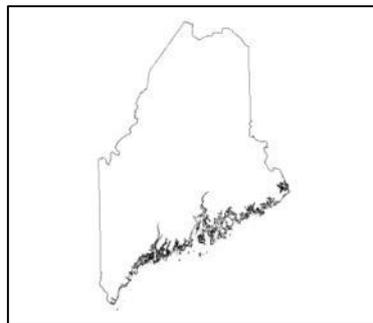


Geologic Site of the Month
January, 2009

***Alkalinity:
An Important Parameter in Assessing Water Chemistry***



Text by
Daniel B. Locke



Introduction

Ground water is the source of drinking water for about 60 percent of Maine's population - 43 percent from private wells and 17 percent from public water supplies (Solley and others, 1995). In spite of this reliance on ground water, very little is currently known about natural ground-water conditions in different bedrock geological settings across the state. In response to numerous concerns about the quality of Maine's ground water, the Maine Geological Survey started investigating Maine's ambient bedrock water quality and associated geochemistry. A long-term monitoring program was initiated to create an ambient ground-water quality database with applications in public health, environmental protection and permitting, economic development, and basic research.

Thus far, 214 bedrock wells have been sampled in the Camden Hills area of coastal Maine, the Range Pond area of south-central Maine, the Presque Isle area in Aroostook County, the Mount Blue area in western Maine, and the Blue Hill, Penobscot, and Ellsworth areas. These samples were analyzed for all of the common water quality constituents as well as trace metals (below).

Field Parameters	concentration	Fluoride	Copper
Specific Conductance	Total Particulate Iron - obtained by	Silica	Lead
pH	subtracting total dissolved iron	Nitrate as nitrogen	Gold
Temperature	concentration from total iron	Phosphorus	Silver
Dissolved oxygen	concentration	Iron	Zinc
Oxidation Reduction Potential (ORP)	Arsenic III and V species separation using ion exchange columns	Manganese	Chromium
Alkalinity - gran plot titration conducted in the field	Laboratory Parameters	Bromide	Aluminum
Total Iron - using a portable spectrophotometer on an unfiltered sample	Hardness	Nickel	Uranium
Ferrous Iron - or Fe +2 using a portable spectrophotometer on an unfiltered sample	Calcium	Cadmium	Tungsten
Ferric Iron - or Fe +3 obtained by subtracting the ferrous iron concentration from the total iron	Magnesium	Tin	pH
	Sodium	Arsenic - Total arsenic, total dissolved arsenic, total particulate arsenic, Arsenic III, and Arsenic V (For early homeowner test results where total arsenic was equal to or greater than 10 ppb)	Standard air equilibrated pH
	Potassium	Antimony	
	Bicarbonate		
	Alkalinity		
	Sulfate		
	Chloride		



Alkalinity and Acid Neutralizing Capacity

Alkalinity and acid neutralizing capacity (ANC) are typically defined as a measure of the capacity of water to neutralize a strong acid. Frequently, the terms alkalinity and ANC are used interchangeably. Technically, alkalinity is determined from filtered samples (using at least a 0.45 μm filter) whereas ANC is determined from a non-filtered or whole water sample. Although alkalinity or ANC consists of the sum of titratable carbonate and non-carbonate chemical species in a sample which act to neutralize acid, in most natural waters alkalinity or ANC is attributed to the dissolved carbon dioxide species, bicarbonate and carbonate. Carbonate alkalinity therefore specifically refers to acid neutralizing capacity attributed to bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) species and is typically reported in terms of milliequivalents or microequivalents per liter or milligrams per liter as a carbonate species and titrated on a filtered sample. In many aqueous systems, alkalinity is attributed to carbonate chemistry and more commonly attributed to bicarbonate and less commonly to carbonate.

Waters highly buffered by calcium carbonate may have somewhat elevated hardness. Hardness is a measure of the abundance of cations, primarily calcium and magnesium which react with soap to form insoluble compounds or precipitate from heated water to form encrustations (Hem, 1985). Other divalent cations including strontium, iron, and manganese can contribute to hardness. Hard water requires considerable amounts of soap to produce lather and is the cause of scale wherever water is heated. Water is considered soft if it contains 0 to 60 mg/L of hardness, moderately hard if it contains more than 120 mg/L of hardness, and very hard if it contains more than 180 mg/L of hardness (Hem, 1985).



A Brief Discussion of pH

Typically, pH is a measure of the acidity or basicity of a substance or solution. In technical terms, pH is defined as the negative base-10 logarithm of the hydrogen ion concentration or activity expressed in moles per liter of solution. The reason why a logarithmic scale is used is because in most natural waters the hydrogen ion activity is too small to be easily expressed in common concentration units such as milligrams or micrograms per liter. The pH range is typically reported within a range of 0 to 14 with 7 being neutral, less than 7 being acidic, and greater than 7 being basic or alkaline. Another way of looking at this is that solutions are considered acidic when the hydrogen ion (H⁺) concentration or activity is greater than the hydroxide (OH⁻) concentration or activity. When the hydroxide (OH⁻) activity or concentration is greater than the hydrogen ion (H⁺) activity or concentration, the solution is considered basic or alkaline. Expressing pH in terms of a logarithmic scale therefore means every whole unit change is actually a ten-fold change from the preceding unit. It should be noted that while the pH range is commonly from 0 to 14, it is possible to have pH values less than 0 and greater than 14 in extreme situations or environments.

For further information on pH, how it is measured, and its importance refer to the following:

- USGS Office of Water Quality [National Field Manual](#)
- [Wikipedia definition of pH](#)
- USGS Water Science for Schools [Water properties: pH](#)
- [Water on the Web: pH](#)



Alkalinity and pH

Alkalinity and pH are among the most common and important water quality parameters measured in both surface and ground water. Why is this important in our everyday lives? Alkalinity, the buffering capacity of water or its resistance to pH change, is critical in the proper metabolism of most forms of life, maintenance of aquatic life forms, understanding the geochemical nature of water, and how best to deal with problems associated with both drinking water and waste water. Alkalinity of surface and ground waters is directly related to the underlying sediment and bedrock (Weddle and Loiselle, 1996). For example, areas underlain by rocks and sediment rich in calcium from limestone would tend to be more resistant to changes in pH caused by acid rain. On the other hand, water bodies underlain by granite and sediment containing little calcareous material would tend to have less resistance to pH changes. Alkalinity is also an important factor in maintaining such things as [aquariums](#) and [swimming pools](#) to name just a few. The bottom line is that alkalinity plays an essential role in all aspects of aquatic chemistry.

Alkalinity is often related to [hardness](#) because the main source of alkalinity is usually from carbonate rocks (limestone) which is mostly CaCO_3 . Hard water makes nearly every cleaning job in the home a nuisance since more soap and detergent are necessary. Soap used in hard water combines with the minerals to form a sticky soap curd. Dishes washed in hard water often appear spotted, clothes often appear dingy or feel scratchy, and scale deposits appear on plumbing fixtures and water-using appliances. Whenever hard water is heated, scale deposits of calcium and magnesium minerals occur which can clog pipes or adhere to heating elements. Hard water is not unsafe to drink, but practical uses may be limited. [Water softeners](#) are used to treat hard water.



Alkalinity and pH

Alkalinity is measured by [titration](#). In some instances, scientists add small amounts of chemicals known as acid-base indicators to water samples to indicate end points as acid is incrementally titrated. Certain acid-base indicators result in color changes when an end point is reached. End points occur when only small amounts of acid are added to impart a significant change in pH. Knowing the volume of the sample, normality of the acid, and the volume of acid needed to reach an endpoint, the alkalinity can be calculated.

Determining alkalinity using the various acid-base indicators works reasonably well with highly buffered waters, but with low alkalinity water, full incremental titrations are the preferred approach. There are a number of methods of handling the data which include the inflection point method, Gran function plot method, and fixed endpoint method. For a detailed description of proper water quality sampling techniques as well as further information on alkalinity titration methodology, refer to the [National Field Manual for the Collection of Water-Quality Data](#) as well as [Chapter 6 - Alkalinity and Acid Neutralizing Capacity](#).



Ground-water Sampling at the Maine Geological Survey

When collecting ground water samples, the Maine Geological Survey utilizes a closed cell for measuring important field parameters such as pH, temperature, specific conductance, dissolved oxygen, and oxidation-reduction potential (Figures 1-2).

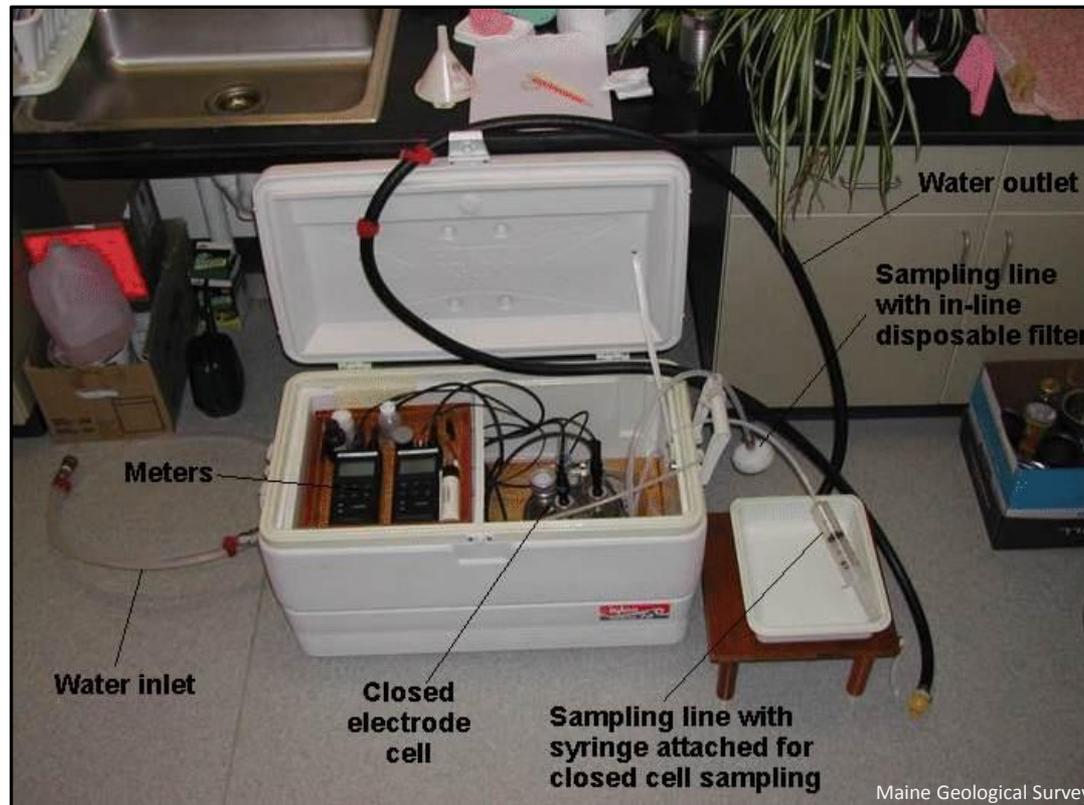


Photo by Daniel B. Locke

Figure 1. View of MGS water sampling device. With this equipment, pH, temperature, specific conductance, dissolved oxygen, and oxidation reduction potential data can be collected on samples prior to exposure to atmosphere.



Ground-water Sampling at the Maine Geological Survey

Inflow is controlled by a needle valve and maintained at a rate of approximately 0.5 gallons per minute. All parameters are noted every five minutes over typically a 30 minute period to verify that stabilization has occurred.

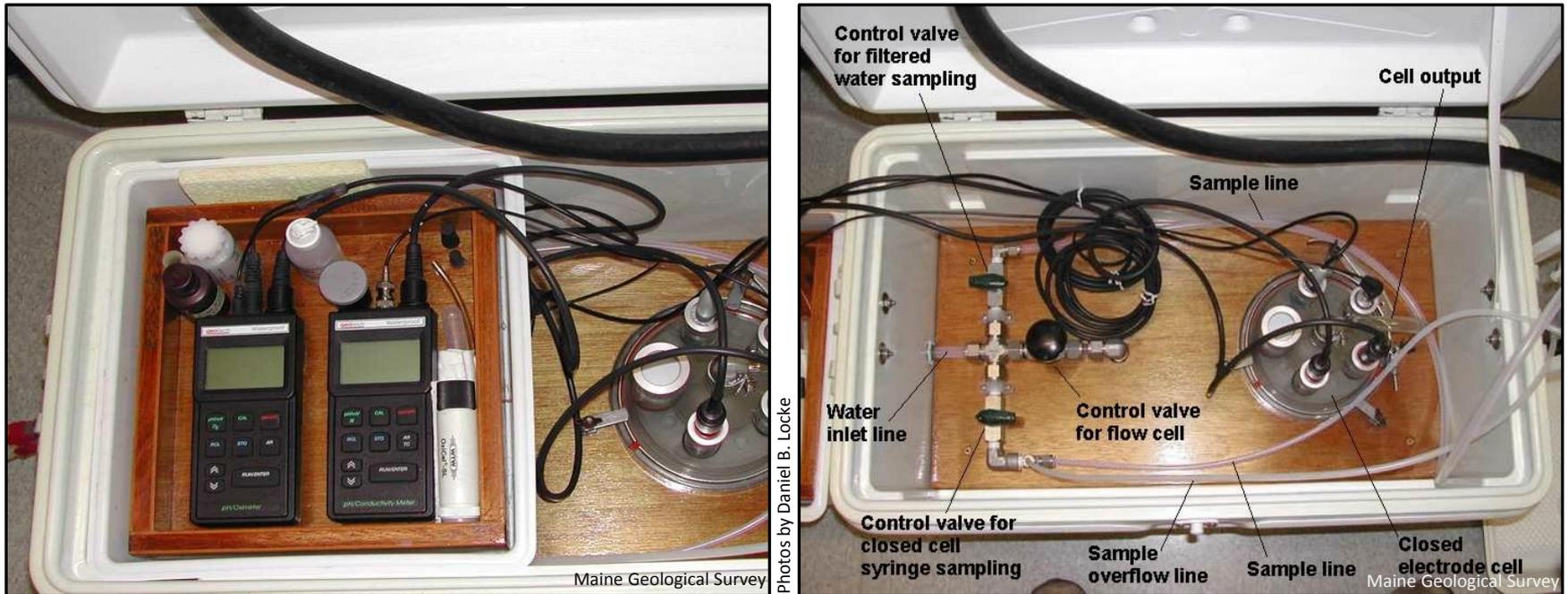


Figure 2. (Left) Enlarged view of meters used with MGS water sampling device. (Right) View of MGS water sampling device with meters set aside to the left.

Ground-water Sampling at the Maine Geological Survey

At this point, samples for laboratory and field analyses are collected. Most samples (including those for alkalinity analyses) are filtered using a disposable 0.45 μm inline filter (Figure 3). Samples for alkalinity analyses are typically examined both in the field and in the laboratory using the [Gran function plot method](#).



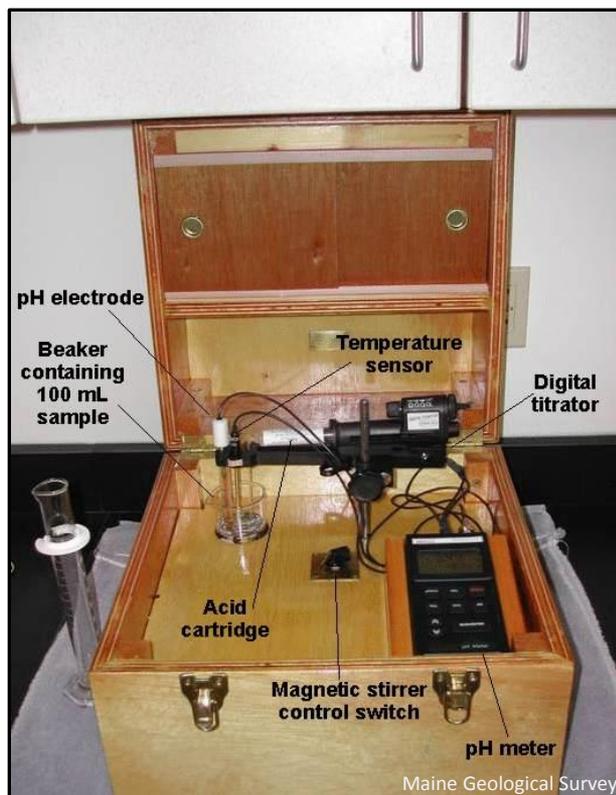
Photos by Daniel B. Locke



Figure 3. (Left) Water sampling line. (Right) Water sampling line with filter.

Ground-water Sampling at the Maine Geological Survey

In an effort to enhance collection of high quality field alkalinity data, staff at the Maine Geological Survey designed a self-contained alkalinity field titration device utilizing a digital titrator, pH meter with electrodes, and battery-operated variable speed magnetic stirrer (Figures 4-5).



Photos by Daniel B. Locke

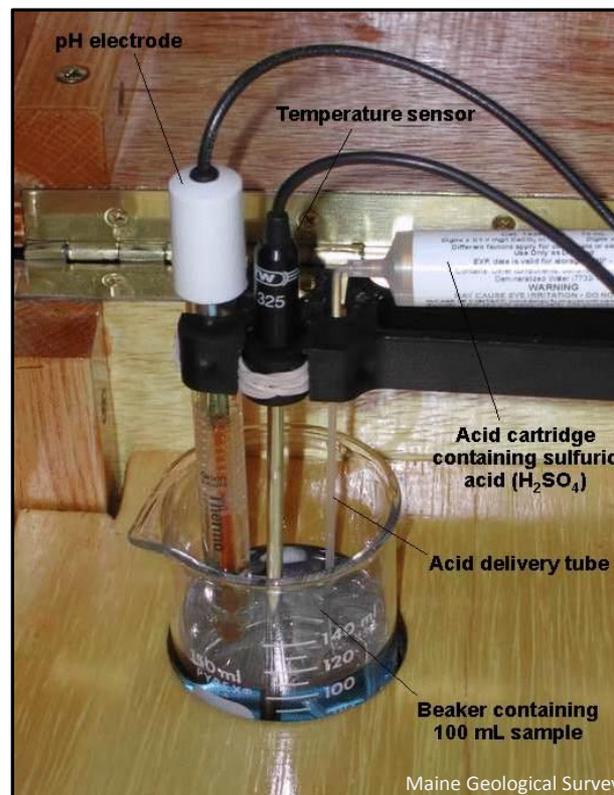


Figure 4. (Left) View of MGS field titration device. (Right) Enlarged view of beaker, pH electrode, temperature sensor, and acid cartridge with delivery tube.



Ground-water Sampling at the Maine Geological Survey

With this device, we are able to conduct the titration shortly after sample collection in an effort to avoid chemical and physical reactions which can alter carbonate and bicarbonate concentrations in a matter of minutes. In some instances, field titration immediately following sample collection is not possible. In such cases, samples are collected in 250 mL containers with no headspace and maintained at a temperature of 10° C until the procedure can be accomplished (as soon as possible).

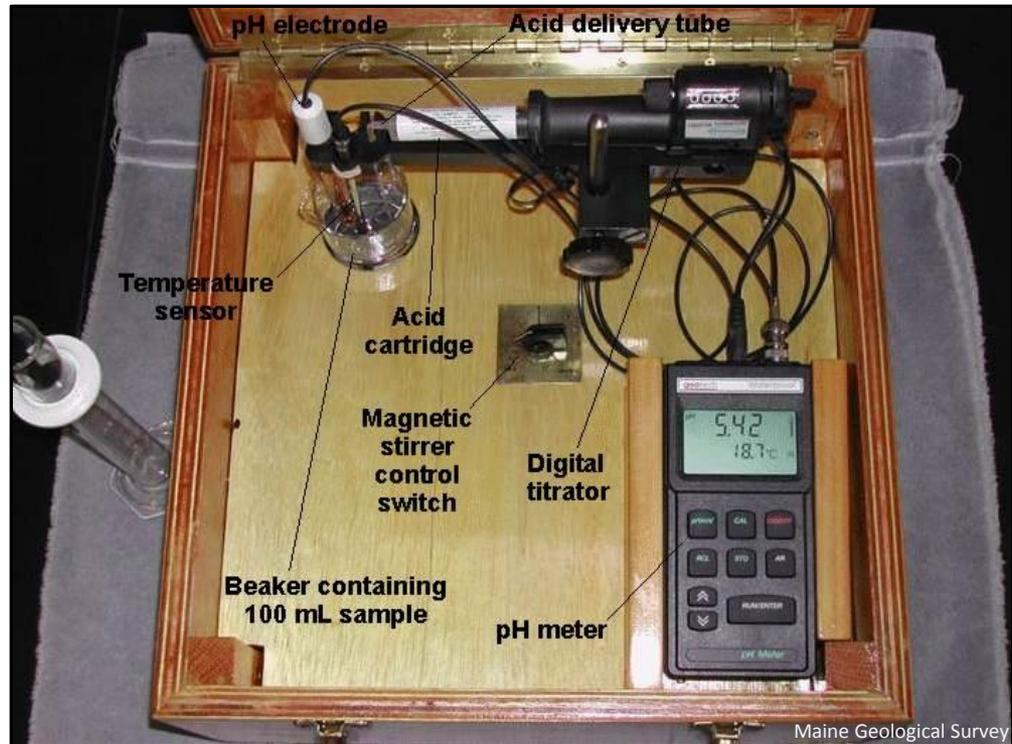


Figure 5. Enlarged view of MGS field titration device.

Ground-water Sampling at the Maine Geological Survey

Titration data are collected for analysis using the Gran function plot method. In the past, data was examined using a relatively simple spreadsheet analysis for total alkalinity, but no speciation of carbonate, bicarbonate, and hydroxide was performed. Fortunately, the U.S. Geological Survey developed what is known as the "[Alkalinity Calculator](#)" which takes titration data and performs all calculations using a [variety of methods](#).

The collection and analysis of ambient bedrock water quality information by the Maine Geological Survey is continuing and a summary report detailing findings will be published in the future.



References and Additional Information

- Hem, J.D., 1985, [Study and interpretation of the chemical characteristics of natural water \(3rd edition\)](#): U.S Geological Survey Water-Supply Paper 2254, 263 p.
- Solley, W. B., Pierce, R. R., and Perlman, H.A., 1998, [Estimated Use of Water in the United States, 1995](#): U.S. Geological Survey, Circular 1200, 71 p.
- Weddle, T. K., and Loiselle, M. C., 1996, Background water quality in significant sand and gravel aquifers in Maine, in Loiselle, M., Weddle, T. K., and White, C. (editors), Selected papers on the hydrogeology of Maine: Geological Society of Maine, Bulletin 4, p. 53-80.

