a weak cold front passage, return in a NE flow down the bay from the urban area along the New Brunswick coast.

2. HISTORY AND RESULTS

2.1 1938, 1939

During 1938, the first summer of fog studies, the author built a $1m^2$ copper screen collector held perpendicular to the wind by a large vane. In 1939, Prof. Houghton of MIT loaned the author a $1m^2$ Nickel screen. The important presence of the SO_4 ion was demonstrated even in the marine location of Kent Island. It is shown by the results of the analysis of 23 samples from '38 and '39 where a majority (12) contained more marine-corrected SO_4 ion (xSO_4) than Cl ion. Back trajectories were computed for the 1939 samples and a marked difference was found in the chloride content. The values were higher for air that traveled over some warm ocean water (> 18°C) than air that only passed over cold water (Cunningham 1940). This relation has not been found for later samples. Measured pH values averaged 7.2, a questionable value, but understood better in later years

2.2 1983, 1984

By 1983, interest in the chemistry of fog water had been revived due to the increase in the anthropogenic sources and the resulting increase of pollutants downwind (in our case, xSO_4 NO_3 NH_4 and H+ ions in fog). Peter Summers (AES) and the author arranged for the re-installation of the simple nickel screen fog collector from its long storage on the island and for the analysis of the fog water samples by H. Samant of the Canadian EPS. The samples were analyzed for pH, alkalinity, acidity, conductivity as well as nitrite, nitrate, sulfate, chloride, and ammonia. Back trajectory analyses were also run. The program for drawing these back tracks was developed and run at AES Downsview. The results of the measurements, analysis and trajectory calculations for the three years 1939,1983 and 1984 are shown in Table 1. The pH values measured before 1988 are incorrect so that a computed value is shown. It was derived by a method discussed in section 2.3.

Table 1 Kent Island Fog Chemistry for Three Years and Three Trajectory Sources

YEAR	Source	# Samp	Cl	NO_3	NH_4	xSO_4	computed H+	computed pH
1939	OCEAN	6	371	--	--	116	88	4.06
	URBAN	5	151	--	--	127	99	4.00
	RURAL	7	47	--	--	110	82	4.09
1983	OCEAN	8	461	60	--	163	137	3.86
	URBAN	5	382	224	--	397	380	3.42
	RURAL	7	176	44	--	265	243	3.61
1984	OCEAN	16	661	99	91	187	162	3.79
	URBAN	6	288	114	130	361	343	3.47
	RURAL	6	180	171	132	594	585	3.23

Conversion of xSO_4 to average pH based on 1988 and 1989 data. Units of ionic concentration in μeq/l

The OCEAN back trajectory is defined as a path that is over the open ocean for at least the last four days, URBAN back trajectory must have left the east coast from Portland ME down to just north of Cape Hatteras, NC within the last four days, while RURAL are those that pass over some other land mass within the most recent four days. It should be noted that RURAL includes the urban cities of St. John and Halifax. The trajectories for several samples that trace over St. John show high SO_4 content. The chloride content as one would expect is larger for the OCEAN trajectories. Note that the SO_4 values are about the same for all three classes in 1939 but are much higher in the RURAL AND URBAN classes in '83 and '84. The increase in the SO_4 content for the OCEAN class from 1939 to '83 '84 is not significant statistically but the SO_4 increase by nearly a factor of four for the URBAN and RURAL classes combined is. The pH values follow the SO_4 history, in this case by definition, decreasing from 4.1 to 3.4. A second way to illustrate the effects of trajectory path on the chemical content of fog has some advantages. The data was separated into two groups, 1/3 with the highest SO_4 content and 1/3 with the lowest. Two maps were drawn showing the trajectories for these two cases. The difference between an ocean and non-ocean trajectory "source" was obvious. The cases that should be followed up with further study were also apparent. The path in one case in the low SO_4 group traveled directly over the city of Boston.

2.3 1987, 1988.

In 1987, a long association began with Dr. Jagels at the Forest Biology Dept of the University of Maine and his acid fog program along the coast of Maine. Kent Island became the furthest east of his string of from six to eight stations. This time the interest in acid fog was based on a forestry problem, the dieback of Red Spruce (Jagels *et al.* 1989). On Kent Island, this program meant first resolving the suspected problem with the nickel collector. As mentioned and discussed by Houghton (1955), the pH readings from the Kent Island screen were a puzzle, the mean value found was a pH of 7.2. Later values found through 1987 were also high. Three large passive screens (Nickel, SS, and Teflon) were installed plus one much smaller active Teflon collector identical to the other collectors of the Maine group (Daube et al 1987). Laboratory tests (Jagels *et al.* 1989) and the analyzed results from a summer's field tests confirmed that the nickel screen pH values were too high (probably due to corrosion). Field tests showed the values for most of the other ions were in reasonable agreement. Table 2 lists the results of these comparisons.

Table 2 Fog Water Collector Comparison

Screen Name	Count	pH+	H+	pH from avg. H+	NH_4	NO_3	Cl	SO_4	xSO_4	Ion Bal Ratio
Ni	18	4.51	83	4.08	114	141	204	263	241	0.75
SS	18	4.02	224	3.65	118	143	210	252	230	0.99
Teflon	18	4.04	181	3.74	97	119	167	203	186	1.01
Active	18	3.96	245	3.61	161	148	222	323	300	1.02

The Teflon screen was made up of many long (1.2 meter) Teflon strings, held vertically but unsupported horizontally, that sang in the wind. The vibrations may have caused some selective drop separation, a possible explanation for its lower ionic concentration. Also the high average values for SO_4 and xSO_4 measured by the active collector are a puzzle, much of the difference appears to be an offset of 45.4, R^2=0.98. The slow collection rate of fog water of the active collector could also be a factor. As the measurements from the nickel collector and the SS collector will be used together to look at historical changes, it should be noted, that the ionic averages in this 1988 set compare very well. The correlation for xSO_4 between the nickel and SS screens is quite high as shown by the regression equation constant of 8.7 and coefficient of 1.01.

To approximate the pH for the early years it was assumed that sulfuric acid was the major source of fog acidity. The xSO_4 ion should therefore be a good predictor for the H+ ion value before the fog water was contaminated by the screen. A regression equation was developed using data from the later years (1988 & 1989), when a stainless steel (SS) screen was used.

(1) $H+ = 1.04* (xSO4) -32\ 83.$ $R^2 = 0.89$, $n = 35$.

Similar equations have been derived for combined data from Cape Race, Newf. and Cape Forchu, NS. (Beauchamp 1993). A regression equation using 50 recent samples from Cape Forchu was developed (Beauchamp 1998) and matches rather closely the Kent Island data. It has a constant of -27.1 and coefficient of 1.18. $R^2 = 0.93$.

2.4 1992 Pollution Plumes and Trajectory Studies.

Differences in interpreting conflicting results from the two collectors with six-hour sample intervals suggested that marked changes could occur over short periods. The addition of a versatile data logging system (a Campbell CR10) made it possible to record pH changes over 10-minute intervals from the high flow SS collector. The pH, fog water flow, solar radiation, rainfall, and the usual weather parameters were recorded at 10-minute intervals. A pH probe remained in a small "spoon" of 15ml of water continuously re-supplied by a 2m tube from the SS collector. Both fog water flow rate and rainfall were recorded. A special study was made of one pollution plume which illustrated how quickly they can pass by in comparison to the exposure time of paired samples used for comparing collectors, which are often of 6 hours duration. The trace of 10-minute samples from this plume looked almost like a square wave dropping, first from a pH value of 3.9 to 3.0, reaching a minimum of 2.9 and then, after 3 hours, starting a fairly rapid rise, returning to a value of 3.7. The wind remained from the south 3-6m/s. Back trajectory analysis suggested that the "source" of the air came from off the New Jersey coast, some 3 days before reaching Kent Island on an all ocean path. It can be imagined that plumes from the NYC and NJ area could have been "captured" by the maritime flow as it passed off and up the coast. The trajectory analysis was based on a modified, PC compatible, EPA program. Surface observations from the ocean buoys, c-man stations, and a few coastal stations were used every 3 hours as input.

2.5 1993, 1994

In 1993, the Kent Island site became part of an expanded fog water and air quality network of stations supplying data to GOMOS and NARE field programs. In this connection Forest Canada loaned an AES type passive fog water collector from their Point Lepreau network and AES Bedford, NS loaned a conductivity meter and arranged for chemical analysis of the fog water collected by the AES device. UMaine continued its support with pH equipment and chemical analysis. The added AES collector permitted the continued comparison between the simple SS screen and a more sophisticated semi-standard collector. This comparison effort continued through 1997. Results so far are challenging to explain and need more high valued data points. Briefly, the concentration of the ions of volatile compounds from the SS samples are close to the values obtained by the AES collector (except for the NH_4 ion). The ions originating from sea salt nuclei are found in higher concentrations in the SS samples than in the corresponding AES samples. The results look rather similar to those obtained at Point Magu, CA with two collectors having different collection efficiencies (Collett, et al 1990). The reason for the excess sea salt ions found in the SS samples probably lies in the fact that, by measurement, only 60% of the air flows through this collector while the AES collector presents very little resistance to the air flow. More of the larger fog drops will be collected by the SS than the AES collector as the drops would not all follow the flow as well as the smaller drops. As the non-sea salt ions are from volatile compounds, their concentration is presumed not dependent on drop size and therefore not affected by this collection efficiency problem. It should be noted that the collection efficiency problem is not simple in this case as the individual wires in the SS screen are about half the size of the Teflon strings in the AES collector. Other than the collector efficiency differences, the pH values of the AES samples were higher than those measured from the SS samples. On many comparison samples, the NH_4 values were also higher. This suggests possible contamination by sea gull guano, which has a pH of ~6 (Kent Island is a major sea gull nesting area). It appears that the AES collector is more sensitive to local presence of ammonia than the SS screen, possibly because the droplets may not run off the collection strings as rapidly as in the other collector. It should be noted that the AES collector is well roofed but the collection flow rate is about 1/10th that of the SS collector. Collections were also made with both collectors in 1997 at nearby Ingalls Head, Grand Manan Island, a site without the gull effect where 8 out of 11 double samples gave very nearly the same pH values.

2.6 The Historical Record

The average values for the ion concentrations in Kent Island fog are summarized in Table 3. Some of the missing values are filled in with estimates using the methods described above.

Table 3 Fog Water Chemistry Spanning a 59 Year Period. Data From Kent Island N.B. Canada.

Year	'38	'39	'83	'84	'87	'88	'89	'91-'92	'93	'94	'95	'96
Collector	C	N	N	N	N	SS	SS	SS	SS	SS	SS	SS
# samples	5	18	20	31	25	28	5	6	26	18	9	19
pH (measured)	--	--	--	--	--	3.7	3.5	3.9	4.1	3.9	3.8	3.8
pH (computed)	3.9	4.1	3.6	3.5	3.6	3.7	3.5	3.8	3.8	3.8	3.8	--
Cl	328	184	341	449	353	168	184	573	504	470	155	--
xSO_4	167	117	257	339	272	206	305	184	178	176	195	--
NO_3	--	(77)	96	123	236	118	189	98	135	132	180	--
NH_4		(123)	--	103	106	105	175	130	136	99	71	--
H+ (measured)		--	--	--	--	181	284	115	87	113	177	158
H+ (computed)	141	89	234	320	250	181	284	158	152	150	170	--

Units of ionic concentration in μeq/l. (x) notes values estimated by using ionic balance and conductivity.

Note that the pH values reach a minimum in the 80's, and partly recover to a steady 3.8 in the '90's. The chloride ion values are erratic reflecting high sensitivity to the number of samples with past or present high winds. The average xSO_4 ion value inversely follows the pH. The NO_3 ion values have increased but not dramatically, there is one abnormally high value in '87. The average NH_4 values have fallen considerably in the last two years.

2.7 Conclusions and Recommendations

The main results of this long-term measurement program have been summarized in Table 3 and show a large increase in xSO_4 from 1939 to 1984. In recent years, the xSO_4 values are more steady and lower. The pH values have risen from lows in 1984 and 1989. The NO_3 values follow a similar trend as xSO_4, but are now rising. Two important auxiliary results are: one, a comparison with more sophisticated fog water collectors have shown that the passive stainless steel $1m^2$ collector (SS) with its high water flow is a simple and possibly adequate fog water sampling device. Further study of the complex collection efficiency question should be pursued. And, two, the high flow rate of the SS collector permits frequent fog water sampling (a pH and/or conductivity measurement every 10 min). This arrangement on Kent Island has revealed short periods of very acid fogs (probably pollution streaks or plumes). Trajectory analysis should accompany further plume detection.

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