TECHNICAL MEMORANDUM

ALKALINITY IN THE POTOMAC AT THE FALL LINE

Report to:

Office of Environmental Programs

MD Department of Health and Mental Hygiene

by the

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Introduction

One conclusion of the Expert Panel engaged by the Potomac Strategy State/EPA Management Committee to study the 1983 algae bloom in the Potomac was that the estuary's ability to buffer against alkaline pH shifts has apparently declined since the late 1970's (Thomann, et.al., 1985). It was also concluded that the low alkalinity condition during the summer of 1983 enabled a large rise in pH to occur due to the normal algal photosynthesis process, which subsequently led to mobilization of absorbed sediment phosphate and its release to the water column, thus fueling the algae bloom. The Panel surmised that some, but certainly not all, of the estuary's reduced buffering capacity may be attributed to the implementation of advanced wastewater treatment processes which changed acid/alkalinity characteristics of wastewater treatment plant effluents discharging to the tidal Potomac. While some technical questions about the Panel's interpretation of the relationship between alkalinity and buffering capacity and the importance of the wastewater treatment plants as a source of alkalinity have surfaced (MWCOG, 1985a), there is no question that lower than normal alkalinity conditions were observed during 1983 in the vicinity of the algal bloom.

In simple chemical terms, alkalinity as measured in units of calcium carbonate ($CaCO_3$) represents the capacity of a solution of water to neutralize acid. The purpose of the investigation described herein was to evaluate the long-term behavior of alkalinity in Potomac waters entering the tidal estuary at the Fall Line. It was thought that changes or variability in this prime source of alkalinity may offer some explanation for the apparent lowering of alkalinity conditions in the Potomac during 1983, and for what the Panel described, perhaps incorrectly, as a reduction in buffering capacity. This investigation was undertaken for the Maryland Department of Health and Mental Hygiene, Office of Environmental Programs, with funds provided with a grant under Section 205(j) of the Clean Water Act.

Sources of Data

The principal source of alkalinity data was the record of observations made by the Washington Aqueduct Division of the U.S. Army Corps of Engineers at their water supply intake structures near Little Falls and Great Falls. The observations at both of these points are made from grab samples taken from the Potomac. These observations are generally made on a daily basis from Monday through Friday. The period of record at Little Falls extended from January, 1963 to March, 1985. At Great Falls the record extended from January, 1977 to May, 1984. An additional source of alkalinity data was the daily observations made by the Washington Suburban Sanitary Commission at their water supply intake and water treatment facility near Watkins Island. The record at this station extended from January, 1978 to December, 1983, and typically covered seven days per week. Alkalinity was measured and recorded in units of mg/l of $CaCO3$ at all of these stations.

By way of reference, the Little Falls intake facility lies approximately one mile above the head of the Potomac Estuary and tidal water, and hydrologically it is located virtually at the Fall Line. Great Falls lies approximately ten miles above tidal water, and Watkins Island is located another three miles upstream. Given the vast extent of the Potomac basin and the drainage area of 11,560 square miles above Little Falls, the location of all three stations at the lower end of the basin (Figure 1) suggests that

Figure 1. The Potomac River Near the Fall Line and Washington, D.C.

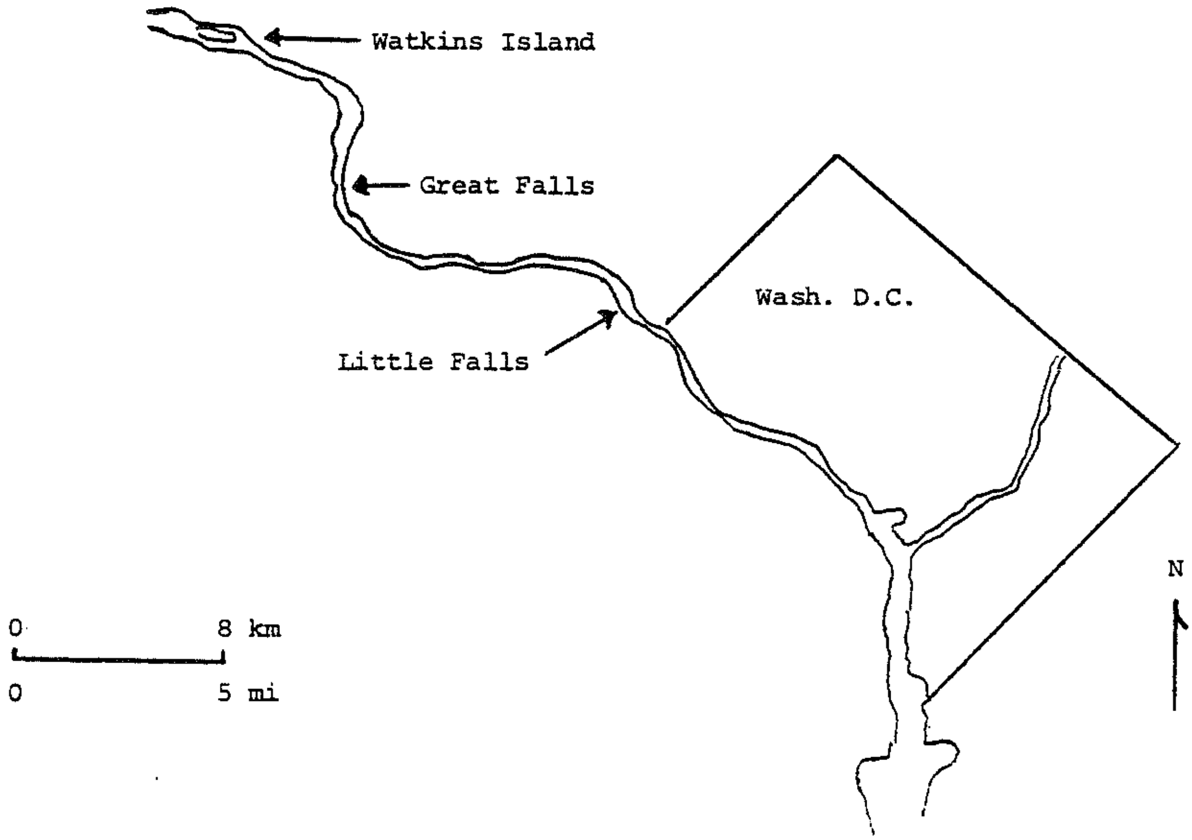
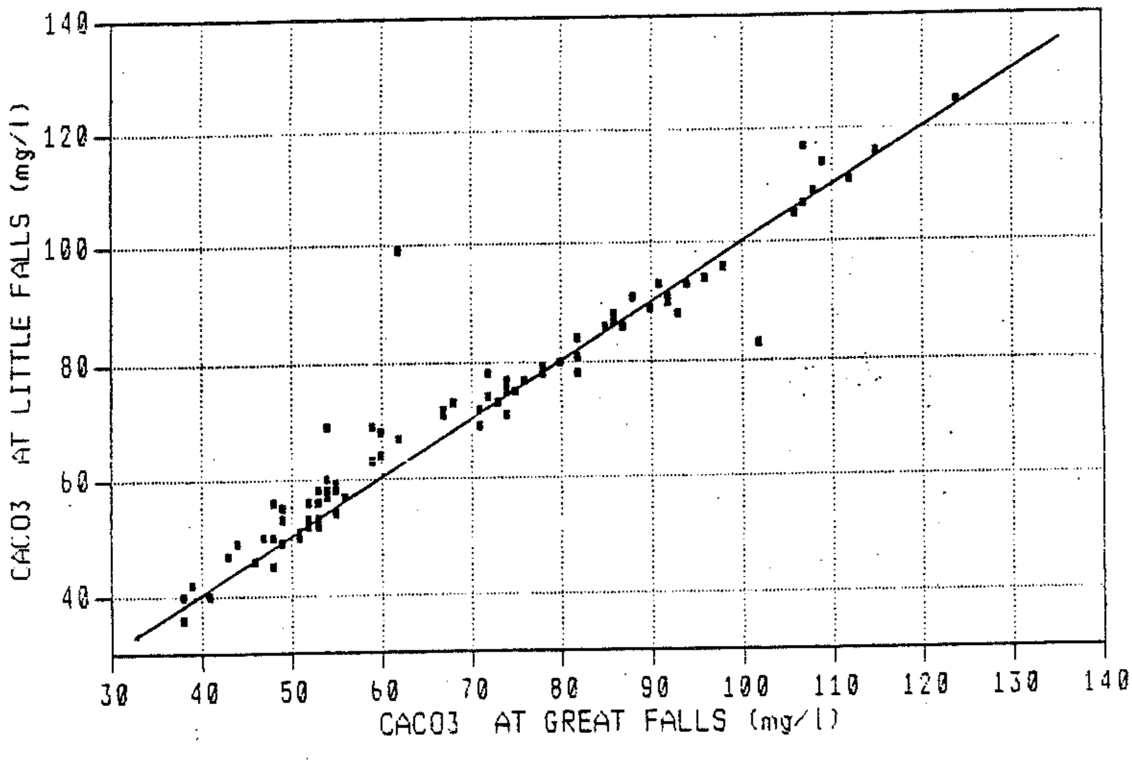


FIGURE 2
COMPARISON OF ALKALINITY
LITTLE FALLS vs GREAT FALLS



water quality could be expected to be rather similar at these stations and representative of "Fall Line" conditions.

Analysis of the Data

Statistical Analysis

For the purpose of conducting this analysis, monthly mean values for alkalinity in units of mg/l of $CaCO_3$ were utilized for all three stations. Use of monthly means was viewed as a reasonable aggregation of the daily data and appropriate for the evaluation of long term trends. The monthly mean alkalinity values were subjected to a standard statistical analysis to determine measures of central tendency as well as the maximum and minimum occurrences. This information is presented in Table 1.

The data for all three stations was quite comparable. The mean, standard deviation and median values were very similar from station-to-station, and the maximum and minimum values were essentially the same as well. The distribution of alkalinity values at all three stations was approximately normal, but with a very slight positive skew as indicated by the nearly identical low skewness coefficients in Table 1. The distributions all had a certain "flatness" to them, especially Great Falls and Watkins Island, where fewer observations were available. This "flatness" is reflected in the fairly low coefficient of Kurtosis values shown in Table 1.

A comparison of mean monthly alkalinity values at Little Falls and Great Falls is presented in Figure 2. This graph illustrates that periods of high or low alkalinity at Little Falls nearly always correspond with similar levels of alkalinity at Great Falls.

Table 1. Analysis of Monthly Alkalinity Data in mg/l CaCO3

	Little Falls	Great Falls	Watkins Island
n (# obs.)	241	89	72
mean	73.6	69.3	70.0
std. dev.	16.9	20.6	19.8
median	73	67	68.5
maximum	125	124	112
minimum	36	38	35
skewness	0.48	0.64	0.50
kurtosis	0.05	-0.44	-0.75

Table 2. Comparison of Average Monthly Alkalinity and Streamflow Conditions at Little Falls

Month	Alkalinity (mg/l CaCO3)	Streamflow (cfs)*
January	69.5	13,645
February	60.5	16,662
March	56.4	22,931
April	60.6	19,422
May	67.0	14,610
June	73.6	8,812
July	78.3	4,956
August	80.4	5,018
September	88.0	4,568
October	94.8	6,001
November	87.8	6,694
December	70.9	10,410
Annual	73.6	11,119

* 50-Year Averages, U.S. Geological Survey.

Table 3. 1983 Monthly Alkalinity and Streamflow Conditions at Little Falls

Month	Alkalinity (mg/l CaCO3)	Streamflow (cfs)
February	40	15,830
March	36	25,270
April	45	48,260
May	58	24,560

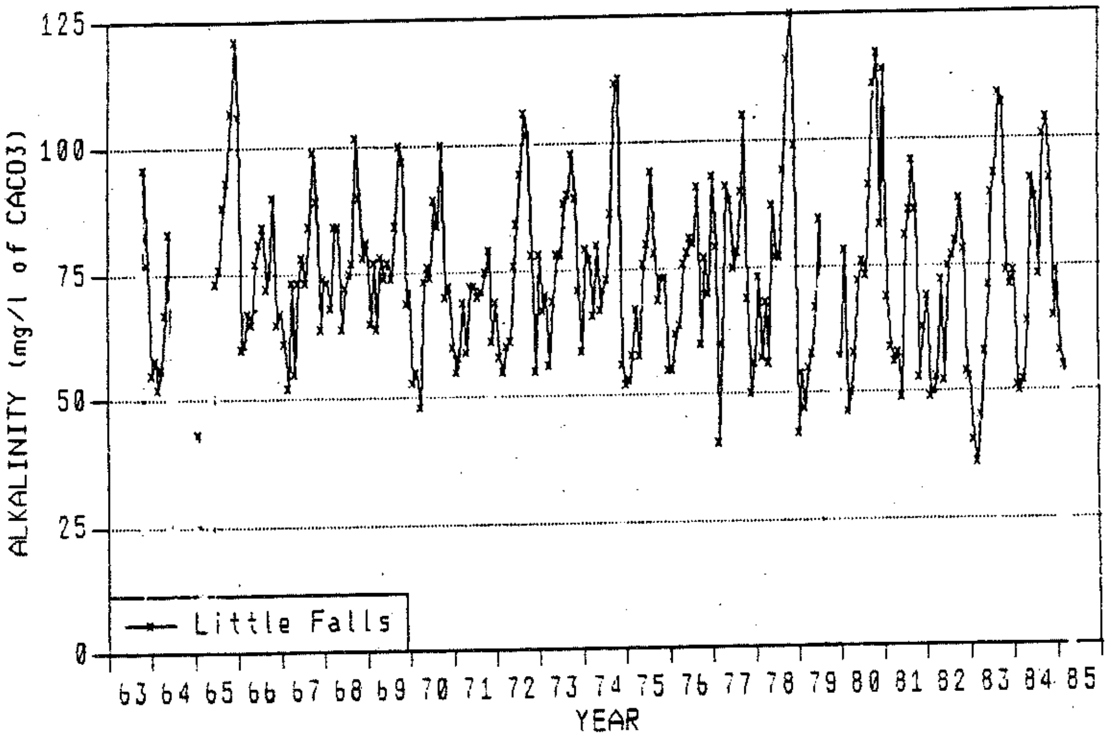
This analysis was interpreted to mean that there is no substantial difference in alkalinity conditions in the stretch of the Potomac between Little Falls and Watkins Island. Further, the twenty-three year record at Little Falls is considered to be representative of Fall Line conditions for the purpose of evaluating trends.

Trends and Relationships

Time series plots of monthly mean alkalinity values for all three stations are presented in Figures 3, 4 and 5. Mean monthly streamflow values at Little Falls as measured by the U.S. Geological Survey are also included in Figure 3. While there is a great deal of scatter and variability in these graphs of alkalinity, there was no statistically significant rising or declining trend. This was determined through regression analysis to evaluate the change in alkalinity over time. The results of this regression for each of the three stations were essentially the same. Each had a regression line with a nearly horizontal slope, and a student's t value of less than 2.0 which indicated that the slope was not statistically different than a slope of zero. This was particularly significant at Little Falls where the alkalinity pattern has remained the same over a twenty-three year period. In a separate analysis of trends and seasonality of Potomac water quality variables using this same data set, Obeysekera and Yevjevich (1985) also found that there was no definite trend in the time series plot of monthly mean alkalinity, and that no significant trend was determined with the application of a variety of regression models and nonparametric tests.

There does appear to be a distinct relationship between streamflow and alkalinity. Mean monthly alkalinity values at Little Falls are graphed with mean monthly streamflow measurements at Little Falls in Figure 6. The

FIGURE 3
FALL LINE ALKALINITY AT LITTLE FALLS



PLOT OF MONTHLY AVERAGE POTOMAC FLOW

LITTLE FALLS

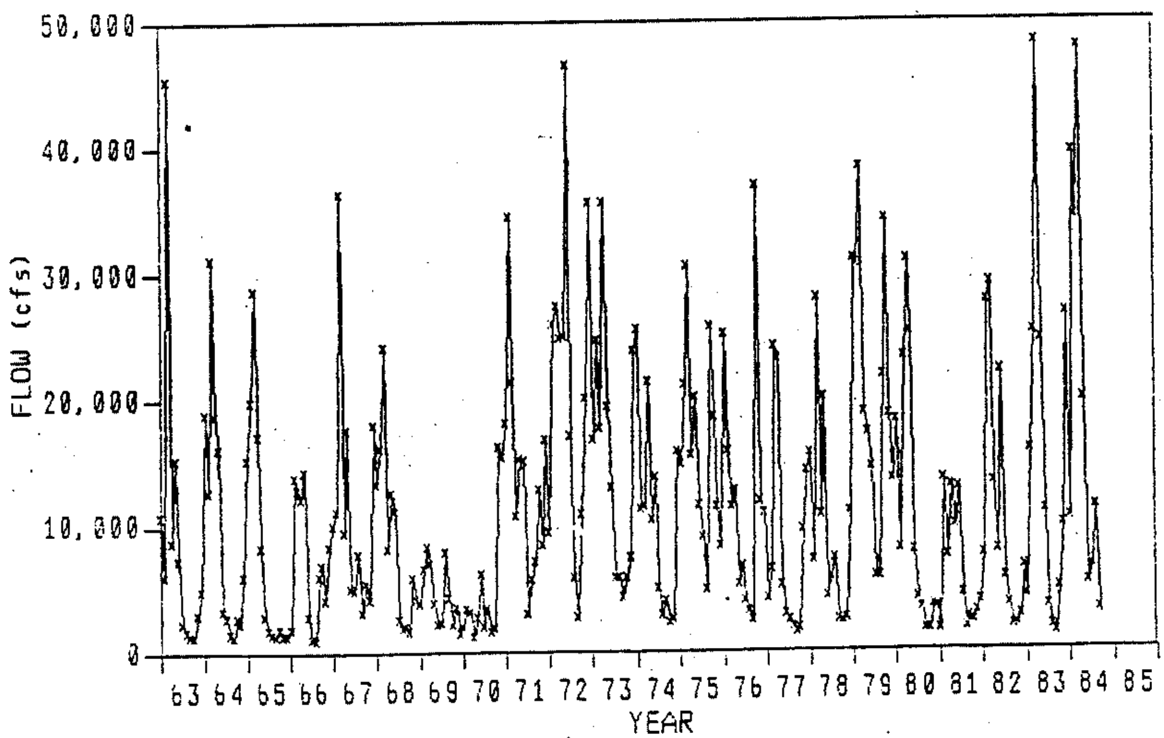


FIGURE 4
FALL LINE ALKALINITY AT GREAT FALLS

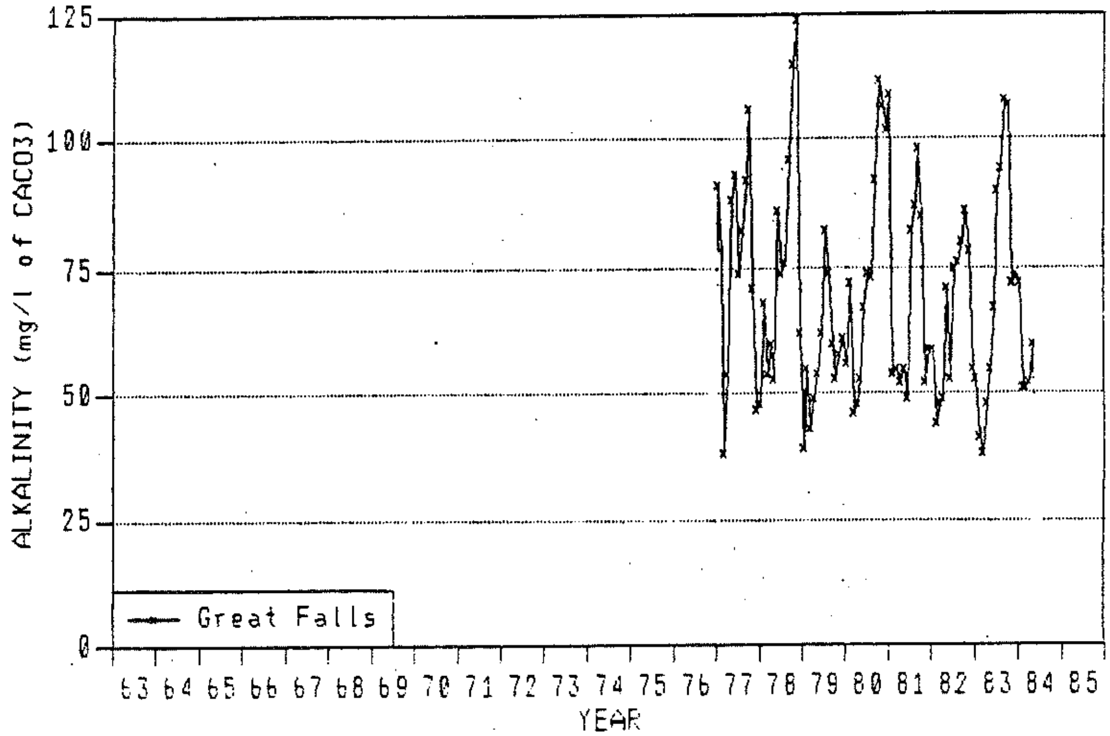


FIGURE 5
FALL LINE ALKALINITY AT WATKINS ISLAND

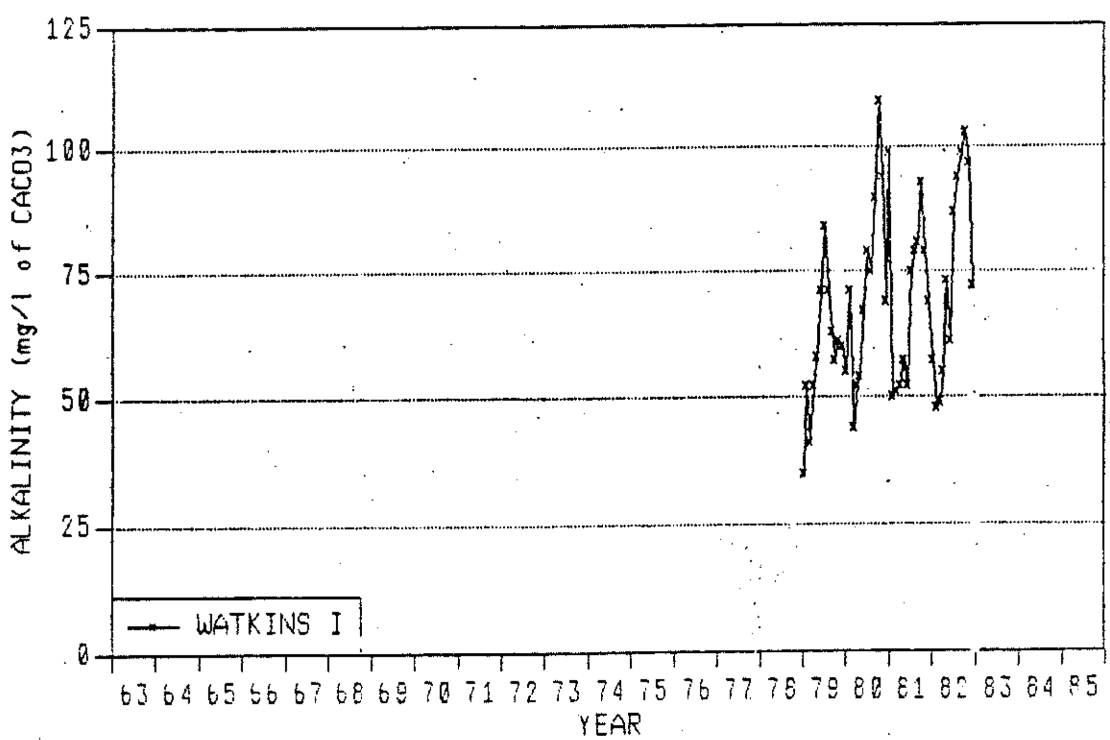


FIGURE 6
RELATIONSHIP BETWEEN FLOW AND ALKALINITY
MONTHLY MEAN VALUES AT LITTLE FALLS

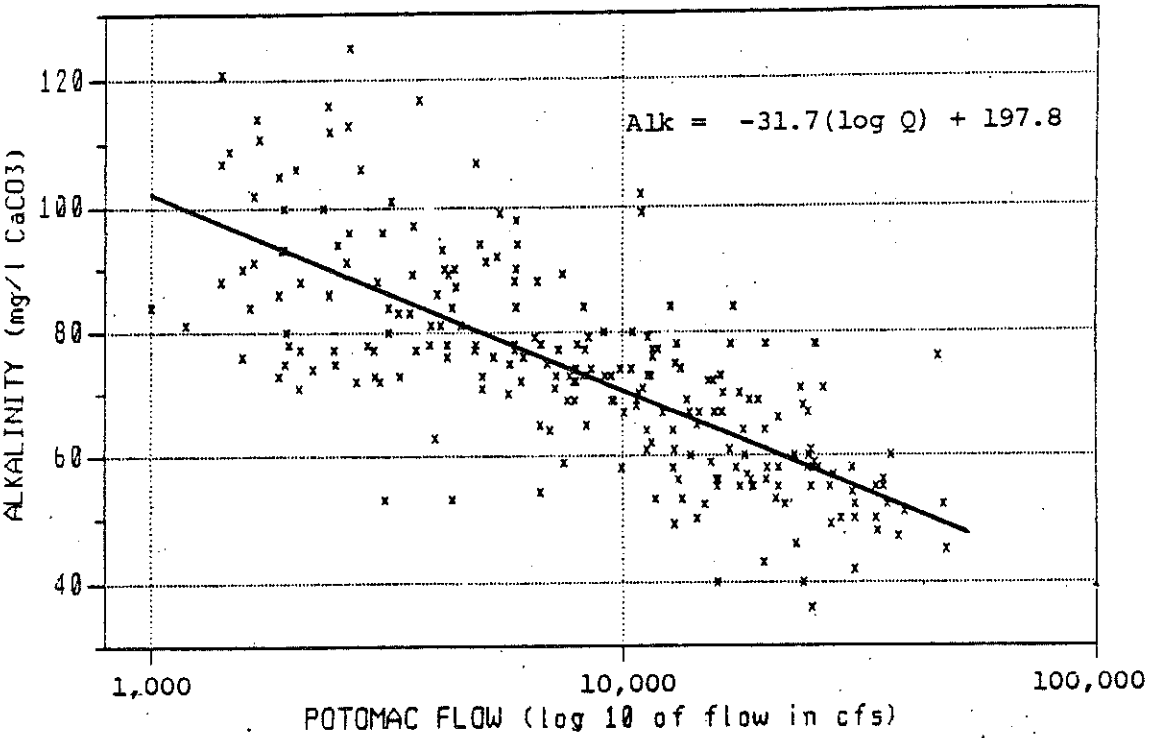
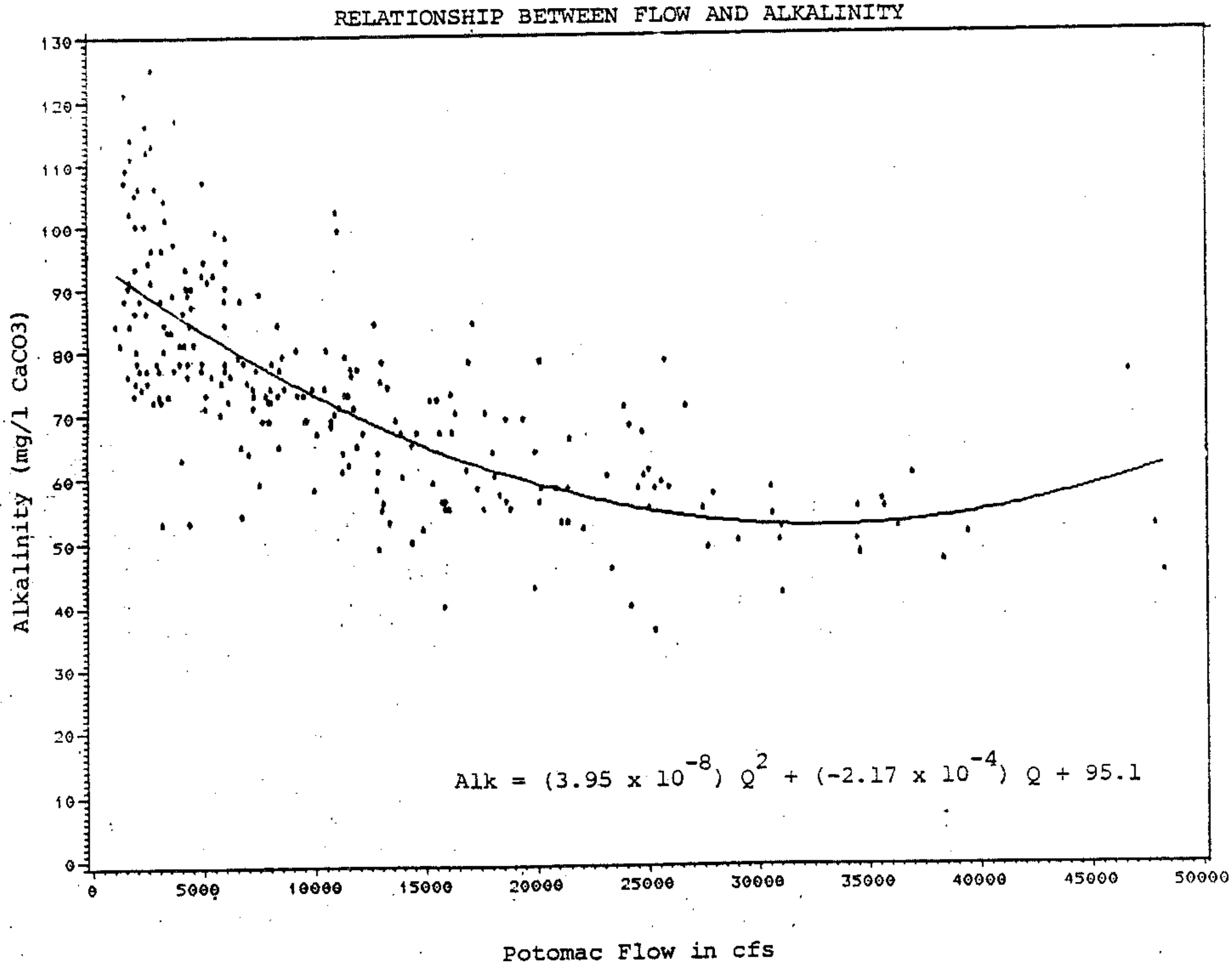


FIGURE 7

RELATIONSHIP BETWEEN FLOW AND ALKALINITY



streamflow values have been placed on a logarithmic scale to account for the log-normalcy of this variable. As shown, there is a definite trend with the higher alkalinity conditions occurring during the lower flow periods. In contrast, the lower alkalinity conditions occur during the higher flows. The regression describing this relationship has an r^2 of 0.56, suggesting that slightly more than half of the variability in alkalinity can be associated with variability in streamflow. A regression analysis utilizing a quadratic equation was also applied and tested with the streamflow and alkalinity data at Little Falls. As shown in Figure 7, this regression also produced a strong relationship which also has an r^2 of 0.56.

Alkalinity conditions in the Potomac appear to follow a distinct pattern from season to season that is probably related to streamflow. On a broad scale, the average alkalinity condition from December through May is 64.1 mg/l. Average streamflow over this six month period is 16,280 cfs. During the other half of the year from June through November, when streamflow is lower and averages 6,118 cfs, the average alkalinity at Little Falls is 83.7 mg/l, nearly 20 mg/l higher.

As shown in Table 2, month-to-month differences in average alkalinity and streamflow conditions are also quite pronounced. The lowest alkalinity conditions typically occur in March, which is usually the month of peak spring runoff in the Potomac. Highest alkalinities can be expected in October, which is typically a month characterized by low streamflow.

Summary and Discussion

While there is a great deal of seasonal and month-to-month variability in the alkalinity condition of waters entering the tidal portion of the Potomac at the Fall Line, no long-term changing trends were found. It had been thought that changes in the acidity of rainfall or other human induced conditions such as mine drainage or agricultural practices may have caused changes in alkalinity at the Fall Line, but this was not evident in the data and analysis. The analysis of twenty-three years of data from the little Falls station indicates that alkalinity at the Fall Line has not changed over time. This analysis suggests that the basic natural determinants of alkalinity such as geology, soils, climate, and meteorological conditions remain dominant and essentially unchanged.

With regard to streamflow, distinct seasonal and month-to-month relationships with alkalinity were found. High streamflows are associated with low alkalinity conditions, and low streamflow with high alkalinity. This suggests that baseflow, the primary component of flow during low flow periods, has a tendency to produce higher alkalinity conditions. Taking this a step further, the natural groundwater environment, i.e., the underlying geology and aquifers of the Potomac basin out of which baseflow originates, probably accounts for the higher Potomac alkalinity conditions that are observed. In contrast, the relatively lower alkalinity conditions that occur during periods of high streamflow are probably due to low alkalinity in surface runoff, and the attendant dilution of the baseflow component with the runoff.

Concerning the broader question about the decline in Potomac Estuary alkalinity conditions from the late 1970's to 1983, as reported in the previously noted Algal Bloom Expert Panel Report, it appears that a decline over time cannot be attributed to inflow to the estuary from above the Fall Line. No discernable declining or rising trend was apparent over the twenty-three year period from 1963 to 1985. However, the specific conditions during the late winter and early spring of 1983, as shown in Table 3, produced particularly large volumes of runoff characterized by rather low concentrations of alkalinity. In fact, the flow-weighted mean concentration of alkalinity at Little Falls for the February through May period of 1983 was 45.1 mg/l. It may be that this large influx of low alkalinity water dominated the estuary throughout the remainder of the summer of 1983, and could have been instrumental in establishing favorable conditions for the development of the 1983 algal bloom. However, a rigorous examination of circulation in the estuary would be required to determine if this was the case or not.

In a separate analysis, the results of a preliminary evaluation of alkalinity in the Potomac with the Potomac Eutrophication Model (PEM) suggested that alkalinity is not conservative under bloom conditions (MWCOG, 1985b). Thus another possible explanation for low alkalinity is that there was an alkalinity sink or loss mechanism present in the vicinity of the bloom. It was further pointed out in a previously noted MWCOG memorandum (1985a) that the precipitation of calcium carbonate could have occurred under 1983 bloom conditions, and that this process could account for alkalinity loss.

A complete accounting of 1983 alkalinity input loads to the tidal Potomac from the two primary sources, the Potomac River at Little Falls and the Blue Plains WWTP in Washington, D.C., is presented in Table 4. The Potomac load was obviously dominant during all of 1983. In fact, on a monthly basis the Potomac load was always greater than the Blue Plains load by a factor of six, and often by one or two orders of magnitude.

A long-term Potomac Studies Program to be undertaken at COG during the late 1980's will investigate the importance of alkalinity in the Potomac and its relationship to algal growth. The Potomac Eutrophication Model (PEM) will be modified to include the appropriate alkalinity chemistry, and model inputs will be modified to include alkalinity inputs. PEM will then be used to examine alkalinity issues.

Reference

Metropolitan Washington Council of Governments, 1985a, "Technical Memorandum: The Role of Alkalinity in the 1983 Potomac Algal Bloom, Follow-up to The Expert Panel Study," Washington, D.C.

Metropolitan Washington Council of Governments, 1985b, "A Simple Potomac Estuary Alkalinity Model: Application to 1983 Data," draft report to the ICPRB, Washington, D.C.

Obeysekera, J.T.B ., and V. Yevjevich, 1985, "Modeling Water Quality Variables of the Potomac River at the Entrance to its Estuary, Phase I: Trend and Seasonality," International Water Resources Institute, George Washington University, Washington, D.C.

Thomann, R.V., and N.J. Jaworski, S.W. Nixon, H.W. Paerl, and J. Taft, 1985, "The 1983 Algal Bloom in the Potomac Estuary," prepared for the Potomac Strategy State/EPA Management Committee, EPA Region III, Philadelphia, PA.

Table 4. Comparison of Potomac River and Blue Plains WWTP Monthly Alkalinity Loads to the Potomac Estuary, 1983

	LITTLE FALLS			BLUE PLAINS		
1983	CaCO mg/l	FLOW cfs	LOAD lbs x 10^3/day	CaCO mg/l	FLOW cfs	LOAD lbs x 10^3/day
January	53	4,373	1,250	33	399	70
February	40	15,830	3,406	37	431	86
March	36	25,270	4,899	26	469	66
April	45	48,260	11,693	30	533	86
May	58	24,560	7,674	27	494	73
June	71	11,080	4,237	26	522	73
July	89	3,595	1,725	35	469	88
August	93	1,906	955	47	477	121
September	109	1,471	871	51	494	136
October	107	4,925	2,827	60	494	161
November	74	9,899	3,953	43	484	112
December	71	26,600	10,188	31	558	92

Sources of Data:

Little Falls Flow: U.S. Geological Survey
Little Falls Alkalinigy: Washington Aqueduct Division, COE
Blue Plains Flow and Alkalinity: Monthly Discharge Records, D.C. WASUA