An Experimental Study On The Properties Of Specific Electrical Conductance For Use In Tracing The Components Of Flow

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Abstract

The use of specific electrical conductance of water (C) as a geochemical tracer in flow component separation has been based primarily on certain assumptions about its physical and chemical properties. These assumptions, however, are based on unrelated data, such as in temperature conversions, or based purely on intuition, such as in mixing functions. However, a better approach would be to experimentally analyze these assumptions. This paper studies the basic relationships between C, temperature & pH and also their respective mixing functions. An understanding of these properties would lead to better modeling using C.

This study found that different C-temperature function exists for each kind of flow water source, and a complete sampling is required for an accurate estimate of this function. This study also found that the quality of water should be considered for future studies using C.

Keywords: Tracer, Specific Electrical Conductance, pH

I. Introduction.

Tracing the components of flow for use in the detection of mass transport or in hydrograph separation brings about more information on the flow phenomenon if an unstable tracer is used. Because of the changes that takes place in an unstable tracer as it is carried by the flow, an understanding of its physical and chemical properties may provide information of the flow path and the soil type encountered, among others. One tracer in this category is the specific electrical conductance of water (C). This tracer is not only a function of the volume of flow, but is also a function of quantities that define water quality, such as the time of contact between the flow and the soil, water temperature, and soil condition during flow. It is obvious that in order to understand the information of the flow using C as a tracer, we must first understand the properties that govern C both physically and chemically. Certain models already utilize physical and chemical assumptions with regards to C properties. One example is the model used by Matsubayashi *et al.* (1991) where the combination of surface and sub-surface flows and the incorporation of the effect of long and C-varying rainfall for separating flow components utilizes volumetric averaging for C, and temperature conversions by Pilgrim *et al.*(1979). Since there has been very little data regarding these assumptions, save for those by Hem (1959), it is only logical to investigate them through laboratory experimentation before proceeding into a more complicated modeling using the above mentioned quantities.

II. Current C-pH-Temperature Functions

If we are to consider the separation equations of flow in terms of the tracer C,

$$Q_n + Q_o = Q_t \quad ; \quad C_n Q_n + C_o Q_o = C_t Q_t \tag{1}$$

where Q represents flows, and C the specific conductance of flows. The subscripts n, o and t represents new, old and total flow in that order. Raw data cannot be used in equation 1 as is. This is because field data is usually taken at a variety of temperatures. To be able to compare data with other researchers, it is usual for data to be converted to a standard temperature for reporting. Although in the rigorous meaning, all C data should be affected by temperature, for equation 1, this effect is usually assumed to be for total flows only. This means that new water (rainfall) and old water (pre-event water) are usually taken as is, or directly from whatever function they are derived from (Pilgrim *et al.*1979, Matsubayashi *et al.* 1991) and only total

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flows are converted to a standard temperature. The standard C conversion schemes from field to standard temperature has been based solely on the report by Hem (1959), wherein it is stated that C is affected linearly by temperature. Pilgrim in his 1979 paper described this function as *"the C at 17°C is 65% of that at 25°C,"* which gives the general formula of C conversion as:

$$C_T = C_{25}(1+0.04375(T-25)), \tag{2}$$

where C_T is the C at T temperature, C_{25} is the C at 25°C. This formula describes a conversion function that varies the slope of the C-temperature line in terms of a percentage of the C at 25°C. Nakamura (1971) uses a similar expression for temperature conversion but at a different standard temperature of 18°C, and he expressed this as:

$$C_T = C_{18}(1+0.025(T-18)), \tag{3}$$

where C_{18} is the C at 18°C. However, after Hem's study, nobody have made a more descriptive analysis of the effect of temperature on C, probably reasoning that temperature conversions does not affect model performance but merely varies the magnitude of the reported data. Nevertheless, if we are to understand the flow phenomenon through the use of C, then a complete study of its functions is in order. As for pH, there has been very little data regarding its effect on C in flow. This also requires some study for a complete analysis of the C function.

Regarding mixture functions for C, it has been generally taken that it behaves like any other stable tracer, where it can be averaged volumetrically for mixtures of two waters of different C's (Pilgrim *et al.* 1979). Whether or not C behaves in this fashion is still in question and is discussed further in this study.

III. Experiments

To verify these and other assumptions, several experiments were conducted. The first set are the C-pH-temperature function experiments. In these experiments, temperature was varied (because it is the easiest to control), and C and pH were noted. This was conducted on five kinds of water (with two samples each) from the experimental basin in Inuyama, namely, (a) base flow water or flow at a downstream region where there was no visible surface flow and after a period of no rainfall, (b) stream water or water at a region where there are visible surface flows, (c) city or tap water, (d) water from weir or stagnant water flowing out of the observation weir at the foot of the basin slope, and (e) deep groundwater or water coming out of an observation tunnel through the basin slope. The experiment was done by placing the sample's plastic container on a large pan with hot water, and gently heating the pan from beneath. After reaching a certain temperature, the sample was removed from the pan and was let to cool by putting it in another large pan with cold water. After reaching room temperature, ice was added to the water on the pan until the sample water temperature was within 10 to 20°C.

The second set of experiments were for C and pH mixing. For each of these experiments, two samples of different C were mixed and the C and pH of the mixture were noted. Two types were made for these mixing experiments. One set used actual rain and stream water while the other set used distilled and city water.

IV. Experimental Results And Discussions

•The experiments produced the following results. For the C-pH-temperature experiments, the data was graphed as a combination function of C, pH and temperature as can be seen on figures 1 to 10. In these figures it is clear that there are separate curves for heating and for cooling. This hysteresis may be attributed to the release of oxygen and hydroxyl either through ion exchange or vaporization during the heating process. Since this process is either irreversible or would require the re-introduction of oxygen to return the water to its original state, it is not surprising that the resulting curve for the cooling process follows a different path than that of the heating one. Simply put , it can be assumed that the water in the cooling process is different from that of the heating process, as far as ionic quality is concerned. To check this process, it can be seen from figure 3 that using two samples from the same source but heated to a different maximum temperature, the hysteresis was greater for the sample that
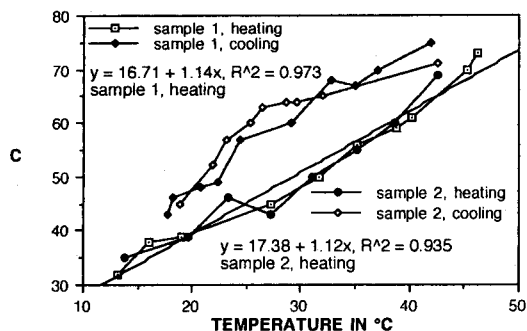
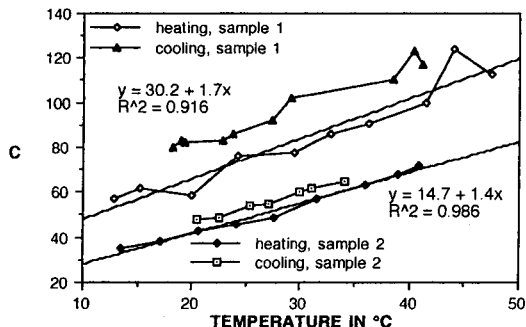**Figure 1 C-Temperature Curves for base flow water (C in μS/cm)**
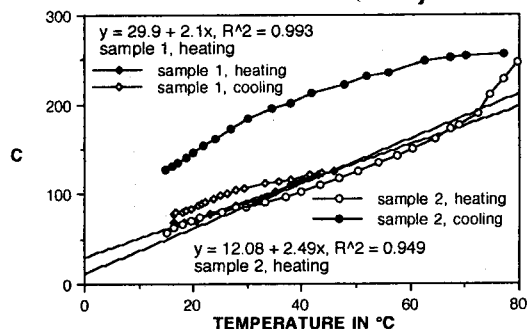
Figure 2 C-Temperature Curves for stream flow water (C in μS/cm)

Figure 3 C-Temperature Curves for city water (C in μS/cm)

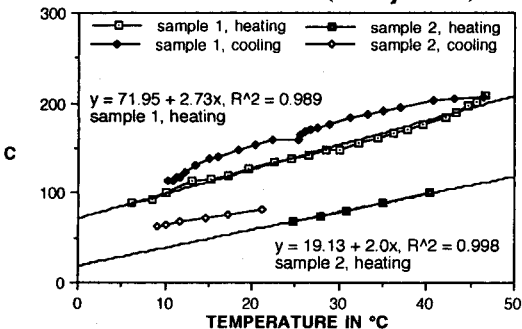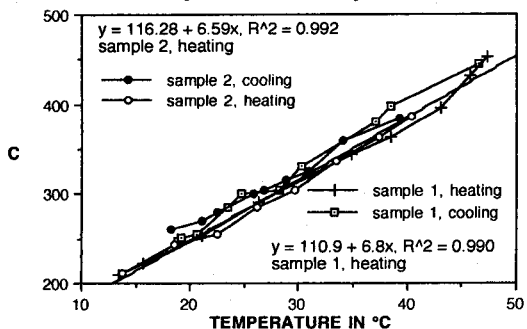**Figure 4 C-Temperature Curves for water from weir (C in μS/cm)**

Figure 5 C-Temperature Curves for deep groundwater (C in μS/cm)
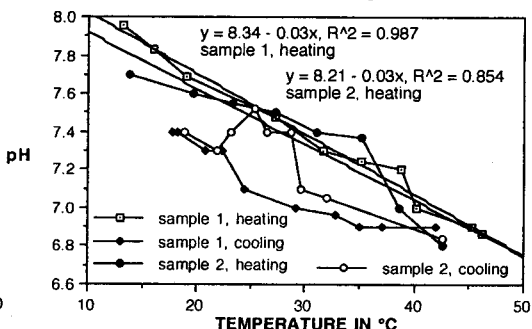
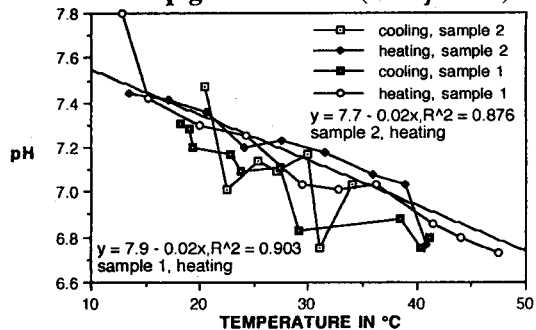**Figure 6 pH-Temperature Curves for base flow water**

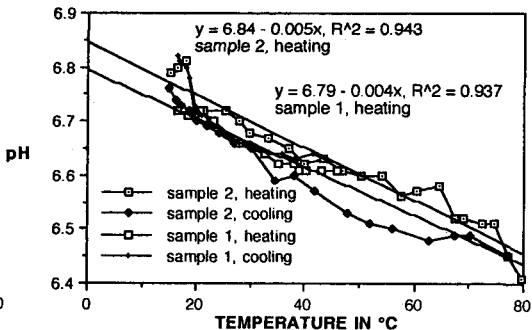**Figure 7 pH-Temperature Curves for stream flow water**

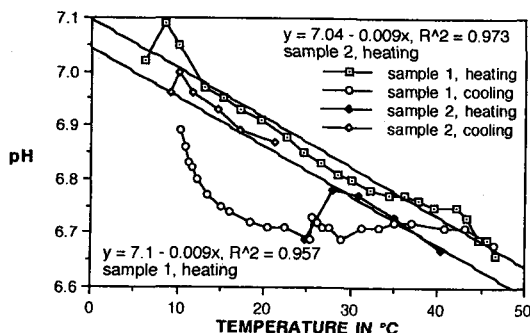**Figure 8 pH-Temperature Curves for city water**

**Figure 9 pH-Temperature Curves
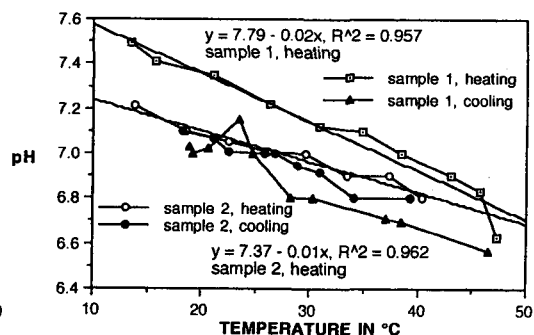for water from weir**

**Figure 10 pH-Temperature Curves
for deep groundwater**

was heated to a higher temperature. Another point that verifies this process can be seen on figures 6 to 10. Here the pH of the sample waters decreases as the temperature increases. Since pH is a negative logarithmic measure of the amount of H^+ ions in solution, a decrease in the pH value corresponds to an increase in H^+ ions in solution. This points to the dissociation of H_2O molecules to H^+ and OH^- ions. Release or reaction of these ions would alter the ionic composition of the water after this heating stage.

Although it may seem that the actual C-temperature function is non-linear, for the sake of simplicity and as a first step, linearity will be assumed in this study. And since the cooling process gives water at a different ionic quality from the original sample, only the heating functions will be utilized, thus the fittings on figures 1 to 5. As can be seen on these figures for same-source samples, the variations in the fitting line slope is small, while this variation is big for the different sample waters. This means that no single line can approximate the C-temperature function for the different waters in a single basin. To check the reason for the variation of the approximate line slope, the functions of the slope of this approximating line was graphed versus the pH and C of the sample at 25°C. This was done by reading the corresponding C and pH for 25°C for each fitting line in figures 1 to 10. Similarly, by plotting the pH at 25°C versus the slope of the fitting line (pH fitting), the reason for pH variation can be determined. The result of these functionality checks are figures 11 and 12.
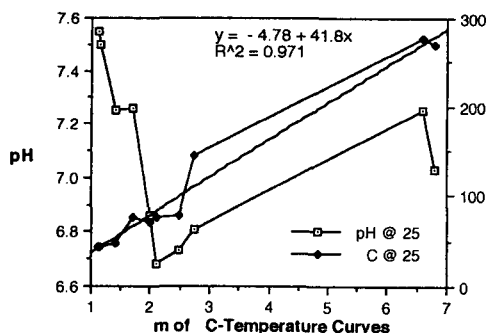

**Figure 11 Relationships Between The
Slopes Of The Fitting Line (for C)
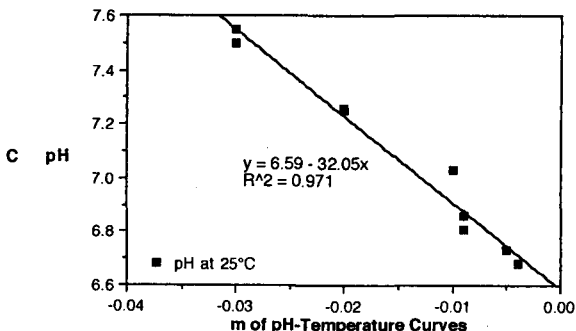And C And pH @25°C (C in μS/cm)**

**Figure 12 Relationship Between The
Slope Of The Fitting Line (for pH)
And pH @ 25°C**

From figure 11, it can be seen that there seems to be a linear relationship between the slope of the approximating line, m, and the C at 25°C. It can also be seen that there is no definite function between pH and m. This means that the quality of the water, in terms of the slope m, cannot be judged with just pH value readings. In figure 12, it can be seen that there seems to be a linear relationship between pH at 25°C and the slope of the fitting line. Thus, if we are to incorporate the above findings in temperature conversion formulation for both C and pH, we will have,

$$C_{25} = C_T - m(T\text{-}25), \qquad (4) \qquad\qquad C_{25} = \text{-}4.78 + 41.8m \qquad (5)$$

where m is the slope of the approximating line. However, as we have seen this slope varies as a function of the C @ 25°C as in equation 5, thus substituting we will get equation 6 as,

$$C_{25} = \frac{C_T - 0.114(T\text{-}25)}{1\frac{T\text{-}25}{41.8}} \qquad\qquad (6)$$

If the right hand side of the numerator in equation 6 is assumed to be zero (the y-intercept of equation 5 becoming zero), we will arrive at the classical formulations by Pilgrim and Nakamura. Although this more simple approach would be better for the mechanical process of C conversions to standard temperature, an understanding of the physical processes involved in temperature variation would require the incorporation of the non-linear terms. Physically, the non-linear term represents the non-linearity of the real C-temperature function as can be seen on figures 1 to 5.

Similarly, by plotting the function between pH and its estimating line slope, we will get a similar equation for pH conversion in terms of temperature. This is expressed as equation 7.

$$pH_{25} = \frac{pH_T - 0.206(T\text{-}25)}{1\frac{T\text{-}25}{32.05}} \qquad\qquad (7)$$

This last expression is useful for pH data coincident with C data. Since all C data are reported at a standard temperature, it is only logical to do also for pH data for studies involving both C and pH.
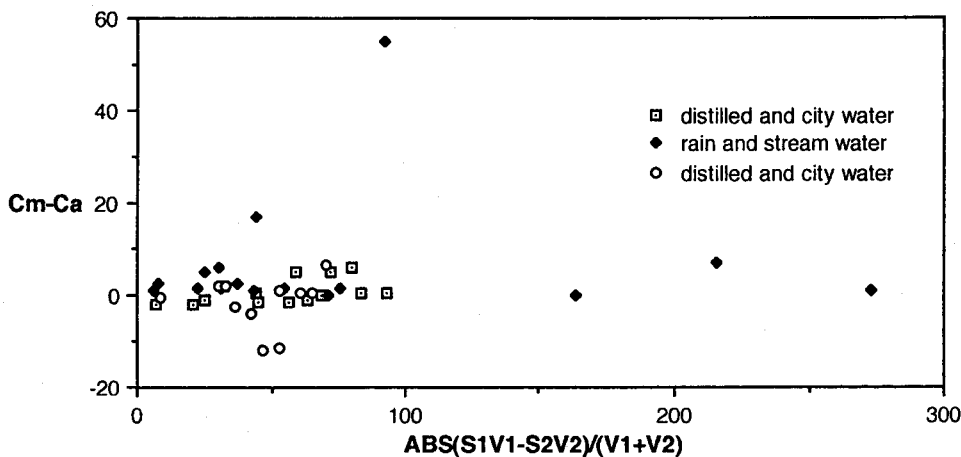
•For the mixture experiments, the results are as follows,

Figure 13 C Mixing Function

In figure 13, Cm stands for the measured C value of the mixture, Ca stands for the volumetric average value, C1 and C2 means the C of samples 1 and 2 respectively and V stands for the volume of the sample. It can be seen that for rain and stream water, the measured values are slightly above the average, while for distilled and rain water, the measured and average value saddles each other. In any case, for the range of values practical for modeling (0 to 100 μS/cm), the Cm-Ca difference can be taken to be equal to zero.
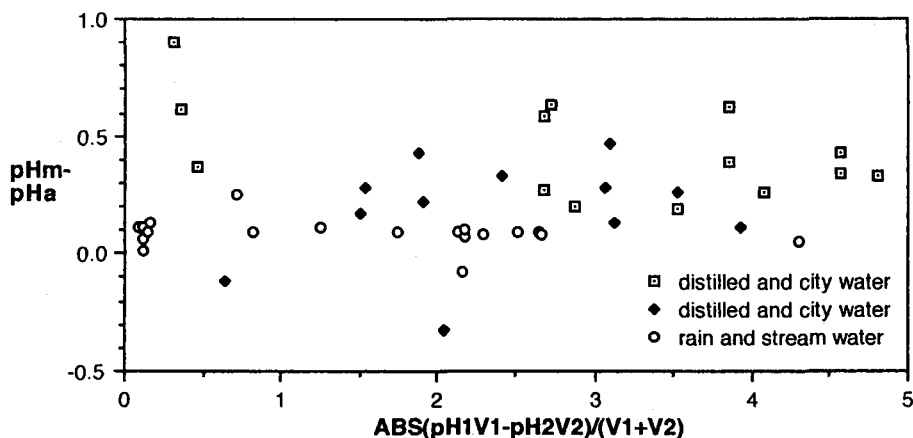
Figure 14 pH Mixing Function

In figure 14, pHm stands for measured value of the mixture while pHa means volumetric average as computed. Here it is obvious that the mixture cannot be averaged volumetrically. For both distilled & city water and rain & stream water experiments, the measured values are constantly above the computed volumetric average. This means that for models involving both C and pH, the latter has to be constantly updated or estimated.

VI. Conclusions
• The determination of a C-Temperature conversion function can be done through the heating of a group of samples within the natural temperature range. Further heating may alter the ionic quality of the sample. Different functions exists for different waters and there is a need to check different possible sources of flow waters for an accurate estimation of the C-temperature conversion.
• The C conversion formula can be expressed in linear form, similar to that by Pilgrim *et al.* and Nakamura, for temperature conversion by assuming linearity between C and temperature, but should be considered in its non-linear form for C function studies that will involve a more rigorous approach in terms of water quality.
• Certain properties such as seasonal variations of the quality of water in a basin and the water quality variations for different basins are still unknown. These and other assumptions that tend to simplify the properties of C will the topic of future studies and research.
•For naturally occurring waters, C mixing can be done volumetrically although fluctuations do occur regularly in actual mixtures. For studies involving both C and pH, it is best not to estimate pH mixing by volumetric averaging. Also, since pH is affected by temperature, those coincident with C data should also be converted to a standard temperature for reporting.

VII. References
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