ALKALANITY TRENDS IN THE POTOMAC RIVER
(for the Potomac Drinking Water Source Protection Partnership (DWSSP) Water Quality Workgroup)

Alkalinity

Alkalinity (the concentration of carbonates, bicarbonates and hydroxide ions in water) is a measure of the buffering capacity of water to resist the change in pH. In nature, alkalinity is primarily the result of the presence of carbonates and bicarbonates. A common source of carbonates and bicarbonates in nature is limestone. When limestone dissolves in water both carbonates and bicarbonates are released. These ions can take up free hydrogen (contributors of high acidity) in environments having low pH values or release hydrogen ions in environments which have high pH values.

pH

pH is a term that is used universally to express the intensity of the acidity of a solution. Acids are compounds that release a proton (H+) and bases are compounds that accept a proton (H+). Therefore the pH is a measure of the hydrogen ion activity. pH stands for 'power of hydrogen' and is numerically defined as the negative log of the molar concentration of the hydrogen ion.

Relationship between pH and Alkalinity

The relationship between pH and alkalinity is complex. The type of alkalinity found in water depends on the pH of water. Although a pH of 7 is neutral, in water chemistry, the pH that separates alkalinity from acidity is approximately 4.3. At a pH of approximately 4.3 and below, no alkalinity is present. There is only Free Mineral Acidity (FMA) and dissolved carbon dioxide (dissolved carbon dioxide is sometimes expressed as carbonic acid, H_2CO_3). As pH increases between 4.3 and 8.3, the dissolved carbon dioxide starts to convert to bicarbonate ion. This conversion is complete at a pH of about 8.3, where only bicarbonate is present. By increasing the pH beyond 8.3, the bicarbonate ion is converted to carbonate ion. Conversion is nearly complete at a pH around 10.2 with almost all the bicarbonate being converted to carbonate. On further increasing the pH beyond 10.2, measurable levels of hydroxide ions along with the carbonate ions is observed.

Increasing Alkalinity in the East Coast Rivers

A recently released study in the peer-reviewed journal *Environmental Science and Technology*, led by Professor Sujay Kaushal of the University of Maryland indicated the changing chemistry in the rivers in eastern United States. Researchers looked at the long-term records of alkalinity trends in 97 streams and rivers from Florida to New Hampshire. It was found that over a time span of 25 to 60 years, two-thirds of the rivers had become significantly more alkaline but more acidic trends were never observed. These trends in increased alkalinity were observed in large rivers like the Potomac River as well as small streams located in urbanized watersheds.

Purpose of this Document
This analysis was completed by the water quality data workgroup of the Potomac Drinking Water Source Water Protection Partnership (Partnership) in an attempt to determine if alkalinity trends similar to those documented in Dr. Kaushal's paper were observed in the stretch of the Potomac River from where the Partnership member utilities withdraw raw water. Seven partner water utilities withdraw raw water from the Potomac River, and supply it to homes, businesses, and key government facilities throughout the Washington Metropolitan Area (WMA), after treatment. The water that occurs in the natural state in the environment, in water bodies, groundwater, rainwater etc., is called raw water. This raw water is treated to remove impurities and make it fit for consumption.

Figure 1: Map Showing Area of Analysis

Chemistry of the raw water often plays an important role in determining the treatment process, especially in the conventional treatment process which includes coagulation, flocculation, clarification, and filtration. Alkalinity is often essential in the coagulation process, to ensure proper floc formation. Adjustments may be required in the treatment process to accommodate for changes in alkalinity. The optimal pH range for coagulation is 6 to 7 when using alum and 5.5 to 6.5 when using iron. For high alkalinity water, excessive amounts of coagulant may be needed to lower the pH to the optimal pH range. The pH controls both the speciation of the coagulant as well as its solubility, and it also affects the speciation of the contaminants. Increased use of coagulants can lead to increase in chemical costs. Hence the interest in alkalinity trends among the partnership members. Figure 1 below shows the map of the general area from which data for this analysis was taken. The analysis is done mostly using raw water data collected by the utilities.

Possible Reasons for Increased Alkalinity

Listed below are some possible reasons for increase in alkalinity in our region:

- Human activities that create acidic conditions are the driving factors for the problem. Naturally formed acids (in the form of acid rain), acidic mining waste, and agricultural fertilizers, can speed the breakdown of limestone, other carbonate rocks, and even concrete and cement as they percolate through the soil and travel over surfaces. This results in carbonate or bicarbonate anions being washed off from the landscape into the waterways.
    - Watershed geology is one of the strongest predictors of river alkalinization. In areas with rivers receiving water from land where geology suggests presence of porous limestone, and other carbonate rocks as in the Potomac Basin, alkalinization is more predominant. Figure 2 below shows the karst regions in the Potomac watershed where there is potential for the phenomenon described above. The shaded regions in the figure show counties where karst geology is prevalent.

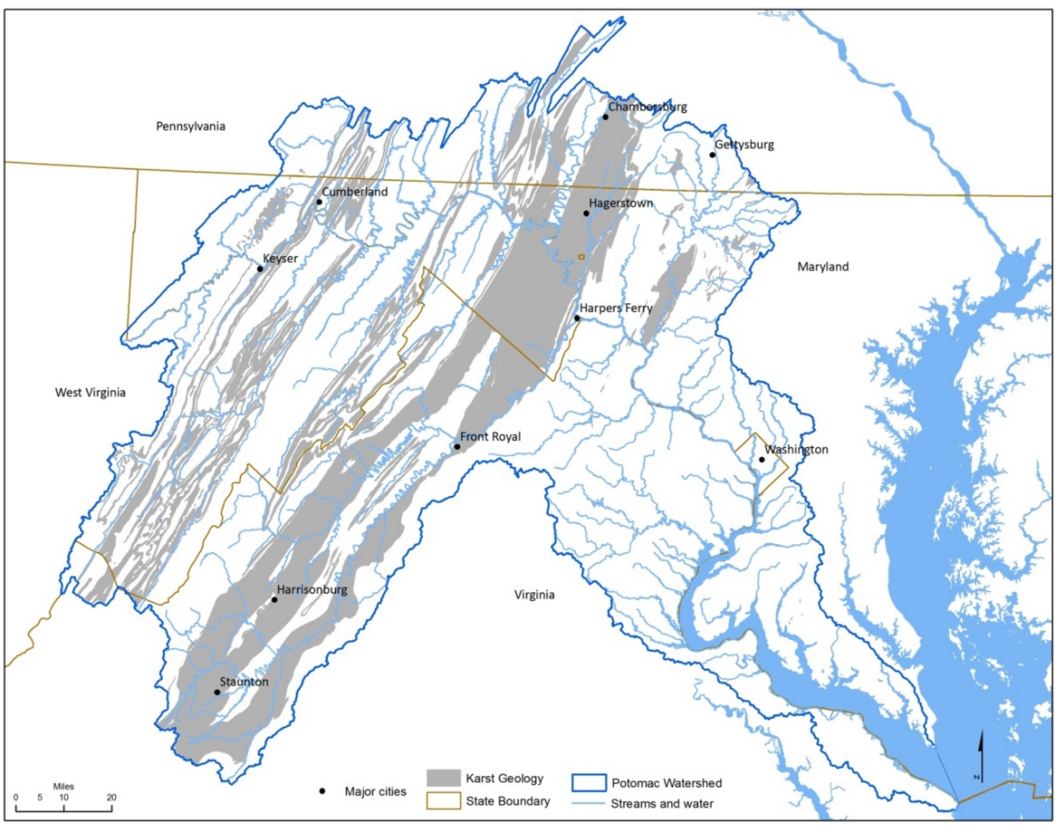

Figure 2 – Karst Regions in the Potomac Watershed

- Topography and pollution are the other triggers. Increased alkalinity observed in the rivers today might be the legacy effect of pollution from decades ago. Acid rain has decreased significantly due to the Clean Air Act regulations. However, lagging effects may be observed for many years to come.

- Acid Mine Drainage (AMD) from abandoned mines is a problem in the North Branch of the Potomac River. Starting in the 1940s, to as recently as the 1970s, abandoned coal mines discharged a significant amount of AMD and impaired an estimated 450 stream miles in the North Branch Potomac. This problem was remediated in 1992 by installing several dosers, which add alkaline material (lime) to the Potomac River and its tributaries to treat AMD. Addition of lime has the potential to increase the pH, as well as the buffering capacity of streams.

Data Sources Used for Analysis

The following sources of data were used to aid in this analysis:

- To evaluate alkalinity and pH trends in the Occoquan Reservoir, data collected by both Fairfax Water and Occoquan Watershed Monitoring Lab (OWML) were analyzed.

- To evaluate alkalinity and pH trends in the Potomac River, data collected by Fairfax Water (FW), Washington Suburban Sanitary Commission (WSSC) and the Town of Leesburg (Leesburg) were analyzed.

Alkalinity Trends in the Occoquan Reservoir

Fairfax Water's data for alkalinity dates back to 1981. Data were collected mostly on a bi-weekly basis. Figure 3 below shows alkalinity values in the Occoquan Reservoir. As seen from the trendline plotted, there is an increasing trend for alkalinity values in the Occoquan Reservoir. Statistical analysis further confirms this. Looking at five years of data at a time, if the 95th percentile and the 5th percentile alkalinity values for the years 1981 to 1986 were compared with the same statistic for the years 2009 to 2013, a significant increase was observed. The values are given in Table 1. Figure 4 below shows the pH values in the Occoquan Reservoir from 1981 to 2013. Data were collected in varying frequencies ranging from weekly to monthly values for certain times of the year. The trendline shows an increasing trend for pH values in the Occoquan Reservoir. The statistical analysis (Table 1) also shows a slight increasing in pH values.

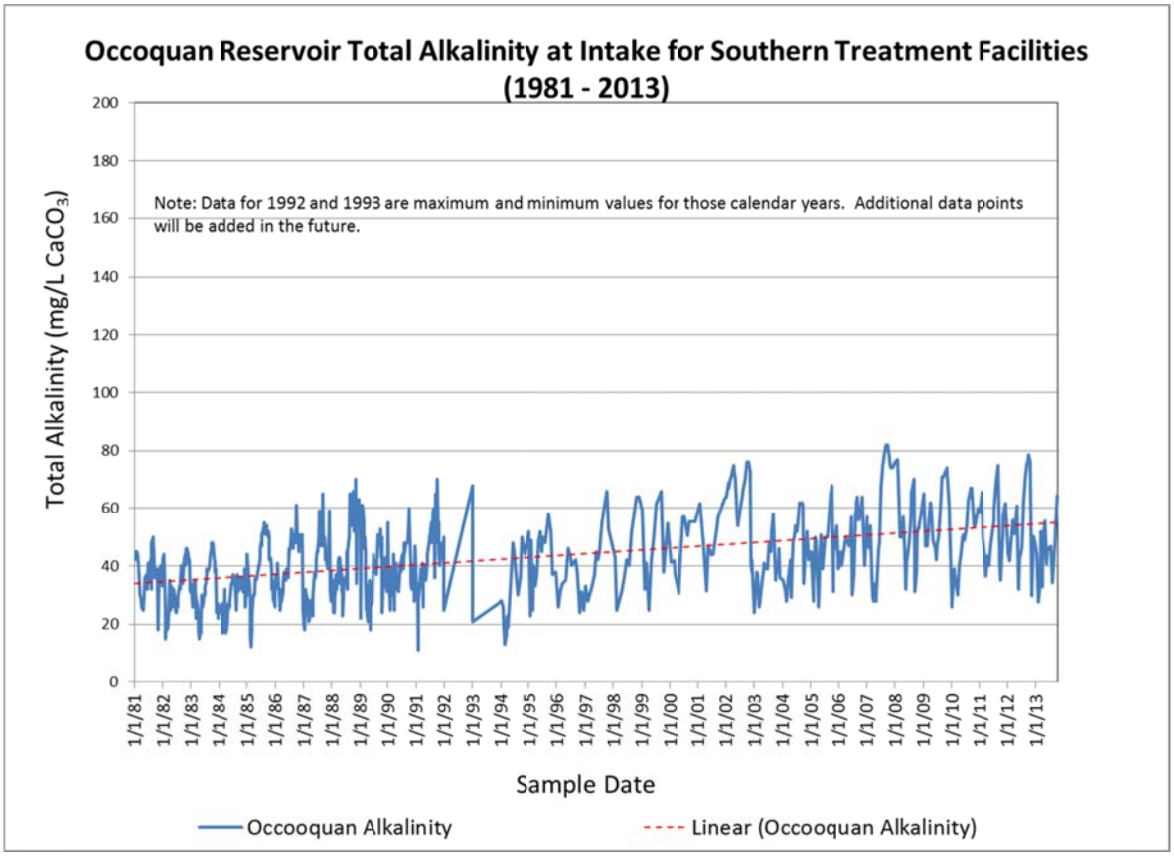

Figure 3 – Alkalinity in the Occoquan Reservoir (FW Data)

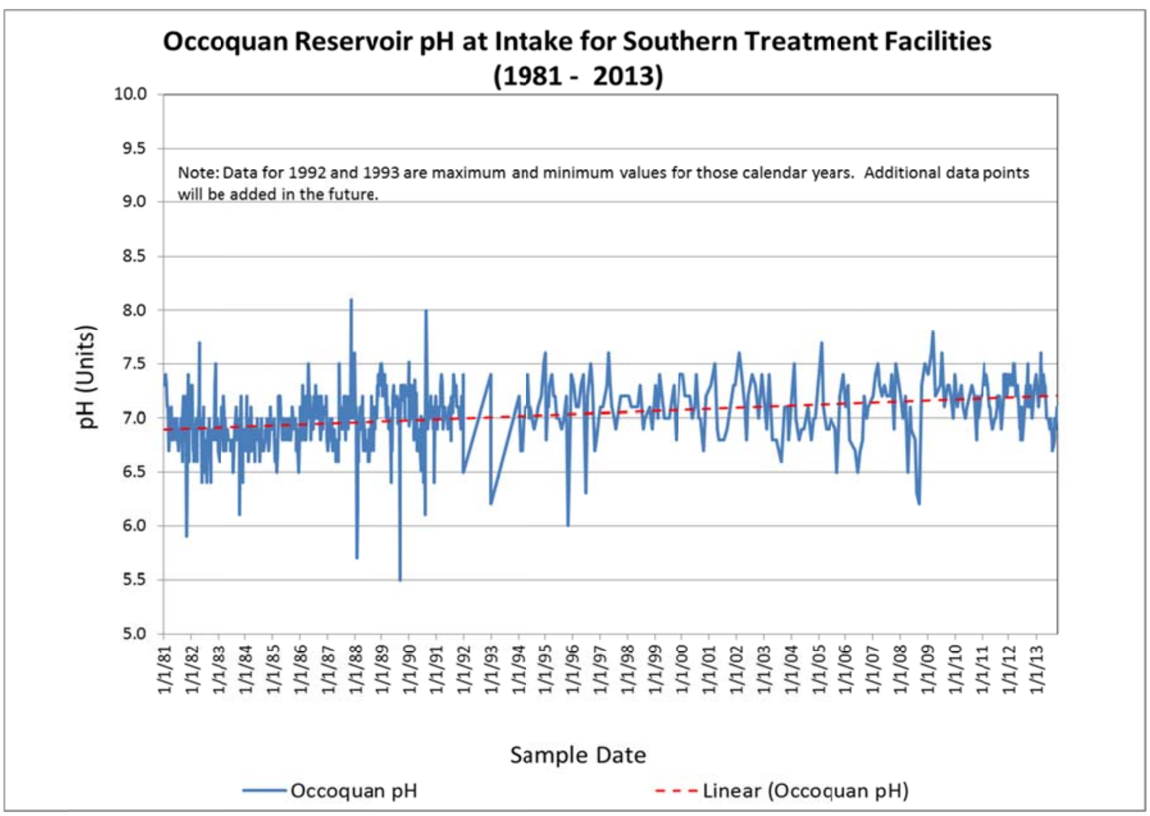

Figure 4 - pH in the Occoquan Reservoir (FW Data)

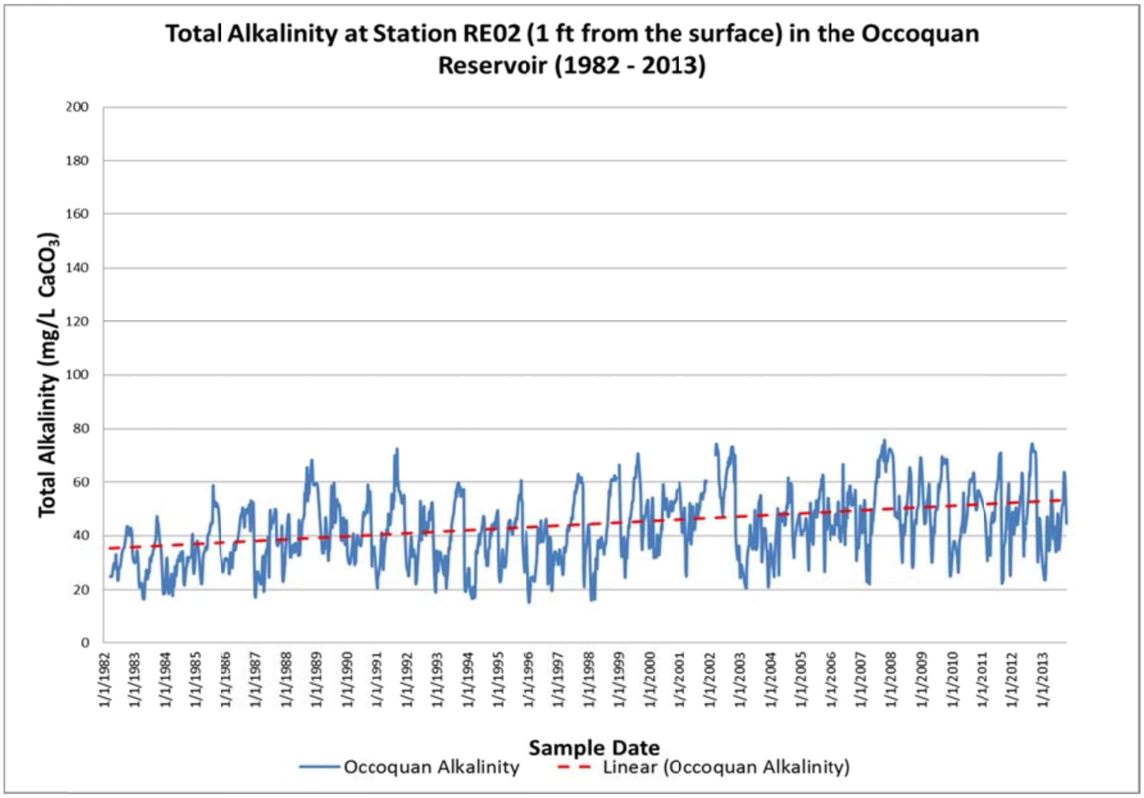

Figure 5 - Alkalinity in the Occoquan Reservoir (OWML Data)

Table 1 – Statistical Analysis of Alkalinity and pH in the Occoquan Reservoir (FW and OWML data)

Organization	Parameter	Year	95th Percentile Value	5th Percentile Value
Fairfax Water	Alkalinity	1981 - 1986	51	18.8
		2009 - 2013	74.5	30.3
	pH	1981 - 1986	7.2	6.6
		2009 - 2013	7.5	6.8
OWML	Alkalinity	1982 - 1987	51.2	20
		2009 - 2013	70	30.7
	pH	1982 - 1987	8.2	6.1
		2009 - 2013	8.9	6.8

Data from OWML for station RE02 in the Occoquan Reservoir (nearest to the Upper Dam) were analyzed for the years 1982 to 2013. Data were collected generally weekly, except during the winter months when it was collected bi-weekly. Figure 5 shows trends in alkalinity and Figure 6 shows trends in pH. The trends observed are very similar to the trends observed by analyzing Fairfax Water data. Similar to the analysis done for the Fairfax Water data, a statistical analysis was performed on OWML data. The results are tabulated in Table 1. The statistical analysis also shows an increasing trend for both pH and alkalinity in the Occoquan Reservoir.

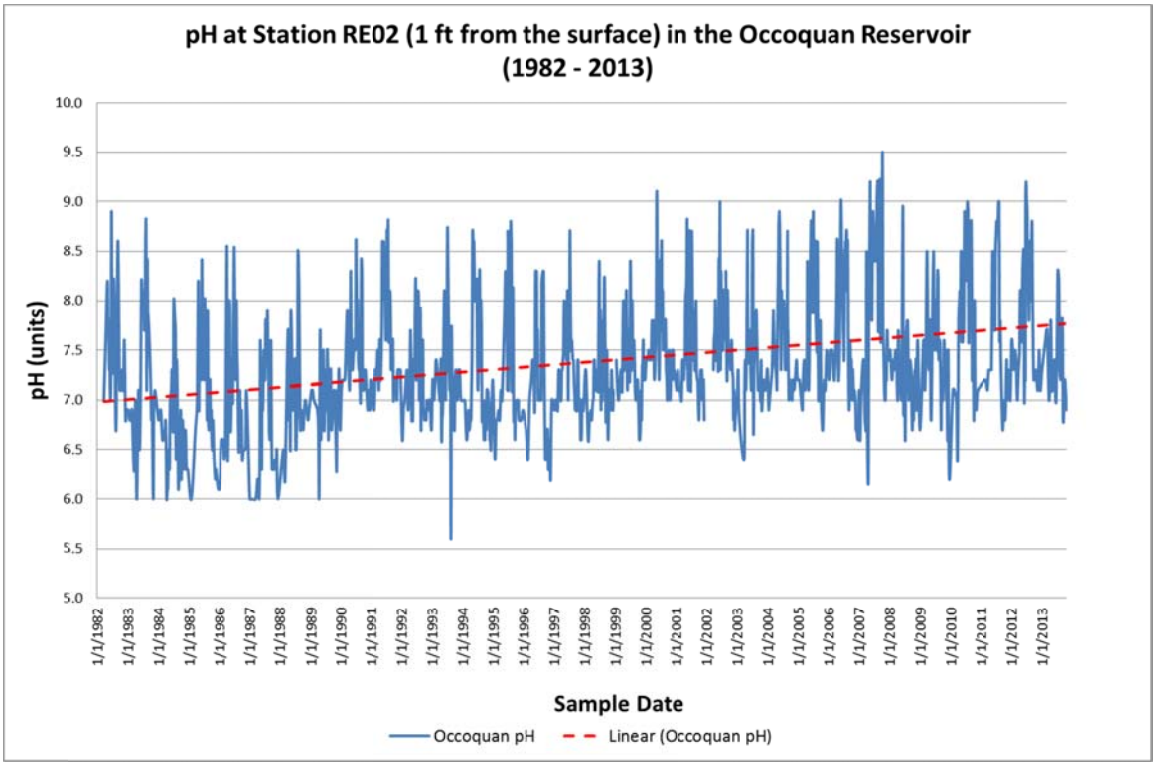

Figure 6 - pH in the Occoquan Reservoir (OWML Data)

Alkalinity Trends in the Potomac River

Fairfax Water's alkalinity and pH data for the raw water from the Potomac River were analyzed for the years 1981 to 2013. The data were collected in varying frequencies ranging from weekly to monthly for various times of the year. Figure 7 below shows alkalinity values in the Potomac River. Statistical analysis similar to the one done for the Occoquan Reservoir was done. The values are given in Table 2. As seen from Figure 7, the graph shows that the range of values for alkalinity have decreased in the recent years as is seen from the tapering nature of the graph as indicated by the green lines drawn in Figure 7. The statistical analysis in Table 2 confirms this. The trendline shows an increasing trend for alkalinity values. Figure 8 below shows the pH values in the Potomac River for the years 1981 to 2013. The trendline shows consistent pH values. The statistical analysis (Table 2) further confirms this.

WSSC and Leesburg are two other utilities that withdraw water from the Potomac River. To confirm the trends for alkalinity observed in the Potomac source waters, similar analysis was done on data from WSSC and Leesburg. Figure 9 and Figure 10 respectively show alkalinity and pH data from WSSC. WSSC has daily alkalinity and pH data for the years 1982 to 2013. Figure 11 and Figure 12 respectively show alkalinity and pH data from Leesburg. Daily alkalinity and pH values for the years 2000 to 2013 were generally available from Leesburg.

Statistical analysis similar to that done for the Occoquan Reservoir was done. The values are given in Table 2. There is a slight variation in values of alkalinity between the samples collected from the three different locations along the Potomac River. This could be due to subtle differences in characteristics specific to the different locations. However, similar increasing trends were observed for alkalinity values. The pH values and trends observed were similar for all three locations, except for a slightly decreasing trend for Leesburg data. This is further supported by the statistical analysis. It might be worth noting that the Leesburg dataset had comparatively fewer years of data. The tapering in the range of alkalinity values in recent years observed in the Fairfax Water data were not observed in the data for alkalinity from the other two locations in the Potomac River.

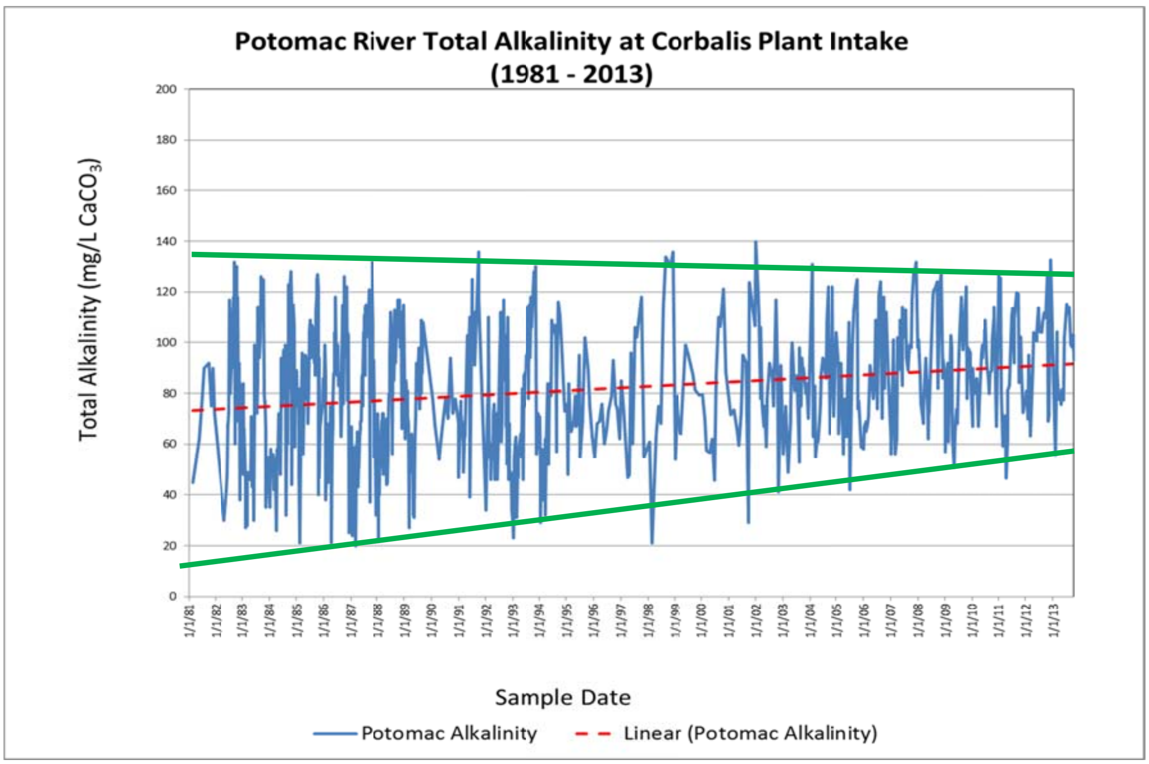

Figure 7 – Alkalinity in the Potomac River (FW Data)

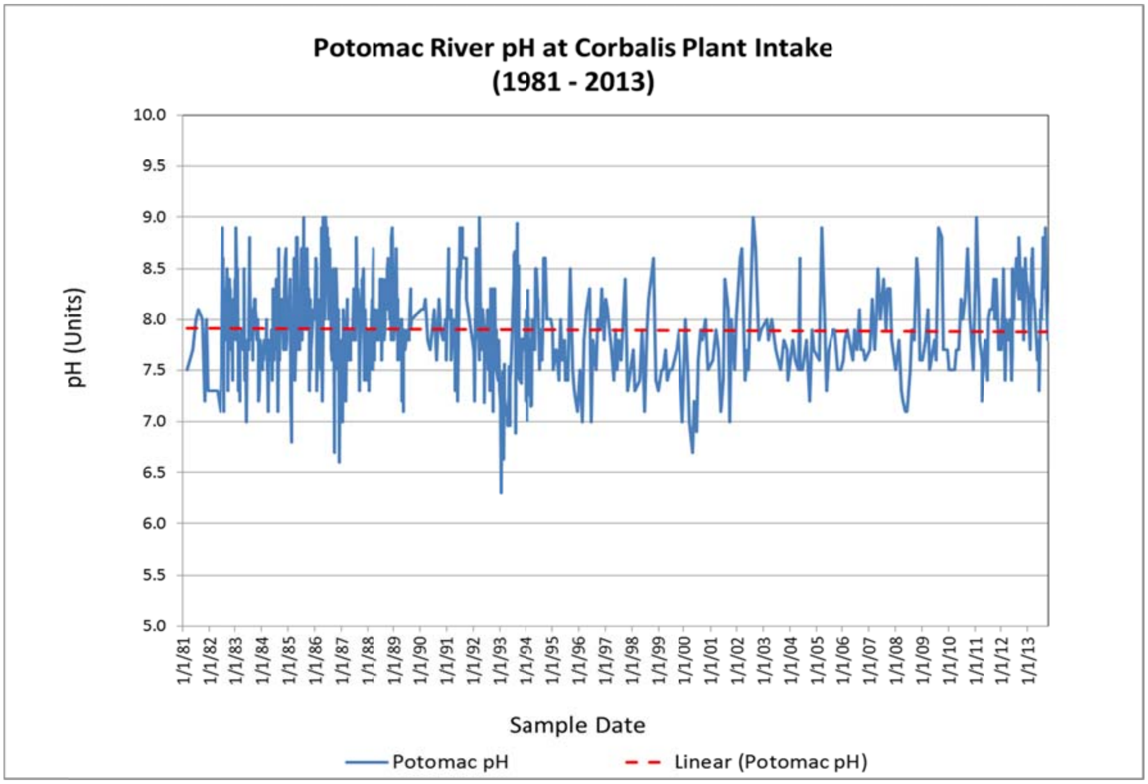

Figure 8 – pH in the Potomac River (FW Data)

Table 2 – Statistical Analysis of Alkalinity and pH in the Potomac River (FW, WSSC and Leesburg Data)

Organization	Parameter	Year	95th Percentile Value	5th Percentile Value
Fairfax Water	Alkalinity	1981 - 1986	123	38
		2009 - 2013	120.5	60.3
	pH	1981 - 1986	8.8	7.2
		2009 - 2013	8.8	7.4
WSSC	Alkalinity	1982 - 1987	106	45
		2009 - 2013	109	59
	pH	1982 - 1987	8.4	7.5
		2009 - 2013	8.7	7.3
Town of Leesburg	Alkalinity	2000-2005	144	64
		2009-2013	147	69
	pH	2000-2005	8.86	7.72
		2009-2013	8.44	7.52

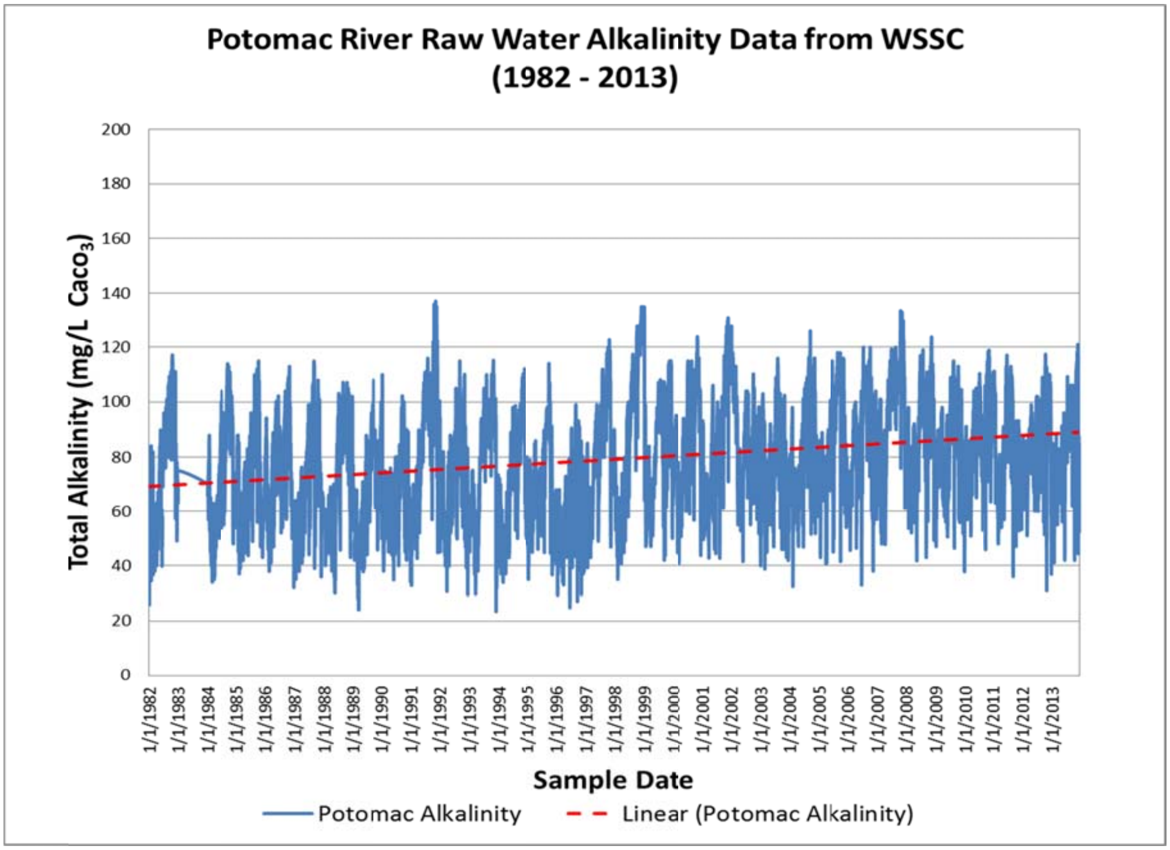

Figure 9 – Alkalinity in the Potomac River (WSSC Data)

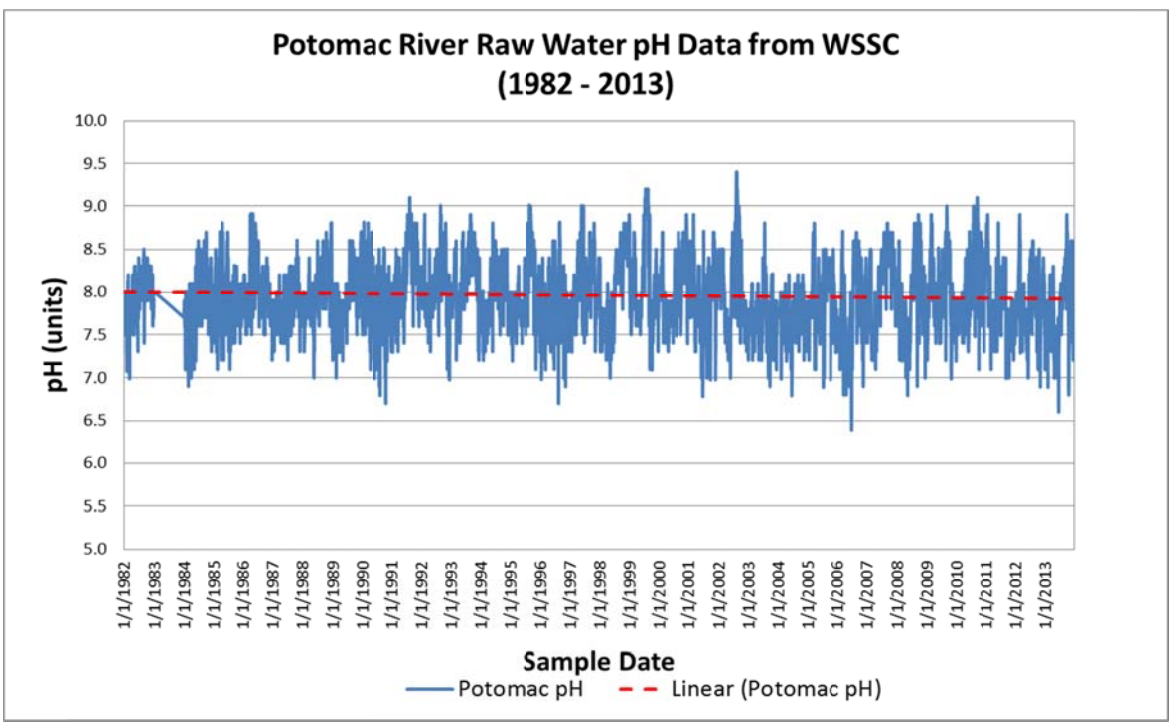

Figure 10 – pH in the Potomac River (WSSC Data)

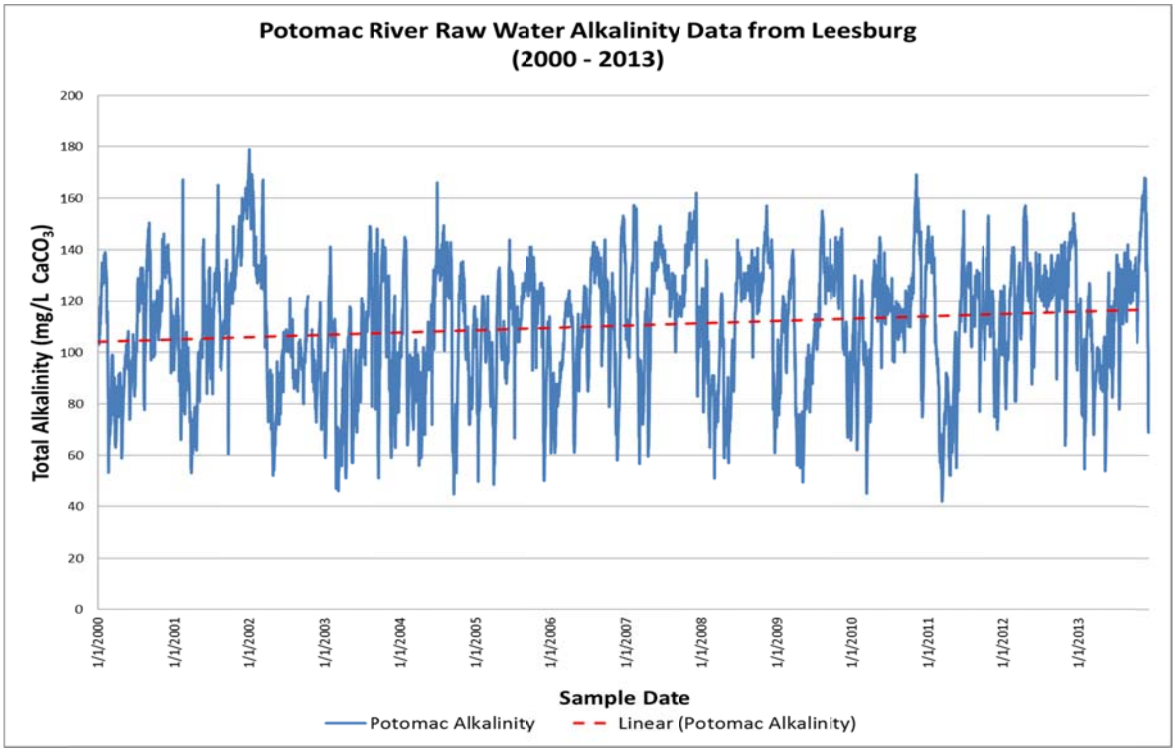

Figure 11 – Alkalinity in the Potomac River (Leesburg Data)

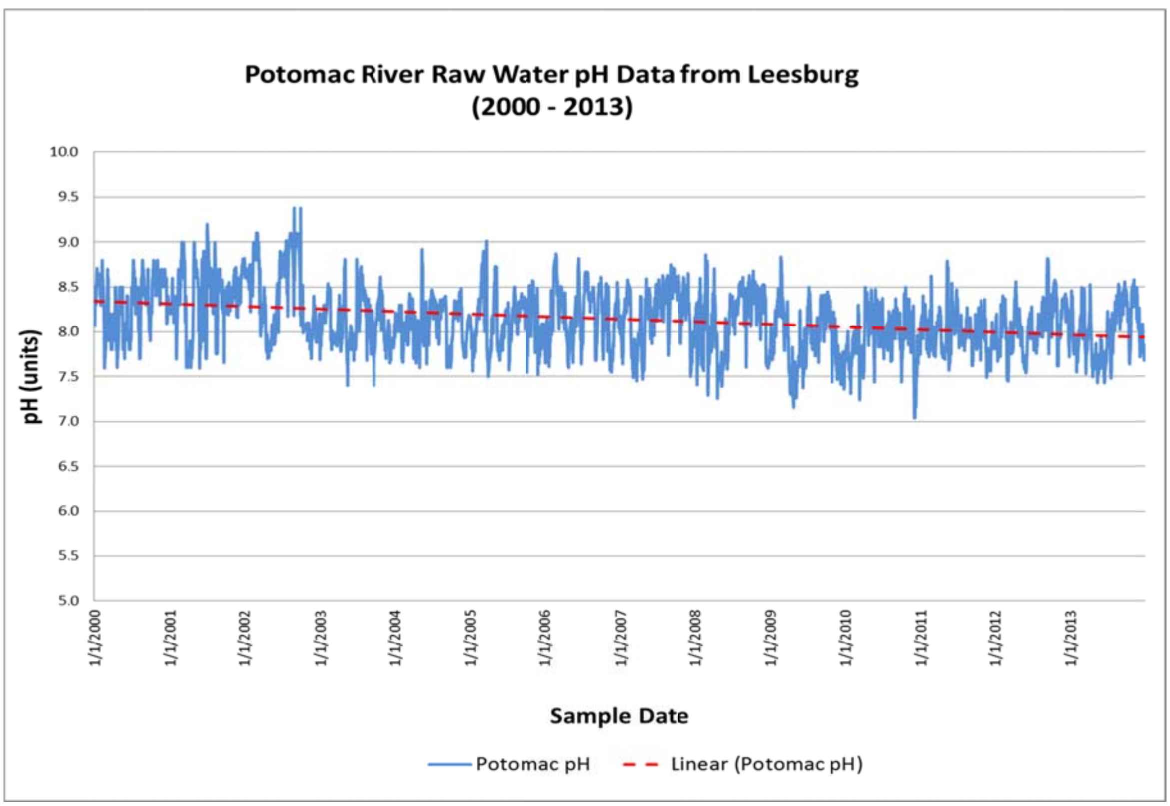

Figure 12 – pH in the Potomac River (Leesburg Data)

The following trends were observed in the Occoquan Reservoir, based on the available data as discussed:

- An increasing trend in alkalinity values was observed in the Occoquan Reservoir.
- An increasing trend in pH values was observed in the Occoquan Reservoir.

The following trends were observed in the Potomac River based on the available data, as discussed:

- An increasing trend in alkalinity values was observed in the Potomac River.
- A consistent trend in pH values was generally observed in the Potomac River, except for the Leesburg data where a slightly decreasing trend was observed.

References

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