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Spatial and Temporal Patterns in Water Chemistry of the Narraguagus River: A Summary of Available Data from the Maine DEP Salmon Rivers Program

Mark C. Whiting
Maine Department of Environmental Protection, mark.c.whiting@maine.gov

William Otto
University of Maine at Machias

Narraguagus River Watershed Council

Downeast Salmon Federation

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In collaboration with the Narraguagus River Watershed Council
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I. Introduction:

Background:

The Narraguagus River is one of eight Maine rivers within the Gulf of Maine Distinct Population Segment with endangered Atlantic salmon (*Salmo salar*). In 1999, a volunteer-based water quality monitoring program was established to evaluate water quality in these rivers. This program is managed by the Maine Department of Environmental Protection (DEP), which works cooperatively with local grass-roots watershed councils. The results of these studies have been previously published as progress reports. The river-specific reports available so far, include the Sheepscot River (Whiting 2006a), Kenduskeag Stream (Whiting 2006b) and the Ducktrap River (Whiting 2007a). No river-specific summaries exist for the downeast rivers (i.e., the Washington County salmon rivers, namely the Narraguagus, Pleasant, Machias, East Machias, and Dennys Rivers). However, more general overviews of all the Maine salmon rivers do exist (Whiting 2001, 2002, 2003).

The purpose of this study is to evaluate present water quality in the Narraguagus River, provide a baseline for the detection of trends, and present a single river summary for this river. Particular attention was devoted to three different water quality issues, namely acid rain effects, the potential for bacterial contamination in downtown Cherryfield, and an evaluation to see if this river meets its state water quality classification standards. Information reviewed by this paper comes from several different sources including volunteer monitors and from DEP staff with the Salmon Rivers and the Biomonitoring Programs.

A recent review of what is currently known about Maine's endangered salmon populations (Dill et al, 2002) identified acid rain and agricultural pesticides as the water quality issues most likely to be inhibiting the recovery of Atlantic salmon. With this in mind, we have evaluated episodic acidification in the mainstem and its principal tributary, the West Branch. We also evaluate the influence of the water chemistry of the West Branch and smaller tributaries on the mainstem. Pesticides are being evaluated by different programs, including Maine's Bureau of Pesticides Control (Chizmas 2001, Jackson 2003) and more recently acid rain and pesticide interactions are being investigated by a collaboration of scientists at the University of Maine (contact Adria Elskus).

In the lower river, within the town of Cherryfield, there are a number of older homes with variance septic systems known as overboard discharges (OBD's). These are built like typical septic systems, but the leach field is installed in a sandy fill. Because the native soils were unsuitable for a leach field, the wastewater could not be infiltrated. An impermeable barrier is installed under the leach field where the water is collected in pipes and is routed to a discharge pipe in the river. Due to the possibility of bacteria and viruses from the leach bed, a chlorinator is added before the wastewater is discharged. When the OBD's are working properly, there is a chlorine discharge to the river. If chlorine tablets are not manually added as needed, the OBD can discharge bacteria and viruses to surface water. Because there are 37 OBD's in the downtown Cherryfield area, we were looking for any evidence of failed or improperly maintained septic systems.

The final goal of this paper is to evaluate conformity with Maine water quality classification goals. The Narraguagus River from its headwaters in Eagle Lake to the confluence with the West Branch are rated ClassAA (see Table 1). The West Branch, Baker, Pork, Schoodic, and Shorey Brooks are also rated Class AA, while other tributaries above the confluence with the West Branch are rated Class A (Sinclair, Bobcat, Crotch Camp, and Lawrence Brooks). The mainstem below the West Branch and all the tributaries below the West Branch are rated Class B. We used available data to determine if the Narraguagus River meets the standards.

Table 1. Maine's water quality classification system with narrative standards. There are also numerical standards for water temperature, DO, pH etc. which are not included here.

Class	Management	Biological Standards
AA	High quality water for recreation and ecological interests. No discharges or impoundments permitted.	Habitat shall be characterized as natural and free flowing. Aquatic life shall be as naturally occurs.
A	High quality water with limited human interference. Discharges limited to non-contact process water or highly treated wastewater of quality equal to or better than the receiving water. Impoundments allowed.	Habitat shall be characterized as natural. Aquatic life shall be as naturally occurs.
B	Good water quality. Discharges of well treated effluent with ample dilution permitted.	Habitat shall be characterized as unimpaired. Discharges shall not cause adverse impacts to aquatic life. Receiving waters shall be of sufficient quality to support all aquatic species indigenous to the receiving water without detrimental changes in the resident biological community.
C	Lowest water quality. Maintains the interim goals of the Federal Water Quality Act (fishable/swimmable). Discharges of well treated effluent permitted.	Haibitat for fish and other aquatic life. Discharges may cause some changes to aquatic life, provided that the receiving waters shall be of sufficient quality to support all species of fish indigenous to the receiving waters and maintain the structure and function of the resident biological community.

Impoundments	Riverine impoundments classified as Great Ponds and managed for hydropower generation.	Support for all species of fish indigenous to those waters and maintain the structure and function of the resident biological community.

To evaluate conformance with water classification requirements, we evaluated bacteria, dissolved oxygen, nutrients, and used DEP Biomonitoring Program summaries.

Watershed Description:

The Narraguagus River originates in Eagle Lake in T34 MD and flows for 69 km (43 miles) to the head of tide in Cherryfield (Figure 1). The estuary then flows another 8 km (5 miles) to the river mouth in Milbridge. The watershed drains 601 square km (232 square miles) and has 402 km (250 miles) of tributaries (Baum & Jordan, 1982). The headwater topography is characterized as "rugged" with rocky hills and ridges from 61 m (200 ft) to almost 460 m (1,500 ft) high on either side of the river valley (Baum & Jordan, 1982). Lead Mountain is the most prominent peak with an elevation of 450 km (1,475 feet). There is a relatively rapid loss of elevation in the river below Beddington Lake, located on the mainstem just below Route 9. Below river km 29 (river mile 18 measured from headtide), the river is relatively flat and takes on a winding morphology that is dominated by alternating riffles and runs. The West Branch, with headwaters below Route 9 in Beddington, is the largest tributary of the Narraguagus River, is 39 km (24 miles) long, and drains 181 square km (70 square miles). The West Branch is influenced by Denbo Heath and other smaller riparian wetlands. The West Branch and mainstem combine in Cherryfield in the lower part of the watershed. Within the towns of Deblois and Cherryfield, the land consists of extensive flat and sandy barrens where blueberries are a major agricultural crop. In this area, the mainstem and the West Branch have cut channels that range from 3 to 15 m (10 to 50 ft) below the surrounding land surface. Sections of this part of the river are bordered by fringing marshes and bogs. For more detailed characterizations of the river see Baum & Jordan (1982).

The Narraguagus and the other downeast Maine salmon rivers are primarily underlain by nutrient-poor and carbonate-poor bedrock, primarily of a granitic nature. However, the headwaters have some marine and volcanic/marine deposits that can be sources of alkaline or acidic water chemistry (Figure 1). These latter formations, especially the Bucksport Formation and the Penobscot Formation are useful in interpreting some of the spatial variability in water chemistry.

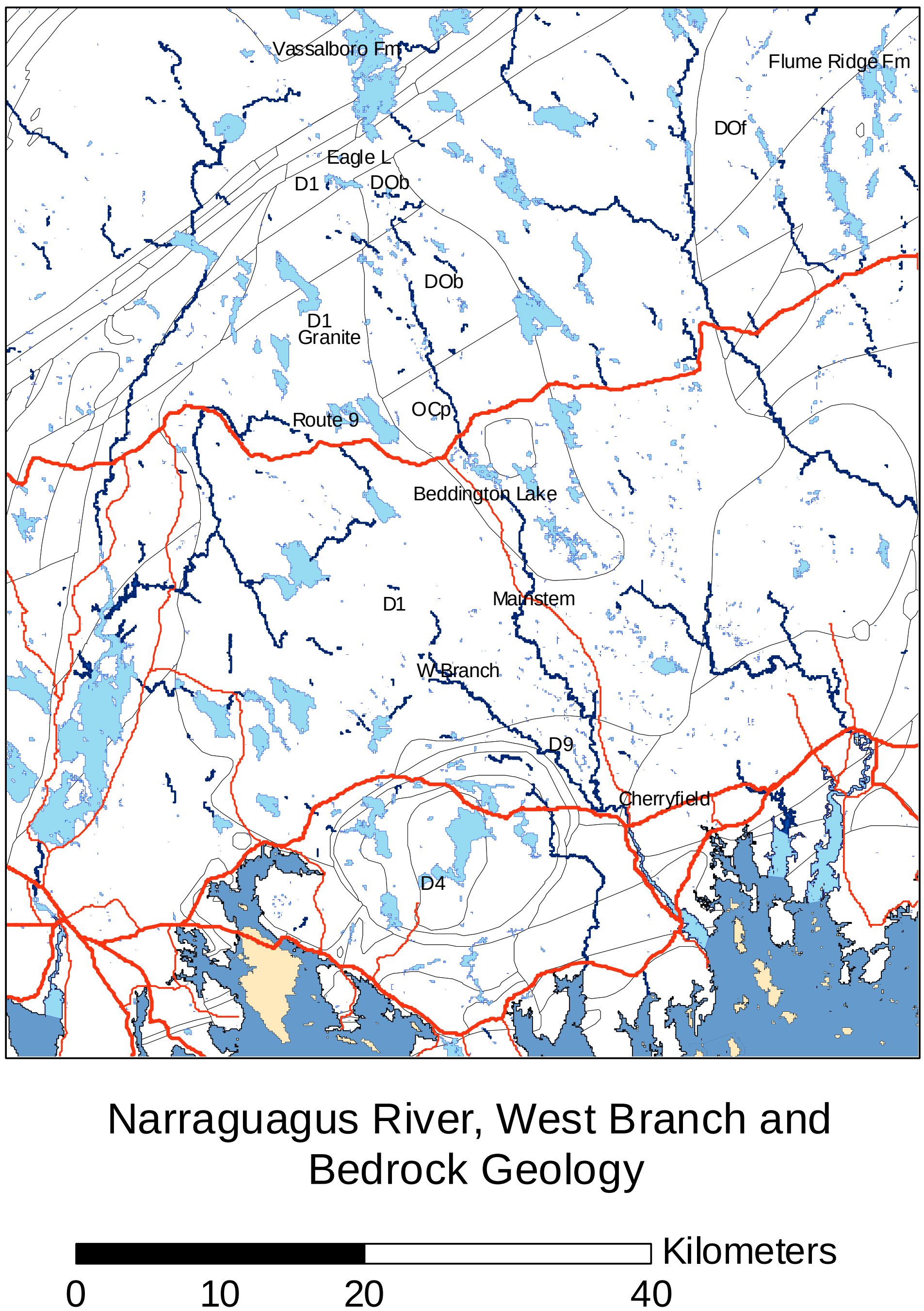


Figure 1. Map of the Narraguagus River watershed, with headwaters at Eagle Lake, showing the mainstem, Beddington Lake, the West Branch, and the town of Cherryfield. The river is superimposed on bedrock geology, which is mostly granitic (D1, D4, and D9), but there are carbonate sources in the upper watershed (i.e., alkaline sources, labeled DOb, the Bucksport

Formation) or combined sulfidic/carbonate (respectively acidic and alkaline sources, labeled OCp, the Penobscot Formation).

Methods:

There are three sources of information for this paper. Almost all field samples were taken by volunteers from the Narraguagus River Watershed Council during the 1999-2002 field seasons. DEP staff tended data sondes in three locations on the river in 2005, took some total nitrogen and total phosphorus (TN and TP) samples in the summer of 2006, and did some phosphorus speciation in 2008. DEP also collected carbon dioxide data during 2006 and 2007. The biomonitoring data in this report is from the DEP Biomonitoring Program (Davies & Tsomoides 1997, Davies et al 1999).

Volunteers took both summertime monthly samples and targeted storm flow samples in the spring and fall. Storm events were sampled if rainfall exceeded 1.0 inch in 24 hours and were generally taken the next day. Baseflow was defined as any sample taken when there were no significant storm events in the last seven days.

The volunteers collected water samples for lab analysis, recorded water temperature, and performed dissolved oxygen (DO) tests in the field. All lab chemistry from the 1999-2002 period is from the George Mitchell Center environmental laboratory at the University of Maine (which has since been disbanded). DEP samples for nutrients, including phosphorus speciation is from the Sawyer Environmental Chemistry Research Lab, also at the University of Maine. The volunteer chemistry included major cations (calcium, sodium, potassium, and magnesium), major anions (chloride, sulfate, nitrate), dissolved organic carbon (DOC), lab pH, alkalinity (measured as acid neutralizing capacity, or ANC), and total phosphorus (TP). Total suspended solids (TSS) and turbidity were measured whenever cloudy water was observed on a given sample day. The DO analysis was performed by volunteers using a LaMotte syringe-style titration kit in the field. Selected downtown Cherryfield sites were evaluated for *Escherichia coli (E. coli).* The *E. coli* samples were processed at the Bangor Regional Office of DEP using the IDEXX method (EPA website, see References section). DEP staff used a Hach field titration kit to determine carbon dioxide concentrations.

Field DO, water temperature, bacteria samples, and DEP Biomonitoring summaries were used to evaluate whether the Narraguagus River and principle tributaries meet state water quality standards. The biomonitoring studies essentially used invertebrate species and abundances to assess whether a given site is typical of natural or disturbed systems and whether it meets state water quality standards. The DEP Biomonitoring Program is described elsewhere (Davies et al 1999).

Because grab samples cannot provide the detail needed to characterize water chemistry extremes, especially those found in highly variable storm events, hourly measurements of field chemistry (pH, specific conductance, dissolved oxygen, and water temperature) were obtained using automated data sondes. In the 2005 field season, DEP, NOAA Fisheries Service and the Maine Atlantic Salmon Commission (ASC) collaborated to place data sondes in the Narraguagus watershed to obtain water quality time series that could evaluate spatial patterns in water chemistry. The sondes were placed in the West Branch and at two locations on the mainstem (upstream and downstream of the West Branch confluence) in an attempt to compare the two major branches of the Narraguagus River, and to determine the extent to which the chemistry of the mainstem is influenced by its largest tributary, the West Branch.

Sample Locations

For the baseline study, sample sites were chosen from the mainstem, some of the larger tributaries to the mainstem, the West Branch and Pork Brook (a tributary to the West Branch). Most samples were taken from knee-high water near the edges of the mainstem or from ankle to knee-deep water in the lower reaches of tributaries. Grab samples were collected at sites reported in Table 2. Sites for DO, bacteria and invertebrate biomonitoring are provided in Table 3. Data sondes were deployed in the mainstem at Little Falls, in the West Branch at Sprague Falls, and in Cherryfield below the confluence. A map of the sonde deployments is provided in Figure 2.

Table 2. Grab sample sites for the volunteer-based monitoring program are identified below. The number of samples from each site are given, and the locations in UTMs are provided for the baseline study. All samples were analyzed at the George Mitchell Center at the University of Maine. All sites are arranged in order from the headwaters to the bottom of the watershed.

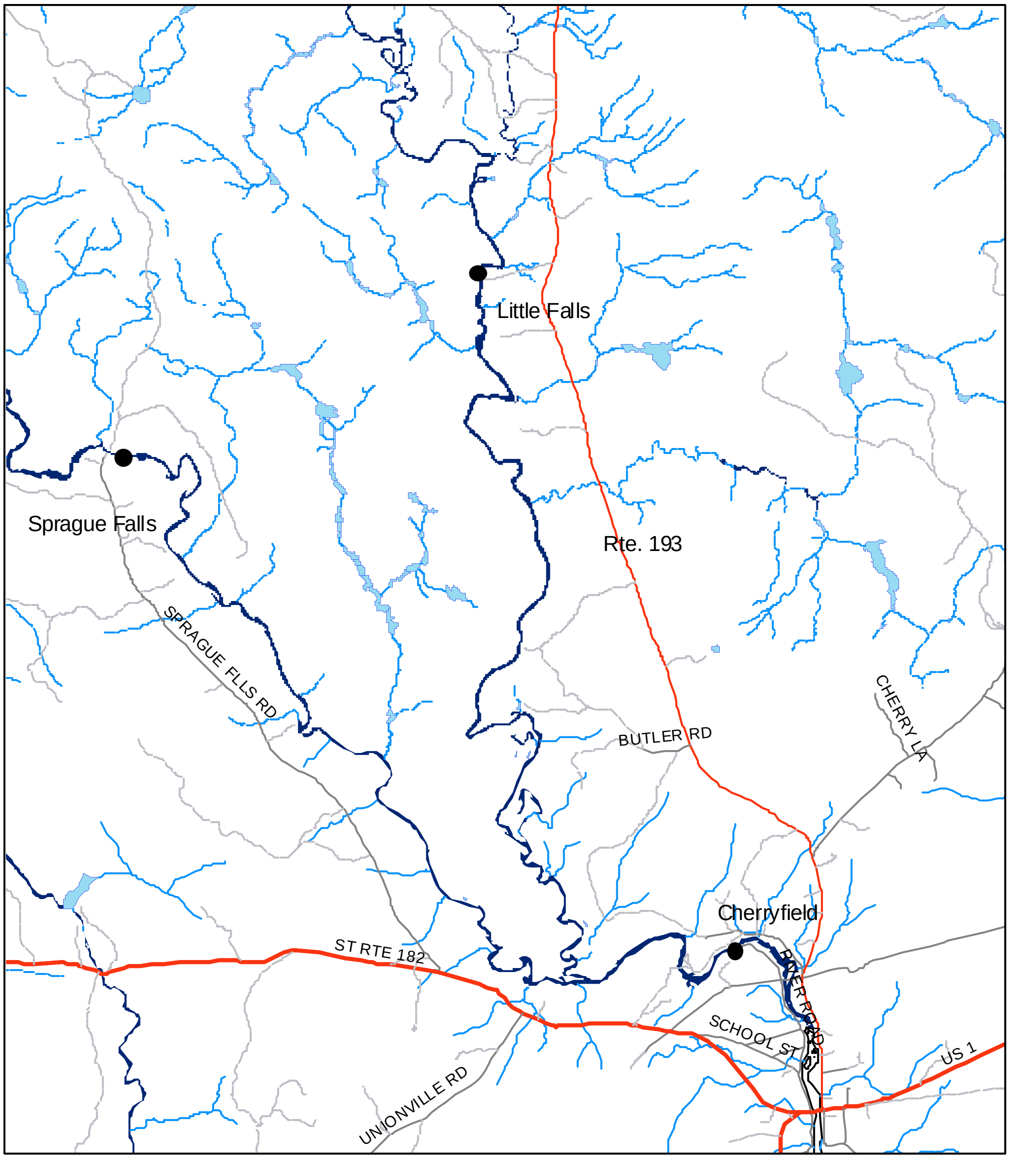
Branch	Site Name	Samples	UTMs in NAD 83	
		N	Easting	Northing
Mainstem	Bracey Ford	8	570485	4978372
Mainstem	Route 9	10	573501	4965912
Mainstem	Beddington L	8	576406	4961965
Mainstem	Route 193	8	578101	4954611
Mainstem	Little Falls	4	582638	4945447
Mainstem	Cable Pool	18	584280	4939888

Tributary Name	Location	N	UTMs in NAD 83	
			Easting	Northing
W Branch of Mainstem	30-00-0 Rd	1	569780	4977198
Barrel Br	30-00-0 Rd	1	569582	4977101
Baker Br	45-00-0 Rd	5	571429	4977549
Gould Br	30-00-0 Rd	1	570578	4973134
Rocky Br	45-00-0 Rd	5	572067	4972124
Humpback Br	30-00-0 Rd	1	571964	4969192
Sinclair Br	45-00-0 Rd	6	571964	4969192
Bobcat Br	45-40-1 Rd	1	574553	4969512
Shorey Br	65-00-0 Rd	2	575436	4964422
Bog Str	Velvet Rd	5	578677	4959967
Pork Br	73-00-0 Rd	1	572018	4957945
W Branch	Sprague Falls Rd	8	579705	4944049

Table 3. Sample locations for field measured dissolved oxygen and water temperature (WQ), *Escherichia coli* (Bact), and aquatic invertebrate biomonitoring (INV) are provided below. All sites are arranged in order from the headwaters to the bottom of the watershed.

Branch	Site Name	Sample Type	UTMs in NAD 83	
			Easting	Northing
Mainstem	Stud Mill Rd	WQ	569052	4980108
Mainstem	Bracey Ford	WQ	570485	4978372
Mainstem	Route 9	WQ	573501	4965912
Mainstem	Beddington L	WQ	576406	4961965
Mainstem	Route 193	WQ, INV	578101	4954611
Mainstem	Little Falls	WQ	582638	4945447
Mainstem	Cable Pool	WQ, Bact	584280	4939888
Mainstem	Academy Pool	WQ, Bact, INV	585265	4939354
Mainstem	Boat Landing	Bact	585291	4938579

Tributary Name	Location	Sample Type	UTMs in NAD 83	
			Easting	Northing
35-Brook	43-04-0 Rd	WQ	572653	4973516
Baker Br	45-00-0 Rd	WQ	571429	4977549
Gould Br	30-00-0 Rd	WQ	570578	4973134
Rocky Br	45-00-0 Rd	WQ	572067	4972124
Humpback Br	30-00-0 Rd	WQ	571964	4969192
Sinclair Br	45-00-0 Rd	WQ	571964	4969192
Bog Str	Velvet Rd	WQ	578677	4959967
McCoy Br	Wyman BB Rd, at dam	WQ	576418	4952878
Great Falls Branch	Rt 193	WQ	581698	4951728
Schoodic Br	Rt 193	WQ	583131	4948404
Lawrence Br	Rt 193	WQ	583315	4943697
Mill Br	Cherryfield	WQ	585317	4938943
W Branch	Sprague Falls Rd	WQ	579705	4944049



Narraguagus River, Lower Watershed, Study Sites

0 0.5 1 2
Kilometers

Figure 2. Map of the lower watershed of the Narraguagus River showing data sonde deployment sites, indicated with a ●. The Cherryfield site is located just below the railroad bridge. Sites above and below the confluence were used to assess the influence the West Branch on the water quality of the mainstem.

II. Results & Discussion: General Water Chemistry

pH and Alkalinity:

The grab samples from the Narraguagus River baseline study had pH values ranging from 5.59 to 7.44 (Table 4). The range of ANC, a measure of buffering capacity, measured in the Narraguagus River was 36-273 ueq/L (Table 5). We have never observed the depletion of the ANC in any of the downeast rivers. Even when the pH is below 4.8 (where the carbonate buffering system is exhausted), ANC values are still well above zero (these extreme pH conditions have not been observed in the Narraguagus River, but are seen in the Pleasant and Machias Rivers). Dissolved organic carbon (DOC) is a source of acidity as well as a source of buffering capacity from the weak organic acids. We assume that any observed ANC below pH 4.8 is due to the presence of weak organic acids.

Table 4. A comparison of pH means, standard deviations and ranges for all mainstem and West Branch sites is provided below.

Comparison of pH in Narraguagus

Branch	Sites	Mean	N	Std Dev	Range
Mainstem	Bracey Ford	6.56	8	0.35	6.02-7.10
Mainstem	Route 9	6.79	10	0.58	6.28-7.44
Mainstem	Beddington L	7	8	0.16	6.68-7.23
Mainstem	Route 193	6.79	8	0.43	5.78-7.17
Mainstem	Little Falls	7.07	4	0.65	6.79-7.26
Mainstem	Cable Pool	6.71	18	0.45	5.59-7.15
W Branch	Sprague Falls	6.68	8	0.45	6.1-7.15

Table 5. A comparison of ANC means in ueq/L, standard deviations and ranges for all sampled sites is provided below.

Comparison of ANC by sites

Branch	Sites	Mean	N	Std Dev	Range
Mainstem	Bracey Ford	205	8	45	147-257
Mainstem	Route 9	197	10	75	50-257
Mainstem	Beddington L	192	8	13	172-205
Mainstem	Route 193	158	8	10	139-170
Mainstem	Little Falls	212	4	17	188-226
Mainstem	Cable Pool	167	18	71	36-273
W Branch	Sprague Falls	140	8	45	79-185

When mainstem and tributary sites are arranged in sequence from the top of the watershed to the bottom, we see that there is little discernable pattern in water pH. The only obvious conclusions are that Sinclair Brook and Bog Stream are more acidic that the upper tributaries. Baker Brook and Rocky Brook occur in the Bucksport Formation, which is a relatively good source of bicarbonate buffering (Osberg et al 1985). Sinclair, Bobcat, and Shorey Brooks, and Bog Brook Flowage occur in the Penobscot Formation, which has carbonate-rich rocks but is also described as “sulfidic,” a source of sulfuric acid. Bog Brook Flowage and the outlet stream are very acidic, probably due in part to the sulfidic underlying bedrock, but also due to the flat and boggy terrain and accumulation of organic acids (DOC). Even lower in the watershed, tributaries like Great Falls Branch, Crotch Camp Brook, Schoodic Brook, and Lawrence Brook are also quite acidic (unpublished data) and are found in calcium-poor igneous intrusions of granite, quartz monzonite, and gabbro/diorite. The West Branch is underlain by granitic bedrock and has water chemistry that is similar to these lower tributaries. There is a general decline in calcium from the upper tributaries to the lower mainstem.

To measure the seasonal variation in pH and examine the influence from the West Branch, data sondes were employed to measure pH at Sprague Falls, Little Falls, and Cherryfield (Figure 2). Due to technical difficulties with the sondes, the Cherryfield record has data gaps (Figure 3). The Cherryfield and Sprague Falls sondes were removed before fall rains and deeper water complicated their retrieval. However, even with the limited Cherryfield record, the mainstem and West Branch base flows are remarkably similar.

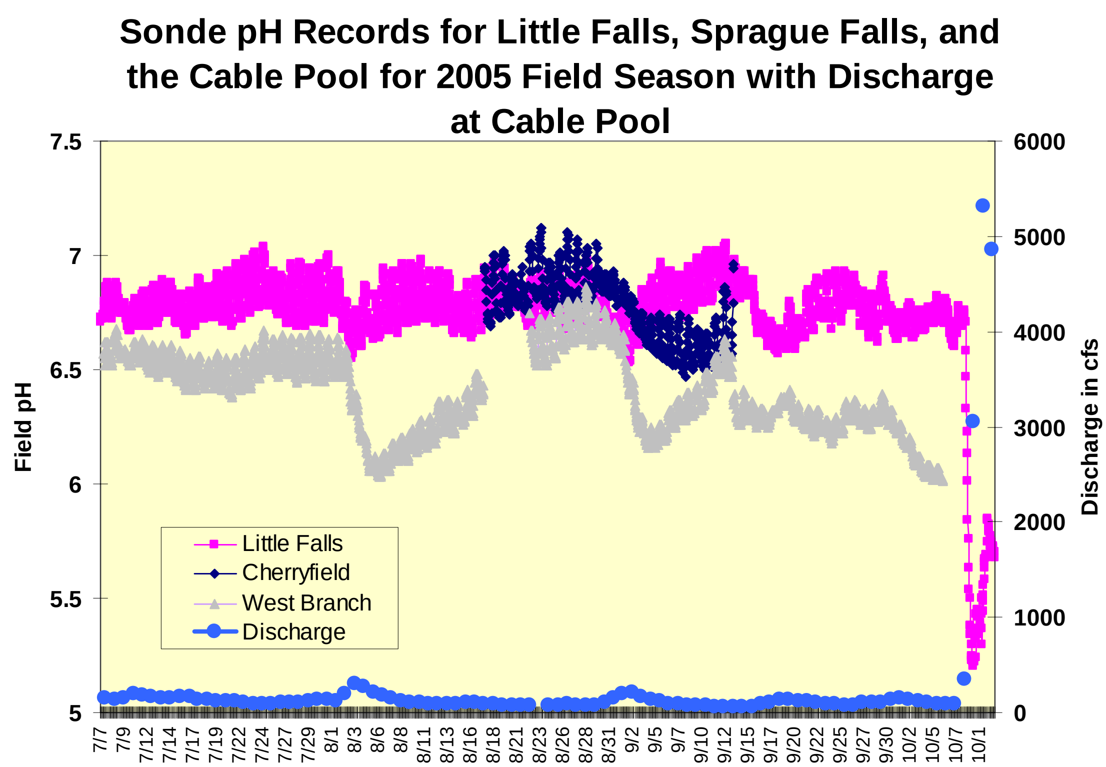


Figure 3. Graph of pH records measured with data sondes from the Narraguagus River mainstem upstream site (Little Falls), the West Branch site at Sprague Falls, and the mainstem

below the confluence with the West Branch at the Cable Pool in Cherryfield. On a separate axis, river discharge at the Cable Pool site is given in cubic feet per second. The sonde record from Little Falls was provided by NOAA.

The pH and ANC are generally lowest in the spring and fall and coincide with high flow events. These low values can be attributed to dilution of ANC by rainfall and to increased DOC due to the flushing of bogs and upper soil layers. However, low pH can occur any time of year if storms are intense enough (Whiting 2005), and are common in the “wet seasons” from October to May (Whiting et al 2007b). It takes more rain to impact water chemistry during the summer due to the soil moisture deficit, i.e., when evapotranspiration losses exceed rainfall inputs. The development of seasonally waterlogged soils represents the formation of a perched water table above the normal water table. This perched water flows down but also laterally through shallow organic soil layers before it breaks out in downhill springs. The soil-influenced flow path has a strong impact on runoff chemistry (see discussion of DOC below). Thus, the seasonal pattern is governed by stream flow, the relative balance between stormwater runoff and groundwater input, and the relative balance between precipitation and evaporation. Both the Mainstem and the West Branch experience acidic conditions that are stressful to salmon (less than pH 6.0), but generally do not experience conditions that are thought to lead to acute toxicity and the death of fish (pH less than 5.6, Staurnes et al 1996).

The data also demonstrate that the mainstem at Little Falls responds to rainstorms with shorter and less extreme acidic episodes than the West Branch. Mild rain began on August 1 with a total of 0.5 inches, intensifying that evening with an overnight storm total of 0.7 inches on August 2. Light rain, a total of 0.2 inches, continued on August 3 resulting in a 48 hour total of 1.4 inches. The mainstem discharge, measured in Cherryfield, went from 122 cfs on August 1 to a peak of 299 cfs on August 3. This 48-hour rain event caused the pH in the mainstem to fall 0.3 pH units, recovering to the base flow pH in 6 days. Our experience with this river suggests recovery would have been faster except the rainfall was extended over three calendar dates. On the West Branch, the pH fell 0.5 units and recovery took at least 18 days.

On August 29, there was light rain with a total of 0.2 inches. There was heavy rain overnight with another 0.5 inches by the end of August 30. River discharge went from 70 cfs on Ausust 29 to 208 cfs on September 2. During this period, the mainstem at Little Falls dropped 0.2 pH units and recovered in about 5 days, while the West Branch went down 0.5 pH units and had not completely recovered in 16 days (when a subsequent storm event arrived on September 15, 17 and 20). The Mainstem at Cherryfield had a pH intermediate between the two branches and took at least 16 days to recover. Clearly, the West Branch has an impact on the mainstem, making it more acidic with longer acidic episodes. Unfortunately, the West Branch and Cherryfield sondes deployments was terminated prior to the storm on October 8-9 which resulted in 8.1 inches of rain over a period of 48 hours. The data from October 9 provides the lowest pH ever recorded in the Narraguagus River (pH 5.2 at 11:00 AM). The pH record never did fully recover to typical fall baseflow pH due to waves of storms in rapid succession.

The sonde records show that pH rises during the day and falls at night. This diurnal cycle is strongest in the summer and is very weak or absent in the winter (Whiting et al 2007b). These patterns are due to the relative balances of respiration and photosynthesis. Carbon dioxide acts as an acid in water (forming carbonic acid). Photosynthesis increases pH by consuming carbon dioxide while respiration releases more carbon dioxide. In these rivers, the pH effects of high carbon dioxide collecting at night (generally 6-8 ppm in the Narraguagus River in the early morning) is followed by partial depletion of CO2 by photosynthesis during the day (to around 2 ppm). In the Narraguagus River, this diurnal cycle seems to account for a pH range of about 0.1-0.3 units. In contrast, daily ranges of 0.5 pH unit are common in the summer in the Crooked River (a tributary to the Machias) and the East Machias River at Route 9 (Whiting et at 2007b).

To determine other chemical sources of the pH, a correlation analysis was used to examine relationships between pairs of water chemistry variables (Figure 4). All of the cations are highly correlated with each other, thus only calcium is shown. The best relationships are between ANC and calcium (a strong positive relationship), sulfate and nitrate (also positive, and both found in acid rain), and DOC and pH (a strong negative relationship). DOC includes organic acids that affect the pH of river water. This is especially visible in storm water runoff where DOC is often found at elevated concentrations. Based on these regressions sulfate and nitrate, the two primary components of acid rain apparently have no relationship with pH. Similar results were used by Kircheis & Dill (2006) to suggest that sulfate does not affect river pH. While it is commonly understood that a good correlation should not be used as proof of a causal relationship, it is not often appreciated that a lack of a correlation should not be interpreted as proof of a lack of a relationship. It only means that the relationship does not conform to a linear model. Clark et al. (2006) also discuss the problems with regressions between pH sulfate and DOC and point out how the relationship is complicated and non-linear. They mention how often people are led to erroneous conclusions by this apparent lack of a relationship. We know that acid rain does affect our rivers (Haines & Akielaszek 1984). Sulfate is an acidic anion, it is abundant in our rivers, and is mostly of anthropogenic origins. However, sulfate does not occur in our rivers as sulfuric acid. Since there is always some buffering capacity present, strong acids will be neutralized by buffers until one or the other is exhausted. Since we never see the ANC depleted, sulfate must occur in surface water as a neutral salt. So in this sense, it does not affect surface water pH. To understand the relationship between acidity and sulfate, the relationship of ANC and sulfate will be more closely examined below.

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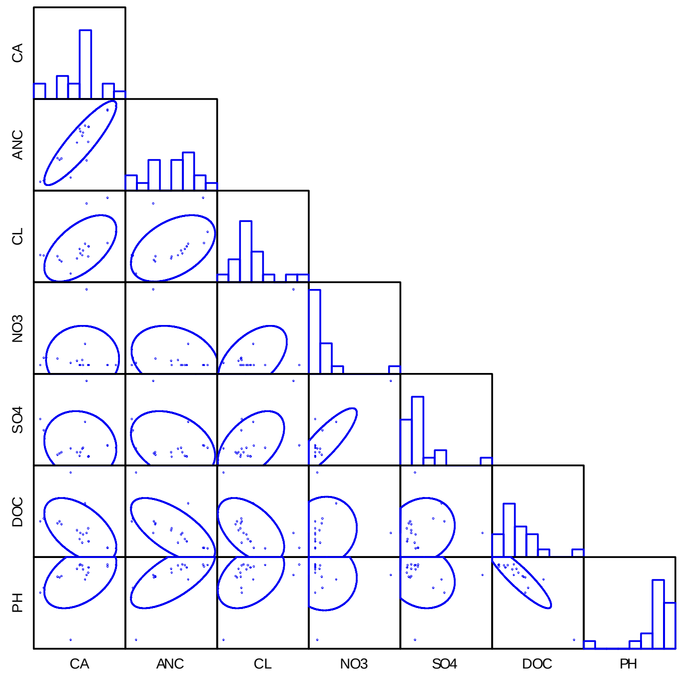


Figure 4. A correlation matrix of pH, ANC, cations (represented here by Ca) and major anions for all samples (baseflow and storm flows) from the Cable Pool in Cherryfield. The bar graphs at the ends of rows show the distribution of the raw data for each parameter

ANC can be both measured as well as calculated. In fact, calculating the alkalinity is a quality assurance check on lab data. The following equation can be used (Kahl et al 1992):

$$ANC = (\sum BC) - (\sum AA)$$

Where BC are the base cations expressed in equivalents
And AA are the acidic anions in equivalents

The dominant base cations in our samples are (in order of importance) calcium, sodium, potassium, and magnesium. The dominant acidic anions (also listed in order) are chloride, sulfate, and DOC (nitrate is very low in abundance and often below detection limits). Since the acidic anions are subtracted from the alkaline earth metals in the above equation, the acidic anions from sea salt (Cl), acid rain and to a lesser extent from marine aerosols (SO_4^{2-}), and organic acids from watershed soils, all represent significant losses of alkalinity. If it is assumed that the oceanic and soil carbon influences are ancient and have not been significantly altered by human activity, then acid rain is the new impact on our watershed. Essentially, the acid rain effect is that some river alkalinity has been replaced by anthropogenic sulfate (Ophardt 2003). This problem is thought to be widespread in northeastern USA and Canada (Ophardt 2003). A recent paper by Johnson & Kahl (2005) created the impression that our salmon rivers are controlled by natural processes and that DOC controls river acidity. However, we maintain that river pH is controlled by an acid-base balance, with several acids and several important bases. Our second most important acid (sulfate) is dominated by acid rain inputs. If salmon recovery is inhibited in part by low pH (Dill et al 2002), and if these rivers were naturally acidic and low in calcium (Norton personal communication), then a historic increase in acidity due to sulfate with concomitant loss of calcium and increase in aluminum flux from soil (Lawrence et al 2007) will clearly make salmon survival even more marginal. The impacts of acid rain, and especially sulfate and aluminum, are not trivial.

Dissolved Organic Carbon (DOC):

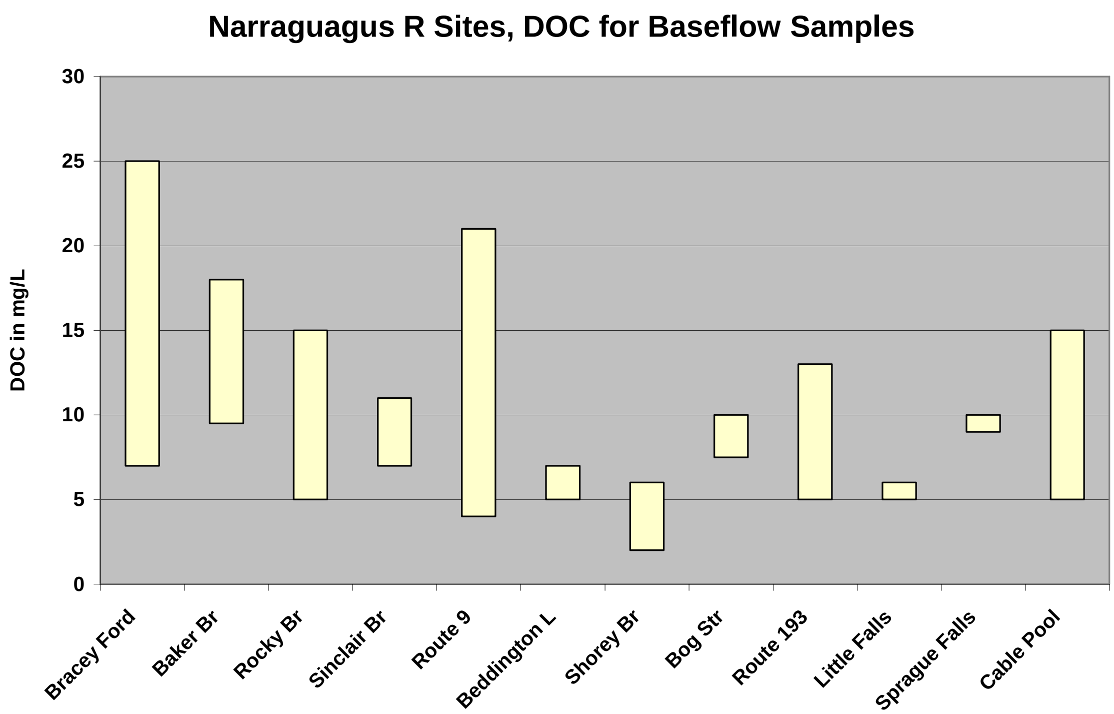
DOC comes from the decomposition of organic matter, especially plant materials, in soils and wetlands. In a review of DOC in streams, Mulholland (2003) reports that DOC is sometimes concentrated, and at other times diluted by storm flows. In general, DOC is diluted when wetlands are the dominant source in the watershed, and is concentrated in high flows when soils were the dominant source. This is due to the fact that north temperate forests are dominated by spodsolic soils which strongly retain DOC under normal circumstances (McDowell & Wood 1984, Aitkenhead & McDowell 2000). Water percolating into upland soils carry DOC to a lower soil horizon (the spodic zone, usually part of the B horizon) where DOC becomes bound with iron and aluminum sesquioxides. However, during fall, winter and spring rains, soils become saturated and water tables develop which are perched above the normal water table. Rainwater passes through shallow organic-rich soil horizons, traveling laterally in the saturated zone, and breaks out again downhill in seasonal springs (McDowell & Wood 1984, Mulholland 2003). Enriched with organic matter, this runoff causes DOC peaks corresponding to high flows in rivers. In contrast, when wetlands are flooded, rainwater runs off the wetland surface and the contact with subsurface organic sediments is reduced, resulting in reduced DOC.

These generalizations about DOC in runoff appear to hold in our salmon river watersheds. Since the downeast rivers have the pattern where DOC is generally highest during high flows, we conclude that most of the DOC in our rivers is probably from upland soils. Wetlands are abundant in the watersheds of our downeast rivers, and are very important landscape features. Some especially large wetlands such as Denbo Heath in the Narraguagus watershed and the Great Heath in the Pleasant watershed come to mind. However, wetlands, both open and forested, account for only about 10-13% of the area of these watersheds (see Table 6). Note that the West Branch has about the same percentage of total wetland than does the mainstem. In contrast, in Fox Brook, a headwater stream in Ellsworth and a tributary to Graham Lake, has a water chemistry pattern where high flows almost always contain less DOC than do baseflows (Whiting, unpublished data). This small perennial stream is located entirely within forested wetland.

Table 6. A breakdown of land cover type for the watershed drainage at each of the data sonde deployment sites (West Branch to Sprague Falls, main stem to Little Falls, and the overall watershed to Cherryfield) is given below (from Michael LaChance, UMM, quantified using GIS).

COVERTYPE	West Branch-Sprague Falls % coverage	Main stem up to Little Falls % coverage	Mainstem up to Cherryfield % coverage
Developed High Intensity	0.01	0.08	0.07
Developed Medium Intensity	0.00	0.14	0.10
Developed Low Intensity	0.06	0.03	0.04
Developed Open Space	0.00	0.04	0.02
Cultivated Land	0.18	0.07	0.19
Pasture/Hay	0.54	0.06	0.27
Grassland/Herbaceous	0.19	0.26	0.23
Deciduous Forest	9.07	13.94	13.61
Evergreen Forest	27.16	24.89	24.50
Mixed Forest	36.62	31.47	32.73
Scrub-Shrub	2.21	2.52	2.41
Forested Wetland	9.16	5.03	7.48
Wetlands	3.83	5.40	4.82
Road/Runway	0.06	0.74	0.53
Unconsolidated Shore	0.20	0.46	0.36
Bare Land	0.04	0.06	0.05
Open Water	1.05	2.49	1.83
Blueberry Field	3.70	8.19	6.18
Light Partial Cut	0.89	1.07	0.96
Heavy Partial Cut	3.24	1.25	1.95
Forest Regeneration	1.80	1.78	1.67

In addition to storm flows, DOC shows a seasonal pattern. Relatively darkly colored water dominates in the late summer to early fall and is diluted in the winter. This is apparently related to temperature-related decomposition rates in soils and release of DOC accumulated during dry weather, and mobilized by wet weather and saturated soils in September-October. Autumn leaf fall occurs in this period, and is a likely fresh source of DOC. With respect to spatial patterns, Figure 5 shows that DOC is generally high in the upper watershed, low at Beddington Lake, with some increase in DOC by the road crossing of Route 193 at Great Falls. The small range at Little Falls is due to the small number of samples from this site (N=2). Surprisingly, the DOC range on the West Branch at Sprague Falls is small despite the relatively large number of samples (N=6). The Cable Pool has a wide range like other mainstem sites except Beddington Lake. The low DOC found at Beddington Lake is probably due to the oxidation of DOC by UV light, (Norton personal communication) and the recovery downstream is due to high DOC concentrations contributed by the lower tributaries. While the average residence time for Beddington lake is only about one month (PEARL website), the photo-oxidation process is fast, with noticeable reductions in a matter of days (Norton personal communication). Lakes are collectors of organic matter and precipitated minerals due to solar oxidation of soluble organic matter, conversion into insoluble organic complexes, and relatively limited turbulence (Norton). Groundwater inputs below Beddington Lake, a region of rapidly declining elevation for the mainstem, probably also contributes to the decrease in DOC content. The average DOC for all baseflow samples is 9.12 mg/L (the range is 2.16-24.60 mg/L).



<u>Figure 5</u>. A bar graph of DOC showing ranges in all baseflow samples from the Narraguagus River. Both tributary and mainstem sites are arranged from the top to the bottom of the watershed.

<u>Calcium and Al:</u>

Calcium ranged from 0.82 mg/L in a stormwater sample from Bog Stream to 5.10 mg/L in a baseflow sample from Baker Brook (Table 7). Baseflow samples have more calcium than storm flows, reflecting the dilution of base cations during high flows. The upper Narraguagus River (from the headwaters above Route 9 to Shorey Brook) had the highest calcium, reflecting the carbonate-rich bedrock (Bucksport and Penobscot Formations) that underlies this region. All of these mean values were low in comparison to known calcium requirements for salmon. In fish hatcheries 50-100 mg/L are recommended (Pennell & Barton 1996), where ideal values in rivers are above 10 mg/L, and 2.5 mg/L is given as the critical lower survival threshold (Brockson et al 1992). In a recent review of brook trout nutrition, Danner (unpublished) notes that salmonid calcium uptake is accomplished primarily from ambient water (not from food) and is absorbed through gills and skin. In Maine salmon hatcheries (which use commercial feeds in which calcium was supplied in excess of metabolic needs), brook trout held at calcium concentrations at or below 2.5 mg/L appeared to be outwardly healthy but had classic hyperparathyroid pathologies, including tooth loss, skeletal and renal deformities, catastrophic loss of egg viability (Danner unpublished data). Oddly, hatchery fish grew fastest and were the largest when grown at low calcium concentrations, and thus appeared to be healthy. This demonstrates that (1.) food sources cannot make up for ambient water concentrations that are too low, (2.) that 2.5 mg/L of calcium is not adequate for brook trout and that we actually do not know what the lower threshold really is, and (3.) that we cannot tell from the outward appearance of fish if they have adequate calcium nutrition. In our waters, the upper Narraguagus has mean calcium concentrations exceeding 2.5 mg/L, the Narraguagus River below Beddington Lake has means that are close to this value, the West Branch and some other tribuataries have mean calcium values that are below 2.5 mg/L. The upper tributaries on the mainstem have the best calcium environment in the watershed. Depending on what the actual minimum river calcium concentration is, part or all of the Narraguagus River may have trouble sustaining salmonids, especially when there are other stressors.

Table 7. A comparison of calcium concentrations in mg/L found in mainstem and West Branch sites, with tributary sites listed separately.

Calcium Baseflow in Mainstem sites

Branch	Sites	Ca Mean	N	Std Dev	Range
Mainstem	Bracey Ford	3.56	5	0.84	2.76-4.60
Mainstem	Route 9	3.84	7	0.29	3.42-4.08
Mainstem	Beddington L	3.49	6	0.2	3.18-3.67
Mainstem	Route 193	2.99	6	0.84	2.44-4.60
Mainstem	Little Falls	2.72	2	0.01	2.71-2.73
Mainstem	Cable Pool	2.52	8	0.28	2.33-3.22
W Branch	Sprague Falls	1.8	4	0.13	1.62-1.89

Calcium Baseflows in Tribs

Trib Name	Ca Mean	N	Std Dev	Range
W Branch of Mainstem				
Barrel Br				
Baker Br	4.26	3	0.66	3.49-5.10
Gould Br				
Rocky Br	4.14	3	0.72	3.03-4.79
Humpback Br				
Sinclair Br	2.3	3	0.26	1.44-1.92
Bobcat Br				
Shorey Br	3.95	2	0.83	3.36-4.54
Bog Str	0.85	3	0.03	0.82-0.88

Pork Br W Branch	1.8	4	0.13	1.62-1.89

Like DOC, aluminum comes from acidic soils. Natural processes, such as strong organic acids, work in combination with atmospheric deposition (sulfate, nitrate and seasalt) to mobilize aluminum from soils (Lawrence et al 2007). In the Narraguagus watershed, total dissolved aluminum ranged from 29 to 245ug/L; and both extremes are from storm flow samples (Table 8). The low value was observed at the Cable Pool in Cherryfield while the highest values were observed in the West Branch at Sprague Falls. The limited number of data points show high values throughout the mainstem and West Branch, and we don't have many measurements from tributaries. Since we do not trust our Al speciation data from this period, therefore we have not reported them. However, Norton & Wilson (personal communication) report high exchangeable Alx (25-35 ug/L) in baseflow samples from the Route 9 and Cherryfield bridges. Frode Kruglund (2007) notes that 5 ug/L Alx is about the smallest amount of Alx that can confidently be detected with present technology. He concludes from his own studies and from a literature review that "there is no safe measureable concentration" of exchangeable Al. Storm flows in the Narraguagus mainstem probably have higher exchangeable Al values because pH is lower, total Al is higher, and the seasonal patterns cause these high flows to occur during the colder seasons. The solubility of inorganic Al increases at lower pH and at lower temperatures (Norton personal communication). When pH is below 5.7 and Alx is greater than 20 ug/L, then salmon mortality can be expected to be high (Kruglund 2007). When pH is above 5.7 and Alx is below 15 ug/L then no mortality is expected, but the fish are clearly stressed (Kruglund 2007). Even low Alx can harm fish if pH is low, for instance McCormick & Monette (2007) report high plasma chloride and reduced saltwater tolerance when fish are held at pH 5.3 with Alx at only 10ug/L.

Table 8. A comparison of total dissolved aluminum in ug/L found in the mainstem and West Branch sites. Baseflow and storm flow conditions are compared in different tables.

dissol Al Baseflows

Branch	Sites	Al Mean	N	Std Dev	Range
Mainstem	Bracey Ford	80	2	23	59-100
Mainstem	Route 9	46	2	16	37-64
Mainstem	Beddington L	45	2	4	42-49
Mainstem	Route 193	45	2	3	43-48
Mainstem	Little Falls	46	2	6	43-53
Mainstem	Cable Pool	65	4	22	37-98
W Branch	Sprague Falls	129	4	65	91-226

Dissolved Al during Stormflow

Branch	Sites	Al Mean	N	Std Dev	Range
Mainstem	Bracey Ford				
Mainstem	Route 9	165	2	42	135-194
Mainstem	Beddington L				
Mainstem	Route 193				
Mainstem	Little Falls				
Mainstem	Cable Pool	139	9	70	29-205
W Branch	Sprague Falls	237	2	11	229-245

In terms of spatial distribution, while many sites have few samples, there appears to be high dissolved Al in the upper river above Route 9, low values and ranges in the middle river, and an obvious impact on the lower mainstem from the high Al contriution from the West Branch. If we believe the apparent pattern, then there is a lake effect from Beddington Lake, where the exposure to sunlight has cleared some of the DOC from the water and resulted in large reductions in complexed Al (and presumably precipitation of organic complexes of Fe and phosphorus as well). If high exchangeable Al is present at Route 9 and in Cherryfield, then we can hope that exchangeable Al is much lower in the middle river where total dissolved Al is relatively low.

Nutrients:

Like the downeast lakes, the downeast rivers are thought of as oligotrophic (nutrient poor with relatively unproductive fisheries). This is certainly true of nitrate (median stream concentration is below detection limits). Total N (TN) was not measured in the baseline study, but was measured in 2006. However, TN is abundant in all samples so far and is apparently predominantly organic nitrogen (the TN average is 0.34 and range was 0.28-0.38 mg/L during baseflows at the Cable Pool, N=6). To compare our results to regional studies, a study of 63 minimally impacted streams in the US, for the glaciated Midwest and northern New England (Ecoregion VIII, Smith et al 2003), northern New England reports an expected background for baseflow conditions of 0.25 mg/L for Total N (including corrections for atmospheric deposition) (Table 9). In an EPA review of available literature (EPA 2001), a suggested background baseflow TN for New England was given as 0.38 ug/L. Thus, the measured TN level appears to be on the high end of normal.

Table 9. A comparison of our average TN and TP values in the Narragugus River with regional studies suggesting baseline conditions for minimally impacted New England streams.

	Total N mg/L	Total P ug/L
Narraguagus Mainstem Sites Measured Mean	0.34	13.7
Smith et al, 2003 study Background Conditions	0.25	15
EPA Recommended Nutrient Criteria (EPA 2001)	0.38	10

In freshwater, phosphorus is normally expected to be the limiting nutrient for ecosystem productivity. In the downeast area, the TP values are also on the high end of normal. The mainstem and West Branch averaged together are 13.7 ug/L, ranging from 3.5 to 35 ug/L for all baseflow and storm water samples. However, high TP tells little about phosphorus availability. The phosphorus was not partitioned into species (i.e., particulate and dissolved, organic and inorganic, ortho-P and other inorganic species). Given the abundance of Al in the water, much of the phosphorus may not be biologically available due to the formation of iron, aluminum and organic complexes (Norton personal communication). Thus, the type of complex but not the phosphorus concentration *per se*, may be limiting ecosystem productivity. In terms of TP and flow, there appears to be a weak relationship (Figure 6). In general, the highest TP values were during high flows.

Maine DEP does not currently have nutrient criteria, as such, but has developed nutrient-based "indicators" of water quality to help interpret the statutory criteria. The draft rules are entitled Chapter 583, Nutrient Indicators for Classification Attainment of Fresh Surface Waters. While this is currently an internal working document only, the proposed threshold for Class A and AA waters is 20 ug/L for TP. These rules actually suggest using several indicators, and the interpretation is conditional on those other factors. However, just looking at TP, and provided this draft rule were to be adopted, then the Narraguagus River currently meets this standard.

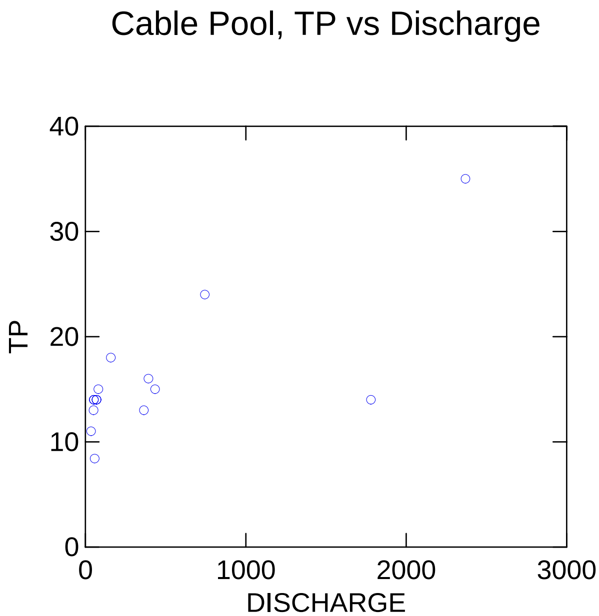
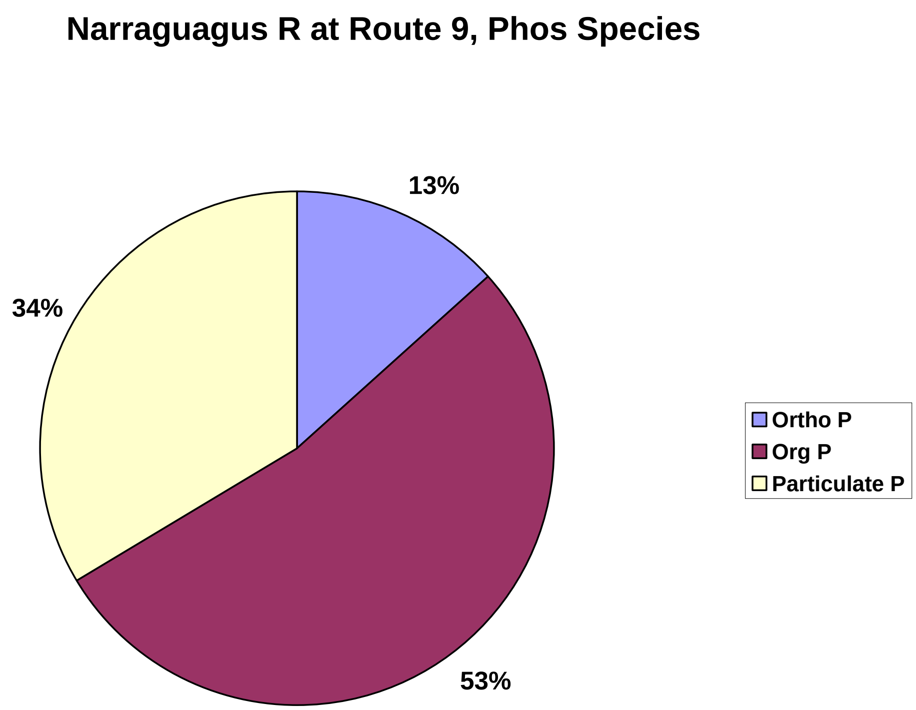


Figure 6. TP in ug/L is plotted against stream discharge in cfs for all Cable Pool samples.

In the spring of 2008, the DEP Salmon Rivers Program took phosphorus samples from Maine salmon rivers in order to investigate the forms of phosphorus present. The result for the Narraguagus River at Route 9 is given below (Figure 7). Samples from the Narraguagus R, Pleasant R, Mopang Stream, Machias R, Crooked R, and Sheepscot R were separated into total P, total dissolved P, ortho-P, and organic dissolved P. Total P ranged from 6.7 ug/L (Mopang Str) to 15.5 ug/L (Pleasant R). In all cases, the particulate and organic fractions were dominant and ortho P was much smaller. The dissolved organic fraction ranged from 35% (Sheepscot R) to 53% (Narraguagus R) and the particulate fraction ranged from 34% (Narraguagus, Pleasant and Crooked Rivers) to 56% (Sheepscot and Machias Rivers). Ortho P was always a small part of the total, ranging from 3% (0.2 ug/L in the Machias R) to 15% (2.4 ug/L in the Pleasant R). Ortho P is available for biological uptake, while particulate and organic fractions must be converted to ortho P before they can be used. This is accomplished by bacterial decomposition and by exposure to sunlight (especially ultraviolet light). We sometimes observe periphyton blooms in the downeast rivers in wide shallow spots in the river. The Cable Pool in Cherryfield is a good example. Because these spots are sunny, these algal blooms might be due to the photo-oxidation and bacterial digestion of organic matter and release of nitrate and ortho-phosphorus. This partitioning of nutrients appears to explain why the Narraguagus River has a lot of phosphorus and nitrogen (TP and TN) while also being extremely unproductive. It might also explain how local hot spots of productivity develop in the summer time.

Algal blooms are mentioned in Maine's draft nutrient indicators (Chapter 583) and are one of the conditions on which water quality attainment is judged. If phosphorus levels are acceptable but one or more of the environmental indicators are not acceptable (such as poor secchi depth, high chlorophyll a, high Diatom Trophic Index, high percent cover of algae, patches of bacteria or fungi, low DO, high pH due to photosynthesis, or when aquatic biological communities are impaired) then the body of water in question is classified as "indeterminate" (i.e., there has to be more study and a best professional judgement must be made). Algal blooms on the Narraguaugus River would be in this indeterminate category, and could result in a decision that local reaches are in non-attainment.



<u>Figure 7</u>. Partitioning of total P in the Narraguagus River into different fractions (based on a single sample from 2008). Total P in this sample was 13.4 ug/L. The organic P is actually dissolved organic P (the fraction that passed through a 0.45 um filter).

<u>Sediment and Turbidity</u>:
Volunteer water quality monitors only sampled for turbidity when there was obviously a turbidity event occurring on a monitoring day. Turbidity is observed only rarely in the downeast salmon rivers, and is always associated with a high flow event. Often, turbidity appears to be associated with the washing out of beaver dams. Generally, these occur only during the highest flows of the year. TSS ranged from 0-20 mg/L, while turbidity ranged from 0-7.5 NTU. Even the highest TSS and turbidity values are comparatively mild (e.g., maximum TSS was 100 mg/L and Turbidity was 40 NTU in Cove Brook, Whiting 2001).

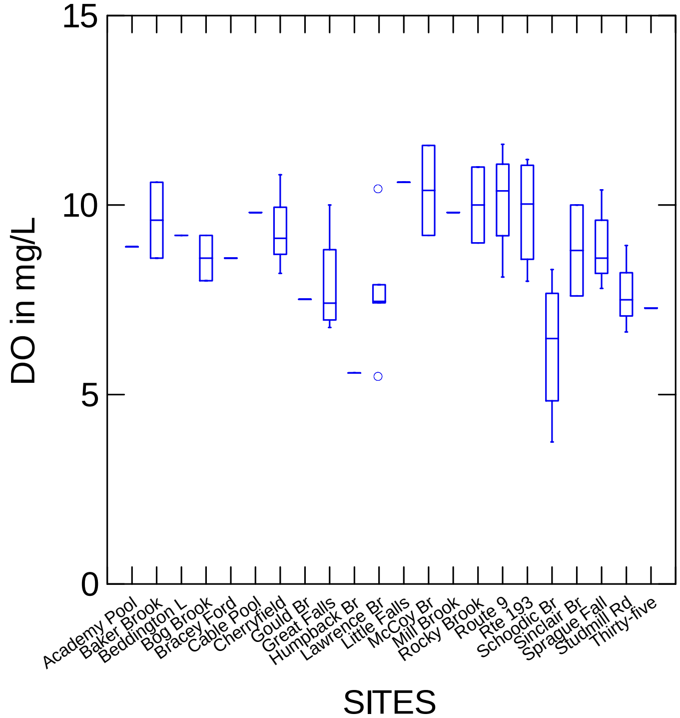
III. Results and Discussion: Water Quality Classification, Bacteria, Oxygen and Biomonitoring

Water Classification:
Maine uses a water quality classification system for its surface waters and uses it to prevent water quality degradation (Maine Water Classification Program, 38 M.R.S.A. § 464-470). Under this system, Class AA and Class A freshwater streams are the highest quality, Class B is next, and Class C is the most impacted by human activities (Table 7). Existing discharges are to be eliminated when possible, pollutants cannot be discharged without treatment adequate for receiving waters to maintain their classification, and water quality is supposed to be adequate to support aquatic life and recreation. All of the downeast salmon rivers are rated "AA", except some river sections rated lower to reflect existing commercial and residential developments. For the Narraguagus, the mainstem from the headwaters in Eagle Lake to the confluence with the West Branch in Cherryfield is rated AA. The West Branch, Baker Brook, Pork Brook, Schoodic Brook, and Shorey Brook are all rated AA. All of the other upper tributaries are rated A, while the mainstem from the confluence with the West Branch and all the tributaries below the confluence are rated B (due to two blueberry canning plants and 37 residential sewage overboard discharges (OBDs)).

Bacteria Chlorine and Dissolved Oxygen:
All of the existing OBDs in Cherryfield are single homes with septic tanks and leach fields built using a variance procedure in the Maine Plumbing Code. This variance allows sandy fill to be used where native soils are inadequate for normal septic systems. Water treatment is good in the sand filter, since it is similar to a normal septic system. However, because the wastewater cannot be infiltrated in the native soils, treated water is collected and chlorinated before being discharged into the river, representing a pollutant discharge to the river. Hypochlorous acid, the active ingredient in chlorination, reacts with natural organic matter in surface waters to form trichloromethane and other toxic chemicals in trace amounts.

Chlorine is extremely reactive and is difficult to test for in natural waters. Field test equipment was found to be not sensitive enough to detect trace amounts of chlorine (these kits are used primarily in waste water treatment plants to detect chlorine in ppm concentrations). Trace amounts of chlorine must be evaluated by laboratory equipment, but the holding time is "as soon as possible" and not more than one hour. The closest available lab is at the University of Maine, which is more than an hour's driving time away. Thus we were not able to evaluate in-stream reactive chlorine.

Dissolved oxygen (DO) is one of Maine's water quality criteria. In order to support aquatic life in Class AA streams, DO must be "as naturally occurs." For Class A and B streams, DO must be 7.0 mg/L or more, or more than 75% saturation, whichever is greater. The percent saturation allows for variability due to temperature effects (oxygen is less soluble in warm water). DO was measured in the field from 2002-2005 along with water temperature, and the measured DO levels were mostly good (Figure 8).



<u>Figure 8</u>. Narraguragus River sites with dissolved oxygen (DO) data in mg/L. Sites are arranged alphabetically, not by position in the watershed.

All sites have adequate dissolved oxygen (DO) for salmonid populations, except for some summer samples from Humpback, Lawrence, and Schoodic Brooks. These streams are predominantly slow-moving beaver flowages with peaty bottoms. Because the low DO is apparently due to natural conditions (a combination of beaver activity, slow currents and poor mixing, high summer temperatures, and organic-rich stream bed) these streams meet their water quality classifications under the "as naturally occurs" part of the narrative standards.

Bacteria sample sites were located in the lower river in Cherryfield because of the concentration of residential development and the OBDs in the lower river. *Escherichia coli*, which are symbiotic with warm blooded animals (mammals and birds), was measured. We were not able to identify any failed systems or straight pipe discharges. In fact, most of the high bacteria results were apparently related to wildlife (such as ducks and cormorants at the Cable Pool, located above all the OBDs). Other than evaluating bacteria occurrences relative to human population density and development, there is currently no convenient way to distinguish wildlife sources from human or domestic animal sources. Based on our information and best professional opinion, bacteria in the lower river do not seem to be of human origin.

Biomonitoring:
The DEP biomonitoring program has two sites on the Narraguagus, one in Deblois on the mainstem just above the Route 193 bridge at Great Falls (a Class AA site), and the second site in Cherryfield below the two blueberry canneries (a Class B area). After being colonized for one month, rock baskets or riffle bags were collected and invertebrates were identified and quantified. The results were put into a multivariate computer model to see if the sites were supporting the numbers and types of invertebrates expected of Class AA or Class B waters (Davies & Tsomoides 1997). The results for our sites show improvement in water quality at Cherryfield (Table 10), probably due to improvements in one discharge and the elimination of the other discharge by the blueberry packing plants in the late 1990's. In addition to the model results, the number of taxa and the kind of species present indicate that Cherryfield is experiencing some nutrient enrichment but that otherwise the water quality is good.

Table 10. DEP biomonitoring results for both Narraguagus study sites, with the classification of the river at the study site (Class), the results of the multivariate model given the taxa and abundances of the invertebrate community (Results), and the total number of individuals present in the collection (Abundance). NA stands for "non-attainment" of any stream classification. For the purposes of the model, there is no difference between an AA classification and A results.

Location	Year	Class	Results	Abundance
Cherryfield	1984	B	NA	364
	1993	B	C	1054
	2001	B	A	1465
Deblois	1987	AA	A	282
	1989	AA	A	602
	1996	AA	B	542
	2001	AA	A	660

IV. Summary:

Grab samples show that the Narraguagus River has good water quality overall, and the downtown Cherryfield site appears to have improved and currently exceeds Class B water quality standards. The upper river is a strong source of calcium, ANC, DOC and Al. The river widens at Beddington Lake and solar radiation causes the oxidation and loss of DOC (and although our data does not clearly show it, there is probably a lot of sedimentation of Al, iron and phosphorus too). The lower tributaries rebuild DOC levels in the lower river. The West Branch is similar to the lower tributaries in that these are important sources of DOC and Al, they are acidic and calcium-poor. Data sonde records show that there is a close linkage between water chemistry and stream flow. Alkaline components in the river come primarily from soils and bedrock while acidic components come from marine aerosols, acid rain, and from soils. There are several important acids and several important bases, all of which have an important impact on the acid-base balance. Dilution is the dominant process affecting storm flows, but there is also generally an increase in DOC from soil runoff. The effect of sulfate and acid rain is primarily a reduction in surface water alkalinity which makes our rivers more prone to pH extremes. Acid rain has also probably caused reductions in calcium concentrations in our soils, streams and rivers, while simultaneously increasing aluminum concentrations in soil water, streams and rivers. While pH in the Narraguagus River mainstem is moderate, aluminum and calcium levels are at harmful thresholds. Inorganic aluminum (what we have called Alx) is "an unambiguous indicator of acidic deposition effects" (Lawrence et al 2007). Less is known about temporal variation in water chemistry in tributary streams, especially headwater areas which have not been sampled at all in our study.

Acid rain is an important problem for many aquatic ecosystems throughout the northeastern USA and Canada. New York, Vermont, and New Hampshire have a number of listed water bodies (mostly lakes) that do not meet their state water quality classifications due to acid rain. These states have developed draft or final TMDL assessments for these impaired waters. Maine currently has no bodies of water listed under the Clean Water Act for acid rain problems, but probably should. At the very least, the White Mountain ecosystems in Maine and the downeast salmon rivers have impaired bodies of water. To our east, Nova Scotia has 14 former salmon rivers that are thought to have lost their populations due to acid rain problems (Amiro & Gibson 2007). Currently, only Cape Breton has enough freshwater salmon production and returning sea-run fish to sustain wild populations. All other salmon rivers are currently without salmon or have declining populations (Amiro & Gibson 2008). In the northeastern USA, it is thought that the average lake may have lost approximately 40% of its buffering capacity (Ophardt 2003), while some better buffered lakes may have lost nothing at all, and vulnerable lakes may have lost all of their buffering and are chronically acidic. In Maine, Davis et al (1978) showed reduced buffering capacity increased acidity in lowland lakes over broad regions of the state, presumably due to acid rain. Acid rain is not just a problem found in alpine watersheds.

The mainstem of the Narraguagus River and the West Branch have similar chemistry during baseflow conditions. During high flow events, the lower river is affected by the West Branch. The mainstem becomes more acidic and the acidic episodes last longer than they otherwise would. In our study, the impact of the West Branch on the mainstem amounted to a reduction of 0.2-0.3 pH units during typical high flows. The West Branch is more like the Pleasant and Machias Rivers, which experience acidic episodes which last for weeks (Whiting et al 2007b), than it is like the mainstem of the Narraguagus River where acidic episodes last only a few days. Even in the extremely wet fall of 2005, pH values below 5.6 on the lower mainstem were rare and fleeting. We concur with the analysis of Dill et al (2002), that salmon restoration in the downeast rivers is inhibited by low pH, low calcium and high Al. This is the typical acid rain complex (Jenkins et al 2005, Lawrence et al 2007). Even during baseflow conditions, the Narraguagus River has marginal water quality; pH is good, but calcium and aluminum levels are near or exceed harmful thresholds. The episodic acidification events during high flows, result in low ANC and depressed Ca, which are even more problematic to salmon recovery than pH *per se*. We conclude that mitigation programs should be pursued even in the Narraguagus River, the downeast salmon river with the best water quality.

The Narraguagus River currently meets its state water quality classification. However, Maine currently does not have specific acid rain-related water quality criteria. The Narraguagus River mainstem has some indications of acid rain impairment. Some headwater streams are likely to be severely impaired. Moreover, except for the Dennys River, the other downeast salmon rivers are in worse shape than the Narraguagus in terms of episodic acidification and calcium. We believe that Maine will probably have to develop a program to address acid rain effects for salmon and brook trout conservation in eastern and western Maine watersheds.

The Narraguagus River is rich in nutrients, but most nitrogen and phosphorus are in organic and particulate forms. These nutrients become available to aquatic life as these forms are modified by biological processes and sunlight. Overall, the river and tributaries are oligotrophic, but wide shallow river reaches have been observed to support algal blooms in the summer. Localized algal blooms could result in some reaches being considered "impaired" under draft administrative rules currently under consideration.

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