Water quality assessment in the Cherry Creek watershed: Patterns of nutrient runoff in an agricultural watershed

V.J. Alarcon and G.F. Sassenrath

Abstract: Access to safe, high quality water for consumption, agriculture, industry, and recreation is critically important. Continuous agricultural and mining activities have impaired the waters of the Grand Lake watershed in the central Great Plains region of the United States. The Grand Lake watershed encompasses portions of southeast Kansas, southwest Missouri, northwest Arkansas, and northeast Oklahoma, and drains into Grand Lake in northeast Oklahoma. The Cherry Creek watershed drains approximately 882.2 km² (218,000 ac) of land in southeast Kansas and is a contributor of water to the Grand Lake watershed. This paper presents a water quality assessment in the Cherry Creek watershed, with an end toward mitigation of nonpoint source pollutants that are a major contributor to sediment and nutrient contaminants in Grand Lake. A hydrological model was developed using the Hydrological Simulation Program Fortran code and was updated, calibrated, and verified with measured data reported by US Geological Survey (USGS) and the Kansas Department of Health and Environment (KDHE). The model was extended to simulate water quality within the study area. Nitrate (NO₃⁻–N), total ammonia (TAM), total phosphorus (TP), and orthophosphate (PO₄³⁻–P) concentrations measured at the USGS stations were used to calibrate the model, and concentrations reported by KDHE at downstream locations were used to verify the model. Results indicate good performance of the hydrological model as tests of fitness were within levels established in previous studies (root-mean-squared-error to standard deviation ratio [RSR] < 0.75; 30% < percentage bias [PBIAS] < 30%; R² > 0.6; NS > 0.5). Nutrient measurements below the minimum quantifiable limit (MQL) hampered precise simulation of nutrient changes, though simulated values were acceptable in terms of ranges of contaminant concentration values and seasonal trends. The calibrated model was used to estimate the probability that nutrient levels would exceed established water quality criteria for rivers and streams. Concentration values of NO₃⁻–N and TAM are shown to be low for an agricultural watershed: 75% of the NO₃⁻–N and TAM concentrations are lower than 0.41 mg L⁻¹. The probability of NO₃⁻–N and TAM concentrations being toxic for aquatic communities is lower than 9%. Although model-estimated PO₄³⁻–P concentrations were low in numerical value (ranging from 0 to 2.60 mg L⁻¹), they could still promote eutrophication according to the accepted 0.05 mg L⁻¹ criteria for maximum PO₄³⁻–P concentrations in streams. Concentrations of PO₄³⁻–P in Cherry Creek have a 30.4% probability of exceeding that threshold. Extensive use of animal manure (primarily poultry) or manure from cattle grazing on pasture may account for the elevated levels of PO₄³⁻–P observed in the watershed. Although nutrient runoff from agricultural watersheds is anticipated to be a major contributor to elevated stream nutrient loads, these results indicate minimal contamination from Cherry Creek.

Key words: hydrological modeling—nitrate—nutrient modeling—orthophosphate—total ammonia—water quality

Secure access to clean, safe water is critical to support society. Water in many geographical areas is critically impaired due to sediment and nutrient contamination from both point and nonpoint sources. Soil and nutrient loss reduces the productive capacity of agricultural lands (Pierce et al. 1983; Pimentel 2006) and fills water reservoirs, reducing their capacity and creating potentially toxic algal blooms (Reilly 1999). This reduces the water security and creates potential trans-boundary contamination issues as negative environmental consequences of agricultural practices in one region or state impact neighbors (McKinney 2011).

The Grand Lake watershed encompasses portions of four states that drain into the Grand Lake in northeast Oklahoma. Extensive agricultural and mining operations in the watershed have severely impaired the waters of the region (OWRB 2001; Juracek 2008; Mignogna et al. 2012; Manders and Aber 2014; Dong et al. 2016). Grand Lake is a primary recreational area in northeast Oklahoma, but most of the watershed originates in other states. Of the rivers draining into Grand Lake, the Neosho River contributes one-half to three-fourths of all water, making it the primary contributor, and hence determinant, of pollutants in the system. The Middle Neosho watershed (MNW) begins in Neosho County in southeast Kansas and ends where the Neosho River crosses the Kansas–Oklahoma state line (Branson 1967). The MNW is the critical watershed draining the southeast area of Kansas into the Grand Lake watershed. As such, it is the transfer point of Kansas agricultural activities to Oklahoma water. The location of the MNW is representative of typical interstate and trans-boundary contamination cases that are becoming more relevant in the United States (DeLaune et al. 2006; McKinney 2011) and the rest of the world (Wouters 2013; Li et al. 2014), and will increase in intensity and negative impact as environmental consequences heighten.

To avoid potential litigious actions that have occurred in the area (City of Tulsa vs. Tyson Foods 2003) and address the critical contamination issues of water supplies, Kansas and Oklahoma have coordinated the development of Watershed Restoration and Protection Strategy plans (GLCWAF 2008; MNW 2011) that identify critical areas within adjoining watersheds and develop preliminary plans for remediation. These management plans emphasize the essential
need to identify and quantify all pollutant sources in the basin, including both non-point and point sources, through the use of computer models that incorporate data on soil type, topography, land use practices, and climate for estimation of pollutant loadings and transport throughout the watersheds of the region (GLCWAF 2008). The highest priority impairments in the Neosho River watershed are nutrients, sediments, and bacteria. The MNW does not meet state water quality standards and fails to achieve aquatic system goals related to habitat and ecosystem health. It has been designated a priority for restoration (MNW 2011).

Land use in the MNW is primarily intensive agricultural production, with historical mining activity. Agricultural production includes row crop and grain production, and cattle production on pasture. Most of the crop production relies on conventional tillage for weed control and seed bed preparation. Although there are some animal confinement operations (swine, poultry, or beef cattle feedlots) within the watershed, most of the animal manures are imported from the extensive poultry production facilities in neighboring states (Tomlinson et al. 2014). Average annual rainfall in excess of 100 cm (39.3 in) exacerbates nutrient and sediment erosion from fields and pastures; climate models predict future rain events will increase in amount and intensity (IPCC 2007). Significant agricultural production in the area continues to erode soil resources and impair the watershed.

Cherry Creek is one of the main tributaries to the Neosho River (figure 1), located in the southeast MNW. The Cherry Creek watershed encompasses primarily agricultural lands, with no major urban areas. Historical mining activities have left strip mine pits that have filled with rain to form strip pit wetlands. The Middle Neosho Watershed Restoration and Protection Strategy study (MNW 2011) lists the Cherry Creek watershed as a targeted area for agricultural best management practices (BMPs) to meet sediment and nutrient load reductions. The Grand Lake Watershed Plan (GLCWAF 2008) also lists Cherry Creek as a high-priority stream for a total maximum daily load (TMDL) study oriented toward reducing nutrient and sediment loads that cause the stream to be listed for a dissolved oxygen (DO) TMDL. Implementation of conservation practices may reduce nutrient and sediment losses within the watershed (Parajuli et al. 2013; Alarcon and Sassenrath 2015; Padedda et al. 2015), and improve water quality in the Cherry Creek watershed, as well as waters of the region.

A TMDL report (KDHE 2002) prioritized the development of a DO TMDL for Cherry Creek based on several observations of low DO levels during a 10-year study period (1991 to 2001). It was recommended that the biological oxygen demand (BOD) be allocated to achieve concentrations lower than 2.65 mg L⁻¹ in order to comply with the 5 mg L⁻¹ standard for DO (USEPA 2002). Since nutrient concentrations were reported to be at very low levels (<0.89 mg L⁻¹), the low DO episodes were attributed to biological contamination (BOD). The primary land use of the region is agricultural (crops and pasture). The use of chemical and manure fertilizers is extensive, and if BMPs for fertility management are not followed, fertilizers and animal manure can contribute significantly to nutrient pollution in water bodies. A comprehensive approach to nutrient loss control has been identified as critical to mitigate eutrophication of fresh waters (Tomer et al. 2013). Continuous water quality monitoring in conjunction with event-based water sampling collection may reveal the actual contribution of nonpoint source runoff to nutrient concentrations in the Cherry Creek watershed. However, this approach is time consuming, labor intensive, and expensive in terms of laboratory analysis. Water quality modeling may provide an alternative tool to assess nonpoint source nutrient contributions.

This study was undertaken to develop an accurate, robust method of tracking nutrient and sediment sources in the MNW using a critical subwatershed within the MNW, Cherry Creek, as a model. We use hydrological and water quality modeling to estimate nitrate-nitrogen (NO₃⁻–N), total ammonia (TAM) as N (comprising NH₄⁺ or nonionized ammonia, and ionized ammonia, i.e., ammonium, NH₄⁺), total phosphorus (TP), and orthophosphate (PO₄³⁻–P) concentrations for streams within the Cherry Creek watershed for an extended period of time (1976 to 2008). Based on the nutrient concentrations estimated by the model and an analysis of current agricultural practices in the area, we explore potential factors contributing to water quality issues in the area. The water quality of the stream is also categorized based on a compounded water quality indicator. This research contributes to the ongoing interstate collaboration to improve the water quality within the Grand Lake watershed, and improve water security for the region and the nation. This modeling tool will allow us to delineate environmentally sensitive areas and identify potentially critical production management practices that can be implemented or altered to reduce nutrient loss from agronomic fields.

Materials and Methods
Study Area. The Cherry Creek catchment and stream drains approximately 882.2 km² (218,000 ac) in southeastern Kansas (figure 1). Historical annual average stream flows at USGS gauge station 07184300 (figure 2) range from 1.50 to 1.72 m³ s⁻¹ (53 to 60.7 ft³ sec⁻¹). Recorded weather data at the National Weather Service station at Columbus, Kansas (figure 2), report an average total annual precipitation of 1,131 mm (44 in), with a range from 601 mm (23.7 in) to 1,676 mm (66 in).

The Cherry Creek catchment physiography is typical of an agricultural watershed and similar to surrounding watersheds in the Middle Neosho River hydrological unit (USGS HUC 11070205). The Cherry Creek watershed is a contributor of water to the Neosho River, and hence to Grand Lake, Oklahoma. Hydrological and water quality processes modeled in Cherry Creek could be extrapolated to neighboring hydrological units.

Agricultural Practices in the Area. Most agricultural practices in the watershed are conventional, large-scale (8 to 12 row equipment) crop production. The crop rotation system produces three crops in two years (corn [Zea mays L., March to August]/ winter wheat [Triticum aestivum L., October to June] /soybeans [Glycine max L., June to November]), with some rotation to sorghum (Sorghum bicolor L.) or other small grains. Row crops are commonly planted in 76 cm (30 in) rows with commercial planting equipment. Wheat is commonly drilled. The management includes surface tillage (15 cm [6 in] deep, disk or field cultivator) prior to planting corn or winter wheat; soybeans are more commonly planted no-till immediately after wheat harvest. Fertility is commonly performed by knitting in urea at recommended rates for the area (corn: 68 kg N [150 lb N]; wheat: 45 kg N [100 lb N]; phosphorus (P: 21 kg [46 lb]) and potassium (K: 20 kg [45 lb]) are applied at recommended rates to all...
crops prior to planting (Leikam et al. 2003). Micronutrients are usually abundant in the soil and not commonly added. Poultry litter, imported from confinement poultry operations in neighboring states, is often used to supplement fertility, especially P (Thomlinson et al. 2014). Herbicides, insecticides, and fungicides are applied as needed to control pests and diseases. Because of the high rainfall common to the area, fungicides are commonly used, especially in wheat production (Bockus et al. 2001).

The agricultural practices described above were introduced to the model in the subroutines related to nutrient loading and timing of fertilization and harvesting. The level of hydrological and water quality modeling employed in this study was at a watershed level, and hence did not utilize different field-scale operations such as tillage, planting, or other field operations.

Hydrological Code and Geographic Information Systems Software. Hydrological modeling of the Cherry Creek watershed was performed with the Hydrological Simulation Program Fortran (HSPF) (Bicknell et al. 1997). The HSPF code was developed by the Environmental Research Laboratory in Athens, Georgia, and most of the continued development has been sponsored by the USGS Water Resources Division in Reston, Virginia (Bicknell et al. 1997). The HSPF code is a computer model designed for simulation of nonpoint source watershed hydrology and water quality. Time-series of meteorological data and digital maps characterizing land use, soil, and topography are used to estimate stream flows and pollutant concentrations. The model simulates interception of rainfall, soil moisture, surface runoff, interflow, base flow, snowpack depth and water content, snowmelt, evapotranspiration, and groundwater recharge. Simulation results are provided as time-series of runoff, sediment load, and nutrient and pesticide concentrations, along with time-series of water quantity, at any point in a watershed. Additional software (Watershed Data Management Utility [WDMUtil; Hummel et al. 2001] and Generation Scenarios [GenScn; Kittle et al. 1998]) is used for data preprocessing and postprocessing, and for statistical and graphical analysis of input and output data (Alarcon and O’Hara 2010). The Better Assessment Science Integrating Point and Nonpoint Sources, BASINS 4.1, GIS system (USEPA
Environmental Protection Agency (USEPA) server for download (USEPA 2008), were used for initial parameterization of the model for Cherry Creek. The National Elevation Data (NED) data set was downloaded for characterizing the topography of the Cherry Creek watershed. The NED data set has a spatial resolution of 30 m (98.4 ft) and is provided with elevation values in centimeters. The use of this data set is facilitated by the BASINS GIS system as it is automatically reprojected from geographical coordinates to the coordinate system in which the BASINS project is established. In this research, all preprocessing and modeling operations were performed in Universal Transverse Mercator (UTM), Zone 15 North.

The National Land Cover Data (NLCD) 2001 derived from the early to mid-1990s Landsat Thematic Mapper satellite data is a 21-class land cover classification scheme applied consistently across the United States (Homer et al. 2007). The spatial resolution of the data is 30 m (98.4 ft) and was reprojected from its original Albers Conic Equal Area projection to UTM Zone 15 North.

Moriasi and Starks (2010) found that there were no significant differences in statistical indicators from hydrological modeling between the higher resolution Soil Survey Geographic Database (SSURGO) and the lower resolution State Soil Geographic Database (STATSGO). In this research we used the STATSGO soil characterization.

**Land Use Change in the Area.** Model development was performed using the NLCD 2001 land use digital raster. The validation of the model output was done for dates ranging from 1991 to 2008. Although it would be possible to compare the results to the NLCD 1992 data set, a direct comparison of this data set with any subsequent NLCD data sets is not suggested due to changes in the methods of legend and map development (MRLC 2016). Therefore, to verify that the land cover map was still valid for simulation dates close to 2008, the “NLCD 2001 to 2011 Land Cover Change” digital raster (USGS 2014) was used to determine if significant land use changes have occurred that would invalidate the model output. This data set is a raster layer in which the spectral signature of each pixel has been identified as dissimilar when comparing NLCD 2001 to NLCD 2011 Land Cover products. Pixels identified as unchanged contain a generic value of zero. The raster layer is the result of the application of a new comprehensive change detection method that includes spectral-based change detection algorithms able to extract change information from pairs of Landsat images (Jin et al. 2013).

The polygon representing the Cherry Creek watershed was overlaid on the NLCD Land Cover Change raster to assess land use change in the area of study. Standard zonal statistics tools were used to identify the number of pixels that underwent spectral signature change from 2001 to 2011 (i.e., land use change) and also to count the pixels without change.

**Hydrological and Water Quality Modeling.** Two model applications were developed in this research, each designed with different watershed delineations. The initial model described a hydrological model for upper Cherry Creek (subbasins 1, 2, 3, 5, and 6; figure 2) and was calibrated for stream flow comparing simulated output to measured data reported at USGS station 07184300 (Hallowell). Six years of measured data were available at this station (September 2, 1976, to September 30, 1982; table 1). After the statistical fit analysis indicated good agreement between simulated and measured stream flows at Hallowell, the model output was compared against measured data collected at USGS station 07184220 (West Mineral). This process was repeated until statistical fit between simulated and measured hydrology data at both stations was good. The comparison at West Mineral was performed for several different time periods from 1976 to 1979 since daily stream flow data were only available in discrete intervals (table 1). The HSPF parameters used for hydrological calibration were the following: INFILT (index to the infiltration capacity of the soil), LZSN (lower zone nominal storage), INTFW (interflow inflow parameter), LZETP (lower zone evapotranspiration), KVARY (groundwater recession flow), IRC (interflow recession parameter), and UZSN (upper zone nominal storage), defined in table 2.

The development of the water quality portion of the model was performed in a similar fashion, although the limited availability and quality of measured data did not allow full statistical comparison of simulated and measured data. Nitrate-N, TAM, and TP concentrations measured at Hallowell (USGS 07184300) for several dates between January of 1977 and March of 1978 (table 1) were used to calibrate the model. The minimum
quantifiable limit (MQL) is the concentration or amount below which the analytical laboratory methods cannot operate with an acceptable level of precision (Bernal 2014; USEPA 2010). Since 11 to 29 measured data records were reported at this station (with the actual number of records dependent on the specific water quality parameter), and several of those concentration values were below the MQL, the calibration and subsequent verification processes focused on replicating trends and range of concentration values as much as fitting simulated data to measured data when these data were available. Sensitivity analysis was one of the criteria followed during calibration. Alarcon and Sassenrath (2015, 2016) provided the basis for the calibration process that also looked for parameter values that made physical and chemical sense and were within ranges recommended by the literature. Verification of the model outputs were performed comparing NO\textsubscript{3}–N, TAM, and TP simulated output to measured data at the West Mineral USGS station (USGS 07184220). The following HSPF water quality parameters (Ouyang et al. 2015) were used during the water quality calibration process: MON\textunderscore ACCUM (monthly value of accumulation rates of nutrients at start of each month), MON\textunderscore SQOLIM (monthly values limiting storage of nutrients at start of each month), MON\textunderscore IFLW\textunderscore CONC (monthly value of nutrient concentrations in interflow outflow at start of month), MON\textunderscore GRND\textunderscore CONC (monthly value of nutrient concentrations in groundwater outflow at start of month), ALNPR (fraction of N requirements for phytoplankton growth satisfied by NO\textsubscript{3}–N), MALGR (maximal unit algal growth rate for phytoplankton), and POTFW (wash-off potency factor) (table 2).

The KDHE collected additional and updated water quality data downstream from the USGS Hallowell station at KDHE Station 605 near Faulkner (figure 2). Since the model for upper Cherry Creek did not cover this downstream location, a second hydrological and water quality model covering both the upper and lower Cherry Creek watersheds (subbasins 1, 2, 3, 5, 6, and 7; figure 2) was developed for modeling flow and water quality estimations at KDHE Station 605. The new hydrological delineation of the area produced an additional subbasin 4 that was external to the Cherry Creek catchment area, and hence was not included in the HSPF model. Hydrological and water quality parameters were extrapolated to this bigger watershed model. Meteorological, land use (NLCD 2001), and topographical (NED) data sets were the same as in the previous model, but covered a larger geographical area and extended temporal meteorological time-series. However, to verify if the extrapolation of hydrological and water quality parameters was correct, the locations of the USGS stations at Hallowell and West Mineral were set up to be catchment exits so that the watershed delineation of the bigger model included them as catchment exits. In this way a comparison of the output of both models, in terms of stream flow and water quality estimations, was possible.

**Table 1**

<table>
<thead>
<tr>
<th>Data set</th>
<th>Station</th>
<th>Location</th>
<th>Records dates</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitation</td>
<td>NWS KS141740</td>
<td>Columbus, Kansas</td>
<td>Aug. 1, 1948, to Dec. 31, 2009</td>
<td>Input data</td>
</tr>
<tr>
<td>Evapotranspiration</td>
<td>NWS KS141740</td>
<td>Columbus, Kansas</td>
<td>Aug. 1, 1948, to Dec. 31, 2009</td>
<td>Input data</td>
</tr>
<tr>
<td>Wind</td>
<td>NWS KS141740</td>
<td>Columbus, Kansas</td>
<td>Aug. 1, 1948, to Dec. 31, 2009</td>
<td>Input data</td>
</tr>
<tr>
<td>Air temperature</td>
<td>NWS KS141740</td>
<td>Columbus, Kansas</td>
<td>Aug. 1, 1948, to Dec. 31, 2009</td>
<td>Input data</td>
</tr>
<tr>
<td>Dew point</td>
<td>NWS KS141740</td>
<td>Columbus, Kansas</td>
<td>Aug. 1, 1948, to Dec. 31, 2009</td>
<td>Input data</td>
</tr>
<tr>
<td>Solar radiation</td>
<td>NWS KS141740</td>
<td>Columbus, Kansas</td>
<td>Aug. 1, 1948, to Dec. 31, 2009</td>
<td>Input data</td>
</tr>
<tr>
<td>Water quality (NO\textsubscript{3}–N, TAM, PO\textsubscript{4}–P)</td>
<td>USGS 07184300</td>
<td>Hallowell, Kansas</td>
<td>11 to 29 records between January of 1977 to March of 1978 depending on WQ constituent</td>
<td>Water quality calibration</td>
</tr>
<tr>
<td>Water quality (NO\textsubscript{3}–N, TAM, PO\textsubscript{4}–P)</td>
<td>USGS 07184220</td>
<td>W. Mineral, Kansas</td>
<td>15 to 29 records between January of 1977 to March of 1978 depending on WQ constituent</td>
<td>Water quality calibration</td>
</tr>
<tr>
<td>Water quality (NO\textsubscript{3}–N, TAM, PO\textsubscript{4}–P)</td>
<td>KDHE 605</td>
<td>Near Faulkner, Kansas</td>
<td>21 records between 1991 and 2008</td>
<td>Water quality verification</td>
</tr>
</tbody>
</table>

Table 2
Parameters used in hydrological and water quality calibration of the Cherry Creek watershed model.

<table>
<thead>
<tr>
<th>Calibration</th>
<th>Definition</th>
<th>Range (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrological calibration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>INFILT</td>
<td>Index to the infiltration capacity of the soil</td>
<td>0.12 to 0.18</td>
</tr>
<tr>
<td>LZSN</td>
<td>Lower zone nominal storage</td>
<td>3.00 to 5.50</td>
</tr>
<tr>
<td>INTFW</td>
<td>Interflow inflow parameter</td>
<td>2.00 to 4.00</td>
</tr>
<tr>
<td>LZETP</td>
<td>Lower zone evapotranspiration</td>
<td>0.40 to 0.60</td>
</tr>
<tr>
<td>KVARY</td>
<td>Groundwater recession flow</td>
<td>1.90 to 2.10</td>
</tr>
<tr>
<td>IRC</td>
<td>Interflow recession parameter</td>
<td>0.46 to 0.48</td>
</tr>
<tr>
<td>UZSN</td>
<td>Upper zone nominal storage</td>
<td>0.90 to 1.20</td>
</tr>
<tr>
<td>Water quality calibration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MON_ACCUM</td>
<td>Monthly value of accumulation rates of nutrients at start of each month</td>
<td>TAM: 0.007 to 0.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₃⁻–N: 0.01 to 1.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄³⁻–P: 0.003 to 0.01</td>
</tr>
<tr>
<td>MON-SQOLIM</td>
<td>Monthly value limiting storage of nutrients at start of each month</td>
<td>TAM: 0.005 to 0.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₃⁻–N: 0.07 to 3.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄³⁻–P: 0.004 to 0.02</td>
</tr>
<tr>
<td>MON-IFLW-CONC</td>
<td>Monthly value of nutrient concentrations in interflow outflow at start of month</td>
<td>TAM: 0.03 to 0.80</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₃⁻–N: 0.10 to 3.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄³⁻–P: 0.009 to 0.10</td>
</tr>
<tr>
<td>MON-GRN-CONC</td>
<td>Monthly value of nutrient concentrations in groundwater outflow at start of month</td>
<td>TAM: 0.04 to 1.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NO₃⁻–N: 0.05 to 5.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PO₄³⁻–P: 0.005 to 1.0</td>
</tr>
<tr>
<td>ALNPR</td>
<td>Fraction of nitrogen requirements for phytoplankton growth satisfied by nitrate</td>
<td>0.60 to 0.80</td>
</tr>
<tr>
<td>MALGR</td>
<td>Maximal unit algal growth rate for phytoplankton</td>
<td>0.40 to 0.60</td>
</tr>
<tr>
<td>POTFW</td>
<td>Wash-off potency factor</td>
<td>50 (Alarcon and Sassenrath 2015)</td>
</tr>
</tbody>
</table>

Notes: TAM = total ammonia. NO₃⁻–N = nitrate-nitrogen. PO₄³⁻–P = orthophosphate.

compares to measured data. While the coefficient of determination ($R^2$) is commonly used for assessing statistical fit, additional recommended tests include quantifying statistical error (root-mean-squared-error to standard deviation ratio [RSR]); estimating bias of simulated data with respect to measured data (percentage bias [PBIAS]); and using the Nash-Sutcliffe coefficient (NS) to assess how well the plot of observed versus simulated data fits the 1:1 line (Moriasi et al. 2007). All four standard statistical indicators of fitness (Moriasi et al. 2007) are used in this research, as outlined in table 3.

The calculation of probabilities of exceedance for the water quality variables included in this study are performed using the standard approach detailed in Searcy (1959) and summarized in table 3. Since the model was trained with limited nutrient data, and long-term simulations are required for the calculation of exceedance probabilities, confidence bounds are calculated for the exceedance probability curve. For this, the 32-year continuous daily water quality simulation (1976 to 2008) was considered to be a series of 32 realizations of water quality events. The empirical distribution function of these realizations is considered an estimate of the true water quality distribution function. The uncertainty of this estimate is quantified in terms of 1-α confidence bands. Since the variance of the distribution is not known and the number of samples is only 32, the t distribution with $\alpha = 0.01$ (i.e., $t = 2.744$) was used to calculate the upper and lower confidence bands of the mean probability of exceedance.

A water quality indicator (WQI) is used to summarize and classify the water quality of Cherry Creek and other water bodies in the Cherry Creek watershed with a single numerical value (Terrado et al. 2010). The WQI index ranges between 0 (worst water quality) and 100 (best water quality) in five categories:

1. $0 < \text{WQI} < 44$: poor water quality, almost always threatened or impaired;
2. $44.1 < \text{WQI} < 64$: marginal water quality, water quality is frequently threatened or impaired;
3. $64.1 < \text{WQI} < 79$: fair water quality, usually protected but occasionally threatened or impaired;
4. $79.1 < \text{WQI} < 94$: good water quality, the water body is protected, with only a minor degree of threat or impairment; and
5. $94.1 < \text{WQI} < 100$: excellent water quality, the water body is protected with a virtual absence of threat or impairment.

The WQI was chosen for this study because it is a flexible index that can be used with several different parameters. Since three water quality variables are modeled and/or simulated in this research (NO₃⁻–N, TAM, and PO₄³⁻–P), each with specific water
indicate poorer water quality. Positive values of cumulative WQI deviation can be negative (i.e., larger negative values are calculated relative to the mean WQI, they of the surface water. Since cumulative values algebraic sense), the better the water quality smaller the cumulative WQI values (in the wetlands could absorb excess nutrients from through time, and also allows comparison of shows the WQI evolution for each subbasin from the mean were also calculated for each subbasin (table 3). This cumulative indicator shows the WQI evolution for each subbasin through time, and also allows comparison of water quality status between subbasins. The smaller the cumulative WQI values (in the algebraic sense), the better the water quality of the surface water. Since cumulative values are calculated relative to the mean WQI, they can be negative (i.e., larger negative values mean better water quality). Conversely, larger positive values of cumulative WQI deviation indicate poorer water quality.

Results and Discussion

Land Use/Land Cover and Change. The Cherry Creek watershed is primarily an agricultural watershed, with 78% of the watershed dedicated to agricultural activities (52% croplands and 26% pasture) according to the NLCD 2001 digital raster (figure 3). Total urban area covers less than 6%, and other land use/land cover categories are the only other significant land cover in that these ranges need to be modified appropriately for shorter simulation time-steps. They also recommended that these ranges need to be modified appropriately for shorter simulation time-steps. For example, for daily time-steps the requirements are less stringent because model simulations are not as accurate for shorter time-steps than for longer time-steps. The following ranges for indicators of fit at a daily simulation level were suggested: \( R^2 > 0.5 \) and NS > 0.5, when stream flow is simulated with a monthly time-step. They also recommended that these ranges need to be modified appropriately for shorter simulation time-steps. For example, for daily time-steps the requirements are less stringent because model simulations are not as accurate for shorter time-steps than for longer time-steps. The following ranges for indicators of fit at a daily simulation level were suggested: \( R^2 > 0.5 \) and NS > 0.395. In this research, all hydrological and water quality simulations were at a daily simulation level, so the following ranges for indica-
tors of fit were adopted: RSR < 0.75, PBIAS < 30%, R² > 0.6, and NS > 0.5. All of the statistical indicators of fit for the stream flow model output were well within these requirements: RSR = 0.60, PBIAS = -0.50%, R² = 0.64, and NS = 0.64 (figure 4).

To verify that the statistical quality of the calibration results was replicated with an independent data set, model-estimated daily stream flow was compared to measured flows at the upstream West Mineral USGS station (07184220) (figure 5). Six time periods of continuous daily measured data were available at this location. For brevity, model verification results from only three of the time period comparisons are presented: best, intermediate, and worst statistical fit. Results from both the hydrological calibration (September 2, 1976, to September 30, 1982) and the verification process (April 24, 1977, to September 30, 1977; October 18, 1977, to June 23, 1978; and April 11, 1979, to May 16, 1979) are summarized in table 5.

Three of the four statistical indicators demonstrate that the fit of simulated stream flow to measured stream flow is good based on our requirements (table 5). The comparison for the most extended simulation time period (September 2, 1976, to September 30, 1982) that covers all the geographical area of the upper Cherry Creek watershed had the second best combination of statistical indicators of fit. The second longest comparison time period (April 24, 1977, to September 30, 1977) in the verification step has the best statistical indicators of fit. For the shortest comparison time period (April 11, 1979, to May 16, 1979), during which an extreme flash-flood event occurred, the event is very well replicated by the model output with the highest R² and NS coefficients (closer to the optimal value of 1 in both cases), and the lowest RSR coefficient (closer to the optimal value of 0). The statistical indicators for the comparison period October 18, 1977, to June 23, 1978, are moderate: RSR and PBIAS are well within the ranges specified as good, and R² and NS are of moderate quality. During this period of time there were several flood events and subsequent stream flow recession limbs that are captured appropriately by the model. Nevertheless, from January 15 to February 28, 1978 (figure 5b), the model simulates two flood events that are not consistent with observed stream flow data. The weather station at Columbus (figure 2) recorded precipitation events consistent with the simulated stream flow peaks. This means that the precipitation events were not homogeneous across the entire region. The rain events that occurred within the Cherry Creek watershed were of much lower magnitude than those registered at Columbus and therefore did not result in flood events in Cherry Creek. However, during the majority of the simulation, the statistical indicators were good. Therefore, the model was considered calibrated and verified for stream flow.

**Water Quality Calibration and Verification.** The calibration of the water quality portion of the modeling effort was performed by comparing simulated and measured concentration values for NO₃⁻-N, TAM, and TP at the Hallowell USGS station (07184300). Validation of the model output was performed comparing NO₃⁻-N, TAM, and TP simulated output to measured data at the West Mineral USGS station (07184220). Figure 6 summarizes the statistical and graphical comparison.

Due to the limited availability of measured data and also because several data values were reported as below minimum quantifiable level, statistical fit indicators were calculated only for NO₃⁻-N and TAM (figure 6). For simulation of water quality, Moriasi et al. (2007) reported wide ranges of statistical fit. For example, while NS values for hydrology were set to >0.395 as an acceptable level, for NO₃⁻-N ranges were calculated from -0.08 to 0.26. This variability in conditions for water quality parameters permits more lenient fitness coefficients. Our results find R² and NS for NO₃⁻-N were good at both locations. However, simulated results for TAM were not as good at either location. RSR was out of range for all simulated results, while PBIAS showed much greater variability, with only one simulated level out of range (NO₃⁻-N at West Mineral). Overall, the statistical fit indicators achieved for NO₃⁻-N and TAM in our model of Cherry Creek watershed (table 6) were of moderate
quality, but acceptable for daily simulations of these nutrient components.

For TP (table 6 and figure 7) the statistical indicators of fit show weaker performance of the model to measured data. All of the statistical measures were well outside of the optimal ranges, with the exception of PBIAS, which was near 12% at both locations. It is interesting to see that at least half of the reported measured data are lower than 0.05 mg P L–1 at both locations. The reported data from USGS for both stations did not include minimum quantification limits. In fact, several of the reported data were 0.0 mg L–1, which is inconsistent with current reporting and laboratory procedure. The USEPA (Wayman et al. 1999) uses two important concepts when setting detection limits of water quality samples: the minimum concentration of a substance that can be measured and reported with 99% confidence that the true value is greater than zero (method detection limit [MDL]), and the lowest level that can be reliably achieved within the specified limits of precision and accuracy during routine laboratory operating conditions (practical quantitation level [PQL]). For P, common values for MDL and PQL are 0.01 mg L–1 and 0.05 mg L–1 as P (CDPH 2015). Although concentration values between the MDL and PQL are uncertain, they should be reported because those values give indications or trends of water quality constituent concentrations (USEPA 2006). These considerations led the calibration and subsequent verification processes to be focused on replicating trends and range of concentrations rather than fitting simulation results to measured values that may have a high degree of uncertainty. In this context, the model simulations are consistent with the order of magnitude and trends of the measured P concentrations.

An additional verification with a completely independent data set was performed for NO3–N, TAM, and PO43–P using data collected near Faulkner, Kansas, downstream of USGS station 07184300 (figure 8). Because several concentration values were flagged as below the MQL (0.1 mg L–1 for NO3–N and TAM, and 0.25 mg L–1 for PO43–P), calculation of statistical indicators of fit was not possible. As with TP, this additional verification focused on replicating trends and range of concentration values.

**Water Quality Simulation, Probability of Exceedance, and Water Quality Indicators.**

The hydrological and water quality model for Cherry Creek correctly simulated water transport, and simulated NO3–N, TAM, and PO43–P transport within acceptable limits. The model was next used to explore potential sources or patterns of pollutants by simulating continuous daily concentrations of NO3–N, TAM, and PO43–P for a 32-year period of time from 1976 through 2008. Figure 9 shows simulated time-series for NO3–N, TAM, and PO43–P. Numerical values of statistical descriptors of the simulated values are included for each parameter over the 32-year period. In general, concentrations follow a seasonal pattern: low concentrations are observed early in the calendar year and high concentrations are simulated during or at the end of summer. This seasonal trend is consistent with the extensive use of fertilizer applications in the spring with planting, followed by additional applications later, and potentially indicates that the nonpoint source of nutrient concentrations is due to agricultural activity. For NO3–N, the model estimates a maximum concentration of 10 mg L–1 with a median of 0.011 mg L–1. Twenty-five percent of the simulated concentration values are lower than 0.005 mg L–1 while 75% of the concentrations are below 0.072. Overall, NO3–N concentrations are low in Cherry Creek. Total ammonia concentrations calculated by the model are lower than NO3–N concentrations. The maximum concentration for TAM is 2.6 mg L–1, and 75% of the simulated concentrations are lower than 0.41 mg L–1. The interquartile range (IQR) of TAM simulations is 0.28 mg L–1 while the IQR for NO3–N is 0.40. Since the maximum concentration for TAM is much lower than for NO3–N, extreme concentration events for NO3–N (outliers) are more frequent and follow a seasonal pattern (figure 9). This pattern is also seen for PO43–P. The maximum simulated concentration for PO43–P is 1.62 mg L–1, with an IQR equal to 0.067 mg L–1. Therefore, events with extreme PO43–P concentrations are also more frequent for this water quality constituent. Seventy-five percent of the PO43–P concentration values calculated by the model are lower than 0.072. The use of manure (from poultry or cattle grazing) as fertilizer could be the source for the excess nutrients in general and P in particular.

With long-term continuous daily simulations of NO3–N, TAM, and PO43–P concentrations, we can now calculate the percentage probabilities that the water quality constituents would equal or exceed...
concentration values that are critical either for human health or for aquatic ecosystems (table 7). Ninety-nine percent confidence bands were also calculated to account for the uncertainty inherent in the long-term water quality simulations. Upper confidence bands were used to establish probabilities of exceedance because upper bounds are more appropriate when water quality criteria are set up as maximum concentrations. The maximum simulated concentration of NO$_3^-$-N was 10 mg L$^{-1}$. The USEPA established 10 mg L$^{-1}$ as the maximum NO$_3^-$-N level allowed in drinking water (USEPA 2016; Reilly et al. 1999). The probability of exceedance of this concentration is minimal in Cherry Creek (lower than 0.01%; figure 10). The established water quality criteria for aquatic ecosystem health sets NO$_3^-$-N levels at a concentration of 0.98 mg L$^{-1}$ or lower. Higher levels of NO$_3^-$-N promote the growth of eutrophic species (table 7). Based on the simulations performed here, the probability that NO$_3^-$-N levels will exceed this lower limit in Cherry Creek is 9%. For TAM, 1 mg L$^{-1}$ is identified in the literature as a threshold value of impairment for aquatic life (table 7). The exceedance probability for this concentration is 3%, while the probability corresponding to a concentration of 1.24, identified by KDHE (2015) as a toxicity threshold for surface waters where fish are present, is 1.6%. For PO$_4^{3-}$-P, the maximum acceptable concentration that would avoid algal blooms and subsequent eutrophication is 0.05 mg L$^{-1}$. The probability of exceedance of a PO$_4^{3-}$-P concentration of 0.05 in Cherry Creek is 30.4%.

Water quality assessed for individual water quality constituents may obscure compound effects of multiple pollutants in stream water quality. The WQI numerical value takes into consideration the compounding effect of NO$_3^-$-N, TAM, and PO$_4^{3-}$-P estimations and their corresponding water quality criteria to produce a single water quality index attributable to a stream (Terrado et al. 2010). The WQI was calculated for each subbasin within the Cherry Creek watershed and for the entire watershed over the 32-year period from 1976 until 2008. The deviation of the WQI for each subbasin relative to the total watershed is presented in figure 11. The data not only demonstrate the temporal variability over the 32-year time span, but also the spatial variability in water quality within the individual subbasins in the Cherry Creek.
Table 5
Results of the hydrological calibration and verification of the Cherry Creek watershed Hydrological Simulation Program Fortran (HSPF) model.

<table>
<thead>
<tr>
<th>Comparison period</th>
<th>RSR &lt; 0.75</th>
<th>PBIAS &lt; 30%</th>
<th>R² &gt; 0.6</th>
<th>NS &gt; 0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sept. 2, 1976, to Sept. 30, 1982*</td>
<td>0.60</td>
<td>-0.50</td>
<td>0.64</td>
<td>0.64</td>
</tr>
<tr>
<td>Apr. 24, 1977, to Sept. 30, 1977†</td>
<td>0.51</td>
<td>1.35</td>
<td>0.74</td>
<td>0.74</td>
</tr>
<tr>
<td>Oct. 18, 1977, to June 23, 1978*</td>
<td>0.73</td>
<td>-9.53</td>
<td>0.42</td>
<td>0.37</td>
</tr>
<tr>
<td>Apr. 11, 1979, to May 16, 1979†</td>
<td>0.51</td>
<td>-29.97</td>
<td>0.85</td>
<td>0.73</td>
</tr>
</tbody>
</table>

Notes: RSR = root-mean-squared-error to standard deviation ratio. PBIAS = percentage bias. R² = coefficient of determination. NS = Nash-Sutcliffe efficiency.

*Calibration, Hallowell station.
†Verification, West Mineral station.

Figure 6
Water quality calibration at (a and c) Hallowell station and verification at (b and d) West Mineral station for (a and b) nitrate-nitrogen (NO₃⁻-N) and (c and d) total ammonia (TAM). Statistical parameters of fitness were calculated according to equations detailed in table 3.
6. The time of concentration of a watershed measures the response of a watershed to a rain event and is defined as the time needed for water to flow from the most remote point in a watershed to the watershed outlet. Since the stream catchment does not collect water efficiently, dilution effects are limited. Also, water entering the stream from the vadose zone (interflow) is also limited by the length of the stream segment and the distances travelled laterally in the subsurface to reach the stream. Subbasin 6 contains approximately 83% of lands dedicated to agriculture (crops and pasture). Therefore, the water that washes off the nearby area and reaches the stream may contain relatively high nutrient concentrations. These waters, although small in volume, rather than diluting the receiving waters instead further enrich its nutrient concentrations.

To further compare WQI values between subbasins, nonparametric statistical indicators were computed for WQI values of each subbasin (minimum, first quartile, median, and third quartile; figure 12). The first quartile indicates the amount of time that 75% of the readings are above a given value. For the Cherry Creek watershed, the first quartile of WQI values for all subbasins is above 74.2, indicating that water quality is at least fair (usually protected but occasionally threatened or impaired). The median value shows that WQI is higher than 93.3 for 50% of the time (i.e., water quality has only a minor degree of threat or impairment). Moreover, the upper quartile WQI shows that WQI is above 96.7 for 25% of the time. Hence, water quality is excellent in all subbasins, with a virtual absence of threat or impairment. Nevertheless, a slight degrading trend of the water quality in the Cherry Creek watershed is observed from subbasin 1 to subbasin 7. For all subbasins, water quality is poor (WQI < 44) less than 1% of the time and water quality is marginal (WQI < 64) less than 6% of the time.

Summary and Conclusions

The Cherry Creek watershed, located in southeast Kansas, is a contributor of water to the Grand Lake watershed via the Neosho River. The watershed drains approximately 882.2 km² (218,000 ac) of land, of which at least 78% are agricultural lands. Several studies have identified the watershed as a targeted area for agricultural BMPs to meet sediment and nutrient load reductions, and for TMDL design oriented toward reducing nutrient and sediment loads. This paper presents a water quality assessment in the Cherry Creek watershed by means of a hydrological and water quality model, developed using the HSPF code. The model was calibrated and verified with measured data reported by USGS and the KDHE. The development of the model was performed in two phases: (1) modeling of the upper Cherry Creek watershed (catchment exit at Hallowell), and (2) modeling of the entire Cherry Creek watershed (catchment exit at Faulkner). The model was designed to simulate water quality in terms of NO₃⁻N, TAM, TP, and PO₄³⁻P concentrations.

Hydrological calibration and verification and subsequent extrapolation of hydrological parameters from the upper Cherry Creek model to the entire Cherry Creek watershed model were successful given the relatively small number of water samples of nutrient analysis used to build the model. Although water quality calibration and verification were hindered by measured nutrient concentration values that were lower than the MQL, by orienting the calibration and verification toward replicating trends and ranges of measured nutrient concentrations, a model was produced that was able to simulate comparable measured concentration values recorded at an independent water quality station downstream of the upper Cherry Creek model.

Our results show that concentration values of nitrogenous contaminants (NO₃⁻N and TAM) are generally low for this agricultural watershed: 75% of the NO₃⁻N and TAM concentrations are lower than 0.41 mg L⁻¹. However, peak values of NO₃⁻N can reach concentration values above 5 mg L⁻¹ up to 10 mg L⁻¹, usually in mid-year (summer or early autumn). This indicates that NO₃⁻N is related to crop production activities and/or low flow conditions in the river. A similar pattern is observed for TAM. The likelihood that the NO₃⁻N and TAM concentrations could become toxic for aquatic communities is low: 9% and 3%, respectively. Although low concentrations are also observed for PO₄³⁻P, if the USEPA criteria for PO₄³⁻P in surface waters (maximum 0.05 mg L⁻¹) are taken into account, even these low concentrations may promote eutrophication. According to our simulation results, concentrations of PO₄³⁻P in Cherry Creek have a probability of exceeding that maximal level 30.4% of the time. With a maximum simulated concentration of 1.62 mg L⁻¹ and an IQR of only 0.067 mg L⁻¹, indicating the existence of frequent extreme concentration events, future research is needed for assessing the PO₄³⁻P activity in Cherry Creek. Extensive use of animal manure, either imported from neighboring confinement operations (primarily poultry) or from cattle grazing on pasture, would contribute excess levels of nutrients, especially P (Tomlinson et al. 2014, 2015). This may account for the elevated levels of PO₄³⁻P observed in the watershed, and indicate the need to target improved methods of animal manure management within the watershed to improve water quality.

The results indicate the suitability of the HSPF model for tracking and predicting nutrient flows in agricultural watersheds. The methodology for assessing overall water quality is also shown to be appropriate. The WQI calculations showed that water quality in upstream subbasins is better than in downstream subbasins, although agricultural activity was present in all subbasins. A slight degrading trend of water quality within the Cherry Creek watershed (from subbasin 1 to subbasin 7) was identified. No appar-

<table>
<thead>
<tr>
<th>Table 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statistical fitness results of the water quality calibration and verification process.</td>
</tr>
<tr>
<td>Comparison period</td>
</tr>
<tr>
<td>NO₃⁻N: Feb. of 1976, to Mar. of 1979*</td>
</tr>
<tr>
<td>TAM: Jan. of 1977, to Mar. of 1978*</td>
</tr>
<tr>
<td>NO₃⁻N: Feb. of 1976, to Mar. of 1979†</td>
</tr>
<tr>
<td>TAM: Jan. of 1977, to Mar. of 1978-3/78†</td>
</tr>
<tr>
<td>TP: Jan. of 1977, to Mar. of 1978*</td>
</tr>
<tr>
<td>TP: Jan. of 1977, to Mar. of 1978†</td>
</tr>
</tbody>
</table>

Notes: RSR = root-mean-squared-error to standard deviation ratio. PBIAS = percentage bias. R² = coefficient of determination. NS = Nash-Sutcliffe efficiency. NO₃⁻N = nitrate-nitrogen. TAM = total ammonia. TP = total phosphorus.

*Verification, Hallowell station.
†Verification, West Mineral station.
Figure 7
Water quality calibration and verification for total phosphorus (TP) for (a) Hallowell and (b) West Mineral.

(a) RSR = 2.99
PBias = 12.00
R² = 0.11
NS = 0.01

(b) RSR = 2.39
PBias = 12.25
R² = 0.16
NS = 0.05

Legend
— Simulated • Measured

Figure 8
Water quality verification for (a) nitrate (NO₃⁻), (b) total ammonia (TAM), and (c) orthophosphate (PO₄³⁻) for simulated and measured values at Faulkner, Kansas. The charts show the minimum quantifiable limit (MQL; concentrations below which analytical methods cannot operate with precision) for each of the water quality constituents.
Figure 9
Water quality simulation for October 20, 1976, to December 20, 2008. (a) Daily nitrate-nitrogen (NO$_3^-$-N), (b) total ammonia (TAM), and (c) orthophosphate (PO$_4^{3-}$-P) concentrations.

- **Figure 9a**
  - Minimum = 0.00
  - 1st Quartile = 0.00
  - 3rd Quartile = 0.10
  - Maximum = 10.00
  - Date: Oct 1976 to Oct 2008

- **Figure 9b**
  - Minimum = 0.00
  - 1st Quartile = 0.13
  - 3rd Quartile = 0.41
  - Maximum = 2.60
  - Date: Oct 1976 to Oct 2008

- **Figure 9c**
  - Minimum = 0.000
  - 1st Quartile = 0.005
  - 3rd Quartile = 0.072
  - Maximum = 1.620
  - Date: Oct 1976 to Oct 2008

Acknowledgements

This research was funded by a grant from CONICYT REDES 140045. This manuscript is contribution number 16-274-J from the Kansas Agricultural Experiment Station. This work was supported in part by the USDA National Institute of Food and Agriculture, Hatch project 1003478.

References


Table 7
Concentration values and criteria reported critical for human health or aquatic ecosystems.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration (mg L⁻¹)</th>
<th>Associated risk</th>
<th>Contaminant source</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₃⁻-N</td>
<td>10</td>
<td>Infants below the age of six months who drink water containing nitrate in excess of the MQL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome (USEPA 2016).</td>
<td>Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits.</td>
</tr>
<tr>
<td>NO₃⁻-N</td>
<td>0.98</td>
<td>Eutrophic macroinvertebrate communities are likely when nitrate exceeds 0.98 mg L⁻¹ (MCEA 2010).</td>
<td>Runoff from fertilizer use; leaking from septic tanks, sewage; erosion of natural deposits.</td>
</tr>
<tr>
<td>TAM</td>
<td>&gt;1</td>
<td>Impairment of the aquatic life use: toxicity may result if high ammonia levels (e.g., TAM &gt; 1 mg L⁻¹) are present (MCEA 2013).</td>
<td>Major evacuative product of animals. TAM-based fertilizer not used by plants can percolate into groundwater. TAM converts to nitrate when oxygen (O) is present.</td>
</tr>
<tr>
<td>TAM</td>
<td>1.24 at pH: 6.5 &lt; pH &lt; 8.3, and temperature: 0°C &lt; T &lt; 30°C</td>
<td>pH- and temperature-dependent chronic aquatic life criteria for total ammonia early life stages of fish present (KDHE 2007, 2015).</td>
<td>Main evacuative product of animals. Fertilizer not used by plants can percolate into groundwater. TAM converts to nitrate when O is present.</td>
</tr>
<tr>
<td>PO₄³⁻-P</td>
<td>0.05</td>
<td>Although levels of 0.08 to 0.10 mg L⁻¹ orthophosphate may trigger periodic blooms, long-term eutrophication will usually be prevented if total phosphorus levels and orthophosphate levels are below 0.5 mg L⁻¹ and 0.05 mg L⁻¹, respectively (Dunne and Leopold 1978).</td>
<td>Natural processes. Main man-made sources are partially treated and untreated sewage, runoff from agricultural sites, and application of lawn fertilizers.</td>
</tr>
</tbody>
</table>

Notes: NO₃⁻-N = nitrate-nitrogen. MQL = minimum quantifiable level. TAM = total ammonia. PO₄³⁻-P = orthophosphate.

Figure 10
Probability of exceedance. Percentage of the time that (a) nitrate-nitrogen (NO₃⁻-N), (b) total ammonia (TAM), and (c) orthophosphate (PO₄³⁻-P) concentration values will exceed the established water quality criteria detailed in table 7.
Figure 11
Relative water quality indicator (WQI) deviations from the mean WQI for each of the six subbasins conforming Cherry Creek watershed. High relative positive deviation values indicate that WQI for that particular subbasin tends to be lower than the mean WQI for the subbasin. Conversely, lower or negative relative deviations indicate that WQI for the subbasin tends to be higher than the mean WQI.
Figure 12
Minimum, first quartile, median, third quartile, and maximum water quality indicator (WQI) per subbasin. Water quality is shown to be mostly fair to excellent through time in all subbasins.


