Predicting Calcium and Magnesium for Streams in the Great Smoky Mountains National Park

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UNIVERSITY HONORS PROGRAM

SENIOR PROJECT - APPROVAL

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College: Engineering

Department: Civil & Environmental

Faculty Mentor: Dr. R. Bruce Robinson

PROJECT TITLE: Predicting Calcium and Magnesium for Streams in the Great Smoky Mountains National Park

I have reviewed this completed senior honors thesis with this student and certify that it is a project commensurate with honors level undergraduate research in this field.

Signed: [Signature], Faculty Mentor

Date: 5/6/02

Comments (Optional):
Calcium (Ca) and Magnesium (Mg) are vital to the overall health of a forest ecosystem. Their concentrations impact the soil and water chemistry, thereby having a direct effect on plant and animal life. There is currently some concern that acid rain in the Great Smoky Mountains National Park may be causing the Ca and Mg in the soil to be leached out and washed into the streams. If this is the case, obviously there could be vast consequences for the future of the Park ecosystem.

A recent study by Harwell (2001), using data collected from 90 stream sites throughout the Park, analyzed many water quality characteristics for trends and influencing factors. At the time of the study accurate Ca and Mg data were not available for analysis. However, since May 2000 reliable Ca and Mg concentrations have been measured for those same 90 sites on a quarterly basis. The work of Harwell included the compilation of a database to describe the physical attributes of each watershed, or basin, where the stream samples are collected. This information was used to identify correlations between various water quality measures and the basin characteristics and to formulate mathematical models to predict the values of the water quality constituents from the physical data.

The purpose of this study was a parallel examination of the newly available Ca and Mg concentrations using the watershed database created by Harwell (2001). In light of the aforementioned importance of these two ions to the health of the overall Park ecosystem, discovering associations between them and the physical basin descriptions, and possibly even developing models that could soundly predict the former from the latter, would obviously prove invaluable. Granted, “...the presence of statistically significant correlations between basin characteristics and water quality constituents do not establish cause and effect relationships, [but] they can certainly provide insight into possible and reasonable causes” (Harwell 2001). The research and statistical procedures of Harwell were used extensively as a guide for this investigation, both to aide in understanding of the concepts and to maintain consistency within the information available regarding the water quality in the Park (2001).
PREDICTING CALCIUM AND MAGNESIUM FOR STREAMS IN THE GREAT SMOKY MOUNTAINS NATIONAL PARK

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May 2002
University of Tennessee, Knoxville
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Introduction

Calcium (Ca) and Magnesium (Mg) are vital to the overall health of a forest ecosystem. Their concentrations impact the soil and water chemistry, thereby having a direct effect on plant and animal life. There is currently some concern that acid rain in the Great Smoky Mountains National Park may be causing the Ca and Mg in the soil to be leached out and washed into the streams. If this is the case, obviously there could be vast consequences for the future of the Park ecosystem.

A recent study by Harwell (2001), using data collected from 90 stream sites throughout the Park, analyzed many water quality characteristics for trends and influencing factors. At the time of the study accurate Ca and Mg data were not available for analysis. However, since May 2000 reliable Ca and Mg concentrations have been measured for those same 90 sites on a quarterly basis. The work of Harwell included the compilation of a database to describe the physical attributes of each watershed, or basin, where the stream samples are collected. This information was used to identify correlations between various water quality measures and the basin characteristics and to formulate mathematical models to predict the values of the water quality constituents from the physical data.

The purpose of this study was a parallel examination of the newly available Ca and Mg concentrations using the watershed database created by Harwell (2001). In light of the aforementioned importance of these two ions to the health of the overall Park ecosystem, discovering associations between them and the physical basin descriptions, and possibly even developing models that could soundly predict the former from the latter, would obviously prove invaluable. Granted, “...the presence of statistically significant correlations between basin characteristics and water quality constituents do not establish cause and effect relationships,
[but] they can certainly provide insight into possible and reasonable causes” (Harwell 2001).

The research and statistical procedures of Harwell were used extensively as a guide for this investigation, both to aide in understanding of the concepts and to maintain consistency within the information available regarding the water quality in the Park (2001).

Data

Calcium and Magnesium

The Ca and Mg data used for this study were obtained from stream samples collected in the Park from May 2000 to November 2001. There were between four and seven observations recorded during that time period for each of the ninety sites referred to previously, depending on the weather and other related factors for every location at the various collection times. The lab instrument used to measure the ionic concentrations of the constituents in each water sample was an Atomic Absorption Spectrophotometer.

The median value of the available records for Ca and Mg at each site were compiled to use for all analysis. The median, instead of the sample mean, was used as the method of measuring central tendency because it is less sensitive to extreme values. Also, “the median is an average of position, making it often the better representative value” (Lapin 1997). Seven of the ninety sample sites are natural springs, as opposed to surface water streams, so the watershed concept does not apply as well to them. Therefore, these sites with ID numbers 183, 195, 201, 218, 219, 220, and 290 were eliminated from consideration, leaving a total of 83 in the data set.

Basin Characteristics

As mentioned before, the physical details used in this study regarding each basin came from the database developed by Harwell in 2001. Not all the information in the database was included in this study though. The variables utilized were elevation, mean elevation, elevation
class, stream order, basin length, basin area, stream density, average basin slope, channel slope, maximum channel length, basin width, basin shape, geology type, vegetation type, and disturbance history. Eight geology types, ten vegetation types, and five types of disturbance history were used to characterize each watershed. Harwell provided the following descriptions for the physical variables (2001):

- **Elevation**—Elevation in meters above mean sea level of the sample site. Sample sites are usually located at points along a stream where either roads or trails that appear on USGS 1:24,000 scale quadrangle maps intersect. For sampling sites that are not located at easily recognizable points on USGS quads, the sampling site location and elevation were estimated. All elevations are probably accurate to within 6.1 meters since contour intervals are 12.2 meters.
- **Mean Elevation**—Average elevation in meters above mean sea level of the contributing area to the sample site determined from the GIS database.
- **Elevation Class**—A whole number between two and eleven indicating which of the ten elevation ranges in the National Park the sample site is located in. The ten classes and their corresponding elevation ranges in meters are: 2: 305-457; 3: 457-610; 4: 610-762; 5: 762-914; 6: 914-1,067; 7: 1,067-1,219; 8: 1,219-1,372; 9: 1,372-1,524; 10: 1,524-1,676; and 11: >1,676.
- **Stream Order**—Stream order for the sample site using Horton’s method. Any streams that appeared as blue lines on USGS 1:24,000 scale quadrangle maps were counted to determine stream order.
- **Basin Length**—Map distance in kilometers along a straight line from the sample site to the point on the drainage divide used to determine maximum channel length (see below). Digitized USGS quadrangle maps allow a user to select these two points and determine distance.
- **Basin Area**—Contributing area in hectares to the sample site determined from the GIS database.
- **Stream Density**—Ratio of stream distance in kilometers to basin area in square kilometers. Stream distance is the total stream length contributing to the sample site. The length of any stream that appeared as a blue line on USGS 1:24,000 scale quadrangle maps was used to determine the amount of stream distance within the basin.
- **Average Basin Slope**—Average land slope of the contributing area expressed as a percentage and determined from the GIS database.
- **Channel Slope**—Slope of the channel expressed as a percentage determined by the elevation difference between points located 10 and 85 percent of the distance along the main stream channel from the sample site to the drainage basin divide, divided by 75 percent of the length of the main stream channel from the sample site to the drainage divide. This information was determined from the USGS 1:24,000 scale quadrangle maps (Choquette 1988).
- **Maximum Channel Length**—Distance in kilometers from a sample site to the drainage divide following the longest flow path determined from the GIS database.
o Basin Width—Width of contributing area in kilometers obtained by dividing the basin area in square kilometers by the basin length in kilometers.

o Basin Shape—Dimensionless ratio of basin length squared to the basin area.

o Geology Type—Percentage of the contributing area to the sample site covered by the different geology types in the GIS database. The eight types considered were Thunderhead Sandstone, Limestone, Cades Sandstone, Elkmont Sandstone, Anakeesta, Metadiorite, Great Smoky Group, and Basement Complex. Geology data are available for all sites except those within Hazel Creek watershed. The geology data in the GIS database are based upon work done in 1968 (King et al 1968).

o Vegetation Type—Percentage of the contributing area to the sample site covered by the ten different vegetation types considered. This information comes from the GIS database and is based upon work done in 1993 (MacKenzie 1993). Additional habitat information for the different species was obtained from The Audubon Society Field Guide to North American Trees, Eastern Region (Little 1980). A detailed description of each vegetation type follows.

- Spruce Fir—The Eastern Spruce (Picea rubens) often grows in pure stands in the rocky, high elevation (1,372-1,981 meters) soils of the Great Smoky Mountains.

- Northern Hardwood—Major species in this group include the American Beech (Fagus grandifolia) and the Sweet Birch (Betula lenta). Minor species include the Red Maple (Acer rubrum), Sugar Maple (Acer saccharum), and the Northern Red Oak (Quercus rubra). All of these species prefer the cool and moist conditions found at higher elevations. They generally occur at elevations above 1,075 meters and often in pure stands.

- Cove Hardwood—These forests generally do not have a single dominant species that occurs in pure stands like the Spruce Fir or the Northern Hardwood forests. However, major species in this group include White Basswood (Tilia heterophylla), Carolina Silverbell (Halesia carolina), Red Maple (Acer rubrum), Sugar Maple (Acer saccharum), Yellow Buckeye (Aseculus octandra), American Beech (Fagus grandifolia), Cucumber Magnolia (Magnolia acuminata), Sweet Birch (Betula lenta), and Eastern Hemlock (Tsuga canadensis). Some of the species in this group are also found in the Northern Hardwood forest. However, when they occur in a Cove Hardwood forest, they are typically not pure stands. The elevation range for this type of forest is broad. Cucumber Magnolia and White Basswood trees are found in the lower elevations (about 60 meters), and other species are found at higher elevations. The Yellow Buckeye is found at elevations as high as 1,920 meters, and the Eastern Hemlock as high as 1,524 meters. The Eastern Hemlock is the only species in this group that does occur in pure stands. All of the species in the Cove Hardwood forests prefer moist soil conditions. Moist soil conditions are found at the higher elevations and at lower elevations along streams and in ravines.

- Mesic Oak—Major species in these forests include Northern Red Oak (Quercus rubra), Chestnut Oak (Quercus prinus), and White Oak (Quercus alba). This forest can occur throughout the Great Smoky Mountains at almost any elevation. It is common on ridges and south-facing slopes at higher elevations and ridges.
and side slopes at lower elevations. The trees in this forest often grow in pure stands.

- **Mixed Mesic Hardwood**—This forest type has no clear dominant species. It may contain any combination of the following: Oaks (*Quercus*), Elms such as the American Elm (*Ulmus americana*), Pines (*Pinus*), Hickories such as Bitternut Hickory (*Carya cordiformis*) and Pignut Hickory (*Carya glabra*), Tulip Poplar (*Liriodendron tulipifera*), Red Maple (*Acer rubrum*), Black Walnut (*Juglans nigra*), Sweetgum (*Liquidambar styraciflua*), Sycamore (*Platanus occidentalis*), and Black Locust (*Robinia pseudoacacia*). Some of these species, such as the Sweetgum, American Sycamore, and Tulip Poplar, are found in areas that have been cleared in the last 80 years as a result of farming or logging operations. These areas are usually found at the lower elevations of the Great Smoky Mountains. The Mixed Mesic Hardwood forests are typically found at elevations less than 750 meters. Some of the species can be found at higher elevations.

- **Tulip Poplar**—The Tulip Poplar, mentioned as part of the Mixed Mesic Hardwood forests, also occurs frequently enough in stands within the Great Smoky Mountains to be classified as a unique forest type. The Tulip Poplar is usually found in coves and valleys with moist, well-drained soils at elevations from 300 meters to as high as 1,372 meters. Most of the stands are found at lower elevations that have been logged or farmed prior to establishment of the Park.

- **Pine**—Major species in the Pine forests include Pitch Pine (*Pinus rigida*), Table Mountain Pine (*Pinus pungens*), and Shortleaf Pine (*Pinus echinata*). Minor species include Eastern White Pine (*Pinus strobes*) and Virginia Pine (*Pinus virginiana*). The Pine forests typically occur at the middle to lower elevations of the Great Smoky Mountains. They prefer well-drained soils such as sands and sandy loams. The Eastern White Pine can be found as high as 1,524 meters. The remainder of species in these forests is below 1,300 meters. The Virginia Pine is another species, which tends to do well in areas that were farmed or logged prior to establishment of the Park.

- **Heath Bald**—The Heath Bald forests are dominated by evergreen ericaceous shrubs, which form dense thickets in the understory of other mountain forests. Species within these forests include Mountain Laurel (*Kalmia latifolia*), Catawba Rhododendron (*Rhododendron catawbiense*), and Rosebay Rhododendron (*Rhododendron maximum*). These plants, especially the Mountain Laurel, prefer acidic soils. They are found over a broad elevation range, but most are found at the middle to upper elevations (900 to 2,000 meters).

- **Xeric Oak**—Major species in this group include Scarlet Oak (*Quercus coccinea*), Chestnut Oak (*Quercus prinus*), Black Tupelo or Blackgum (*Nyssa sylvatica*), Sourwood (*Oxydendron arboreum*), and Black Locust (*Robinia pseudoacacia*). The trees in this forest can occur at high elevations in the Great Smoky Mountains, but typically this forest occurs on ridges and slopes below 1,050 meters. These trees typically grow in mixed forests with other oaks or pines. The exception to this is the Chestnut Oak. As already mentioned, the
Chestnut Oak often grows in pure stands. In this situation, it is part of what was classified as a Mesic Oak forest. When the Chestnut Oak occurs in Xeric Oak forests, it grows along with other species.

- Pine/Oak—This forest type contains an even mixture of pine and oak. It has the same site characteristics as the Pine forests. Species included in these forests can be any combination of the types typically found in the Pine forests or the Mesic Oak forests.

- Disturbance History—Percentage of the contributing area to the sample site with a certain type of historical land use. The types of disturbance history include undisturbed, light cut, settlement, selective cut, and heavy cut. This information comes from the GIS database and is based upon work done in 1985 and 1988 (Pyle 1985; Pyle 1988).

**Preliminary Analysis**

*Scatter Plots*

The Ca and Mg median values for each sample site were graphed against the basin descriptors listed in the previous section in scatter plots. A separate plot was made for each individual watershed characteristic, or independent variable. These were produced to begin getting a feel for the data set and to look for possible trends that could play an important role in the eventual modeling process. The graphs are included as Figures A-1 thru A-35 in Appendix A.

It was quickly realized during the creation of these scatter plots that the information could not be seen very effectively because of the broad range of Ca concentrations. However, only three of the observations with very large values seemed to be causing this problem. Sites 156, 174, and 489 with Ca concentrations in μeq/L of 226.65, 1,067.50, and 766.00 respectively were determined to be the outliers. These identical sites also had the highest Mg concentrations in the data set. In the same order, their Mg values in μeq/L were 117.70, 226.34, and 176.54. For perspective, the next highest concentrations of Ca and Mg in the data set were respectively 122.00 and 81.07 μeq/L.
A second group of scatter plots were made exactly as the first except without the three outlying sites. This set of figures is shown in Appendix B numbered B-1 to B-35. As can be seen, the points are much more evenly distributed in this second group of graphs giving a better view of the data, yet very few clearly defined relationships can be spotted by looking only at the observations themselves. Linear trend lines were added to both sets of scatter plots using Microsoft® Excel in order to better identify existing trends. These trend lines are shown on all the figures in both Appendices A and B.

Without the influence of the outliers, the watershed characteristics that visually appeared to have the strongest linear connection with Ca and Mg are average basin slope, Limestone, Anakeesta, Spruce Fir, Mesic Oak, and heavy cut, although this determination is somewhat subjective. See the figures in Appendix B. Of these associations, Mesic Oak and heavy cut are the only independent variables that vary inversely with Ca and Mg concentrations.

Inspection of the scatter plots in Appendix A, which include the three outlying observations, painted a different picture. Ca and Mg seemed to have the most noteworthy trends with Limestone, Cades Sandstone, Pine, Xeric Oak, Pine/Oak, and settlement. Each of these basin characteristics varies directly with the Ca and Mg concentrations. Note that Limestone is the only basin descriptor that turns up in the list of strongest relationships with Ca and Mg for both sets of graphs. Limestone, because of its chemistry (CaCO3), was expected to play a significant role in this study, and this is the first evidence supporting that assumption.

Correlations

Correlation analysis was performed on the data set for similar purposes as the scatter plot exercise and to provide more quantitative, rather than subjective, conclusions. In addition, the correlation results would later be used to evaluate the prediction models developed. The
procedures were done with SPSS statistical software, version 10.0 and 10.1 (SPSS 1999), and Kendall’s Tau correlation coefficient (τ) was the selected as the technique “because it is a rank-based procedure for data which are not normally distributed and is resistant to [the] effects of outliers” (Harwell 2001).

The Ca and Mg concentrations were tested for correlations with each of the watershed variables, and Table 1 details the results. These findings give insight to possible associations between the amount of Ca and Mg in the streams and the physical characteristics of each stream basin. A Kendall’s Tau value near ±1.000 denotes a strong interaction and near 0.000 a weak one. The positive or negative sign of τ indicates either a direct or inverse correlation respectively. The highest correlation discovered exists between Ca and Mesic Oak, but the τ for this relationship is still only −0.391. Only four other associations were found with a τ > ±0.300. They are Ca and Limestone with τ = 0.315, Ca and undisturbed with τ = 0.346, Mg and Limestone with τ = 0.331, and Mg and Pine/Oak with τ = 0.325. Notice that Limestone is mentioned in regards to both the Ca and Mg concentrations. Again, the importance of Limestone is affirmed.

The median concentrations of Ca and Mg were tested for their association with one another in the stream water also. A fairly notable relationship was revealed with τ = 0.621. Obviously, this number suggests a much higher correlation between Ca and Mg themselves than either has with any of the watershed descriptors.

Finally, the relationships among the physical basin characteristics themselves were explored with correlation analysis. The outcome of this work is shown in Table 2. Strong correlations between assorted watershed variables could potentially cause multi-collinearity problems during model formulation.
Table 1: Kendall’s Tau (τ) Correlations

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<th>ca</th>
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Note: Normal font denotes statistical significance at 0.01 level, bold at 0.05 level, and blank cells are not significant.
Table 2: Kendall's Tau (\(\tau\)) Correlations (continued)

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Note: Normal font denotes significance at 0.01 level, bold at 0.05 level, and blank cells are not significant.
Modeling Process

Formulation

Multiple linear regression was the chosen technique for attempting to predict Ca and Mg concentrations from the basin characteristics. Of the various types of multiple linear regression, "it was concluded that stepwise procedures would be adequate for model selection..." (Harwell 2001). SPSS statistical software, version 10.0 and 10.1, was used once again for this analysis (SPSS 1999). The physical watershed descriptors served as the multiple independent variables available for use in the regression equations, and either Ca or Mg was the dependent variable for each regression performed. The independent variables "were set to enter the model if the probability of the partial F statistic was less than or equal to 0.05 and set to leave if the partial F statistic was greater than or equal to 0.10" (Harwell 2001).

Additionally, the program was fixed to exclude cases pairwise in the event of missing values.

Evaluation

After a model was developed by linear regression, an array of tests mostly patterned after the work of Harwell was employed to determine its accuracy (2001). The statistical significance and adjusted $R^2$ of the overall model were first assessed. Next, the constant and coefficients of the equation were checked for statistical significance ($p < 0.100$). The sign of all coefficients was also compared to the sign of their corresponding Kendall's Tau correlation coefficients found previously. The signs of the two should be the same.

The condition index of each predictor was used to evaluate the model for multi-collinearity problems, and an index of over 30 was considered unacceptable (Harwell 2001). Cook's D statistic was calculated to test the leverage, or influence, of each sample observation on the
model. A Cook’s D value above 1.000 was regarded as suspect enough to investigate removal of the observation (Anderson, Sweeney, and Williams 1993).

Partial regression scatter plots for each independent variable selected by the regression were also produced and examined. A linear trend is desired on these graphs. They “are useful for detecting influential data and can reveal nonlinearity (Fox, 1997)” (Harwell 2001). Graphing the standardized residuals against the unstandardized predicted values created residual plots. These were used to check for a normal distribution of the residuals. A random scattering that is roughly equal above and below zero is desired, and a detectable pattern on the residual plot could indicate the need to perform some transform of one or more of the variables. The normality of the distribution was determined by calculating the kurtosis and skewness of the unstandardized residuals. These indicators are equal to 3.00 and 0.00, respectively, for an ideal normal distribution, so those values were considered to be best (Tamhane and Dunlop 2000). Moreover, a box plot of the unstandardized residuals was constructed to visually inspect for normality.

The unstandardized predicted concentrations were plotted versus the actual ones to assess the mathematical model. Theoretically, if the expression were perfect, this graph would have an intercept of 0.000 and slope equal to 1.000. The intercept and slope were found for the plot and tested for statistical significance ($p < 0.100$). Lastly, the reasonableness of the predicted values was checked. “Reasonable values were defined as not negative. The model should not predict negative values for water quality constituents” (Harwell 2001).

**Predictive Models**

A number of regression models were developed and evaluated during this study by the above-described methods. All the models were formulated to predict either Ca or Mg from the
physical basin characteristics where the samples were collected. Each predictive equation is
displayed in Table 3 along with its overall adjusted $R^2$ and statistical significance. Further
information about the models is provided in the following sub-sections. A discussion is also
included concerning their applicability. Use of the models reported here should not occur for
applications beyond the scope of the limitations and guidelines recommended therein.

*All Sites*

Initially, regression models were formed to predict Ca and Mg utilizing data from all
83 stream sites. The resulting equations can be seen in Table 3. Both are statistically
significant and have high $R^2$ values. Nonetheless, the other evaluation procedures uncovered
substantial problems with the models.

In the Ca expression, the coefficient for Cades Sandstone is negative, whereas the related
Kendall’s Tau correlation coefficient listed in Table 1 is positive. In addition, Table 2 gives a
Kendall’s Tau coefficient for Cades Sandstone and Limestone of 0.800, but their respective
equation coefficients have opposite signs. Three of the individual site observations returned
Cook’s D statistics larger than 1.000. Kurtosis and skewness of the unstandardized residuals
were 12.80 and 2.32 respectively, denoting a non-normal distribution. Of these two, clearly the
kurtosis of 12.80, which is considerably greater than 3.00, raises more concern. See the box
plot of unstandardized residuals in Figure 1. Finally, the intercept of 2.548 for the predicted
versus actual plot was relatively close to 0.000 but was not statistically significant
($p$ not < 0.100).

The formulated expression for Mg had its troubles as well. The coefficient of Thunderhead
Sandstone shown in Table 3 is positive, and the associated Kendall’s Tau in Table 1 is
negative. The Cook’s D for one stream site was over 1.000, and again, although better, the
### Table 3: Model Summary

<table>
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<tr>
<th>Sites Included in Analysis</th>
<th>Regression Equation</th>
<th>Adjusted $R^2$</th>
<th>Statistical Significance</th>
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</thead>
<tbody>
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<td>All</td>
<td>Ca = 42.844 + 54.2941(Limestone) - 4.394(Cades Sandstone) + 0.283(undisturbed)</td>
<td>0.967</td>
<td>$p = 0.000$</td>
</tr>
<tr>
<td>All</td>
<td>Mg = 20.703 + 9.809(Limestone) + 0.293(Anakeesta) - 0.138(heavy cut) + 0.796(Xeric Oak) - 1.884(Heath Bald) + 8.29E-02(Thunderhead Sandstone)</td>
<td>0.909</td>
<td>$p = 0.000$</td>
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<tr>
<td>With Limestone</td>
<td>Ca = 347.137 + 60.142(Limestone) - 210.788(basin shape)</td>
<td>0.988</td>
<td>$p = 0.001$</td>
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<tr>
<td>With Limestone</td>
<td>Mg = 25.683 + 12.931(Limestone)</td>
<td>0.993</td>
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<tr>
<td>Without Limestone</td>
<td>log(Ca) = 1.669 + 2.724E-03(undisturbed) + 2.001E-02(maximum channel length) - 2.78E-02(basin length) - 2.29E-02(Heath Bald) - 1.62E-03(Elkmont Sandstone) - 1.87E-03(Northern Hardwood)</td>
<td>0.558</td>
<td>$p = 0.000$</td>
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<tr>
<td>Without Limestone</td>
<td>log(Mg) = 1.266 + 2.945E-03(Anakeesta) + 4.798E-03(Mixed Mesic Hardwood) + 1.443E-03(undisturbed) - 2.60E-03(Elkmont Sandstone) - 2.24E-02(Heath Bald) - 9.902E-03(Pine)</td>
<td>0.616</td>
<td>$p = 0.000$</td>
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</table>
unstandardized residuals distribution did not turn out normal. The kurtosis was 6.40, and skewness 1.59.

It was suspected that some of the problems with these original models might be due to the outlying data points discovered during the preliminary scatter plot analysis. To illustrate this idea, the predicted versus actual concentrations for each model are displayed in Figures 2 and 3. It can easily be seen that a few individual points in each plot are separate from the fairly well clustered majority. Furthermore, the exceptionally strong effects of Limestone, alluded to previously, apparently played a role. The influential status of Limestone in the models is plainly evident by comparing the relative magnitudes of the Limestone coefficients to the other coefficients in each equation.

For these reasons it was decided to split the data set into two distinct sets for modeling purposes, one for stream sites located in basins with Limestone and the other for sites without
Figure 2: Predicted versus Actual Concentrations—All Sites

Figure 3: Predicted versus Actual Concentrations—All Sites
Limestone. Inspection of the data revealed that only six of the 83 sample sites had any Limestone existing in their watershed area. These were sites 13, 24, 156, 173, 174, and 489. Interestingly, the three observations earlier identified as outliers in preliminary analysis are all included in this small group.

Sites With Limestone

Multiple linear regression was performed on the data set for the six sites containing some percentage of Limestone within their basins. Predictive expressions for both Ca and Mg were explored, and models with particularly high $R^2$ values were the outcome for each. This is largely believed to be an outcome of the powerful impacts of Limestone on the concentrations of Ca and Mg in the water.

Calcium

The first mathematical equation produced to predict Ca explained much of the variability among the points and had few problems upon evaluation. No observations were designated as high leverage points by Cook's D statistic. The kurtosis of the unstandardized residuals was 1.16, and their skewness was 0.40. Also, the predicted versus actual plot had a statistically insignificant ($p > 0.100$) intercept of 2.801.

A $\log_{10}$ transformation of the Ca values was executed and regression attempted a second time to see if an improved model would result. The expression formed had a considerably lower $R^2$ value and some of the checks still exposed weakness. Therefore, the first equation created was chosen as the best model to predict Ca for basins that include Limestone. This model is given as part of the model summary in Table 3.
Magnesium

The Mg modeling process encountered a few more difficulties. Regression procedures formed an expression with an $R^2$ of 0.951, but testing revealed a stream site with a Cook's D of 5.961. Additionally, kurtosis and skewness of the unstandardized residuals in order were -0.61 and 0.87. The intercept of the predicted versus actual plot was equal to 4.208, and once again, as with Ca, it was not significant ($p$ not < 0.100).

Endeavoring for a better model, a second linear regression was attempted after removal of the highly influential point. The $R^2$ value increased slightly, and kurtosis of the unstandardized residuals improved to 1.37. However, their skewness worsened to -1.00. The intercept for the predicted and actual concentrations graph decreased to 0.42 but was still not statistically significant ($p$ not < 0.100). This model did provide a little improvement, although more was pursued.

A third equation was formulated using the same data points as the second model, except the log$_{10}$ of the Mg median values was used as the dependent variable. This model yielded a smaller $R^2$ and had yet another observation with a Cook's D statistic greater than 1.000. So, the second expression created was determined to be the optimum model for predicting Mg where Limestone is present in the watershed. Table 3 displays this equation.

Sites Without Limestone

Predictive models of Ca and Mg were produced utilizing linear regression techniques for the basins with no Limestone as well. This data set included 77 stream sample sites from around the Park. The $R^2$ values were not nearly as high as for the Limestone basins, but they were still fairly good for this type of modeling.
Calcium

The initial expression to predict the Ca concentrations had an R² of 0.513. The equation coefficient for Elkmont Sandstone was negative, and preliminary correlation analysis gave a positive corresponding Kendall’s Tau. Two other selected watershed characteristics, basin length and maximum channel length, curiously had model coefficients with opposite signs yet a Kendall’s Tau shown in Table 2 of 0.923. In addition, partial regression plots for the model did not appear to be linear. An example for one basin variable, undisturbed, can be viewed in Figure 4. The standardized residuals plot had a noticeable “fanning” pattern and is included as Figure 5. On the other hand, the kurtosis and skewness of the unstandardized residuals were respectively 2.44 and 0.19, indicating a distribution quite close to normal. Plotting the predicted Ca values against the related actual ones resulted in poor intercept and slope values also. The intercept was 24.813 and slope 0.551, both of which were statistically significant (p < 0.100).

Other regressions were tried using various transformations of the dependent and independent variables in an attempt to discover a better equation. The transforms investigated were a log₁₀ conversion of the Ca concentrations, a log₁₀ conversion of both Ca and the favored predictors simultaneously, and transformations where the chosen predictors were individually raised to assorted powers. The exponents surveyed for each were −1, ½, and 2. The best mathematical model was formed with the first transformation listed. This equation did explain more of the variation, but the issue of the opposing signs for Elkmont Sandstone was not resolved. The kurtosis of the unstandardized residuals decreased to 0.30 while their skewness essentially did not change. The intercept and slope for the predicted versus actual plot improved and remained significant (p < 0.100). They were 0.700 and 0.593, in that order. This
Figure 4: Partial Regression Plot for Undisturbed—Sites Without Limestone

Partial Regression Plot

Dependent Variable: ca

Figure 5: Standardized Residuals Plot—Sites Without Limestone
predictive expression for the Ca concentrations in basins without Limestone is reported in Table 3.

**Magnesium**

Multiple linear regression gave similar conclusions when first applied to Mg. The $R^2$ value was a low 0.427. Again the partial regression plots did not seem strongly linear, and a pattern was evident on the plot of standardized residuals. Figure 6 displays this pattern. Kurtosis was calculated to be 9.37 and skewness 2.17 for the unstandardized residuals. The intercept of the predicted versus actual plot was 15.324 and significant ($p < 0.100$). Its slope, which was significant ($p < 0.100$) as well, was determined to be 0.450. Obviously this was not a satisfactory model.

The search for an improved predictive equation for Mg was approached in a parallel manner to that described above for Ca. Regression analyses were performed using the same assortment of transforms, and as for Ca, the model of choice used a $\log_{10}$ transformation of the dependent variable. The consequent enhancement of $R^2$ to 0.616 for this expression was quite drastic. Also, the unstandardized residuals distribution became much closer to normal. Its kurtosis was 3.76 and skewness 1.01. The graph of the predicted Ca concentrations against actual ones gave better intercept and slope values. The intercept was 0.500 and slope 0.647, both still significant ($p < 0.100$). Table 3 shows the equation for this model selected to predict Mg for watersheds with no Limestone.

**Model Application**

Before using any of the predictive equations detailed in Table 3, careful consideration regarding the applicability of the model for the intended use is strongly encouraged. The regression models should not be applied to situations greatly dissimilar to those from which the
raw data used to create them originated. Circumstances where the terrain, forest, climate, groundwater movement, air quality, and other factors are most comparable to the Great Smoky Mountain National Park will provide the best opportunity for utilization of the equations. Their accuracy and dependability should be at its highest when those conditions are met. Examination of the other information presented in this document concerning the models should be helpful in determining applicability. It should be noted in addition that all the specifics of this study are not included in this report.

Range guidelines for each regression equation are listed in Table 4. Recorded there are the minimum, maximum, and median values for the predicted and actual Ca and Mg concentrations for each model. The same values are provided for all independent variables selected as predictors in the expressions. Application of any model outside of its reported variable ranges is not recommended.
Table 4: Model Application Information

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Model</th>
<th>Sites Included</th>
<th>Predicted</th>
<th>Min., Max., Median Actual</th>
<th>Independent Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>All</td>
<td>23.17, 1127.74, 54.17</td>
<td>28.50, 1067.50, 50.50</td>
<td>Limestone: 0, 21, 0</td>
<td>Cades Sandstone: 0, 33.2, 0</td>
</tr>
<tr>
<td></td>
<td>With Limestone</td>
<td>42.81, 1062.07, 181.19</td>
<td>62.50, 1067.50, 164.25</td>
<td>Limestone: 0.4, 21, 4.6</td>
<td>basin shape: 1.4, 2.6, 1.8</td>
</tr>
<tr>
<td></td>
<td>Without Limestone</td>
<td>31.80, 89.95, 52.77</td>
<td>28.50, 122.00, 49.85</td>
<td>undisturbed: 0, 100, 37.5</td>
<td>basin length: 0.4, 18.2, 5.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Heath Bald: 0, 9.2, 1</td>
</tr>
<tr>
<td>Mg</td>
<td>All</td>
<td>13.95, 243.62, 26.73</td>
<td>15.06, 226.34, 25.43</td>
<td>Limestone: 0, 21, 0</td>
<td>Anakeesta: 0, 100, 0</td>
</tr>
<tr>
<td></td>
<td>With Limestone</td>
<td>30.86, 176.97, 55.42</td>
<td>35.56, 226.34, 83.09</td>
<td>heavy cut: 0, 100, 0.2</td>
<td>Xeric Oak: 0, 26.5, 0.8</td>
</tr>
<tr>
<td></td>
<td>Without Limestone</td>
<td>16.16, 50.73, 25.74</td>
<td>15.06, 81.07, 24.24</td>
<td>Heath Bald: 0, 9.2, 0.9</td>
<td>Thunderhead Sandstone: 0, 100, 49.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Pine: 0, 14, 0.2</td>
</tr>
</tbody>
</table>
Summary and Conclusion

The goal of this study was to formulate mathematical models to predict the Ca and Mg concentrations in surface water streams using the physical watershed characteristics of the individual streams as predictors. The water quality data and basin information used were collected from a number of sample sites in the Great Smoky Mountains National Park. Similar work done recently by Harwell with other water quality information from the Park served as a pattern (2001). Some preliminary investigation of the data set was performed using scatter plots and Kendall’s Tau correlation coefficients before modeling actually began. These analyses provided valuable insight for the subsequent modeling process and aided in evaluation of the various equations produced. Stepwise multiple linear regression was the method of choice for modeling.

Regression procedures were initially attempted using information from the complete set of applicable sites, and expressions with high R squared values resulted for both Ca and Mg. Upon evaluation of the models though, considerable weakness was discovered. This was apparently due to the strong influence of Limestone on the Ca and Mg concentrations, so it was decided to break the data into two separate sets for regression analysis, one for sample sites with Limestone in their watershed and the other for sites without.

Modeling results improved for these separate data sets. The predictive equations for Ca and Mg at sites with Limestone in their basins had R squared values of 0.988 and 0.993 respectively. Important predictors selected for Ca were Limestone and basin shape, whereas the only watershed descriptor used to predict Mg was Limestone. The significance of Limestone existing within the watershed on the Ca and Mg concentrations in the streams is clearly obvious from this outcome. The expressions formed using the data from sample sites without
Limestone in their basins explained somewhat less of the Ca and Mg variability, but the $R^2$ values were still rather good for this type of modeling. The Ca equation had an $R^2$ of 0.558, and the $R^2$ for the Mg model was 0.616. The independent variables selected for the Ca expression were undisturbed, maximum channel length, basin length, Heath Bald, Elkmont Sandstone, and Northern Hardwood. The watershed characteristics determined to predict Mg were Anakeesta, Mixed Mesic Hardwood, undisturbed, Elkmont Sandstone, Heath Bald, and Pine.

It is of interest that the $R^2$ values of the regression models attained for both Ca and Mg using sample sites with Limestone are substantially greater than those for sites without Limestone. This is probably further evidence of the importance of Limestone to the concentrations of those ions. However, this conclusion is only logical considering the chemical makeup of Limestone and was a theory from the onset of the study. Also, the relative $R^2$ values of the models should not diminish the fact that a significant amount of Ca and Mg variability was explained even for the sample sites without Limestone included in their basins.

A final observation is that no elevation variables were chosen as predictors in any of the models formulated. In the work of Harwell, elevation was found to be quite influential in relation to some other water quality constituents, namely pH and nitrate (2001). Therefore, it is worthy of noting that elevation does not seem to play a major role in the concentrations of Ca and Mg in the Park streams.
REFERENCES


Figure A-2: Mean Elevation Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-3: Elevation Class Trends

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-4: Stream Order Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-5: Basin Length Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-6: Basin Area Trends?

The figure shows a scatter plot with data points for Mg and Ca concentrations against basin area (ha). The trends for Mg and Ca are indicated with symbols and linear regression lines. The x-axis represents the basin area in hectares, while the y-axis represents the concentration in mg/L.
Figure A-7: Stream Density Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)

![Graph showing stream density trends with Mg, Ca, linear Mg, and linear Ca lines.]
Figure A-8: Average Basin Slope Trends?

- Mg
- Ca
- Linear (Mg) - - Linear (Ca)
Figure A-9: Channel Slope Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-10: Maximum Channel Length Trends?
Figure A-11: Basin Width Trends

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-12: Basin Shape Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)

Axes:
- y-axis: mg/L
- x-axis: basin shape

Data points and trend lines indicating Mg and Ca concentrations with linear fits.
Figure A-13: Thunderhead Sandstone Trends?
Figure A-14: Limestone Trends?

- Mg (diamonds)
- Ca (squares)
- Linear (Mg) (solid line)
- Linear (Ca) (dashed line)
Figure A-15: Cades Sandstone Trends?

- **Mg**
- **Ca**
- Linear (Mg)
- Linear (Ca)
Figure A-16: Elkmont Sandstone Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-17: Anakeesta Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-18: Metadiorite Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-19: Great Smoky Group Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-20: Basement Complex Trends?
Figure A-22: Northern Hardwood Trends?
Figure A-23: Cove Hardwood Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-24: Mesic Oak Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-25: Mixed Mesic Hardwood Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-26: Tulip Poplar Trends?
Figure A-27: Pine Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-28: Heath Bald Trends?
Figure A-29: Xeric Oak Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-30: Pine/Oak Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure A-31: Undisturbed Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)

ueq/L vs light cut (% area)
Figure A-32: Light Cut Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)

undisturbed trends (% area)
Figure A-33: Settlement Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)

Settlement (% area)
Figure A-34: Selective Cut Trends?

- Diamond: Mg
- Square: Ca
- Solid line: Linear (Mg)
- Dashed line: Linear (Ca)

Axes:
- Y-axis: mg/L
- X-axis: Selective cut (% area)
Figure A-35: Heavy Cut Trends?

![Graph showing heavy cut trends for Mg and Ca](image-url)

- **Mg**
- **Ca**
- Linear (Mg)
- Linear (Ca)
Figure B-1: Elevation Trends?

![Graph showing elevation trends](image-url)
Figure B-2: Mean Elevation Trends?
Figure B-3: Elevation Class Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-4: Stream Order Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-5: Basin Length Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-6: Basin Area Trends?
Figure B-7: Stream Density Trends?
Figure B-8: Average Basin Slope Trends?

Mg  Ca  Linear (Mg)  Linear (Ca)
Figure B-9: Channel Slope Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-10: Maximum Channel Length Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-11: Basin Width Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-12: Basin Shape Trends?
Figure B-13: Thunderhead Sandstone Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-14: Limestone Trends?
Figure B-15: Cades Sandstone Trends?

![Figure B-15: Cades Sandstone Trends Diagram]
Figure B-16: Elkmont Sandstone Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)

Elkmont Sandstone (% area)
Figure B-17: Anakeesta Trends?
Figure B-18: Metadiorite Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-19: Great Smoky Group Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-20: Basement Complex Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-21: Spruce Fir Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-22: Northern Hardwood Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-23: Cove Hardwood Trends?
Figure B-24: Mesic Oak Trends?

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Mesic Oak (% area)

ueq/L

Mg
Ca
Linear (Mg)
Linear (Ca)
Figure B-25: Mixed Mesic Hardwood Trends?
Figure B-26: Tulip Poplar Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-28: Heath Bald Trends?
Figure B-29: Xeric Oak Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-30: Pine/Oak Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-31: Undisturbed Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-32: Light Cut Trends

undisturbed trends (% area)
Figure B-33: Settlement Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-34: Selective Cut Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)
Figure B-35: Heavy Cut Trends?

- Mg
- Ca
- Linear (Mg)
- Linear (Ca)