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# Chloride Sources and Losses in Two Tile-Drained Agricultural Watersheds

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## Abstract

Chloride is a relatively unreactive plant nutrient that has long been used as a biogeochemical tracer but also can be a pollutant causing aquatic biology impacts when concentrations are high, typically from rock salt applications used for deicing roads. Chloride inputs to watersheds are most often from atmospheric deposition, road salt, or agricultural fertilizer, although studies on agricultural watersheds with large fertilizer inputs are few. We used long-term (21 and 17 yr) chloride water quality data in two rivers of east–central Illinois to better understand chloride biogeochemistry in two agricultural watersheds (Embarras and Kaskaskia), the former with a larger urban land use and both with extensive tile drainage. During our sampling period, the average chloride concentration was 23.7 and 20.9 mg $L^{-1}$ in the Embarras and Kaskaskia Rivers, respectively. Annual fluxes of chloride were 72.5 and 61.2 kg $ha^{-1}$ $yr^{-1}$ in the Embarras and Kaskaskia watersheds, respectively. In both watersheds, fertilizer chloride was the dominant input (~49 kg $ha^{-1}$ $yr^{-1}$), with road salt likely the other major source (23.2 and 7.2 kg $ha^{-1}$ $yr^{-1}$ for the Embarras and Kaskaskia watersheds, respectively). Combining our monitoring data with earlier published data on the Embarras River showed an increase in chloride concentrations as potash use increased in Illinois during the 1960s and 1970s with a lag of about 2 to 6 yr to changes in potash inputs based on a multiple-regression model. In these agricultural watersheds, riverine chloride responds relatively quickly to potash fertilization as a result of tile-drainage.

## Core Ideas

- Chloride inputs in agricultural tile-drained watershed respond quickly to inputs.
- Chloride inputs from potash could be used to predict riverine concentrations.
- Chloride results suggest that nitrate response would also be rapid in these watersheds.

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CHLORIDE has typically been viewed in two different ways in past research: as a conservative tracer in forested watersheds (e.g., Svensson et al., 2012), where we can learn about the source of water (Kirchner et al., 2010), or as a contaminant in urban watersheds and streams where concentrations are periodically elevated as a result of runoff of road salt applied as a deicer during winter storms, potentially harming biota (e.g., Gardner and Royer, 2010; Trowbridge et al., 2010). Atmospheric deposition and rock weathering are the major natural inputs of chloride to a watershed, with larger deposition inputs near coastal areas (Kelly et al., 2008). Road salt, wastewater effluent, and agricultural fertilizer can all be important anthropogenic inputs in various watersheds. Chloride has mostly been thought to be unreactive in ecosystems with little uptake or release by either soils or vegetation, allowing it to be used as a conservative tracer, often to determine water residence times or the mass balances of nonconservative elements (Svensson et al., 2012). Kirchner et al. (2010) used chloride and water isotopes to demonstrate that although flow responds quickly to storm precipitation in watersheds, the source of the water reflects storage and mixing of waters over long time scales. However, Chen et al. (2002) found that adsorption or adsorption-like processes influenced stream chloride concentrations in a watershed in Wales, although the actual process was not identified.

Svensson et al. (2012) compiled chloride budgets from 32 forested watersheds and found that sites with low chloride deposition (<6 kg $ha^{-1}$ $yr^{-1}$) had a net release of chloride indicative of an internal source or declining internal pool. Watersheds with greater deposition had a more conservative balance of chloride (Svensson et al., 2012). Their results followed several recent studies that concluded chloride is more reactive than previously thought and actually has a complex biogeochemical cycle with conversion of chloride to organic chlorine forms important for retention (e.g., Bastviken et al., 2007; Öberg and Bastviken, 2012). Soil organic matter and oxic conditions are thought to be controlling factors for this conversion (Bastviken et al., 2007).

Many studies have focused on road salt and acute impacts of elevated chloride concentrations on stream biota (e.g., Kelly et al., 2008; Gardner and Royer, 2010; Trowbridge et al., 2010).

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Of the 44.5 Tg of salt that was used in the United States during 2014, ~43% was used for highway deicing (USGS, 2015). Kelly et al. (2008) observed a steadily increasing trend in stream chloride concentrations as a result of road salt applications during a period when applications did not change. They attributed the steady increase to a lag effect of long-term use and subsurface buildup of chloride (Kelly et al., 2008). Gardner and Royer (2010) measured concentrations as high as 2100 mg Cl $L^{-1}$ as a result of road salt, with the concentration of a reference site <22 mg $L^{-1}$. They concluded, however, that the chloride concentrations measured did not appear to be an important threat to aquatic life based on toxicity testing. Kaushal et al. (2005) documented increasing chloride concentrations in rivers of the northeastern United States from road salt and increasing impervious surfaces. They observed that if the increase in chloride concentrations continued, many surface waters in the northeastern United States would be toxic to aquatic organisms and not potable for humans (Kaushal et al., 2005).

Few studies have evaluated agricultural watersheds where the primary input is likely fertilizer derived chloride from potash. Böhlke (2002) termed chloride from potash an agricultural contaminant to groundwater, although there are no published papers documenting drinking water problems from this source. A recent study conducted a mass balance of chloride on a large watershed in the Czech Republic evaluating changes in agricultural fertilizer inputs, road salt, and land use change on chloride (Kopáček et al., 2014). They observed major changes in inputs and outputs in response to changes in fertilizer inputs and land drainage and observed retention that was attributed to both chloride immobilization as organic chlorine as well as changes in Cl storage in ground water (Kopáček et al., 2014). van der Velde et al. (2010) developed numerical approaches of time-varying travel time distributions to evaluate nitrate and chloride transport in a small (6600 ha) tile-drained watershed in the Netherlands. They found that the surface water concentrations were a result of mixing a large volume of old water with a relatively constant chloride concentration with a discharge-dependent contribution of younger water with variable concentrations (van der Velde et al., 2010). In further chloride transport analysis on the same watershed, Benettin et al. (2013) showed that root zone residence times were affected by short-term events, with transport times for chloride of weeks to months. Chloride that reached groundwaters was released at slower rates and accumulated and persisted for much longer times, with mean travel times of ~2.7 to 3.6 yr (Benettin et al., 2013).

Given the limited research on chloride balances and fluxes in agricultural watersheds, our goal was to use long-term data to better understand chloride biogeochemistry in two dominantly agricultural watersheds: one with a larger urban land use and both with extensive tile drainage. We evaluated the major inputs and outputs of chloride to each watershed as well as long-term changes in stream loads.

# Materials and Methods

## Site Description

Two watersheds in east–central Illinois were used in this study: the Upper Embarras River and the Lake Fork of the Kaskaskia River (Supplemental Fig. S1). Both watersheds have been previously reported on for riverine studies of nitrate and phosphorus (David et al., 1997; Royer et al., 2004, 2006; Gentry et al., 2007, 2014) as well as dissolved organic C (Royer and David, 2005). Nearly all of the land use in these watersheds (>90%) is in a corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] crop rotation with almost no farm animals; so, there are no important manure inputs. Soils are Mollisols formed in about 100 cm of loess, with Drummer the dominant series (fine-silty, mixed, superactive, mesic Typic Endoaquolls). Sewage effluent from Champaign–Urbana does not flow into the Embarras or Lake Fork of the Kaskaskia Rivers. The landscape is flat and has been extensively hydrologically modified with numerous dredged drainage ditches and field tile installations (David et al., 1997; Royer et al., 2006). The tile systems are typically 1 to 1.5 m below the soil surface and include both older random tile systems as well as newer patterned systems. Precipitation is typically about 100 cm annually, with ~10 cm as snow. The Embarras River watershed is mostly in the southern half of Champaign County and northern part of Douglas County, IL. The Lake Fork of the Kaskaskia River watershed is mostly in Piatt County, IL.

## Riverine and Tile Sampling

We used long-term river flow and chloride concentrations datasets from these two agriculturally dominated watersheds. From June 1993 through September 2014 we collected water samples ($n$ = 1147) from the Embarras River at the USGS gauging station (#003343400) near Camargo, IL (39°47′30″ N, 88°11′09″ W) where the watershed area is 48,100 ha. From October 1996 through September 2014 we collected water samples ($n$ = 1223) from the Lake Fork of the Kaskaskia River at the USGS gauging station (#05590800) near Atwood, IL, (39°48′23″ N, 88°28′34″ W) where the watershed area is 38,600 ha. Maps of these watersheds have been previously published by David et al. (1997) and Gentry et al. (2007). Water samples were collected weekly to daily depending on flow. We attempted to sample all high-flow periods (>28 $m^3 s^{-1}$) on a daily basis. River samples were filtered (0.45-μm pore size) and analyzed for chloride by ion chromatography (Dionex). We used linear interpolation to estimate a chloride concentration for every daily discharge value to determine daily and annual loads. We also obtained monthly chloride data for the Embarras River at Camargo from 1962 through 1971, sampled and measured by the Illinois State Water Survey (Harmeson and Larson, 1969; Harmeson et al., 1973) and data collected by Illinois EPA sampled on a 6-wk-interval basis from 1979 through 1993 (USEPA, 2015). Again, linear interpolation was used to estimate daily chloride concentrations that were combined with measured USGS flow data. The analysis of 1962 through 1993 data was used to obtain annual flow-weighted chloride concentrations.

The Kaskaskia River watershed has no large towns, but southern portions of Champaign (2013 population of 83,424) and Urbana (2013 population of 41,752) and nearly all of Savoy (2013 population of 7681) drain into the Embarras River (US Census, 2015). We sampled the urban drainage from Champaign and Urbana as they formed the upper Embarras River with drainage areas of 571 ha for Champaign and 135 ha for Urbana. We also sampled the upper Embarras River just south of the cities at Curtis Road, where the drainage area was 1594 ha, as well as at a location midway down the watershed at road 300N (drainage area of 11,269 ha, location marked on David et al. [1997] published map as well as Supplemental Fig. S1). These locations had water quality samples collected weekly to daily from 1994 through 1996 to assess chloride and sodium from urban drainage in the watershed. Chloride was again determined using ion chromatography, and sodium was determined by flame emission using an atomic absorption spectrophotometer (American Public Health Association, 1989).

To assess the response of chloride in tile drainage to KCl fertilization at the field scale in the Embarras Watershed, we used data from four biofuel feedstock crops (miscanthus [*Miscanthus ×giganteus* J. M. Greef & Deuter ex Hodk. & Renvoize], switchgrass [*Panicum virgatum* L.]), restored prairie [28 species, see Zeri et al. {2011} for species composition], and a corn–corn–soybean rotation) on the University of Illinois Energy Farm located in upper part of the watershed near the Curtis Road sampling location. Each crop was planted on a 4-ha block in 2008 with patterned tile drains that were installed during the fall of 2007 at a spacing of 30.5 m between laterals and a depth of 1 to 1.5 m to allow collection of drainage water from each crop type (see Smith et al. [2013] for complete details). Each tile outlet had an Agri Drain structure with a pressure transducer to measure continuous flow (15-min basis) with autosamplers (American Sigma 900MAX portable sampler) to collect flow-proportional water samples for chloride analysis by ion chromatography. Few tile water samples were collected during 2012 as a result of the drought that occurred. These fields had previously been in alfalfa (*Medicago sativa* L.) and before planting a grid-based soil test with samples collected on 28 Nov. 2007 was conducted. Based on the November soil test, potash was added across the fields using variable-rate technology on 17 Apr. 2008 with 58, 179, 233, and 237 kg potash $ha^{-1}$ added to the corn, switchgrass, prairie, and miscanthus plots, respectively, to achieve a uniform K soil test value of 336 kg K $ha^{-1}$. The corn plot was again fertilized with 224 kg potash $ha^{-1}$ on 1 Oct. 2012 (the other biofuel plots were not fertilized).

## Chloride Balance

An annual chloride balance was estimated using the riverine chloride export determined above along with atmospheric deposition inputs, crop fertilization, and crop harvest. Wet deposition was from the Bondville, IL, station of the National Atmospheric Deposition Program, which is located in between the two watersheds just outside the borders of each (National Atmospheric Deposition Program, 2015). Crops in Illinois are typically fertilized with K every other year as potash (KCl). We used USDA National Agricultural Statistics Service (USDA–NASS) survey values of $K_2O$ fertilization rates for Illinois, which were available annually from 1993 through 2003 and then again in 2005 and 2010 (USDA–NASS, 2015b). Interpolation was used to fill in missing years. These rates were reported on a per-acre basis of corn or soybean each year along with the percentage of acres receiving K fertilization for the state. We assumed that the state fertilization rates were typical of these watersheds. We used planted acres of corn and soybean in Champaign, Douglas, and Piatt Counties each year to obtain the fraction of cropland in corn and soybean (USDA–NASS, 2015b) and then used those fractions to estimate acres of corn and soybean each year in each watershed. Fertilization rates of K were then applied to these acres in each watershed using the rate and percentage of acres receiving K fertilization. Crop harvest of chloride was estimated using a similar approach as for fertilizer. Annual corn and soybean harvests were obtained for Champaign, Douglas, and Piatt Counties each year (USDA–NASS, 2015b) and then scaled to each watershed using the fraction in corn and soybean of the total area of each watershed. The amount of chloride in corn and soybean grain was 0.04% for corn and 0.03% for soybean (Batal et al., 2011).

Historical potash fertilizer sales in Illinois were obtained from annual Illinois Agricultural Statistics bulletins, annual USDA Agricultural Bulletins, and fertilizer tonnage reports from 1945 through 2014 (USDA–NASS, 2015a; Illinois Department of Agriculture, 2015). Fertilizer sales are reported on a crop-year basis July through December of the previous year plus January through June of the actual crop year and were converted to a Cl basis. Recent road salt inputs were estimated as described in the Supplemental Information.

## Linear Regression Modeling

We used multiple linear regression using SAS v. 9.3 (SAS Institute, 2011) to model annual flow-weighted Embarras River chloride concentrations from 1962 through 2014 (except for the 1972–1978 water years, where no data were available, $n$ = 46 yr) with two variables: (i) water yield and (ii) lagged, multiple-year moving average Cl (potash) sales. Both current and the previous-year's water yield were evaluated along with different previous-years' potash sales (moving averages of 2–6 yr) lagged from 0 to 3 yr. Models with the lowest Mallows' values and those with Cp values (a statistic that compares the precision and bias of the full model to models with a subset of predictors) approximately equal to one plus the number of variables in the model were considered additionally. The PRESS statistic for each model was calculated; the model with the lowest PRESS statistic was selected as the best model (Montgomery et al., 2006). A plot of predicted vs. modeled chloride concentrations in the final model is shown in Supplemental Fig. S2. Model residuals (shown in Supplemental Fig. S3) were tested for normality of distribution using the Anderson–Darling $A^2$ test. Final models results are given in Supplemental Table S1.

# Results

## Chloride Concentrations

Annual flow-weighted chloride concentrations averaged 23.7 and 20.9 mg $L^{-1}$ for the Embarras (1994–2014 water years) and Kaskaskia Rivers (1998–2014 water years), respectively (Fig. 1). The Kaskaskia River often had chloride concentrations >50 mg $L^{-1}$, particularly during 2012 and 2013. High chloride concentrations were typical during the fall and always at low flow in this river. The Kaskaskia was nearly stagnant when these high chloride concentrations were measured, and 2012 and 2013 were low-flow years leading to a larger number of samples with high chloride concentrations. Flow-weighted chloride concentrations were not greater during the winter months (January–March) in either river compared with the other seasons (means not shown).

Concentrations of chloride in the head waters of the Embarras River watershed were much more variable and reached much greater concentrations than downstream locations during

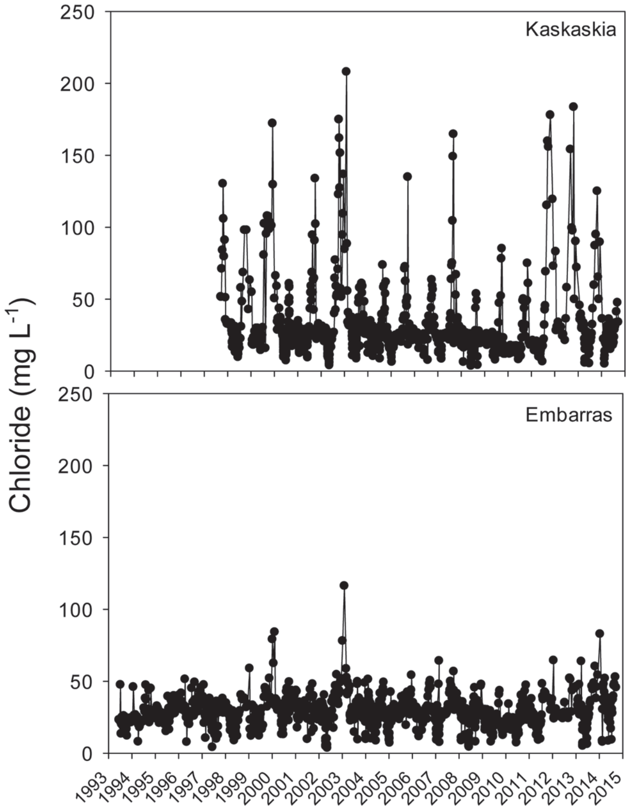

**Fig. 1. Chloride concentrations in grab samples in the Embarras River at Camargo, IL, and the Kaskaskia River at Atwood, IL.**

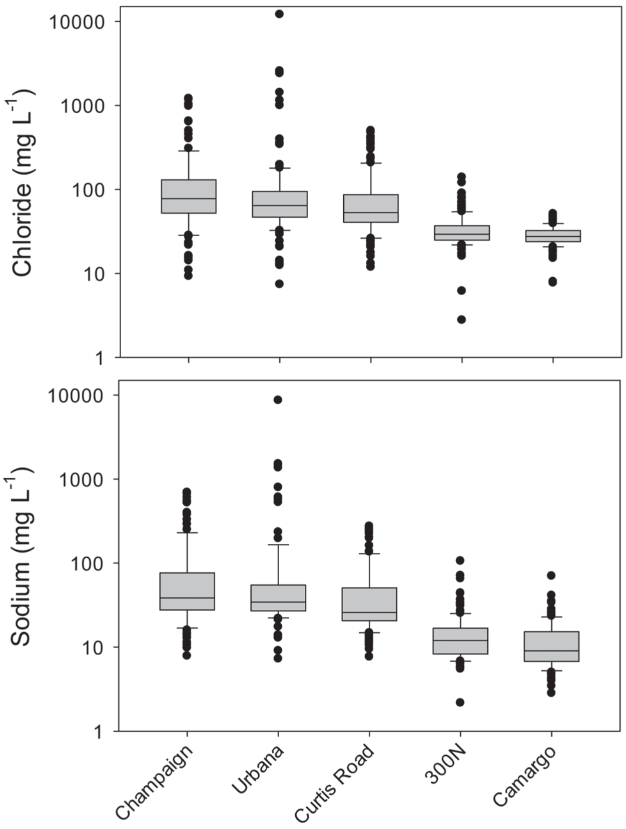

**Fig. 2. Box plots of chloride and sodium concentrations for headwater (Champaign, Urbana, and Curtis Road), midwatershed (300N), and outlet (Camargo) locations in the Embarras River watershed during 1994 through 1996.**

the monitoring period of 1994 through 1996 (Fig. 2). Median chloride concentrations from the urban drainage areas of Champaign and Urbana were 63.6 and 59.4 mg L$^{-1}$, respectively, and decreased to 47.1 mg L$^{-1}$ by Curtis Road (Supplemental Table S2). At 300N, where the drainage area was 11,269 ha (23% of the entire watershed), the median concentration had decreased to 27.8 mg Cl L$^{-1}$, just above the median value at the Camargo outlet (25.7 mg Cl L$^{-1}$). During several winter runoff events, concentrations from the small urban drainage areas concentrations increased rapidly to a maximum chloride concentration of 12,063 mg L$^{-1}$ on 11 Jan. 1996 in the Urbana drainage. On that same day, the concentration in the Champaign drainage was 1017 mg Cl L$^{-1}$. By the next day chloride in the Urbana drainage had decreased to 2569 mg Cl L$^{-1}$ and remained above 1000 mg L$^{-1}$ for 4 d. Sodium concentrations followed the same pattern as chloride and were much greater in the upper watershed than the outlet (Supplemental Table S2). The molar ratio of sodium to chloride was about 0.80 in the three upper watershed sampling sites compared with 0.72 downstream (300N and outlet) in the watershed.

## Stream Export

Average annual chloride yields were 72.5 and 61.2 kg Cl ha$^{-1}$ yr$^{-1}$ for the Embarras and Kaskaskia watersheds, respectively, and varied across a large range, similar to water yields (Table 1; Fig. 3). Chloride yield varied linearly with water yield for both watersheds ($r^2 = 0.95$ and 0.89 for the Embarras and Kaskaskia rivers, respectively) with the exception of two high flow years in the Kaskaskia River, where yields were lower than the overall trend. Average annual flow-weighted concentrations decreased linearly with increasing water yields, with the Kaskaskia River having lower concentrations than the Embarras River (Supplemental Fig. S4).

## Tile Chloride Concentrations

Based on the soil test results, a larger amount of potash was applied to the prairie and miscanthus plots in the fall of 2007 than corn and switchgrass, and this was reflected in the larger chloride concentrations in tile drainage water during the next 4 yr (Fig. 4). Chloride concentrations were greater in the prairie and miscanthus plots in 2008 and 2009 than the corn and switchgrass plots. In the miscanthus, switchgrass, and prairie

**Table 1. Average chloride inputs (wet deposition, fertilizer) and outputs (grain harvest, stream export) for the Embarras River watershed at Camargo, IL, for 1994 to 2014 and Lake Fork of the Kaskaskia River watershed at Atwood, IL, for 1998 to 2014 along with standard errors in parentheses. The overall long-term balance and estimated recent (2010–2014) road salt inputs of chloride are also given.**

| | Embarras | Kaskaskia |
|---|---|---|
| | ———— kg Cl ha$^{-1}$ yr$^{-1}$ ———— | |
| Inputs | | |
| Wet deposition | 1.0 (0.04) | 1.0 (0.04) |
| Fertilizer | 47.1 (0.7) | 51.9 (0.9) |
| Outputs | | |
| Grain harvest | 2.4 (0.1) | 2.6 (0.1) |
| Stream export | 72.5 (5.4) | 61.2 (6.6) |
| Balance | −26.7 | −10.9 |
| Road salt | 23.2 | 7.2 |

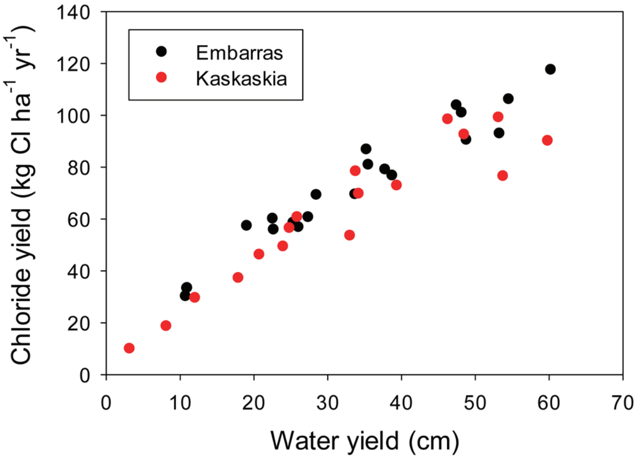

**Fig. 3. Annual chloride and water yields for the Embarras River watershed at Camargo, IL, and the Kaskaskia River at Atwood, IL.**

plots, chloride concentrations in tile drainage decreased each year to a concentration of 1 to 3 mg $L^{-1}$ by 2013 and 2014. The corn plot also had decreasing concentrations from 2008 through 2012, which then increased to a chloride concentration of 25 to 30 mg $L^{-1}$ in 2013 following fertilization with potash in the fall of 2012.

### Chloride Balance

We were able to calculate most inputs and all outputs on an annual basis, with the exception of road salt, where we could only estimate recent inputs (Table 1). Wet deposition of chloride was a minor input (1 kg ha$^{-1}$ yr$^{-1}$) to both watersheds, with fertilizer the dominant source of chloride through KCl applications. Grain harvest and export of chloride from the watershed was a small output, averaging just 2.5 kg ha$^{-1}$ yr$^{-1}$ in the two watersheds. The largest chloride output and largest flux overall was stream export as described previously. The 21-yr chloride balance for the Embarras watershed (inputs–outputs) was −26.7 kg ha$^{-1}$ yr$^{-1}$ and for the 17 yr of data for the Kaskaskia was −10.9 kg ha$^{-1}$ yr$^{-1}$. During the last 5 yr (2010–2014), that matches our road salt estimate period: the chloride balances were −20.9 and 0.9 kg ha$^{-1}$ yr$^{-1}$ for the Embarras and Kaskaskia watersheds, respectively. Our estimated road salt inputs of 23.2 and 7.2 kg ha$^{-1}$ yr$^{-1}$ for the Embarras and Kaskaskia watersheds, respectively, compared well with the balances, with a much larger chloride input from road salt in the Embarras River watershed as a result of its larger urban drainage areas of Champaign, Urbana, and Savoy (and more street surface area). There also could be small inputs of chloride from sewage effluent from some of the towns in each watershed that we had no data for. However, these towns were just a few thousand people and unlikely to be a large source of chloride. Again, there were no large sewage effluent sources in either watershed, as Champaign–Urbana's effluent was not discharged into either of these watersheds.

## Discussion

### Riverine and Tile Chloride and Balances

Our overall chloride balances for the Embarras and Kaskaskia watersheds suggest that in these dominantly agricultural watersheds with extensive tile drainage, chloride added through

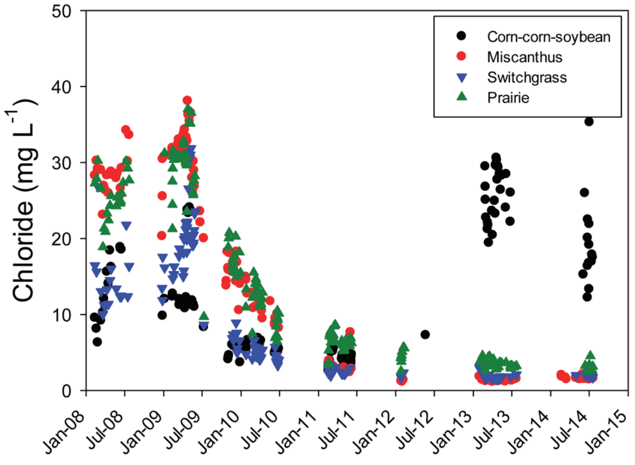

**Fig. 4. Chloride concentrations in tile drainage water during 2008 through 2014 by biofuel crop. Rotation was in corn in 2008, 2009, 2011, 2012, and 2014 and soybean in 2010 and 2013.**

fertilizer and road salt is transported to the river system and out of the watershed. In both watersheds, chloride export increased linearly with annual stream flow, and concentrations were diluted, suggesting a finite pool available for leaching each year. Basu et al. (2010) noted that nutrients from managed watersheds followed this pattern as a result of a legacy of accumulated nutrients providing a memory.

Average chloride concentrations were >20 mg $L^{-1}$ in both watersheds and demonstrate that concentrations can be elevated from mainly agricultural inputs. Kaushal et al. (2005) discussed the role of road salt in streams of the northeastern United States increasing concentrations to similar levels or above, but fertilizers can also increase concentrations. However, since fertilizer inputs are not increasing, it is not likely that the streams we monitored would have increased chloride concentrations in the future.

Although chloride concentrations could be quite high in the urban drainage areas in the Embarras watershed following snowmelt events, they were of short duration and were diluted quickly downstream as watershed drainage area increased. The decrease in the molar sodium to chloride ratios in the Embarras from the urban drainage areas to the watershed outlet are consistent with road salt being a larger source of chloride in the upper reaches. Trowbridge et al. (2010) compared road salt chloride concentration exceedances in New Hampshire streams with USEPA standards for the protection of aquatic life. They discussed the chloride data that were needed for a stream given the 4-d chronic exposure average concentration of 230 mg $L^{-1}$ and 1-h average of 860 mg $L^{-1}$ where USEPA (1988) standards consider a water body impaired. Corsi et al. (2010) also compared a wide range of stream monitoring data with these standards and found that in many northern sites both acute and chronic concentrations were exceeded. We measured concentrations well beyond the 1-h average concentration standard in both Urbana and Champaign drainage, but these were small drainage areas and streams. Just a few kilometers downstream, concentrations were greatly reduced at the Curtis Road sampling location, and concentrations were never near the aquatic life standards along the main stem of the river further downstream.

Fertilizer chloride was the major input in both watersheds, followed by road salt. Little chloride was removed through crop harvest of corn and soybean. The long-term history of chloride added through potash fertilization in Illinois increased after World War II, followed by relatively stable sales during 1955 through 1965, with increasing sales through the late 1960s and 1970s, peaking at 578,000 Mg Cl yr$^{-1}$ in 1980 (Supplemental Fig. S5). Since 1980, there has been more variability in Cl inputs from potash sales with an overall decreasing trend through 2005 and then a steady increase during the next 10 yr. Using other available data, we observed that the annual flow-weighted long-term chloride concentration in the Embarras River at Camargo increased steadily from about 7 mg L$^{-1}$ in 1962 and 1963 to a peak of 31 mg L$^{-1}$ in 1988 (Fig. 5). Since 1994, using our data, the average annual flow-weighted concentration has been 23.7 mg L$^{-1}$. Limitations in our road salt estimates prevent us from being more precise with our chloride balances and may have affected our long-term estimates of inputs beyond fertilizer.

The best multiple regression model of annual flow-weighted stream chloride concentrations in the Embarras River at Camargo used 4-yr average potash sales for Illinois lagged 2 yr and annual stream flow (Supplemental Table S1). The relationship between potash sales and stream chloride concentrations suggests that there was a short lag in stream chloride concentrations in response to potash sales, and that average sales over multiple years best represented the buildup or draw down of added chloride. This pattern in stream chloride concentrations was observed during both the increase in potash sales in the 1960s and 1970s as well as the period of decreasing use in the 1980s and 1990s. Chloride concentrations were also greater during low-flow years, which is why annual stream flow was a significant variable. These results indicate that riverine chloride responds in a relatively short time period to changing fertilizer inputs to agricultural fields as a result of transport from both root-zone water and shallow groundwater, each with different water transit times, as discussed below.

It is possible that our regression equation only explained 73% of the variation in annual chloride concentrations as a result of variable road salt inputs. We cannot quantify this input during the regression period, and it is likely that some of the unexplained variation is due to year-to-year variation of road salt to the Embarras River watershed. However, it is not likely that road salt use was greater in the past than our recent estimates but likely was less and fluctuated yearly depending on snow fall and probably started to increase during the 1960s, similar to potash (Jackson and Jobbágy, 2005). However, given that road salt is a smaller input than potash fertilizer that is added in large amounts every year, we think our analysis is appropriate.

Further evidence for a rapid response to chloride inputs is shown in our tile monitoring data (Fig. 4). Following potash applications, all four tile systems had rapid decreases in chloride concentration during years 3 to 6. This pattern of decreasing chloride concentrations from individual fields during a 3- to 6-yr time period is similar to our long-term watershed-scale result that integrates hundreds of tile-drained fields and again suggests chloride concentrations respond relatively quickly to both inputs and removal by drainage water. The Embarras River watershed was estimated to have 75 to 80% of the land area drained in 1997 (David et al., 1997), and this likely has increased with new patterned systems since that time. The field tile and overall watershed data are similar to results reported by Benettin et al. (2013), who stated that chloride in streams comes from both root-zone water with short transport times of weeks to months combined with groundwater chloride with travel times of several years. This would account for the lag times we have observed.

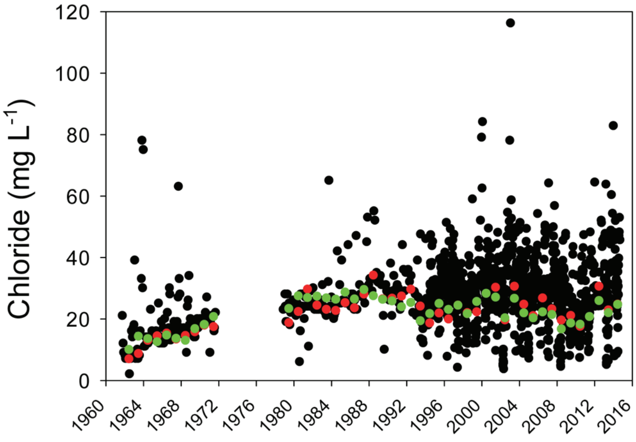

**Fig. 5. Embarras River at Camargo, IL, grab sample chloride concentrations from 1962 through 2014 and annual flow-weighted concentrations for the same period (red circles). Also shown are linear regression modeled flow-weighted chloride concentrations in green. Data before 1994 from Harmeson and Larson (1969), Harmeson et al. (1973), and USEPA (2015).**

## Comparisons with Other Watershed Chloride Studies

This result is somewhat in contrast with Kelly et al. (2008) for a forested watershed in eastern New York with some urban areas, where the major input was road salt. They observed a storage effect from long-term road salt use that led to a subsurface build-up of salt with steadily increasing stream water concentrations of chloride. Road salt use was not estimated to have changed during the 20-yr period of stream monitoring data in the study, but chloride concentrations in the stream continued to increase, suggesting a large amount of retention in the subsurface. Our response may have occurred more quickly as a result of the presence of drainage tiles, which effectively move shallow water through our watersheds and limit the loss of chloride to deeper groundwater reserves.

Other studies on forested ecosystems with smaller inputs of chloride have also observed more complex biogeochemical processing of added chloride thought to be due to immobilization and mineralization of chloride bound in organic matter (Svensson et al., 2012). We do not believe this was likely to have occurred in our agricultural soils, although these watersheds are mainly Mollisols with relatively high organic C concentrations (David et al., 2009). However, this amount of C is still much less than a forested watershed with a forest floor, and our inputs were much larger than watersheds where immobilization of chloride by organic matter has been observed (Svensson et al., 2012).

Kopáček et al. (2014) is the only study that we are aware of that evaluated chloride fluxes in a watershed with large and documented agricultural fertilizer inputs of chloride. In addition, their watershed had substantial tile drainage that increased from 4 to 43% in the agricultural portion of the watershed between 1960 and 1990. They had similar chloride inputs as our watersheds (23 to 64 kg ha$^{-1}$ yr$^{-1}$) during the 1950s to 1980s, which then decreased to about 14 kg ha$^{-1}$ yr$^{-1}$ during 1990 to 2010. Output stream water chloride fluxes estimated by Kopáček et al.

(2014) peaked at about 50 kg ha$^{-1}$ yr$^{-1}$, less than our average riverine fluxes (Table 1) and substantially below our maximum flux of 117 kg ha$^{-1}$ yr$^{-1}$ in 2002 for the Embarras watershed. Kopáček et al. (2014) discussed that chloride retention occurred during the time period where fertilizer inputs of chloride were increasing, followed by release when fertilizer inputs decreased greatly. Similar to Svensson et al. (2012), they speculated that chloride was immobilized in soils by formation of organic chlorine and adsorption. However, the lag could have been due to the time required to reach the maximum chloride concentration in the shallow groundwater, as we speculate occurred in our study.

Both Kelly et al. (2008) and Kopáček et al. (2014) found lags in chloride release as a result of subsurface storage, the former in a forested watershed receiving road salt inputs and the latter in a more agricultural watershed where fertilizer was the source of chloride. During the period of our monitoring data (from 1993 through 2014) we did not see any long-term evidence of storage (inputs were less than outputs). However, there did appear to be storage or lag during the period of increasing potash use during the 1960s and 1970s, as discussed previously. A limitation of our study, however, is that we do not have annual road salt inputs throughout our study period, and we do not know how they have changed through time.

## Implications of Rapid Chloride Response to Input Changes

Recent papers evaluating changes in nitrate flux for the Mississippi River basin have suggested that a response to management changes in corn and soybean might have considerable lags and take decades for a response to be observed (Sprague et al., 2011; Sprague and Gronberg, 2012; Tesoriero et al., 2013). Our chloride analysis suggests that for the tile-drained Corn Belt, where the largest fluxes of nitrate have been observed (USEPA, 2008; David et al., 2010), the response would be relatively rapid. This is consistent with other work on nitrate in the Embarras River watershed, where the previous year's management was shown to affect nitrate export (David et al., 1997; Gentry et al., 2014), and for the entire Mississippi River basin, where the drought of 2012 in the upper Midwest had an immediate effect on the next year's nitrate concentration (Pellerin et al., 2014). In addition, McIsaac et al. (2001) found that net N inputs affected riverine nitrate fluxes for the Mississippi River basin, with a lag of as much as 9 yr but most of the response in Years 2 through 5. Smith et al. (2013) showed that for the same fields where our biofuel chloride concentrations were measured, tile nitrate concentrations responded on the same time scale. Jaynes (2015) found a rapid response to a large input of fertilizer N to a tiled field (concentrations increased greatly in the first spring after the previous fall application) and continued to affect concentrations for at least 4 yr.

Likely, a part of the response in both chloride and nitrate riverine fluxes is due to recent (within 1 yr) management and weather with rapid transport from the root zone, with a long-term change as a result of the response of the shallow ground water pool (Benettin et al., 2013). Based on our chloride results, this pool likely responds on a multiyear period ranging from 2–6 yr, similar to the 2.7 to 3.6 yr mean travel time reported by Benettin et al. (2013) for a small tile drained watershed in the Netherlands.

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