

The Impact of Large Storm Events on Nutrient Loadings in Texas Rivers

Paul Bireta

Fall 2012



Nutrients can be damaging to natural water bodies, harming both human and ecological health. One of the primary sources of these nutrients in river systems is runoff from agricultural land. Nutrients are added to the land in the form of fertilizers. Storm events can strip some of the nutrients off the agriculture land and carry them into river systems. The goal of this project is to examine the impact of these large storm events on rivers in Texas and to determine if the storms events are the main driver of nutrients loadings in the river. In order to assess this, water quality data, land cover data, and precipitation data will be examined.

There are several water quality parameters that can be used to assess nutrient impacts on rivers. For this project, nitrate, ammonia, phosphorous, and dissolved oxygen were chosen. Nitrate, ammonia, and phosphorous are nutrients or direct byproducts of nutrient breakdown. Examining dissolved oxygen will show the impact of the nutrients on the water bodies instead of directly showing the amounts, which can be a more useful measure of potential ecological effects. Nitrate can be dangerous to human health as is it transformed to nitrite within the body. Nitrate is the cause of blue baby syndrome and the EPA has set a drinking water MCL of 10 mg/L. The rest of the target contaminants are not directly dangerous to human health and instead have ecological risks associated with them. Ammonia is still under investigation by the EPA for toxicity to wildlife. Phosphorous is not associated with wildlife toxicity. Instead, it is a risk because of its potential to lead to eutrophication. The phosphorous causes a bloom in algae which eventually die off and are decomposed by bacteria. This decomposition consumes dissolved oxygen within the water. Low dissolved oxygen levels can be harmful to wildlife. Dissolved oxygen levels are a good indicator of overall health of a water system as low level can be caused by several negative factors.

The Texas Commission for Environmental Quality (TCEQ) runs a program for gather surface water quality data. The Continuous Water Quality Monitoring Network (CWQMN) provides data for 12 Texas basins and 2 conservation districts. Stations, such as the one show in Figure 1, are set up near a river and take water quality data continuously. The data is available in near real time. The only intermediate step is a TCEQ QA/QC check to ensure the quality of the data. Sites collect many different water quality parameters. For this project, nitrate, ammonia, phosphorous, and dissolved oxygen have been chosen for their relation to nutrient contamination in rivers. The major issue with the CWQMN data is that many sites are no longer active and that there are some holes in the data. The gaps in the data are primarily due to maintenance issues with the sampling stations. These stations operate continuously over several years and are exposed to varying environmental conditions. Since they are not manned continuously, maintenance issues can arise and are often not immediately dealt with.



Figure 1 - Example TCEW CWQMN Station

The complete CWQMN data set was examined in order to determine the area of Texas with the most complete data. The Brazos basin contained the most stations that had both the water quality parameters of interest and relatively continuous data over at least one year. Figure 2 shows the CWQMN stations in the Brazos basin in red. Figure 3 shows a close up of the Brazos basin.

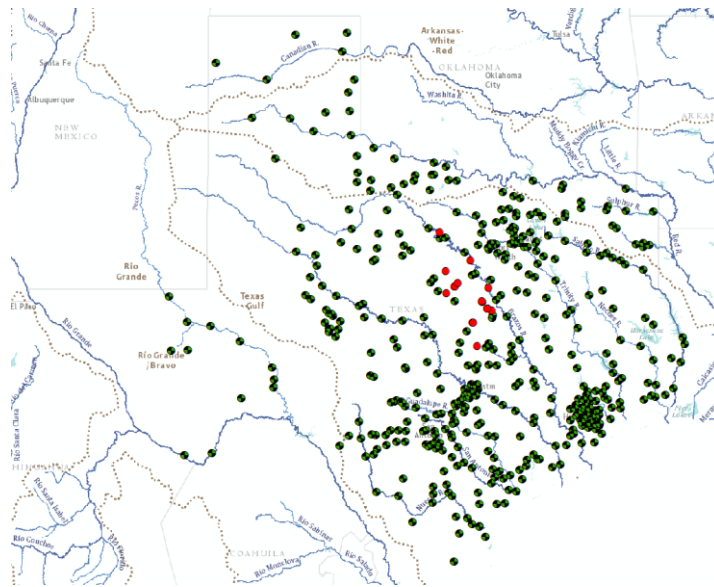


Figure 2 - Map of Texas with USGS Flow Gages and TCEW CWQMN Stations

The other important factor in selecting CWQMN stations to analyze is the availability of flow data. The green dots in Figure 3 show the location of USGS flow gages. In order for a CWQMN station to be selected, it needed the correct water quality parameters, relatively continuous data, and a nearby coupled USGS gage. Three of the stations in the Brazos basin were selected and they are marked in light blue in Figure 3. The three stations selected were Bosque River and Coopers Crossing, Bosque River at Clifton, and Leon River at Gatesville. Bosque River at Coopers Crossing has phosphorous and dissolved oxygen data available from August 2007 to July 2008. Capturing an entire year is important so that seasonal variations can be examined. Bosque River at Clifton has data for nitrate and ammonia for 2005 and dissolved

oxygen for 2002. Leon River at Gatesville has data for nitrate and ammonia for 2005 and dissolved oxygen for 2002. These data sets work very well because there are two watersheds that have three of the same water quality parameters over the same time periods. A more direct comparison can be made between these watersheds.

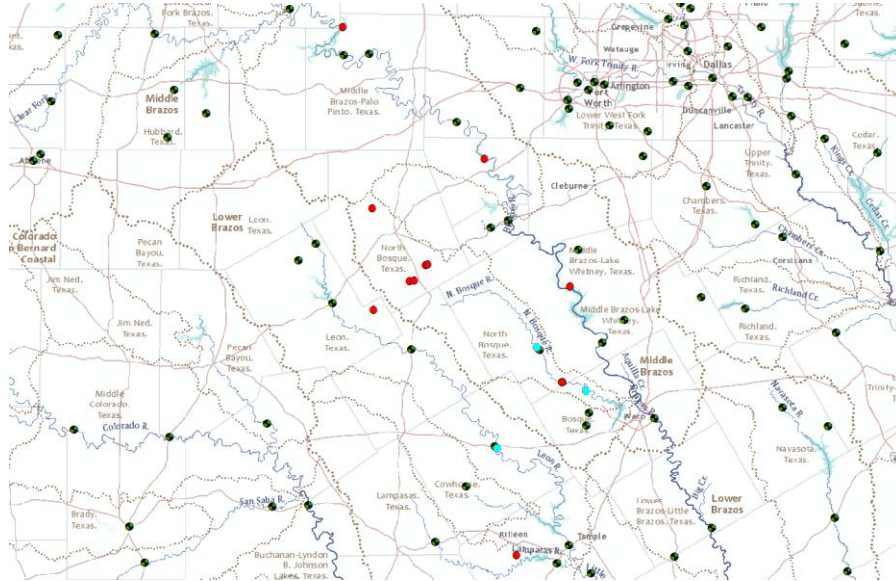


Figure 3 - Map of Selected TCEQ CWQMN Stations

Watersheds were delineated for each CWQMN station. The drainage area for each station was found using the ‘Watershed_nosimp’ tool from Worldwatershed. The outlet point was selected as the CWQMN station location. Figure 4 shows the total drainage area of each delineated watershed. Figure 5, Figure 6, and Figure 7 show the delineated drainage area for each CWQMN station. These shapes were used as the area which would influence each CWQMN station. The shapes were carried forward into further analysis to see what would affect each station.

Watershed	Total Area (square miles)
Bosque River at Coopers Crossing	1141
Bosque River at Clifton	962
Leon River at Gatesville	2381

Figure 4 - Total Area of Delineated Watersheds

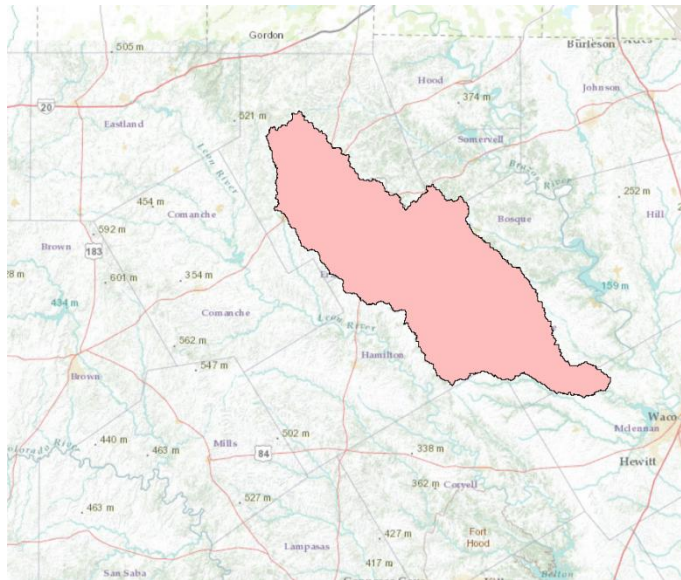


Figure 5 - Bosque River at Coopers Crossing Watershed

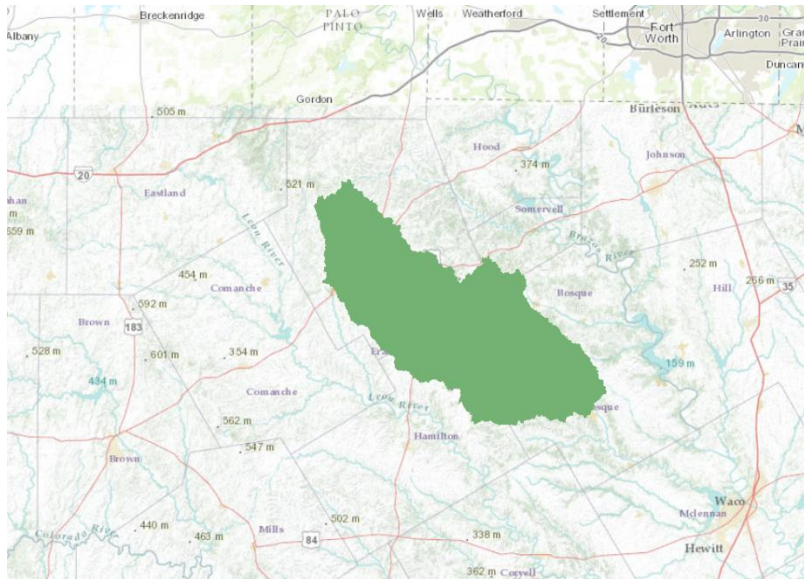


Figure 6 - Bosque River at Clifton Watershed

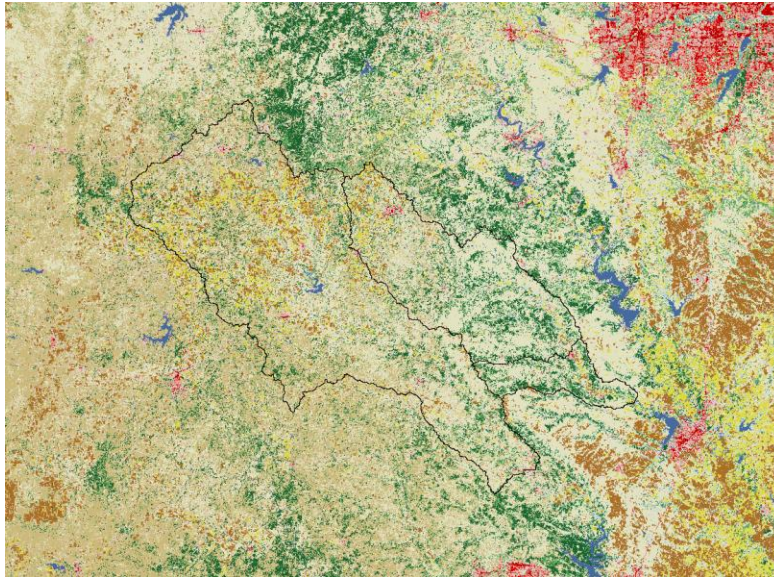


Figure 8 - National Land Cover Dataset with Delineated Watersheds

Figure 8 shows the NLCD raster with each delineated watershed. In order to determine the land cover breakdown in each watershed, the histogram tool was applied to the NLCD raster with the area being each watershed, individually. This produced the total number of cells of each subcategory within the watershed. The percentage of each subcategory was then determined. The complete results of this analysis can be found in the appendix and the most important data can be found in Figure 9. The important thing to notice for this data is that the Leon River at Gatesville watershed has a significantly higher percentage of both Hay/Pasture and Cultivated Crops.

Watershed	Hay/Pasture (% Area)	Cultivated Crops (% Area)
Bosque River at Coopers Crossing	3.4	3.3
Bosque River at Clifton	3.4	3.2
Leon River at Gatesville	6.7	7.4

Figure 9 - NLCD Agriculture Percentages

Precipitation data was gathered from the National Climactic Data Center, which is run by the National Oceanic and Atmospheric Administration. Hourly precipitation data is gathered at rain gages across the country, although there is not data available for every hour. Figure 10 shows the locations of the precipitation gages used for this project.

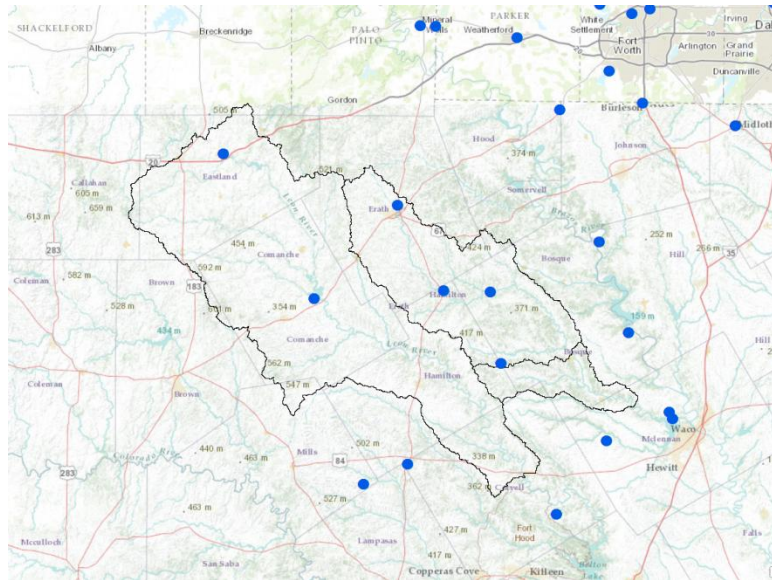


Figure 10 – National Climactic Data Center Precipitation Gage Locations

Thiessen polygons were created in order to interpolate between precipitation gages. This may not have been the most statistically accurate interpolation, but in this case the absolute magnitude of the storm events is not the most important parameter. In this project, it is more important to be able to identify the timing of large storm events within the watershed. After the polygons were created, each watershed shape was then extracted. Figure 11 shows the extracted shapes. This data allowed each precipitation gage to be weighted by percentage of area in the watershed in order to determine the total precipitation in each watershed. To determine the total precipitation within a watershed, the precipitation from each gage within the watershed was summed after being corrected by the proper weight.

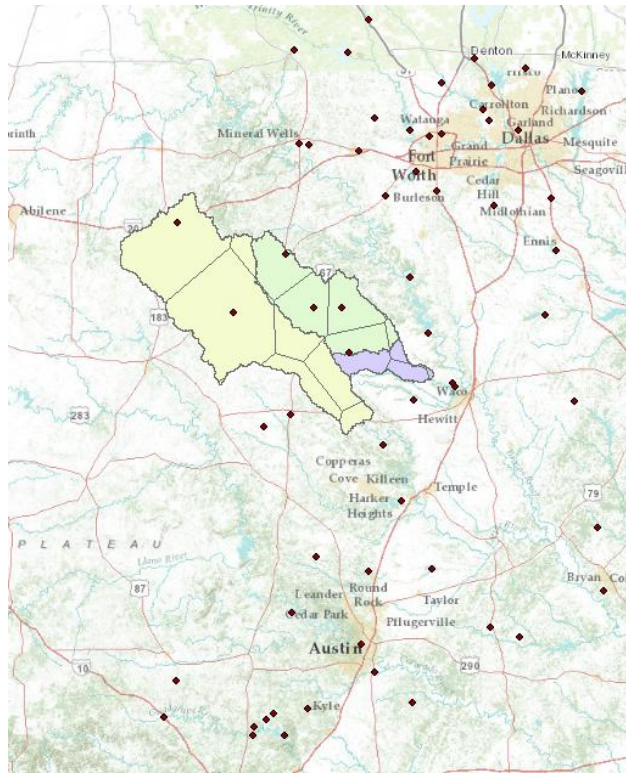


Figure 11 - Thiessen Polygons for Watersheds

The Bosque River at Coopers Crossing has water quality data for phosphorous and dissolved oxygen. The precipitation data for this watershed is shown in Figure 12. The major storm events are marked with red lines. The phosphorous data had several gaps in the data and so it was difficult to draw any definitive conclusions. The phosphorous data can be seen in the appendix as Figure 35.

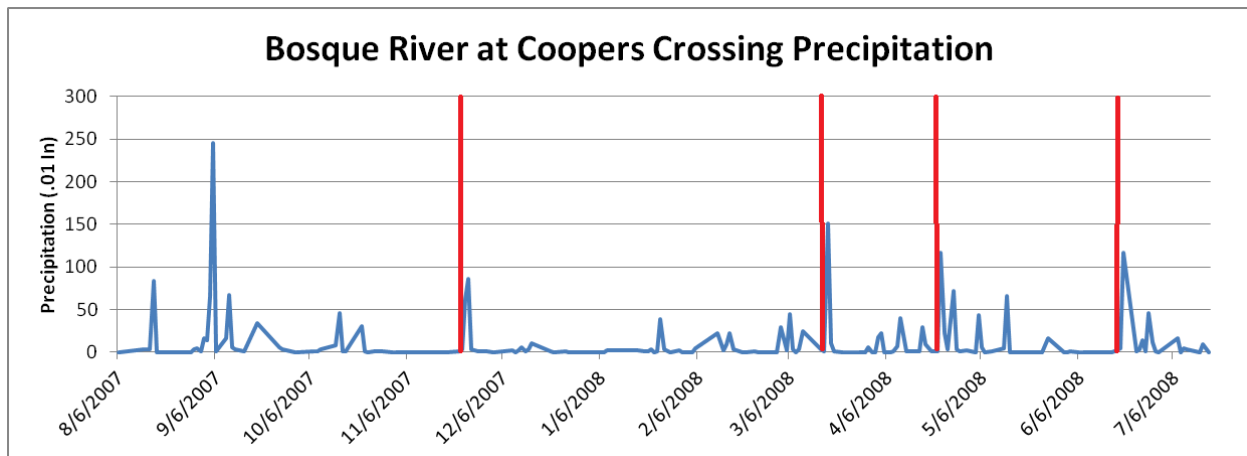


Figure 12 - Precipitation Data for Bosque River at Coopers Crossing

The dissolved oxygen data for this watershed is shown in Figure 13. It is difficult to draw any relationship between the storm events and dissolved oxygen because of the obvious seasonal trend. Instead it is more important to look at changes in the dissolved oxygen percentage of saturation. The saturation concentration of dissolved oxygen is strongly temperature dependent, explaining the seasonal variation.

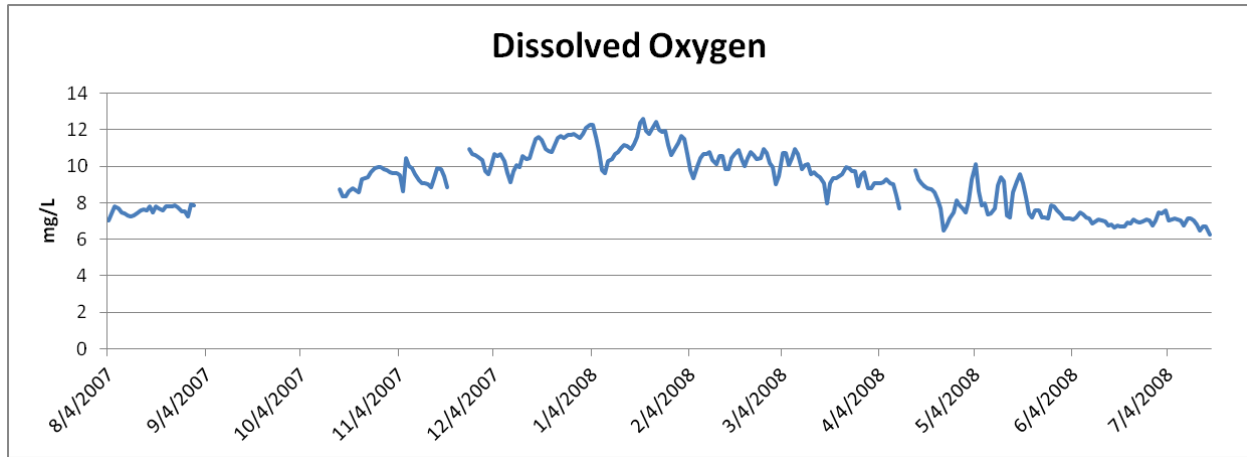


Figure 13 - Bosque River at Coopers Crossing Dissolved Oxygen

The dissolved oxygen saturation concentration was calculated using the water temperature data from the CWQMN station. Figure 14 shows the dissolved oxygen data as a percentage of saturation. The time points that correlate with the storm events are also marked in red. At each storm event, there is a small decrease in the dissolved oxygen percent saturation. Many other factors can affect dissolved oxygen and so there is a lot of noise in the data. It is difficult to say positively that the decreases are due to the large storm event, but it seems likely as it occurs for each event. The dissolved oxygen data for Bosque River at Clifton and Leon River at Gatesville has even more variability and so a complete analysis was not completed on this data set.

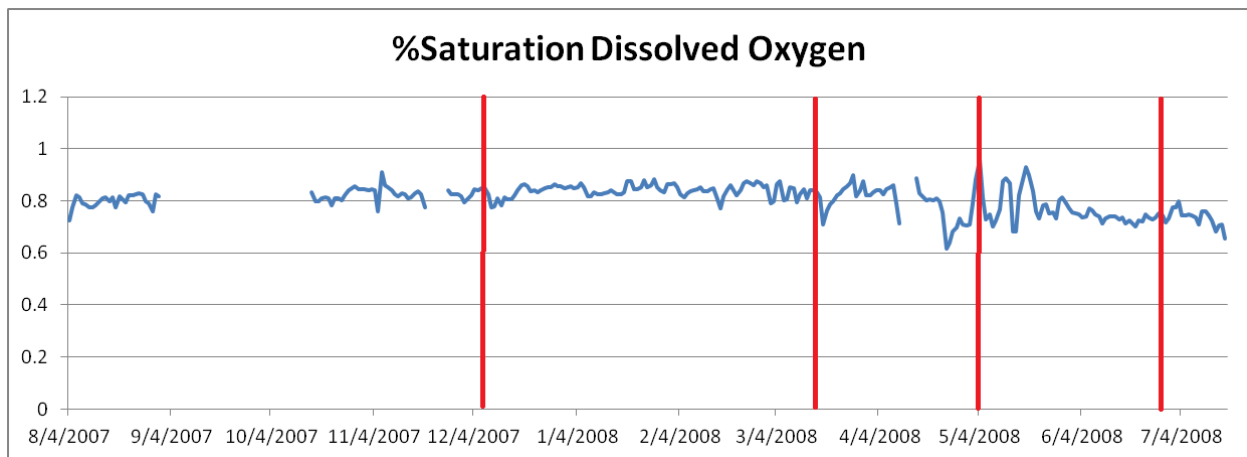


Figure 14 - Bosque River at Coopers Crossing Dissolved Oxygen %Saturation

Bosque River at Clifton had good data for both nitrate and ammonia. This watershed has 3.4% Hay/Pasture and 3.2% Cultivated Crops of the total area. Figure 15 shows the precipitation data for the Bosque River at Clifton in 2002. Figure 16 shows the nitrate water concentration data for 2002. There appears to be small decreases in the nitrate concentration when storm events occur, however this does not hold for all storm events. These small decreases may be due to dilution that is occurring from runoff. There is a definite seasonal trend in the water column concentration as the nitrate levels increase in winter and decrease during the summer.

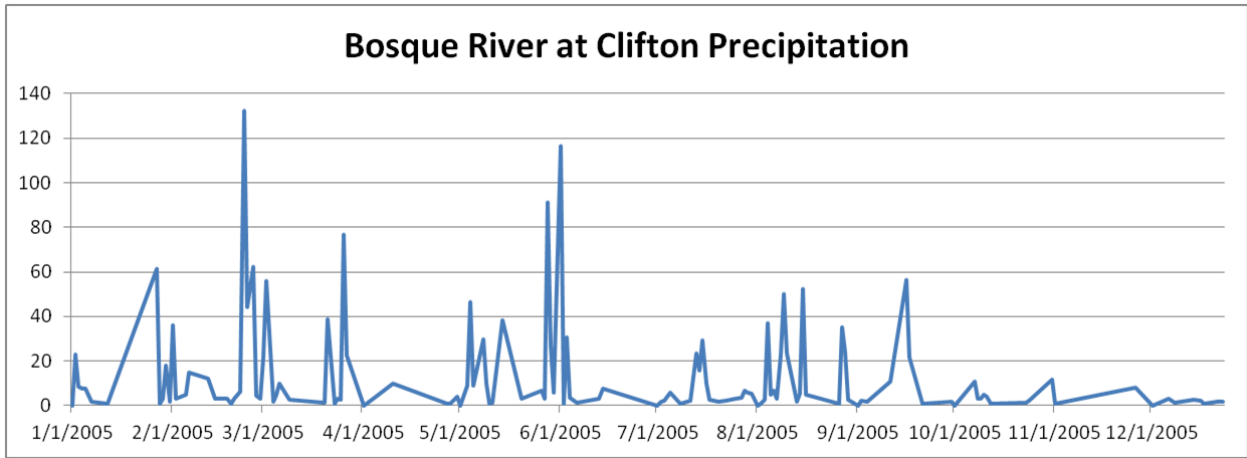


Figure 15 - Precipitation Data for Bosque River at Clifton

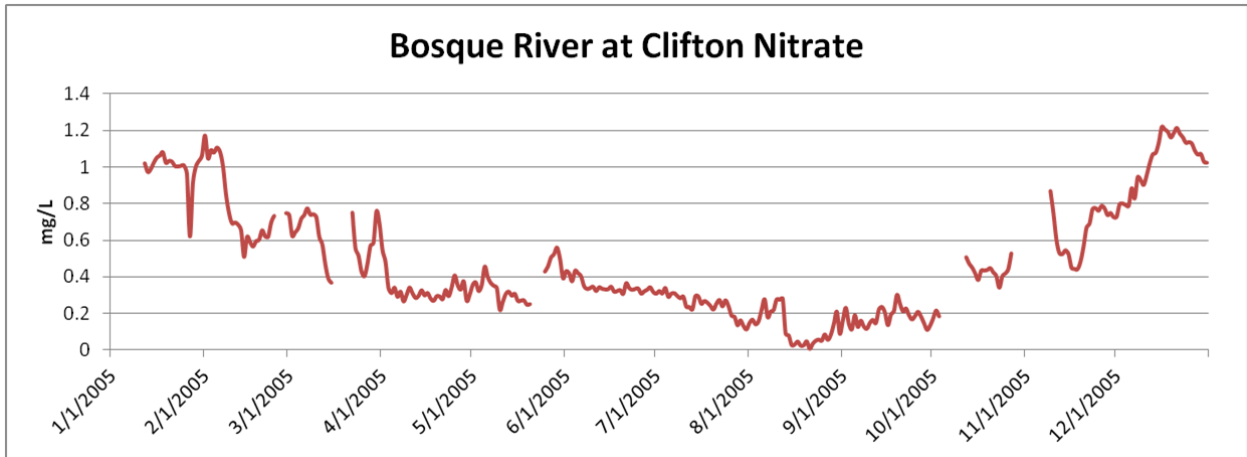


Figure 16 - Nitrate Concentration for Bosque River at Clifton

When trying to determine the nutrient loading to the river, the water concentration is not the most accurate metric. What is really important is the total amount of nutrients that are being flushed into the river. To find this, the water concentration is multiplied by the flow rate to find the mass loading of nitrate in the river. This mass loading is shown in Figure 17. The mass loading shows a more accurate picture of the nutrient impact on the river. The seasonal trend that is shown in the water concentration is not shown in the mass loading. The majority of the nutrients are transported by the river during the spring. The water column concentrations are actually lower during these peak mass discharges. The high precipitation during this time greatly increases the flow of the river, causing the high mass of nitrate to be diluted to a lower concentration. The timing of the large mass loading peaks correlate to a large storm event, but the following large storm events, such as early June, do not cause the same effect. This is due to the majority of readily removable nitrate already being washed off during earlier storm events, as nitrate is typically not continuously applied.

Figure 1

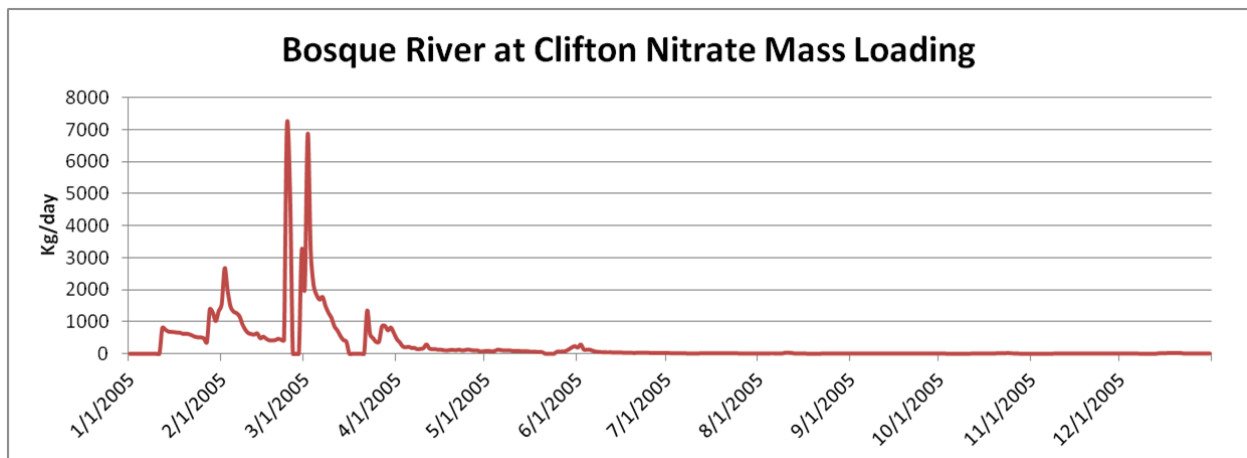


Figure 17 - Nitrate Mass Loading for Bosque River at Clifton

The ammonia data follows very closely with the nitrate data. The water column ammonia data is shown in Figure 18. There is not the same seasonal trend in the water column for ammonia. Instead there is an increase during the fall and then a slow decrease through the rest of the year. The same calculation was done to produce the mass loading of ammonia and that data is shown in Figure 20. The ammonia mass loading follows very similar pattern as the nitrate, although not to the same absolute level of mass loading. This is due to the increased flow rates driving the pattern in the mass loading. The majority of ammonia is transported by the river during the later winter and spring. The storm events occurring later in the year do not cause an increase in ammonia mass loading, agreeing with the nitrate data. This reinforces the idea that all of the available nutrients are washed off during the earliest major storm events after application.

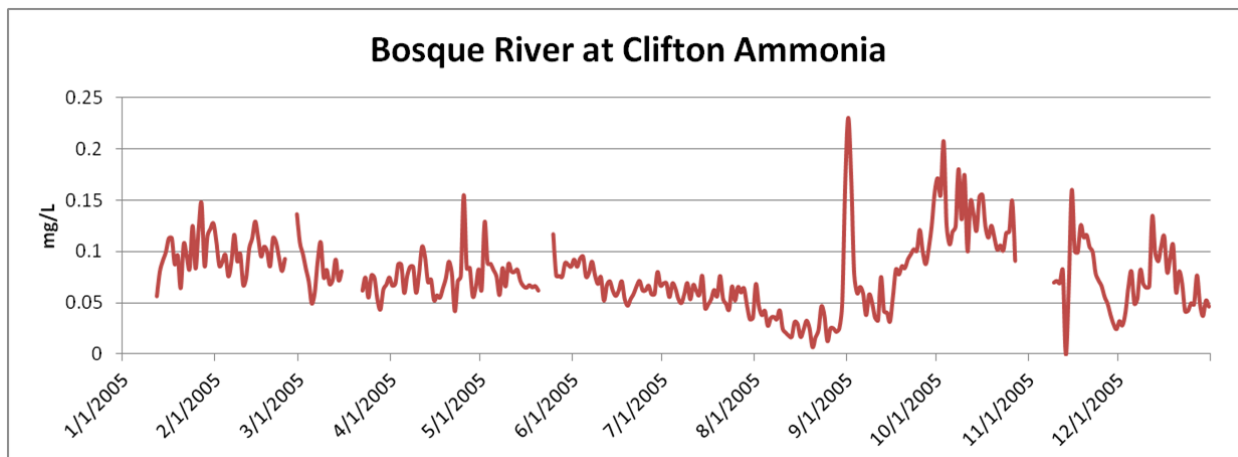


Figure 18 - Bosque River at Clifton Ammonia Concentration

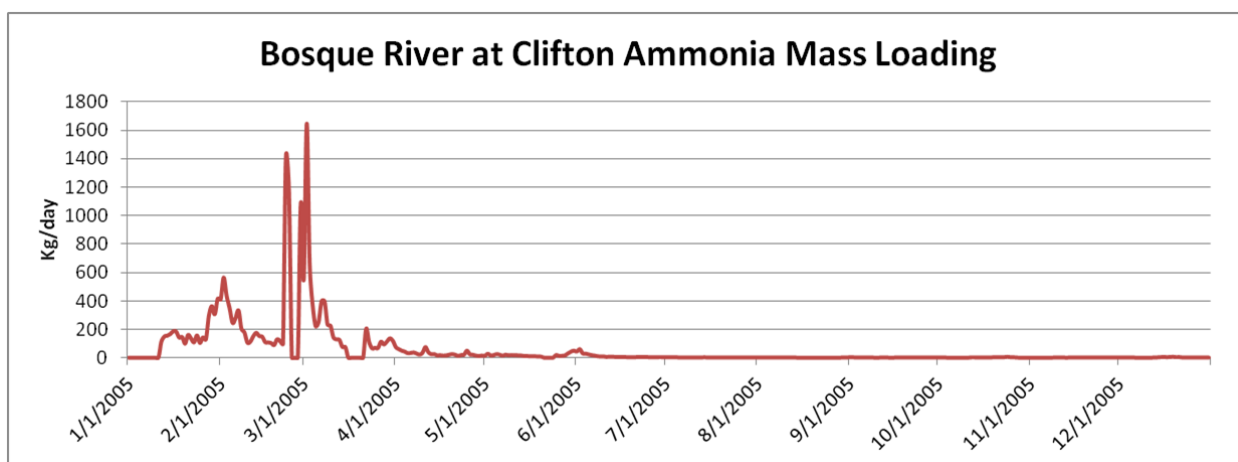


Figure 19 - Ammonia Loading for Bosque River at Clifton

Dissolved oxygen data for this site was not analyzed fully due to high variability within the data and the high quality of the nitrate and ammonia data.

Leon River at Gatesville also has data for both nitrate and ammonia for 2005. The precipitation data for this watershed can be found in Figure 20. There are not quite as many large storm events in this watershed, but the magnitude of the largest events are greater. This watershed has 6.7% Hay/Pasture and 7.4% Cultivated Crops of the total area, both values slightly more than double of the watershed for Bosque River at Clifton.

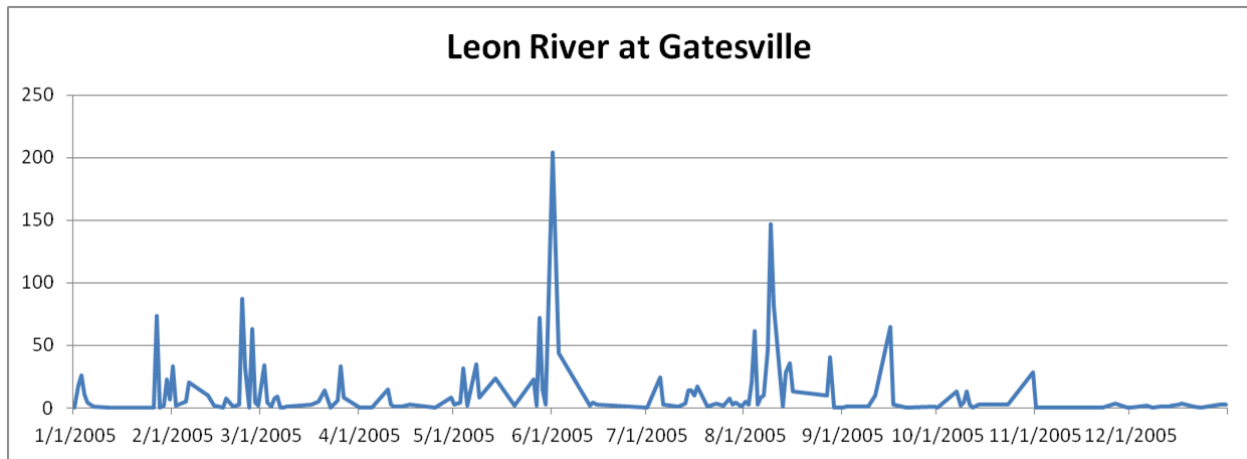


Figure 20 - Precipitation data for Leon River at Gatesville

Figure 21 shows the nitrate concentration data for the Leon River. There are not any defined seasonal trends. The concentration stays between 1 and 2 mg/L for the majority of the year. The one spike in concentration that does occur in October does not seem to correlate to a major storm event. There is a small rise in concentration in March which corresponds well with a series of medium storm events.

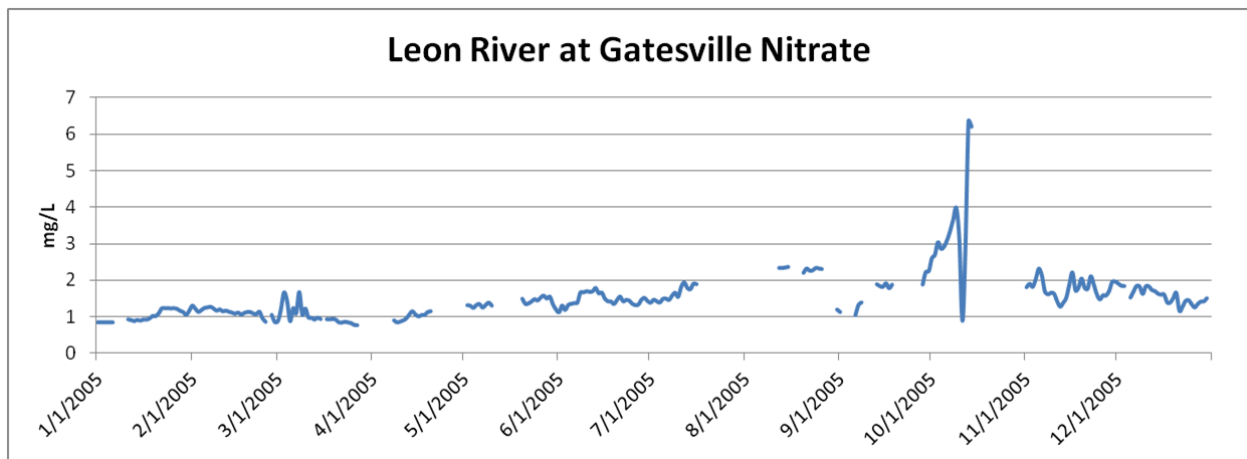


Figure 21 – Nitrate Concentration for Leon River at Gatesville

Again, the water concentration data is not the most accurate metric and so the mass loading was calculated and is shown in Figure 22. The majority of nitrate was carried through the river in the spring. There is one spike in August which corresponds to the second largest storm event of the year. The magnitude of the mass loading for nitrate is significantly higher than it was for the Bosque River.

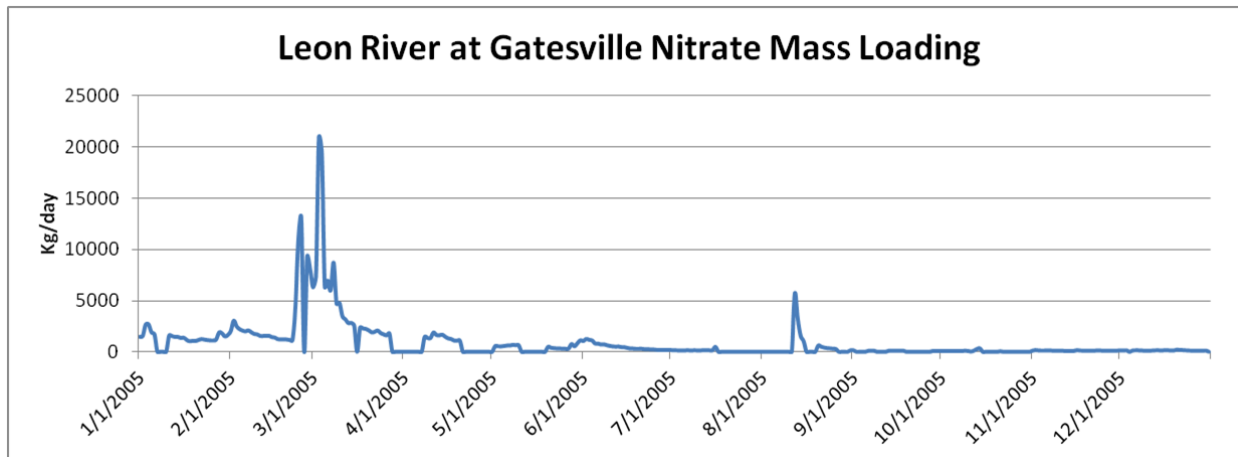


Figure 22 – Nitrate Mass Loading for Leon River at Gatesville

The mass loading data for ammonia in the Leon River can be seen in Figure 23. The trends are very similar to the ones seen in the nitrate data. However, an even higher proportion of the ammonia is carried during a shorter period. There is an additional spike in mid October which does not seem to relate to a specific storm event. The rest of the ammonia data can be seen in the appendix in Figure 36.

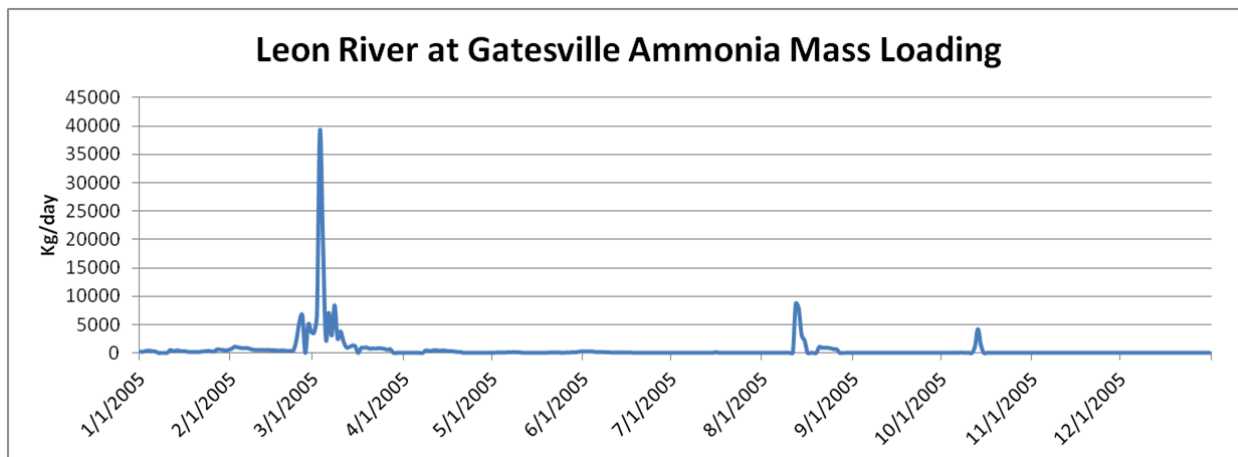


Figure 23 - Ammonia Mass Loading for Leon River at Gatesville

Data from the Bosque River at Clifton and Leon River at Gatesville can be easily compared since they have the same environmental parameters over the same time. Figure 24 shows a comparison of the water concentrations. The Leon River has higher nitrate concentrations over the entire year. However, it has been discussed that the water concentration does not show the most complete representation of nutrient impacts. The water concentration is most applicable when looking at acute or chronic toxicity impacts. The nitrate levels never cross

the EPA MCL, which would be a very conservative acute limit since humans would not be directly ingesting this water.

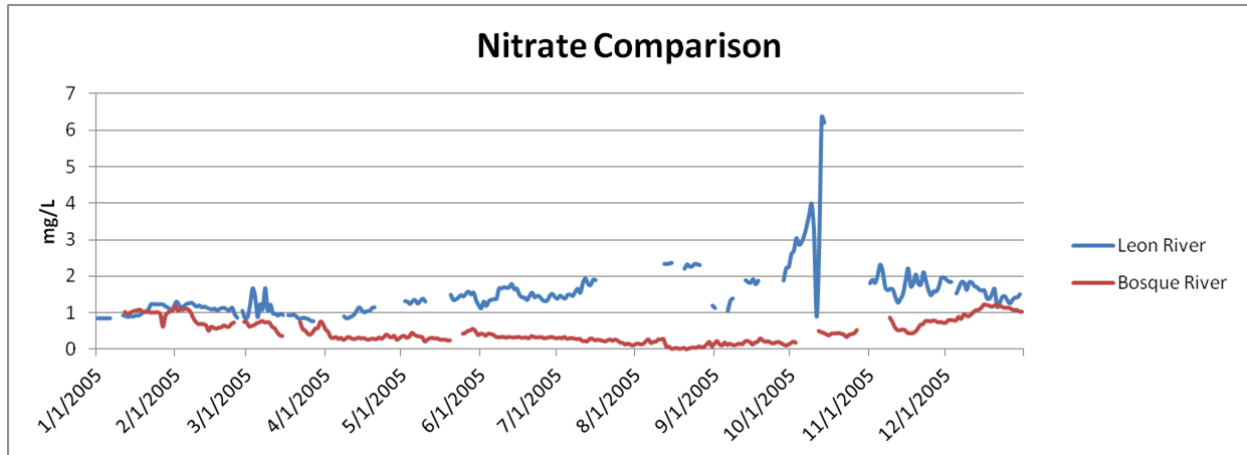


Figure 24 - Comparison of Nitrate Concentrations

Figure 25 shows the nitrate data converted into mass loading. This shows the Leon River transports a significantly higher amount of nitrate. If you just looked at this data, one could assume that the drainage area of the Leon River is a significantly higher source of nitrate. However, the drainage areas of these two locations are not the same size. The Bosque River at Clifton drains an area of 962 square miles while the Leon River at Gatesville drains an area of 2381 square miles. It is expected that the Leon River would transport more nitrate since it drains a larger area.

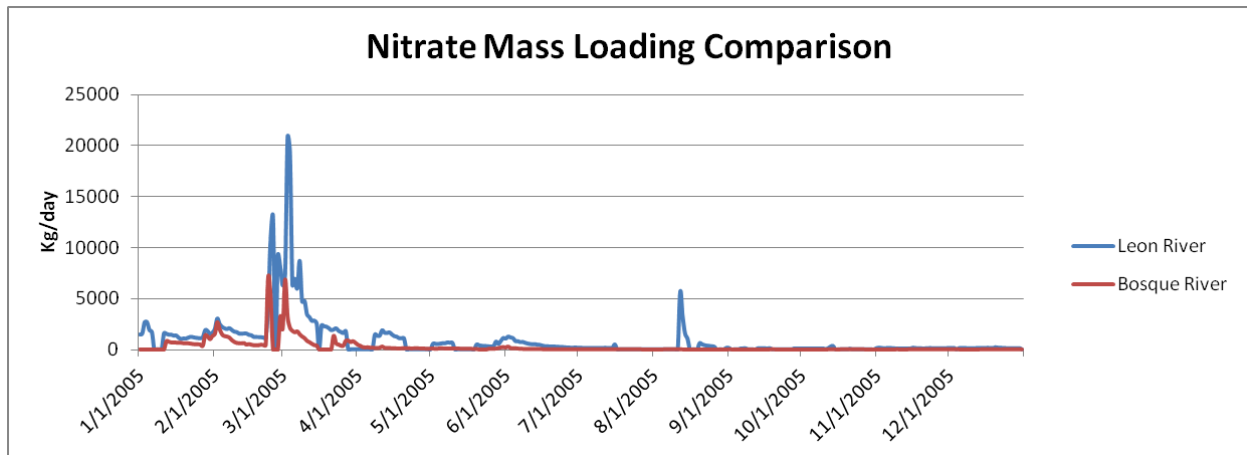


Figure 25 - Comparison of Nitrate Mass Loadings

The nitrate mass loading can be normalized by the total drainage area. This data is shown in Figure 26. After this area correction, the data matches up very well. The nitrate mass loading can also be normalized by the agriculture land area, since that is a primary source of the non-point contamination. Figure 27 shows the nitrate mass loadings normalized by cultivated

agriculture area. Only cultivated agriculture area was used because pasture land is less likely to have fertilizer applied. These two graphs show different results. After normalizing to cultivated area, the Bosque River shows a higher nitrate mass loading. It is difficult to determine which of these graphs is a more accurate representation of actual conditions because both make some assumptions. Normalizing to the total area assumes that the non-point source nitrate loading is relatively constant over the watershed. Normalizing to the cultivated area assumes that agriculture is the primary source of nitrate. Neither of these takes into account point source pollution, which could be a problem if there are large sources within the watershed. The actual nitrate loading probably lies somewhere in between these two representations. Agriculture is probably a major source of nitrate into the river, so Figure 27 over compensates. However, all land types do not contribute equally and so Figure 26 is not entirely accurate. Most accurately, some weighting for different land types could be applied along with identification of major point sources.

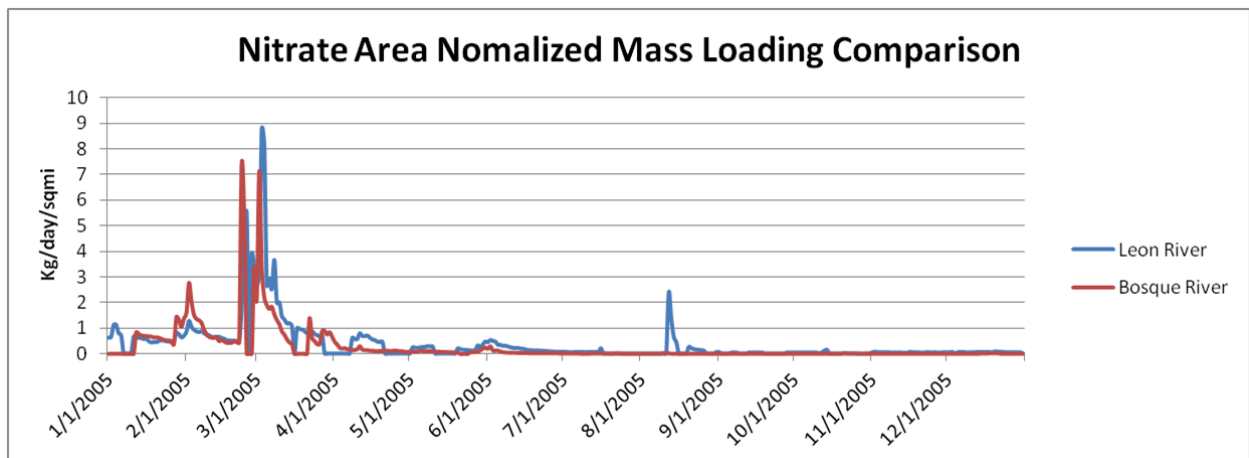


Figure 26 - Comparison of Nitrate Mass Loadings Normalized by Total Drainage Area

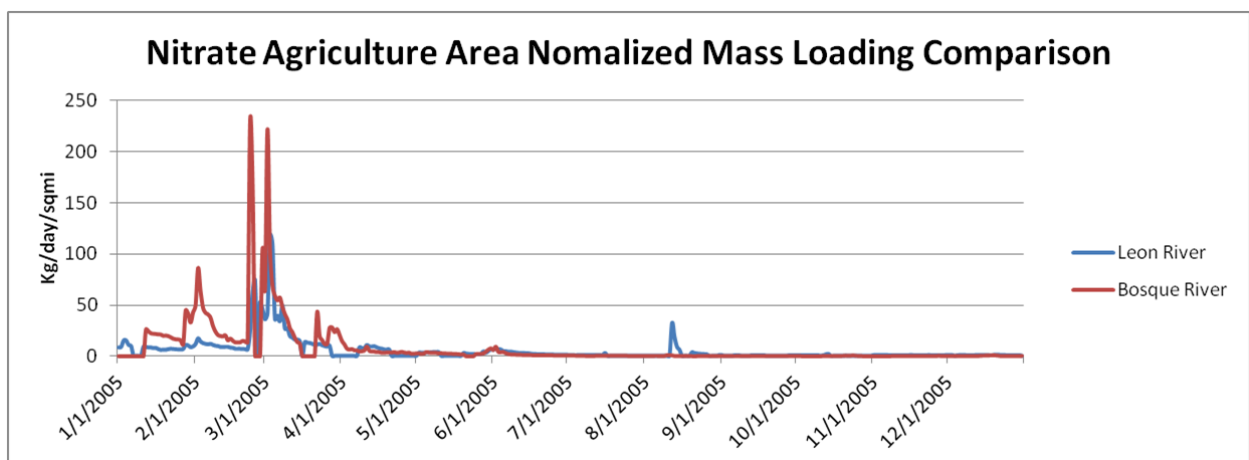


Figure 27 - Comparison of Nitrate Mass Loadings Normalized by Agriculture Area

The mass loadings for ammonia can also be compared for these two watersheds. Figure 28 shows the ammonia mass loading normalized by total drainage area. Figure 29 shows the ammonia mass loading normalized by cultivated agriculture area. The conclusions are easier to draw from this data. Both graphs show that the Leon River has a significantly higher ammonia mass loading, whether it is normalized by total area or agriculture area. The actual magnitude of the mass loading may not be quantitatively accurate because there are still assumptions in both calculations. Again, there are point sources for ammonia that are not being taken into account. The different land types provide different amounts of ammonia per unit area but there is no data to find these weights.

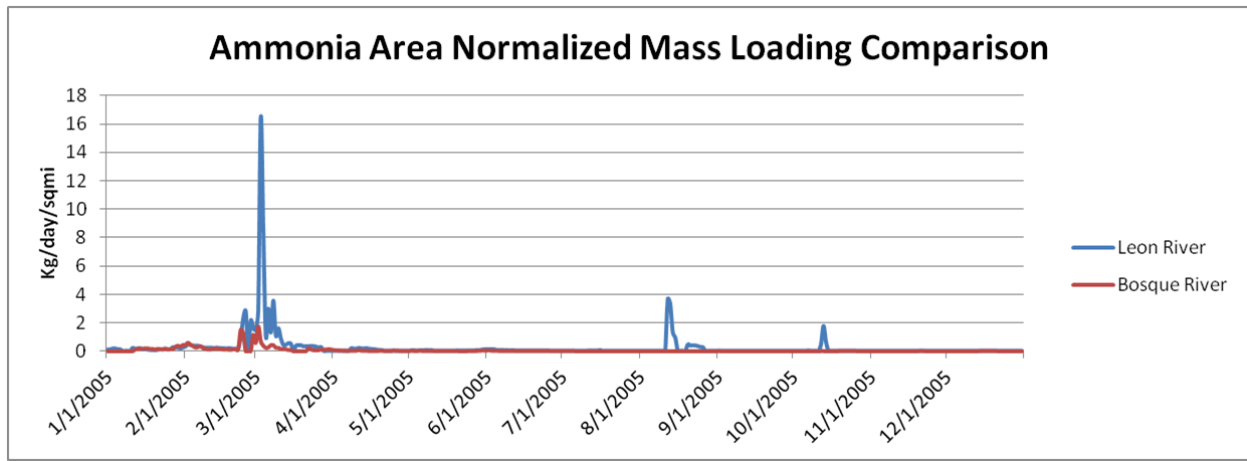


Figure 28 - Comparison between Bosque River and Leon River Ammonia Area Normalized

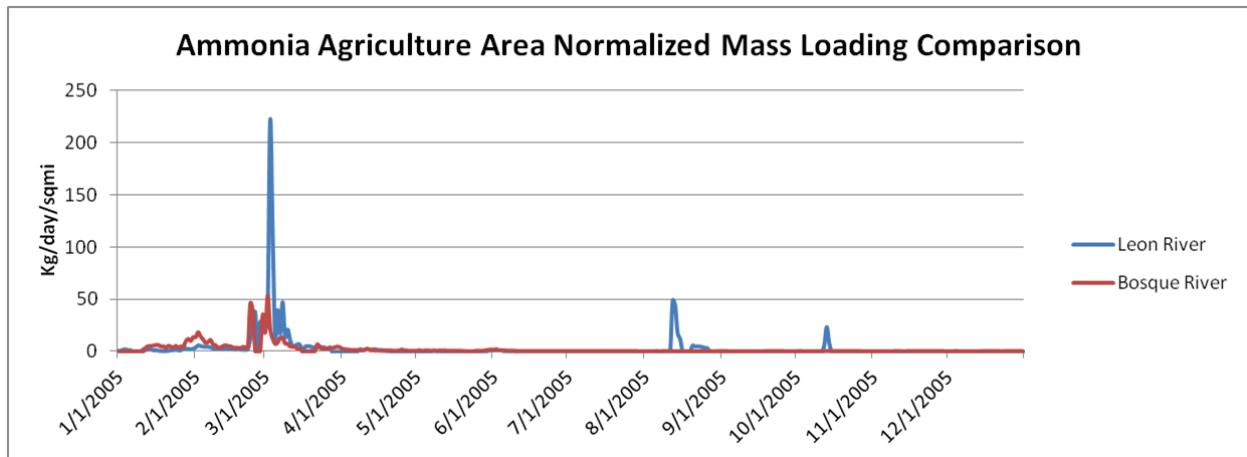
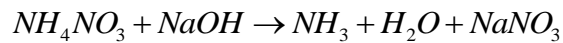


Figure 29 - Comparison of Ammonia Mass Loadings Normalized by Agriculture Area

Using these mass loadings per unit agriculture area, a simple mass balance can be performed on the fertilizer applied to agriculture area. There are a few assumptions that need to be made to carry out this mass balance. The first assumption is that the only fertilizer being applied is ammonium nitrate. This is one of the most popular fertilizers, but there are several others commonly used. Ammonium nitrate allows for the most direct translation to the ammonia

and nitrate levels in the river. Ammonium nitrate (NH_4NO_3) is changed to ammonia (NH_3) and nitrate (NO_3) through a reaction as shown below.



This reaction is important because it corrects the mass added as ammonium nitrate to resultant masses of ammonia and nitrate. Each gram of ammonium nitrate reacts to form .213 grams of ammonia and .774 grams of nitrate. This allows for the comparison of mass added to agriculture land as ammonium nitrate to ammonia and nitrate measured in the rivers. The second assumption is that the cultivated agriculture land is the only source of ammonium nitrate. This is probably not entirely accurate, but these areas are a primary source. If it is assumed that the ammonia and nitrate found in the rivers only come from ammonium nitrate added to agriculture land, then a percent loss from the agriculture land can be calculated. Because of this assumption, the percent loss will be overestimated.

Depending on soil conditions and crop type, between 50 and 150 pounds of ammonium nitrate is added per acre of agriculture land. To find the total amount of ammonia and nitrate found in the river per acre of agriculture area, the area under the curve in Figure 27 and Figure 29 is integrated for the year. The output is then converted to per acre from per square mile. The resultant values are found in Figure 30.

	Ammonia (kg/acre)	Nitrate (kg/acre)
Leon River	1.79	2.85
Bosque River	1.03	4.71

Figure 30 - River Ammonia and Nitrate per Acre of Agriculture Land

The 50 and 150 pounds of ammonium nitrate are corrected for mass changes due to the chemical reaction to form ammonia and nitrate. The masses totaled in the river can then be divided by the masses added as fertilizer to determine what percentage of the fertilizer was lost to runoff. The runoff losses can be found in Figure 31. The runoff losses are given as a range to account for the different amounts of ammonium nitrate added and so the lower percentage is for 50 pounds added and the higher percentage is for 150 pounds. This data shows that a significant percentage of the applied fertilizer is lost to runoff. However, it is important to remember that these are overestimates due to the assumption that all of the ammonia and nitrate found in the rivers are from agriculture runoff.

	Ammonia Runoff Loss (%)	Nitrate Runoff Loss (%)
Leon River	12.4-37.1	5.4-16.2
Bosque River	7.1-21.3	8.9-26.8

Figure 31 - Runoff Losses

The goal of this project was to examine the impact of large storm events on nutrient loadings in Texas rivers. The storm events do seem to have a small impact on dissolved oxygen levels as shown in the Bosque River. However, there is a lot of natural variability in the data and

so it is difficult to determine exactly how much of an impact the storm events have. The outcome is more pronounced for nitrate and ammonia loadings in the Bosque River and Leon River. The storm events do have an impact on the nutrients being flushed into the river but the larger impact seems to be from the timing of nutrient application. Nutrients are typically applied at the beginning of the growing season. The majority of nutrients are flushed off during the first major storm events after application. Subsequent storm events do not cause the same level of nutrients to runoff into rivers. This is similar to 'first flush' in stormwater runoff in urban regions where the earliest rain washes most of the contamination into storm sewers. After the early rain carries out built up contaminants, subsequent rain runoff is much cleaner. This analysis did not take point sources into account which may provide some baseline nutrient loadings that are not as seasonally dependent. The mass balance performed on nitrate and ammonia show that a significant amount of applied fertilizer can be lost to runoff. Up to 37.1% of nutrients added as fertilizer could be lost to runoff, however, this is probably an overestimate because it assumes that all nutrients found in the river can be attributed to agriculture runoff.

Data Sources

Texas Commission on Environmental Quality – Continuous Water Quality Monitoring Network.
<http://www.tceq.texas.gov/waterquality/monitoring/swqm_realtime.html>

Multi-Resolution Land Characteristics Consortium – National Land Cover Database 2006.
<<http://www.mrlc.gov/nlcd2006.php>>

United States Geologic Survey – Water Quality Data for Texas.
<<http://waterdata.usgs.gov/tx/nwis/qw>>

National Oceanic and Atmospheric Administration – National Climactic Data Center, Online Climate Data Directory.
<<http://www.ncdc.noaa.gov/oa/climate/climatedata.html>>

References

“Is it Worth Fertilizing Alfalfa with Current Fertilizer Prices?” Steve Orloff, Dan Putnam, and Rob Wilson. UC Davis Agronomy and Range Science Department

“Nitrogen – Best Management Practices” Division of Plant Sciences – University of Missouri.
<<http://plantsci.missouri.edu/nutrientmanagement/nitrogen/practices.htm>>

“Nitrogen Fertilizer Management in Good Economic Times and Bad.” Purdue University, Agronomy Department. 2003.

“Quality Assurance Project Plan for Continuous Water Quality Monitoring Network Program.” Texas Commission on Environmental Quality, Water Quality Planning Division. March 2012

“Source Water Protection Practice Bulletin.” Environmental Protection Agency, Office of Water, 2010

Appendix

These graphs were not directly used for data analysis but may be of interest.

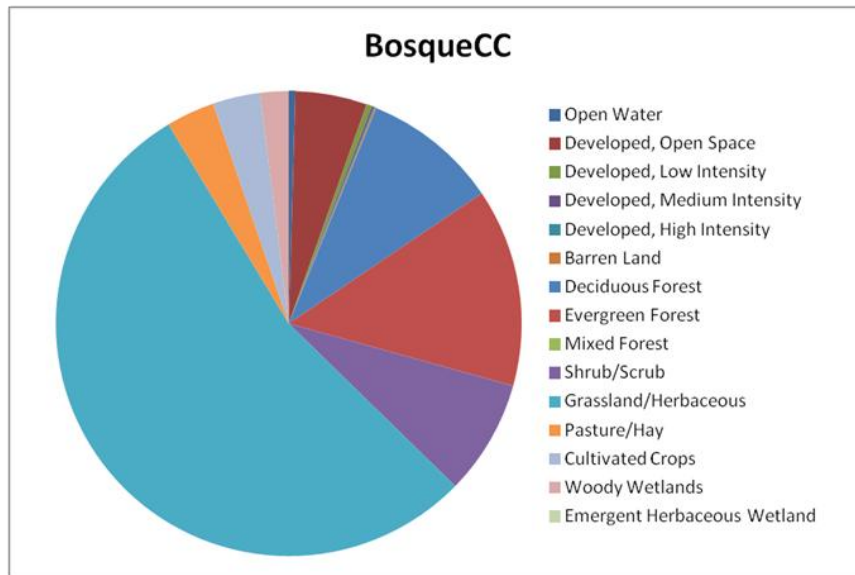


Figure 32 - Land Cover for Bosque River at Coopers Crossing Watershed

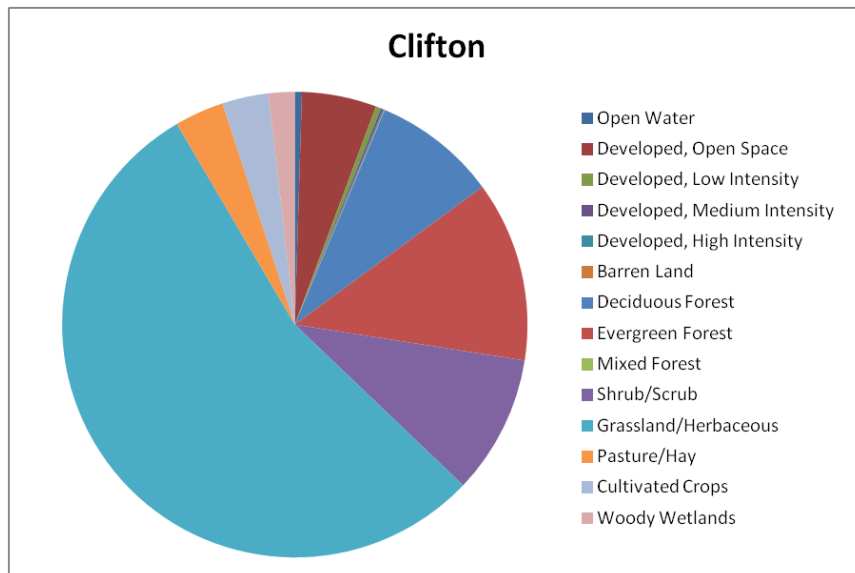


Figure 33 - Land Cover for Bosque River at Clifton Watershed

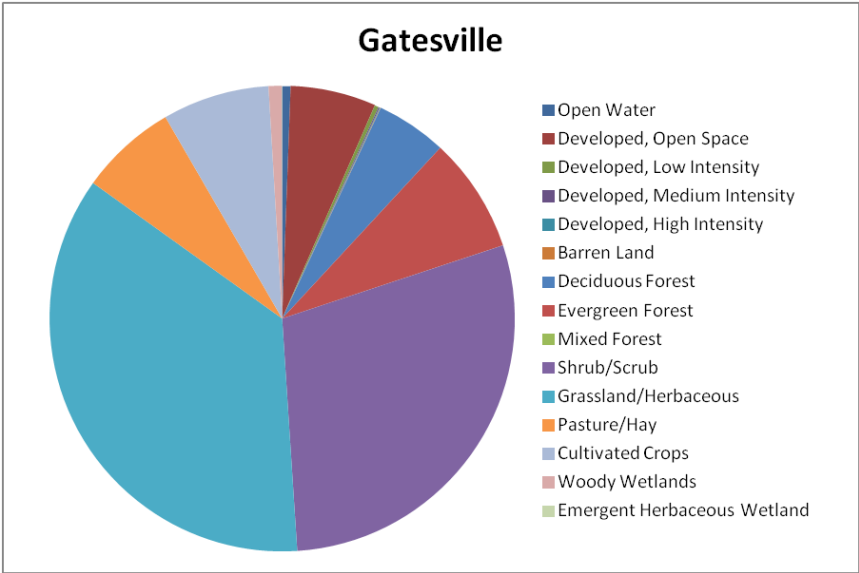


Figure 34 - Land Cover for Leon River at Gatesville

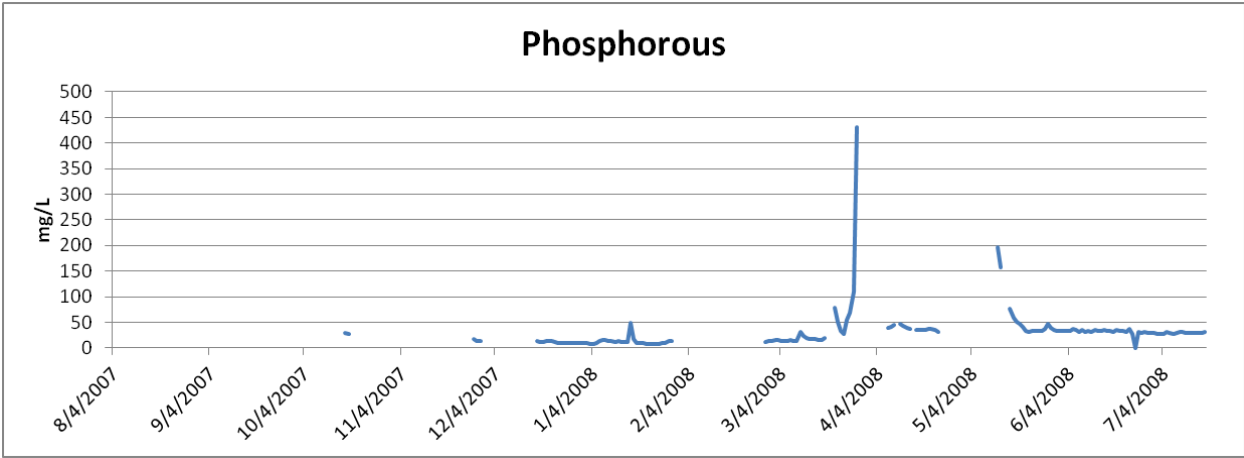


Figure 35 - Bosque River at Coopers Crossing Phosphorous Concentration

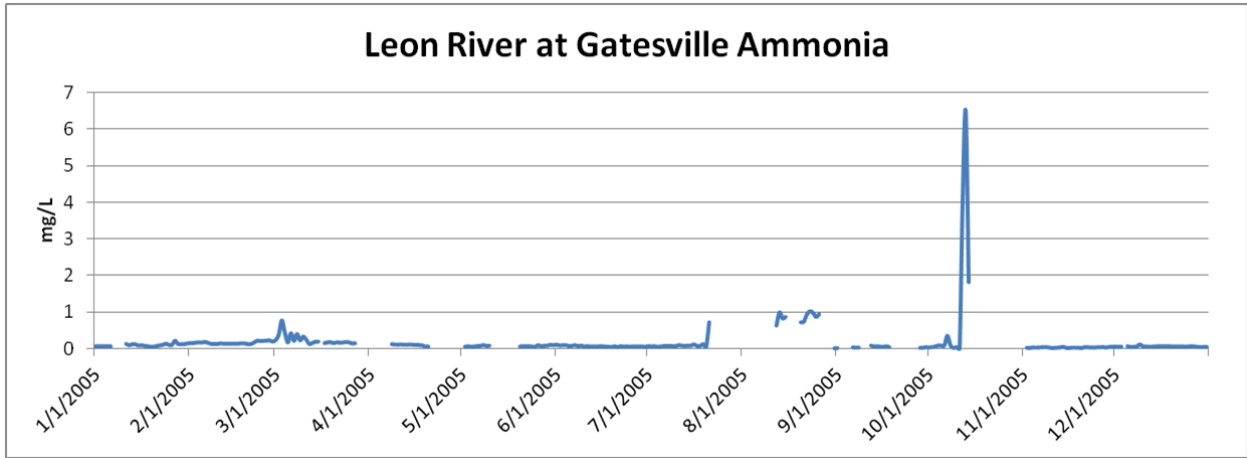


Figure 36 - Leon River at Gatesville Ammonia Concentration

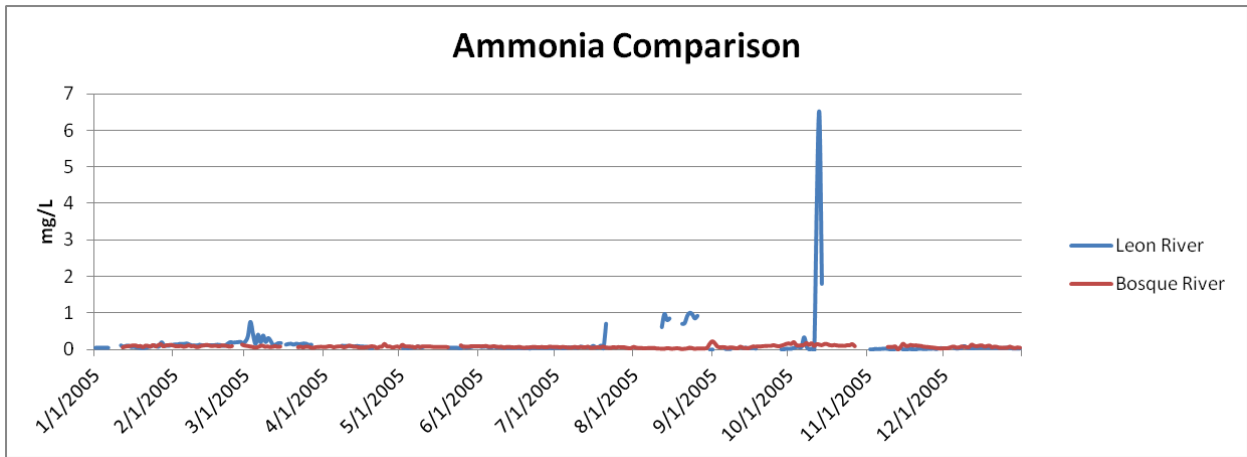


Figure 37 - Comparison between Bosque River and Leon River Ammonia Concentrations

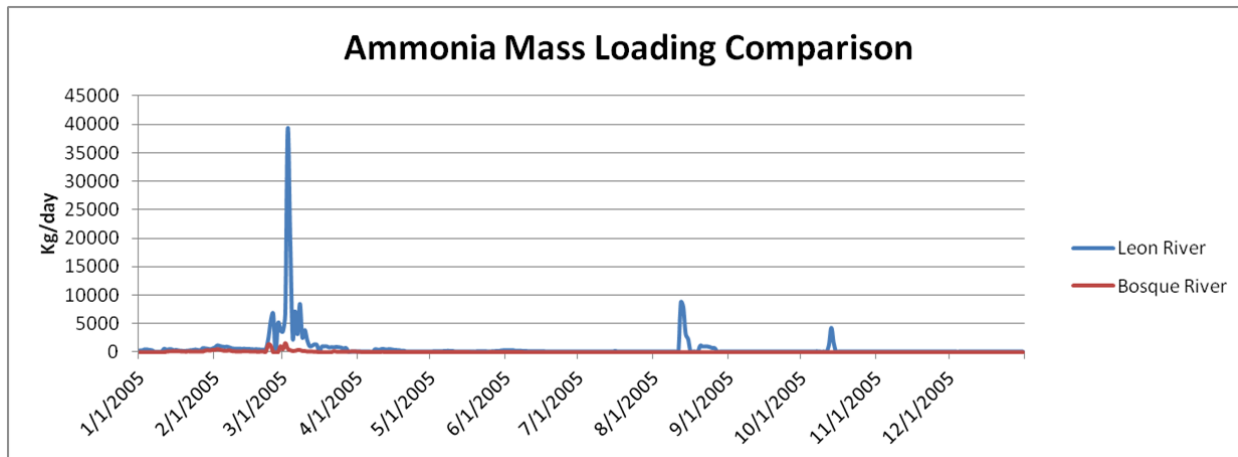


Figure 38 - Comparison between Bosque River and Leon River Ammonia Mass Loading