

SURFACE WATER AND SEDIMENT GEOCHEMISTRY IN UNDERSTANDING
MOBILITY OF NITRATES IN MESIC KANSAS GRASSLAND

by

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Abstract

To understand ambient nitrate dynamics in an unmanaged grassland environment, the stable isotope chemistry of various substrates at the Konza Prairie Biological Station were studied. Sediments consisted of alluvium, loess and bedrock materials are mostly limestone and shale. To gain a better understanding of the biogeochemistry of N cycling in this unmanaged grassland, 34 water samples have been collected along a full stretch of the major onsite creeks (Kings and Shane Creeks). These samples have been analyzed for δD , $\delta^{18}O$, and $\delta^{15}N$ to determine the manner by which water allows nitrates to be leached into sediment, and to determine if additional nitrate is contributed from weathering of the bedrock. The anion chemistry of the waters show the presence of bicarbonates, sulfates, chlorides, nitrates, and fluorides. Although an obvious correlation among the anions is not present, data shows high alkalinity content due to the presence of shallow bedrock that is continuously being weathered. Using a hydraulic geoprobe, sediment cores were collected up to 8 ft deep using 2 ft core liners adjacent to the creeks to study $\delta^{15}N$ and $\delta^{13}C$ spatial variation of the sediments. This research also indicated the presence of C_3 and C_4 derived soil organic carbon with the latter being dominant. There is also an approximate 1:9 correlation between the total nitrogen and carbon content of these core sediments including NO_3 and NH_4 that are mostly concentrated in the upper 2 – 4 ft of the sediment profile. The results of this study provide a broader context for ambient nitrate cycling in unmanaged grassland and a baseline comparison for nitrate levels in surrounding agricultural lands.

Table of Contents

List of Figures	vi
Acknowledgements	vii
Dedication	viii
Chapter 1 - Introduction	1
Nitrogen Cycle	1
Nitrogen in agriculture	2
Stable isotopes of nitrogen	2
Sources of nitrate pollution	3
Health and environmental effects of nitrates	3
Health	3
Environment	4
Geology of the Konza Prairie and its Relation to nitrates	4
Why study nitrates in the Konza	5
Chapter 2 - Background	6
Nitrates	6
Konza Prairie geology	6
$\delta^{15}\text{N}$ studies in water	7
$\delta^{15}\text{N}$ studies in sediment	8
Nitrates in Kansas	8
Konza Stream Work	9
Use of $\delta^{18}\text{O}$ in nitrate studies	10
Use of $\delta^{13}\text{C}$ in nitrate studies	10
Chapter 3 - Objectives and Hypotheses	12
Objectives	12
Hypotheses	12
Chapter 4 - Methods and Materials	14
Study Area Description	14
Sample Collection	15
Water sampling	15

Sediment Sampling	16
Analyses	17
Water Analyses	17
Sediment Analyses	21
Chapter 5 - Results	26
Sediment Characterization	26
Color of sediment analysis	27
X-Ray diffraction of sediment (Mineralogy)	29
Ammonium	32
Nitrate vs ammonium concentrations	35
Total carbon and total nitrogen analysis	37
Analysis of total $\delta^{15}\text{N}$ of Sediment	39
Analysis of total $\delta^{13}\text{C}$ of sediment	40
Water Chemistry	40
Cations	40
Anions	41
Hydrogeochemical source	42
Analysis of $\delta^{15}\text{N}$ of Water	45
δD and $\delta^{18}\text{O}$	46
Chapter 6 - Discussion	49
Sediment Geochemistry	49
Mineralogy of sediment cores	49
Ammonium	50
Nitrate	50
$\delta^{15}\text{N}$ of sediment	51
$\delta^{13}\text{C}$ of sediment	51
Water Chemistry	52
Anions and cations	52
$\delta^{15}\text{N}$ of water	53
Hydrogen and oxygen isotopes as indicators of groundwater recharge	54
Chapter 7 - Conclusions	56

Sediment	56
References	58
Appendix A - Water Analyses	63
Water Chemistry Data/ Table 1	63
Str: Stream	64
KC: Kings Creek.....	64
SC: Shane CreekCations/ Table 2.....	64
Cations/ Table 2	65
Str: Stream	65
KC: Kings Creek.....	65
TDS of water samples/ Table 3.....	66
Stable Isotope measurements $\delta^{15}\text{N}$, $\text{NO}_3\text{-N}$, NO_3 and pH/ Table 4	67
$\delta^2\text{H}$ & $\delta^{18}\text{O}$ / Table 5.....	68
General sediment characteristics	69
Total carbon % and total nitrogen % of sediment samples/ Table 6	70
NH_4 and NO_3 in sediment measurements/ Table 7.....	71
Stable isotopes/ Table 8	72
$\delta^{13}\text{C}$ & $\delta^{15}\text{N}$ of sediment samples	72
X-Ray Powder Diffraction (XRD)/ Table 9	73

List of Figures

Figure 1. Making use of the hydraulic geoprobe out in the Konza.....	16
Figure 2. The Picarro G1301.	19
Figure 3. The Delta plus mass spectrometer.....	21
Figure 4. The Carlo Erba NC2500 elemental analyzer.....	23
Figure 5. The Delta V + isotope ratio mass spectrometer (IRMS).....	24
Figure 6. Sample identification points.....	27
Figure 7. Sediment cores from a sample point in Zone 1.....	28
Figure 8. Sediment cores from a sample point in Zone 2.....	28
Figure 9. Sediment cores from a sample point in Zone 3.....	29
Figure 10. XRD of sediment in sample location Geop 9, core # 4.....	31
Figure 11. Ammonium with depth at each of the Zones.....	33
Figure 12. Nitrate with depth at each of the Zones.....	35
Figure 13. NO ₃ and NH ₄ levels within 2 inches from the top of 2 feet cores.	36
Figure 14. NO ₃ and NH ₄ levels within 2 inches from the top of 4 feet cores.	36
Figure 15. NO ₃ and NH ₄ levels within 2 inches from the top of 6 feet cores.	37
Figure 16. NO ₃ and NH ₄ levels within 2 inches from the top of 8 feet cores.	37
Figure 17. Total C with total N (%)......	38
Figure 18. Sample points (Geop 1-10) within their zones, where stable isotope analysis for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of sediment cores were taken.	40
Figure 19. Relationship of nitrates with anions.....	41
Figure 20. Piper diagram.....	43
Figure 21. Gibbs Diagram.....	44
Figure 22. Ranges of $\delta^{15}\text{N}$ values.	45
Figure 23. Graph of nitrate-N with $\delta^{15}\text{N}$ using groundwater and surface water.....	46
Figure 24. Stable isotope plots of δD and $\delta^{18}\text{O}$	47
Figure 25. Stable isotope plots of δD and $\delta^{18}\text{O}$ water sample locations when compared to precipitation (pptn).....	48

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Dedication

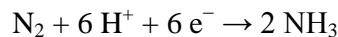
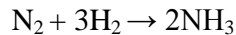
This thesis is dedicated to my parents, Mr. Edward Eke (RIP) and Mrs. Felicia Eke for both instilling in me the value of education.

Chapter 1 - Introduction

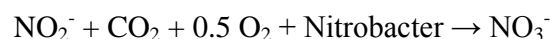
Nitrogen (N) is a key limiting resource in grassland ecosystem. They are available within microscopic cells and constitute the structural building block for both plants and animals. The whole earth abundance of N is 0.03%, with 97.76% of the total N located in rocks, 2.01% in the atmosphere, and 0.23% in the hydrosphere and biosphere (Kendall, 1998). Nitrogen as N₂ gas is about 78% of the total air content within the atmosphere (Berner and Berner, 1987). However most of the nitrogen in the atmosphere is unavailable for use by organisms due to the presence of triple bonds between the N atoms in N₂ molecules, thus making it relatively inert (Chang, 2001). In fact, in order for plants and animals to be able to use nitrogen, N₂ gas must first be converted to more a chemically available form such as ammonium (NH₄⁺), nitrate (NO₃⁻), or organic nitrogen (e.g. urea - (NH₂)₂CO) (Harrison, 2003). Although NO₃⁻ is used by particular plants with the help of microbes, it becomes soluble after precipitation and leaches downwards. This can become a problem on groundwater resources within aquifers because of the potential for exposure to nitrate contamination.

Nitrogen Cycle

Nitrogen fixation (N₂ → NH₄⁺) Nitrogen is fixed in the soil by lightning and mostly by bacteria. The process by which nitrogen is fixed by lightning is due to the high energy created by the phenomenon which breaks the N₂ triple bonds and releases reactive N atoms. Bacteria engage in nitrogen fixation ensuring that nitrogenase enzyme combines nitrogen gas with hydrogen gas to produce ammonia and eventually to ammonium for plant accessibility (Howarth, 2004). The enzyme, nitrogenase acts as a catalyst enabling the biochemical reaction. This reaction can also be done industrially through the Haber-Bosch process as shown below.

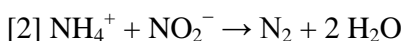
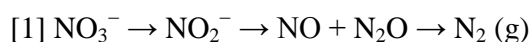


Nitrification (NH₄⁺ → NO₃⁻) Nitrosomonas bacteria oxidize ammonium or ammonia and convert it to nitrite. Subsequently it is further oxidized by the nitrobacter bacteria to eventually convert nitrite to nitrates as shown below. These reactions take place exclusively in aerated soil and are necessary for plant nutrients which are taken up by plants through their root system.





Denitrification ($\text{NO}_3^- \rightarrow \text{N}_2$) The denitrification process involves the conversion of nitrates and to a smaller extent, ammonium (NH_4^+) under anoxic conditions through a series of reducing steps ending with the release of nitrogen gas (N_2) which goes back to the atmosphere (Holloway, 2002; Holloway et al., 2001; Holloway et al., 1998). This is shown below in two ways. Since the nitrogen cycle is continuous, nitrogen gas is released constantly into the atmosphere.



Other processes within the nitrogen cycle consist of *nitrogen uptake* and *mineralization* (Harrison, 2003). The former involves the conversion of NH_4^+ to organic N and can also be referred to as immobilization. The latter which is mineralization, is the antithesis to nitrogen uptake signifying the conversion of organic N to NH_4^+ .

Nitrogen in agriculture

An increase in nitrogen in the soil can be achieved by planting crops such as maize which rarely utilizes nitrogen for growth. To maintain some balance and prevent excess nitrogen from leaching to the water table in the form of nitrates, crops are alternated by farmers. Maize can be alternated with root nodular or nodular crops such as peanuts, alfalfa, or beans which contain bacteria residing in their nodules. The bacteria breaks down nitrogen into their bio-available forms of ammonium ion, nitrate, and to a smaller extent, nitrite. This whole process of maintaining balanced nitrogen content in soils is regarded as crop rotation among farmers.

Stable isotopes of nitrogen

There are two major stable isotopes of nitrogen which are ^{14}N and ^{15}N . These isotopes are critical in isotopic analysis as it pertains to using it as an isotopic signature (Robinson, 2001). The average terrestrial abundance of ^{14}N is 99.636% and ^{15}N is 0.364%. The air has a constant abundance of 0.366% for ^{15}N , and hence the air isotope composition has served as the primary standard for isotopic analyses of nitrogen (Kendall, 1998). This is important in sediment and water studies because the ratio of $^{15}\text{N}/^{14}\text{N}$ can be used to indicate an enrichment or depletion of ^{15}N in relation to the standard, which could be used to trace or indicate a point and non-point contaminated locations. Most ecologists usually use isotopes of nitrogen to understand the relationship between microbes and plant nutrients as nitrogen moves within the various steps of its cycle. Geologists mainly conduct

studies in hydrology by using nitrogen isotopes as tracers. Although as an isotope signature/tracer, analyzing stable isotopes of nitrogen could be quite problematic due to overlaps in nitrogen source ranges. Analysis of this kind is usually done in conjunction with additional isotope studies of other elements such as $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water.

Nitrogen compounds containing both of the isotopes undergo fractionation whereby the lighter isotope, ^{14}N is used in biological processes such as denitrification and during volatilization of ammonia gas. The heavier isotope that is retained by the substrate can be utilized by using isotope ratios (i.e., $^{15}\text{N}/^{14}\text{N}$ ratio) incorporated into compounds with N_2 gas (air) as a standard. The same calculations involving isotope ratios are multiplied by 1000 to produce results in $\delta^{15}\text{N}$ with permil (‰) as the unit.

$$\delta^{15}\text{N}_{\text{sample}} (\text{‰}) = \left\{ \left(\frac{^{15}\text{N}/^{14}\text{N}}{^{15}\text{N}/^{14}\text{N}} \right)_{\text{sample}} / \left(\frac{^{15}\text{N}/^{14}\text{N}}{^{15}\text{N}/^{14}\text{N}} \right)_{\text{air}} - 1 \right\} \times 1000$$

Sources of nitrate pollution

Although small amounts of nitrates and nitrites are necessary for biological life, but in excess amounts are harmful. These excesses are most often due to anthropogenic sources including:

- *Industrial waste and nitrogen containing accidental spills* Nitrates are usually made on a large scale as nitrogen gas for usage as it pertains to preservation. Nitrates also form during the nitrogen extraction process as waste. This causes groundwater and surface water nitrogen concentration (as nitrates) to increase.
- *Vehicular combustion* Combustion processes from vehicles and industries (Savard et al., 2009) could also enhance the nitrate and nitrite supplies, due to the emission of nitrogen oxides that can be converted to nitrates and nitrites in the environment.
- *Commercial fertilizer* Humans have done much to change the natural supplies of nitrates by the addition of fertilizer to soil (Kerr-Upal et al., 1999; Keskin, 2010). This is done by the extensive use of fertilizers by farmers which eventually leach to the water table and contaminates groundwater (Townsend, 2003).

Health and environmental effects of nitrates

Health

Blue baby syndrome, which often affects infants of less than 6 months in age (Comly, 1987), happens when excess nitrates make it to the infant's bloodstream, where they act as an oxidizing

agent that oxidizes Fe^{2+} to Fe^{3+} . In turn, nitrates become reduced to nitrites (NO_3^- to NO_2^-). With the dominance of Fe^{3+} , the hemoglobin within a victim's bloodstream is unable to carry oxygen through the circulatory system to energize the cells. This creates an oxygen deficiency, which is indicated by a display of a pale blue color on the skin (Johnson et al., 1987). The altered form of blood protein which prevents the blood cells from absorbing oxygen, leads to slow suffocation of an infant that may lead to death (Gustafson, 1993; Finley, 1990).

Environment

After precipitation, soluble ions including nitrates (Smith, 2010), are transported as runoff and some are leached to the subsurface waters. Runoff can accumulate in a lake, pond, or coastal waters and if excess amount of nitrates are present, it is likely to cause eutrophication (Nebel et al., 1999). The condition of eutrophication is characterized by an abundance of dissolved plant nutrients (Chang, 2001) which initiates an algal bloom including the presence of other aquatic plants on the surface of the water. Once these plants die, aerobic bacteria decomposes them using oxygen from the water causing an oxygen deficiency beneath the water surface (Nebel et al, 2001). This nutrient over-enrichment has been blamed for increased frequencies of coastal fish-kill events, increased frequencies of harmful algal blooms, and species shifts within coastal ecosystems (Harrison, 2003).

Geology of the Konza Prairie and its Relation to nitrates

The Konza Prairie Biological Station contains 34.87 km² land located in the Flint Hills of northeastern Kansas. Surficial deposits are generally thin and accumulated in temporary storage sites, such as ridge tops and valley bottoms, before being transported away from the Konza toward the Kansas River (Oviatt, 1998). The upland region of the Konza consists of loess which contains clay minerals and rich organic matter. The total thickness of loess is three to four feet, and it was dropped on the Konza during multiple episodes of deposition for at least the last 100 ka (Ross, 1995). Drainage densities (stream length/drainage-basin area) are 5.8 km/km² in a typical low-relief basin on the Konza and 7.2 km/km² in a typical high relief basin, values that are within the expected range of dendritic stream systems that drain non-resistant, flat-lying sedimentary strata in humid-temperate regions (Oviatt, 1998). Valley floors which contain the streams such as Kings Creek, were formed during the Holocene. Kings Creek and Shane Creek flow northward to the Kansas River where weathered material leave the site. These valley floors undergo cycles of deposition and downcutting which transports reworked alluvial sediments throughout the Konza. Prior work shows that concentrations of nitrate decreased downstream from permanent sources of water in the headwaters,

although local reaches have elevated concentrations due to inputs from seeps and tributaries (Gray et al., 1998). Between watersheds within the Kings Creek basin, nitrate levels show a significant negative correlation with watershed area (Dodds et al., 1996). The Konza, like other lands in the region is used dominantly for grazing, with other parts of the larger valley bottoms used to grow crops (Sophocleous et al., 2003; Macpherson et al., 2008). The Konza retains a pristine quality with no presence of excess $\delta^{15}\text{N}$, which indicates no nitrate pollution within the unconfined aquifer present including the surface waters (Macpherson, 1996; Macpherson et al., 2004). The low $\delta^{15}\text{N}$ value also indicates nitrate formation from soil nitrogen (Townsend et al., 2003), with no commercial fertilizer applied to soil.

Why study nitrates in the Konza

Nitrates in the Konza is important to study to have a better understanding of the way nitrates relate with sediments and move with water. This also includes how these two materials (sediment and water) with regards to nitrates, relate to one another within a pristine site when compared to a contaminated one. This is achieved by determining the factors that increase or decrease nitrate content within sediment and water, factors that enrich $\delta^{15}\text{N}$ values, and how minerals, including dissolved ions, affect nitrate and $\delta^{15}\text{N}$ values. Nitrates in the Konza could also be used as a baseline study to better trace enriched levels of $\delta^{15}\text{N}$ and interpret its source using the aid of other stable isotopes such as $\delta^{13}\text{C}$, δD , and $\delta^{18}\text{O}$, when applied to an actual contaminated area.

Chapter 2 - Background

Nitrates

Nitrate concentrations greater than 2 mg/L in groundwater indicate possible anthropogenic sources (Townsend et al., 2003). Nitrate-N values greater than the U.S. EPA drinking water limit of 10 mg/L occur with $\delta^{15}\text{N}$ values greater than +10‰.

In 150 counties, TX, nitrate was detected in more than half of the groundwater samples measured. The nitrate problem is more pronounced in western Texas. Relatively low nitrate levels were found throughout eastern Texas, where organic-rich soils and moist conditions promote denitrification (Hudak, 2000). More than half of the observations in each of those counties surpassed the drinking water standard (Hudak, 2000).

In earlier work conducted by Tang et al. (2004), in Japan, it was found that nitrate in groundwater mainly came from fertilizers used in the upstream recharge area of the study site. When the groundwater moved up across the wetland, nitrate concentrations in the groundwater decreased rapidly in the shallow water-table zone due to denitrification (Tang et al., 2004).

Konza Prairie geology

The bedrock layers within the Konza Prairie consist of limestone and shale which is Permian (Oviatt, 1998). Limestone units form benches, and shale units form slopes, giving rise to the “terraced” topography of the Konza and the Flint Hills. There are no faults or folds that occur in the bedrock and the only structures are a system of vertical joints or fractures in two orthogonal sets, N 25 - 35°W and N 55 - 65°E (Smith, 1991). The Florence Limestone Member of the Barneston Limestone underlies the highest hills on the Konza Prairie and contains a large volume of chert that weathers out to mantle ridge tops and slopes. It is the youngest bedrock unit on the Konza and forms the drainage divide in Kings Creek. The Shroyer Limestone includes the drainage divide between Kings and Shane Creek (Oviatt, 1998). Two older limestone units, the Shroyer Limestone and Threemile Limestone Members of the Wreford Limestone, also contain chert. Two types of Quaternary deposits have been identified in the Konza. The oldest deposit consists of windblown silt deposits which range between three to four feet (Ross, 1995; Oviatt, 1998). They were likely deposited during the period of late Pleistocene glaciation, when the climate in Kansas was much drier and colder than it is today and eolian-dust deposition rates were greater (Smith, 1991). The youngest

deposits on the Konza consist of colluvium and alluvium which are less than 10,000 years old (Oviatt, 1998). They range in thickness from a few centimeters to meters.

$\delta^{15}\text{N}$ studies in water

Isotope analysis involved establishing the ratio of ^{15}N to ^{14}N on the nitrogen in nitrate compared to the ratio observed in the standard, which is atmospheric nitrogen (air) at 0‰ (Townsend, 2007). Comparisons of these values indicate whether there were more (positive) or less (negative) ^{15}N in the sample than the standard. The values thus indicated whether the samples were enriched (+) or depleted (-) in relation to the standard (Townsend, 2008). Studies showed that lighter isotope ^{14}N was preferentially used by microbes and plants leaving behind the heavier isotope, ^{15}N (Townsend, 2003). It has also been shown that $\delta^{15}\text{N}$ values in nitrate from commercial fertilizer sources range from -2 to +8‰, soil nitrogen are in the range of +5 to +7‰, and animal waste is generally greater than +10‰ (Townsend, 2007; Townsend, 2008). Although animal waste has starting $\delta^{15}\text{N}$ values around +5‰, animal waste also has a high ammonia component, and the release of the ammonia when the waste is produced causes an immediate enrichment of the $\delta^{15}\text{N}$ because the ^{14}N in the waste is released by volatilization (Townsend 2007). As a result, the $\delta^{15}\text{N}$ of the remaining nitrogen is much higher (in the range of +10‰ or more). In general, animal waste sources contain high nitrate-N concentrations which are usually higher than the EPA set limit of 10 mg/L (Townsend, 2008). As the lighter ^{14}N isotope is released into the atmosphere with N_2 gas, the remaining nitrogen becomes enriched with $\delta^{15}\text{N}$ (Townsend, 2007). Because of possible volatilization of anhydrous ammonia by bacteria and conversion of the ammonia to nitrate, the $\delta^{15}\text{N}$ values frequently are +2 to +8‰ (Townsend, 2005). Denitrification was another process that resulted in the enrichment of $\delta^{15}\text{N}$ values. This process may be explained by the degradation of nitrate to nitrogen gas by bacteria with nitrogen gases eventually released to the atmosphere. The ^{14}N of the nitrate is preferentially utilized, resulting in an enriched $\delta^{15}\text{N}$ occurring in the remaining nitrate. Signs of possible denitrification were low nitrate values, enriched $\delta^{15}\text{N}$ values, and high levels of bicarbonate, which is a byproduct of the denitrification process (Townsend, 2008). If the pH is around six or less and iron, manganese, ammonium, chloride, and sulfate are present in measurable quantities, then the water is considered reducing and the nitrate concentration is generally very low (Nielsen et al., 1998; Tor et al., 2000; Tang et al., 2004). In this situation, it is likely that the nitrate is reduced to ammonium and nitrogen gas by bacterial action (denitrification) and this process will be reflected in its isotopic signature (Townsend, 2007). With a pH above eight, a chemical volatilization process of ammonium to ammonia may occur, causing a release of N_2 gas and an enrichment of ^{15}N in the remaining

ammonium (Townsend, 2007; Townsend, 2008) due to fractionation processes. If the chemistry of the water changes by mixing with a lower pH water, then the ammonium may be nitrified to nitrate by bacteria and the ^{15}N signature will become more enriched (Townsend, 2007).

$\delta^{15}\text{N}$ studies in sediment

When it comes to reservoir sedimentation, the sediments present play a role in carrying along contaminants, which are coated around the soil particles. Once in water the potential contaminant, nitrogen, dissolves to form nitrogen oxides such as the nitrates and nitrites (Townsend, 2008). Alternatively, there is an inverse relationship when it comes to sediments within a reservoir and water. This is because the increase of sediments within a reservoir reduces the volume of water present within it (deNoyelles et al., 2008). Hence this causes an increase in concentration of other contaminants. Previous work done by Townsend (2007) showed that volatilization occurred in the soils and rocks with carbonates. The carbonate rocks increased the pH of water towards 8.5, which made the water more basic. In this range, nitrate can be converted to ammonia gas (Townsend et al., 2007, Townsend, 2008). Work also done by Townsend (2008) showed that most nitrogen found in soil samples is organic. The increase of nitrate in the sandy zone suggested that more oxygenated water is available that resulted in the conversion of ammonium-N to nitrate-N (Townsend et al., 2007, Townsend, 2008). This indicated that $\delta^{15}\text{N}$ values generally increased with depth, which may be due to bacterial degradation of the nitrate. However, nitrogen content (nitrate) usually decreased with depth indicating denitrification processes have occurred. In this study, the measurable nitrate and ammonium concentrations with depth suggested that the original source of the nitrogen may have had a higher $\delta^{15}\text{N}$ signature than soil organic nitrogen, and animal waste may be such a source (Townsend, 2008).

Nitrates in Kansas

Groundwaters in urban and rural areas are susceptible to nitrate contamination from leaking septic and sewer systems as well as from previous land use where farmland has been developed (Ridder et al., 1974). However an increase in nitrate levels due to applications of commercial fertilizers and manure was found in mostly in rural areas and now is recognized as an evolving public health crisis in many parts of the world. Some of the areas worked on that have had nitrate problems include city of Hays, Ellis County, in west central Kansas (Townsend, M.A., and S.A. Macko, 2007); Reno County, City of Oberlin located in Decatur County, northwestern Kansas (Townsend et al., 2003); the city of Lincolnton, Kansas (Townsend, 2007); McPherson County, Kansas (Townsend,

2005), and Leavenworth County, Kansas (Townsend, 2008). According to studies done in Kansas, sources of nitrates consist of three factors: (1) animal waste source, (2) lagoon seepage of waste products from feedlots that move downwards, and (3) from fertilizers applied by farmers to crops (Townsend et al., 2008). Remedial actions have been taken to deal with this problem. Although sometimes limited and not completely effective, they help to remove some of the nitrate contaminants. There is the use of treatment processes, such as ion exchange, reverse osmosis, biological denitrification, chemical reduction which actually removes portions of the pollutant, and blending of contaminated water with cleaner water to reduce contaminant levels (Kendall, 1998). Nitrate concentrations exceed the maximum contaminant level (MCL) for drinking water of 10mg/L as N established by the U.S. EPA in 12 to 46 percent of the wells sampled in the agricultural regions in Kansas (Hamilton et al. 1995). Apparent cases of high nitrates in groundwater have been reported extensively by Kansas Geological Survey in the last five years (3-60 times higher in agricultural areas relative to undisturbed areas) (Townsend and Macko 2007, Wankel et al. 2009). There has been a growing interest in the field of nitrates and sometimes nitrites within the scope of their interaction with groundwater (Townsend and Macko 2007, Wankel et al. 2009, Mattern et al. 2009, Kennedy, 2009). Townsend (2007) concluded that ^{15}N analysis was critical in tracing source of nitrate contaminants within wells and shallow aquifers. It was also stated that chloride and bromide ions in water were considered to be conservative tracers because they were not affected by bacterial degradation and also there is a relationship between increasing nitrate-N with increasing chloride concentrations (Townsend, 2008). In addition, it has been observed that movement of anions such as chloride through clay liners can occur whereas positive ions such as ammonium will be retained in the clays due to adsorption onto them (Townsend et al. 2007). The use of pH helps to determine if water has reducing water chemistry (Townsend, 2007).

Konza Stream Work

Nitrate studies in the Konza Prairie streams have shown that nitrate concentrations do vary seasonally and are high during dry periods and low during high amounts of precipitation (Gray et al., 1998). The NO_3^- concentrations of stream water in lowland reaches were lowest during times of high precipitation due to a decrease in concentration and rapid transport off site. Additionally, this could also occur when the relative influence of groundwater drainage is minimal and water in the channel is primarily derived from prairie land types which are generally flat. The groundwater from cropland increased stream NO_3^- concentrations about four-fold during low-discharge periods, even though significant riparian forest corridors exist along most low stream channels on Konza (Kemp et al.

2001). Earlier work by Dodds et al. (1996), described the discharge and N content of surface water flowing from four Karst watersheds on Konza Prairie, managed with different burn frequencies, and were monitored from 1986 to 1992. Climate, fire, and bison grazing were the natural processes that were taken into consideration on N transport and concentration in streams. Dodds et al. (1996) concluded that annual N transport by streams, averaged across all watersheds and years, was 0.16 kg N ha⁻¹ yr⁻¹. Annual N transport per unit area also increased as the watershed area increased and as precipitation increased. The total annual transport of N from the prairie via streams ranged from 0.01 to 6.0‰ of the N input from precipitation. Nitrate and total N concentrations in surface water decreased ($P < 0.001$, r values ranged from 0.14-0.26) as the length of time since last fire increased. It was also suggested that between NH₄⁺ and NO₃⁻, a preference for NH₄⁺ was indicated as an N source (O'Brien and Dodds, 2010). The efficiency at which N is cycled and retained decreases with increasing nutrient concentration so in low-NO₃⁻ streams, available NO₃⁻ was transported very quickly and traveled a relatively short distance before being taken up again. As the concentration of NO₃⁻ increased, the magnitude and length of travel also increased (O'Brien et al., 2007).

Use of $\delta^{18}\text{O}$ in nitrate studies

Although isotope analysis using d¹⁵N is capable of differentiating between animal and organic N including inorganic fertilizer derived nitrate, it still has its limitations. It is still quite inconclusive when it comes to determining various animal sources. The use of $\delta^{18}\text{O}$ in conjunction with $\delta^{15}\text{N}$, (Wankell et al. 2009) for differentiating between animal sources has not been useful likely due to similarities within their broad isotopic range of 10‰ to 23‰. However isotope studies are still a viable means in understanding the nature of the heavy nitrogen isotope present within an aquifer after the lighter isotope has been denitrified and volatilized (Townsend and Macko 2007, Wankell et al. 2009, Mattern et al. 2009, Kennedy, 2009). Datta et al. (1997) proposed that high nitrate levels are associated with high $\delta^{18}\text{O}$ values, clearly indicating that significant quantities of evaporated (isotopically enriched) irrigation water infiltrate along with fertilizer nitrate to the groundwater system.

Use of $\delta^{13}\text{C}$ in nitrate studies

Studies using stable carbon isotopes in the city of Hays, Ellis County, KS, (Townsend and Macko, 2007) provide supporting evidence that indicates soils are not a major contributor to the observed nitrate-N concentration in the ground water. $\delta^{13}\text{C}$ values of the dissolved organic carbon (DOC) in soils generally were more enriched (-11.6 to 18.8‰) while corresponding groundwater

$\delta^{13}\text{C}$ values were more depleted (-19.9 to 22.2‰), suggesting that the source of the DOC in groundwater is not from the soils (Townsend and Macko, 2007).

In another study, computer modeling suggested by Magette et al. (1989), indicate that corn whether produced under no-till or conventional methods, can result in average $\text{NO}_3\text{-N}$ concentrations leaving the root zone greater than 10 mg/L in 4 to 6 of 10 years.

Chapter 3 - Objectives and Hypotheses

Objectives

The purpose of this study was to compare the spatial variation of nitrate using geochemistry and mineralogy of sediments along with water chemistry using stable isotopes (δD , $\delta^{18}\text{O}$, and $\delta^{15}\text{N}$) (Koh et al., 2005) of both surface water and groundwater on the Konza Prairie. This work focused on four zones of the Konza Prairie which include areas around Kings Creek (Zone 1), (N4D) area grazed by bison (Zone 2), area adjacent to Interstate 70 (Zone 3), and Shane Creek (Zone 4). The main objective was divided into three different sub-objectives:

1. Determine the manner by which recharge water (precipitation) allows nitrates to be leached into sediment, and to see if additional nitrate is contributed from source rocks or the extent that nitrate from sediment feed into adjacent running streams, subsequently into groundwater using studies of δD , $\delta^{18}\text{O}$, and $\delta^{15}\text{N}$ analyses.
2. To determine the spatial variation of water chemistry, major minerals, and $\delta^{15}\text{N}$ values of both sediment and water along the four above mentioned zones, to aid in understanding the extent of nitrogen cycle processes such as nitrification, denitrification, and mineralization (ammonification) within this unmanaged grassland.
3. The significance of the mineralogy in controlling nitrates and the spatial variation with regards to the mineralogy of the four zones using XRD analysis. Additionally, how does this if at all affect nitrate distribution within the Konza.

Hypotheses

Because the study area is situated within the Flint Hills which is characterized by alternating layers of permeable limestone and impermeable shale, calcite, clay minerals and quartz should be the major minerals present within the environment. The presence of loess which is rich in nutrients, coats the surface of the majority of the study area. The nutrients present should comprise of clay minerals, NH_4^+ , and NO_3^- . Some of the NO_3^- is probably very soluble and can be transported by water. During precipitation, gravity will transmit NO_3^- downwards to groundwater level within the subsurface.

With the help of stable isotope study of $\delta^{15}\text{N}$, one can compare a grazed site from a non-grazed site because an enrichment of $\delta^{15}\text{N}$ could be from the feces of bison, which graze in N4D (Zone 2) of the Konza. These feces made up of complex ammonium compounds that decay to inorganic nitrogen gas and will be available for use by plants. During these processes the lighter

isotope ^{14}N is preferentially utilized compared to ^{15}N which is left behind. We should see this signature from the ^{15}N studies.

There should be some ^{15}N progression and variation within the biochemical cycle as it reflects in the grassland. This should help to transfer nitrates from sediment to water or water to sediment. And also there should be a time progression of a 10 year variation of ^{15}N with nitrate as it relates to time. The major limestone-shale mineralogy should control the nitrate movement from weathering of these rocks to produce in situ sediments of them leaching into groundwater

Precipitation is the most likely groundwater recharge mechanism in this study. Surface water may not be a contributor to the recharge of groundwater, especially Kings Creek since the stream flows to McDowell Creek and from there to the Kansas River. The hypothesis here is that the variation of the spatial distribution of $\delta^{15}\text{N}$ within the Konza, should be minimal and $\delta^{15}\text{N}$ values should increase with depth (Townsend et al. 2007) indicating denitrification processes have occurred.

Chapter 4 - Methods and Materials

Study Area Description

The Konza Prairie Biological Station is a 34.87 km² native tallgrass prairie located in the Flint Hills of northeastern Kansas. It is located south of Manhattan, within Riley County, Kansas. It is 10 km south from Kansas State University. The southern boundary of the Konza Prairie is adjacent to Interstate 70. The Flint Hills, on which the Konza Prairie developed, cover about 212,380 km² throughout a portion of eastern Kansas. The Flint Hills northern end is on the Kansas-Nebraska border and it extends as far as north-central Oklahoma. Konza Prairie is located within the largest remaining area of unplowed tallgrass prairie in the Flint Hills. Hence, the vast majority of Konza Prairie retains its native characteristics.

The Konza Prairie along with the Flint hills was formed during the Permian period at about 250 million years ago. The current location of the Konza was dominated by warm shallow waters and marine biota which facilitated the production of limestone. Some of the limestone contains fine-grained silica-rich microcrystalline quartz in the Florence Limestone bed layer. The upland region of the Konza, consists of loess which contain clay minerals.

Its vegetation is mainly comprised of several plant species with the major one being the native tallgrass prairie. Also present are the big bluestem, little bluestem, switchgrass, indiagrass, legumes, and forbs. The tallgrass canopy reaches over 2.5 m in height in the most productive years. The grassland habitats include upland prairie on thin loess soils, hill prairie along alternating limestone benches and slopes, and areas of lowland prairie on deep alluvial-colluvial soils which accumulated during the Kansan Glacial Epoch (KPBS, 2011).

It has a continental climate characterized by warm, wet summers and dry, cold winters with elevation ranging from 320 m to 444 m. Average monthly temperature ranges from a January low of -2.7° C to a July high of 26.6° C. It also has an average annual precipitation of 32.9 inches, which is sufficient to support woodland vegetation. However, drought, fire and grazing are important in maintaining this grassland.

In addition to the native prairie habitat, the two branches of Kings Creek originate on the station and run 10 km through it. An additional stream is Shane Creek, which is east of Kings Creek. Gallery forests dominated by bur and chinquapin oaks and hackberry occur in bands along the major stream courses and cover approximately 7% of the preserve area (KPBS, 2011). Several agricultural

fields and restored prairie on former cultivated fields occur on the deep soil lowlands along the lower stretches of Kings Creek.

Sample Collection

Water sampling

During the course of several field trips (May, June, July 2010 and June 2011) surface waters from Kings Creek (Zone 1) and its tributary, Shane Creek (Zone 4); some ephemeral streams located in the N4D region - area grazed by native herbivores such as bison (Zone 2) of the Konza Prairie; and from a stream adjacent to Interstate 70 (Zone 3). Well water samples were collected from wells ranging in water level elevation above mean sea level of 360 m to 397 m with the use of a bailer. Wells were pumped for approximately 1–2 minutes until the water ran clear.

Before heading to the field sites, each sample bottle was pre-washed following a specific protocol. Each bottle was rinsed three times with tap water, rinsed three times with de-ionized water, soaked in RBS (detergent) overnight, rinsed three times again with de-ionized water, soaked in an acid bath (10% Trace Metal grade HCl) overnight, rinsed with de-ionized water three times, and air-dried on Kim-wipes.

All samples were collected in duplicate, and some in triplicate (May, June, July 2010) after rinsing the bottles three times with the water to be collected—one in a white Fisherbrand® 500 ml Nalgene® high-density polyethylene narrow-mouth bottle (Cat. No. 2006-0016); and in two amber, 125 ml Nalgene® high-density polyethylene narrow-mouth bottles (Cat. No. 2004-0004). Sample bottles were filled to the top leaving no head space in the bottle. Filtered, unacidified samples were collected in plastic 50 ml centrifuge tubes (Fisherbrand® Disposable Centrifuge Tube, Sterile, Polypropylene, 50 ml; Cat. No. 06-443-20). Filtering was done using disposable plastic syringes (25 ml) pushing the water through a 0.45 µm polypropylene filter (Whatman syringe filter, 25 mm GD/X Disposable Filter Device, PP Filter Membrane with Polypropylene Housing, Cat. No. 6878-2504) into its respective sample bottles. Twelve water samples (ten surface water and two well water samples) were collected in 1 gallon jugs during May 2010 and June 2011 for the analysis of $\delta^{15}\text{N}$.

Each sample bottle was labeled with the location from which it came from i.e. Kings Creek (KC), Shane Creek (SC), etc. Sample number, geographic coordinates and dates were taken at each sampling location with a hand-held Global Positioning System (GPS, Garmin eTrex Vista HCx). This information was also recorded manually in a field notebook including longitude and latitude of

sample locations. For each respective type of water sample bottle the following analyses were performed (when applicable):

1. 500 ml white Nalgene® bottles (unfiltered, unacidified) – Anions
2. 125 ml amber Nalgene® bottles (unfiltered, unacidified) – stable isotopes ($\delta^{18}\text{O}$ and $\delta^2\text{H}$)
3. 125 ml amber Nalgene® bottles (unfiltered, unacidified) – cations
4. 3.785 ml (1gallon) jugs (unfiltered, unacidified) – stable isotopes ($\delta^{15}\text{N}$)

Sediment Sampling

In this study, a hydraulic geoprobe was used to take sediment core samples from ten locations covering all zones within the Konza (Fig. 1).



Figure 1. Making use of the hydraulic geoprobe out in the Konza.

The geoprobe went as far as 8 feet into the ground with the use of 4 core liners. The coring device was pressed down into the ground, collecting sediments into the core liner. When a core was fully inserted (~2 feet in length), it was carefully removed from the ground, taking care not to lose any sample. The top of the corer had a threaded cap which could be unscrewed to expose ~2 cm of the core liner. An additional metal pipe fitted with a plastic core liner internally, could be attached to allow for further drilling into the subsurface. The core liner was then cautiously pulled out from the

metal corer, and a plastic cap was placed over the end of the core liner and closed. Once the cap was secured on the top end of the liner, the other end of the liner was removed from the metal corer completely and closed with a cap as well. The core name, location, and sample ID were written on each of the core liners onsite and this information was also written in field notebook (appendix B). This process was repeated up to four times and at least once at each location. Subsequently all samples (water and sediment) were taken to Kansas State University, Geology Department and stored in a freezer until further analyses were performed.

Analyses

Water Analyses

Anions in waters

Major anions (F^- , Cl^- , NO_3^- , SO_4^{2-}) for ~34 water samples collected during 2010 and 2011 were measured at the Kansas Geological Survey (KGS) and the Kansas Soils lab (KSU) using the Dionex IC-3000, Ion Chromatograph (IC). Five standards were prepared using 0.2 μm filtered de-ionized distilled water and stock standard solutions of 1000 mg/l. The standards for each element were made for the following in mg/l: F^- [0.1, 0.2, 0.4, 0.8, 1.0]; Cl^- [5, 10, 40, 60, 100]; NO_3^- [1.0, 2.5, 5, 15, 25]; SO_4^{2-} [5, 10, 40, 60, 100]. Samples were prepared by filtering through 0.2 μm filters (Cat. No. 09-927-26C), with an approximate range of 0.5 to 2.5 ml of sample added to the Ion Chromatograph (IC) vials which were then loaded into the autosampler. The five standards, along with a blank, were run for calibration of the machine. Then the 34 water samples were analyzed for their respective anion concentrations. Some the water samples such as Stream 4 (Str 4), Stream 8 (Str 8), and Shane Creek 4 (SC 4) were run in duplicates while Shane Creek (SC4) was also ran as a triplicate.

Bicarbonate or alkalinity was measured for the same 34 water samples (by HACH® Alkalinity Test Kit (~2 months after collection in the field) Alkalinity was measured for the samples using a HACH® Alkalinity Test Kit (10-4000 mg/l, Model AL-DT; Cat. No. 20637-00), Digital Titration method. For each sample, about 20 ml of water sample was used. The 20 ml sample was added to a 100 ml graduated cylinder, and one Phenolphthalein Indicator Powder Pillow (Cat. No. 942-99) was added to the sample, swirling the cylinder to mix the contents. Since the Phenolphthalein Indicator Powder did not turn any of the sample solution pink, it was concluded that no value for $CaCO_3$ -P alkalinity was important for these samples. Then a Bromcresol Green-methyl Red Indicator Powder Pillow (Cat. No. 943-99) was added to the sample and swirled till it was

dissolved and homogenized. A digital titration cartridge of 1.6 N H₂SO₄ (Cat. No. 14389-01) with a delivery tube was attached to the HACH® digital titrator and inserted in the 20 ml water sample. Titration of the sulfuric acid into the sample proceeded until a light greenish blue-grey (pH 5.1), a light violet-grey (pH 4.8), or a light pink (pH 4.5) color was achieved. The total number of digits displayed on the titrator was recorded and multiplied by 5 (the respective digit multiplier for a 20 ml sample) to obtain the amount (mg/l) as HCO₃⁻ which is also regarded as Total Alkalinity. The resulting liquid was discarded. Before the next sample was analyzed for alkalinity, the graduated cylinder and the delivery tube were rinsed three times with de-ionized water and three times with water from the next sample to be analyzed to maintain precision and reduce error.

Cations in waters

Sub-samples were taken from 22 water samples that were collected in 2010 and 2011 from the Konza, were filtered with 0.45 µm polypropylene filter (Whatman syringe filter, 25 mm GD/X Disposable Filter Device, PP Filter Membrane with Polypropylene Housing, Cat. No. 6878-2504) and placed in 50 ml Polypropylene Disposable centrifuge tubes (Fisherbrand Cat. No. 06-443-18). Then they were acidified to a pH of <2 with high purity Optima HNO₃ and placed in a sample-holder rack. Then they were packaged and shipped to Actlabs, a division of Activation Laboratories in Ontario, Canada. Using an Inductively Coupled Plasma Optical Emission Spectroscopometer (ICP-OES), five multi-element standards were prepared with concentrations of each element made from stock solutions. The instrument was calibrated with the standards and the samples were analyzed in concentrations of mg/l. The most common line with least interference was chosen for each element.

δ²H and δ¹⁸O of water samples from the Konza Prairie

Stable isotope values of δ²H and δ¹⁸O for 17 water samples were measured using the Cavity Ringdown spectrometer (Picarro G1301) in the Stable Isotope Mass Spectrometry Lab in the Department of Biology at Kansas State University (Fig. 2). After filtering through a 0.2 µm filter, approximately 2 µg of sample was injected into the Picarro water analyzer for determination of δ²H and δ¹⁸O. Inside the Picarro analyzer, the injected water sample was converted to vapor and carried by a N₂ flight tube to the analyzer where the relative abundance of heavy and light isotopes was measured. Due to the adsorptive nature of water, there is a slight memory effect between samples as water molecules from one injection linger on the surface of the analyzers internal plumbing. To remove the memory effect, a total of six injections were made into the analyzer per sample. The data from the first three were removed from the analysis (due to memory effect), and the last three were

averaged (as recommended in the Picarro instrument user's manual). The average value represents a raw data point that is standardized to three standards which are Evian bottled water [$\delta^2\text{H} = -78.07\text{‰}$ and $\delta^{18}\text{O} = -10.01\text{‰}$], KSU de-ionized water [$\delta^2\text{H} = -40.72\text{‰}$ and $\delta^{18}\text{O} = -5.30\text{‰}$], and KSU de-ionized enriched water [$\delta^2\text{H} = -8.36\text{‰}$ and $\delta^{18}\text{O} = 4.03\text{‰}$] that are analyzed along with each batch of samples. The standards have been calibrated to National Institute of Standards and Technology (NIST) accepted standards (Greenland Ice Sheet Precipitation (GISP: $\delta^2\text{H} = -189.5\text{‰}$ and $\delta^{18}\text{O} = -24.78\text{‰}$), Standard Light Arctic Precipitation (SLAP: $\delta^2\text{H} = -428.0\text{‰}$ and $\delta^{18}\text{O} = -55.5\text{‰}$), and Vienna Standard Mean Ocean Water (VSMOW: $\delta^2\text{H} = 0\text{‰}$ and $\delta^{18}\text{O} = 0\text{‰}$) (Coplen, 1994). The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values of the standards span the entire range of expected isotope values for the samples submitted. In order for correction of drift in the analyzer during a batch of samples, a working standard of known isotope ratios was analyzed every four samples. Finally, the raw isotope data was corrected to the three standards analyzed with the measured water samples.



Figure 2. The Picarro G1301 used to analyze stable isotopes of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of water.

$\delta^{15}\text{N}$ of water samples

Analysis of $\delta^{15}\text{N}$ of water was done following the protocol outlined in the Lotic Inter-site Nitrogen eXperiment II (LINX II) (O'Brien et al. 2007). Water from each of the 3.785 liter (one gal) jugs (two well and ten surface water samples) was placed in two white Fisherbrand® 500 ml

Nalgene® high-density polyethylene narrow-mouth bottle (Cat. No.2006-0016). The two 500 ml bottles represent each location that was sampled. The water samples were taken to KSU- Biology Department and transferred to an acid washed 2000 ml beaker. Added to the beaker were 5 g of ashed NaCl and 3 g of ashed MgO to make the solution basic. The 2000 ml beaker with its 1000 ml contents was then placed on a hot plate and boiled down to roughly 100 ml after about three to four hours. After cooling somewhat, the boiled down sample was placed into an acid-washed 250 ml and then placed in refrigerator for the meantime.

A filter packet was made to entrap NO_3^- and converted it to NH_4^+ . This was done by placing Small glass fiber filter (GF/D filter) in a 600 °C degree oven for 3 days to remove any organic content. Aluminum foil was spread across the work space and cleaned with 95% ethanol to remove impurities that could hamper precise results. Teflon filter of about 1.5 inches strip was cut with a sterilized pair of scissors (cleaned with 95% ethanol) and placed on the aluminum foil with the ashed GF/D filter placed on one end of the Teflon filter. KHSO_4 of 25 uL volume, 2.5 M concentration, was retrieved with a pipette and transferred to completely soak the ashed GF/D filter. The other end of the Teflon filter was then lifted with sterilized tweezers and placed over the GF/D filter. The Teflon filter was then sealed by rolling the open end of a scintillation vial around the outside portion of the Teflon filter, making sure the filter pack remained stuck together.

The 250 ml bottle was taken from the refrigerator and 0.5 g of ashed MgO, 0.5 g of Devardas alloy, and the filter pack was added to the bottle. The bottle was then capped tightly with a piece of parafilm and placed in a 60 °C oven for two days. The bottles were then taken from the oven and placed on a shaker for seven days at room temperature. The bottles were open and the filter packs were taken out with sterilized tweezers and blotted with Kim wipes to remove excessive water droplets. The filter pack was placed in an open labeled scintillation vial and transferred to a dessicator to dry for four days. An open vial of 2.5 M KHSO_4 was also placed in the dessicator to absorb any ammonia in the air. Subsequently the filter pack was then removed and placed on the sterilized aluminum foil surface alongside Costech Analytical Technologies pressed tin capsules (5 x 9 mm). Using a couple of sterilized forceps, the enclosing teflon filter was removed and the Whatman #2 GF/D filter was retrieved and placed in a tin capsule that was immediately closed and folded from the open end to seal in the filter. The encapsulated filter was then placed in a closed well tray set and sent to Ackert Hall, KSU for $\delta^{15}\text{N}$ analysis (Fig. 3).



Figure 3. The Delta plus mass spectrometer used to analyze $\delta^{15}\text{N}$ of water entrapped in filter.

All 12 water samples followed the aforementioned procedure. An entry of a dry mass of 1 mg for all filter samples and %N value for each sample was taken into consideration by the isotope lab to allow calculation of N recovery during processing of each sample.

Sediment Analyses

Analysis for NO_3^- and NH_4^+ in sediment

The total number of cores to be analyzed was 34. These were sampled in July and August 2010. For NO_3^- and NH_4^+ analysis for each core section, only top 2 inches was sectioned out to measure their bulk content. The sediment was removed and stored in 50 ml polypropylene disposable centrifuge tubes (Fisherbrand Cat. No.06-443-18). They were taken to the KSU Soil Testing Laboratory, Throckmorton Hall and placed in a 60°C oven for two days with the centrifuge tubes slightly opened to drive out the moisture content. They were then ground to sand sized particles while making sure to wash the ceramic mortar and pestle with acetone and rinsing it three times with deionized water after grounding each sample. The samples were then weighed to ~ 2.00 g and transferred to a tray made out of Styrofoam with openings and a series of plastic small sized conical flasks attached to its bottom. 1M of KCl was made and 20 ml of KCl was poured into each of the tray openings, containing the 2 g samples. The trays were placed on a shaker and shaken for 30 minutes and the contents were turned over into glass vials attached to filters. The filtrate within the vials contained NO_3^- and NH_4^+ which had been displaced by K^+ and Cl^- ions respectively (Laima, 1993; Laima, 1994; Kowalenko, 2006). The equipment used to determine this analysis was the ALPKEM autoanalyzer made up of component 301, 302, 305A, 313, and 314. The ALPKEM analyzed for both $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ in ppm. The standard consisted of soil solution with known content amount, with

a standard for every 12 sample slots, an unknown sample at slot # 25 and a vial containing water in the final slot.

Analysis for total carbon and nitrogen

About 2 inches from the top of a 0-2 feet core liner from each of the sediment sample locations, was used for analysis. This brought the number of samples to be analyzed for total carbon percentage and total nitrogen percentage to 10. The samples were taken to the KSU Soil Testing Laboratory to determine total nitrogen percentage and total carbon percentage. The samples were weighed at ~350 mg each and enclosed in Costech Analytical Technologies tin cups and wrapped and pressed at the top to seal it. The samples were then taken to the LECO TruSpec® CN 2000 combustion analyzer (LECO Corp., 1995), to undergo combustion. The standards used were made of reference material NIST RM 8704, Buffalo River Sediment at 3.351% carbon; and NIST RM 8433, Corn Bran at 0.884% nitrogen. Total levels (inorganic and organic) of C and N were determined on a dry-weight percent basis using the LECO CN 2000 combustion analyzer (LECO Corp., 1995).

X-Ray diffraction of sediment

The sediment samples that were to undergo X-Ray diffraction for its mineralogical content, were Core 2 and 3 from Geop 1, Core 2 and 4 from Geop 3, Core 2 and 3 from Geop 6, Core 2 and 4 from Geop 8, Core 2 and 4 from Geop 9, and Core 2 and 3 from Geop 10. Each of the core liners were cut to about an inch depth from their core tops and the sediment was laid on a plate in the Department of Geology to dry. A tungsten-carbide shatterbox was used to grind the samples to clay sized particles. After grinding each sample, the shatterbox puck and assemblage were washed with acetone, distilled water, and dried with compressed air. The ground samples were placed in separate small 20 ml HDPE scintillation vials (Wheaton; Cat. No. 0334172) and shipped to the Department of Geological Sciences and geological Engineering, Queen's University, Ontario, Canada. The samples were scanned with a Philips PANalytical X'Pert Pro MPD diffractometer fitted with an X'Celerator high speed strip detector. Samples were mounted as thin smears of fine powder on glass disks. Cu K α radiation (Ni filtered), 0.02 rad incident beam sollar, 15 mm mask, 1/2° divergence slit, 1° anti-scatter slit, 0.02° diffracted beam sollar. Count time was 20 sec at 0.02° 2 θ increments scanned from 3° to 70° 2 θ ; the sample was rotated at 2 sec/revolution. PANalytical High Score software was used for phase identification. The software compared the peak positions and peak intensities for the unknown sample to data in a large database of known phases inputted into the software.

$\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of sediment samples

Selected core liners had about 2 inches from their tops cut out with their sediment extracted and placed in 50 ml polypropylene disposable centrifuge tubes (Fisherbrand Cat. No. 06-443-18). They were taken to Throckmorton Hall – KSU and placed in a 60°C oven for two days with the centrifuge tubes slightly so moisture could escape. They were then ground to sand sized particles using a ceramic mortar and pestle. The ceramic mortar and pestle were cleaned with 95% ethanol and rinsed three times with deionized water after each sample. The sediment samples were also acidified to remove oxides and carbonates. The ground samples were measured out in masses ranging from 2 to 10 mg according to the CASIF (Central Appalachians Stable Isotope Facility) sample weight calculator, using the Mettler Toledo Analytical Balance and then enclosed in Costech Analytical Technologies pressed tin capsules (5 x 9 mm). Samples were then packed in a paraffin sealed well tray and shipped to University of Maryland, Center for Environmental Science for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ analysis. The samples were analyzed using a Carlo Erba NC2500 elemental analyzer interfaced with a Thermo Delta V+ isotope ratio mass spectrometer (IRMS) (Fig4 & 5).

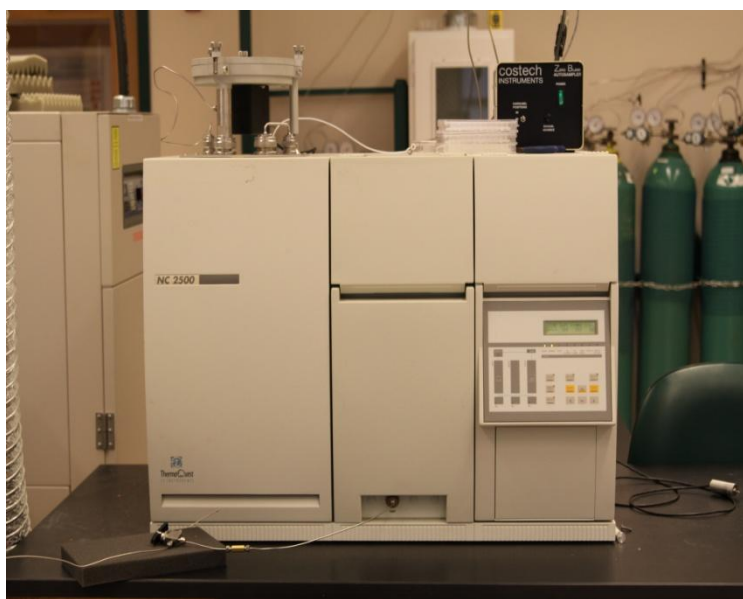


Figure 4. The Carlo Erba NC2500 elemental analyzer.



Figure 5. The Delta V + isotope ratio mass spectrometer (IRMS).

They were combusted in an oxygenated column (900°C) packed with silver cobaltous and chromium oxide. The sample gases and helium carrier gas then flow into a reduction column (650°C) packed with copper granules that convert the oxides of nitrogen into molecular nitrogen (N₂). The CO₂, N₂, and water vapor travelled through a magnesium perchlorate water trap including a GC column (50°C) for peak separation before entering the IRMS. Samples are compositionally matched with a quality control (QC) in-house standard, which are interspersed among the unknown samples. QC materials have been previously calibrated against internationally known reference materials. Two different known standards (USGS 40 and USGS 41 or in-house standards that have been calibrated against the internationally known standards) are run in every analysis to normalize values for each batch of samples. One blank is included to detect any background CO₂ or N₂. Each run is started with an acetanilide “bypass” sample (~1mg) to prime the system and to check for any irregularities (e.g. in the timing or shape of C and N peaks). Three samples of atropine in a specific range of weights are included in order to obtain %C and %N data. The long-term standard deviation (1σ) of QC standards is 0.12 for δ¹³C and 0.11 for δ¹⁵N. If the δ¹³C and δ¹⁵N values for >1 of the QC samples in a given sample set exceeds the 2σ range of the known value for that QC material then the samples are

reanalyzed. The final isotopic values are expressed relative to international standards V-PDB (Vienna PeeDee Belemnite) and Air for carbon and nitrogen, respectively.

Chapter 5 - Results

Sediment Characterization

Sediments were derived from regions adjoining Kings Creek (Zone 1), N4D (Zone 2), and Interstate-70 (Zone 3). The choice of the Zone 1 was mostly based on the main stream of the Konza Prairie which flows to the Kansas River and has several tributaries. Zone 2 was chosen because it is located within the vicinity of the groundwater wells, the presence of surface water which is an extension of King Creek, and a grazing site for bison. Zone 3 was chosen to observe any relationship of NO₃ to highway activity due to vehicular emissions.

Sediment types were observed in this study and these sediments were loess, colluvium, and alluvium. Loess is formed by the accumulation of wind-blown silt, which also contains sand and clay to a lesser extent. Precipitation of calcite between the grains of loess loosely cements them together and subsequently makes them usually homogeneous and highly porous. The total thickness of the loess is three or four feet (Oviatt, 1998) and it was deposited on the Konza during multiple episodes of dust deposition during the Pleistocene. Loess could be intermixed with alluvium which were derived from areas of high elevation located south of the Konza and washed northwards by gravity. Alluvium is also found as stream deposits in the terraces present in the Kings Creek valley. Alluvium is loose sediment which are eroded and deposited by water. The major difference between loess and alluvium within this study is that the genesis of alluvium is a recent process which is related to water, while loess is a Pleistocene deposit, formed via air. The major mineral contributed from the bedrock strata is calcite. The limestone is Permian in age and was deposited almost 300 million years ago in, or near the margins of shallow interior seas, which fluctuated in depth and extent (Smith, 1991). The particle sizes within the sediment cores that were analyzed ranged from silt to sand, excluding those consisting of bedrock material (limestone), since it was biochemically derived.

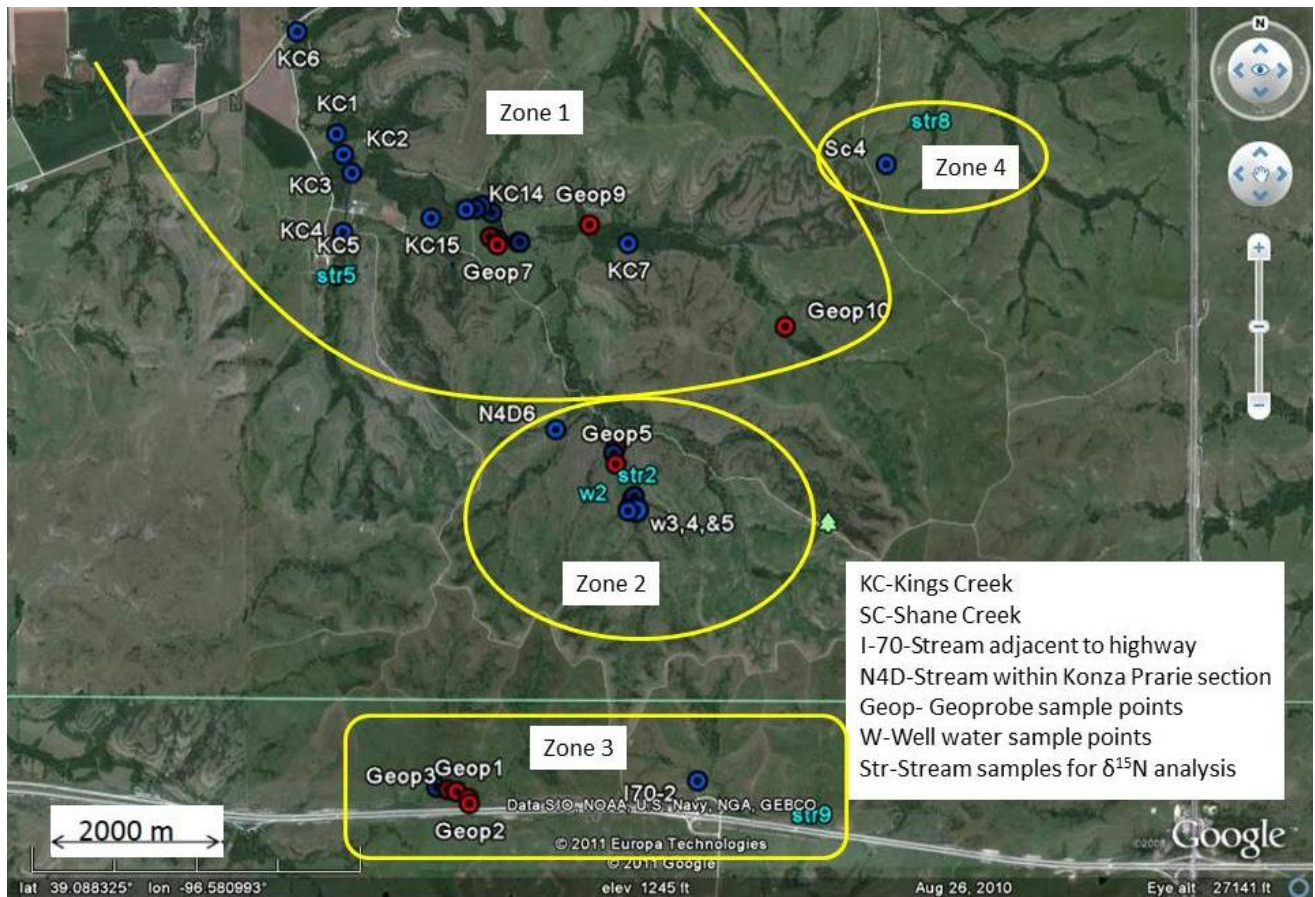


Figure 6. Identification points from where water (blue) and sediment samples (red) were collected from for analysis within the Konza. Zone 1 represents the lowland region, Zone 2 represents the upland region, Zone 3 represents alluvium and colluvium deposits adjacent to the highway, and Zone 4 represents Shane Creek.

Color of sediment analysis

Kings Creek (Zone 1)

Sediment sample identification points consisted of Zone 1 (Geop 7, 8, 9, and 10) (Fig. 6). Sediments were 5YR (Yellow-Red), 4 value, and 3 chroma which is 5YR 4/3 according to Munsell soil color chart with many variable-size clay aggregates situated within a finer-grained matrix, which also encircles few larger grains of quartz, feldspars, and calcite (Fig. 7). These sediments, especially from the core just beneath the surface, mostly consist of various clay minerals as examined by X-Ray diffraction and also are rich in organic matter. No significant depth-dependent variation in color was observed in these core.



Figure 7. Sediment cores from a sample point in Zone 1 located by Kings Creek (N39°06.111', W096°35.688')



Figure 8. Sediment cores from a sample point in Zone 2 located in the N4D region of the Konza Prairie (N39°05.324', W096°35.075').

N4D (Zone 2)

Sediment sample identification points were Geop 5 and Geop 6 (Fig. 6). A depth-dependent variation in the color of the sediment was observed in this sample location. The core was 5YR (Yellow-Red), value 3, and chroma 4 - 5YR 3/4 according to Munsell soil color chart. They contain organic material, quartz, feldspar, and clay minerals. At two feet and four feet depths, the sediment core color changes from 5YR 3/4 to 2.5Y 6/2 color (Fig. 8). These core sediments were comprised of mostly calcite, with quartz and feldspar.



Figure 9. Sediment cores from a sample point in Zone 3 adjacent to Interstate 70 (N39°03.995', W096°35.782').

I-70 (Zone 3)

Sediment sample identification points consisted of Geop 1, 2, 3, and 4. A depth-dependent variation in the color of the sediment was observed in this sample location (Fig. 9), which is adjacent to Interstate 70. Surficial sediment core was 5YR 3/4 according to Munsell soil color chart. They contain various clay minerals, and organic matter, including dead leaves and roots (Fig. 9). Deeper cores consist of fine grained sediments, 2.5YR 4/4 and sandy in texture. The deepest sediment core which is between 6-8 feet, contain clay sized particles, and range from 10YR 5/8 to 2.5YR 3/6 according to Munsell color chart.

X-Ray diffraction of sediment (Mineralogy)

Cores were collected from different zones which consisted of Zone 1, Zone 2, and Zone 3. X-ray diffraction (XRD) analysis of sediment cores from the Zones revealed spatial variability of minerals present. XRD detection indicated the presence of quartz, feldspars, calcite and clay minerals as shown below (Fig. 10, rest in appendix B*). The sediments in general did not reveal much distinction in mineralogy with depth. The mineralogy of sediment in all areas was predominantly quartz, smectite group of clay minerals, and calcite. Among the smectites, nontronite might be present but detection was not possible without clay mineral diffraction. Some of the minerals that were not consistently detected in all the zones are albite, dolomite, microcline, and muscovite.

The relative proportion of quartz is fairly constant throughout the sampled zones. Abundance of muscovite, feldspars (albite and microcline), muscovite, and smectite were more prominent in the

areas enclosing the stream valley of the Konza, in which the Kings Creek and its tributaries lie (Zone 1). Areas of higher elevation (Zone 2), had smectite, quartz, and calcite, but not a wide variety of minerals as Zone 1 and 3. In Zone 3, the presence of the mineral dolomite or magnesium calcite differentiated it from the other zones which had no magnesium calcite detected. Illustrations of X-Ray Diffraction peaks and height, are in Appendix B; a, b, c, d, e, f, g, h, I, j, k, and l. Powder X-Ray Diffraction of the sediments analyzed indicated quartz had an average intensity of 69.90 with d-spacing of 3.3432, albite had an intensity of 40.34 with d-spacing of 3.7755, K-feldspar (microcline) had an intensity of 100 with d-spacing of 3.2463, calcite had an intensity of 100 with d-spacing of 3.0337, dolomite intensity was 100 with d-spacing of 2.8854, and smectite group clay mineral had an intensity of 60 with d-spacing of 5.01. The summary of the mineralogy is as follows:

ZONE 1 Geop 8, core #2 quartz, muscovite, albite, and microcline

Geop 8, core #4 quartz, muscovite, albite, and microcline

Geop 9, core #2 quartz, muscovite, albite, and smectite group clay minerals

Geop 9, core #4 quartz, albite, microcline, and smectite group clay minerals

Geop 10, core #2 quartz, albite, microcline, and smectite group clay minerals

Geop 10, core #4 quartz, albite, calcite, and smectite group clay minerals

ZONE 2 Geop 6, core#2 quartz, smectite group clay minerals, and calcite

Geop 6, core #3 quartz, smectite group clay minerals, and calcite

ZONE 3 Geop 1, core #2 quartz and smectite group clay minerals

Geop 2, core #3 quartz, smectite group clay minerals, dolomite or magnesium calcite

Geop 3, core #2 quartz, smectite group clay minerals, muscovite, albite

Geop 3, core# 4 quartz, smectite group clay minerals, muscovite, albite

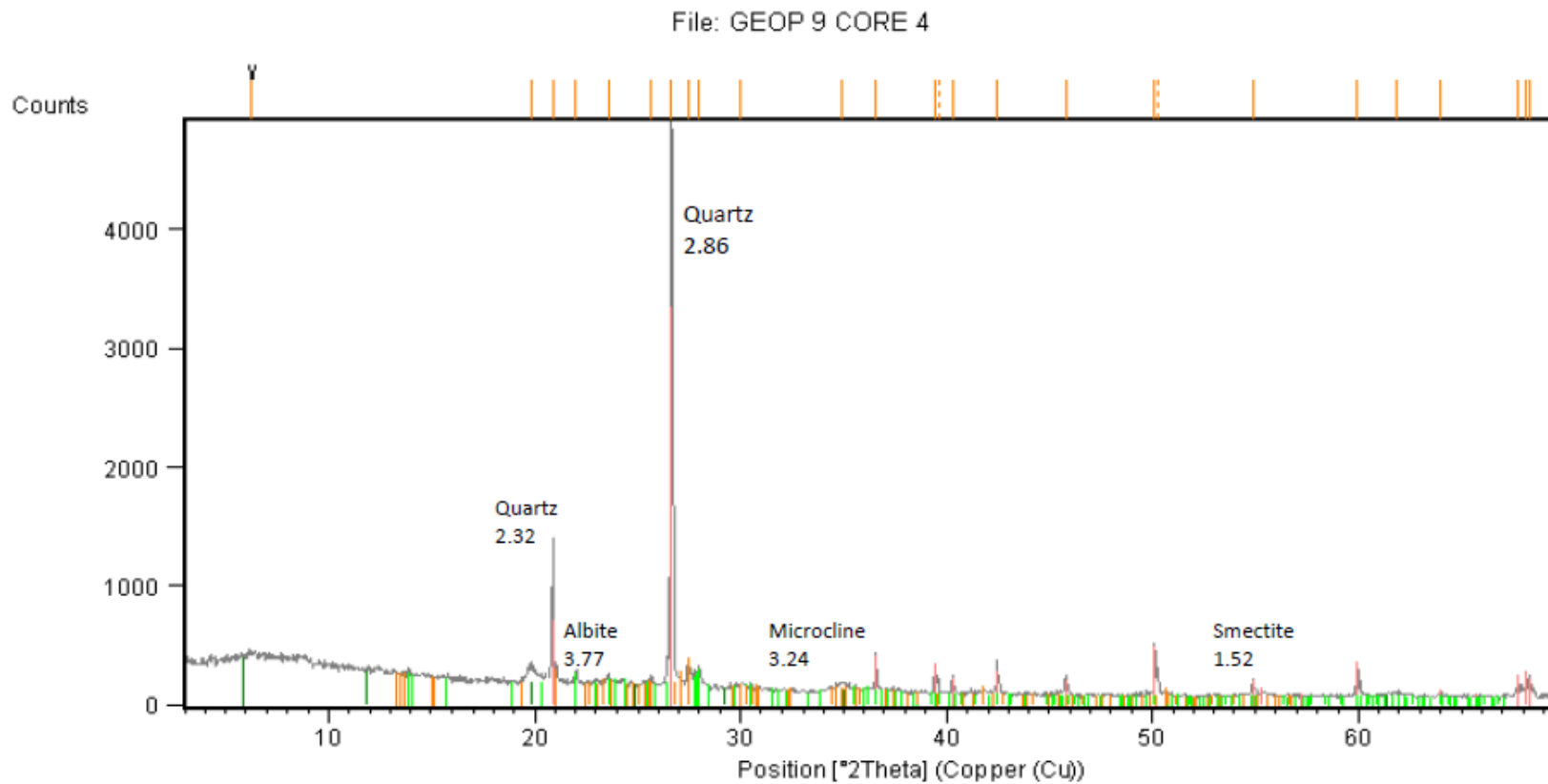


Figure 10. XRD of sediment in sample location Geop 9, core # 4 shows presence of quartz, albite, microcline, and smectite, based on peak position and height. (The peak intensities of smectite and microcline were very little).

Ammonium

Sediment cores were analyzed for NH_4 an average depth of 2 inches from the surface. The result from this analysis shows that NH_4 is highest in concentration at the top and it generally decreases with depth (Fig. 11). At Geop 5 (Zone 2), no core could be retrieved because of hard bedrock beyond 1 foot. The mean values of ammonium concentration within all the cores from Zone 1, was 63 mg/L, Zone 2 was 79.1 mg/L, and Zone 3 was 47 mg/L. So essentially, Zone 1 and 2 had similar proportion of NH_4 , but less in Zone 3. [The detection limit used was 0.1 mg/L]. For Zone 1, $p = 0.0008$; Zone 2, $p = 0.18$; and Zone 3, $p = 0.02$. Probability (p) values which are greater than 0.05 or 5 % indicate that the relationship of ammonium with nitrate with regards to depth is not statistically significant. Standard Error of the Mean (SEM) testing was calculated using Zone 1, 2, and 3 for 0 ft depth, 2 ft depth, 4 ft depth, and 6 ft depth. The formula used for SEM was (standard deviation, STD)/ (square root of n) as shown below:

Depth in feet	Zone 1 (mg/L)	Zone 2 (mg/L)	Zone 3 (mg/L)	n (number of applicable zones)	Mean	STD	SEM
0	150.5	142.1	138.7	3	143.8	6.1	3.5
2	49.3	23.2	15.5	3	29.3	17.7	10.2
4	33.1	8.8	19.7	3	20.5	12.2	7.0
6	19.3		4.7	2	12.0	10.3	7.3

So Zone 1, mostly being constituted of quartz, albite, calcite, muscovite, microcline, and smectite group clay minerals showed NH_4 to decrease by 87.2% from surface to 6 ft depth. In Zone 2, the minerals were calcite, quartz, and smectite, with a percentage decrease in NH_4 of 93.8%. In Zone 3, the minerals consisting of quartz, muscovite, albite, dolomite and smectite group clay minerals, showed a percentage loss of NH_4 from the surface to 6 ft depth was 96.6%.

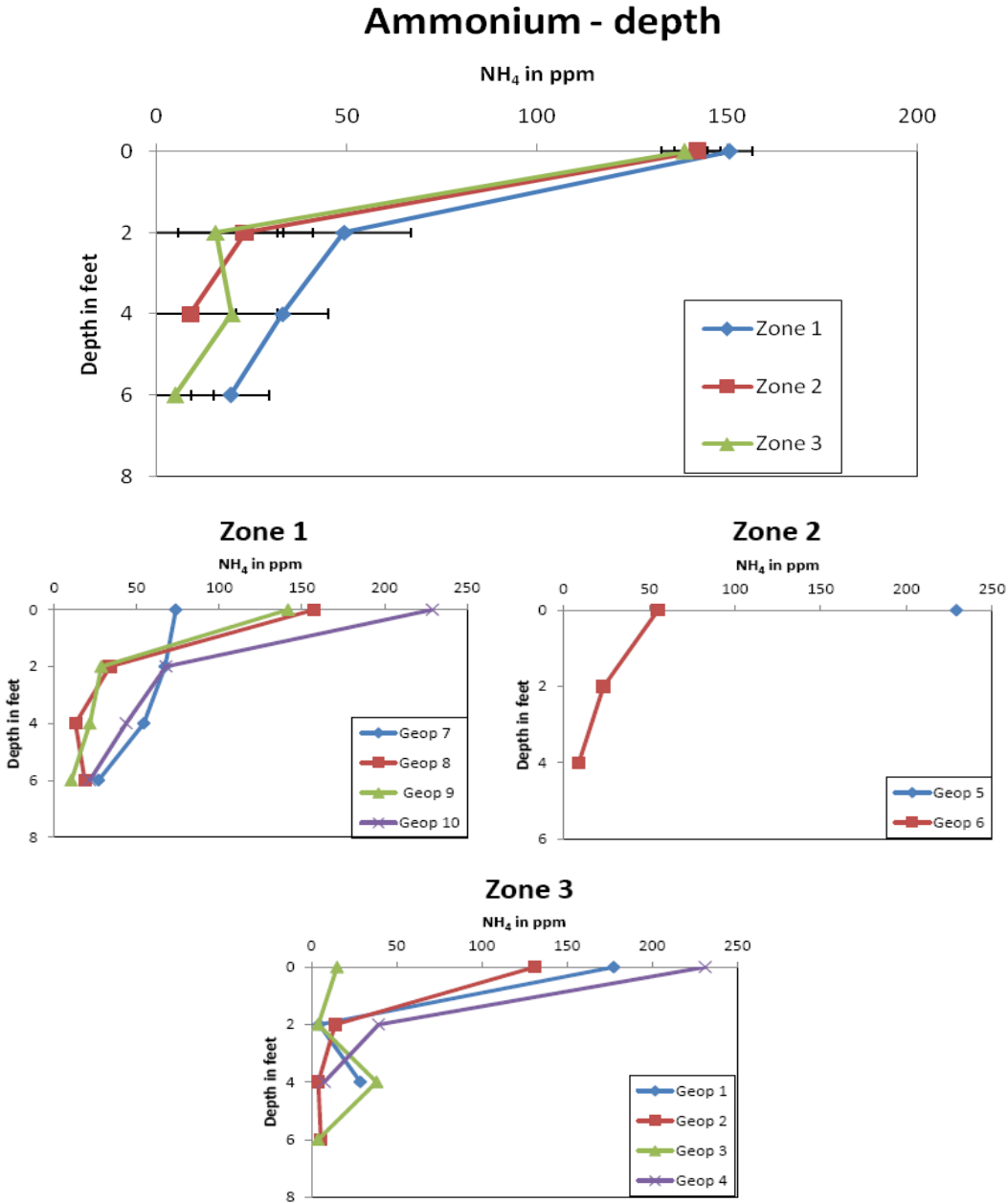


Figure 11. Ammonium with depth at each of the Zones. Each sediment sample was from ~ 2 inches from the top of each core liner.

Nitrate

There is a general decrease in nitrate concentration except for a slight general increase in nitrate concentration within two feet beneath the subsurface (Fig 12). After 2 feet, nitrate concentration steadily decreases with depth (Fig 12) in similar manner to NH_4 . At Geop 5 sample location (Zone 2), the core liner could go no farther in depth than 2 feet due to the presence of hard

bedrock material. The mean values of nitrate concentration within all the cores examined from Zone 1, was 5.61 mg/L, Zone 2 was 2.56 mg/L, and Zone 3 was 3.25 mg/L. [The detection limit used was 0.1 mg/L]. Student t-testing values were calculated for Zone 1, 2, and 3. For Zone 1, $p = 0.002$; Zone 2, $p = 0.23$; and Zone 3, $p = 0.03$. Probability (p) values which are greater than 0.05 or 5 % indicate that the relationship of nitrate with ammonium with regards to depth is not statistically significant. Standard Error of the Mean (SEM) testing was calculated using Zone 1, 2, and 3 for 0 ft depth, 2 ft depth, 4 ft depth, and 6 ft depth. The formula used for SEM was (standard deviation, STD)/ (square root of n) as shown below.

So Zone 1, mostly being constituted of quartz, albite, calcite, muscovite, microcline, and smectite group clay minerals showed NO_3 to decrease by 32% from surface to 6 ft depth. In Zone 2, the minerals were calcite, quartz, and smectite, with a percentage decrease in NO_3 of 11.5%. In Zone 3, the minerals consisting of quartz, muscovite, albite, dolomite and smectite group clay minerals, showed a percentage loss of NH_4 from the surface to 6 ft depth was 38.1%.

Depth in feet	Zone 1 (mg/L)	Zone 2 (mg/L)	Zone 3 (mg/L)	n (number of applicable zones)	Mean	STD	SEM
0	5.0	2.6	4.2	3	3.9	1.2	0.7
2	8.2	2.7	3.7	3	4.9	2.9	1.7
4	5.7	2.3	2.3	3	3.4	1.9	1.1
6	3.4		2.6	2	3.0	0.6	0.5

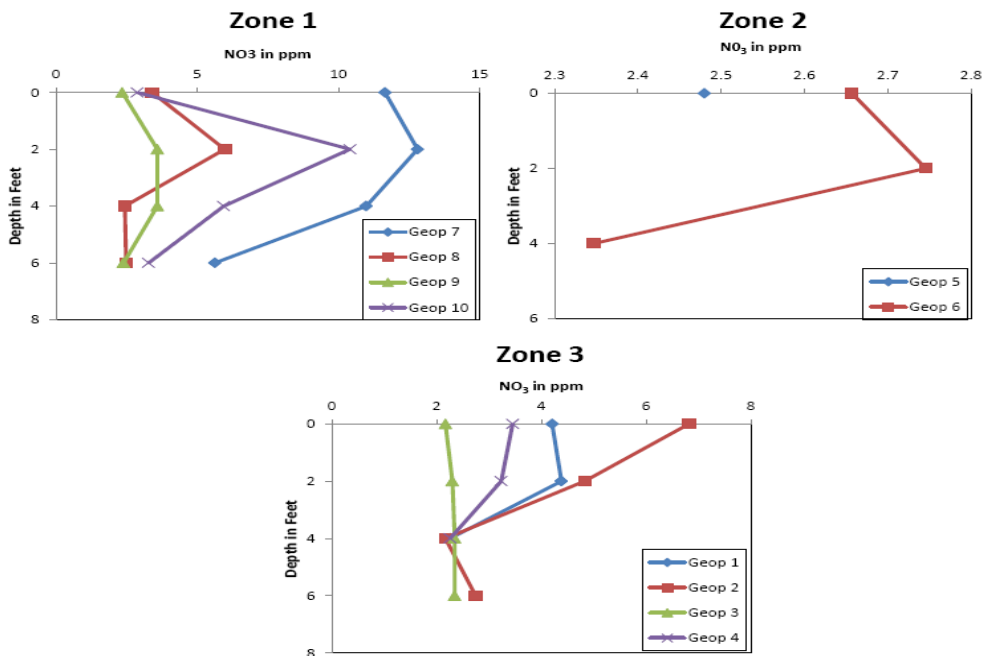
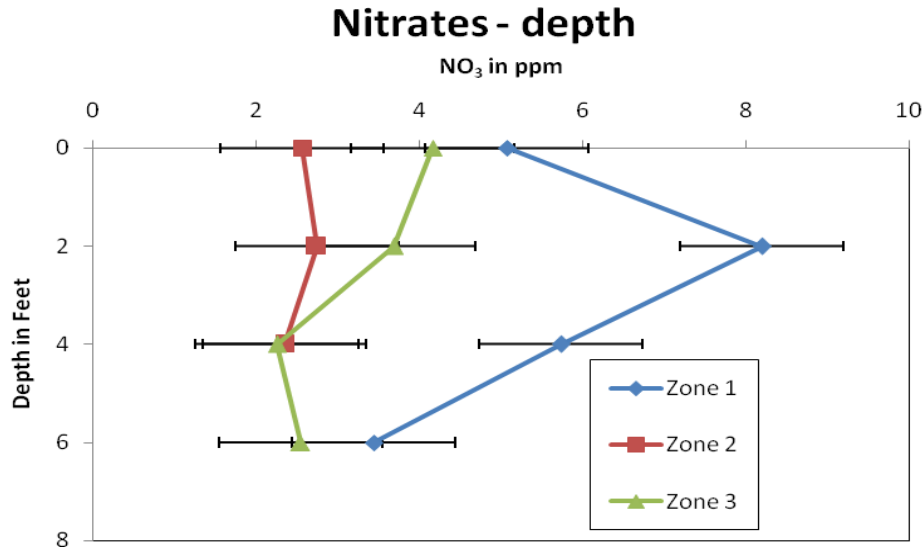


Figure 12. Nitrate with depth at each of the Zones. Each sediment sample was from ~ 2 inches from the top of each core liner.

Nitrate vs ammonium concentrations

Here the depth distributor was not considered but only zones were. $\text{NO}_3^- - \text{NH}_4^+$ was plotted among the zones to see any marked relationship among them. Graphs plotted with NO_3^- against NH_4^+ with regards to 2 ft core, (0-2 ft core); 4 ft core, (2-4 ft core); 6 ft core, (4-6 ft core); and 8 ft core, (6-8 ft core) were illustrated, to show a significant relationship between the ions (Fig 13, 14, 15, and 16). Using NO_3^- as a function of NH_4^+ within the 0-2 ft cores, it was shown that there was no obvious

relationship because of the presence of an open system towards the surface. Additionally, the dissolution of nitrates in water reduces its concentration on the surface as it moves downward with water. However, as the core progressed deeper to 4 ft, 6 ft, and 8 ft, a fairly moderate positive correlation exists between NO_3 and NH_4 .

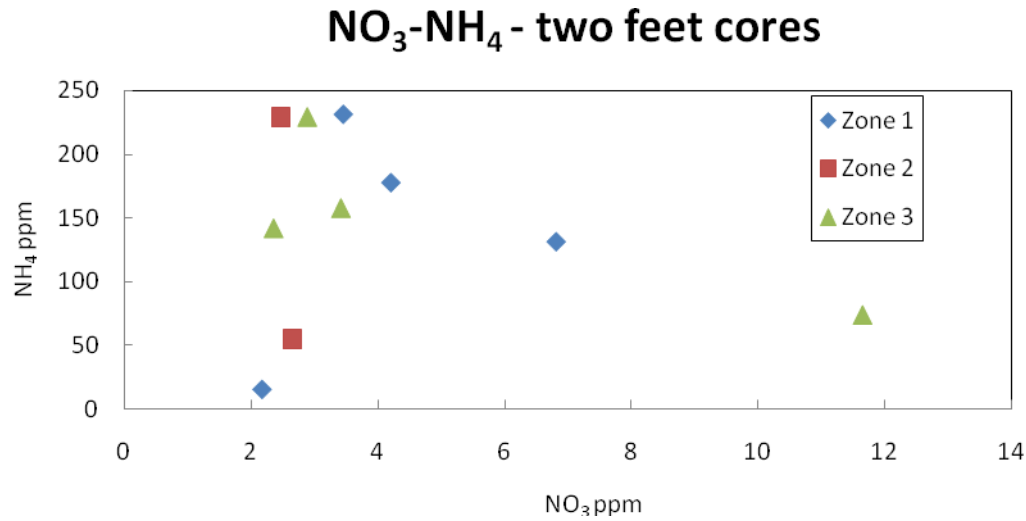


Figure 13. NO_3 and NH_4 levels within 2 inches from the top of 2 ft cores. There is no correlation between NO_3 and NH_4 with regards to the cores zero to two feet from ground surface.

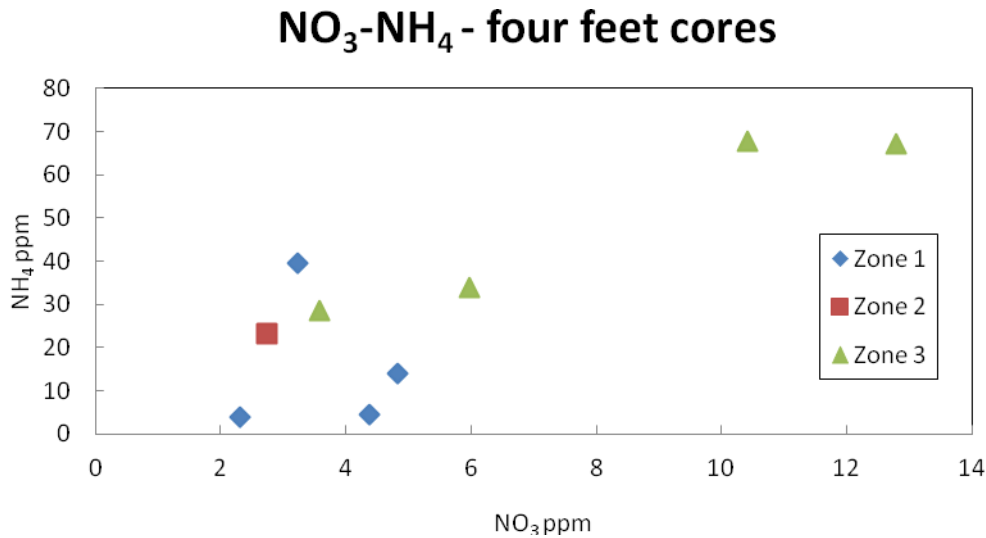


Figure 14. NO_3 with NH_4 levels are also compared among the the three zones within 2 inches from the top of 4 ft cores. A moderate correlation between them is shown with regards to the cores within two to four feet of the subsurface.

NO₃-NH₄ - six foot cores

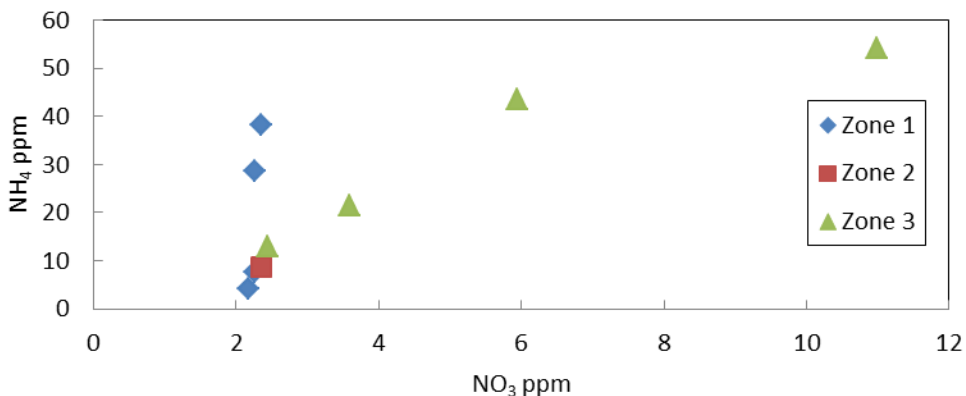


Figure 15. NO₃ with NH₄ levels are also compared among the three zones within 2 inches from the top of 4 ft cores. A moderate correlation between them is shown with regards to the cores within four to six feet of the subsurface.

NO₃-NH₄ - eight feet cores

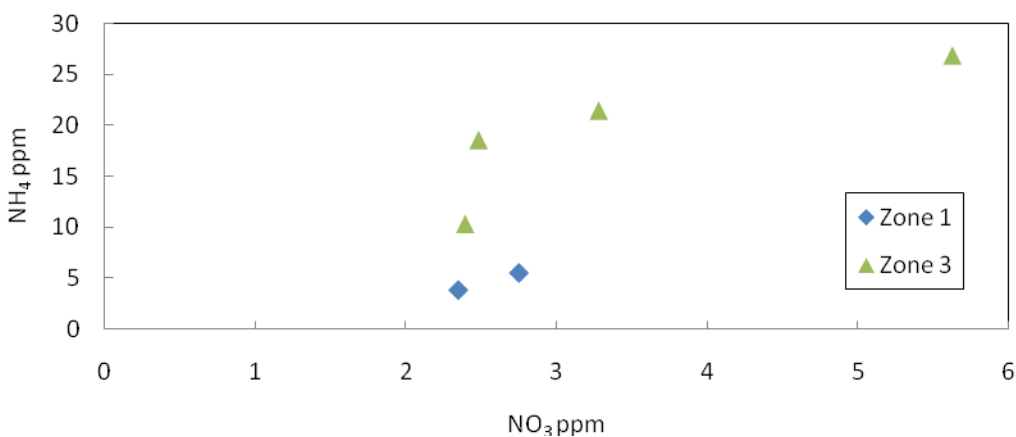
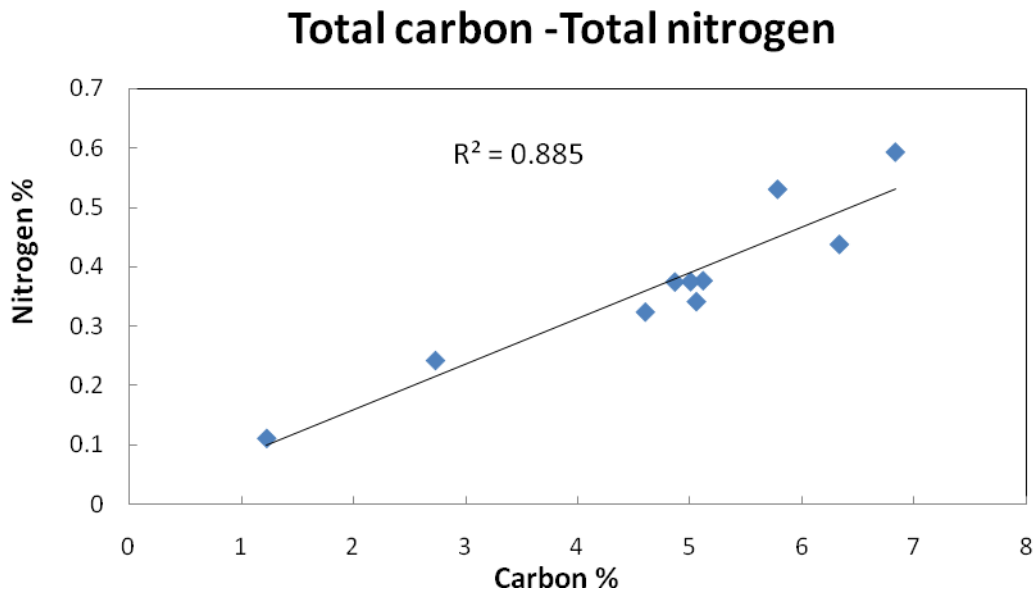


Figure 16. NO₃ with NH₄ levels are also compared among the the three zones within 2 inches from the top of 4 ft cores. A moderate correlation between them is shown with regards to the cores within six to eight feet of the subsurface.

Total carbon and total nitrogen analysis

Selected sediment cores were selected to compare between total C and total N. For this comparison we only chose the 0-2 ft of all cores (from each zone) and total C and N was analyzed for 2 inches of bulk sediment from the top. This was done to differentiate from the earlier NO₃ and NH₄

values and their depth distribution, which focused on the inorganic contribution of N. While total C to total N included more of the organic contribution for both C and N. Results show a positive correlation (See et al., 2005) between total carbon and nitrogen (Fig. 17). Total carbon and nitrogen were considered because it took into account organic carbon and organic nitrogen including inorganic carbon and nitrogen, present on the surface (within 0-2 inches). This differentiated it from ammonium and nitrate analyses of sediment which focused on the inorganic aspect.

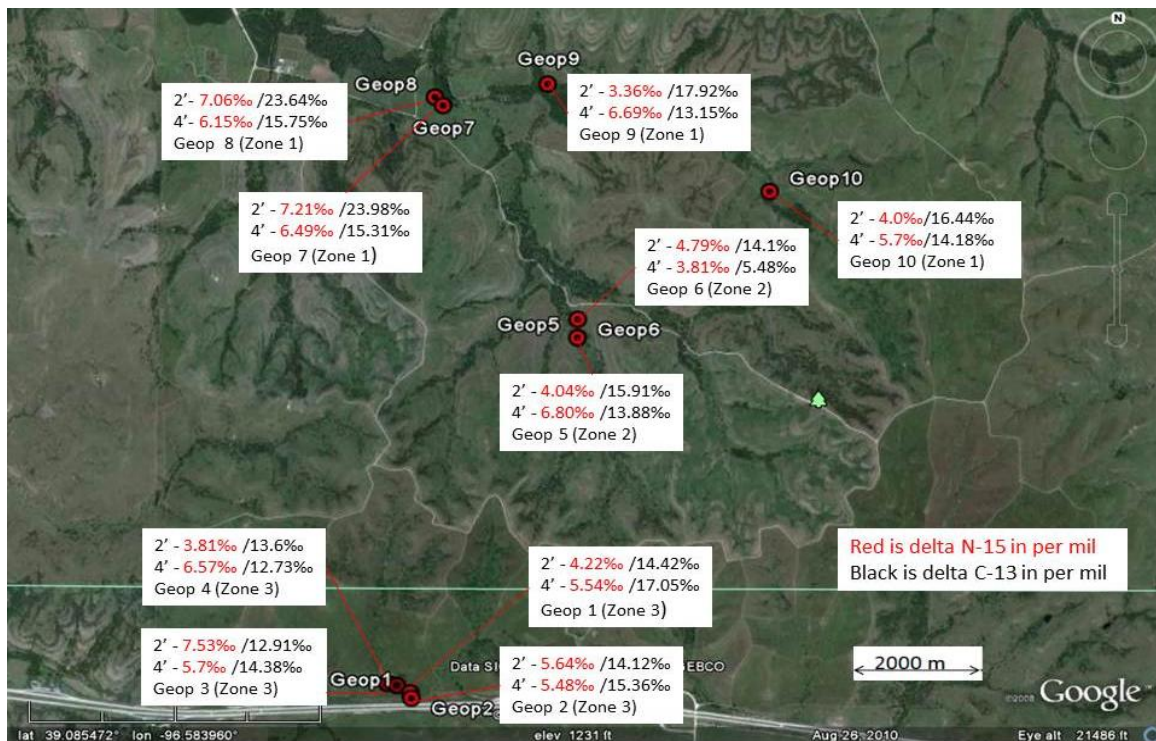


Zone	Sample ID	Carbon %	Nitrogen %
1	Geop 7-1	6.8	0.6
1	Geop 8-1	5.8	0.5
1	Geop 9-1	2.7	0.2
1	Geop 10-1	4.9	0.4
2	Geop 5-1	5.0	0.4
2	Geop 6-1	4.6	0.3
3	Geop 1-1	5.1	0.3
3	Geop 2-1	5.1	0.4
3	Geop 3-1	1.2	0.1
3	Geop 4-1	6.3	0.4

Figure 17. Total C with total N (%) indicating a relationship that reveals on average, a 9:1 ratio in carbon versus nitrogen.

Analysis of total $\delta^{15}\text{N}$ of Sediment

The results for total $\delta^{15}\text{N}$ of sediment within the Konza Prairie indicate enrichment and depletion within the sample locations with regards to 2 ft depth from the ground surface. From each zone, top 2 inches of bulk sediment was analyzed for $\delta^{15}\text{N}$. There is an enrichment of $\delta^{15}\text{N}$ with depth (~ 2 ft from the ground surface) in Zone 1, 2 and 3 (Geop 1, 4, 5, 9, and 10) but this does not necessarily coincide with an increase in nitrate-N (Fig. 12 & 18). Meanwhile there is some level of depletion of $\delta^{15}\text{N}$ with depth at sample regions Zone 1, 2, and 3 (Geop 2, 3, 6, 7, and 8) (Fig. 18). In this study (Fig. 18) we considered the depths that would contain the maximum NO_3 in sediment and then analyzed for $\delta^{15}\text{N}$ to understand the contribution of NO_3 .



	Sample ID	$\delta^{15}\text{N}$ at 0 feet	$\delta^{15}\text{N}$ at 2 feet	NO_3 at 0 feet	NO_3 at 2 feet
Zone 1	Geop 7	7.21 ‰	6.49 ‰	11.6 mg/L	11.8 mg/L
	Geop 8	7.06 ‰	6.15 ‰	3.4 mg/L	51.6 mg/L
	Geop 9	3.36 ‰	6.69 ‰	2.3 mg/L	15.1 mg/L
	Geop 10	4.00 ‰	5.70 ‰	2.9 mg/L	10.4 mg/L
Zone 2	Geop 5	4.04 ‰	6.80 ‰	2.5 mg/L	
	Geop 6	4.79 ‰	3.81 ‰	2.7 mg/L	11 mg/L
Zone 3	Geop 1	4.22 ‰	5.54 ‰	4.2 mg/L	18.6 mg/L
	Geop 2	5.64 ‰	5.48 ‰	6.8 mg/L	30.2 mg/L
	Geop 3	7.53 ‰	5.70 ‰	2.2 mg/L	9.6 mg/L
	Geop 4	3.81 ‰	6.57 ‰	3.5 mg/L	15.3 mg/L

Depth in feet	Zone 1 ‰	Zone 2 ‰	Zone 3 ‰	n	STD	SEM
0	5.4	4	5.3	3	0.8	0.5
2	6.3	5.3	5.8	3	0.5	0.3

Figure 18. Sample points (Geop 1-10) within their zones, where stable isotope analysis for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of sediment cores were taken.

Analysis of total $\delta^{13}\text{C}$ of sediment

There was depletion of $\delta^{13}\text{C}$ with depth at sample locations within Zone 3 (Geop 1, 2, and 3); (Fig. 6). There was an enrichment of $\delta^{13}\text{C}$ with depth at sample locations of Zone 1 and 2 (Geop 4, 5, 6, 7, 8, 9, and 10); (Fig. 18). Isotope analysis for $\delta^{13}\text{C}$ also indicates the presence of C_3 type soil within Zone 1 of the Konza as shown below. Zones 2 and 3 are prevalent with C_4 type soils. The presence of C_3 type soil within this study was limited to two sediment sample locations, Geop 7 and 8.

Depth in feet	Zone 1 in ‰	Zone 2 in ‰	Zone 3 in ‰	n	STD	SEM
0	-20.5	-15.0	-13.8	3	3.6	2.1
2	-14.6	-9.7	-14.9	3	2.9	1.7

Water Chemistry

Cations

Calcium dominates the cationic components of the Konza, with a mean value of 82.34 mg/L followed by magnesium, with mean value of 18.84 mg/L. Next to magnesium is sodium with mean value of 5.51 mg/L and followed by Potassium with mean value of 2.22 mg/L. Dissolved Fe was relatively low within Zone 1 with values of ~ 0.01 mg/L except for KC 1 which contained 0.02 mg/L of Fe (II). The well samples (Zone 2) contain significant amount of dissolved iron which range from 0.01 mg/L – 0.02 mg/L. Well 2, well 4, well 5, and stream 1 of the N4D section (Zone 2) also contained 0.02 mg/L of Fe (II) when sampled surface water was analyzed. Dissolved calcium within Kings Creek and its tributaries (Zone 1) ranged from 37.3 to 89 mg/L. In the wells (Zone 2), they ranged from 91.5 to 126 mg/L, and the surface water within the N4D region (Zone 2) ranged from 48.9 to 70.8 mg/L. Magnesium within Kings Creek ranged from 16 to 18.8 mg/L. In the wells they ranged from 19.2 to 24.6 mg/L, and the N4D region ranged from 17.6 to 17.7 mg/L. The detection limit used was 0.1 mg/L except for iron (II) and manganese (II) which were 0.01 mg/L.

Anions

Analytical result presents the abundance of these anions in the following order: Bicarbonate > Sulfate > Chloride > Nitrate > Fluoride. Bicarbonate is the dominant anion found during this study. The average concentration of bicarbonate was 233 mg/L with a range of 190 mg/L – 337 mg/L. Mean value for chloride was 6.72 mg/L with a range of 0.71 mg/L – 16.99 mg/L. Sulfate had an average concentration of 18.80 mg/L with a range of 5.78 mg/L – 37.38 mg/L. Total nitrate values of water in the Konza, range from 0.0033 – 1.286 mg/L, with a mean value of 0.47 mg/L. Fluoride contained the least amount of anions in the water with an average of 0.41 mg/L and range of 0.2703mg/L – 0.76mg/L. Well samples within Zone 2 have low nitrate values which range from 0.004 – 0.025 mg/L compared to Konza surface waters which range from 0.003 – 1.286 mg/L (Dodds et al., 1996). There was no obvious relationship among the anions as shown in the graphs below in Fig. 19.

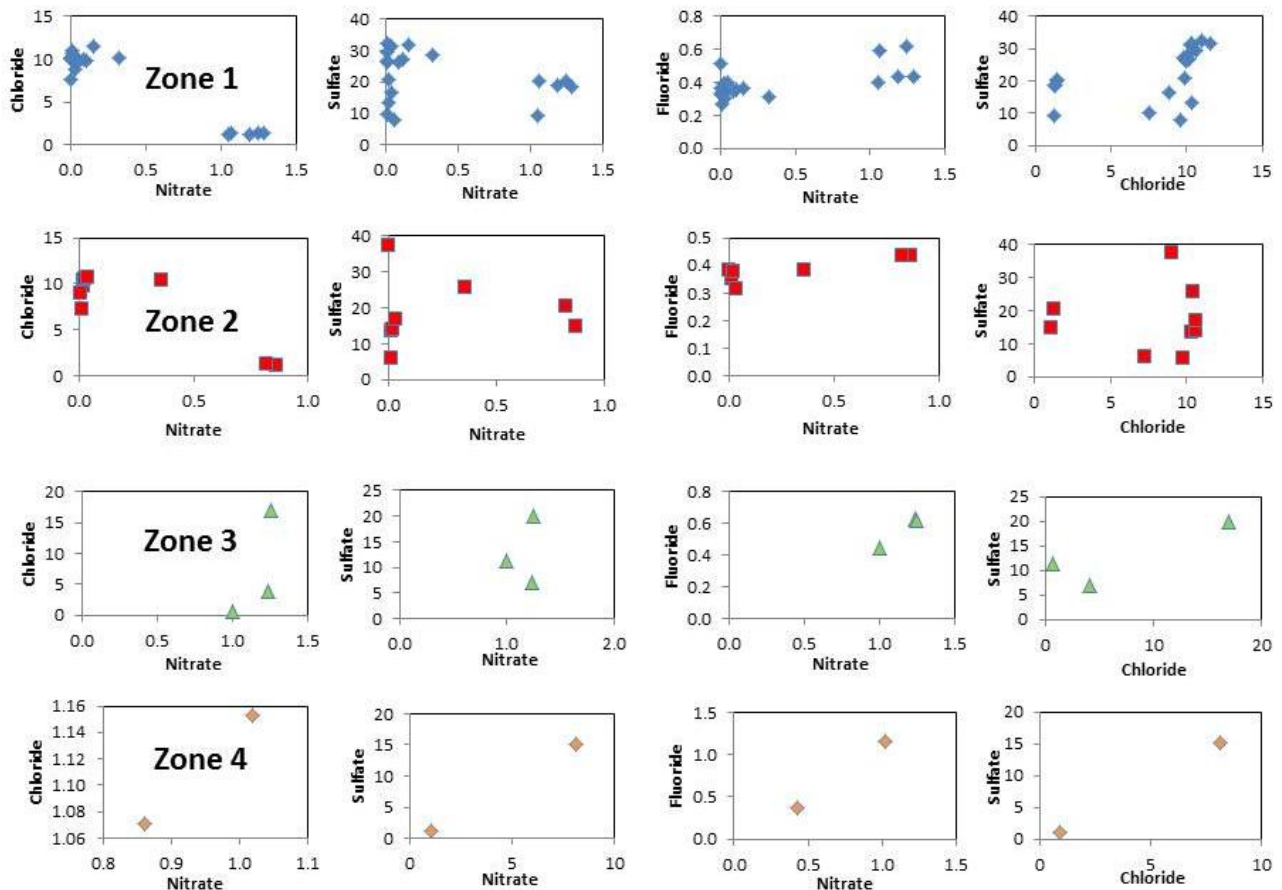


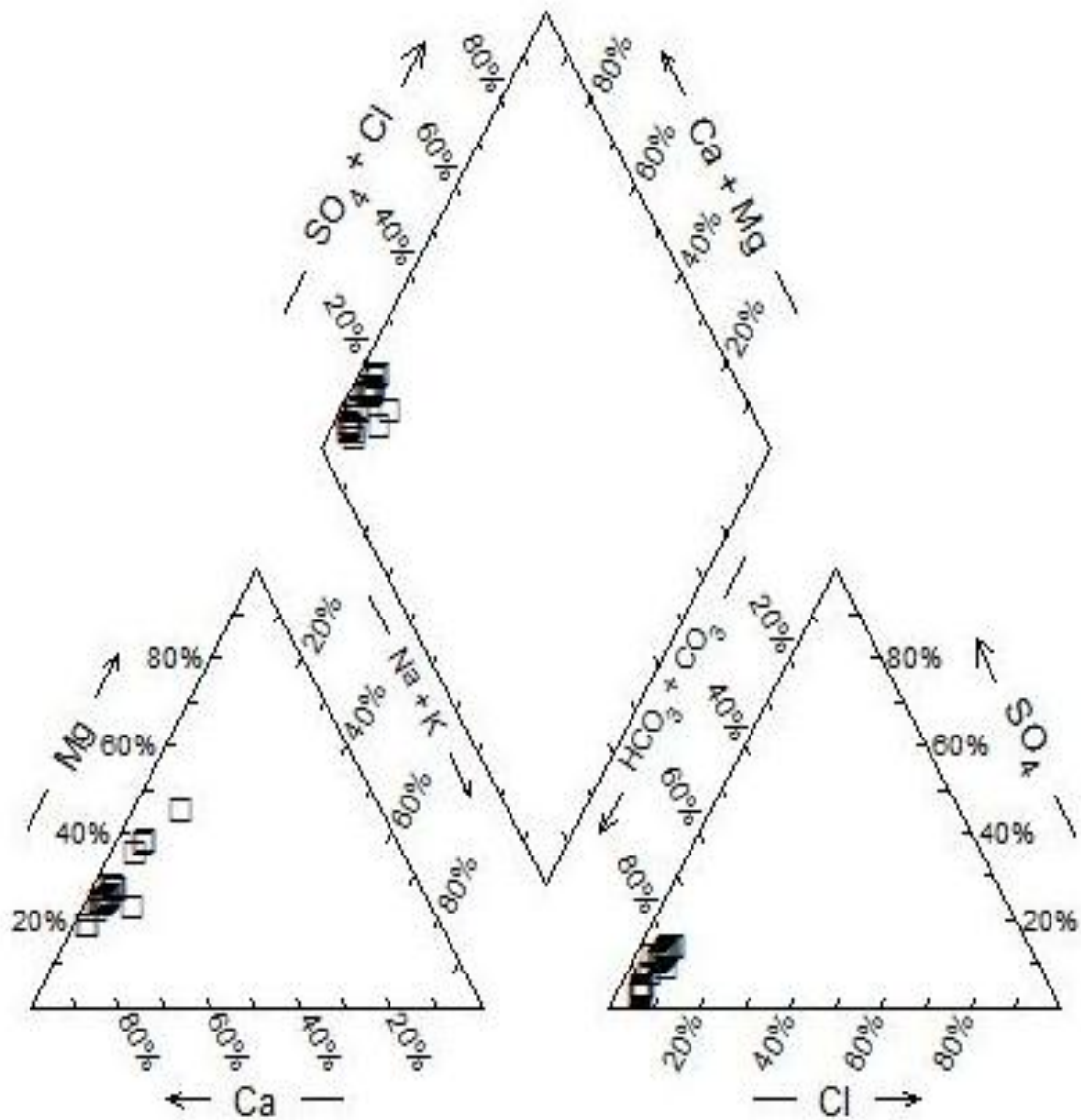
Figure 19. Relationship of nitrates with anions present in the Konza in ppm.

Hydrogeochemical source

Water analysis was performed for Kings Creek (Zone 1), N4D zone for surface water and groundwater from the wells located in N4D (Zone 2), surface water adjacent to Interstate 70 (Zone 3), and Shane Creek (Zone 4). A Piper diagram (Fig. 20) was used to establish the Konza hydrogeochemical variation of the stream water. The piper diagram was constructed using the Geochemist Workbench program in units of milliequivalents per liter (meq/L). This was done by using the ratio of atomic weight to valence, which is called equivalent weight. Meq/L units are equal to the concentration (mg/L) divided by the equivalent weight.

A Gibbs diagram was plotted (Fig. 21) to assist in determining the hydrogeochemical sources of waters within the zones. Total Dissolved Solids (TDS) calculated ranged from 355.92 to 489.99 mg/L with an average TDS of 412.47 mg/L of all the water. TDS was plotted against $\text{Na}/(\text{Na}+\text{Ca})$ to determine the origin of the major ions within the stream and groundwaters within the various zones (Fig. 21). The Results showed that well and N4D surface water samples (Zone 2), are likely from the dissolution of weathered rock material. Kings Creek surface water samples (Zone 1), were mostly derived from an evaporation-crystallization source.

Definitely the N4D surface and well waters are influenced by bedrock weathering. The bedrock in the N4D zones is comprised mostly of limestone and shale. When $\text{Na}/(\text{Na}+\text{Ca})$ are plotted against TDS, it shows that major ions in the streams and deeper wells have a large control from the content of bedrock weathering. The Kings Creek surface waters are more in the spread out ridges of the Konza (valleys) and are dominated by evaporation-crystallization processes. Dry climate evaporation (hot summer month average temperature of 90°F) and recrystallization of salts show very low $\text{Na}/(\text{Na}+\text{Ca})$ but other ions are of higher contribution.



Robin Mon Jul 22 2011

Figure 20. Piper diagram illustrating the presence of Ca-HCO₃ and to some extent SO₄ which reflects the sources and mixing of water is derived from the dissolution of limestone including, dolomite and gypsum (to some extent).

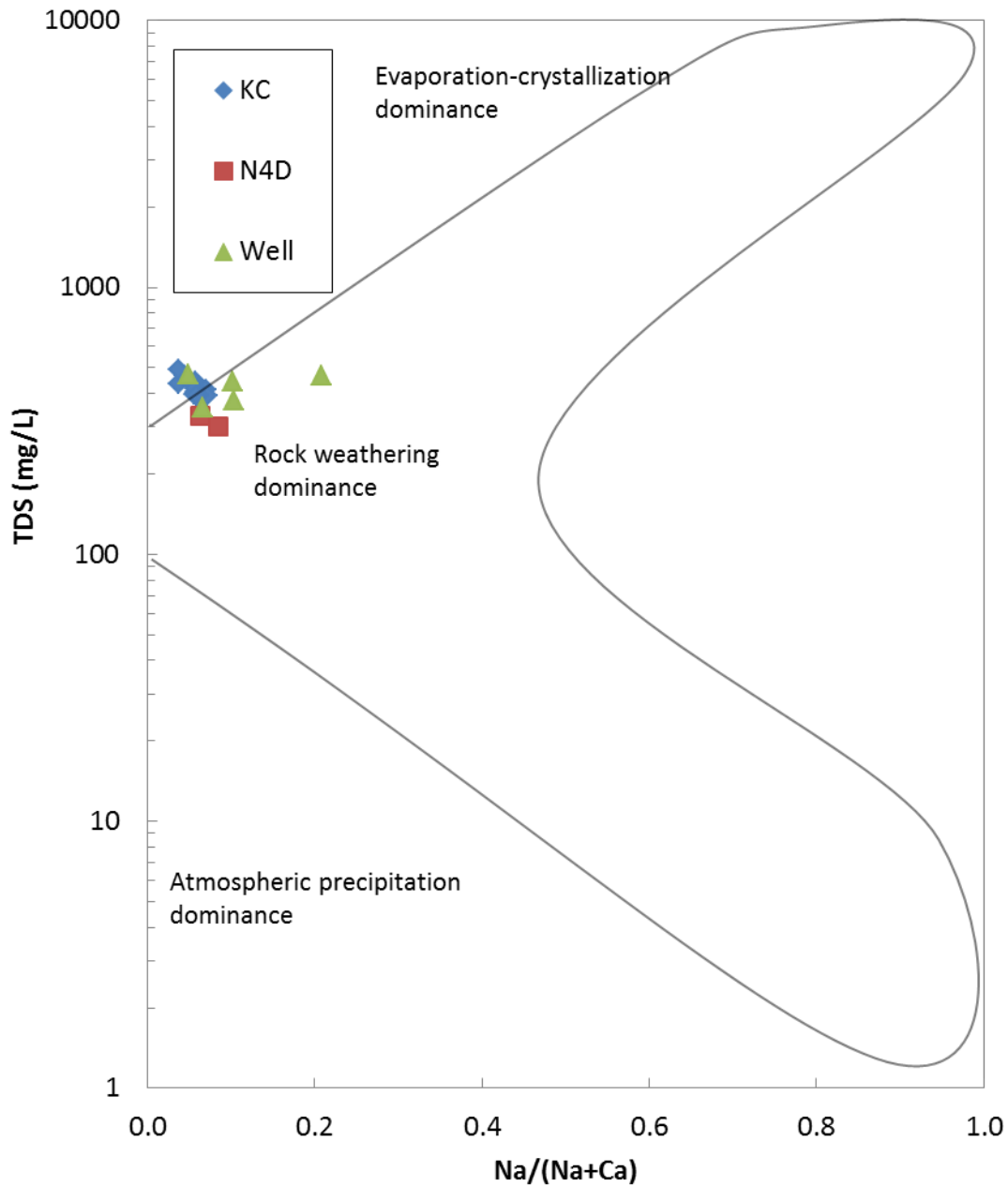


Figure 21. Gibbs Diagram (Guo et al. 2011) illustrates Na/(Na+Ca) plotted against Total Dissolved Sediments (TDS) to display the origin of Kings Creek (KC), Zone 1; and N4D surface and well water, Zone 2 – the three water types according to the hydrogeochemical source can be categorized under two sources a) rock weathering dominance b) evaporation-crystallization dominance.

Analysis of $\delta^{15}\text{N}$ of Water

Water samples used for $\delta^{15}\text{N}$ analysis, were derived from surface water and well water from all the zones. Water samples were taken from Kings Creek (KC), Zone 1; N4D well samples (Well), Zone 2; N4D surface water, Zone 2; stream adjacent to highway I-70 (I-70), Zone 3 and Shane Creek (SC), Zone 4. Groundwater samples from the wells within the N4D region (Zone 2), ranged from 0.07‰ – 6.13‰ in $\delta^{15}\text{N}$ value. Well samples were not enriched in $\delta^{15}\text{N}$ when compared to the $\delta^{15}\text{N}$ values of the analyzed surface waters. Well samples 1 and 2 analyzed for $\delta^{15}\text{N}$ had values of 3.98‰ and 4.78‰ respectively (Fig. 23), while the surface waters had a value range of 0.07‰ – 6.13‰ (Fig. 23). Generally the surface waters were more enriched in $\delta^{15}\text{N}$ relative to the well sample values. Figure 22 illustrates that the ranges of the well and surface water $\delta^{15}\text{N}$ values, indicate a soil (organic nitrogen) source for the N. As illustrated in Fig. 23, the differences between the two graphs indicate a smaller concentration of nitrate in groundwater when compared to surface water. However $\delta^{15}\text{N}$ values of both surface water and groundwater do not vary much. This reveals that denitrification took place in the well samples of Zone 2. Denitrification is noted as a process where nitrate levels decrease as $\delta^{15}\text{N}$ values are enriched (Townsend et al., 2003).

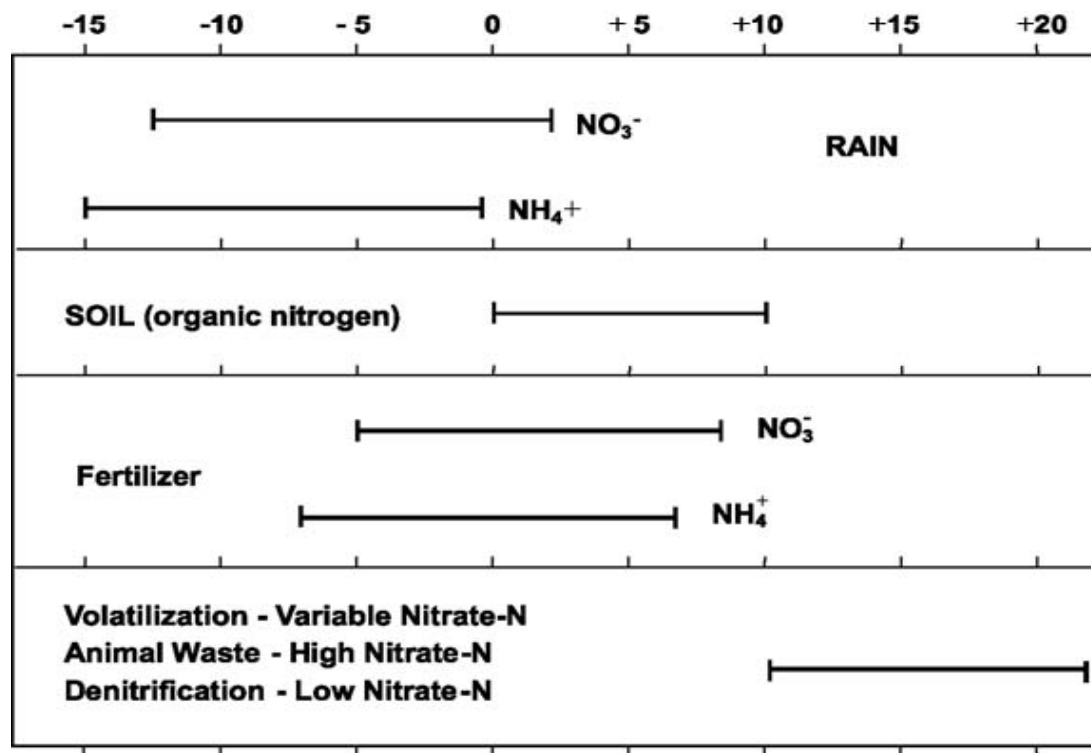


Figure 22. Ranges of $\delta^{15}\text{N}$ values associated with identified sources of groundwater nitrate and enrichment processes. Data from (Townsend et al., 1994; Townsend, 2001; Townsend et al., 2003).

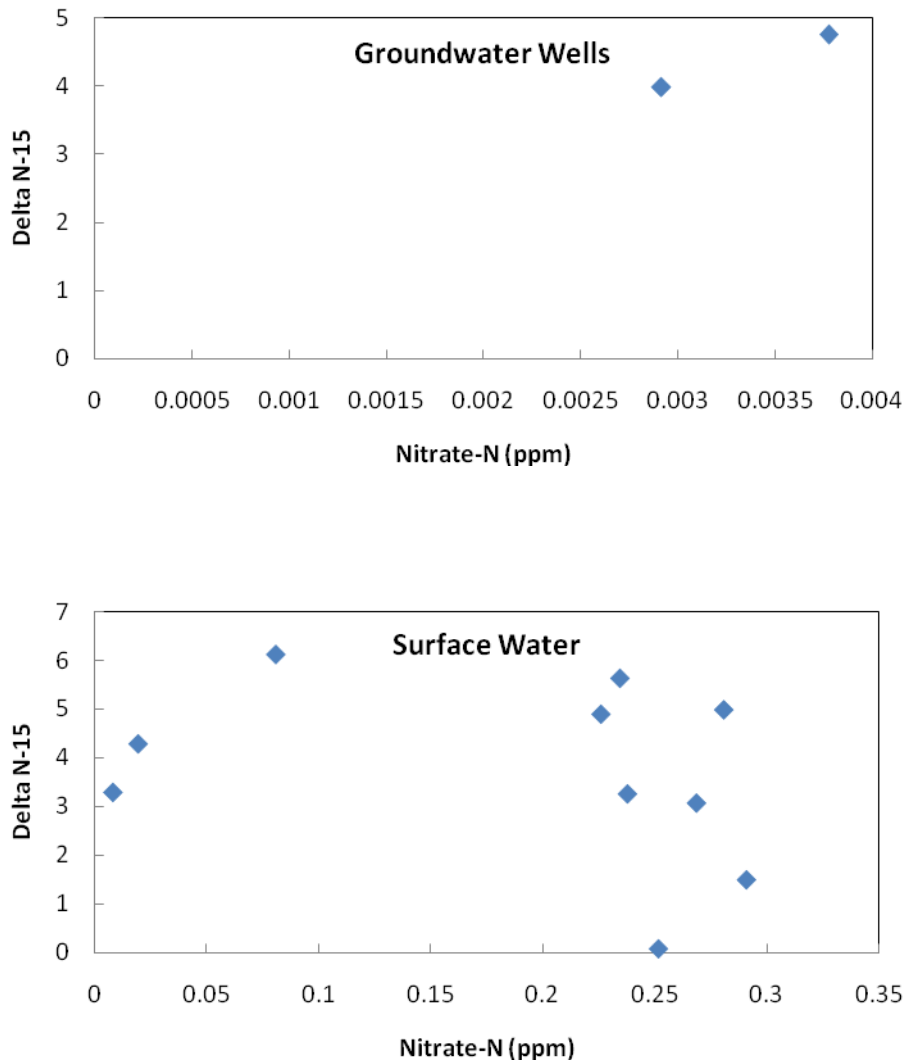


Figure 23. Graph of nitrate-N with $\delta^{15}\text{N}$ using groundwater and surface water.

δD and $\delta^{18}\text{O}$

Stable isotope values of δD and $\delta^{18}\text{O}$ of Kings Creek (KC), Zone 1; N4D well samples (Wells), Zone 2; surface water within N4D (N4D), Zone 2; surface water adjacent to I-70 (I-70), Zone 3 and Shane Creek (SC), Zone 4, all show a relationship (Fig. 24). There was a range from -5.74 to -5.34‰ with an average of -5.56‰ for $\delta^{18}\text{O}$ and -37.65 to -34.66‰ with an average of -35.84‰ for δD . Surface water plotted just below the GMWL except for N4D. Surface waters ranged from -5.70‰ to -5.34‰ for $\delta^{18}\text{O}$ and from -37.44‰ to -34.66‰, for δD , while N4D surface water within the location of the wells had values of -35.17‰ and -5.70‰ for δD and $\delta^{18}\text{O}$, respectively.

When δD was plotted against $\delta^{18}O$, the majority of the groundwater from the well fell below the GMWL, a bit farther than the surface water. δD values for well samples ranged from -37.65‰ to -35.84‰, and $\delta^{18}O$ values ranged from -5.74‰ to -5.36‰. It was also noticed that there was not much fractionation when it came to $\delta^{18}O$ values as compared to δD values. In figure 25 there are relatively no precipitation points close together as the well and water samples because the precipitation points fall closely along the Global Meteoric Water Line (GMWL). However precipitation points indicating warmer periods are closer to the sampled points, indicating a link to evapo-concentration which enriches $\delta^{18}O$.

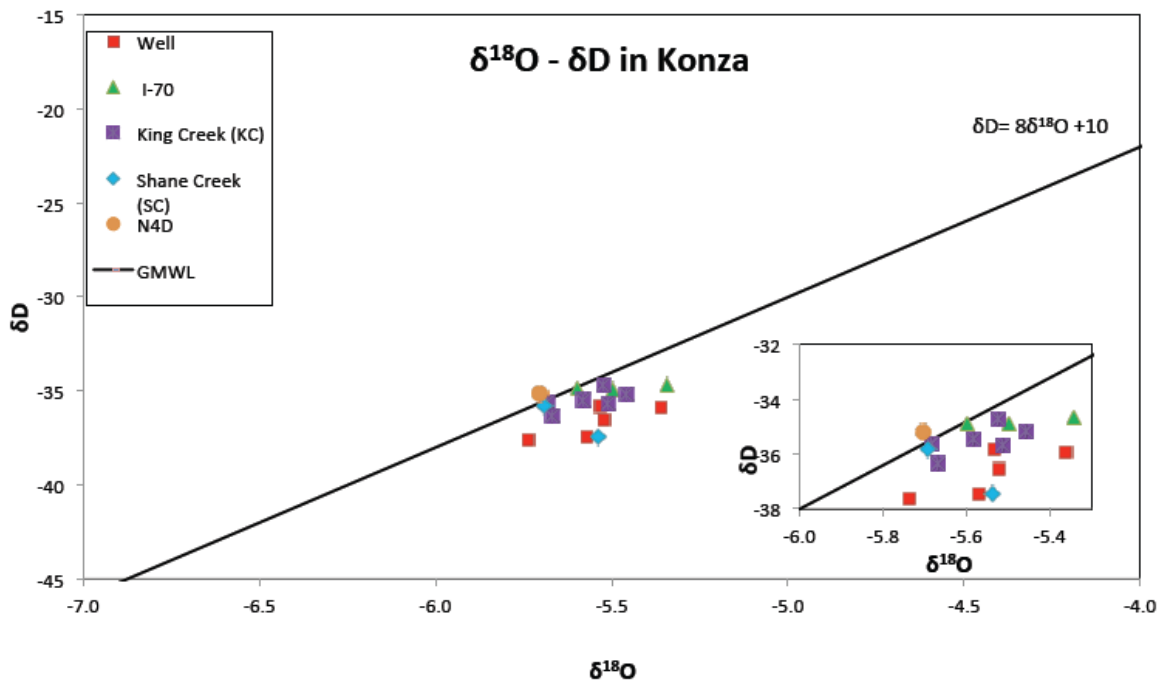


Figure 24. Stable isotope plots of δD and $\delta^{18}O$ calibrated to (Vienna-Standard Mean Ocean Water (V-SMOW) for Kings Creek (KC), Shane Creek (SC), I-70 (stream adjacent highway), N4D (section of Konza Prairie), and Well water from Konza Prairie. Global meteoric water line (GMWL) is shown with its slope-intercept equation. A zoomed in view of the sampled points is also shown.

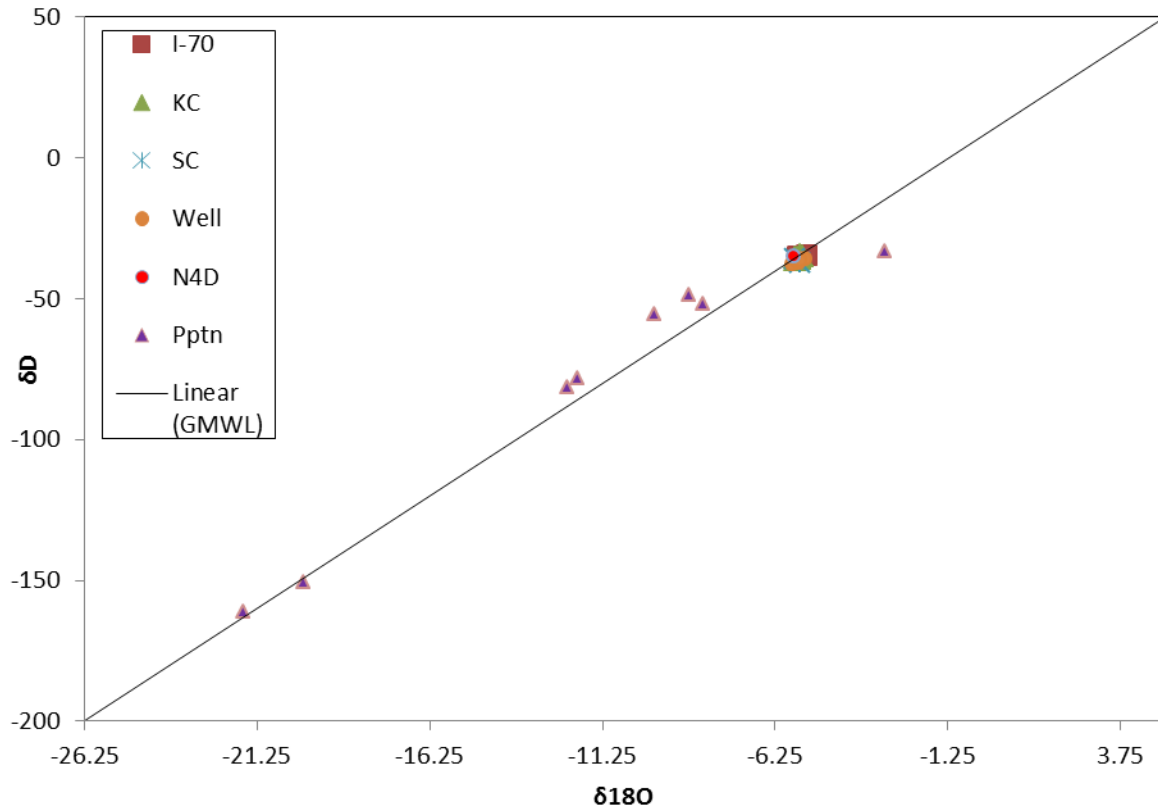


Figure 25. Stable isotope plots of δD and $\delta^{18}\text{O}$ water sample locations when compared to precipitation (pptn) analyzed during several periods of the year in the Konza Prairie with GMWL as standard.

Chapter 6 - Discussion

Sediment Geochemistry

Mineralogy of sediment cores

So if we divide the Konza (sampling locations) among the three zones we see the majority of minerals in Zone 1 are quartz, albite, calcite, muscovite, microcline, and smectite. Zone 2 major minerals are quartz, calcite, and smectite. Zone 3 major minerals consist of quartz, muscovite, albite, dolomite, and smectite.. Smectite was located in all the Zones that were sampled, within the Konza. The presence of clay mineral goes to depths of 6 feet from the surface of the sampling points. Clay minerals were within the upland regions (Zone 2), area containing deposits of alluvium and colluvium (Zone 1), and adjacent the stream valley beds containing Kings Creek (Zone 3). Dolomite was found in sample location Geop 2 (Zone 3), which indicated some displacement of calcium ions by magnesium ions. The magnesium ion is integrated within the crystal structure of the bedrock material made primarily of calcite minerals, and is eventually precipitated as magnesium-rich calcite. Dolomite is not present in the other sample locations or located in the northern part of the Konza Prairie.

Sample locations within Zone 1 and 3 are made of reworked sediments which have undergone extensive weathering and transportation of eroded material along flood plains (Oviatt, 1998). Sample locations Geop 9, (core 2 and core 4) and Geop 10 (core 2 and core 4) may contain traces of the smectite group clay mineral nontronite which is all but similar to montmorillonite except for the presence of iron (III) (Essington, 2003). The presence of iron (III) could have come from bedrock material in the northern part of the Konza. Well 2, well 4, well 5, KC 1 and stream 1 of the N4D section contained 0.02 mg/L of Fe (II) when sampled water was analyzed. Surface water with sample locations KC 3, 5, 6, 7, 8, 11, 13, and stream 2 of the N4D section all contained 0.01 mg/L of iron (II) in water. The well samples analyzed have significant amount of dissolved iron (II) which act as reducing agents of nitrates (Tang et al., 2004) thereby reducing nitrate amount within the groundwater and in the process becomes oxidized to iron (III) (Huang et al., 2004). Iron (II) ions are transported spatially throughout Zone 1 through streams and their minor tributaries. Groundwater could also play a part in this by the transportation of iron (II) through hyporheic zones (Hornberger et al., 1998). As dissolved iron (II) ions makes its way to sediments there is adhesion of the ions to the surface of the sediment which could also be triggered by the high pH of the water(Huang et al., 2004).

A wide variety of minerals are present within Zones 1 and 3 when compared to Zone 2 which likely indicates the extent of sediment accumulation. Mineralogical analyses via XRD show that Zone 2 has calcite, quartz, and smectite group clay minerals signifying the least extent of sediment accumulation since it is within an upland region. Zones 1 and 3 have the same minerals as Zone 2 including microcline, albite, dolomite, and muscovite. This indicates sediment accumulation within Zone 1 and 3 due to weathering and transportation. Microcline which is more resistant to weathering than albite (Essington, 2003) is present in Zone 1 but not in Zone 3 where geoprobe samples were taken. This likely indicates there might be more weathering and sediment accumulation in Zone 1 than in Zone 3.

Ammonium

The significant difference between Zone 1 and Zone 3 with regards to ammonium concentration within sediments, are highlighted below. The average total concentration of ammonium in all cores in Zone 1 and 3 are 63 mg/L and 50.3 mg/L, respectively. This is not the case for Zone 2, where NH_4 values in average reach 79.1 mg/L and hard bedrock layers close to the surface. The bedrock strata limited the number of sampling points and restricted further depth penetration with the hydraulic geoprobe. Organic matter within the sediment probably has a part of clay minerals that are negatively charged. The negative charge on the clay particles retains ammonium ions (NH_4^+) to balance it (Kendall, 1998). Retention of ammonium ions on clay particles prevents the ions from leaching. There is a continuous decrease in ammonium content as the cores penetrate deeper within the subsurface. The highest amount of ammonium was recorded within the surficial sediment, which is made up of colluvium and alluvium.

Nitrate

Nitrates, as found in this study, was on average 20 times less than ammonium. The average nitrate in sediment in all cores in Zone 1 and 3 are 5.6 mg/L and 3.3 mg/L, respectively. At Geop 5 sample location (Zone 2), the core liner could go no further in depth than 2 ft due to the presence of hard bedrock material. At sample point Geop 6 (Zone 2), core liners went no further than 4 ft within the subsurface. Slight increase in nitrate concentration within the sediment were present two feet deep beneath the surface. This trend was present in all the zones, and could be due to the leaching of nitrates with depth (Smith, 2010). At approximately 2 ft deep, after the slight increase of nitrate concentration within the zones, there is a steady decrease of nitrates. This is likely due to the uptake

of nitrates by plant roots (Dodds et al., 1996). According to the sediment sampled locations, there seems to be more available soil nitrogen within Zone 1 than in Zone 2

$\delta^{15}\text{N}$ of sediment

This study was carried out to compare the $\delta^{15}\text{N}$ of sediment to $\delta^{15}\text{N}$ of water and it was shown that $\delta^{15}\text{N}$ of sediment was within the range of 3.36‰ – 7.53‰. At two feet deep, the sediments ranged from 3.81‰ – 6.80‰ of $\delta^{15}\text{N}$.

In this study there was an enrichment of $\delta^{15}\text{N}$ with depth (~ 2 feet from the ground surface) at Zone 1, 2, and 3 (Geop 1, 4, 5, 9, and 10) as nitrate-N increased in amount simultaneously as ammonium-N concentration steadily decreased with depth. A chemical volatilization process of ammonium to ammonia may have occurred releasing N_2 and enrichment of $\delta^{15}\text{N}$ in the remaining ammonium because of fractionation processes (Kendall 1998, Townsend, 2003). Increased $\delta^{15}\text{N}$ values at depth for some of the cores also suggest that microbial action is impacting the nitrogen content of the soil and contributing to the observed increase in $\delta^{15}\text{N}$ values at these sample locations (Townsend, 2005).

There is some level of $\delta^{15}\text{N}$ depletion with depth ~ 2 feet at sample locations Zone 1, 2, and 3 (Geop 2, 3, 6, 7, and 8) coinciding with nitrate-N increase in concentration (but Geop 2 shows nitrate-N concentration decreases after 2 feet). But at Geop 2, the $\delta^{15}\text{N}$ value on the surface was 5.64‰ and two feet beneath the surface was 5.48‰ indicating very little fractionation must have taken place. The increase in nitrate and decrease in $\delta^{15}\text{N}$ values two feet within the subsurface was due to leaching of soluble nitrates (Parker et al., 1987; Perez et al., 2003), which could not be retained to negatively charged clay minerals. This subsequently caused a slight increase in nitrate-N concentration which is depleted in $\delta^{15}\text{N}$ when compared to ammonium isotopic signature (Kendall, 1998). At this depth ^{14}N mixes with ^{15}N resulting in the depletion of $\delta^{15}\text{N}$ values. It is also important to note that mixing of ^{14}N with ^{15}N isotope masses could also enrich $\delta^{15}\text{N}$ values depending on the extent of fractionation within sediments, which is difficult to interpret. The sediments analyzed for this study are generally enriched in $\delta^{13}\text{C}$ and depleted in $\delta^{15}\text{N}$, which is expected with C_4 plants (grasses and crops) and microbial utilization of nitrogen (Townsend and Macko, 2007).

$\delta^{13}\text{C}$ of sediment

The sediments that were analyzed for $\delta^{13}\text{C}$ indicated two pathways of photosynthesis among the plants, which are C_3 and C_4 . Most plants naturally follow the C_3 photosynthesis pathway and have depleted values of $\delta^{13}\text{C}$ (Kendall, 1998). The $\delta^{13}\text{C}$ range of C_3 type soils is between -22‰ and -30‰

(+/- 2‰). Trees, shrubs, cool-weather grasses, and crops are classified as C₃ and have $\delta^{13}\text{C}$ ranging from -20 to -32 ‰ with a mean of -27‰. The carbon isotope analyses of sediment within Zone 1, 2, and 3, reflect the prominence of C₄ type soils. Plants such as corn, sorghum, sugar cane, and warmer-weather grasses, are classified as C₄ plants and have a $\delta^{13}\text{C}$ range from -10 to -17‰, with an average of -12‰ (Townsend and Macko, 2007). The $\delta^{13}\text{C}$ value of sediment depends largely on the type of plant that grew on them. $\delta^{13}\text{C}$ values are depleted when C₃ plants are dominant, and enriched when C₄ plants are dominant.

In this study, analysis for $\delta^{13}\text{C}$ of sediment shows that all the Zones are made up of C₄ type soils except for fewer areas in Zone 1 (Geop 7 and 8) which have C₃ type soils, not more than 2 feet deep. C₄ type soil is confirmed by probably moderate amount of precipitation and a likely warm environment within the Konza. The presence of C₃ type soils within the Kings Creek (Zone 1) flood plain (See, J.H. and D.A. Bronk. 2005) may be due to shrubs within the area along the edges of the stream beds as flowing water proceeds to the Kansas River. In general, the soils collected for this study area were enriched in $\delta^{13}\text{C}$ and depleted in $\delta^{15}\text{N}$, which is expected with current C₄ plants (grasses and crops) and microbial utilization of nitrogen (Townsend, 2007). Flowing water from Zone 2 and other grazing regions SE of the Konza, do not contain a significant amount of high nitrogen and carbon content from bison waste. This signifies almost zero transport of N from bison waste through runoff (Dodds et al., 2002).

Water Chemistry

Anions and cations

The Piper diagram indicates that the water analyzed contains dissolved calcium and magnesium ions. Bicarbonate, sulfate, and chloride are also present. The mean amount of bicarbonate is 234 mg/L, sulfate is 20 mg/L, and chloride is 7 mg/L. The water chemistry in the aquifers at Konza is dominated by calcium and alkalinity (mostly bicarbonate), with the magnesium and sulfate content dependent upon host rock release (Gray et al., 1998). The combined concentration of magnesium, calcium, bicarbonate, and sulfate exceeded 50 % of the total dissolved constituent load in meq/L and as such, the water could be considered hard. The prominence of this group of ions indicates the presence of limestone bedrock, gypsum or anhydrite, and unconsolidated deposits containing abundant carbonate minerals. With TDS at an average of 412mg/L, the water within the Konza is considered fresh water.

The Gibbs hydro-geochemical diagram (Fig. 21), illustrates that the ion sources within runoff on the zones, originate from weathered rock material and evaporation- crystallization processes. The diagram also illustrates that Zone 2 goes through extensive weathering when compared to Zone 1. Zone 1 is generally made up of the remnants of dissolved ions after evaporation-crystallization of precipitate. This validates that Zone 2, which is within the upland region of the Konza, is a stream source. Zone 1 is located within catchment areas where streams flow downstream just as evaporation and precipitation take place. The process of evaporation-crystallization increases TDS within Zone 1 due to relative loss of moisture to the atmosphere.

$\delta^{15}\text{N}$ of water

Water analysis for $\delta^{15}\text{N}$ ranged from 0.07‰ – 6.13‰. This indicates that sediments are a source of nitrates to the streams and groundwater, since the sediments on average have higher $\delta^{15}\text{N}$ values (Townsend and Macko, 2007). It is possible that the chemistry of the water changes by mixing with lower pH water, causing ammonium to be nitrified to nitrate by bacteria resulting in the $\delta^{15}\text{N}$ signature being more enriched (Townsend and Macko, 2007).

Surface water samples

Previous work in Kansas shows that nitrate-N in commercial fertilizer sources have $\delta^{15}\text{N}$ values of -2 to +2‰; soil nitrogen has a range of +5 to +7‰; and animal waste generally has values greater than +10‰ (Townsend et al., 1996; and Townsend and Macko, 2007). There is no known information on the use of commercial fertilizer within the Konza and the results for the $\delta^{15}\text{N}$ analysis of water do not show values of +10‰ or more. This leaves the source of nitrates in water from the soil (organic nitrogen) and precipitation, which is validated by the $\delta^{15}\text{N}$ values which all fall between the general ranges of 0 - 9‰ and -12 to +2‰ respectively (Townsend, 2005).

Analyzed water samples have a pH range of 7.66 – 8.22, confirming the presence of bicarbonates and no carbon species of dissolved carbon dioxide. A high pH indicates the presence of bicarbonates, which release ammonia from ammonium via volatilization (Kendall, 1998; Townsend, 2003). Carbonates can increase the pH of water towards 8.5. In this range, nitrate can be converted to ammonia gas. The lighter ^{14}N isotope is released with the gas. The remaining nitrogen becomes enriched in $\delta^{15}\text{N}$.

Well water samples

Well water samples within the Zone 2 have low nitrate values which range from 0.004 – 0.025 mg/L compared to all sampled surface waters which range from 0.003 – 1.286 mg/L. But these

well samples are not enriched in $\delta^{15}\text{N}$ either when compared to the $\delta^{15}\text{N}$ values of the surface waters. Well samples 1 and 2, within Zone 2, had $\delta^{15}\text{N}$ values of 3.98‰ and 4.78‰ respectively, while the surface waters had a value range of 0.07 – 6.13‰. Generally the surface waters were more enriched in $\delta^{15}\text{N}$ compared to the well sample values. This analysis is contradictory to what was expected. The well samples contain significant amount of dissolved iron which range from 0.01 mg/L – 0.02 mg/L which could act as an oxidizing factor that subsequently depletes nitrate concentration within the groundwater. Additionally a process that usually results in an enriched $\delta^{15}\text{N}$ value is denitrification (Kendall, 1998; Townsend, 2003). During this process, bacteria degrades nitrate to nitrogen gases which is released to the atmosphere. The ^{14}N of the nitrate is preferentially utilized resulting in an enriched $\delta^{15}\text{N}$ occurring in the remaining nitrate. Indicators of possible denitrification are low nitrate values, enriched $\delta^{15}\text{N}$ values and high levels of bicarbonate, which is a byproduct of the denitrification process (Kendall, 1998).

As illustrated in Fig. 23, during this study, the differences between the two graphs indicate a smaller concentration of nitrate in groundwater when compared to surface water. However $\delta^{15}\text{N}$ values of both surface water and groundwater do not vary much. This reveals that denitrification is likely an ongoing process in the well samples of Zone 2.

Hydrogen and oxygen isotopes as indicators of groundwater recharge

Precipitation did not show any indication that it directly recharged the wells. Since 1991, water level measurements in the local limestone and alluvial aquifers of watershed N4D (Zone 2) show that the response of aquifers to recharge events as rainfall is uneven and presumably related to the frequency of rainfall events (Gray et al., 1998). Several periods of precipitation close together were more likely to affect recharge to the aquifers than an isolated rainfall, and significant recharge was less likely during the growing season because of extensive evapo-transpiration (Gray et al., 1998). In this study, there were no such periods of precipitation close together. However, precipitation points indicating warmer periods show closeness to both surface and well water points indicating a link to evapo-concentration which enriches $\delta^{18}\text{O}$.

Overall, plots of $\delta^{18}\text{O}$ versus δD for the water samples showed a significant degree of enrichment due to moderate evaporation effect, with δD and $\delta^{18}\text{O}$ values plotted below the GMWL. Surface water samples had slight evaporative enrichment from the GMWL since they were chiefly fed by precipitation except for Shane Creek (SC) sample 1 (Zone 4). This one exception showed a fair amount of evaporative enrichment which indicated slightly more evaporation than groundwater. This may be due to low discharge rates compared to Kings Creek.

The $\delta^{18}\text{O}$ and δD values for the majority of groundwaters fell below the GMWL, mainly in the range of -5.74 to -5.36‰ and -37.65 to -35.84‰ respectively. Surface waters also plotted just below the GMWL, illustrating that these waters were affected by evaporation, but were not as enriched as the well samples. The $\delta^{18}\text{O}$ and δD values of the surface water range from -5.70 to -5.34‰ and -37.44 to -34.66‰ respectively. The wells are slightly more enriched than the majority of the surface waters sampled, suggesting continuous recharge from the stream valleys and hyporheic zones, where stream and groundwater mixed. This also indicates that not much fractionation takes place within the limestone aquifer since ^{18}O was not incorporated within the calcite mineral structure which would deplete the water within the aquifer of $\delta^{18}\text{O}$. Surface water normally makes its way to limestone aquifers through fractures and joints in a lateral and downward direction, which makes its travel time slower than alluvial aquifers (Macpherson, 2008). Alluvial aquifers take in water sometimes faster than the formation of a stream, since water moves downwards through sediment pores (Gray et al., 1998). It will be plausible to believe that the well waters sampled were slightly younger than the surface waters. This is a conjecture because the standard deviation for $\delta^{18}\text{O}$ values used in this study is 0.11 and it is 0.96 for δD , suggesting more variation of data with δD values and not much differentiation with $\delta^{18}\text{O}$ values for the water samples analyzed. These values indicate enrichment of water samples due to low flow rates of some of the surface waters and well samples. Since groundwater shows a significant amount of evaporative enrichment, it is possible to believe groundwater or well water had a significant contribution of recharge from the surface water in this study.

Chapter 7 - Conclusions

Sediment

From this study we conclude that different processes take place within the Zones, within Konza which is reflected in the spatial variation of sediment $\delta^{15}\text{N}$ values as related to various minerals present within the sampled zones. Some of these processes include denitrification and mixing of $\delta^{15}\text{N}$ values. The mixing of $\delta^{15}\text{N}$ of ammonium and nitrate sediment values, cause spatial variation within Zones 1, 2, and 3, in Konza. In this study it was found that there was an enrichment of $\delta^{15}\text{N}$ with depth (~ 2 feet from the ground surface) at Zone 1, 2, and 3, as nitrate-N increased in amount simultaneously as ammonium-N concentration steadily decreased with depth. A chemical volatilization process of ammonium to ammonia may have occurred causing a release of nitrogen gas (denitrification) and enrichment of $\delta^{15}\text{N}$ in the remaining ammonium due to fractionation processes (Kendell, 1998; Townsend, 2003). There is also some level of $\delta^{15}\text{N}$ depletion with depth ~ 2 feet at Zone 1, 2, and 3 coinciding with nitrate-N increase in concentration except for sample Geop 2 (Zone 1) whose nitrate-N concentration decreases after 2 feet.

A wide variety of minerals are present within Zones 1 and 3 when compared to Zone 2 (upland ridge), which likely indicates the extent of sediment accumulation. XRD mineralogical analyses show that Zone 2 has calcite, quartz, and smectite group clay minerals signifying the least extent of sediment accumulation since it is within an upland region, where sediment transportation originates. Zones 1 and 3 have the same minerals as Zone 2 but also microcline, albite, dolomite, and muscovite. This indicates sediment accumulation within Zones 1 and 3 due to weathering and transportation with the aid of runoff.

Analysis for $\delta^{13}\text{C}$ of sediment concludes that most of our studied zones are made up of C_4 type soils except for fewer areas in Zone 1 (Geop 8 and 7) which have C_3 type soils not more than 2 feet deep. The presence of C_3 type soils within the Kings Creek (Zone 1) flood plain may be due to the presence of shrubs. This is also indicated by the moderate amount of precipitation within the Konza, which supports the prevalence of C_4 type soil. In general, the soils collected for this study area were enriched in $\delta^{13}\text{C}$ and depleted in $\delta^{15}\text{N}$, which is expected with current C_4 plants (grasses and crops) and microbial utilization of nitrogen (Townsend, 2007).

Nitrate concentration and $\delta^{15}\text{N}$ values of surface and well water from the sampled points of Zone 1, 2, 3, and 4; indicate an origin from soil (organic nitrogen). $\delta^{15}\text{N}$ values from surface and well water are generally less than the $\delta^{15}\text{N}$ values of the sediment within the aforementioned Zones in Konza. There is a general low content of nitrates in the deeper wells due to the reduction of nitrates (denitrification) when compared to surface water. And there is also no significant difference between a grazing zone (Zone 2) and a non-grazing zone (Zone 1) within the Konza in this study, in terms of variation in nitrate concentration.

In conclusion, it was shown that rock weathering and evaporation – crystallization dominance are the primary source of dissolved ions in the sampled zones. They are mostly of bicarbonate type water, indicating the dominance of alkalinity (mostly bicarbonates) with some amount of calcium, magnesium, and sulfate. The rocks weathered consist of limestone, rock gypsum or anhydrite, and dolomite. The mean Total Dissolved Solids (TDS) of Zone 1, 2, 3, and 4 is 412 mg/L which classifies the water as fresh water.

Surface water and well waters have similar isotope signatures with regards to δD and $\delta^{18}\text{O}$, varying widely from precipitation. Well waters were slightly more enriched in ^{18}O than surface water, indicating that well waters are recharged with evapo-concentrated surface water, with little to no input from precipitation directly except as a transport medium via flowing water. This corroborates the prevalence of C_4 type soil, using $\delta^{13}\text{C}$ stable isotope analysis indicating moderate precipitation. However precipitation points indicating warmer periods show closeness to both surface and well water points indicating a link to evapo-concentration which enriches $\delta^{18}\text{O}$.

References

- Berner, E. and R. Berner. 1987. *The Global Water Cycle*, Prentice Hall, New Jersey. p. 102-119.
- Chang, R. 2001. *Chemistry*. McGraw-Hill Science/Engineering/Math; 7th edition
- Comly, H. H. 1987. Cyanosis in Infants Caused by Nitrates in Well Water. *Journal of the American Medical Association*. 257, 2788-2792.
- Datta, P.S., Deb, D.L., Tyagi, S.K. 1997. Assessment of groundwater contamination from fertilizers in the Delhi area based on ^{18}O , NO_3^- and K^+ composition. *Journal of Contaminant Hydrology*. 27, 249-262.
- deNoyelles, F., Jakubauskas, M. 2008. Current State, Trend, and Spatial Variability of sediment in Kansas Reservoirs. *Sedimentation in Our Reservoirs: Causes and Solutions*. 9-25.
- Dodds, W.K., Blair, J.M., Henebry, G.M., Koelliker, J.K., Ramundo, R., Tate, C.M. 1996. Water Quality: Nitrogen transport from tallgrass prairie watersheds. *J. Environ. Qual.* 25, 973-981.
- Dodds, W.K., Lopez, A.J., Bowden, W.B., Gregory, S., Grimm, N.B., Hamilton, S.K., Hershey, A.E., Marti, E., McDowell, W.H., Meyer, J.L., Morrall, D., Mulholland, P.J., Peterson, B.J., Tank, J.L., Valett, H.M., Webster, J.R., Wollheim, W. 2002. N uptake as a function of concentration in streams. *The North American Benthological Society*. 21(2), 206-220.
- Essington, M.E. 2003. *Soil and Water Chemistry: An integrative approach*. CRC Press; 1st edition.
- Finley, B. 1990. Well-water Nitrates Endanger N. Colorado, Denver (Colorado) Post, 16 November.
- Gray, L.G., Macpherson, G.L., Koelliker, J.K., Dodds, W.K. 1998. Hydrology and aquatic chemistry. Pages 159-176 in A.K. Knapp, J.M. Briggs, D.C. Hartnett and S.L. Collins, editors. *Grassland Dynamics: Long-term Ecological Research in Tallgrass Prairie*. Oxford University Press, New York.
- Guo, H., Zhang, Y., Xing, L., Jia, Y. 2011. Spatial variation in As and F^- concentrations of shallow groundwater from the Shahai town of the Hetao basin, Inner Mongolia. *School of Water Resources and Environment*. China University of Geosciences, Beijing.
- Gustafson, D. I., 1993, *Pesticides in Drinking Water*. VanHostrand Reinhold, New York, p. 241.
- Hamilton, P.A., Helsel, D.R. 1995. Effects of Agriculture on Groundwater Quality in 5 Regions of the United States. *Groundwater*. 33(2), 217-226.
- Harrison, J.A. 2003. *The Nitrogen Cycle: Of Microbes and Men*. Visionlearning .Vol. EAS-2 (4).

(http://www.visionlearning.com/library/module_viewer.php?mid=98)

- Holloway, J.M. and R.A. Dahlgren. 2002. Nitrogen in rock: Occurrences and biogeochemical implications. *Global Biogeochemical Cycles*. 16(4), 1-17.
- Holloway, J.M., Dahlgren, R.A., Casey, W.H. 2001. Nitrogen release from rock and soil under simulated field conditions. *Chemical Geology*. 174, 403-414.
- Holloway, J.M., Dahlgren, R.A., Hansen, B., Casey, W.H. 1998. Contribution of bedrock nitrogen to high nitrate concentrations in stream water. *Nature*. 395, 785-788.
- Hornberger, G.M., Raffensperger, J.P., Wiberg, P.L., Eshleman, K.N. 1998. *Elements of Physical Hydrology*. The Johns Hopkins University Press
- Howarth, R.W. 2004. Human acceleration of the nitrogen cycle: drivers, consequences, and steps toward solutions. *Water Science Technology*. 49, 7-13.
- Huang, Y.H. and T.C. Zhang. 2004. Effects of low pH on nitrate reduction by iron powder. *Water Research*. 38, 2631-2642.
- Hudak, P.F. 2000. Regional trends in nitrate content of Texas groundwater. *Journal of Hydrology*. 228, 37-47.
- Johnson, C. J., Bonrud, P. A., Dosch, T. L., Kilness, A. W., Senger, K. A., Busch, D. C., and Meyer, M. R. 1987. Fatal Outcome of Methemoglobinemia in an Infant. *Journal of the American Medical Association*. 257, 796-2797.
- Kemp, M.J. and W.K. Dodds. 2002. Comparisons of Nitrification and Denitrification in Prairie and Agriculturally Influenced Streams. *Ecological Applications*. 4, 998-1009.
- Kemp, M.J. and W.K. Dodds. 2001. Spatial and temporal patterns of nitrogen concentrations in pristine and agriculturally-influenced prairie streams. *Biogeochemistry* 53, 125-141.
- Kemp, M.J. and W.K. Dodds. 2002. The influence of ammonium, nitrate, and dissolved oxygen concentrations on uptake, nitrification, and denitrification rates associated with prairie stream substrata. *Limnol. Oceanogr.* 47(5), 1380-1393.
- Kendall, C. 1998. *Isotope Tracers in Catchment Hydrology*. Elsevier Science B.V., Amsterdam. pp. 519-576.
- Kennedy, C.D., Genereux, D.P., Corbett, D.R., et al. 2009. Spatial and temporal dynamics of coupled groundwater and nitrogen fluxes through a streambed in an agricultural watershed. *Water Resources Research*. 45, W09401.
- Kerr-Upal, M., Seters, T.V., Whitehead, G., Price, J., Stone, M. 1999. Assessing the risk of groundwater nitrate contamination in the region of Waterloo, Ontario. *Canadian Water*

- Resources Journal. 24, 225-233.
- Keskin, T.E. 2010. Nitrate and heavy metal pollution resulting from agricultural activity: a case study from Eskipazar (Karabuk, Turkey). *Environ. Earth. Sci.* 61, 703-721.
- Koh, D., Chang, H., Lee, K., Ko, S., Kim, Y., Park, W. 2005. Hydrogeochemistry and environmental isotopes of ground water in Jeju volcanic island, Korea: implications for nitrate contamination. *Hydrological Processes*. John Wiley & Sons Ltd.
- Kowalenko, C.G. 2006. Evaluation of hot KCl extraction as an index of mineralizable N: Ammonium and ultraviolet absorption measurements. *Canadian Journal of Soil Science*. 86, 911-920.
- Laima, M.C.J. 1993. Recovery of $^{15}\text{NH}_4^+$ in labeling experiments on coastal marine sediments. *Marine Chemistry*. 44, 31-42.
- Macpherson, G.L. and M. Sophocleous. 2004. Fast ground-water mixing and basal recharge in an unconfined, alluvial aquifer, Konza LTER Site, Northeastern Kansas. *Journal of Hydrology*. 286, 271-299.
- Macpherson, G.L. Hydrogeology of thin limestones: the Konza Prairie Long-Term Ecological Research Site, Northeastern Kansas. 1996. *Journal of Hydrology*. 186, 191-228.
- Macpherson, G.L., Roberts, J.A., Blair, J.M., Townsend, M.A., Fowle, D.A., Beisner, K.R. 2008. Increasing shallow groundwater CO_2 and limestone weathering, Konza Prairie, USA. *Geochimica et Cosmochimica Acta*. 72, 5561-5599.
- Magette, W.L., Weismiller, R.A., Angle, J.S., Brinsfield, R.B. 1989. A nitrate groundwater standard for the 1990 farm bill. *Journal of Soil and Water Conservation*. 491-494.
- Mattern, S., Fasbender, D., Vanclooster, M. 2009. Discriminating sources of nitrate pollution in an unconfined sandy aquifer. *Journal of Hydrology*. 376, 275-284.
- Nebel, J.B., and Wright R.T. 1999. *Environmental Science: The way the world works*. Prentice Hall College Div; 7th edition
- Nielsen, J.L. and P.H. Nielsen. 1998. Microbial nitrate-dependent oxidation of ferrous iron in activated sludge. *Environ. Sci. Technol.* 32, 3556-3561.
- O'Brien, J.M. and W.K. Dodds. 2010. Saturation of NO_3^- uptake in prairie streams as a function of acute and chronic N exposure. *J. N. Am. Benthol. Soc.* 29(2), 627-635.
- O'Brien, J.M., Dodds, W.K., Wilson, K.C., Murdock, J.N., Eichmiller, J. 2007. The saturation of N cycling in Central Plains streams: ^{15}N experiments across a broad gradient of nitrate concentrations. *Biogeochemistry*. 84, 31-49.

- Oviatt, C.G. 1998. Geomorphology of the Konza Prairie. Pages 35-47 in A.K. Knapp, J.M. Briggs, D.C. Hartnett and S.L. Collins, editors. *Grassland Dynamics: Long-term Ecological Research in Tallgrass Prairie*. Oxford University Press, New York.
- Parker, J.M., Booth, S.K., Foster, S.S.D. 1987. Penetration of nitrate from agricultural soils into the groundwater of the Norfolk Chalk. *Proc. Instn Civ. Engrs, Part 2*. 83, 15-32.
- Perez, J.M.S., Antiguada, I., Arrate, I., Garcia-Linares, C., Morell, I. 2003. The influence of nitrate leaching through unsaturated soil on groundwater pollution in an agricultural area of the Basque country: A case study. *The Science of the Total Environment*. 317, 173-187.
- Ridder, W.E., Oehme, F.W., Kelley, D.C. 1974. Nitrates in Kansas groundwaters as related to animal and human health. *Toxicology*. 397-405.
- Robinson, D. 2001. $\delta^{15}\text{N}$ as an integrator of the nitrogen cycle. *TRENDS in Ecology & Evolution*. 16, 153-162.
- Ross, K.L. 1995. Geomorphology of the N4D watershed, Konza Prairie Research Natural Area, Riley and Geary Counties, Kansas. MS thesis, Kansas State University. 60 pp.
- Savard, M.M., Begin, C., Smirnoff, A. 2009. Tree-ring nitrogen isotopes reflect anthropogenic NO_x emissions and climatic effects. *Environ. Sci. Technol.* 43, 604-609.
- See, J.H. and D.A. Bronk. 2005. Changes in C:N ratios and chemical structures of estuarine humic substances during aging. *Marine Chemistry*. 97, 334-346.
- Smith, G.N. 1991. Geomorphology and geomorphic history of the Konza Prairie Research Natural Area, Riley and Geary Counties, Kansas. MS thesis, Kansas State University. 121 pp.
- Smith, J.G. 2010. *Organic Chemistry*. McGraw-Hill Science/Engineering/Math; 3rd edition.
- Sophocleous, M. and R.C. Buchanan. 2003. Ground-water recharge in Kansas. *KGS Pub. Inf. Circ.* 22.
- Sophocleous, M.A., Townsend, M.A., Willson, T., Vocasek, F., and Zupancic, J., 2006. Fate of Nitrate beneath Fields Irrigated with Treated Wastewater in Ford County, Kansas: Kansas Water Research Institute First-Year Progress Report, Kansas geological Survey, Open-File Report.
- Tang, C., Azuma, K., Iwami, Y., Ohji, B., Sakura, Y. 2004. Nitrate behavior in the groundwater of a headwater wetland, Chiba, Japan. *Hydrological Processes*. 18, 3159-3168.
- Tor, J.M., Xu, C., Stucki, J.M., Wander, M.M., Sims, G.K. 2000. Trifluralin degradation under microbiologically induced nitrate and Fe(III) reducing conditions. *Environ. Sci. Technol.* 34, 3148-3152.

- Townsend, M.A. 2005. Sources of nitrate at McPherson County feeders, McPherson County, Kansas. Kansas Geological Survey Open-file Report.
- Townsend, M.A. 2007. Use of the nitrogen-15 natural abundance method and other chemical tracers to identify nitrate sources at Lincolnville, Kansas. Kansas Geological Survey Open-file Report.
- Townsend, M.A. 2008. Use of the nitrogen-15 natural abundance method to identify potential sources of nitrate-N contamination in ground water utilized by rural Water District #7, Leavenworth County, Kansas. Kansas Geological Survey Open-file Report.
- Townsend, M.A. and D.P. Young. 1999. Nitrate in Kansas Ground Water. KGS Pub. Inf. Circ. 14.
- Townsend, M.A., and Macko, S.A., 2007. Preliminary identification of groundwater nitrate sources using nitrogen and carbon stable isotopes, Kansas: Kansas Geological Survey, Current Research in Earth Sciences, Bulletin 253, part 3, 11p.
- Wankel, S.D., Kendall, C., Paytan, A. 2009. Using nitrate dual isotopic composition ($\delta N-15$ and $\delta O-18$) as a tool for exploring sources and cycling of nitrate in an estuarine system: Elkhorn Slough, California. *Journal of Geophysical Research-Biogeosciences*, 114.

Appendix A - Water Analyses

This section contains general data for water samples and results from laboratory analyses.

Water Chemistry Data/ Table 1

General data for water samples collected from April 2010 to July 2011 (continued on next page).

Sample ID	longitude (W) degree (°)	latitude (N) degree (°)	F mg/L	Cl mg/L	NO ₃ mg/L	NO ₃ -N mg/L	SO ₄ mg/L	HCO ₃ mg/L
KC-1	96.607279	39.108327	0.367	11.531	0.151	0.034	31.705	245
KC-2	96.60672	39.107036	0.343	10.976	0.010	0.002	32.406	230
KC-3	96.606019	39.105862	0.345	10.279	0.031	0.007	31.144	247
KC-4	96.606696	39.102127	0.393	9.900	0.018	0.004	20.770	292
KC-5	96.607174	39.09941	0.394	10.392	0.027	0.006	31.429	225
KC-6	96.610454	39.114702	0.270	10.319	0.013	0.003	13.374	298
KC-7	96.583617	39.101417	0.321	10.640	0.008	0.002	29.433	252
KC-8	96.592375	39.101529	0.313	10.233	0.321	0.073	28.748	235
KC-9	96.592536	39.101529	0.362	9.929	0.007	0.002	26.120	230
KC-10	96.594146	39.101635	0.335	10.138	0.003	0.001	26.605	245
KC-11	96.594677	39.103375	0.357	9.787	0.111	0.025	27.119	250
KC-12	96.59547	39.103832	0.345	10.001	0.084	0.019	26.387	265
KC-13	96.595971	39.103603	0.399	9.575	0.052	0.012	7.771	270
KC-14	96.596743	39.103565	0.512	7.573	0.006	0.001	9.994	250
KC-15	96.599564	39.103004	0.303	8.830	0.032	0.007	16.495	240
Str 1 (N4D)	96.583106	39.085644	0.382	10.385	0.356	0.081	25.673	185
Str 2 (N4D)	96.58291	39.084811	0.313	10.629	0.034	0.008	16.990	190
3-5 Mor (Well 1)	96.58326	39.08549	0.364	7.295	0.013	0.003	5.942	230
3-5-1 Mor (Well 2)	96.58358	39.084877	0.352	9.792	0.017	0.004	5.779	250
4-6 Eis 2 (Well 3)	96.583609	39.08474	0.361	10.384	0.016	0.004	13.533	330
4-6 Eis 1 (Well 4)	96.583609	39.08474	0.386	9.043	0.004	0.001	37.379	334
4-6 Mor (Well 5)	96.583609	39.08474	0.377	10.607	0.025	0.006	14.078	337
Str 3 (KC)	96.610583	39.114983	0.622	1.435	1.241	0.282	20.469	210
Str 4 (KC)	96.60675	39.1071	0.414	1.358	1.036	0.235	19.517	206
Str 5 (KC)	96.6073	39.099333	0.405	1.288	1.051	0.239	9.508	230
Str 6 (KC)	96.595483	39.103767	0.435	1.262	1.187	0.270	18.757	214
Str 7 (KC)	96.592883	39.101433	0.439	1.299	1.286	0.292	18.482	204
Str 8 (SC)	96.559233	39.10895	0.370	1.047	1.112	0.253	14.851	222
	longitude (W)	latitude (N)	F	Cl	NO ₃	NO ₃ -N	SO ₄	HCO ₃

Sample ID	degree (°)	degree (°)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Str 9 (I-70)	96.568944	39.065806	0.450	0.709	0.999	0.227	11.404	118
I70-2	96.578022	39.068007	0.629	4.015	1.236	0.281	6.990	114
I70-3	96.599027	39.067572	0.620	16.988	1.250	0.284	19.915	159
SC 4	96.562814	39.106288	0.437	0.860	1.019	0.232	8.067	146
N4D 2	96.584771	39.088327	0.433	1.139	0.865	0.197	14.641	235
N4D 6	96.589449	39.089813	0.437	1.257	0.822	0.187	20.253	265

Str: Stream

KC: Kings Creek

SC: Shane Creek

Cations/ Table 2

Sample ID	Mg (mg/L)	Ca (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	Fe (mg/L)	S (mg/L)
KC-1	19.2	91.5	5.6	20.9	6.3	0.02	12
KC-2	19.4	89.1	5.7	1.3	6.4	0	12
KC-3	19.0	88.0	5.7	1.6	6.4	0.01	11
KC-4	20.8	102	4.8	1.2	6.9	0	8
KC-5	18.9	126	4.9	2.2	7.8	0.01	9
KC-6	18.4	126	4.8	2.1	7.7	0.01	9
KC-7	18.8	77.7	5.9	1.5	6.4	0.01	10
KC-8	18.3	75.6	5.8	1.2	6.3	0.01	11
KC-9	17.7	89.0	5.2	1.2	6.4	0	10
KC-10	18.0	83.2	5.1	1.2	6.5	0	10
KC-11	18.0	87.1	5.4	1.3	6.5	0.01	10
KC-12	18.1	92.5	5.2	1.3	6.3	0	10
KC-13	18.0	90.1	5.5	1.3	6.4	0.01	10
KC-14	18.4	82.2	5.4	1.4	6.5	0	10
KC-15	18.3	86.8	5.4	1.4	6.6	0	10
Str 1 (N4D)	17.6	70.8	4.8	1.3	5.6	0.02	7
Str 2 (N4D)	17.7	48.9	4.5	1.1	5.6	0.01	6
3-5 Mor (Well 1)	18.3	76.7	5.4	1.0	5.9	0.01	5
3-5-1 Mor (Well 2)	24.6	58.5	6.7	1.4	5.7	0.02	13
4-6 Eis 2 (Well 3)	16.0	88.2	4.5	0.8	5.0	0	5
4-6 Eis 1 (Well 4)	23.1	37.3	9.8	1.2	6.2	0.02	9
4-6 Mor (Well 5)	17.8	44.2	5.0	1.0	5.7	0.02	6

Str: Stream

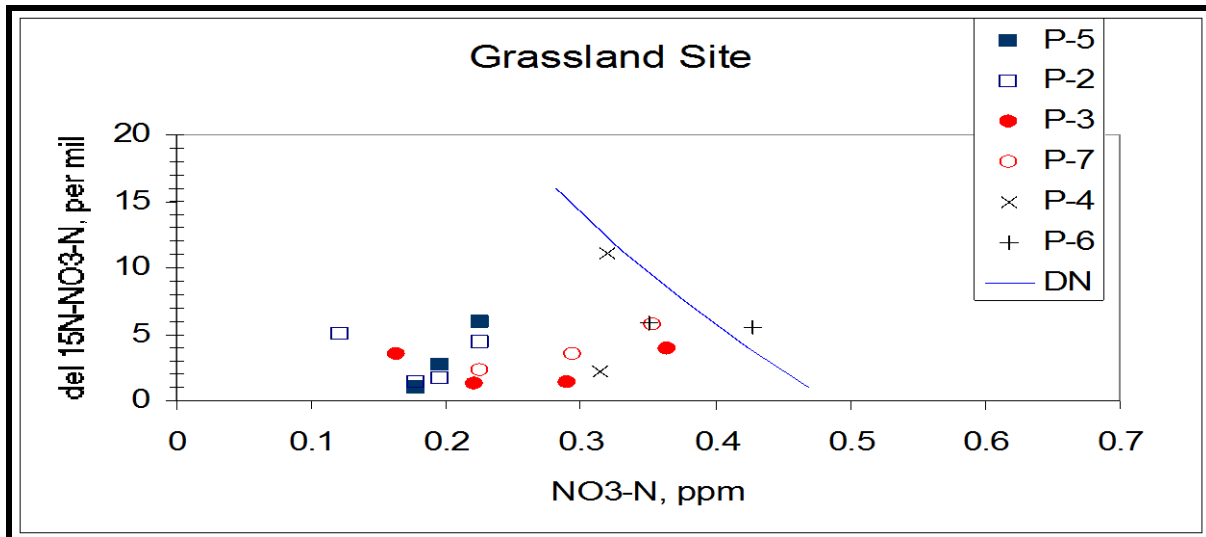
KC: Kings Creek

TDS of water samples/ Table 3

Sample ID	F (mg/L)	Cl (mg/L)	NO3 (mg/L)	SO ₄ (mg/L)	HCO ₃ (mg/L)	Mg (mg/L)	Ca (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	Fe (mg/L)	S (mg/L)	Na/(Na+Ca) (mg/L)	TDS (mg/L)
KC-1	0.4	11.5	0.2	31.7	245	19.2	91.5	5.6	20.9	6.3	0.02	12	0.058	444.3
KC-2	0.3	11.0	0	32.4	230	19.4	89.1	5.7	1.3	6.4	0	12	0.060	407.6
KC-3	0.3	10.3	0	31.1	247	19	88	5.7	1.6	6.4	0.01	11	0.061	420.5
KC-4	0.4	9.9	0	20.8	292	20.8	102	4.8	1.2	6.9	0	8	0.045	466.8
KC-5	0.4	10.4	0	31.4	225	18.9	126	4.9	2.2	7.8	0.01	9	0.037	436.1
KC-6	0.3	10.3	0	13.4	298	18.4	126	4.8	2.1	7.7	0.01	9	0.037	490.0
KC-7	0.3	10.6	0	29.4	252	18.8	77.7	5.9	1.5	6.4	0.01	10	0.071	412.7
KC-8	0.3	10.2	0.3	28.7	235	18.3	75.6	5.8	1.2	6.3	0.01	11	0.071	392.8
KC-9	0.4	9.9	0	26.1	230	17.7	89	5.2	1.2	6.4	0	10	0.055	395.9
KC-10	0.3	10.1	0	26.6	245	18	83.2	5.1	1.2	6.5	0	10	0.058	406.1
KC-11	0.4	9.8	0.1	27.1	250	18	87.1	5.4	1.3	6.5	0.01	10	0.058	415.7
KC-12	0.3	10.0	0.1	26.4	265	18.1	92.5	5.2	1.3	6.3	0	10	0.053	435.2
KC-13	0.4	9.6	0.1	7.8	270	18	90.1	5.5	1.3	6.4	0.01	10	0.058	419.1
KC-14	0.5	7.6	0	10.0	250	18.4	82.2	5.4	1.4	6.5	0	10	0.062	392.0
KC-15	0.3	8.8	0	16.5	240	18.3	86.8	5.4	1.4	6.6	0	10	0.059	394.2
Str 1 (N4D)	0.4	10.4	0.4	25.7	185	17.6	70.8	4.8	1.3	5.6	0.02	7	0.063	328.9
Str 2 (N4D)	0.3	10.6	0	17.0	190	17.7	48.9	4.5	1.1	5.6	0.01	6	0.084	301.8
3-5 Mor (Well 1)	0.4	7.3	0	5.9	230	18.3	76.7	5.4	1	5.9	0.01	5	0.066	355.9
3-5-1 Mor (Well 2)	0.4	9.8	0	5.8	250	24.6	58.5	6.7	1.4	5.7	0.02	13	0.103	375.9
4-6 Eis 2 (Well 3)	0.4	10.4	0	13.5	330	16	88.2	4.5	0.8	5	0	5	0.049	473.8
4-6 Eis 1 (Well 4)	0.4	9.0	0	37.4	334	23.1	37.3	9.8	1.2	6.2	0.02	9	0.208	467.4
4-6 Mor (Well 5)	0.4	10.6	0	14.1	337	17.8	44.2	5	1	5.7	0.02	6	0.102	441.8

Stable Isotope measurements $\delta^{15}\text{N}$, $\text{NO}_3\text{-N}$, NO_3 and pH/ Table 4

Sample ID	$\delta^{15}\text{N}$	nitrate ppm	nitrate-N	pH
Well 1	3.98	0.0129	0.002915	8.20
Well 2	4.75	0.0167	0.003774	8.22
KC-12	4.29	0.084	0.018984	8.10
Stream 1 (N4D)	6.13	0.3561	0.080479	7.71
Stream 2 (N4D)	3.29	0.0342	0.007729	7.68
Stream 3 (KC)	4.99	1.2413	0.280534	7.94
Stream 4 (KC)	5.64	1.036	0.234136	7.93
Stream 5 (KC)	3.26	1.0509	0.237503	7.88
Stream 6 (KC)	3.07	1.1873	0.26833	7.76
Stream 7 (KC)	1.49	1.286	0.290636	7.76
Stream 8 (SC)	0.07	1.1122	0.251357	7.66
Stream 9 (I-70)	4.90	0.9986	0.225684	7.60



Graph indicates denitrification (DN) of nitrate-N with $\delta^{15}\text{N}$ which is a negative correlation. The graph (Grassland site) above is used for comparison (courtesy of Macpherson et al. 1994)

$\delta^2\text{H}$ & $\delta^{18}\text{O}$ / Table 5

Sample ID	$\delta^{18}\text{O}$ (‰ V-SMOW)	δD (‰ V-SMOW)
I-70 1	-5.598306201	-34.87444936
I-70 2	-5.49701083	-34.91451727
I-70 3	-5.343844169	-34.65727454
KPKC 14	-5.683312771	-35.629679
KPKC-02	-5.581825447	-35.46839724
KC-4	-5.52426061	-34.72427886
KC-10	-5.510745369	-35.6949998
KC-8	-5.669132405	-36.33810664
KC-12	-5.458553997	-35.14650712
SC 1	-5.537915867	-37.43812236
SC 4	-5.690752233	-35.84348677
stream 2 (N4D)	-5.703207006	-35.1646892
well 1 3-5 MOR	-5.533521628	-35.84112984
well 2, 3-5 MOR	-5.736496235	-37.64586943
well 3, 4-6 Eis 2	-5.360775364	-35.91789862
well 4, 4-6 Eis 1	-5.571607504	-37.45596772
well 5, 4-6 MOR	-5.522161284	-36.53709938
Precipitation (01/05/10)	-21.66538169	-161.2109371
Precipitation (02/09/10)	-19.89915524	-150.7671217
Precipitation (02/23/10)	-11.9776617	-78.33764831
Precipitation (03/09/10)	-8.326942247	-51.96476001
Precipitation (03/16/10)	-12.26825951	-81.29836652
Precipitation (03/23/10)	-9.744451328	-55.68853955
Precipitation (03/30/10)	-8.746619548	-48.48471754
Precipitation (04/06/10)	-3.060025906	-33.19231128

Str: Stream

KC: Kings Creek

SC: Shane Creek

Appendix B - Sediment Analyses

This section contains general sediment descriptions, in addition to results from lab analyses.

General sediment characteristics

Samples were named according to equipment used (hydraulic geoprobe) and depth in feet.

Date	Sample ID	Number of cores	Length	Latitude	Longitude	elevation
7/27/2010	Geop 1-1	3	~ 2 feet	N39°04.013'	W096°35.787'	1323 feet
	Geop 1-2		~ 2 feet			
	Geop 1-3		~ 2 feet			
7/27/2010	Geop 2-1	4	~ 2 feet	N39°03.995'	W096°35.782'	1323 feet
	Geop 2-2		~ 2 feet			
	Geop 2-3		~ 2 feet			
	Geop 2-4		~ 2 feet			
7/27/2010	Geop 3-1	4	~ 2 feet	N39°04.039'	W096°35.845'	1306 feet
	Geop 3-2		~ 2 feet			
	Geop 3-3		~ 2 feet			
	Geop 3-4		~ 2 feet			
7/27/2010	Geop 4-1	4	~ 2 feet	N39°04.046'	W096°35.886'	1301 feet
	Geop 4-2		~ 2 feet			
	Geop 4-3		~ 2 feet			
	Geop 4-4		~ 2 feet			
7/27/2010	Geop 5-1	2	~ 2 feet	N39°05.259'	W096°35.077'	1293 feet
	Geop 5-2		~ 2 feet			
7/27/2010	Geop 6-1	3	~ 2 feet	N39°05.324'	W096°35.075'	1253 feet
	Geop 6-2		~ 2 feet			
	Geop 6-3		~ 2 feet			
8/2/2010	Geop 7-1	4	~ 2 feet	N39°06.082'	W096°35.652'	1109 feet
	Geop 7-2		~ 2 feet			
	Geop 7-3		~ 2 feet			
	Geop 7-4		~ 2 feet			
8/2/2010	Geop 8-1	4	~ 2 feet	N39°06.111'	W096°35.688'	1102 feet
	Geop 8-2		~ 2 feet			
	Geop 8-3		~ 2 feet			
	Geop 8-4		~ 2 feet			
8/2/2010	Geop 9-1	4	~ 2 feet	N39°06.155'	W096°35.204'	1133 feet
	Geop 9-2		~ 2 feet			
	Geop 9-3		~ 2 feet			
	Geop 9-4		~ 2 feet			
8/2/2010	Geop 10-1	4	~ 2 feet	N39°05.773'	W096°34.257'	1216 feet
	Geop 10-2		~ 2 feet			
	Geop 10-3		~ 2 feet			
	Geop 10-4		~ 2 feet			

Total carbon % and total nitrogen % of sediment samples/ Table 6

<u>Sample ID</u>	<u>Carbon %</u>	<u>Nitrogen %</u>
Geop 1-1	5.059	0.341
Geop 2-1	5.119	0.37617
Geop 3-1	1.228	0.11159
Geop 4-1	6.334	0.43697
Geop 5-1	5.007	0.37456
Geop 6-1	4.604	0.32357
Geop 7-1	6.833	0.59172
Geop 8-1	5.783	0.52941
Geop 9-1	2.732	0.24228
Geop 10-1	4.867	0.37398

NH₄ and NO₃ in sediment measurements/ Table 7

<u>Geop#-Core #</u>	<u>NH4 ppm</u>	<u>Geop#-Core #</u>	<u>NO3 ppm</u>
1-1	177.47	1-1	4.21
1-2	4.62	1-2	4.38
1-3	28.77	1-3	2.26
1-4	0	1-4	0
2-1	131.10	2-1	6.82
2-2	13.91	2-2	4.83
2-3	4.06	2-3	2.17
2-4	5.55	2-4	2.75
3-1	15.11	3-1	2.17
3-2	4.06	3-2	2.30
3-3	38.30	3-3	2.35
3-4	3.90	3-4	2.35
4-1	231.13	4-1	3.45
4-2	39.46	4-2	3.23
4-3	7.61	4-3	2.26
4-4	0	4-4	0
5-1	229.32	5-1	2.48
5-2	0	5-2	0
5-3	0	5-3	0
5-4	0	5-4	0
6-1	54.96	6-1	2.66
6-2	23.23	6-2	2.75
6-3	8.82	6-3	2.35
6-4	0	6-4	0
7-1	73.68	7-1	11.65
7-2	67.18	7-2	12.80
7-3	54.28	7-3	10.98
7-4	26.85	7-4	5.62
8-1	157.54	8-1	3.41
8-2	33.78	8-2	5.98
8-3	12.87	8-3	2.44
8-4	18.59	8-4	2.48
9-1	141.66	9-1	2.35
9-2	28.53	9-2	3.59
9-3	21.57	9-3	3.59
9-4	10.39	9-4	2.39
10-1	229.01	10-1	2.88
10-2	67.69	10-2	10.41
10-3	43.60	10-3	5.9
10-4	21.47	10-4	3.28

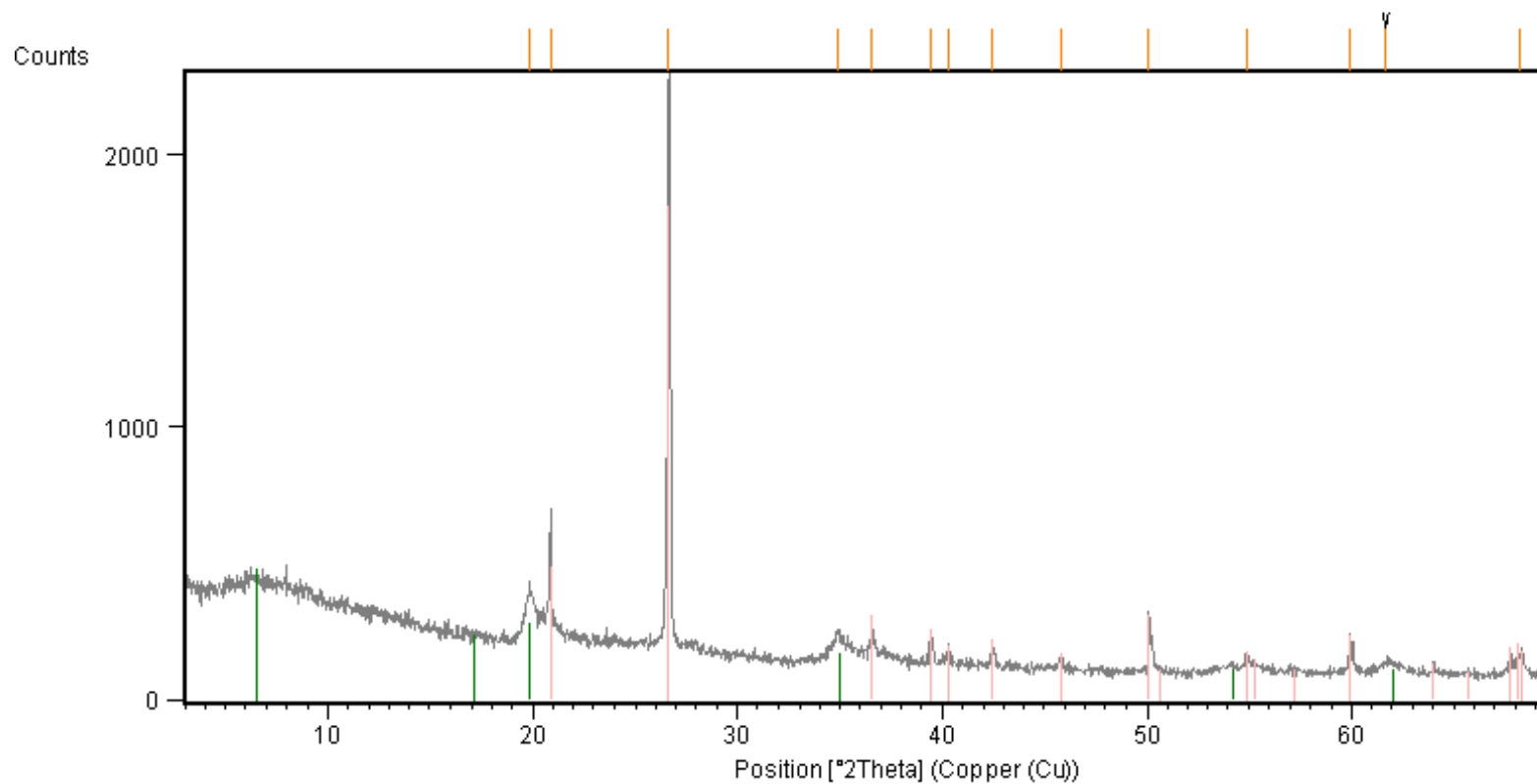
Stable isotopes/ Table 8

$\delta^{13}\text{C}$ & $\delta^{15}\text{N}$ of sediment samples

Sample ID-core	$\delta^{13}\text{C}$	%C	$\delta^{15}\text{N}$	%N
Geop 1-1	-14.42	2.947	4.22	0.232
Geop 2-1	-14.12	2.552	5.64	0.212
Geop 3-1	-12.91	1.244	7.53	0.114
Geop 4-1	-13.6	3.634	3.81	0.286
Geop 5-1	-15.91	3.433	4.04	0.278
Geop 6-1	-14.1	2.893	4.79	0.235
Geop 7-1	-23.98	5.076	7.21	0.472
Geop 8-1	-23.64	4.162	7.06	0.38
Geop 9-1	-17.92	1.994	3.36	0.171
Geop 10-1	-16.44	2.945	4	0.239
Geop 1-2	-17.05	0.331	5.54	0.053
Geop 2-2	-15.36	0.772	5.48	0.075
Geop 3-2	-14.38	0.534	5.7	0.058
Geop 4-2	-12.73	1.092	6.57	0.1
Geop 5-2	-13.88	2.203	6.8	0.179
Geop 6-2	-5.48	7.127	3.81	0.129
Geop 7-2	-15.31	1.952	6.49	0.16
Geop 8-2	-15.75	0.518	6.15	0.062
Geop 9-2	-13.15	1.211	6.69	0.112
Geop 10-2	-14.18	1.823	5.7	0.157

X-Ray Powder Diffraction (XRD)/ Table 9

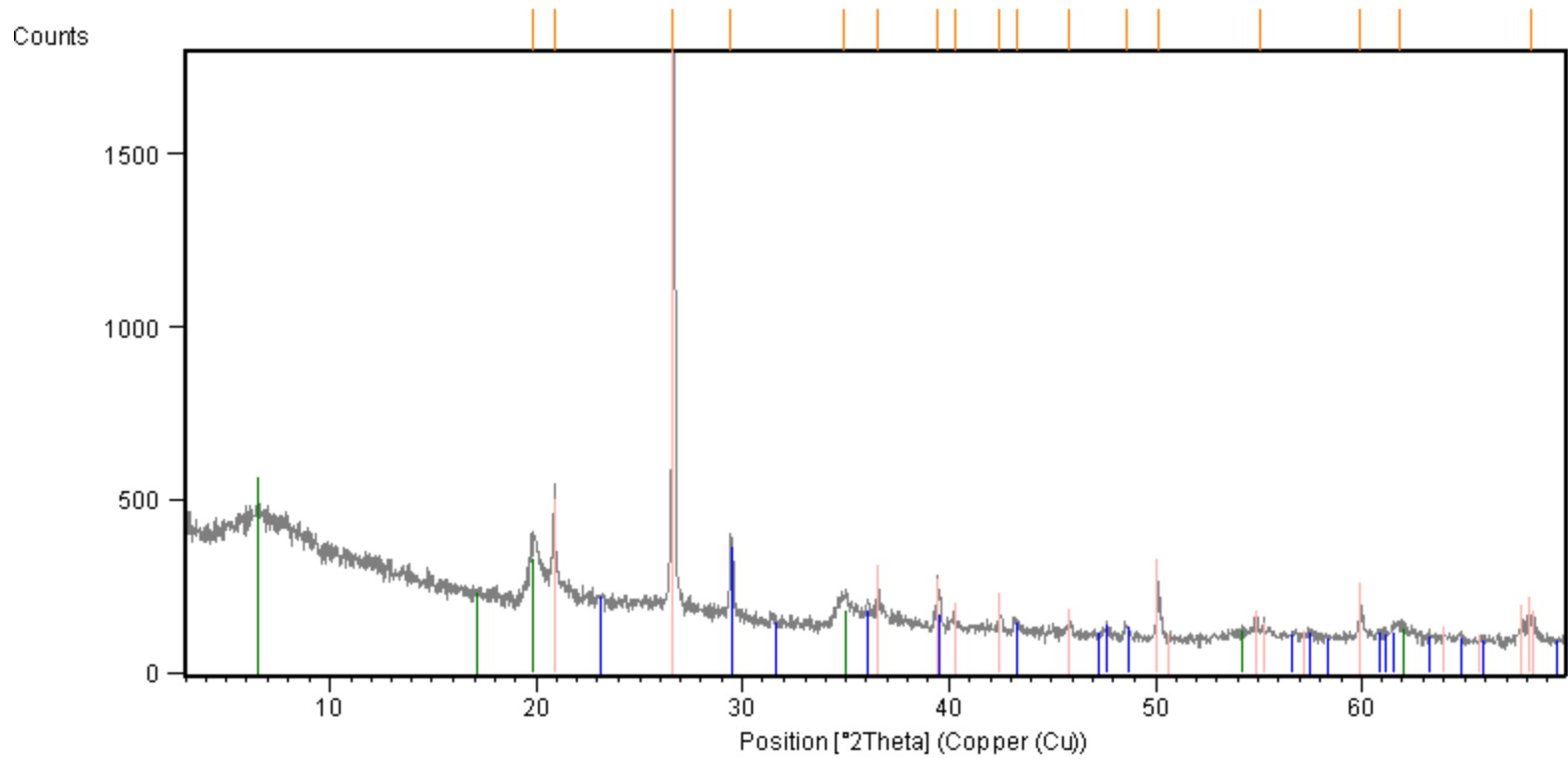
File: GEOP 1 CORE 2



Major Peaks: Quartz, 3.34 Å, (SiO₂)

Smectite group clay minerals, 15 Å

File: GEOP 1 CORE 3

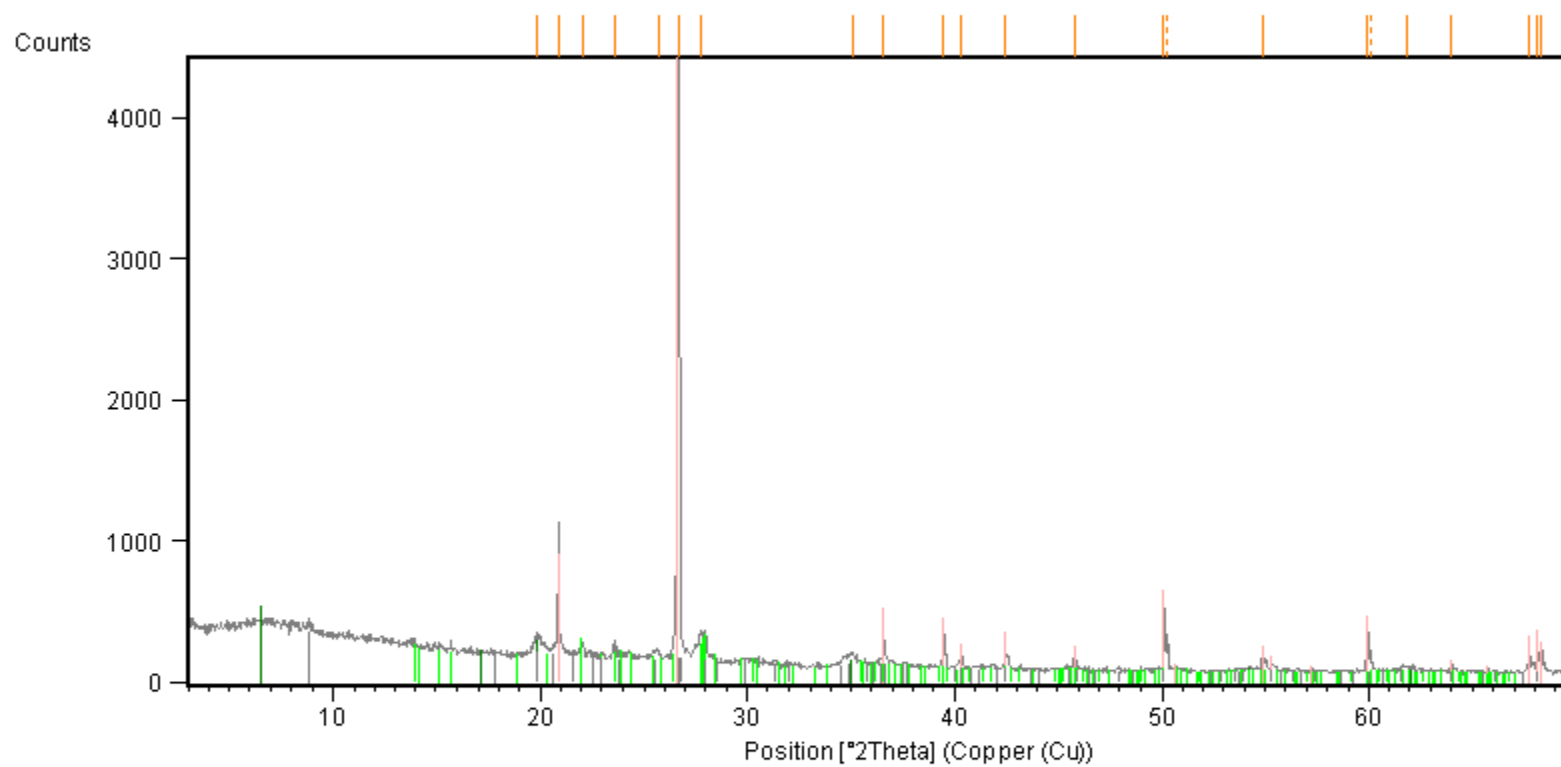


Major Peaks: Quartz, 3.34 Å, (SiO₂)

Magnesium rich calcite, 2.45 Å, (Mg_{0.03}Ca_{0.97})(CO₃)

Smectite group clay minerals, 15 Å

File: GEOP 3 CORE 2



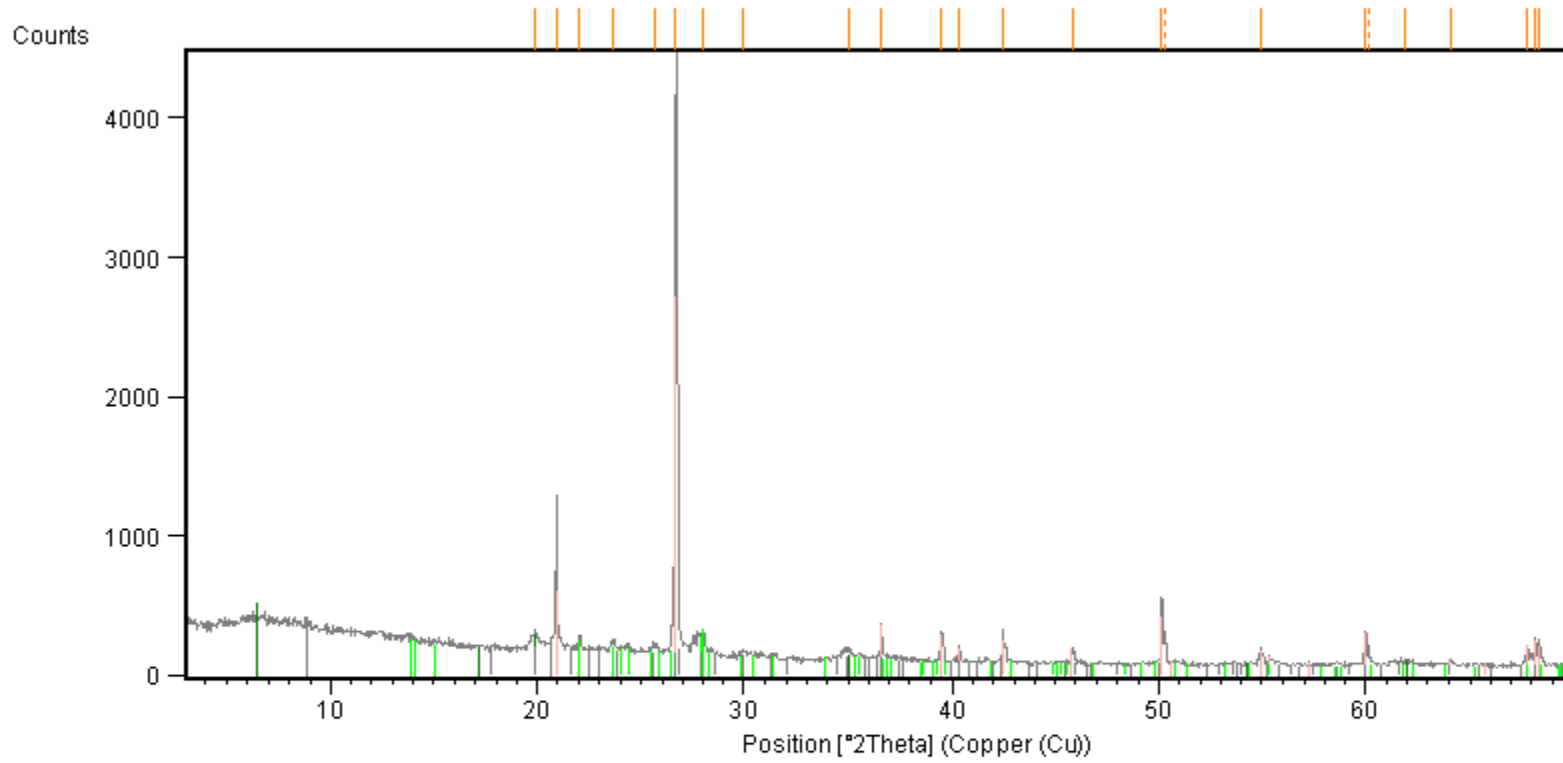
Major Peaks: Quartz, 3.34 Å, (SiO₂)

Smectite group clay minerals, 15 Å

Albite calcium low, 2.27 Å, (Na_{0.84}Ca_{0.16})Al_{1.16}Si_{2.84}O₈

Muscovite, 1.77 Å, KAl₂(Si₃Al)O₁₀(OH,F)₂

File: GEOP 3 CORE 4



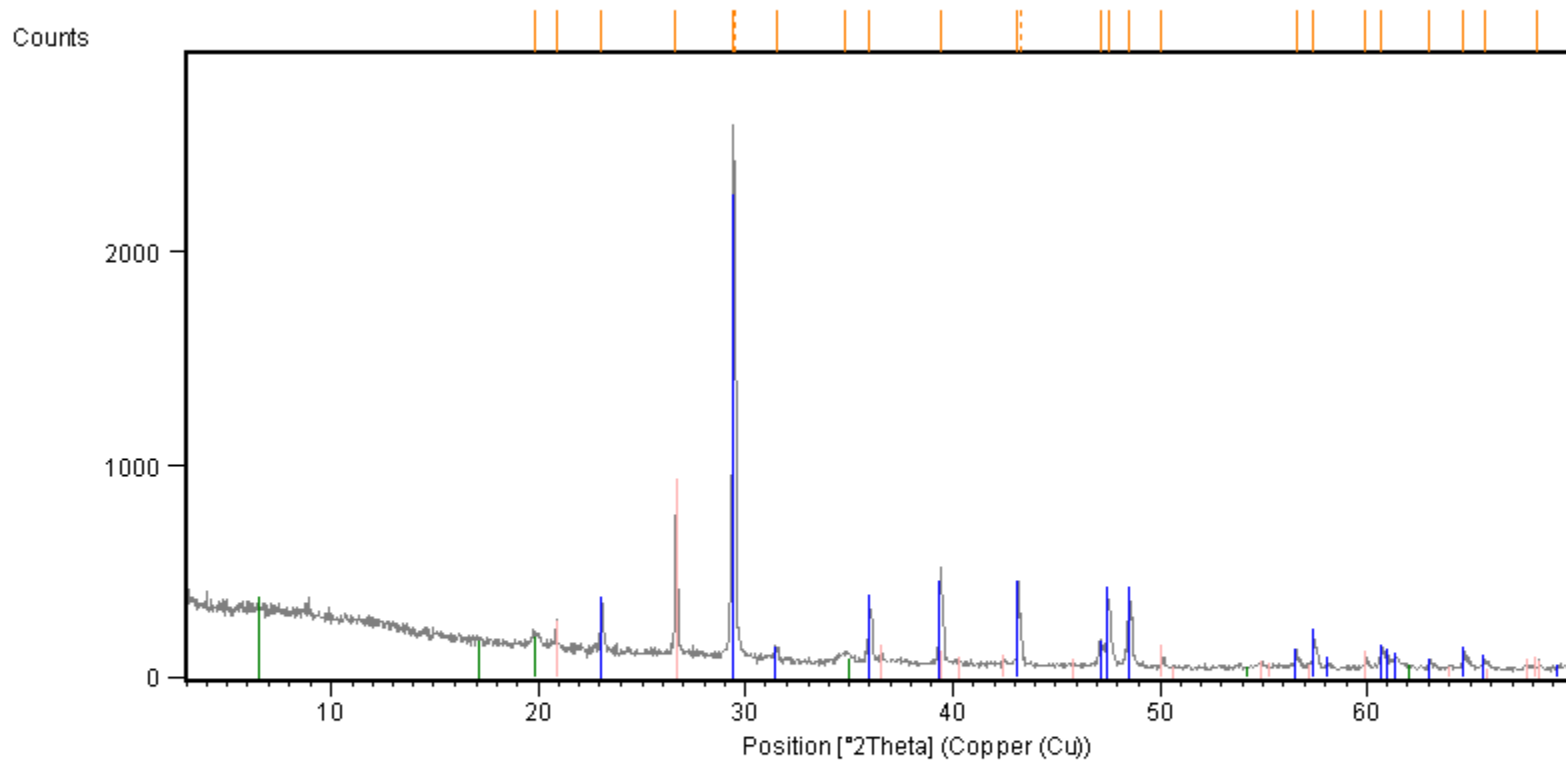
Major Peaks: Quartz, 3.34 Å, (SiO₂)

Albite calcium rich, 4.03 Å, (Na,Ca)Al(Si,Al)₃O₈

Smectite group clay minerals, 15 Å

Muscovite, 1.77 Å, KAl₂(Si₃Al)O₁₀(OH,F)₂

File: GEOP 6 CORE 2

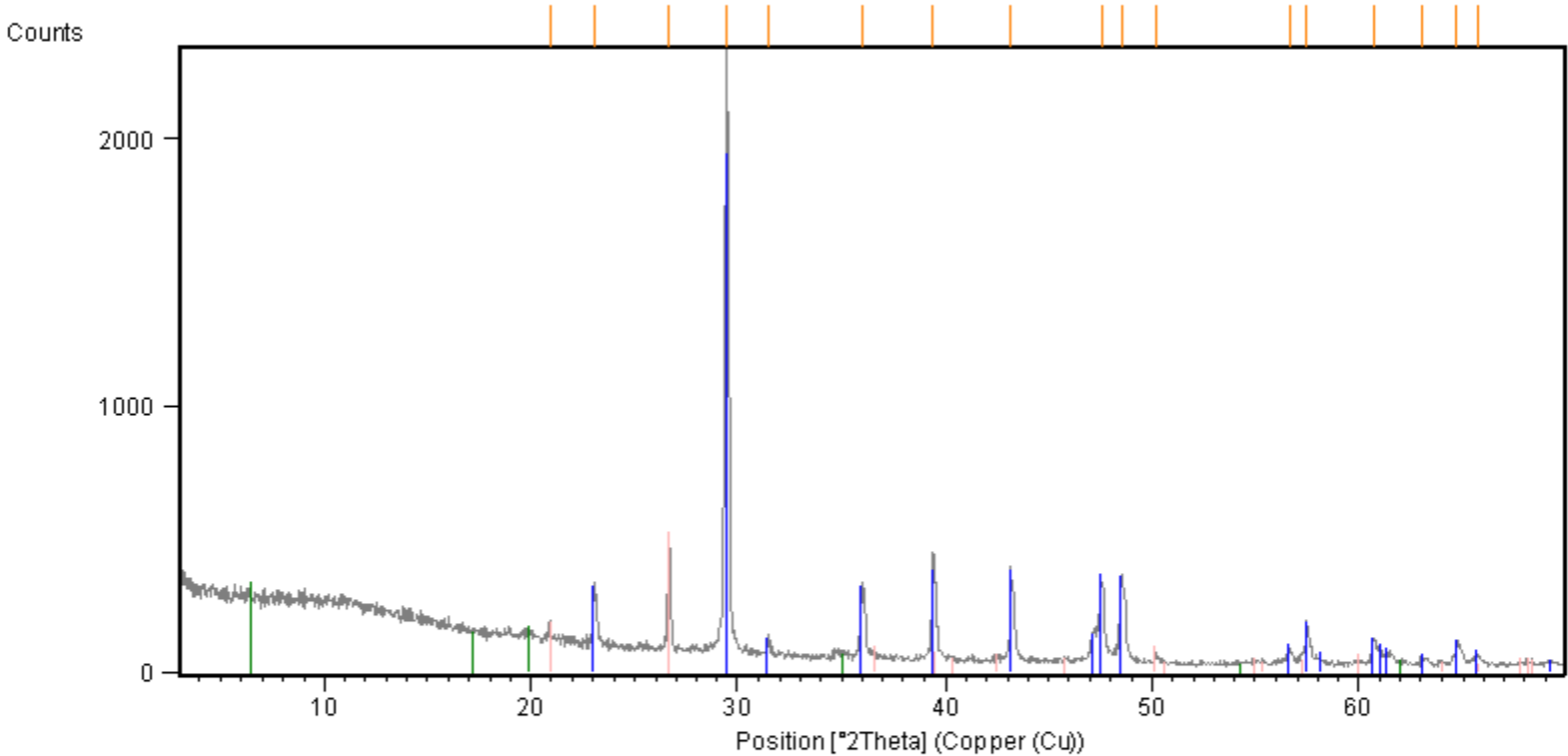


Major Peaks: Quartz, 3.34 Å, (SiO₂)

Calcite, 3.03 Å, (CaCO₃)

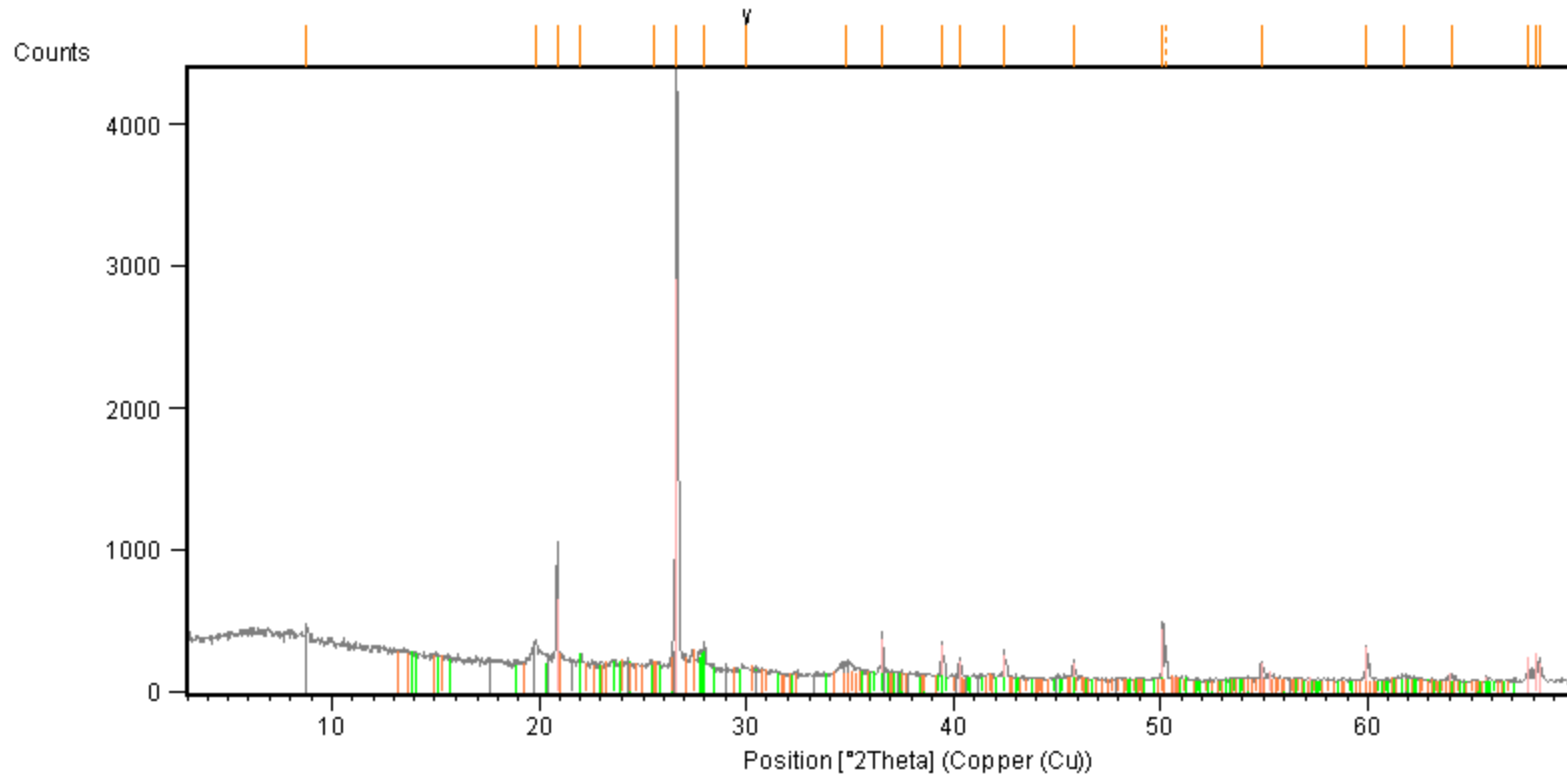
Smectite group clay minerals, 15 Å

File: GEOP 6 CORE 3



Major Peaks: Quartz, 3.34 Å, (SiO₂)
Calcite, 3.03 Å, (CaCO₃)
Smectite group clay minerals, 15 Å

File: GEOP 8 CORE 2



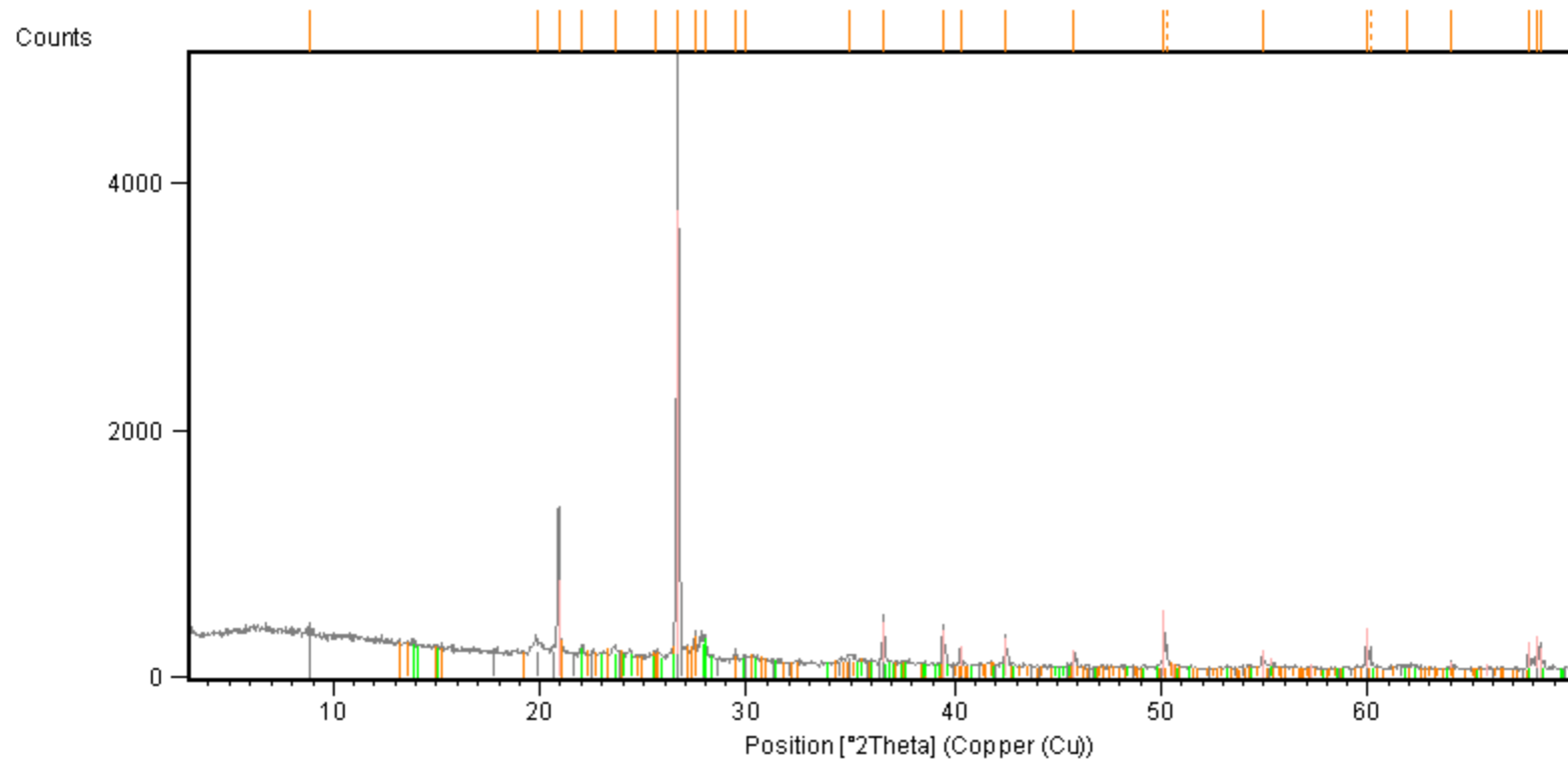
Major Peaks: Quartz, 3.34 Å, (SiO₂)

Albite calcium low, 2.27 Å, (Na_{0.84}Ca_{0.16})Al_{1.16}Si_{2.84}O₈

Muscovite, 1.77 Å, KAl₂(Si₃Al)O₁₀(OH,F)₂

Microcline maximum, 3.37 Å, (KAlSi₃O₈)

File: GEOP 8 CORE 4



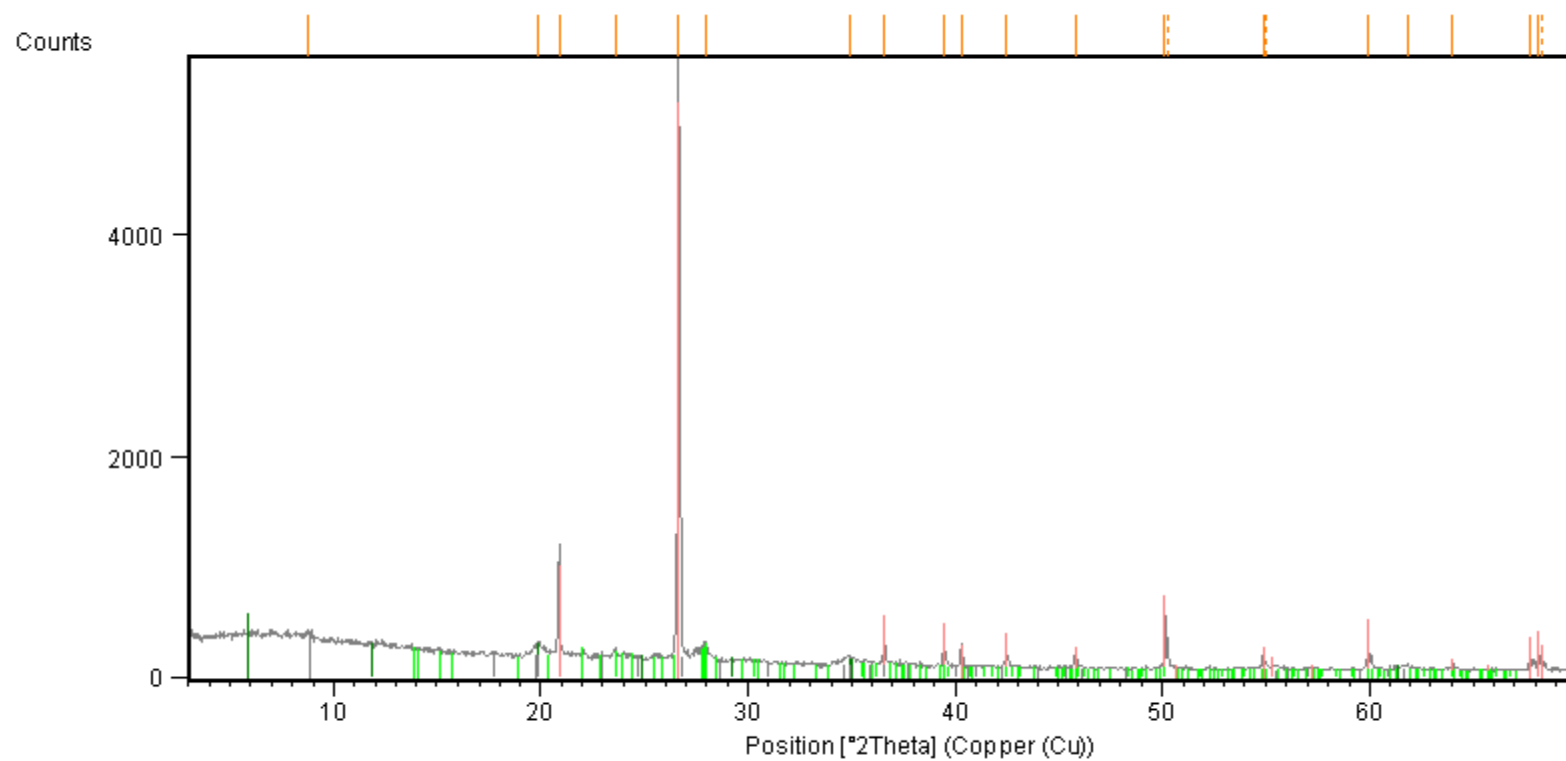
Major Peaks: Quartz, 3.34 Å, (SiO₂)

Muscovite, 1.77 Å, KAl₂(Si₃Al)O₁₀(OH,F)₂

Microcline maximum, 3.37 Å, (K_{0.94}Na_{0.06}Al_{1.01}Si_{2.99}O₈)

Albite calcium rich, 4.03 Å, (Na,Ca)Al(Si,Al)₃O₈

File: GEOP 9 CORE 2

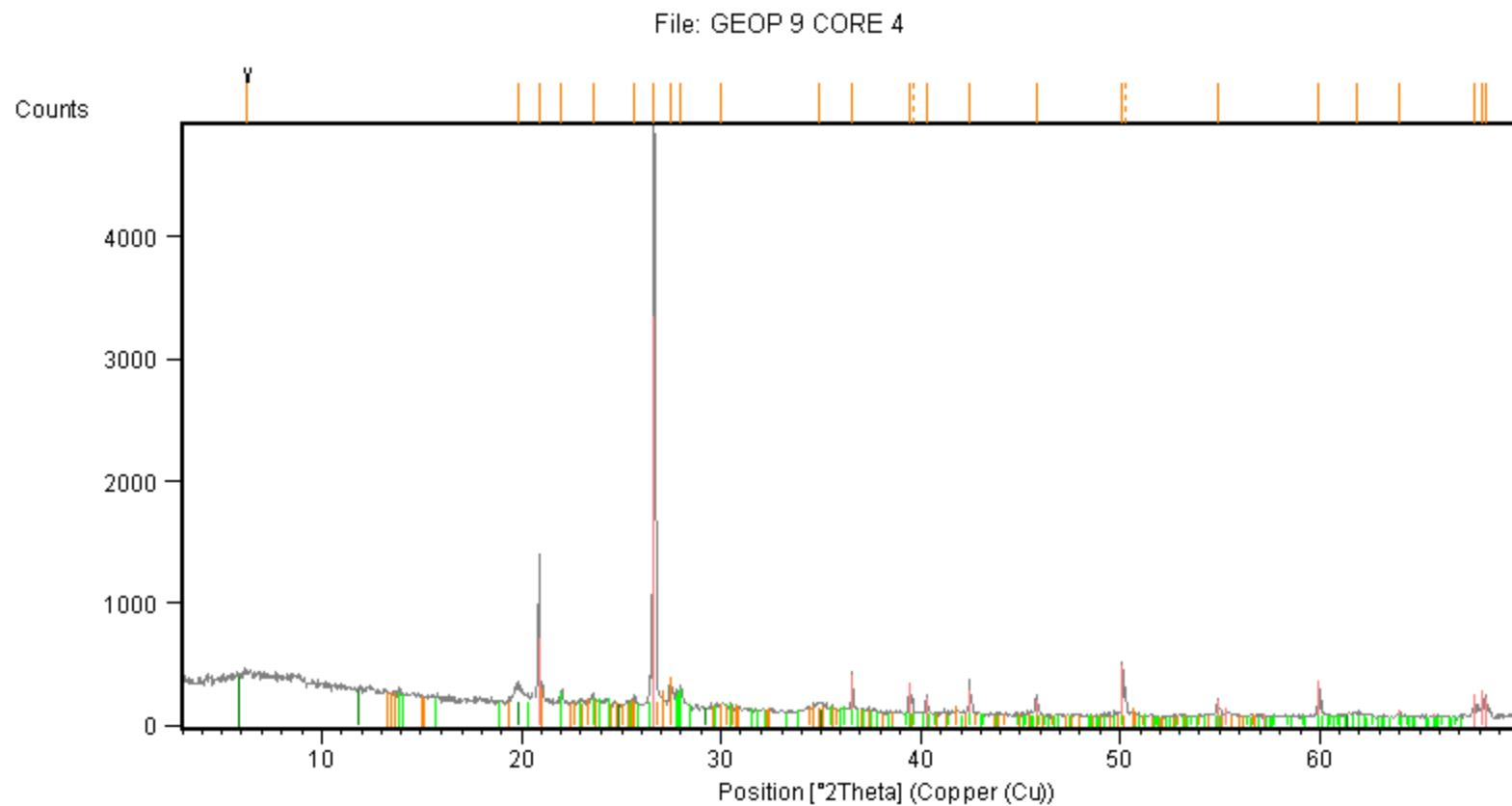


Major Peaks: Quartz, 3.34 Å, (SiO₂)

Albite calcium low, 2.27 Å, (Na_{0.84}Ca_{0.16})Al_{1.16}Si_{2.84}O₈

Smectite group clay minerals, 15 Å

Muscovite, 1.77 Å, (K, Na)(Al, Mg, Fe)₂(Si_{3.1}Al_{0.9})O₁₀(OH)₂



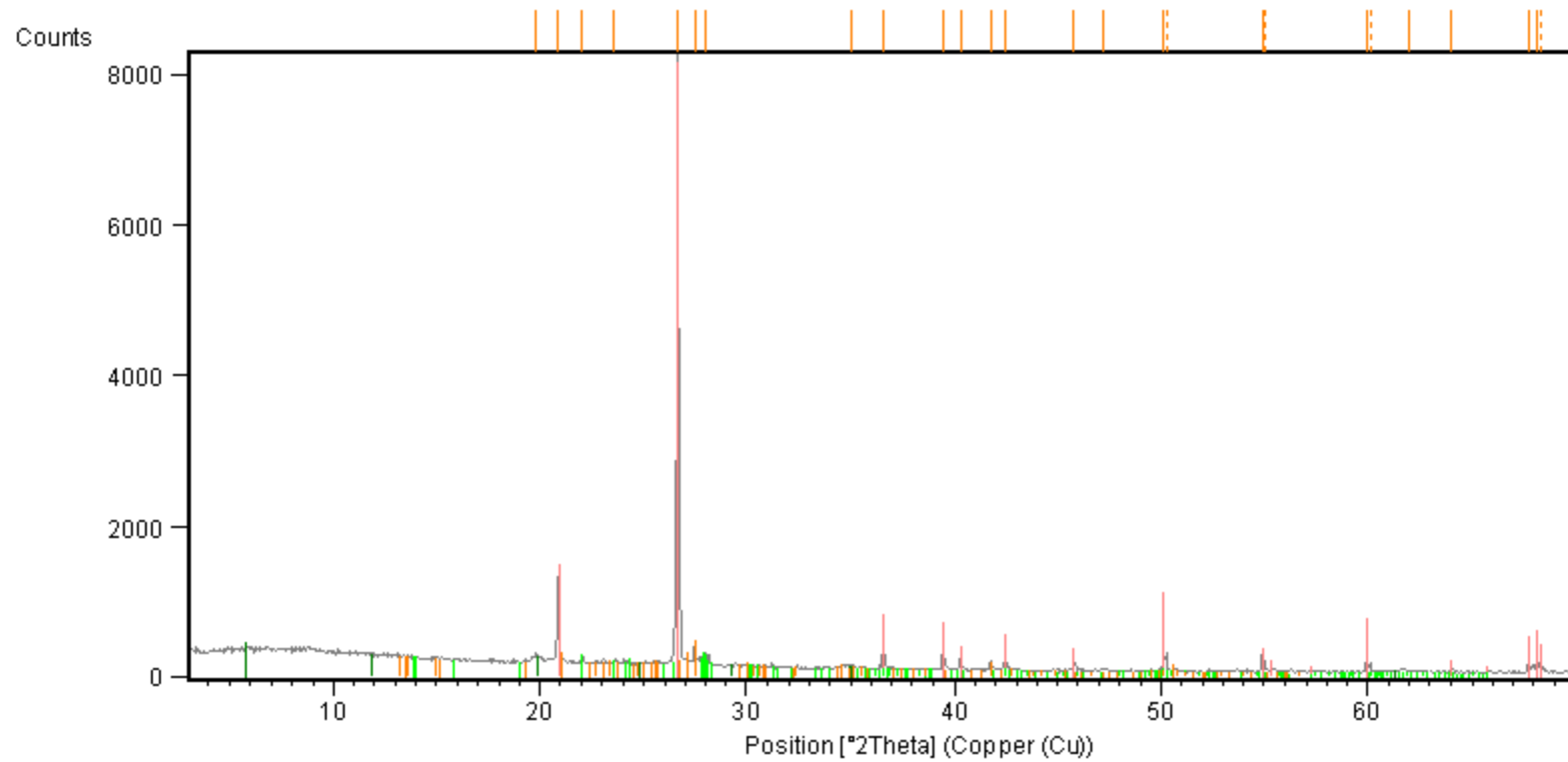
Major Peaks: Quartz, 3.34 Å, (SiO₂)

Albite calcium low, 2.27 Å, (Na_{0.84}Ca_{0.16})Al_{1.16}Si_{2.84}O₈

Microcline intermediate, 3.37 Å, (KAlSi₃O₈)

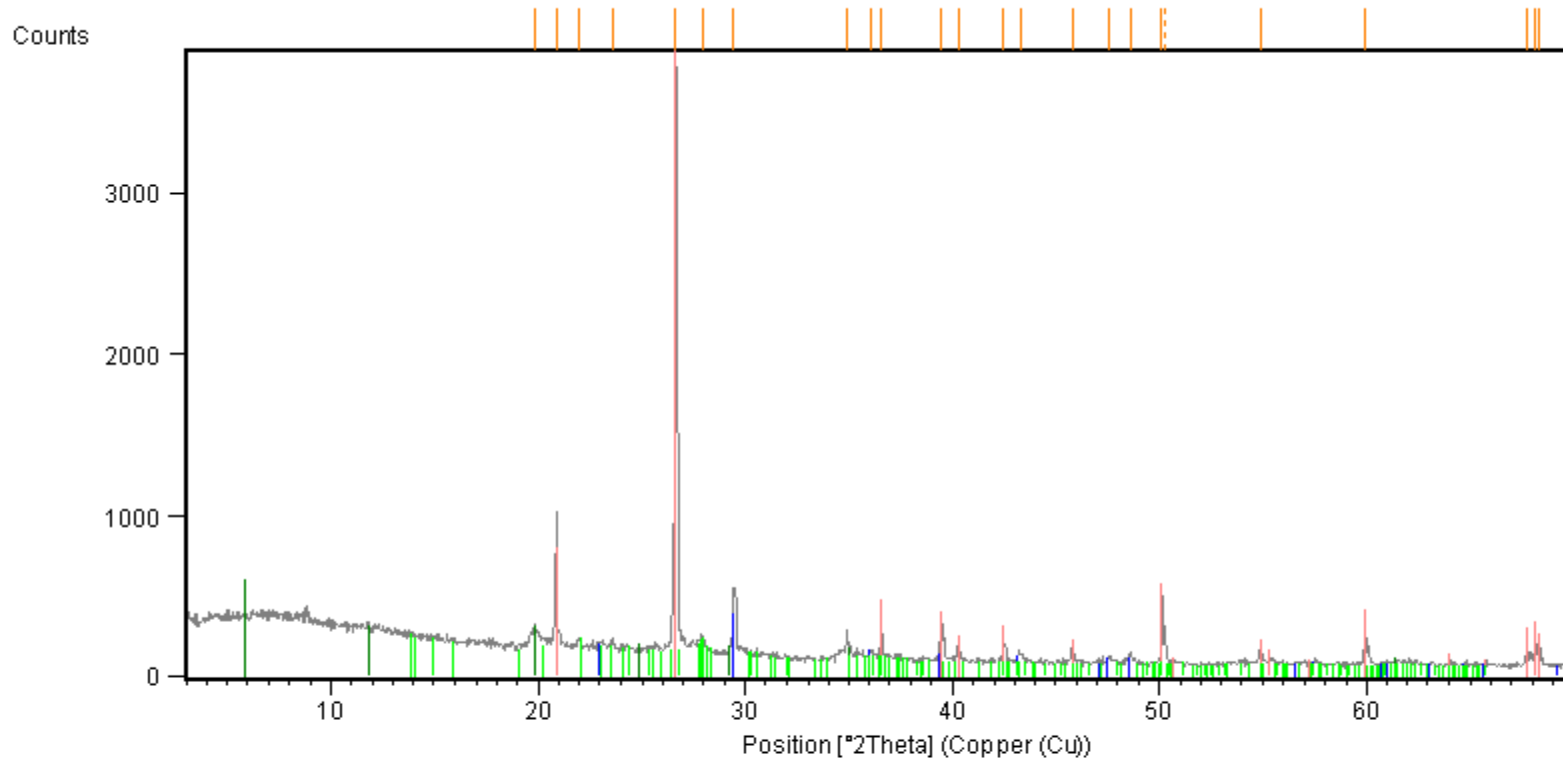
Smectite group clay minerals, 15 Å

File: GEOP 10 CORE 2



- Major Peaks: Quartz, 3.34 Å, (SiO₂)
Albite low, 3.19 Å, Na(AlSi₃O₈)
Smectite group clay minerals, 15 Å
Microcline intermediate, 3.37 Å, (KAlSi₃O₈)

File: GEOP 10 CORE 4



Major Peaks: Quartz, 3.34 Å, (SiO₂)
Calcite, 3.03 Å, (CaCO₃)
Smectite group clay minerals, 15 Å
Albite low, 3.19 Å, Na(AlSi₃O₈)