
RELATIONSHIP BETWEEN TOTAL ALKALINITY,
CONDUCTIVITY, ORIGINAL pH, AND BUFFER
ACTION OF NATURAL WATER

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INTRODUCTION

In an effort to elucidate the properties of water related to the carbon supply for living organisms, the buffer action, conductivity, and total alkalinity of various natural waters were studied. Natural waters around Bowling Green, Ohio, were sampled at various times: Urschel's Quarry in Bowling Green being sampled most frequently; Klein's Well represented a soft ground water drawn directly from the ground by a pump; Poe Ditch was contaminated by sewage.

Dye (1944), using equilibrium equations of Moore (1939), produced nomographs for the relationship between pH, total alkalinity, and the three forms of carbon dioxide (free carbon dioxide, carbonate, and bicarbonate). However, Verduin (1956a) showed that these nomographs do not give a valid relationship between pH change and carbon dioxide change in natural water. The values obtained from the equilibrium equations do not agree with the actual data from Sandusky Bay, ocean water, and Lake Erie which Verduin (*ibid.*) has reported. Moberg et al. (1934) showed that their theoretical values do not completely agree with their computed values for ocean water. In the pH range from 6.0 to 8.0, observed linear increase of carbon dioxide content with decreasing pH is not in

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line with the theoretical values predicting an exponential increase in this region. Thus, other factors appear to influence the buffering capacity of natural waters.

METHODS

The samples were dipped from the surface of the water body in a 1,000 ml flask and returned to the laboratory, where the fresh samples were processed immediately. The aerated samples were allowed to reach equilibrium with the atmospheric CO₂ by standing at a depth of 2 cm in a large pan for at least 24 hr before processing.

A Barnstead Purity Meter (Model PM-3) was used to measure the electrical conductivity (Daniels et al., 1941). The meter was calibrated in megohms (Mohm) resistance and has a built-in temperature correction rheostat. The electrical conductance in mho of a 100-ml sample of distilled water was measured. The equipment was then rinsed thoroughly with distilled water. A sample of natural water was then diluted 1:50 with distilled water, mixed, and the conductivity measured. Then, 1:100 and 1:200 dilutions of the natural water were made and also measured for conductivity. The average of the three readings was computed to make the data more reliable.

A Beckman pH Meter (Model G) was used to support total alkalinity and buffering action titrations by methyl orange and phenolphthalein indicator methods (Kline, 1955; Bull, 1943). After three drops of phenolphthalein indicator had been added, 0.01 N H₂SO₄ or 0.02 N NaOH were titrated into the sample until the end point had been reached. Then, 1 ml of titrate at a time was added in excess until a total of 5 ml had been added. The total alkalinity was measured by titration to the visual end point with 0.01 N H₂SO₄, using methyl orange indicator (Welch, 1948). The pH of the sample was measured before, during (in the case of phenolphthalein), and after titration.

Results of the phenolphthalein titration were graphed on arithmetic graph paper. From these buffer curves the micromoles of CO₂ per liter per pH unit were calculated for each four-tenths of a pH unit change. These data were then graphed against total alkalinity, original pH of the water, and conductivity.

Standard statistical computations were made (Snedecor, 1946). Since Klein's Well and Poe Ditch data were noticeably different from the natural water data, they were omitted from the statistical computations but were placed in the graphs for comparison.

RESULTS

The data were compared by means of graphs. Since the hydrogen ions and the hydroxyl groups react with an equal number of carboxyl groups, the micromoles of carbon dioxide change per unit of pH change can be computed from such a graph as follows:

$$\frac{\text{ml titrate} \times 10 \mu\text{mole CO}_2/\text{ml titrate}}{0.11 \times 0.4 \text{ pH unit}} = \mu\text{mole CO}_2/(\text{l} \cdot \text{pH unit})$$

Typical values for the buffer curve were 462.5 μmole of CO₂/(l · pH unit) for the pH range 7.0–7.4; 475 for the pH range 7.4–7.8; 500 for pH range 7.8–8.2; 450 for pH range 8.2–8.6; 700 for pH range 8.6–9.0; and 1025 for the pH range 9.0–9.4.

The conductivity graphed against the total alkalinity of the natural water samples (fig. 1) increased as the total alkalinity increased. The coefficient of correlation ($r = +0.72$) was highly significant, statistically ($P = <0.01$).

The original pH graphed against the buffer curve (fig. 2) showed a wide scatter with a correlation coefficient of $+0.27$. Similar graphs of original pH vs. total alkalinity and conductivity showed low correlations.

The total alkalinity graphed against the slope of the buffer curve in the pH range 8.2 to 8.6 showed that the buffering capacity of the water increased with

total alkalinity and has a correlation coefficient of $+0.76$ ($P=0.02$). All other pH ranges studied (7.0-9.4) showed similar positive, statistically significant correlations.

Conductivity graphed against the slope of the buffer curve in pH range 7.4 to 7.8 has a correlation coefficient of $+0.32$, and this graph was representative of the other pH ranges. The product of total alkalinity and conductivity was graphed against the slope of the buffer curve (fig. 3) to learn whether this product

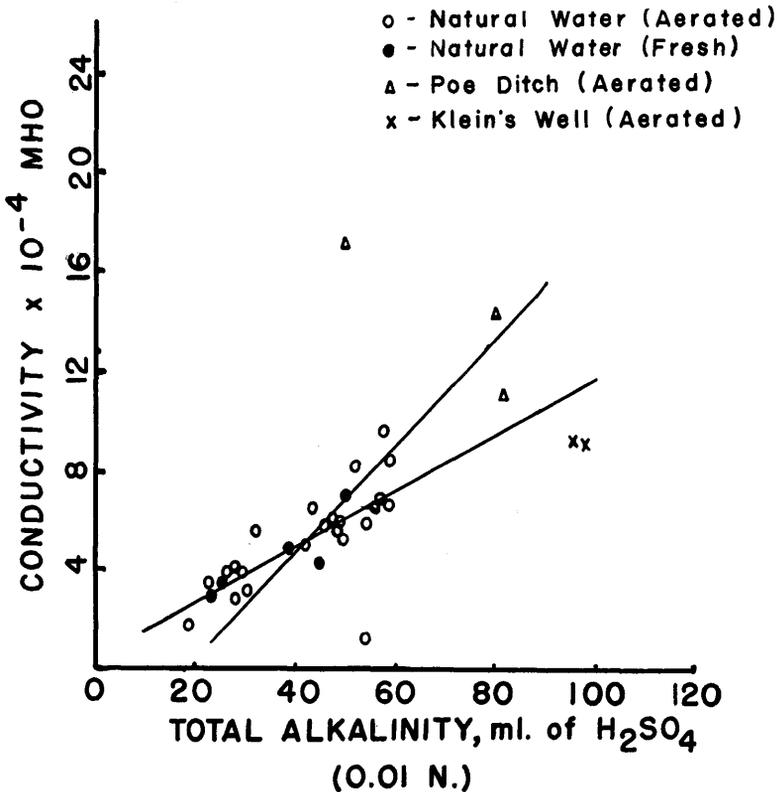


FIGURE 1. Relation of conductivity to total alkalinity.

would show a higher correlation than each property by itself. There is a wide variation to the data; however, a correlation coefficient of $+0.52$ ($P=0.04$) was found. The correlation coefficient is greater than conductivity graphed against the slope, and less than total alkalinity graphed against the slope of the buffer curve. This then showed that factors other than the forms of carbon dioxide affect buffer action, but these have not been investigated. A summary of the statistical analyses appears in table 1.

DISCUSSION AND CONCLUSIONS

Variation in limnological data is normal and to be expected. Powers (1939) found a range of over one pH unit in the blood pH and aerated serum within the same species of fish. The relation of Secchi disc readings to the depth associated with one percent of surface light presents also a scatter of the data (Verduin, 1956b). The photosynthetic rate at optimal light intensity vs. respiration rate demonstrates a wide range with values ranging from 0.25 to $14 \mu\text{mole of CO}_2/ (10 \mu\text{l}\cdot\text{hr})$ (Verduin, 1956a). In terrestrial biological data variation is also observed,

as in a measure of the wood mouse (*Peromyscus leucopus*) population (Jackson, 1952). Environmental variations do occur, and the researcher must accept them.

In graphs presented by Moberg et al. (1934) variations are as great or greater than the variation observed for the present data, and portions of their observed data differ markedly from their theoretical values. This is especially noticeable below the pH range of 7.5. Their theoretical equation apparently does not account for all of the dissolved ions in the water. Even after introducing a correction factor for boron into their equation, they observed values still at wide

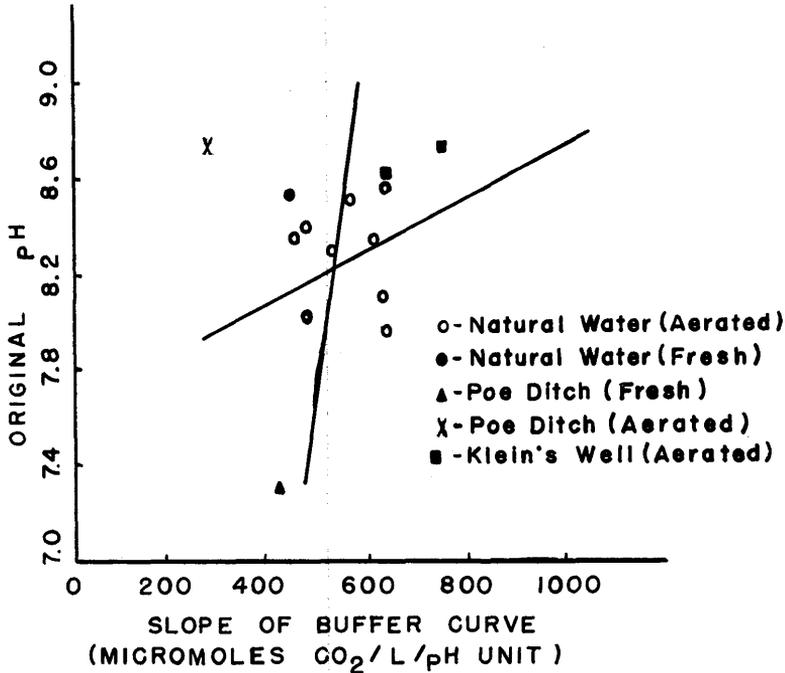


FIGURE 2. Relation of original pH to slope of buffer curve (pH range 7.4-7.8).

variance with their calculated values at low pH. Since the chemical conditions are different for each body, and are constantly varying within each body, wide variance in the data may be influenced by varying chemical conditions of the water.

The literature discusses the effects of many chemicals present in water. While many are present in only trace amounts, they do influence biological processes. Many are essential for the growth of plants and are present in ionic form, thus contributing to the total conductivity. In supporting plant life, they indirectly affect respiration and photosynthesis and the use of carbonates and bicarbonates. Mollusca, *Elodea*, and *Vallisneria* precipitate calcium carbonate as marl and shells. Since calcium carbonate is insoluble, a decrease in the total alkalinity, conductivity, and buffer capacity of the water will result. Chemical conditions of such water therefore vary greatly and thus affect variations in the buffer curve, total alkalinity, pH, and conductivity.

The aerated and fresh samples did not differ significantly from natural water. Since the water was always collected from the surface, it is likely that the fresh sample was already in equilibrium with the atmospheric gases.

The phenolphthalein and methyl orange indicators are used widely in limnological studies. These indicators are assumed to indicate presence of carbonates

and the absence of carbonic acid (Welch, 1948; Verduin, 1959). However, in this study no significant differences were found between the aerated and fresh samples. Thus, an aerated sample must contain some carbonic acid while the carbonates must be practically absent. Carbon dioxide is continually entering the water, converting to carbonic acid, and changing the carbon dioxide into bicarbonates. Thus, phenolphthalein alkalinity measures the hydroxyl ions rather than the carbonates, as one is so often led to believe.

Poe Ditch and Klein's Well differ markedly from natural water. Samples from these two sites had a much higher electrical conductance and total alkalinity,

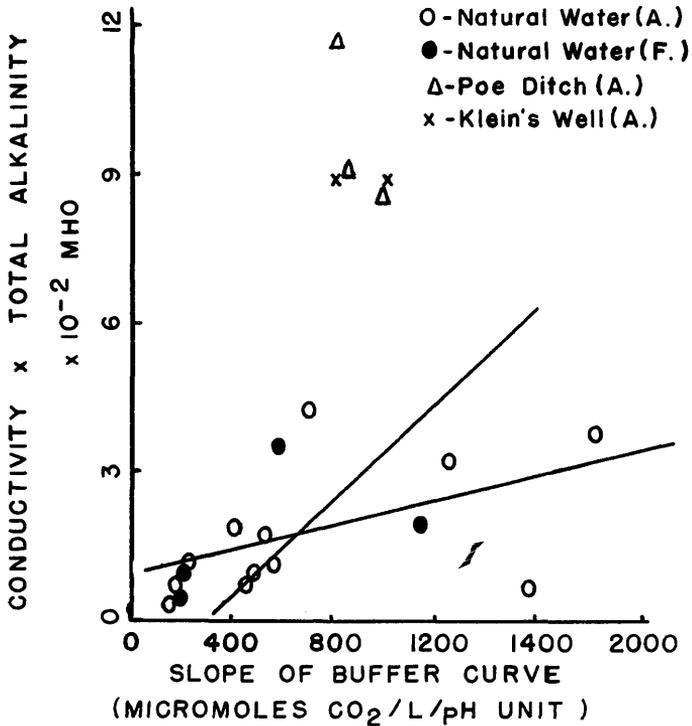


FIGURE 3. Relation of product of conductivity and total alkalinity to slope of buffer curve (pH range 8.2-8.6).

but the slopes of the buffer curves were intermediate to those for natural water. The product of total alkalinity and conductivity, as might be expected, further separated the ditch and well samples from the natural waters.

Factors other than the various forms of carbon dioxide affect buffering action. Since the coefficient of correlation of total alkalinity vs. the slope of the buffer curve ($r = +0.52$) is intermediate between conductivity vs. slope ($r = +0.32$) and total alkalinity vs. slope ($r = +0.76$), other unmeasured ions affect the buffer curve. When the product of conductivity and total alkalinity was graphed against slope, the unmeasured ions were partially masked; when total alkalinity was graphed against slope, the unmeasured ions were entirely absent, thereby, resulting in a high coefficient of correlation.

However, these studies have not explained the wide variation in the slopes of the buffer curves. Verduin (1956a) has shown differences in the buffer curves for a standard sodium bicarbonate solution, ocean water, Sandusky Bay water, and Lake Erie water; and the present study revealed similar results.

TABLE 1
Summary of statistical analyses*

	N	b_{xy}	b_{yx}	t_b	P_b	r	t_r	P_r
pH vs. Slope	11	0.0011	64.24	0.85	<0.01	+0.27	2.63	0.02
Conductivity vs. total alkalinity	34	10.99	0.047	5.36	<0.01	+0.72	5.30	<0.1
Conductivity vs. slope	14	0.47	0.22	0.96	0.34	+0.32	0.99	0.30
Total alkalinity vs. slope	21	0.021	30.34	1.14	0.23	+0.76	2.56	0.02
Total alkalinity × conductivity vs. slope	16	12.74	0.21	1.73	0.11	+0.52	2.25	0.04

*KEY

N = Number of pairs of values used for each analysis.

 b_{xy} = Slope of line for x on y. b_{yx} = Slope of line for y on x. $t_b = b/\Sigma b$. P_b = Probability.r = Correlation coefficient = $\Sigma xy \sqrt{(\Sigma x^2)(\Sigma y^2)}$ $t_r = r\sqrt{(n-2)/(1-r^2)}$ P_r = Probability of correlation coefficient.

SUMMARY

1. Factors other than the three forms of carbon dioxide affect buffering capacity.
2. Buffering action was least efficient between the pH range 8.2 to 8.6.
3. Ions other than the forms of carbon dioxide were found to affect the buffer curve. These are unmeasured at present.
4. Phenolphthalein alkalinity measures the hydroxyl ions rather than carbonate ions alone.
5. Apparently the pH of the natural waters is relatively independent of total alkalinity, conductivity, and buffer capacity of those waters.

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