

A Senior Honors Thesis

**Inorganic Carbon Cycling in Agricultural Lands,  
Coshocton, Ohio**

By

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## ABSTRACT

Alkalinity, or the dissolved inorganic carbon species from chemical weathering exported from soils to streams, is a measureable representation of one of the terrestrial sinks for atmospheric CO<sub>2</sub>. Fluuvially transported alkalinity, derived from soils, can be used to help characterize land management methods and improve future conditions to sequester carbon. This study focuses on how the different land uses affect inorganic carbon (i.e. alkalinity) exportation. The North Appalachian Experimental Watershed, in Coshocton, Ohio is composed of several small watersheds with different agriculture land uses, such as pastured, forested, mixed, no-tillage crops, and tillage crops. During October 2008 to April 2009, water samples were collected from five different watersheds and alkalinity measurements were made during baseflow and stormflow conditions. Baseflow alkalinity yields were nearly indistinguishable among land use types. Carbonate speciation calculations showed the primary species, on average, in all of the water samples to be bicarbonate. Stormflow at the tilled and non-tilled sites showed that the tilled land use exported at least twice the amount of alkalinity than the non-tilled land at times of high flow. Tillage practices release inorganic carbon and ultimately may be a source for atmospheric CO<sub>2</sub>.

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# CARBON CYCLING

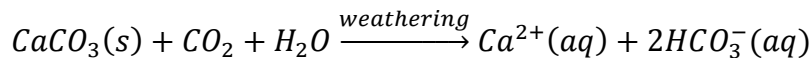
## Introduction

The element carbon is the foundation for all life. Major carbon pools include the atmosphere, soil, vegetation, and the ocean; all of which are connected. Soil is the largest terrestrial global carbon pool and carbon is stored in the soil in both organic and inorganic forms. Higher amounts of carbon in soil enhance soil productivity, fertility, water-holding capacity, and other soil conditions that reduce erosion and control nutrient and pesticide availability (USDA, 2008). One prominent inorganic carbon species, CO<sub>2</sub>, a greenhouse gas, has amplified the interest in studying the storage and release of carbon from various pools. The increase of atmospheric CO<sub>2</sub> has been largely attributed to the burning of fossil fuels. However, other research studies suggest CO<sub>2</sub> has also increased in response to changes in land use and management. Large scale soil studies indicate that agricultural erosion and subsequent burial may be a sink of between 0.06 to 0.27 petagrams of carbon, and hence draw-down atmospheric CO<sub>2</sub> (Van Oost et al., 2008). Conversely, these results are hotly debated, as the fate of eroded carbon is not necessarily immediately buried (Lal et al., 2008). Rather microbial oxidation or mineralization may be accelerated in the disaggregated, redeposited soil and thereby return CO<sub>2</sub> back into the atmosphere (Lal et al., 2008). Thus, to evaluate carbon cycling associated with agricultural land use, mineral-weathering processes must also be considered. For example, the chemical weathering of silicates draws down CO<sub>2</sub>, sequestering it on the order of millions of years, while carbonate weathering only sequesters CO<sub>2</sub> for hundreds to thousands of years (Raymond and Cole, 2003). In terms of geologic time, carbonate weathering results in no net loss or gain of CO<sub>2</sub> to the atmosphere (Cockell et al., 2008). This is because weathering carbonates on land uses one carbon atom from the atmosphere and then precipitating a carbonate

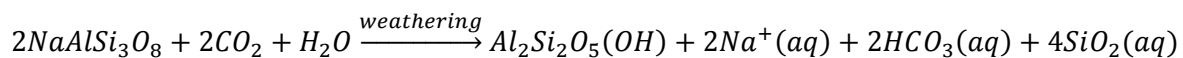
mineral in the ocean releases one carbon atom (Equation 1), leading to no net loss or gain of CO<sub>2</sub> over a long period of time (Cockell et al., 2008). On the other hand, silicate weathering uses two carbon atoms from the atmosphere during weathering (Equation 2), and releases one carbon atom into the atmosphere during precipitation. Hence, silicate weathering removes CO<sub>2</sub> from the atmosphere (Cockell et al., 2008).

Finally, our understanding of gain or loss of CO<sub>2</sub> associated with land use practices depends on evaluating the fate of both organic carbon and inorganic carbon soil pools. Fluxes of carbon must be examined in the soil, the air, and the surface waters that erode and redeposit carbon on the landscapes. This study determines the behavior of dissolved inorganic carbon in surface water draining in several agricultural watersheds in the United States Department of Agriculture's (USDA) North Appalachian Experimental Watershed in Coshocton, Ohio. Results and interpretation of this research will eventually be paired with other soil carbon, respiration, and isotopic data to quantify the total carbon pool; and in particular the release or draw down of atmospheric CO<sub>2</sub>.

**Carbonate weathering** (Equation 1)



**Silicate weathering** (Equation 2)



## Why measure alkalinity?

Alkalinity is a measure of the capacity of a solution to neutralize acids or the ability to resist change in pH. The definition of alkalinity includes all of the following components, where T is the total:

$$A_T = [\text{HCO}_3^-]_T + 2[\text{CO}_3^{2-}]_T + [\text{B(OH)}_4^-]_T + [\text{OH}^-]_T + 2[\text{PO}_4^{3-}]_T + [\text{HPO}_4^{2-}]_T + [\text{SiO(OH)}_3^-]_T - [\text{H}^+] - [\text{HSO}_4^-] \quad (\text{Equation 3})$$

Most of the chemical species represented in Equation 3 are only present in significant amounts in seawater conditions, but fresh surface waters will primarily have only  $\text{HCO}_3^-$  (bicarbonate) and trace  $\text{CO}_3^{2-}$  (carbonate) in considerable amounts to account for  $A_T$ . Thus, it is acceptable to conclude, for fresh water,  $A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}]$ . Terrestrial alkalinity produced during chemical weathering of soils is a process that sequesters atmospheric  $\text{CO}_2$  (Raymond and Cole, 2003).  $\text{CO}_2$  is converted into bicarbonate or carbonate by weathering of parent rocks and minerals (Raymond and Cole, 2003). Finally, dissolved inorganic carbon (DIC) in the form of alkalinity is transported by stream.

## The major objectives of this study were to:

1. Quantify the amount of dissolved inorganic carbon and its chemical speciation for distinct land uses under baseflow and stormflow conditions.

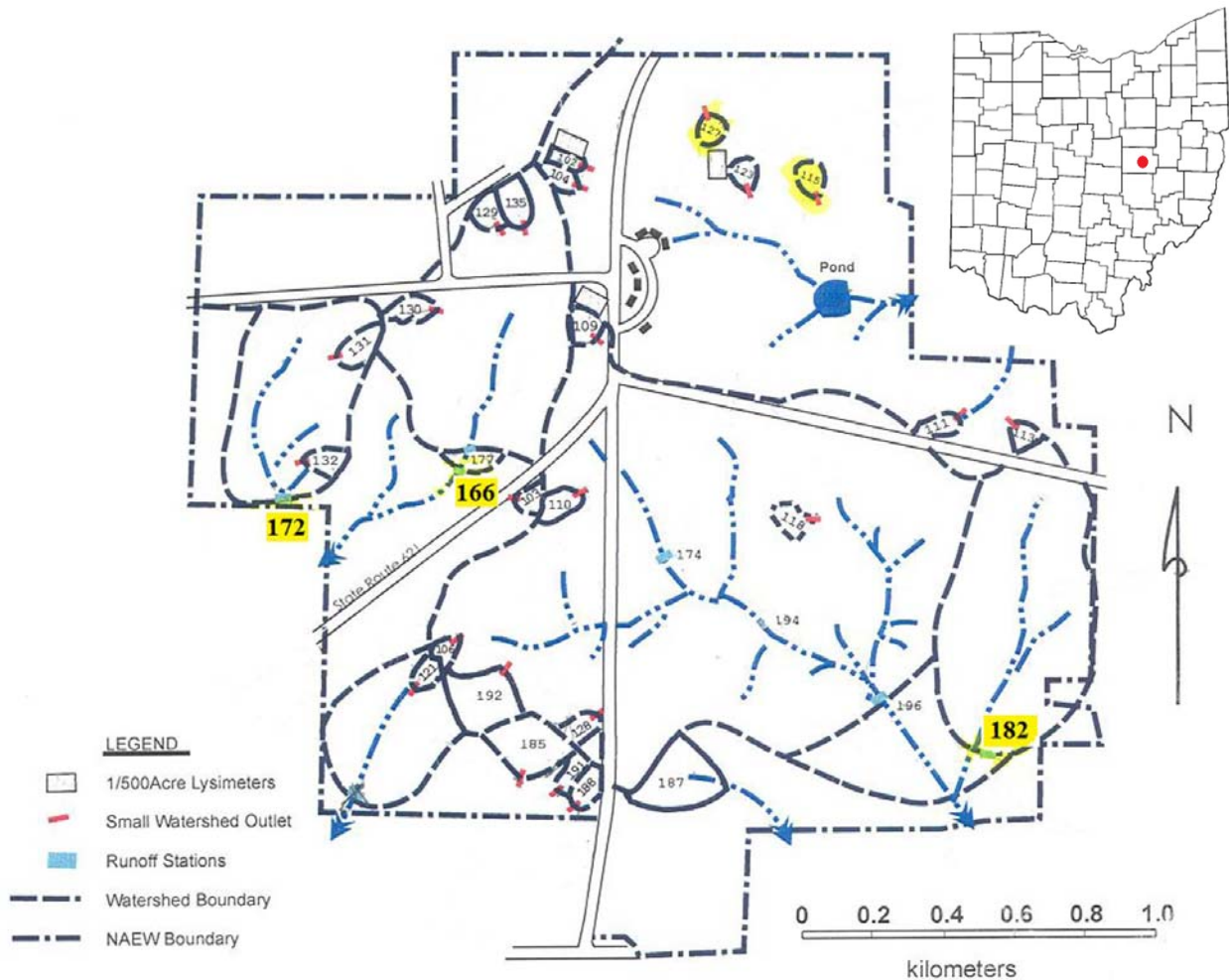
Hypothesis: It is expected that dissolved inorganic carbon will vary land use type and flow conditions. Stormflow may increase the amount of DIC exported.

2. Determine the role of mineral weathering and mineralization of soil organic carbon on dissolved inorganic carbon concentrations.

Hypothesis: Because the groundwater interacts with limestone, the carbonate weathering equation implies that  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  should be prominent water constituents, as also seen by Drever, 1997.



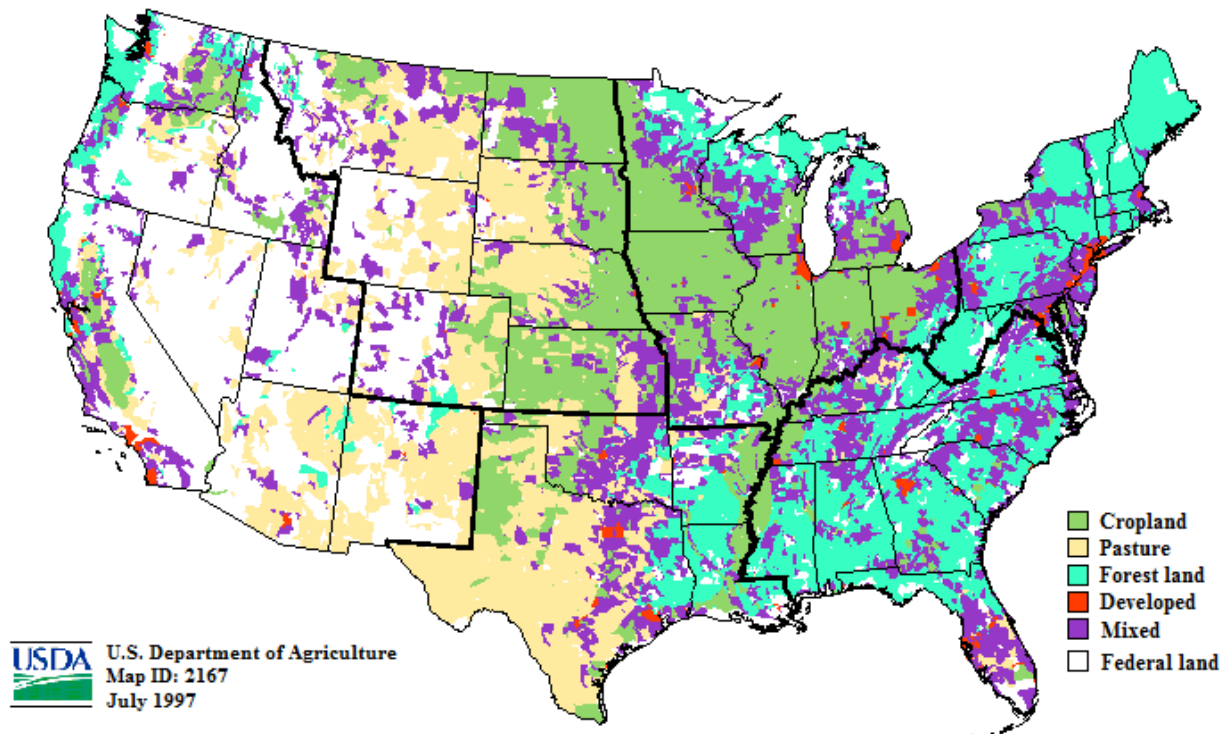
## SITE DESCRIPTION



**Figure 1.** Location map of study area, the North Appalachian Experimental Watershed. Watershed (WS) land uses: WS 115 (corn, tilled), WS 127 (corn, no till), WS 166 (mixed land use), WS 172 (forest), WS 182 (unimproved pasture).

The North Appalachian Experimental Watershed (Figure 1) was established near Coshocton, Ohio in the late 1930s to study the effect of soils, land management, geology and climate on waterflow characteristics from agricultural land (Kelley et al., 1975). The NAEW utilizes 1,047 acres of USDA controlled land. The location of this research station was selected because it was considered geologically representative of 129,500 square kilometers (32,000,000

acres) of land that lies within the states of Ohio, Pennsylvania, West Virginia, Indiana, Kentucky, and Tennessee. Figure 2 shows the United States distribution of land uses selected in this study (developed and federal lands not included in this research) and how the chosen watersheds are a good representation of similar processes in the United States.



**Figure 2.** Dominant U.S. land uses. Data from USDA, 1992.

The bedrock lies within the Allegheny Formation and is composed of unglaciated, sedimentary strata consisting mainly of sandstone and shale with interbedded strata of coal, clay, and limestone (Kelley et al., 1975). The sedimentary rocks were deposited during the late Paleozoic. Later, uplift from the Allegheny Plateau caused streams to carve the landscape during the Tertiary period (Kelley et al., 1975). Subsurface water transport has interaction with limestones, coals, and sandstone that overlie impermeable clays. The geologic structure is characterized by an underlying anticline with the strata dipping less than 1° to the southeast. The principal soil series are Berks, Coshocton, Dekalb, Keene, and Rayne (Kelley et al., 1975).

## METHODS

### Field Collection

Stream water samples were collected at the five different watersheds and their features are tabulated in Table 1. Ongoing sample collection occurs once per month. Preferred collection sites are located upstream of the weir. When it is dry, there is no flow above the weir and samples are taken from below the weir. The water samples were collected in low-density polyethylene bottles, stored in a cooler in the dark, then taken back to the lab to be filtered and chemically analyzed. This collection method is only true for the unimproved pasture (WS 182), the forested site (WS 172) and the mixed land use (WS 166) because they have flowing streams. For the tilled (WS 127) and non-tilled (WS 115), that do not have streams, samples were only collected during storm events using Coshocton wheels, which continuously collected a flow-proportional sample during surface runoff events (Owens et al., 2008). About 70 samples have been collected since October 2008.

### Lab

#### *Titration*

Alkalinity was determined by titration using a pH meter and step-wise additions of a standard hydrochloric acid. The standard acid was a 0.1 N HCl solution from Fisher Scientific. One of two pH electrodes was used: either an Orion 5 Star Triode low maintenance pH (9107BNMD) or an Orion pH Triode (91-57BN). The unfiltered sample's initial pH was recorded. The standard acid was added using a pipet and the resulting pH was recorded after each addition. Acid was added until the pH dropped below 4.5. The volume of acid used to reach a pH of 4.5 was determined by interpolation and this was used to calculate the alkalinity

concentration of the samples, using Equation 4. Accuracy of the titration can be checked from the Gran-alkalinity defined as the sum of the strong base cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) minus the sum of the strong acid anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ ), which equals the acid buffering components ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{H}_2\text{CO}_3^*$ ). Eleven of seventy-three samples were calculated using both the Gran and titration methods with an average error of 7%. Variance between both methods ranged from 0.26–52.9 $\mu\text{eq}$ . The tillage site accounted for most of this error (about 30% error in February). This may be because the Gran method did not reflect the mass  $\text{HCO}_3^-$  exportation or excess cations,  $\text{K}^+$  in particular from manure application that occurred during that month at the tillage site.

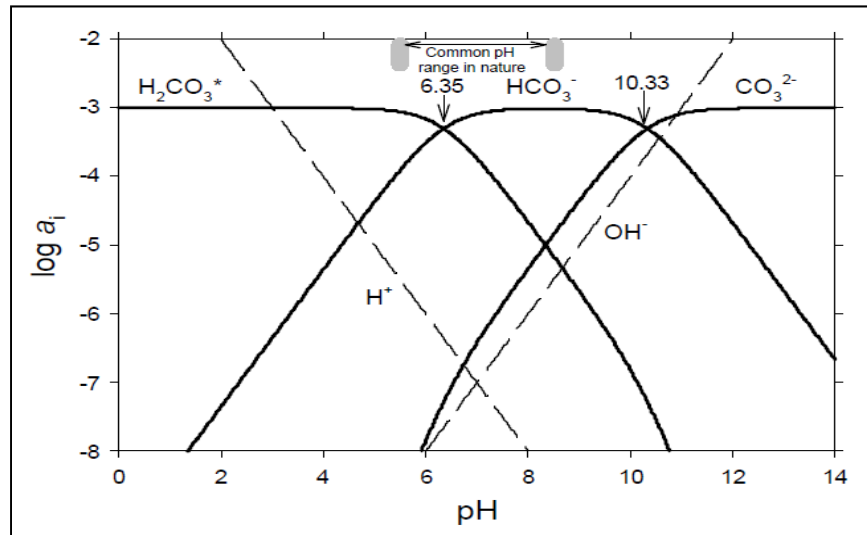
### ***Major Ions***

The samples were first filtered through Whatman glass fiber filters 47mm, GF/F, and then through Whatman-Nuclepore polycarbonate membrane 47mm, 0.4 $\mu\text{m}$  pore size filters. The samples were analyzed on a Dionex DX-120 instrument. The analysis followed the procedure that can be found in the Long Term Ecological Research (LTER) Limnological Methods Manual ([www.homepage.montana.edu/~lkbonney/DOCS/Data.html](http://www.homepage.montana.edu/~lkbonney/DOCS/Data.html)). Samples were filtered through 0.4 $\mu\text{m}$  nuclepore filters using pre-cleaned plastic filtration apparatus. Samples were analyzed for  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . However, the anion data will not be discussed in this work.

A total of 66 samples were analyzed for cations. Accuracy of measurements, calculated from percent error, was less than 4% error and the precision was less than 2% calculated from relative percent difference measured in 8 duplicates.

**Table 1. Information of the five watersheds that were investigated in this study (from Owens et al., 2008)**

<i>Watershed</i>	<i>Area (acres)</i>	<i>Land use</i>	<i>Treatment</i>
<b>172</b>	43.6	All wooded	No chemical treatment
<b>182</b>	69.6	Unimproved pasture (82%) Wooded (18%)	No chemical treatment
<b>166</b>	79.2	Meadow (34%) Medium fertility pasture (23%) Summer pasture (13%)	Manure Fertilization in May
<b>127</b>	1.65	Tillage, corn crops	Manure in February Disked in May Fertilization in May Harvested in October
<b>115</b>	1.61	No-tillage, corn crops	Fertilization in May Harvested in October



**Figure 3.** Bjerrum plot of inorganic carbon species. Activities of different species as a function of pH.  $\text{H}_2\text{CO}_3^* = \text{H}_2\text{CO}_3^0 + \text{CO}_2(\text{aq})$

## Analytical

The following equations are based on the assumption that total alkalinity,  $A_T$ , is equal to  $\text{HCO}_3^-$  because  $\text{CO}_3^{2-}$  does not have a substantial presence until above a pH of 10 (Figure 3). DIC, dissolved inorganic carbon, is the sum of all the carbonate species present in the sample (Equation 4), and each species can be determined using equations 5, 6, and 7 and the equilibrium constants in Table 2. In Equation 5, volume of HCl means the volume added to reach a pH of 4.5, the approximate pH when  $A_T$  has been completely converted to  $\text{H}_2\text{CO}_3^*$ .

$$\text{DIC} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (\text{Equation 4})$$

$$[\text{HCO}_3^-] = A_T = \frac{(\text{Volume of HCl}) \times (\text{Normality of HCl})}{(\text{Sample Volume})} \quad (\text{Equation 5})$$

$$[\text{H}_2\text{CO}_3^*] = \frac{[\text{HCO}_3^-][\text{H}^+]}{K_1} \quad (\text{Equation 6})$$

$$[\text{CO}_3^{2-}] = \frac{[\text{H}_2\text{CO}_3^*]K_1K_2}{[\text{H}^+]^2} \quad (\text{Equation 7})$$

**Table 2. Equilibrium Constants for the Carbonate System (from Drever, 1997).**

[ $\text{p}K = -\log_{10}K$ ]

T(°C)	$\text{p}K_{\text{CO}_2}$	$\text{p}K_1$	$\text{p}K_2$	$\text{p}K_w$
0	1.11	6.58	10.63	14.94
5	1.19	6.52	10.55	14.73
10	1.27	6.46	10.49	14.53
15	1.34	6.42	10.43	14.35
20	1.41	6.38	10.38	14.17

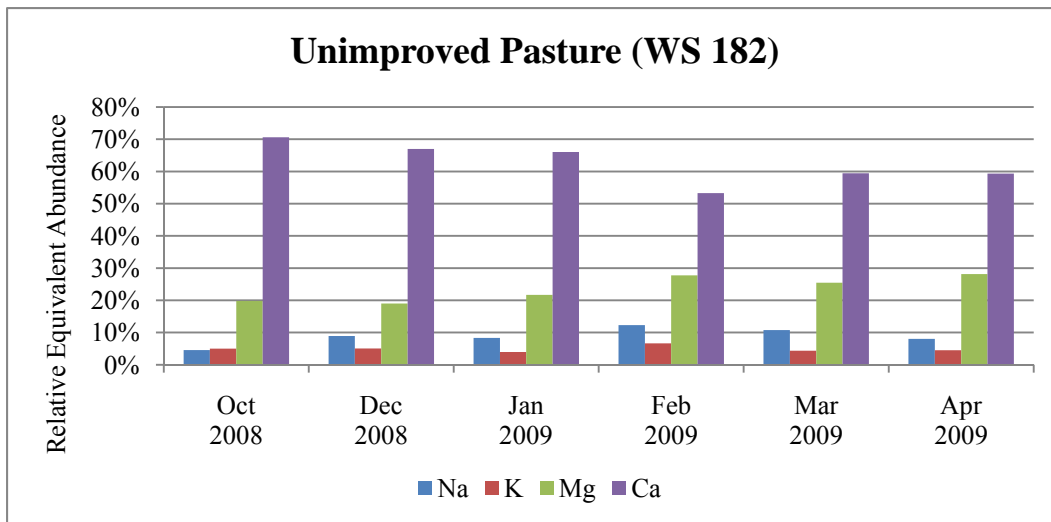
## RESULTS

One observed pattern of the baseflow sites (forest – WS 172, mixed – WS 166, and unimproved pasture – WS 182) is that there is a significant inverse correlation between alkalinity concentration and flow rate based on Pearson's correlation. The forest watershed has a correlation coefficient of -0.76 ( $p < 0.05$ ), while both the unimproved pasture and mixed land uses had values of -0.64 ( $p = 0.12$ ). This implies when flow is high, alkalinity is low or DIC is diluted at high flows. Also, flow is the primary contributor to inorganic carbon yield (flux normalized by area) in the forest, mixed, unimproved pasture, and no-tillage watersheds. Therefore, in the tillage site, it is the inorganic carbon, not the flow, that contributes mostly to the yield. Alkalinity and flow were not correlated in the tilled watershed (WS 127).

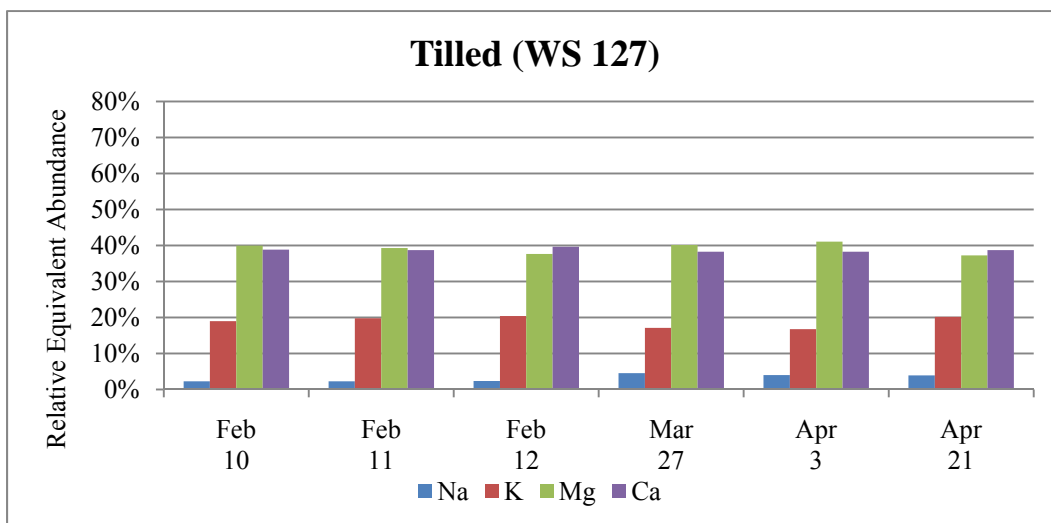
Figures 4 and 5 shows an example of the concentrations of cations, during baseflow and stormflow, respectively, where the cations were summed in equivalents and plotted in terms of relative abundance. During baseflow and stormflow in the forest, mixed, and pastured land uses,  $\text{Ca}^{2+}$  was the most abundant cation (greater than 50% in equivalents).  $\text{Mg}^{2+}$  was the second most abundant (20–35% in equivalents).  $\text{Na}^+$  was less than 15% and  $\text{K}^+$  was less than 10% in occurrence. In both the tilled and non-tilled, stormflow conditions only,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are nearly equal in abundance (both 30 – 40% in equivalents).  $\text{K}^+$  occurred in greater amounts (10–20%) and  $\text{Na}^+$  was less than 5%.

The dissolved inorganic carbon speciation calculations determined that during baseflow conditions, DIC speciation is on average 82.5% bicarbonate, 17.4% carbonic acid (includes dissolved  $\text{CO}_2$ ), and 0.1% carbonate. This is consistent with the Bjerrum plot of the inorganic carbon species. Within the neutral pH range of natural waters, bicarbonate should be the

dominant species and the lower the initial pH, the more carbonic acid was present. This may be due to the presence of snow melt or rain water. Rain has a typical pH of 5.6, but can have a pH range of 4–6 (Berner and Berner, 1996). The average stormflow speciation values were 64.4% bicarbonate, 35.5% carbonic acid (includes dissolved CO<sub>2</sub>), and about 0.02% carbonate. These calculations compared to the baseflow conditions follows that the weakly acidic rain contributed to the increase of carbonic acid.

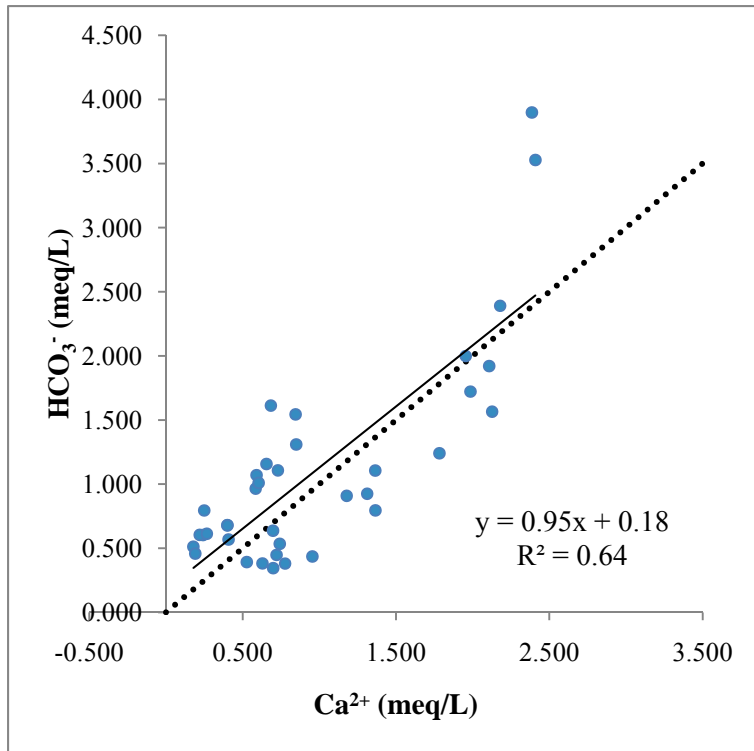


**Figure 4.** Relative cation contributions in baseflow from unimproved pasture lands showing Ca<sup>2+</sup> as dominant cation.



**Figure 5.** Relative cation contributions in stormflow from tillage lands showing very consistent ratios. All of the dates are from the year 2009.





**Figure 6.** Bicarbonate vs. Calcium. Data points include both stormflow and baseflow conditions. The solid line is the regression line. The dotted line represents a 1:1 ratio.

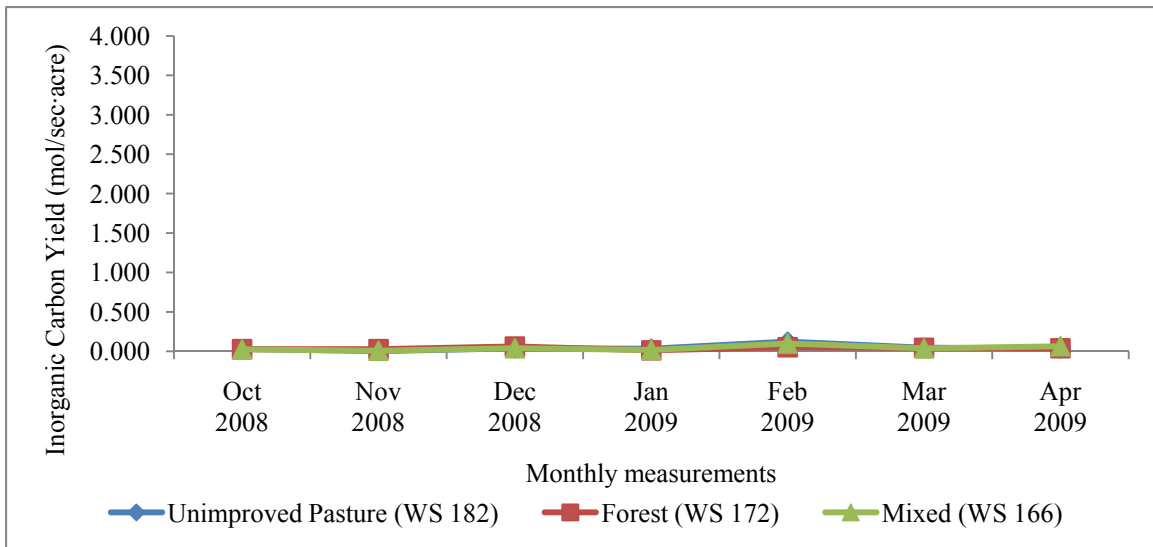
Figure 6 shows a plot of  $\text{Ca}^{2+}$  vs.  $\text{HCO}_3^-$ . If  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  were being controlled by the dissolution of  $\text{CaCO}_3$ , there should be a relationship of 1:1 in equivalents, as shown by the dotted line. The coefficient or slope of calcium when regressed on bicarbonate is 0.95. This coefficient is clearly different from 0 at even a 99% confidence interval (Table 3). The coefficient is then compared to 1 to test whether the 1:1 relationship

is supported by this data. Subtracting 1 and dividing by the standard error normalizes the coefficient so that it can be compared to the values in a t distribution table. For a t distribution with 35 degrees of freedom, the hypothesis that this coefficient is equal to one cannot be rejected at any reasonable confidence interval.

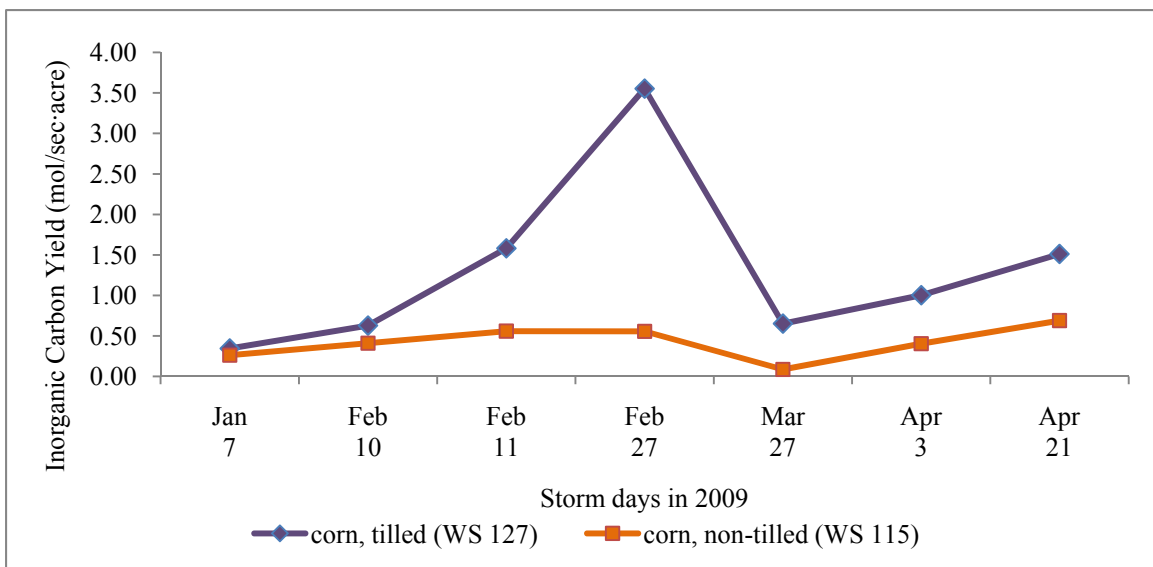
**Table 3. t statistics for data in Figure 6**

Source	Coefficient	Standard error	t	Pr >  t	Lower bound (99%)	Upper bound (99%)
Calcium	0.953	0.120	7.928	< 0.0001	0.625	1.280

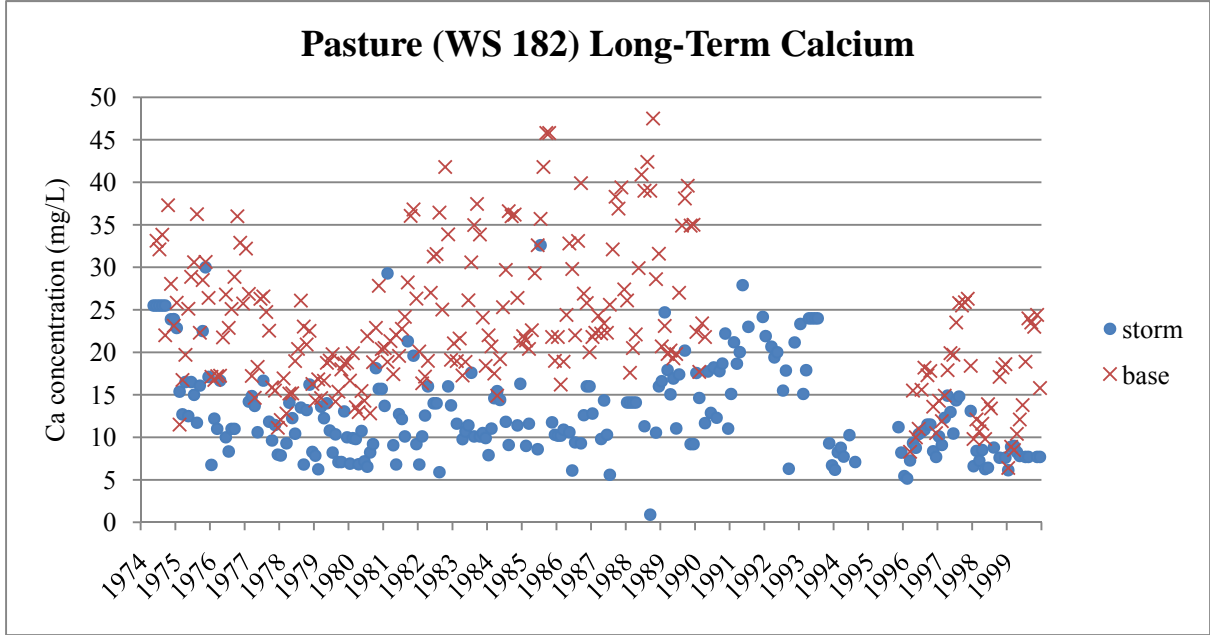
Figures 7 and 8 show inorganic carbon yield (flux normalized by watershed area) in baseflow and stormflow conditions. Compared to stormflow, baseflow alkalinity is indistinguishable between sites, while the tilled and non-tilled greatly diverge during high flow storm events in February.



**Figure 7.** Inorganic carbon yield in baseflow coming from ground water.



**Figure 8.** Inorganic carbon yield in stormflow during rain events.



**Figure 9.** Long term calcium data following the trend of baseflow concentrations being higher than stormflow, as in the study by Jarvie et al., 1997.

## DISCUSSION

### *Cations*

Figure 6 shows a near 1:1 ratio of  $\text{Ca}^{2+}$  with  $\text{HCO}_3^-$ , the two products of carbonate weathering. Therefore, this suggests the system is dominated by carbonate weathering. Regarding baseflow,  $\text{Ca}^{2+}$  is the most abundant cation and this is consistent with Berner et al. (1996), where  $\text{Ca}^{2+}$  is thought to be the most abundant cation based on world average river water, in which 65% of the total calcium is derived from the weathering of calcite (52%) and dolomite (13%,  $\text{Mg}^{2+}$  source). Long-term data from the North Appalachian Experimental Watershed provided by the USDA, Figure 9 shows that concentrations of major ions are higher under baseflow than stormflow conditions, which is clearly demonstrated using  $\text{Ca}^{2+}$  vs. flow in WS 182 (unimproved pasture). This is due to near-surface runoff under stormflow conditions diluting any contributions from groundwater (Jarvie et al., 1997). In stormflow conditions, the increased concentrations of  $\text{K}^+$  may be a result of fertilization. Manure was applied the WS 127 (tillage) in February, which is potassium-rich.

### *Speciation*

The chemical speciation calculations of the dissolved inorganic carbon determined under baseflow conditions show that roughly 70–90% bicarbonate, 10–30% carbonic acid (includes dissolved  $\text{CO}_2$ ), and less than 1% carbonate. This supports Jarvie et al. (1997), where approximately 90% of the mean river dissolved inorganic carbon was  $\text{HCO}_3^-$ , 10% was  $\text{H}_2\text{CO}_3^*$ , and less than 1% was  $\text{CO}_3^{2-}$ . However, some samples were as much as 50%  $\text{H}_2\text{CO}_3$  because rain water is more acidic than surface flows (Cockell et al., 2008). This conclusion makes sense for stormflow events, but does not resolve why some baseflow samples are more acidic.

### ***Tilled vs. Non-tilled***

There is a great difference in dissolved inorganic carbon yields between the tillage and no-tillage watersheds. The tillage site exports at least twice as much inorganic carbon as the no-tillage site when flows are high. January 7, 2009 was a low flow day and WS 127 (corn, with tillage) had not yet been disked; and the two sites had about the same yield (0.27 relative percent difference). There may be two possible reasons for more exportation in WS 127. First, tillage practices disturb soil and release inorganic carbon that may have existed for thousands of years. Secondly, soil temperatures may be higher in cultivated land (due to dark soil being exposed to the sun and absorbing solar energy), consequently increasing microbial activity (Amundson, 2001).

## CONCLUSIONS

There are three prominent conclusions from this study. Because the groundwater interacts with limestone, it was hypothesized that  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  would be major stream water constituents. The first conclusion is that  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  are the main water components, suggesting the area is dominated by carbonate weathering. During baseflow conditions, the inorganic carbon yields were found to be indistinguishable in forest lands (WS 172), unimproved pasture (WS 182), and mixed land use (WS 166). This suggests that the contributions from the groundwater are not significantly altered by different land uses. However, the storm events produced an immense difference between tilled and no-tilled lands. Therefore, the tilled lands exported much higher amounts of inorganic carbon yield.

## FURTHER RESEARCH

One of the remaining aspects of this study is to investigate organic carbon. By doing so, there will be a more complete picture of total carbon exportation off each of the landscapes. It is also necessary to formulate a better comparison with the forest watershed because it represents a controlled group or the watershed that has experienced the least anthropogenic alterations. The winter months are considered dormant for this study and the data in this paper only covers October 2008 to April 2009. It will be interesting to have a full year of data in order to complete the cycle and generate more conclusions.

## **APPENDIX A**

Alkalinity & Carbonate Speciation  
for watersheds 115, 127, 166, 172, 182

### WS 115 (Corn, no-till)

Date	Alk(meq/L)	pH	<sup>β</sup> [H <sub>2</sub> CO <sub>3</sub> *]	<sup>β</sup> [HCO <sub>3</sub> □ ]	<sup>β</sup> [CO <sub>3</sub> <sup>2-</sup> ]	<sup>β</sup> DIC	[H <sub>2</sub> CO <sub>3</sub> *]%	[HCO <sub>3</sub> ]%	[CO <sub>3</sub> ]%
12/20/08	S 0.603	<sup>α</sup> 6.6	0.617	0.603	5.25E-05	1.221	50.57%	49.42%	0.00%
12/25/08	S 0.605	<sup>α</sup> 6.4	0.797	0.605	4.28E-05	1.402	56.86%	43.13%	0.00%
12/27/08	S 0.512	<sup>α</sup> 6.3	0.850	0.512	2.88E-05	1.362	62.40%	37.60%	0.00%
1/07/09	S 1.157	<sup>α</sup> 6.7	0.819	1.157	1.46E-04	1.976	41.45%	58.55%	0.01%
2/08/09	S 0.681	<sup>α</sup> 7.4	0.101	0.681	4.29E-04	0.782	12.88%	87.07%	0.05%
2/09/09	S 0.678	<sup>α</sup> 7.5	0.073	0.678	5.90E-04	0.751	9.67%	90.25%	0.08%
2/10/09	S 1.070	<sup>α</sup> 7.2	0.245	1.070	4.36E-04	1.316	18.63%	81.33%	0.03%
2/11/09	S 0.965	<sup>α</sup> 7.2	0.192	0.965	4.51E-04	1.158	16.63%	83.33%	0.04%
2/27/09	S 1.010	<sup>α</sup> 7.1	0.278	1.010	3.42E-04	1.289	21.59%	78.38%	0.03%
3/26/09	S 0.916	<sup>α</sup> 7.1	0.210	0.916	3.73E-04	1.126	18.63%	81.33%	0.03%
4/03/09	S 1.127	<sup>α</sup> 6.4	1.387	1.127	8.55E-05	2.514	55.16%	44.84%	0.00%
4/21/09	S 0.810	<sup>α</sup> 6.7	0.488	0.810	1.26E-04	1.299	37.60%	62.39%	0.01%

### WS 127 (Corn, till)

Date	Alk(meq/L)	pH	<sup>β</sup> [H <sub>2</sub> CO <sub>3</sub> *]	<sup>β</sup> [HCO <sub>3</sub> □ ]	<sup>β</sup> [CO <sub>3</sub> <sup>2-</sup> ]	<sup>β</sup> DIC	[H <sub>2</sub> CO <sub>3</sub> *]%	[HCO <sub>3</sub> ]%	[CO <sub>3</sub> ]%
12/20/08	S 0.613	<sup>α</sup> 6.6	0.613	0.613	5.46E-05	1.226	50.00%	50.00%	0.00%
12/25/08	S 0.794	<sup>α</sup> 6.4	1.047	0.794	5.62E-05	1.842	56.86%	43.13%	0.00%
12/27/08	S 0.458	<sup>α</sup> 6.4	0.604	0.458	3.24E-05	1.062	56.86%	43.13%	0.00%
1/07/09	S 1.612	<sup>α</sup> 6.6	1.505	1.612	1.54E-04	3.117	48.27%	51.72%	0.00%
2/10/09	S 1.107	<sup>α</sup> 7.2	0.259	1.107	4.41E-04	1.367	18.98%	80.98%	0.03%
2/11/09	S 1.309	<sup>α</sup> 7.5	0.154	1.309	1.04E-03	1.464	10.51%	89.42%	0.07%
2/12/09	S 1.543	<sup>α</sup> 7.1	0.379	1.543	5.87E-04	1.923	19.70%	80.27%	0.03%
2/27/09	S 3.931	<sup>α</sup> 7.1	0.965	3.931	1.49E-03	4.898	19.70%	80.27%	0.03%
3/26/09	S 1.003	<sup>α</sup> 7.0	0.270	1.003	3.48E-04	1.273	21.20%	78.77%	0.03%
4/04/09	S 1.129	<sup>α</sup> 6.7	0.729	1.129	1.63E-04	1.858	39.23%	60.76%	0.01%
4/21/09	S 1.086	<sup>α</sup> 7.2	0.202	1.086	5.44E-04	1.289	15.69%	84.27%	0.04%

<sup>α</sup> estimated pH, measured in lab, not *in situ*

<sup>β</sup> concentration units in mmol/L

S: stormflow

B: baseflow



## WS 166 (Mixed land use)

Date		Alk(meq/L)	pH	<sup>β</sup> [H <sub>2</sub> CO <sub>3</sub> *]	<sup>β</sup> [HCO <sub>3</sub> <sup>-</sup> ]	<sup>β</sup> [CO <sub>3</sub> <sup>2-</sup> ]	<sup>β</sup> DIC	[H <sub>2</sub> CO <sub>3</sub> *]%	[HCO <sub>3</sub> ]%	[CO <sub>3</sub> ]%
10/25/08	B	2.390	7.0	0.658	2.390	8.10E-04	3.050	21.59%	78.38%	0.03%
11/18/08	B	1.921	6.9	0.838	1.921	4.11E-04	2.759	30.38%	69.60%	0.01%
11/18/08	B	1.922	6.6	1.674	1.922	2.06E-04	3.597	46.55%	53.45%	0.01%
12/23/08	B	1.106	7.9	0.052	1.106	2.11E-03	1.160	4.46%	95.36%	0.18%
12/25/08	S	0.568	<sup>α</sup> 6.4	0.803	0.568	3.75E-05	1.371	58.55%	41.45%	0.00%
1/27/09	B	0.909	8.4	0.013	0.909	5.48E-03	0.928	1.45%	97.96%	0.59%
2/12/09	S	0.637	<sup>α</sup> 7.2	0.121	0.637	3.12E-04	0.759	16.00%	83.96%	0.04%
2/27/09	B	0.535	7.6	0.049	0.535	5.47E-04	0.584	8.35%	91.56%	0.09%
3/27/09	B	0.817	7.3	0.129	0.817	4.81E-04	0.947	13.67%	86.28%	0.05%
4/27/09	B	1.486	6.8	0.695	1.486	3.10E-04	2.181	31.86%	68.12%	0.01%

## WS 172 (Forest)

Date		Alk(meq/L)	pH	<sup>β</sup> [H <sub>2</sub> CO <sub>3</sub> *]	<sup>β</sup> [HCO <sub>3</sub> <sup>-</sup> ]	<sup>β</sup> [CO <sub>3</sub> <sup>2-</sup> ]	<sup>β</sup> DIC	[H <sub>2</sub> CO <sub>3</sub> *]%	[HCO <sub>3</sub> ]%	[CO <sub>3</sub> ]%
10/25/08	B	3.528	6.5	3.292	3.528	3.53E-04	6.821	48.27%	51.72%	0.01%
11/18/08	B	3.899	6.9	1.663	3.899	8.53E-04	5.563	29.90%	70.09%	0.02%
12/23/08	B	1.241	7.3	0.221	1.241	6.22E-04	1.462	15.09%	84.87%	0.04%
1/07/09	S	0.382	<sup>α</sup> 6.3	0.711	0.382	1.83E-05	1.092	65.06%	34.94%	0.00%
1/27/09	B	1.292	7.8	0.076	1.292	1.96E-03	1.370	5.55%	94.30%	0.14%
2/12/09	S	0.377	<sup>α</sup> 7.3	0.067	0.377	1.98E-04	0.444	15.09%	84.86%	0.04%
2/27/09	B	0.345	7.3	0.057	0.345	1.94E-04	0.402	14.23%	85.72%	0.05%
3/27/09	B	0.470	7.2	0.094	0.470	2.20E-04	0.564	16.63%	83.33%	0.04%
4/27/09	B	0.549	7.2	0.098	0.549	3.02E-04	0.647	15.09%	84.86%	0.05%

<sup>α</sup> estimated pH, measured in lab, not *in situ*

<sup>β</sup> concentration units in mmol/L

S: stormflow

B: baseflow

## WS 182 (Unimproved pasture)

Date		Alk(meq/L)	pH	<sup>β</sup> [H <sub>2</sub> CO <sub>3</sub> *]	<sup>β</sup> [HCO <sub>3</sub> □ ]	<sup>β</sup> [CO <sub>3</sub> <sup>2-</sup> ]	<sup>β</sup> DIC	[H <sub>2</sub> CO <sub>3</sub> *]%	[HCO <sub>3</sub> ]%	[CO <sub>3</sub> ]%
10/25/08	B	1.565	7.3	0.211	1.565	1.08E-03	1.777	11.88%	88.06%	0.06%
11/18/08	B	1.722	7.0	0.611	1.722	4.53E-04	2.333	26.18%	73.80%	0.02%
12/23/08	B	0.795	8.3	0.017	0.795	3.31E-03	0.815	2.08%	97.51%	0.41%
12/25/08	S	0.392	<sup>α</sup> 6.2	0.819	0.392	1.75E-05	1.211	67.63%	32.37%	0.00%
1/27/09	B	0.925	8.0	0.039	0.925	1.98E-03	0.966	3.99%	95.80%	0.20%
2/12/09	S	0.436	<sup>α</sup> 6.7	0.309	0.436	5.75E-05	0.745	41.45%	58.55%	0.01%
2/27/09	B	0.380	7.8	0.022	0.380	6.03E-04	0.403	5.55%	94.30%	0.15%
3/27/09	B	0.665	7.7	0.039	0.665	1.05E-03	0.706	5.55%	94.30%	0.15%
4/27/09	B	0.713	7.7	0.040	0.713	1.24E-03	0.754	5.32%	94.52%	0.16%

<sup>α</sup> estimated pH, measured in lab, not *in situ*

<sup>β</sup> concentration units in mmol/L

S: stormflow

B: baseflow

## **APPENDIX B**

Cation data for  
watersheds 115, 127, 166, 172, 182

### WS 115 (Corn, no-till)

Date	Flow condition	Na meq/L	K meq/L	Mg meq/L	Ca meq/L
12/20/08	Storm	0.022	0.277	0.235	0.242
12/25/08	Storm	0.019	0.274	0.226	0.220
12/27/08	Storm	0.017	0.221	0.181	0.178
01/07/09	Storm	0.016	0.247	0.737	0.655
02/08/09	Storm	0.014	0.162	0.433	0.400
02/09/09	Storm	0.015	0.164	0.402	0.400
02/10/09	Storm	0.016	0.203	0.567	0.590
02/11/09	Storm	0.035	2.091	0.579	0.585
02/12/09	Storm	0.029	0.303	0.521	0.588
02/27/09	Storm	0.067	0.223	0.619	0.604

### WS 127 (Corn, till)

Date	Flow condition	Na meq/L	K meq/L	Mg meq/L	Ca meq/L
12/20/08	Storm	0.035	0.296	0.277	0.266
12/25/08	Storm	0.023	0.293	0.264	0.249
12/27/08	Storm	0.026	0.233	0.192	0.191
01/07/09	Storm	0.024	0.382	0.783	0.684
02/08/09	Storm	0.016	0.190	n.a	0.290
02/10/09	Storm	0.042	0.356	0.751	0.730
02/11/09	Storm	0.049	0.434	0.863	0.850
02/12/09	Storm	0.050	0.435	0.802	0.845

**WS 166 (Mixed land use)**

Date	Flow condition	Na meq/L	K meq/L	Mg meq/L	Ca meq/L
10/25/08	Base	0.464	0.136	1.389	2.179
11/18/08	Base	0.361	0.148	1.382	2.108
11/18/08	Base	0.312	0.153	1.368	2.120
12/23/08	Base	0.277	0.117	0.795	1.365
12/25/08	Storm	0.082	0.241	0.327	0.408
01/27/09	Base	0.352	0.096	0.821	1.179
02/09/09	Storm	0.175	0.116	0.534	0.643
02/12/09	Storm	0.160	0.137	0.562	0.698
02/27/09	Base	0.199	0.141	0.637	0.742
02/27/09	Base	0.198	0.131	0.652	0.763

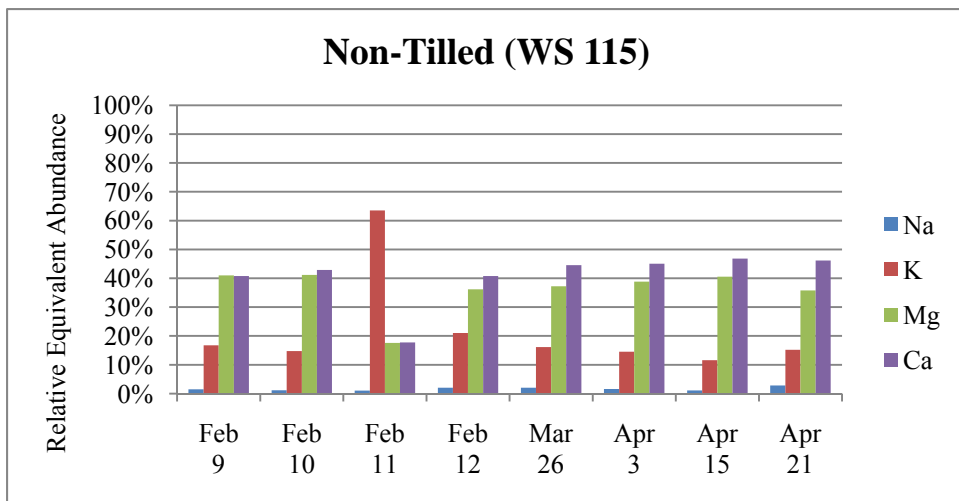
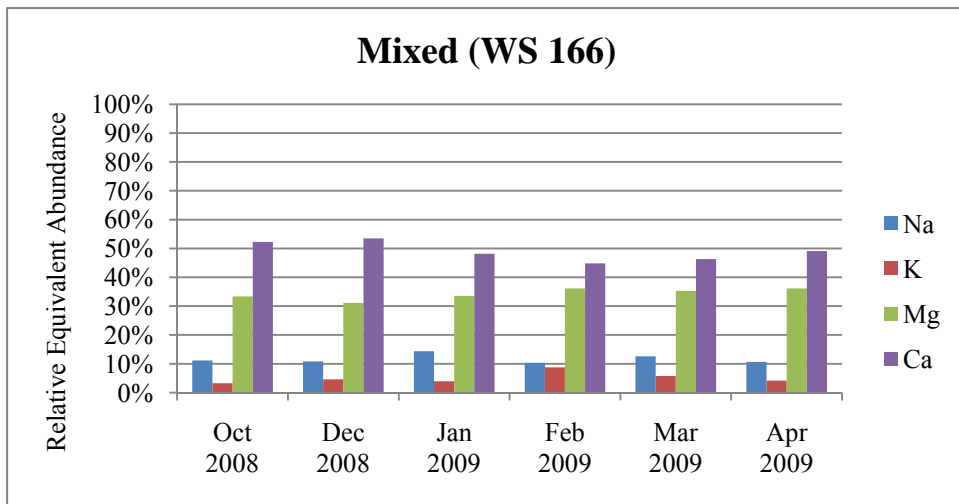
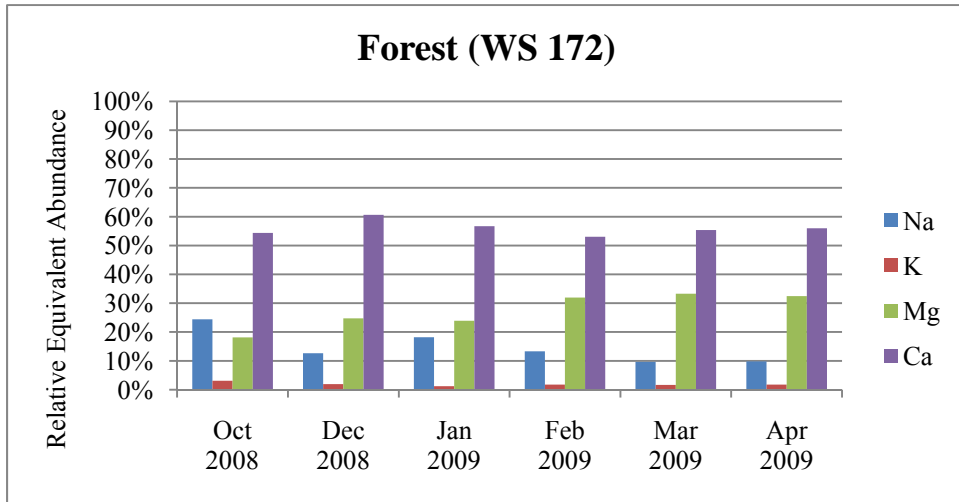
**WS 172 (Forest)**

Date	Flow condition	Na meq/L	K meq/L	Mg meq/L	Ca meq/L
10/25/08	Base	1.081	0.138	0.804	2.409
10/25/08	Base	1.104	0.140	0.808	2.426
11/18/08	Base	1.052	0.114	1.099	2.561
11/18/08	Base	1.022	0.103	1.172	2.386
12/23/08	Base	0.372	0.057	0.727	1.783
12/23/08	Base	0.557	0.076	0.841	2.182
01/07/09	Storm	0.138	0.052	0.396	0.629
01/27/09	Base	0.558	0.038	0.734	1.741
01/27/09	Base	0.483	0.043	0.711	1.625
02/09/09	Storm	0.142	0.024	0.488	0.734
02/09/09	Storm	0.211	0.028	0.506	0.841
02/27/09	Base	0.119	0.028	0.469	0.699
02/27/09	Base	0.162	0.032	0.495	0.806

**WS 182 (Unimproved pasture)**

<b>Date</b>	<b>Flow condition</b>	<b>Na meq/L</b>	<b>K meq/L</b>	<b>Mg meq/L</b>	<b>Ca meq/L</b>
10/25/08	Base	0.137	0.151	0.597	2.127
11/18/08	Base	0.141	0.119	0.848	1.986
11/18/08	Base	0.138	0.114	0.857	1.955
12/23/08	Base	0.182	0.103	0.387	1.366
12/25/08	Storm	0.114	0.126	0.286	0.527
01/27/09	Base	0.166	0.079	0.431	1.312
02/09/09	Storm	0.383	0.072	0.465	0.955
02/09/09	Storm	0.125	0.087	0.384	0.721
02/27/09	Base	0.217	0.086	0.478	0.777
11/18/08	Base	0.195	0.212	0.227	0.352
11/18/08	Base	0.194	0.212	0.229	0.350
12/23/08	Base	0.228	0.263	0.121	0.367
01/27/09	Base	0.130	0.092	0.073	0.422

## Additional cation abundances



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