



# Comparing Urban and Agricultural Nutrient Mass Flux into the Lower Great Lakes

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## 1. Introduction

High concentrations of nitrate and phosphate in water bodies cause harmful algal blooms, which can be toxic to human and aquatic life. When these algae die and decompose, dissolved oxygen is depleted, and the resulting hypoxic zones affect survival of fish and other organisms. **In this study, an agriculture-dominated watershed was compared to an urban-dominated watershed to determine which has a greater contribution of nutrients to the Lower Great Lakes.**

The specific objectives were to:

- Observe the effect of discharge on nitrate and phosphate concentration;
- Use major anions to infer the nutrient source;
- Compare mass fluxes for the summer between the watersheds;
- Observe changes in nitrate, phosphate, and dissolved oxygen concentrations throughout the course of a diurnal cycle during baseflow.

## 2. Field Sites

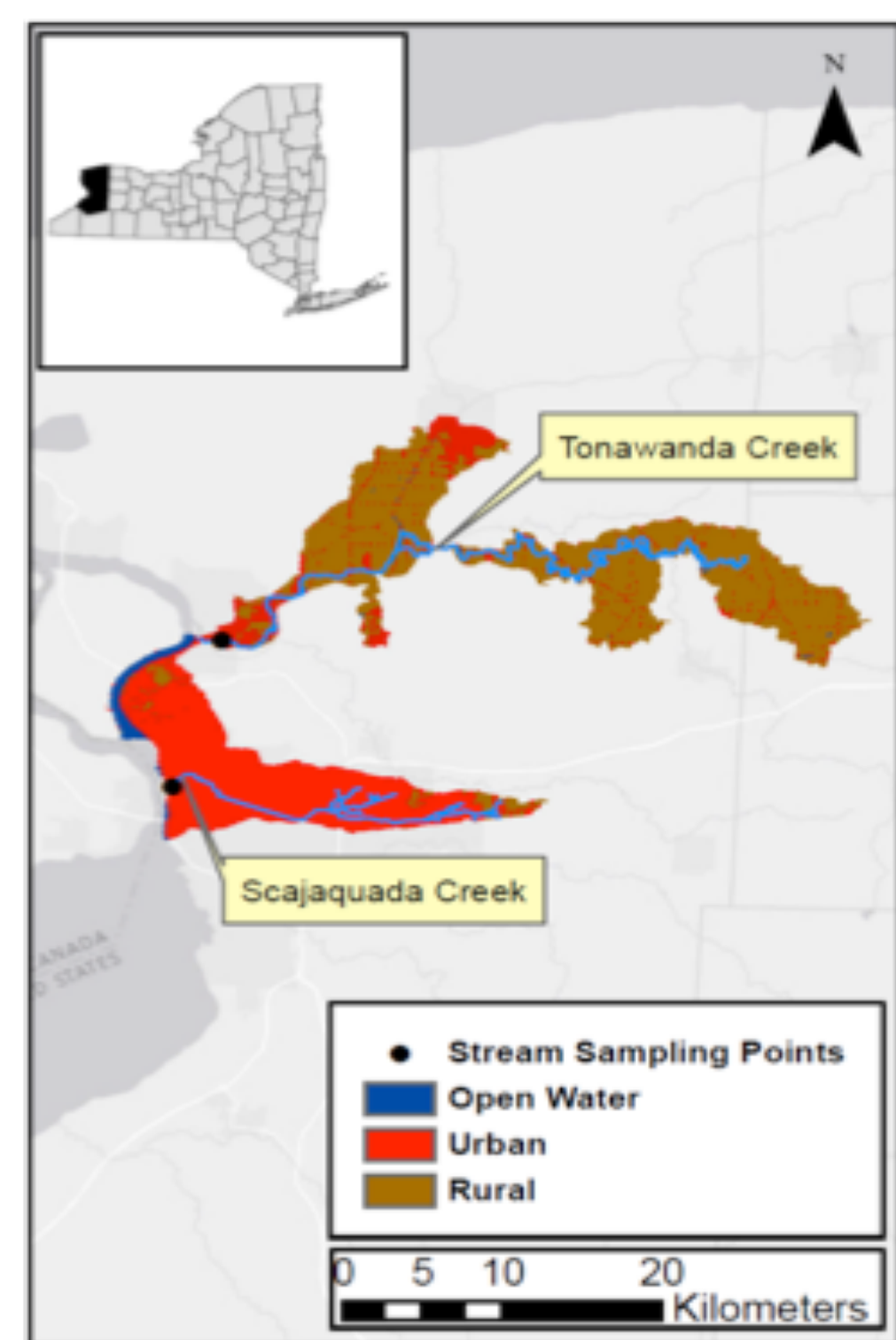


Figure 1: A map showing the two creeks sampled and their watersheds

Nitrate and phosphate can be found in wastewater and in fertilizers used in both urban and agricultural areas. The Tonawanda Creek (Figure 2a) watershed is mostly rural land, and the Scajaquada Creek (Figure 2b) watershed is mostly urban.



Figure 2a: Tonawanda Creek has an agricultural dominated watershed. Samples were collected at the USGS gaging site at Rapids.



Figure 2b: Scajaquada Creek has an urban dominated watershed. Samples were collected where the creek flows out of an underground tunnel.

## 3. Methods

### Field Methods:

- Followed USGS sampling guidelines for stream water quality (Shelton, 1994)
- Used appropriate sampling equipment based on stream velocity (Figure 3a)
- Samples were collected and split uniformly (Figure 3b)
- Samples filtered at 0.45  $\mu\text{m}$  (Figure 3b)
- YSI probe used to collect in situ pH, temperature, specific conductivity, and dissolved oxygen
- Rating curves developed by collaborators (figure 3d) were used to determine discharge at Scajaquada Creek. Discharge data for Tonawanda Creek was taken from the USGS (USGS, 2015)

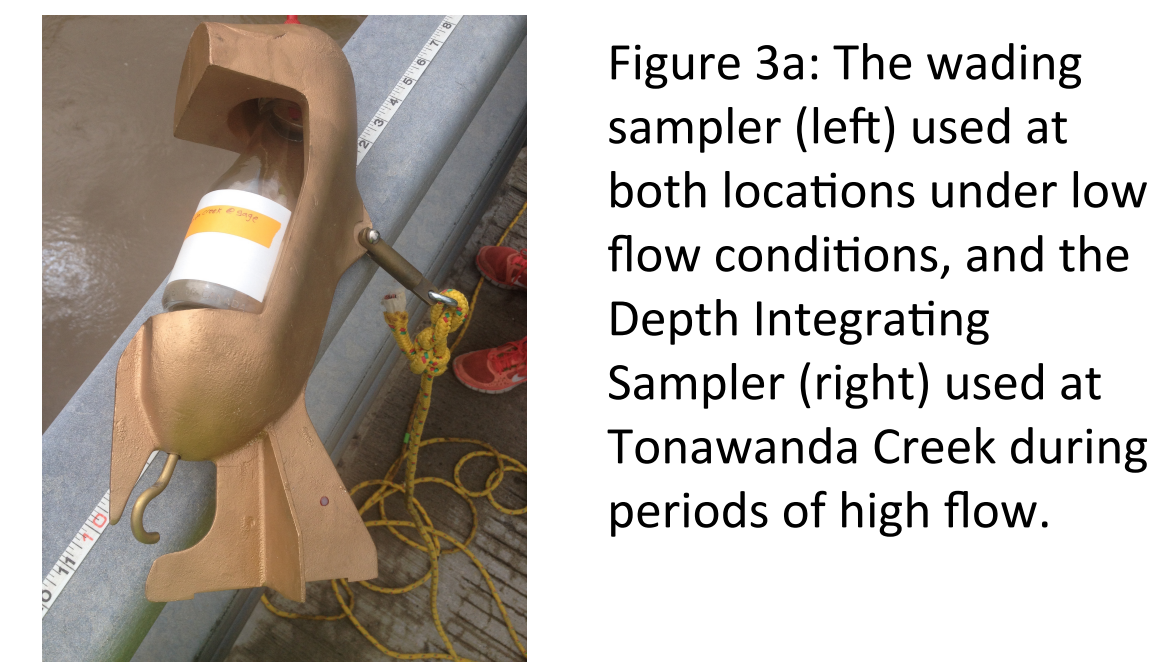


Figure 3a: The wading sampler (left) used at both locations under low flow conditions, and the Depth Integrating Sampler (right) used at Tonawanda Creek during periods of high flow.



Figure 3c: Sampling from the bridge at Tonawanda Creek using the Depth Integrating Sampler



Figure 3b: The sample splitter (left) split the samples uniformly. These samples were then filtered in the field to remove sediment from the water.



### Lab Methods:

1. Determined nitrate and major anions (chloride and sulfate) using ion chromatography (Dionex 1000)
2. Total phosphate determined colorimetrically (Genesys 10S) following persulfate digestion according to established procedures (EPA, 1978; APHA et al., 2010)
3. Bicarbonate concentration determined by alkalinity titration using a Hach titrimer.

## 4. Results

### Stream Chemistry and Hydrology

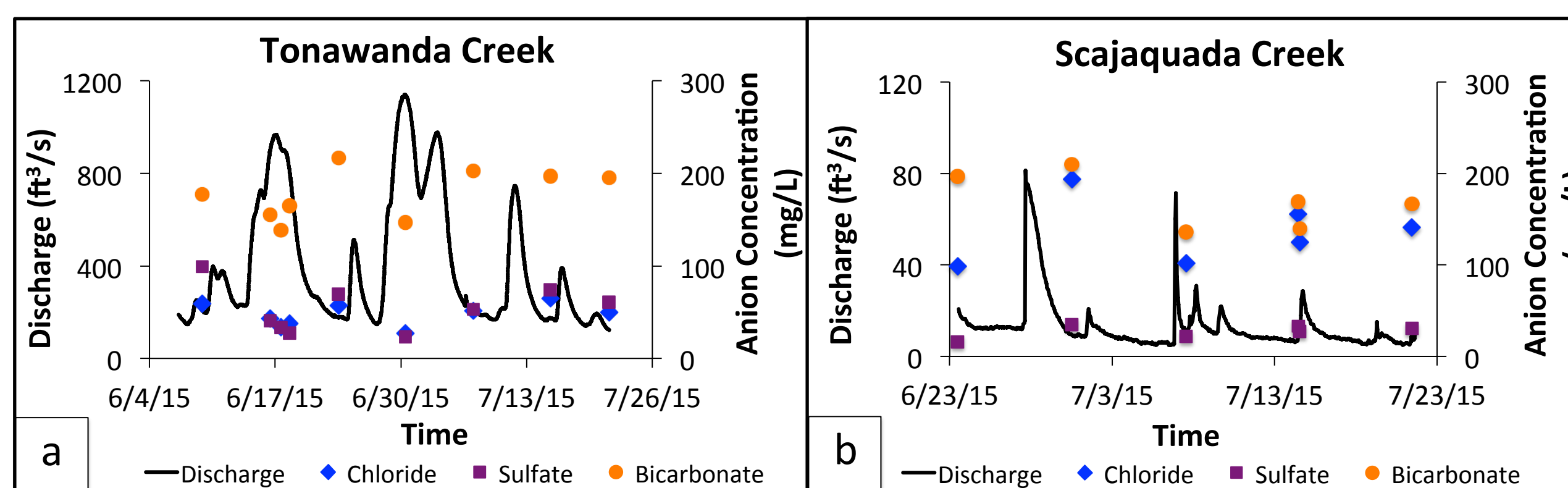


Figure 4.1: Major anions plotted on the flow hydrograph for (a) Tonawanda (b) Scajaquada Creeks. Tonawanda Creek had a slow response to storm events, while Scajaquada Creek had a fast response. When flow is high at Tonawanda Creek, major anion concentrations are low due to dilution. There was no relationship between flow and major anion concentration at Scajaquada Creek.

### Nitrate and TP Loading

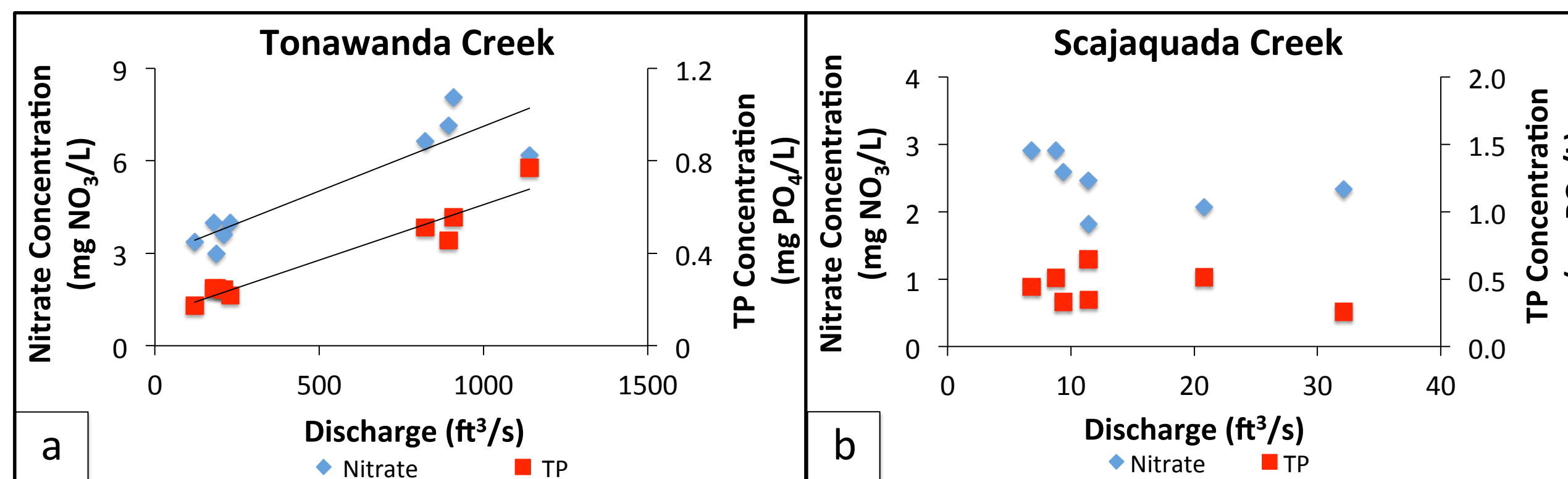


Figure 4.3: Nitrate and TP concentration vs. discharge for the duration of sampling at (a) Tonawanda Creek and (b) Scajaquada Creek. TP values are lower than nitrate values at both locations. At Tonawanda Creek there is a positive correlation between nutrient concentration and discharge. This suggests that the water being added during storm events has both nutrients. No correlation exists at Scajaquada Creek. Nitrate and TP concentrations are relatively high compared to recent research done in different locations.

### Changes over a Diurnal Cycle

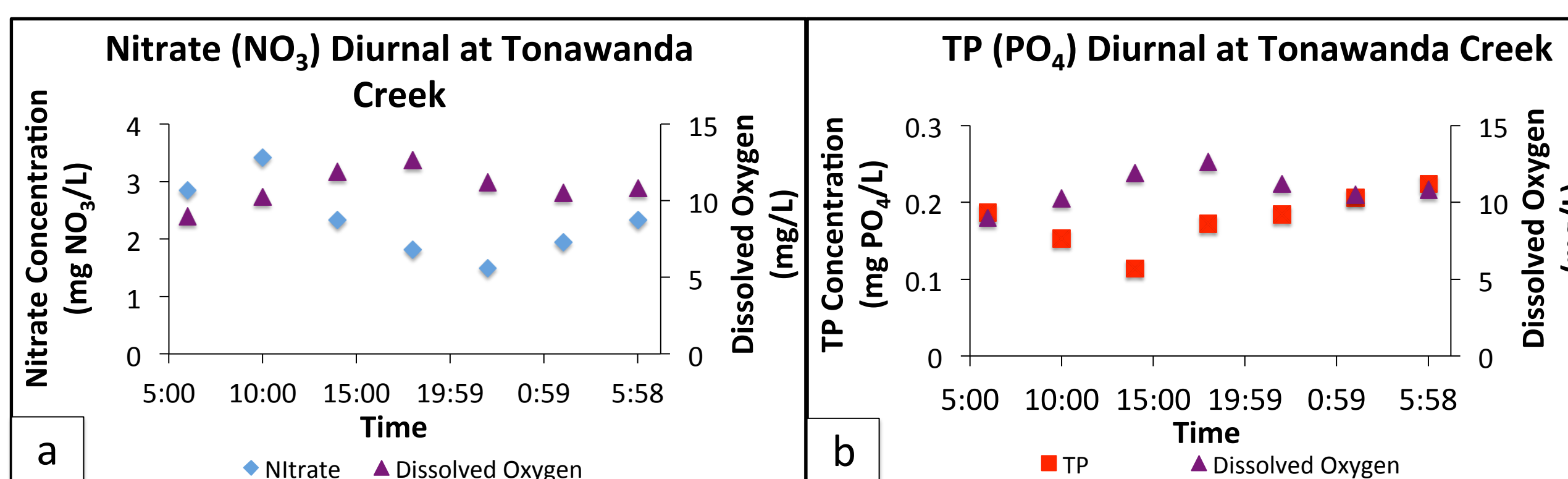


Figure 4.5: Diurnal data from Tonawanda Creek taken 6:00 AM 7/24/15 – 6:00 AM 7/25/15 under baseflow conditions for (a) nitrate and (b) TP. Nitrate and TP decreased during the day due to plant uptake and DO increased due to photosynthesis. Specific conductance was constant as there was no change in flow. The nitrate, TP, and DO minima are not synchronous.

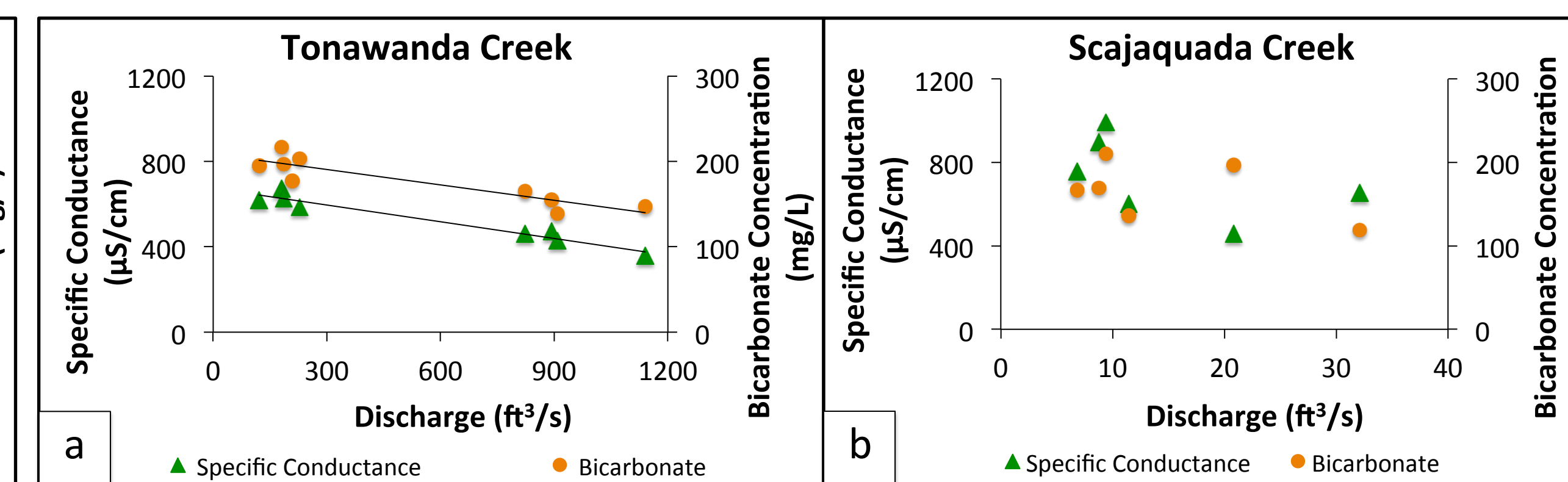


Figure 4.2: Specific conductance and bicarbonate concentration vs. discharge for (a) Tonawanda Creek and (b) Scajaquada Creek for the duration of sampling. Bicarbonate and specific conductance have a similar trend, as bicarbonate is the dominant major anion. At Tonawanda Creek specific conductance and bicarbonate concentration decrease as discharge increases due to dilution. No relationship exists at Scajaquada Creek.

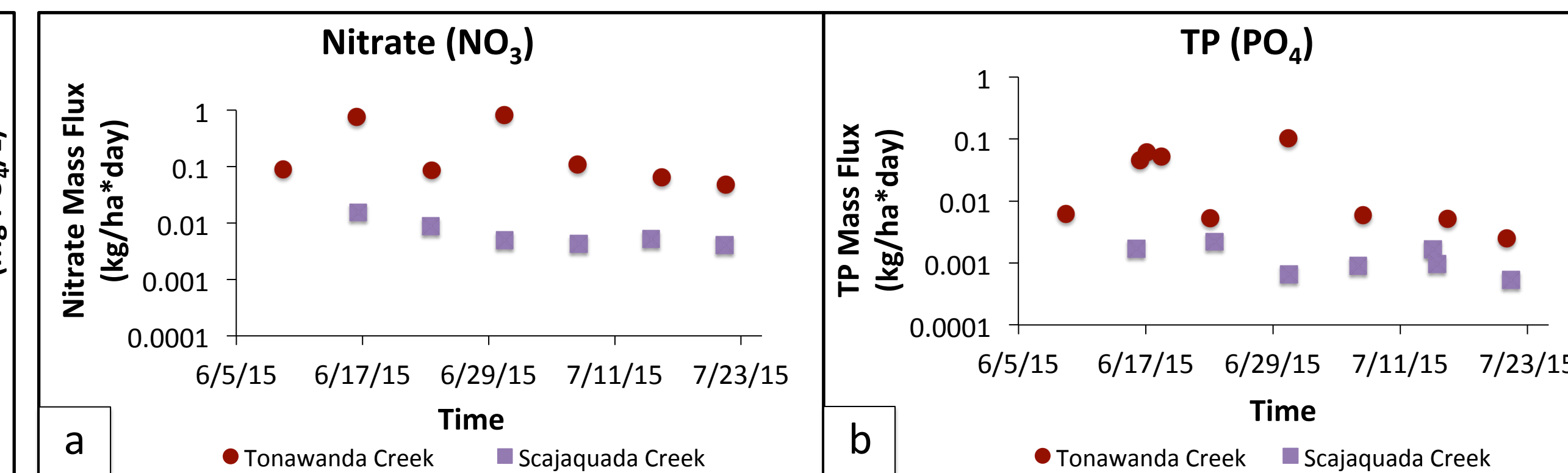


Figure 4.4: Mass flux over the sampling period for (a) Nitrate and (b) TP. Mass flux is consistently higher at Tonawanda Creek (agricultural dominated) than at Scajaquada Creek (urban dominated) for both nutrients by a factor of 10 or more, suggesting agricultural sources contribute more to nutrient concentrations in the Lower Great Lakes.

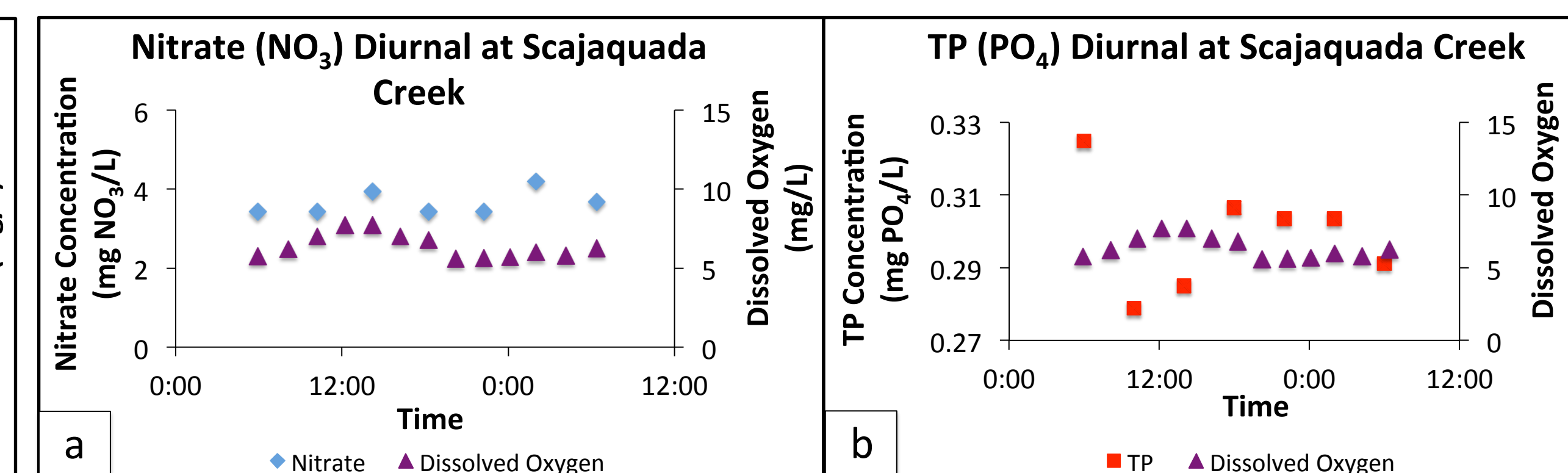


Figure 3.5: Diurnal data from Scajaquada Creek taken 6:00 AM 7/28/15 – 6:00 AM 7/29/15 under baseflow conditions for (a) nitrate and (b) TP. Although DO concentration changed throughout the diurnal period due to photosynthesis, there was no significant change in nitrate or TP, suggesting the existence of unknown processes acting in the creek. Specific conductance was constant as there was no change in flow.

## 5. Conclusions

- The positive correlation between discharge and nutrient concentration in Tonawanda Creek suggests nutrients are derived from fast flow or overland flow.
- The relationship between discharge and specific conductance in Tonawanda creek was supported through major anion analysis, and suggests that the water added during high discharge events dilutes stream water, and is mostly due to overland flow or shallow flow.
- At Scajaquada Creek no correlation between discharge and anion, nitrate, or phosphate concentrations existed. Nitrate and phosphate concentration at Scajaquada Creek was relatively constant, and not dependent on discharge.
- Mass flux was consistently higher for Tonawanda creek than Scajaquada Creek for both nutrients. Although limited to only two stream segments, these results suggest that agricultural streams have a higher nitrate and phosphate contribution to the lower Great Lakes than urban streams.
- Diurnal nitrate and phosphate concentration patterns are consistent with plant uptake at Tonawanda Creek. These processes significantly impact nitrate and phosphate concentrations and mass flux at baseflow.

## Acknowledgements

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