Nitrate-nitrogen patterns in the Raccoon River Basin related to agricultural practices

J.L. Hatfield, L.D. McMullen, and C.S. Jones

Abstract: Nitrate-N concentrations in the Raccoon River have increased beginning in the early 1970s. Since this river is the predominant water supply for the City of Des Moines in Iowa, there is concern about the potential long-term impacts of these trends. Improvements in water quality from agricultural watersheds are critical to protect the water supply, and understanding the factors affecting water quality will lead to potential changes in agricultural management to improve water quality. The historical database of nitrate-nitrogen (NO$_3$-N) concentrations sampled at the Des Moines Water Works have been combined with observations on N fertilizer use, animal production, crop yields, land-use changes, and precipitation patterns to evaluate these interrelationships. Annual NO$_3$-N concentrations in the Raccoon River watershed have increased since 1970 in spite of no significant change in N fertilizer use for the past 15 years. There have been three years with maximum NO$_3$-N concentrations above 18 mg L$^{-1}$. However, these spikes occurred throughout the past 30 years and are not isolated to the last 10 years of record. Nitrate-N loads from the Raccoon River watershed have shown a slight decrease in the past ten years because of the increased crop yields and increased removal of N in the corn (Zea mays L.) and soybean (Glycine max [L.] Merr.) grains. Production numbers for cattle have decreased by 63% since the early 1980s, while hogs have shown a 21% decrease over the same time period. Therefore, N available for application into the basin has decreased by 25%. Annual variations in NO$_3$-N loads are significantly related to precipitation in the first five months of the year. A significant correlation was found between the land area within the watershed cropped to small grains and hay crops and the increase of NO$_3$-N since 1970 ($r = -0.76$). This relationship was caused by alteration in the seasonal water-use patterns and loss of N during the fall or early spring in the water movement in contrast to corn or soybean, which have a limited N uptake pattern concentrated between June and early September. Changes in the water-use patterns caused by shifts in cropping patterns provide an explanation for the positive correlation between precipitation and flow during the early part of the year. Development of agricultural management practices that can potentially affect water quality will have to be more inclusive of all components in agricultural systems, rather than only changing fertilizer rate or timing.

Key words: cropping practices—farming practices—nitrogen management—water balance—water quality—watershed

Nitrate nitrogen loss from agricultural watersheds has become a topic of great interest in the past 20 years. Detections of nitrate-nitrogen (NO$_3$-N) in water above the drinking water standard (10 mg L$^{-1}$) raise questions about the source of N and the potential impact of agricultural practices. Keeney and Deluca (1993) evaluated NO$_3$-N in the Raccoon River watershed from the early 1940s through the 1970s and concluded that the intensity of tillage and the subsequent N mineralization was the primary source of NO$_3$-N in the river that offset the increase in commercial N fertilizer use in the 1970s. MiCIsaac and Libra (2003) assessed the nitrate concentrations in the Des Moines River using current analytical methods and found that there were increases in the mean NO$_3$ concentrations from 1945 to 2001 periods. Schilling and Libra (2000) evaluated 15 Iowa watersheds and concluded that NO$_3$-N concentrations were directly related to the percentage of row crops in the watershed. Thomas et al. (1992) re-sampled seven small agricultural watersheds throughout Kentucky in 1989 and 1990 that they had previously sampled in 1971 to 1972 and found that NO$_3$-N concentrations were almost the same despite the minor doubling of N fertilizer use. The geology of these watersheds is sedimentary and ranges from sandstones to shales, the annual precipitation for these watersheds ranges from 1,110 to 1,330 mm (43.7 to 52.4 in), and the annual runoff ranges from 371 to 481 mm (14.6 to 18.9 in). Thomas et al. (1992) concluded that the parent rock of the soils within the watersheds had a greater effect on NO$_3$-N concentrations than agricultural use patterns, and there was no evidence across these watersheds that fertilizer use was detected in NO$_3$-N or PO$_4$-P levels in the streams. Variation in the results across different watersheds suggests that there is no single answer for the changes in NO$_3$-N concentrations from agricultural watersheds over time.

After repeatedly violating the US Environmental Protection Agency’s drinking water standard of 10 mg L$^{-1}$ for NO$_3$-N, and faced with increasing levels of nitrate in its source water, the Des Moines Water Works (DMWW) constructed the world’s largest ion exchange nitrate removal facility in 1991 (McMullen 2001). Since the facility became operational in 1992, the nitrate standard has not been violated. However in June of 2005, the utility again nearly violated the nitrate standard due to very high water demand concurrent with very high source water nitrate levels, a heretofore rare circumstance. This motivated DMWW staff to extensively review long-term flow and nitrate data for its primary water source, the Raccoon River. United States Geological Survey flow data dating back to 1919, along with nitrate data generated from DMWW’s testing laboratory dating to 1931, are a unique data source to evaluate the interrelationships among water quality and agricultural practices. Understanding the interactions between NO$_3$-N levels in water supplies and agricultural production systems will provide insights into efforts to reduce N levels in drinking water. There have been several studies that have shown the linkage between agricultural...
land use and N concentrations in adjacent water bodies. Studies by Hill (1978), Mason et al. (1990), and Jorden et al. (1997) have all shown that as the intensity of agricultural practices increases, the amount of N moved to adjacent streams also increases.

Nitrate-N concentrations in the Raccoon River and surrounding areas in Central Iowa have been the subject of several studies over the past 20 years. Lucey and Goobhy (1993) reported that NO\textsubscript{3}-N concentrations could be explained by a four-variable model based on streamflow from the previous seven days, soil moisture condition, and the cosine of the day of year (DOY) and sine of the DOY. They estimated the soil moisture condition from a simple hydrologic model for the watershed. This model explained 70% of the variation in the NO\textsubscript{3}-N concentrations (Lucey and Goobhy 1993). Schilling and Zhang (2004) evaluated baseflow in the Raccoon River watershed and found that baseflow contributed nearly two-thirds of the NO\textsubscript{3}-N export from the watershed, which suggested that seasonal patterns in the enrichment of baseflow with NO\textsubscript{3}-N were linked with seasonal crop N uptake patterns. Zhang and Schilling (2005) completed a more detailed analysis of the temporal and spatial patterns of flow in streams contributing to the Raccoon River watershed and baseflow in the river and found NO\textsubscript{3}-N concentrations and loading have half-year cycles, while precipitation, streamflow, and baseflow have yearly cycles. Schilling (2005) discovered that the increase in row crop intensity increased the baseflow and baseflow percentage in the Cedar and Raccoon River Basins. This study addressed the factors affecting daily NO\textsubscript{3}-N concentrations; however, a detailed analysis of the effects of changes in the agricultural practices within a watershed over long periods of time has not been extensively evaluated.

The objectives of this study were to evaluate the long-term patterns in NO\textsubscript{3}-N lost from the Raccoon River watershed and the relationship of these patterns to changes in agricultural practices within the watershed. These analyses will provide details on the potential of improving management practices to reduce NO\textsubscript{3}-N losses from the watershed.

**Materials and Methods**

**Description of the Raccoon River Basin.** The Raccoon River rises in Buena Vista County, Iowa, and travels approximately 300 km (186 mi) to its confluence with the Des Moines River in the City of Des Moines. The mainstem of the Raccoon River, also known as the North Raccoon (Hydrologic Unit Code 07100006) in its upper stretches, has two main tributaries: the Middle and South Raccoon Rivers. The Middle Raccoon River rises in northwestern Carroll County and flows 120 km (74.5 mi) to join the South Raccoon near Redfield, Iowa. The South Raccoon River rises in northwest Carroll County and flows 120 km (74.5 mi) to join the South Raccoon near Redfield, Iowa. The South Raccoon River rises near Van Meter, Iowa, a few kilometers downstream from the South Raccoon watershed. The combined flows of the Middle and South Raccoon (Hydrologic Unit Code 07100007) join the North Raccoon near Van Meter, Iowa, a few kilometers downstream from Redfield. The entire Raccoon River watershed drains land from 17 counties and 9,324 km\(^2\) (3,304,010 ac), 6.4% of Iowa’s total land area (figure 1). Agriculture is dominant in the basin with over 80% of the land area in agriculture production. The soils in the Raccoon River watershed were formed from Wisconsin till under a native prairie grass vegetation, and the basin is predominantly in the Des Moines Lobe that is characterized by a prairie pothole structure with extensive drainage systems installed in the early 1900s that remove water from the landscape into nearby streams. It has been estimated that over 40% of the agricultural land area in this region of Iowa has subsurface drainage (Zucker and Brown 1998). Installation of subsurface drainage has greatly altered the hydrology of the watershed by providing a more direct conduit from fields into adjacent surface water streams. Because of subsurface drains, soluble nutrients, e.g., NO\textsubscript{3}-N are being readily transported from fields into surface water sources.

The Raccoon River as a Source of Drinking Water. The Raccoon River and shallow groundwater influenced by it is the primary source of drinking water for Des Moines Water Works’ (DMWW’s) two treatment plants that serve the Des Moines Metropolitan area. From 1884 until 1948, the utility’s Fleur Drive Treatment Plant obtained water exclusively from an underground collection system known locally as the infiltration gallery. This is a 5 km (3.1 mi) long, 91 cm (35.8 in) internal diameter pipe that runs parallel to the Raccoon River, 10 m (32.8 ft) below grade. Distance from the river varies between 15 and 30 m (49.2 and 98.4 ft). The pipe was installed in short (approximately 1 m [3.28 ft]) sections, with gaps left between the sections that allow water to collect in the pipe. Water quality and volume from these pipes is highly influenced by the river, but the water benefits from bankside filtration which removes much of the solid and suspended matter present in the river water. River water is also diverted to a series of constructed ponds that lies above the gallery, which helps saturate the surrounding soil structure, increasing water yield.

![Figure 1](image-url)
By the late 1940s, water demand had increased to the point where yield from the gallery was not sufficient. The utility constructed a permanent intake on the Raccoon River, and direct use of river water then supplemented the supply from the infiltration gallery. At the utility’s Maffitt Treatment Plant, shallow arrays of infiltration pipes placed in the river bed are used to extract water for this water treatment facility.

**Nitrate Data.** Nitrate-N data were collected by analyzing samples taken from DMWW’s Raccoon River intake at the Fleur Drive Treatment Plant. Grab samples have been collected at or near this site since the 1930s. Prior to the early 1970s, regular samples have been collected at seven o’clock in the morning Central Standard Time at a frequency dependent on the nitrate level in the river; i.e. sometimes daily, but usually never less than weekly. Since 1988, nitrate concentrations have been determined using inorganic anions by ion chromatography techniques, most recently Environmental Protection Agency method 300.0 (National Environmental Methods Index 2008a). Prior to 1988, measurements were made using ion selective electrode and colorimetric techniques (Method 4500-P-F) (National Environmental Methods Index 2008b). Quality assurance/quality control procedures included fortified samples (spikes), replicates, and known concentration samples, all analyzed with each analytical batch since 1974. Concentrations of $\text{NO}_3^-$ are reported as mg L$^{-1}$. Observations that were collected weekly were smoothed using regression techniques to create daily values to link with the discharge data from the Raccoon River and are used throughout this analysis.

**Water Flow Data.** Discharge and flow rates were obtained from the United States Geological Survey gauging station located at the Van Meter site (United States Geological Survey 05484500) on the Raccoon River (USGS 2008). This station has been in use since it was established in 1916, and the data were obtained from the records available from 1970 through 2004. Discharge was converted to daily flows and linked with the daily concentrations to create daily load values expressed as kg day$^{-1}$.

**Agricultural Data.** Crop areas for the counties in the Raccoon River Basin were obtained from the National Agriculture Statistics Service (USDA NASS 2009) for the available records since 1949. These records included all crops produced within the counties; however, emphasis was placed on the changes in corn and soybean area over the period through 2002. Fertilizer use data for each county was obtained from the sales records for each county available from the Iowa Department of Agriculture and Land Stewardship Fertilizer Division (IDALS 2009). Until 2002, records were maintained for each county by the type of fertilizer sold. It was assumed in these analyses that fertilizer sold within the county was applied within the county. To determine the application amounts for counties with a portion of their land area within the Raccoon River watershed, the total fertilizer amount was adjusted by the portion of the county within the watershed and the fraction of crop area within the county to derive the application rate per unit area. Total amount used for the watershed was determined as the sum of yearly sales for all counties within the watershed.

Animal production numbers were obtained from the National Agriculture Statistics Service agricultural inventory data (USDA NASS 2009). Individual county numbers were extracted for total cattle and hog inventory and the county values were summed for each county within the basin area. Estimates of N from manure produced from each species were obtained using values for cattle and swine obtained from the Midwest Plan Service values for cattle and swine (Midwest Plan Service 1993) and then were adjusted for N available for application based on the predominant manure storage for these species. The predominant manure storage system was assumed to be earthen storage for swine and was assumed to be an open lot with a scrape system for cattle.

Crop yields were obtained for all counties for corn and soybean from 1970 through 2003. These data were obtained from the county yield data available from the Iowa Department of Agriculture and Land Stewardship. Total crop production for each county was estimated by the crop area multiplied by the average crop yield for the year. Adjustments to estimated N removed in the grain were made by assuming that corn grain contained 1.5% N and soybean 4.5% (International Dairy Federation 2006).

**Meteorological Data.** Meteorological data for the Raccoon River watershed were obtained from the National Climate Data Center (NCDC 2009). Precipitation data across the watershed were used to estimate total depth of water deposited onto the watershed each year. This was estimated by computing the average precipitation amount across all stations within the Raccoon River watershed to determine the equivalent depth of water deposited onto the watershed and then multiplying by the total watershed area to compute the volume of water deposited over the watershed each day. Daily data were then aggregated into monthly totals for all years since 1930. These data were used to determine the portion of precipitation lost in the river flow each year.

**Data Analysis.** Records of data varied in length depending upon the availability of data from the different sources. All data were checked throughout data collection for consistency in their time series, and any outliers were smoothed using regression models fit to the data surrounding the data point. Data were subjected to various analyses to define the temporal responses to natural and agro-economic changes within the watershed.

**Results and Discussion**

**Agricultural Production Practices.** Agriculture within the Raccoon River watershed has changed significantly since 1949. Cropping systems have changed from a mixture of crops to predominantly corn (*Zea mays* L.) and soybean (*Glycine max* [L.] Merr.) production (table 1). Analysis of the changes of cropping practices within the watershed showed a large decrease in the land area cultivated as small grains (*Triticum aestivum* L.), oats (*Avena sativa* L.), barley (*Hordeum vulgare* L.), as well as hay (alfalfa (*Medicago sativa* L.) and grass within the watershed. Land area for each major crop within each county assembled since 1949 showed that the amount of land area in small grains decreased from 0.3 of the cultivated land area in 1949 to less than 0.005 in 1997 (figure 2). When the land in alfalfa or hay is added to the total, the fraction changes from 0.4 in 1949 to 0.03 in 1997 (figure 2). The total amount of land area in crop production has remained relatively constant over the last 60 years (table 1).

Grain production of both corn and soybeans has increased each year with an annual increase within the Raccoon River watershed of 45,409 Mg y$^{-1}$ (50,054.8 tony$^{-1}$) for corn production (figure 3) and 16,580 Mg y$^{-1}$ (18,276.3 tony$^{-1}$) for soybeans (figure 4). Grain production in the watershed shows
Table 1
Distribution of crop production area in Raccoon River Valley from 1949 through 2002 (USDA NASS 2009).

<table>
<thead>
<tr>
<th>Year</th>
<th>Wheat (ha)</th>
<th>Barley (ha)</th>
<th>Oats (ha)</th>
<th>Corn, grain (ha)</th>
<th>Corn, silage (ha)</th>
<th>Sorghum, grain (ha)</th>
<th>Soybean (ha)</th>
<th>Alfalfa (ha)</th>
<th>Potato (ha)</th>
<th>Total (ha)</th>
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<tbody>
<tr>
<td>1949</td>
<td>4,753</td>
<td>642</td>
<td>186,246</td>
<td>344,936</td>
<td>0</td>
<td>0</td>
<td>66,531</td>
<td>53,832</td>
<td>106</td>
<td>715,703</td>
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<tr>
<td>1954</td>
<td>503</td>
<td>548</td>
<td>175,931</td>
<td>293,391</td>
<td>4,802</td>
<td>437</td>
<td>101,882</td>
<td>172,935</td>
<td>90</td>
<td>751,057</td>
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<tr>
<td>1959</td>
<td>1,115</td>
<td>1,110</td>
<td>122,917</td>
<td>356,293</td>
<td>5,848</td>
<td>1,566</td>
<td>189,214</td>
<td>128,113</td>
<td>37</td>
<td>753,007</td>
</tr>
<tr>
<td>1969</td>
<td>583</td>
<td>64</td>
<td>52,153</td>
<td>285,796</td>
<td>10,841</td>
<td>624</td>
<td>217,250</td>
<td>111,437</td>
<td>68</td>
<td>677,759</td>
</tr>
<tr>
<td>1978</td>
<td>251</td>
<td>29</td>
<td>17,465</td>
<td>361,738</td>
<td>12,622</td>
<td>558</td>
<td>300,328</td>
<td>22,417</td>
<td>0</td>
<td>618,369</td>
</tr>
<tr>
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<td>16,598</td>
<td>362,411</td>
<td>15,926</td>
<td>0</td>
<td>296,671</td>
<td>83,183</td>
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<td>9,828</td>
<td>281,061</td>
<td>4,371</td>
<td>1</td>
<td>300,328</td>
<td>22,417</td>
<td>0</td>
<td>618,369</td>
</tr>
<tr>
<td>1992</td>
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<td>0</td>
<td>6,362</td>
<td>365,402</td>
<td>4,773</td>
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<td>313,037</td>
<td>20,761</td>
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<td>1997</td>
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<td>349,726</td>
<td>4,127</td>
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<td>13,576</td>
<td>0</td>
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<tr>
<td>2002</td>
<td>0</td>
<td>0</td>
<td>2,037</td>
<td>357,696</td>
<td>3,887</td>
<td>1</td>
<td>339,174</td>
<td>18,812</td>
<td>0</td>
<td>721,597</td>
</tr>
</tbody>
</table>

Figure 2
Change in area planted to small grains and alfalfa and hay crops (ha) within the Raccoon River Basin from 1949 through 1997.

Raccoon River Basin (1949 to 1997)

- Small grain
- Alfalfa and hay

a linear increase even though there was no significant change in land area for corn and soybean cultivation. These increases in production are similar to trends within Iowa and the Midwest for these crops.

There have been significant changes in the animal production systems within the Raccoon River watershed. Cattle numbers have declined since the early 1980s, and current production numbers are approximately half of the inventory within the watershed (figure 5). Hog production numbers have declined since the mid-1980s; however, this change is not as large as in the cattle numbers (figure 5). In this analysis, poultry production and other animals were not considered because of the small numbers within the watershed. The changes in cattle and hog numbers creates a decrease of 0.63 less N from cattle and 0.26 less N from swine production compared to the amount of N produced in the early 1970s. The amounts of N produced were estimated based on animal production values (Midwest Plan Service 1993) and do not account for N losses during storage, which would further reduce the N available for land application.

Nitrogen Fertilizer Use. One of the major inputs of N into the basin is the use of N fertilizer, and total N fertilizer sold within the watershed has not significantly changed for the last 15 years (figure 6). There was an increase from 40,000 Mg (44,092 tn) to the current value of 80,000 Mg (88,184 tn) from 1985 through 1990 (figure 6). Although there is variation among years, there is no significant trend in the amount sold over the past 15 years. There was no significant or consistent change in the forms of N applied during this period based on the county fertilizer sales records evaluated in this study, with anhydrous ammonia accounting for nearly 60% of the N sales in the watershed. If we assume that all of the N fertilizer sold is applied to the cropped fields in the Raccoon River watershed, other than soybeans, the application rates vary among years and range from 100 kg ha\(^{-1}\) (86 lb ac\(^{-1}\)) to over 200 kg ha\(^{-1}\) (172 lb ac\(^{-1}\)) with an average of 179 kg ha\(^{-1}\) (154 lb ac\(^{-1}\)) (figure 7). These rates vary with sales because the cropped area with potential N application is predominantly corn, and the corn area varies little among years. The statewide N rate estimated from total N sales and area planted to corn shows a similar pattern to the Raccoon River watershed (figure 7). During the early 1980s, there was a much larger N rate at the state level.
compared to the Raccoon River watershed, and after 1985, the statewide N rate was less than the Raccoon River watershed (figure 7). The statewide average application rate has been 172 kg ha\(^{-1}\) (148 lb ac\(^{-1}\)) over the past 20 years. The N rates within the Raccoon River watershed are not excessive and are near the levels recommended for corn production in Iowa.

**Long-term Trends in Nitrate-Nitrogen Concentrations.** Nitrate-N trends in the Raccoon River have changed dramatically from 1930 through 2004 (figure 8). Monthly concentrations averaged into annual values showed that in the early 1970s, there was a large increase in the annual concentration from an average concentration of less than 2 mg L\(^{-1}\) to an annual average of over 6 mg L\(^{-1}\). Data from 1972 showed that nitrate concentration increased 0.144 mg L\(^{-1}\) y\(^{-1}\) \((r^2 = 0.31)\). The early record from 1930 through 1950 showed concentration averages above 2 mg L\(^{-1}\) followed by a period from 1950 through 1970 with concentrations less than 1 mg L\(^{-1}\) (figure 8). This rapid increase in NO\(_3\)-N concentrations since 1970 has caused concern about potential impacts of agricultural practices on nitrate concentrations. Earlier results reported by Keeney and DeLuca (1993) suggested that the intensive agricultural practices in the mid-1940s were the cause of concentrations being similar to those in the 1980s. Fluctuations in annual concentrations between 2 to 10 mg L\(^{-1}\) over the last 30 years suggest that NO\(_3\)-N concentrations are not solely linked to the intensity of agricultural practices as suggested by Schilling and Libra (2000). The overall record from within the watershed shows the dynamic nature of nitrate concentrations from this complex agricultural basin. The recent analyses by McIsaac and Libra (2003) and Schilling and Zhang (2004) from the Central Iowa Watersheds show that NO\(_3\)-N loss is a result of complex interactions between streamflow and baseflow and that values have been increasing in the recent record.

An analysis of the maximum NO\(_3\)-N concentrations observed in the 1970 through 2003 record showed an annual maximum concentration of 18 mg L\(^{-1}\) in 2002 and raised concern about the trend toward very large daily NO\(_3\)-N values (figure 9). These concerns have continued with 18.7 mg L\(^{-1}\) observed during 2006. Examination of the maximum concentrations showed a linear increase in the maximum concentrations since 1995 except for 2000, when 10 mg L\(^{-1}\) was the maximum concentration observed (figure 9). Daily data were analyzed to identify the maximum concentration recorded each year and the number of days in which the concentration exceeded 10 mg L\(^{-1}\). There have been three years in the data record in which the concentrations exceeded 10 mg L\(^{-1}\); however, these have been distributed throughout the data record in 1974, 1979, and 2002 (figure 9). There were six years (1979, 1992, 1999, 2001, 2002, and 2003) in which there were over 100 days per
year that exceeded 10 mg L\(^{-1}\) (figure 9). In addition, 2004 and 2007 also had over 100 days above 10 mg L\(^{-1}\). Nitrate-N concentrations in the Raccoon River are dynamic and show large variations among years with the last 30 years showing the highest concentrations for the last 70 years. There have been more occurrences of the daily concentrations exceeding 10 mg L\(^{-1}\) in the past ten years than before in the data record (figure 9). These increases in the number of days that have exceedances above 10 mg L\(^{-1}\) have raised questions about the changes in agricultural practices that have occurred within the watershed and the impact of these changes on water quality.

**Nitrate-N loads in the Raccoon River.** The data record for NO\(_3\)-N load was aggregated into four quarters of the year to determine if there had been any change in the pattern of NO\(_3\)-N loss from the watershed since 1970. The predominant quarter was the period from Day of Year (DOY) 91 to 180 for the entire period (figure 10). Although there was large variation in load among years, patterns were consistent with the first and last quarters of the year contributing very little to the annual load. Variation among years can be attributed to the variation in annual rainfall onto the watershed. Precipitation in the first five months of the year was significantly correlated \((r = 0.8)\) to annual concentrations and load, similar to the observations by Lucey and Goolsby (1993), in which streamflow was a dominant factor affecting NO\(_3\)-N concentrations. Since subsurface flow is dominant in the watershed, increases in precipitation are related to increases in streamflow. Hatfield and Jaynes (1998) showed that increases in precipitation were positively related to increases in streamflow in the Walnut Creek watershed. The results by Schilling and Zhang (2004) showed that baseflow and streamflow were related to nitrogen loss from the watershed.

Nitrate-N loads from the Raccoon River Basin vary among years, and there has been no trend towards an increase in load from the watershed (figure 11). When expressed as the amount of NO\(_3\)-N lost per unit of land area, variation among years range from 0 to 16.6 kg NO\(_3\)-N ha\(^{-1}\) (0 to 14.3 lb NO\(_3\)-N ac\(^{-1}\)) for all of the cropland area within the watershed (figure 11). Variations in N lost from the watershed are related to the variation in annual precipitation; however, an analysis of the NO\(_3\)-N load relative to precipitation trends showed no significant change in the fraction of precipitation lost as flow from the watershed during the last 30 years. Schilling (2005) reported an increase in baseflow for the Raccoon River, which could account for the continuing increase in NO\(_3\)-N loads, but he also found an indirect relationship to precipitation. The increase in baseflow coupled with extensive subsurface drainage in the watershed suggest that NO\(_3\)-N leaching from the soil profile is the primary path of N lost from the watershed, which is consistent with the observations by Jaynes et al. (1999) from the Walnut Creek watershed in Central Iowa. They reported N losses that ranged from 4 to 66 kg N ha\(^{-1}\) (3.4 to 56.9 lb N ac\(^{-1}\)) in
this intensively cropped watershed. It would be expected that the Raccoon River Basin would show similar variation in NO$_3$-N per unit area. Nitrogen losses from agricultural watersheds are complex interactions of the hydrologic and landuse practices within the watershed.

Relationship of Nitrogen lost to Agricultural Practices. The increase in grain yield shown in figure 3 results in a significant increase in grain production, causing more N to be removed by grain production. Over the last 30 years, there has been a large variation in N removal as corn grain. It has averaged 0.70 of the N applied as fertilizer (figure 12). The export of N from the watershed as grain represents a large fraction of the amount applied, and the unaccounted for portion in the N balance would be the mineralization term, which could be quite large in these soils because of the soil organic matter contents. The annual rate of yield increase translates to an annual increase of over 1,000 Mg (11,02.3 tn) of N removed by corn and 750 Mg (826.7 tn) from soybean production. Although these values are small compared to the total amounts of N applied, they are significant from the standpoint of a continual increase in N removal without the concurrent increase in N application. The continual increase in NO$_3$-N loads in the Raccoon River over the same period of time, as there is increasing yield and consistent N inputs from fertilizer, suggest that these systems are complex in terms of achieving a balance in N use and N loss. The lack of a significant relationship between N loss and a single agronomic parameter demonstrates the complexities in watershed analyses.

Manure, as a source of nutrients within the basin, has declined in the past 20 years. When expressed as a fraction of the N available from manure compared to the amount of fertilizer N applied, the values have declined from 0.4 to less than 0.2 (figure 3). Reduction in animal numbers has greatly impacted the N inputs into the watershed, and there has not been an increase in commercial N applications to offset this decline. The total N load into the watershed has declined in the past 20 years because of the reductions in manure application.

The variation in N load relative to N applied shows a large amount of variation over the past 30 years with an average of 0.22 (figure 12). This variation can be explained by the strong dependence between N load and precipitation in the early part of the year. There is no significant trend in N load compared to N applied over the past 30 years. The enrichment of baseflow with NO$_3$-N as a result of leaching to baseflow and seasonal crop requirements as suggested by Schilling and Zhang (2004) provides an explanation for the changes in N load.

An interesting aspect is that the increase in NO$_3$-N concentrations in the Raccoon River beginning in 1970 can be linked to reduction of land area in small grain or hay as a portion of the total watershed. The current fraction of the watershed in small grain...
and hay is less than 0.1 of the cultivated land area. The correlation between the fraction of land area in small grain or hay and annual average NO$_3$-N since 1970 is −0.76. There are several explanations for this relationship. Increases in NO$_3$-N concentrations can be linked with the reduction in crop area with an early season NO$_3$ and water removal from the profile. Small grain crops reduce NO$_3$-N leaching, and Bergstrom and Jokela (2001) showed that ryegrass (Lolium perenne L.) used as a cover crop within a barley crop reduced NO$_3$-N from 22 to 8 kg ha$^{-1}$ (18.9 to 6.9 lb ac$^{-1}$). Randall et al. (1997) evaluated the effect of alfalfa and grass systems within the Conservation Reserve Program on NO$_3$-N from corn or corn–soybean systems. They found the presence of these crops reduced leaching due to a change in seasonal evapotranspiration and greater uptake or immobilization of N by the perennial crops. Kaspar et al. (2007) found that rye (Secale cereale L.) reduced in the NO$_3$-N loads in all four years of their study by an average of 19.8 kg N ha$^{-1}$ (17.1 lb ac$^{-1}$). They found that the rye didn't affect the amount of drainage from the soil profile into the tile drain lines. Prueger et al. (1998) showed that rye or oats increased the water use from the soil profile during the off-season, compared to corn or corn–soybean systems, because of the increase in plant water use compared to bare soil water evaporation in the early season. Toth and Fox (1998) demonstrated that NO$_3$-N concentrations leaching from alfalfa in the crop rotation were 0.2 to 0.25 as high as corn with an optimal rate of N fertilizer. However, Hansen et al. (2000) cautioned that the NO$_3$-N reductions due to cover crops may not be as large as expected because of the long-term effects of increased N mineralization caused by the increases in soil organic matter content. One aspect of the change in land use within the Raccoon River watershed was the significant negative correlation (−0.55) between the fraction of land area in small grain and hay and the fraction of water lost in the period between April and June (DOY 91–181). This is in agreement with the findings of Schilling (2005), who observed for 11 Iowa rivers an increase of 33 to 135 mm (1.3 to 5.3 in) in baseflow or a 7% to 31% increase in baseflow percentage compared to the previous 20 years. These values reported by Schilling (2005) of increased baseflow are similar to those estimated from the change in water use.
patterns by decreasing the small grain and hay area within the watershed. Observations from Prueger et al. (1998) and Hatfield and Prueger (Unpublished data) show that in the period from April through mid-June, the average water use by small grain or hay would be approximately 2 mm day$^{-1}$ (0.08 in day$^{-1}$), compared to the bare soil in a corn-soybean rotation of 0.2 mm day$^{-1}$ (0.008 in day$^{-1}$). These estimates show a potential water use difference of 135 mm (5.3 in) over this period. This difference is sufficient to cause the change in baseflow as reported by Schilling (2005). These differences in water use over the past 30 years caused by changes in cropping patterns would have an affect on baseflow and subsurface drainage flow. This is interesting since it suggests that changes in land use would have to be integrated with management systems within the agro-nomic systems in order to develop watershed management changes that would positively impact water quality.

Addition of cover crops or small grains or alfalfa into crop rotations in the Midwest would have a positive impact on the N balance due to water balance and the resultant effect on leaching (Bergstrom and Jokela 2001). These observations suggest a positive impact on water quality would result from a more diversified rotation across the landscape.

**Summary and Conclusions**

Nitrate-N concentrations within the Raccoon River watershed have shown large changes over the past 70 years, with large variation among years. Variations in annual loads are related to the annual precipitation amounts since leaching into the subsurface drains is the primary path into the stream and river network with the most significant relationship with precipitation amounts in the first five months of the year. Increase in mean annual concentration since the 1970s is related to the continual decrease in land area planted to small grains or hay crops, and there is a −0.76 correlation between the land area in these crops and the mean annual NO$_3$-N concentration. There was a −0.55 correlation with discharge in the April to June period and the mean annual NO$_3$-N concentration. The development of other relationships between N applied as commercial fertilizer or manure showed no significant relationships over this period. Changes in land use from a more mixed crop rotation, with small grains and hay, to the current corn—soybean or corn—corn system has altered the annual pattern of crop water use and uptake of N from the soil profile. Reported values of N uptake by small grains or cover crops is similar to the NO$_3$-N losses observed within the Raccoon River watershed that often reach 16 kg ha$^{-1}$ (13.7...
lb ac^-1). Changes in cropping patterns were found to be more significant than changes in N fertilizer use and variations in annual precipitation in affecting NO3-N loads; however, achieving the maximum benefit will require an integrated approach of watershed management and agronomic management. These results suggest that improvements in NO3-N concentrations could be achieved through changes in cropping practices that introduced more small grains, cover crops, or hay crops into the landscape coupled with improved N management in corn production systems. These recommended changes would alter the seasonal water use patterns and directly affect NO3-N leaching.

References


