LAND USE, SEASONAL, AND DROUGHT EFFECTS ON PHOSPHORUS FROM OWASCO LAKE TRIBUTARIES

A Thesis

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by

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ABSTRACT

Non-point source pollution (NPS), especially from agricultural runoff, is a leading contributor to water quality impairments in the U.S. Lately, attention to nutrient pollution, specially to phosphorus, has arisen due to disturbing increases in seasonal toxic blue-green algal blooms. To improve our understanding of how land use and seasonal weather patterns impact runoff and nutrient loading in temperate areas, we investigated the effect of different land uses on P inputs into Owasco Lake, in central NY. In addition, the inputs were evaluated in the context of a prolonged drought that affected the northeastern U.S. during 2016. Monitoring of base and high flow conditions was conducted between December 2015 and November 2016 at sites located along twelve tributaries to the lake, representing the dominating land uses in the watershed (i.e.: agriculture and forest). Small watersheds were chosen to be able to isolate impacts of particular land uses. The results show a strong interaction of seasonal and land use effects, with the drought event masking the effect of agricultural and mixed land use on P loads; and with the highest loads registering during the first rain event after the drought, exacerbating the agricultural impact on water quality. These findings are an important contribution from a management perspective, as projections for the Northeast US suggest that, although total precipitation will remain relatively stable, summer rains are likely to become concentrated in fewer events of higher intensities, interspaced with more prolonged dry periods. We consider it absolutely critical to incorporate detailed timing management practices for fertilizer and/or manure application relative to runoff producing storm events, in order to mitigate climate extremes impact on water quality.

BIOGRAPHICAL SKETCH

Maria Sol Lisboa was born in Buenos Aires, Argentina, in 1986. She completed her first 10 years of education in Mendoza, and then moved to Israel where she completed high school. She returned to Mendoza in 2005 and enrolled at the Universidad Nacional de Cuyo to study Natural Resources Engineering. She graduated in 2011 with an honor's thesis investigating the influences of meteorological parameters on landslides' occurrence in the Aconcagua Park, Argentina. After graduation she joined the Anaerobic Digestion Lab at the University of Maryland as a research intern investigating manure co-digestion substrates for biogas production and waste water treatment. Upon finalizing the internship, she moved to Buenos Aires and worked in an environmental consultant firm on various projects related to the oil and energy sector. In 2015, through a Fulbright scholarship co-funded with the Argentinian Government, she joined the Soil and Water Lab at the Biological and Environmental Engineering Department at Cornell University to conduct her graduate studies.

To my parents, Betty and Juan Carlos, who have loved and supported me, always.

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1. INTRODUCTION

Discharge of pollutants into water bodies is a major concern for water quality protection and a challenge for sustainable development. In the US, non-point source pollution (NPS) is considered the leading contributor to water quality impairments (US EPA, 2013). Nutrients applied to agricultural soils, in the form of either animal manure or chemical fertilizers, are among the main NPS pollutants of concern for water quality. Eutrophication is also considered one of the most important anthropogenic problems on aquatic ecosystems, causing a negative impact on aquatic ecology and a direct impact on human health through disinfection byproducts linked to cancer and toxins associated with harmful algal blooms (Carpenter et al., 1998; Chislock, 2013) Phosphorus (P) and nitrogen (N) runoff from agricultural land to water bodies is among the main causes of eutrophication and algal blooms in natural waters (Rabalais, 2002; US Geological Survey, 1999) Although excess of both P and N can contribute to freshwater eutrophication, literature shows that in temperate freshwater ecosystems, like the northeastern US (NE US), P is usually the major limiting nutrient for primary productivity (Carpenter et al., 1998; Schindler, 1977; Schindler et al., 2016) Excess phosphorus loading was significantly reduced in the 1970's with the limits on detergent P content, however attention to nutrient pollution has again arisen due to a disturbing increase in seasonal blue-green algal blooms. Repeated occurrences of toxic algal blooms have impacted water bodies throughout the NE US, raising concerns for recreational safety and drinking water (Halfman et al., 2016; NYS DEC, 2018).

In agricultural areas of the NE US, P is often introduced to cropped fields through manure applications as a simultaneous mechanism for fertilization and waste disposal (Carpenter et al., 1998; Klausner et al., 1998; Kleinman et al., 2015). This practice induces soil nutrient imbalances leading to nutrient losses. Excess P is primarily transported from the landscape to streams via storm runoff. Verheyen et al., (2015) demonstrated that, in agricultural areas, surface runoff is the main factor driving dissolved P export from the landscape to the streams. However other land uses can also contribute to surface water pollution. For example, dissolved N from septic systems and sediment erosion from steep slopes and new construction are also contributors (McPhillips et al., 2017). Watershed scale management has been widely applied over the past several decades as a holistic approach to deal with water quality issues emerging from the impact of different land uses, and especially in agricultural areas (Hawkins and Geering, 1989; Makarewicz, 2009). Research by Grant and Langpap (2018) has documented the success of efforts by more than 1000 U.S. watershed organizations in improving water quality in the past 15 years.

However, in addition to the impact on water quality from anthropic activities in the watershed, the frequency and intensity of hydrometeorological events will also influence the P excess delivery pattern from the landscape to the water bodies. Nutrient pollution via storm runoff from watersheds is not just driven by land use but is also strongly dependent on patterns of precipitation as these interact with soil properties, vegetative cover, and topography (Dahlke et al., 2012; Dunne and Black, 1970; Horton, 1930, 1941). These findings gain relevance given global climate change predictions for an increase in the frequency of hydrological extremes. There has already been a 74% increase in high intensity rainfall events throughout the NE US over the past several decades (Horton et al., 2014). These intense downpours are leading to increased overland flow, erosion, and associated downstream pollution. Warming air temperatures and shifting seasonal precipitation will likely lead to changes in seasonal snow water equivalent, soil moisture, and evapotranspiration, all leading to modified surface runoff regimes. The timing and amount of stream flows is anticipated to shift to (1) more high flow events in winter, (2) earlier peak flows in spring and (3) extended low flow periods in summer (Frumhoff et al., 2007). In particular, the occurrence of summer droughts is projected to become more frequent, from one every three years to one every year under the highest emission scenario (Hayhoe et al., 2007; Horton et al., 2014). However, how such changes would interact to affect water pollution is less well understood.

Our overall goal was to improve our understanding of how land use and seasonal weather patterns interact to control runoff and nutrient loading into Owasco Lake (OWL) located in central NY. Owasco Lake is part of the Finger Lakes watershed located in Western and Central NY that supports agriculture and industrial activities, and the lake constitutes the main drinking water source for its surrounding community. In the past several years the lake has also been subject to a series of toxic algal blooms, posing a threat for human health and aquatic ecology (Halfman et al., 2016).

In this context, our specific objectives were to:

(1) quantify and compare overall patterns of water quality among twelve different tributaries of Owasco Lake which differ in their dominant types of land use;

(2) determine to what extent seasonal / weather conditions interact with land use to influence nutrient loading into Owasco Lake;

(3) evaluate the impact of an extreme drought event, which took place in the Finger Lakes in 2016, on stream water chemistry and nutrient loading to Owasco Lake.

2. METHODS

2.1 Study Area

Our study was conducted in the Owasco Lake watershed, located in Central NY. The lake is of glacial origin and is part of the Seneca-Oneida-Oswego River Basin, which drains into the Ontario Lake (Schaffner and Oglesby, 1978). The region is characterized by a temperate climate with a mean annual temperature of 8.8°C and a mean annual precipitation of 1209 mm (NOAA, 2017). The Owasco Lake watershed extends over approximately 530 km^2 and its bedrock geology is composed of limestone, sandstone, and shale (Oglesby, 1973). The main tributaries to the lake include the Owasco Inlet, which accounts for 60% of the land area draining to the lake, Dutch Hollow Brook, Venness Brook, and Sucker Brook. Each of these tributaries has several small tributaries, in addition to approximately fifty small and intermittent tributaries that flow directly into the lake (Figure 1). The land is used mainly for agricultural purposes: 21.6% of the watershed area is cultivated with crops and 26.4% with hay and pasture for livestock production. This agricultural production occurs on approximately 200 farms of varying size from 8 to 800 hectares (Wright and Haight, 2011). Of the remaining area, 34% is forested, while the rest is distributed among other uses, 5% of which is classified as developed (Multi-Resolution Land Characteristics (MRLC) Consortium, 2011). The population as of the 2010 census indicated that approximately 16,000 people live in the watershed, predominantly in the towns of Moravia, Groton, Owasco, and spread throughout several small rural aggregates. The lake's shoreline is mainly used for recreational activities and is characterized by seasonal housing. The towns of Groton and Moravia have a developed sewage system, with a waste water treatment plant (WWTP) that uses a tertiary phase treatment for P removal. The rest of the watershed utilizes septic systems (Cayuga County, 2015).

2.2 Sampling design

Twelve small tributaries to the lake were selected for sampling and captured the diverse land uses present in the watershed; small watersheds were chosen in order to isolate impacts of particular land uses. Each catchment represented one of three predominant land uses: agriculture, forest, and mixed land use. We selected three forest-dominated sub-catchments, representing baseline water quality of the natural ecosystem, and nine sub-catchments with different proportions of agriculture. The agricultural watersheds were grouped into two categories: (1) mixed areas (between 40 to 60 percent agriculture), and high intensity agricultural areas (more than 80 percent of agricultural use). The sub-watersheds classified as mix use usually include residential areas with associated septic systems. Sub-watersheds areas ranged between 0.2 to 13.2 km^2 (Figure 1).

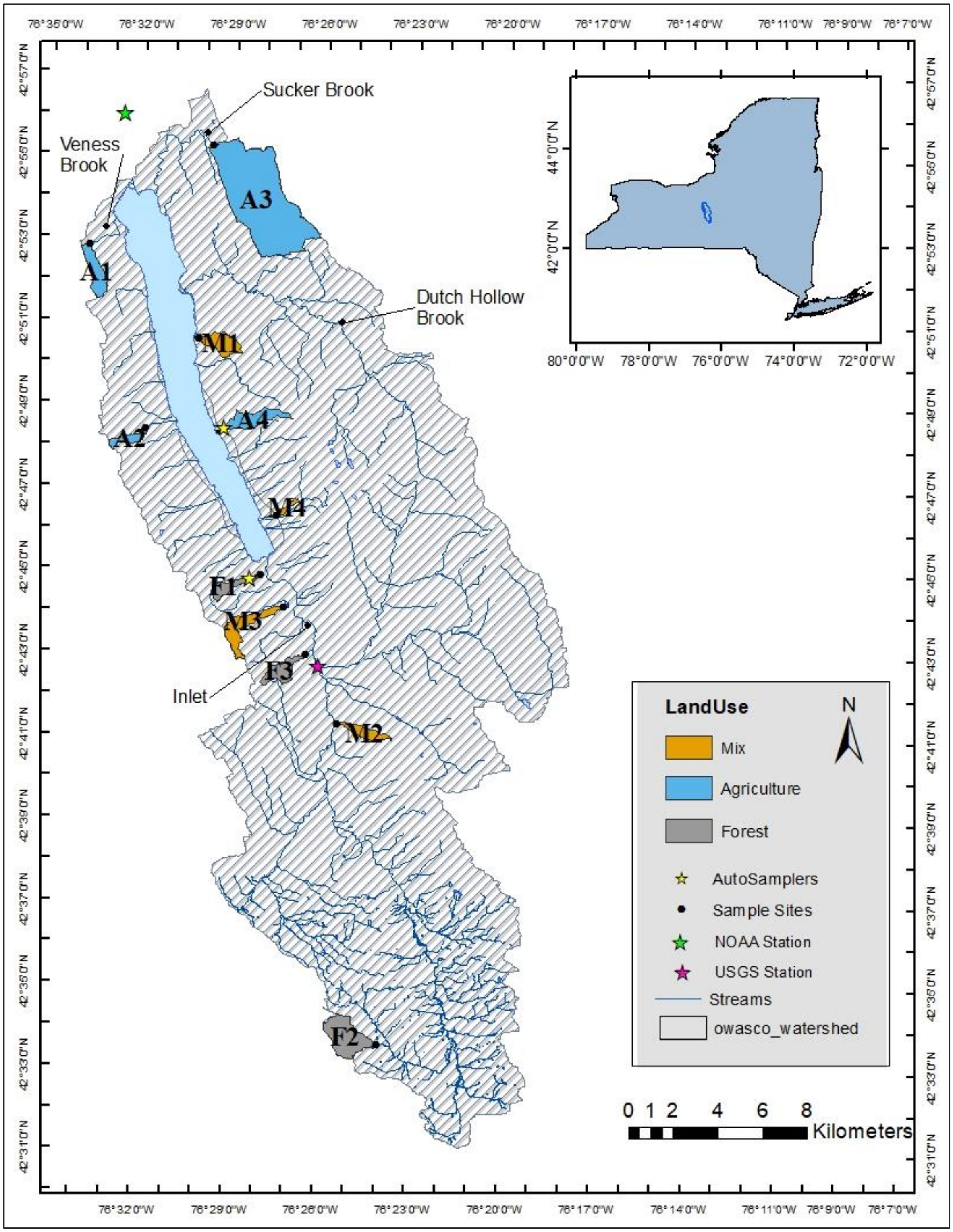

Figure 1. Map of Owasco Lake watershed, NY, showing locations for sampling sites and its respective sub-watersheds and its predominant land uses.

2.3 Water sampling and analysis

Grab samples from each tributary were collected for Total Phosphorus (TP), Soluble Reactive Phosphorus (SRP) and Total Suspended Sediments (TSS) analysis from December 2015 to November 2016, at monthly intervals during the winter and biweekly throughout the rest of the year. Samples were also analyzed for nitrate, but these data will not be reported here (see Appendix 2 for data summaries), but it will be part of a subsequent paper in preparation. Water samples were collected in 1L acid-washed polypropylene bottles, stored at 4°C in a cooler, and transported to the Soil and Water Lab at Cornell University located in Ithaca, New York. Once in the lab, each 1L sample was divided into three parts for the various analyses. Approximately 50 ml were immediately filtered through a 0.45 µm filter (Supor Membrane Disc Filter, 25-mm diameter) and stored for SRP analysis. Additional unfiltered ~550ml subsamples were stored separately for TP and TSS analysis. All the samples were stored at 4°C. To halt potential microbial cycling of nutrients, we decreased the pH to 2 by adding several drops of 30% H_2SO_4 as necessary before storage. Nutrient analyses were run within 4 weeks after collection and TSS was analyzed within 7 days of collection.

Phosphorus analysis was done on an automated wet chemistry analyzer (FS3000; Xylem Analytics O.I. Analytical, Beverly, Massachusetts) screening for phosphate anions (PO3−4) in SRP and TP samples. TP samples were first digested with persulfate and sulfuric acid (US EPA, 1978); and filtered through a 0.45 um filter (Supor Membrane Disc Filter, 25-mm diameter). Reagents for analysis were ammonium molybdate, ascorbic acid, sulfuric acid, and potassium antimonyl tartate (US EPA, 1978). Each run was calibrated using 0.005, 0.05, 0.5, 5, and 10 ppm potassium phosphate standards, with all R^2 values of the standard curves between 0.9998 and 0.9999. Water samples for TSS analysis were filtered using a 0.47 um filter (Supor Membrane Disc Filter, 25-mm diameter) and TSS concentration was determined by calculating the mass difference of the filter before and after oven drying at 60°C for 24hs, divided by the water volume filtered (US EPA, 1983).

When the stream stage allowed access, discharge was calculated using measured velocity and cross- sectional area of the stream (Turnipseed and Sauer, 2010). Water velocity was measured with a portable flow meter (Marsh McBirney, Flo-Mate™ - Model 2000) at several points along the stream transect. As much as possible, the measurements were taken at the same stream section during each sampling event. When water level was too low to use a velocity meter (water depth below 3 cm), a small neutrally buoyant object was used to estimate velocity. Alternatively, if a culvert was nearby, the time required to fill a container of known volume was used to determine discharge. In addition to the chemical analyses, during each sampling event, we measured four environmental variables including pH (AR50; Fisher Scientific Accumet 166 Research, Waltham, Massachusetts), conductivity (Fisher, AR50), dissolved oxygen (YSI 550A; Yellow Springs Instruments, Yellow 167 Springs, Ohio) and temperature (YSI 550A).

In addition to regular grab water samples, several storm events were sampled between April and November. Additionally, two ISCO™ auto-samplers were deployed to capture representative, complete storm events during summer and fall, one in a forested sub-catchment (Site F1) and one in an agricultural area (Site A4) (Figure 1). A water level actuator was used to trigger the auto-sampler every time the stream level increased by a significant amount. Auto-samplers were programmed to collect 250 ml samples every 15-min for 12 hours. The auto-sampler bottles were pre-acidified with 0.5 ml concentrated sulfuric acid to guarantee the sample preservation and were collected within 48 hours of the storm. Since the monitored streams are ungauged, the continuous flow measurements at the nearest USGS station (Owasco Inlet station #4235299) (Figure 1) were used to estimate the discharge at sites F1 and A4 throughout the sampled storms events, by correcting the measurements by sub-watershed area. The samples collected were analyzed individually for sediments and phosphorus concentrations, and then averaged to obtain a daily concentration and load value, which was then incorporated in the final database for analysis.

2.4 Data and Statistical Analysis

The data analysis was structured in two phases. In the first phase, we used a descriptive analysis in order to characterize the hydrology and water quality of the tributaries. To characterize water quality at the tributaries, we computed annual summary statistics for the six water quality parameters measured. Some of these results will be presented and discuss here, but for a complete data summary and a detailed comparison to the appropriate water quality guideline/criteria set by EPA, please see Appendix 1. Due to the ungauged nature of the tributaries, we used data from USGS station at the Owasco Lake Inlet (#4235299) and from the NOAA station at Auburn (#00300321) to plot discharge hydrograph and annual precipitation for the whole watershed for the period 2015-2016. In addition, 2016 annual flow and precipitation statistics were used in a comparison with historical values for the last 30 years period.

In the second phase, we used a two-way Analysis of Variance (ANOVA) with the Tukey Honest Significant Difference (HSD) pairwise comparison to assess the effect of land uses and seasons on conductivity, P, and TSS. Additionally, ANOVA results were used to predict the best concentrations and load estimates for each land use and season combination. As P and TSS concentrations were directly correlated with stream flows, we applied the ANOVA for concentration estimates and calculated loads using the resulting concentration estimates as shown in the equation below.

$$\text{Concentration} = \mu \pm 2 * SE$$

$$Load = \mu\beta \pm 2 * \text{SE}$$

μ: mean concentration estimate

SE: standard error of the concentration estimate

β: Stream flow normalized by area averaged per land use type and season

In order to account for having multiple time measurements from each site, water quality parameters were averaged for each sampling season and site before statistical analyses. Whenever the distribution of water quality measurements was non-normal, a square root transformation was applied before the analysis. Results were considered significant when p-values < 0.05. All statistical analyses were conducted in R (version 3.2.5; R Project for Statistical Computing).

3. RESULTS

3. 1 Hydrology of the Owasco Lake watershed

Hydrology at the Owasco Lake watershed is dominated by snow precipitation during the winter and intense rainfall during spring and fall. Snowmelt process typically begins during early March increasing the runoff during spring months, which later decreases to base-flow conditions by early June. Base-flows then remain constant for the summer and, by the end of the fall (October and November), larger storm runoff typically dominates again (Figure 2). Based on historical data from USGS over the last 16 years (1999-2016), the highest mean monthly discharge usually occurs between March and April and the lowest mean monthly discharge has been observed, between July and September. However, 2016 was an unusually dry year, with a mean annual discharge (3.33 m^3/s) well below the annual mean (4.34 m^3/s) over the last 56 years (1960-2016). The 2016 annual runoff (28.2 mm) was notably lower than the annual mean of the last 56-year period (37.1 mm) (US Geological Survey, 2017, 2016). Mean precipitation for 2016 (1124 mm) was also somewhat lower than the annual mean of the last 20 years (1209 mm), and the precipitation during the growing season was significantly lower in comparison to the historical mean (NOAA, 2017; Sweet et al., 2017) The US Drought Monitor classifies droughts into 5 categories ranging from abnormally dry conditions (D0) to exceptional drought (D5). During 2016, 95% or more of Cayuga County's total area was classified in at least one of the five droughts categories from June 7th to December 12th, with 100% of the area experiencing severe and/or extreme drought conditions (D3-D4) between August 9th and October 24th (NDMC, University of Nebraska, USDA, 2017).

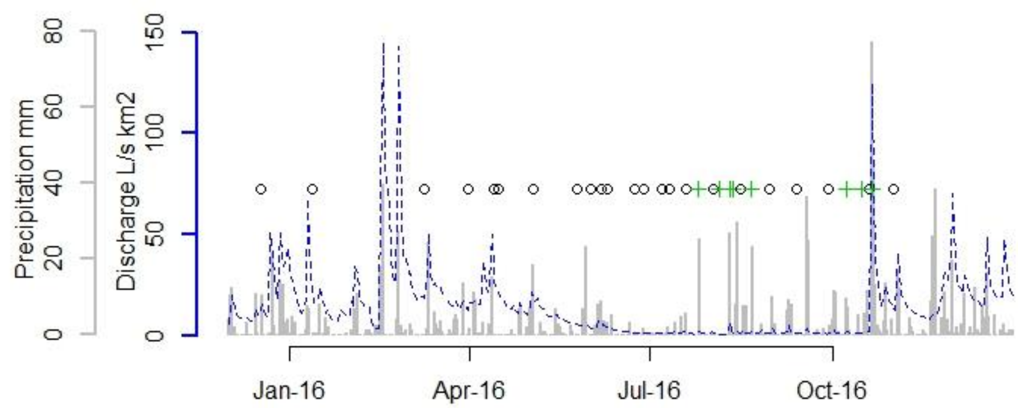

Figure 2. Daily precipitation (NOAA Auburn station GHCNG:USC:00300321) and discharge (USGS station at Owasco Inlet below Aurora street at Moravia NY, #4235299) for 2016 at the Owasco Lake watershed. The points indicate dates when grab samples were collected, and the crosses when auto-samplers were enabled.

When we analyzed the 2016 flow measurements for the 12 small tributaries monitored in this study, the unusual 2016 drought conditions become more evident. Following the typical annual hydrograph, in 2016, the tributaries’ discharge peaks occurred during the spring months, April and May, and then decreased to baseflow conditions by the beginning of June. In all the sites, the period extending from June to October was characterized by extreme low flows with intermittent and in some cases extended periods of no-flow. Of the twelve tributaries monitored in this study, only two sites (M5 and F2) ran continuously between June and October, while the remaining ten sites experienced one or several periods of no flow. Such drought periods varied in length for each site, from a minimum of 1 week and up to 22 weeks. At the end of October (October 20th to 24th), the area experienced the largest rain event of the year (Figure 2), which restored flow in all the streams. During this event, streams located in sites dominated by agricultural and mix uses exhibited a second peak in their annual hydrograph, while streams located in forested areas did not show a significant second peak in their hydrographs, even when flow conditions were restored (Figure 3). Interestingly, the peak flow resulting from the mixed land use was greater than that of agriculture with forested being lowest.

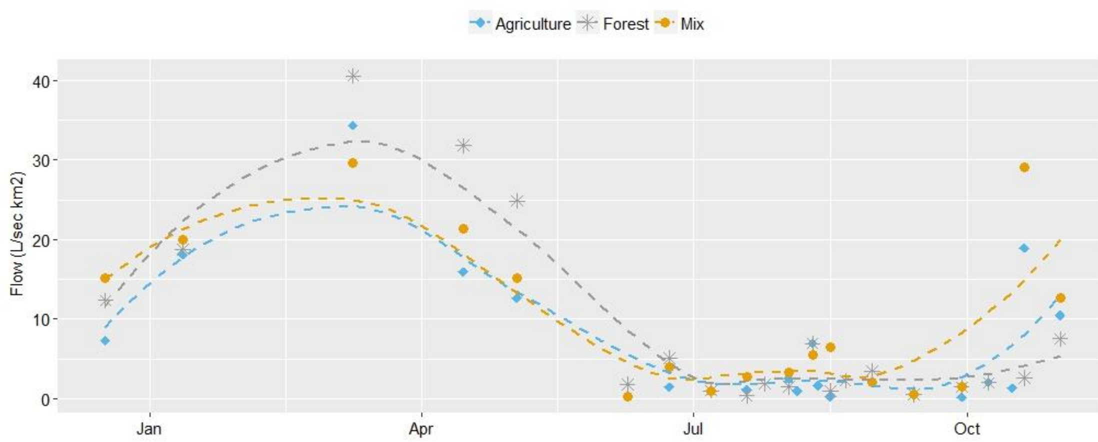

Figure 3. Discharge measurements per sampled date for the interval period December 2015 to November 2016, at the 12 sampling sites averaged by land use type. The points indicate the mean averaged discharge by land use type. The line represents the smooth moving average between the measured discharge

Table 1. Annual mean, minimum (above zero) and maximum measured flow (L/s km^2) for each sampling site, and number of weeks of total drought between June 7th to December 12th).

Land use		**Forest**			**Mix**					**Agriculture**			
Site		**F1**	**F2**	**F3**	**M1**	**M2**	**M3**	**M4**	**M5**	**A1**	**A2**	**A3**	**A4**
Flow L/s km^2	**Mean**	12.52	6.34	11.09	17.83	17.13	33.62	13.96	16.17	15.49	21.91	5.57	6.96
	Min	0.72	0.26	0.10	0.97	1.28	16.02	0.24	0.52	0.00	0.96	0.00	0.15
	Max	60.67	31.41	37.64	50.53	53.53	60.67	57.88	161.44	60.27	86.99	17.88	24.16
# of weeks with no flow		13	0	17	21	21	22	12	0	21	14	19	8
% of weeks with no flow		50.0	0.0	65.4	80.8	80.8	84.6	46.2	0.0	80.8	53.8	73.1	30.8

3.2 Water quality summary for the Owasco Lake tributaries

Analytical results of surface water samples indicated that stream waters were slightly alkaline with annual mean pH values ranging between 7.91 to 8.14. The lowest and highest individual values were observed at site F3, during fall (7.38) and spring (8.56), respectively (Figure 4, Table 4). Mean annual Dissolved Oxygen (DO) ranged between 8.06 to 11.93 mg/L, while individual values ranged between 5.20 to 14.40 mg/L (Figure 4, Table 4). The lowest values were observed during the summer at sites A2, A4, F2, F3 and A5 (ranging between 5.2 and 6.0 mg/l); while the highest values were observed in F1, M1 and M2 (between 14.0to 14.4 mg/l) during the winter (Figure 4). Annual mean conductivity ranged between 129.6 and 483.5 µS/cm, while individual values ranged from 106 to 659 µS/cm (Table 4). The highest individual values were observed at sites A1, A2 and A4 (659, 644 and 644 µS/cm respectively) during the October 20th storm event, while the lowest were measured at sites M3 and M4 during the winter (106 and 107 µS/cm respectively). Annual mean TP concentrations for the tributaries ranged between 0.04 mg/L and 0.20 mg/L. The highest individual values were observed during the October 20th rain event, at sites A3 and A2 (0.86 and 0.43 mg/L, respectively), while the lowest non-zero individual values were observed during the summer at sites F2 and M5 (0.014 and 0.015 mg/L, respectively). The mean SRP concentrations ranged between 0.02 and 0.09 mg/L. Similar to TP concentrations, highest SRP individual values were observed during the October storm event at sites A3 and A4 (0.38 and 0.19 mg/L, respectively), while the lowest individual values were observed during the summer at sites A2 and A1 (0.001 and 0.002 mg/L, respectively). Annual TSS mean ranged between 6.4 and 97.5 mg/L, with the highest individual values at site A2 during the October storm event (301.8 mg/L) and at site F1 during the summer (203 mg/L); The lowest non-zero individual values were observed during the summer at sites A1, M1 and F3 (0.2, 0.4, and 0.4 mg/L, respectively) (Figure 4, Table 4).

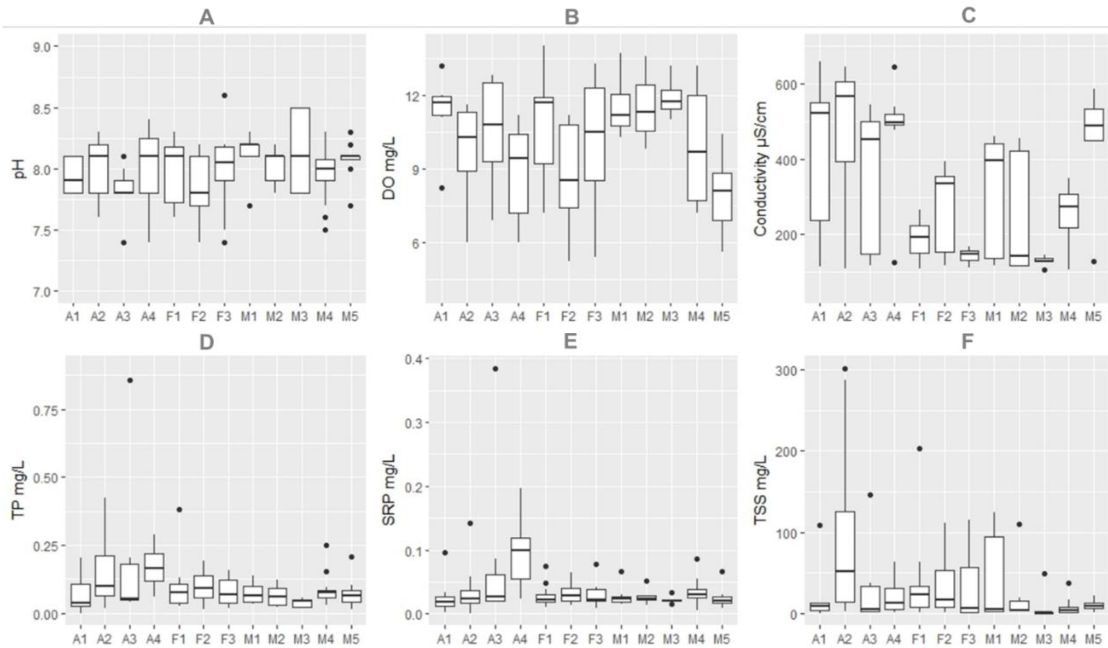

Figure 4. boxplots per site for water quality parameters. A: pH, B: Dissolved oxygen mg/L, C: Conductivity µS/cm, D: TP mg/L, E: SRP mg/L, F: TSS mg/L. Sites A1 to A4 correspond to agricultural areas, M1 to M5 mix areas and F1 to F3 to forested areas

3. 3 Land use and seasonal effect at the OWL tributaries

3.3.1 Conductivity

Conductivity is a measure of dissolved solids concentrations, and the two way ANOVA indicated significant differences between land uses interacting with seasons (F(6, 31) = 2.57, p=0.038) (Table 2). Post hoc comparisons showed significantly higher conductivity values for agricultural areas compared to mixed and forested sites during spring, while during summer and fall, the agricultural areas were significantly higher than the forested areas, but not different from mix areas (Figure 5A).

Forested watersheds consistently had the lowest conductivities, with seasonal means ranging between 133 to 246 µS/cm; mixed and agricultural areas had seasonal means ranging between 123 to 393 and 133 to 537µS/cm, respectively (Table 4). Seasonally, conductivity remained low during winter (~130 µS/cm) and increased over the year for all land uses, however these seasonal changes were significant only for agricultural areas from winter to spring (p<0.01).

3.3.2 Phosphorus (TP and SRP)

There was significant temporal and spatial variability of P concentrations, with seasonal patterns differing among the three land uses. The two way ANOVA indicated a strong effect of land uses interacting with seasons for both TP (F(6, 31) = 3.89, p=0.005) and SRP (F(6, 31)=3.05, p=0.018) (Table 2). For both, post-hoc comparisons demonstrated significantly higher concentrations at agricultural sites during the fall (p < 0.001), while there were no significant differences between land uses during winter, spring and summer (Figure 5B&D). In agricultural and mixed areas, the highest predicted TP concentrations were observed during the fall (means of 0.23 mg/L and 0.08 mg/L, respectively), while in forested areas the maximum concentrations were observed during the summer (0.14 mg/L) (Table 3, Figure 5B).

TP Loads follow a similar pattern with agricultural and mixed areas peaking during the fall (2.70 and 1.17 mg/s km^2, respectively), while forest maximum values were during winter and spring (1.07 and 0.86 mg/s km^2, respectively). For all the three land uses, the lowest loads were observed during the summer (0.32, 0.26, and 0.31 mg/s km^2 for forested, mix, and agricultural areas, respectively) (Table 3, Figure 5C). SRP follows a similar pattern to TP, where, for agricultural and mix areas, concentrations and loads peak during the fall (0.12 mg/L and 1.36 mg/s km^2; 0.035 mg/L and 0.49 mg/s km^2, respectively), while for forested areas the concentrations peak during the fall (0.039 mg/L) and the loads peak during winter and spring (0.58 and 0.53 mg/s km^2, respectively). The lowest loads for all land uses were observed during the summer (Table 3, Figure 5 D&E).

3.3.3. Total Suspend Sediments

TSS concentrations were highly variable and there were no clear seasonal patterns among land uses. ANOVA results showed no significant effect from land use and/or season on TSS concentrations (F (6, 31) = 1.54, p=0.19) (Table 2). Agricultural areas had their highest concentrations and loads during the fall (52.3mg/L and 609 mg/s km^2, respectively). For mixed areas, concentrations also peaked during the fall (18.6 mg/L), while the maximum loads were observed during the spring (336 mg/s km^2). Forested areas presented an unexpected pattern; the concentrations peaked during summer (61.37 mg/L) and loads during winter (185 mg/s km^2) (Table 3, Figure 5 F&G).

Table 2. ANOVA results for conductivity, phosphorus (TP, SRP) and sediments (TSS) concentrations against land use, season and land use - season interaction. Bold letters represent statistical significance (<0.05)

Independent variable	Response variable											
	Conductivity			TP			SRP			TSS		
	Sum squares	F-value	p-value	Sum squares	F-value	p-value	Sum squares	F-value	p-value	Sum squares	F-value	p-value
Land use	288.61	20.12	***2.51E-06***	0.059	7.38	***0.0023***	0.2554	5.927	***0.00661***	16.316	1.2009	0.31453
Season	375.41	17.45	***8.06E-07***	0.211	17.6	***7.47E-07***	0.0706	10.928	***5.64E-05***	52.417	2.5721	0.07
Land use*Season	110.88	2.577	***0.0383***	0.093	3.89	***0.0052***	0.0394	3.052	***0.0182***	62.874	1.5426	0.19737

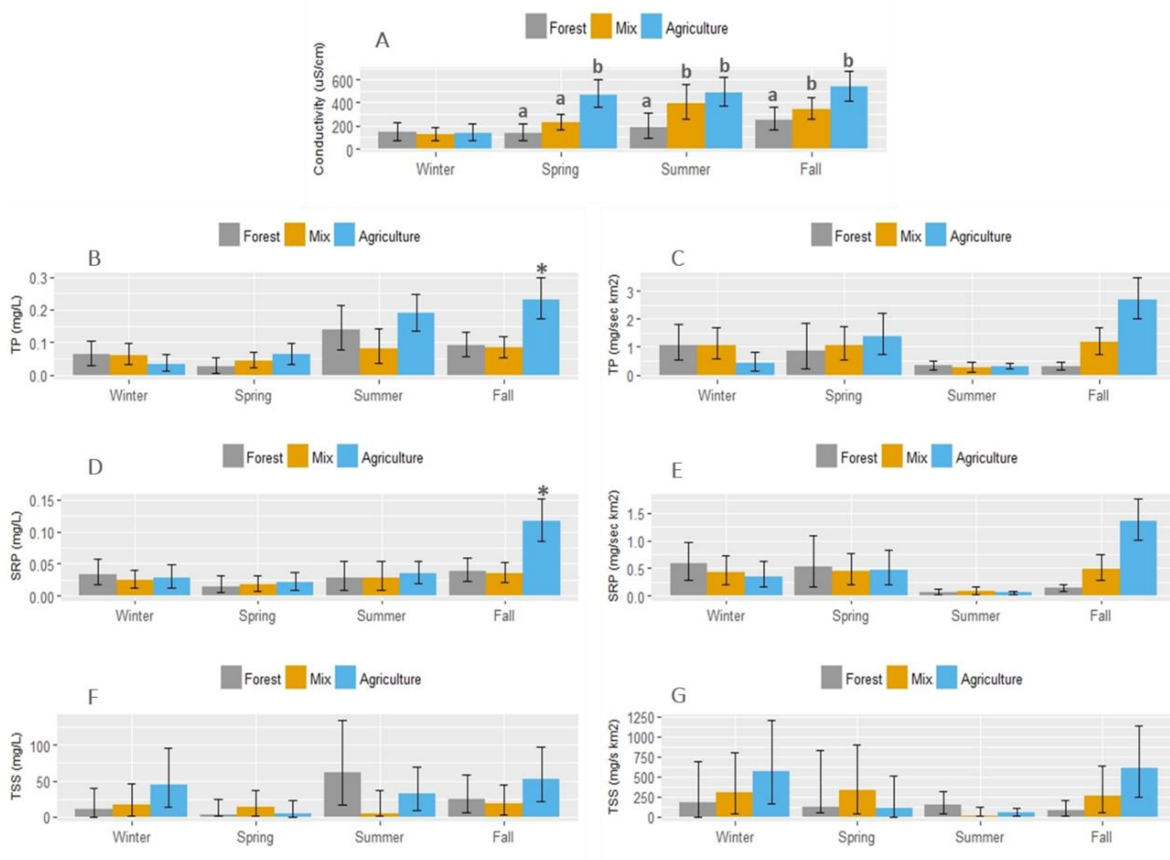

Figure 5. Predicted conductivity, P and TSS concentrations (left) and loads (right) per land use and season. Bars represent estimated means and arrows represent 95% confidence interval for the means. Different letters and asterisk indicate significant differences between land uses, within seasons ($p<0.05$). A: Conductivity µS/cm, B: TP mg/L, C: TP mg/s km^2, D: SRP mg/L, E: SRP mg/s km^2, F: TSS mg/L, G: TSS mg/s km^2

Table 3. Predicted estimates and 95% confidence intervals (lower limit, upper limit) for Conductivity, TP, SRP and TSS concentrations and loads.

Land use	Season	Conductivity µS/cm		Concentration mg/L						Loads mg/ s km^2					
				TP		SRP		TSS		TP		SRP		TSS	
		Estimate	95% CI	Estimate	95% CI	Estimate	95% CI	Estimate	95% CI	Estimate	95% CI	Estimate	95% CI	Estimate	95% CI
Forest	**Winter**	141	76.3, 226	0.062	0.031, 0.105	0.034	0.017, 0.057	10.8	0.05, 40.3	1.07	0.52, 1.80	0.582	0.29, 0.98	185	0.779, 693
Mix	**Winter**	123	70.0, 191	0.061	0.033, 0.097	0.024	0.012, 0.041	17.1	2.17, 46.1	1.06	0.58, 1.69	0.425	0.21, 0.72	299	38.1, 808
Agricul-ture	**Winter**	133	70.0, 215	0.032	0.011, 0.065	0.028	0.013, 0.049	44.9	13.2, 95.5	0.41	0.14, 0.82	0.355	0.16, 0.63	569	167, 1209
Forest	**Spring**	132	70.0, 215	0.025	0.007, 0.054	0.015	0.005, 0.032	3.42	1.49, 24.2	0.86	0.24, 1.87	0.530	0.17, 1.10	118	51.5, 836
Mix	**Spring**	234	165, 302	0.043	0.023, 0.070	0.018	0.008, 0.031	13.7	1.74, 36.9	1.06	0.55, 1.73	0.445	0.21, 0.77	336	42.8, 907
Agricul-ture	**Spring**	471	360, 597	0.062	0.034, 0.098	0.021	0.010, 0.037	4.64	0.25, 23.2	1.39	0.76, 2.20	0.473	0.21, 0.83	204	5.67, 519
Forest	**Summer**	189	98.0, 311	0.137	0.078, 0.213	0.028	0.010, 0.055	61.4	16.6, 134	0.32	0.18, 0.50	0.067	0.02, 0.13	145	39.3, 318
Mix	**Summer**	393	255, 562	0.081	0.037, 0.141	0.028	0.010, 0.054	5.15	2.22, 36.3	0.26	0.12, 0.46	0.090	0.03, 0.18	16.7	7.23, 118
Agricul-ture	**Summer**	490	376, 618	0.188	0.136, 0.248	0.035	0.019, 0.054	31.6	8.78, 68.5	0.31	0.22, 0.41	0.057	0.03, 0.09	52.2	14.5, 223
Forest	**Fall**	245	167, 359	0.089	0.055, 0.132	0.039	0.023, 0.060	25.0	5.50, 58.7	0.32	0.20, 0.47	0.139	0.08, 0.21	89.3	19.6, 209
Mix	**Fall**	347	262, 444	0.083	0.053, 0.119	0.035	0.021, 0.053	18.6	3.74, 44.7	1.17	0.75, 1.69	0.494	0.30, 0.74	263	52.9, 633
Agricul-ture	**Fall**	537	418, 671	0.231	0.173, 0.297	0.116	0.086, 0.151	52.3	20.9, 97.7	2.70	2.02, 3.47	1.355	1.01, 1.76	609	244, 1139

4. DISCUSSION

Results of this research provided valuable insights into the processes driving chemical loading into Owasco Lake. This study found that agricultural land uses were an overall greater P contributor, both in concentration and loads, relative to forests. There were noteworthy differences in seasonal contributions, with forested areas presenting higher P loads in winter, possibly due to leaf litter entering streams. TSS followed expected patterns for agricultural watersheds with highs in spring and fall when farm fields are uncovered and exposed to erosion. However, the most interesting findings, were behaviors associated with the occurrence of the 2016 summer drought followed by a large rainstorm in October. This event provided a unique opportunity to evaluate how predicted climate change would affect patterns of nutrient loading from watersheds in coming decades. The first rain event post-drought resulted in significant transfer of P and sediment from the landscape to the tributaries. The highest peak flows were associated with mixed land use, possibly due to contributions from greater impervious surface area. However, the greatest P concentrations and loads came from agricultural land use, while the lowest flows and P inputs were from forested landscapes. These finding have important implications for managing lake water quality in order to reduce drivers of eutrophication in the context of climate change. We find that it is absolutely critical to implement certain management practices such as cover crops, riparian buffers and cattle fencing along streams and roadside ditches, as well as paying special attention to timing of fertilizer and/or manure application relative to runoff producing storm events, in order to mitigate climate extremes impact on water quality.

Land uses among the different catchments around OWL play key roles in how much they contribute to nutrient loading. ANOVA results showed a strong interaction effect of land use and season for TP and SRP. Post hoc comparisons showed that, during the fall season, TP and SRP concentrations in agricultural areas were significantly higher than those of forested and mixed land uses. A close examination of the time series for TP and SRP concentrations (Figure 6 B&C) seem to indicate that the fall effect was driven by the storm event occurred on October 20th, when TP and SRP concentrations almost tripled in magnitude compared with previous seasons. Overall, our results suggest that in 2016 the prolonged drought followed by an intense rain event was the process driving seasonal P dynamics in the OWL tributaries, masking the land use effect during spring and summer on stream P concentrations and loads. This prolonged drought, dated between June and October 2016 (NDMC, University of Nebraska, USDA, 2017; Sweet et al., 2017), provoked extremely low flow levels in the Owasco Lake tributaries, until a rain event in October 20th restored regular flow levels (Figure 1). Overall, P concentrations and loads for agricultural subwatershed were higher than the reported for Dutch Hollow Brook sub-watershed in 2016 (Halfman et al., 2016), highlighting the importance of small tributaries as nutrient contributors to OWL. However, it is worth noticing that the major differences were observed for the fall season, which might be explained by the fact that our results include high and base flow sampling while Halfman et al., (2016) only includes baseflow. On a regional scale, spring and fall seasonal loads were relatively similar to the estimated by Makarewicz et al., (2015), for Genesee River. Likewise, Prestigiacomo et al., (2016), reports SRP concentrations for Fall Creek ranging between 0 and 0.045 mg/L for April-October interval of 2013, while in our study agricultural sub-watersheds spring and summer mean SRP concentration were 0.021 and 0.35 mg/L, respectively.

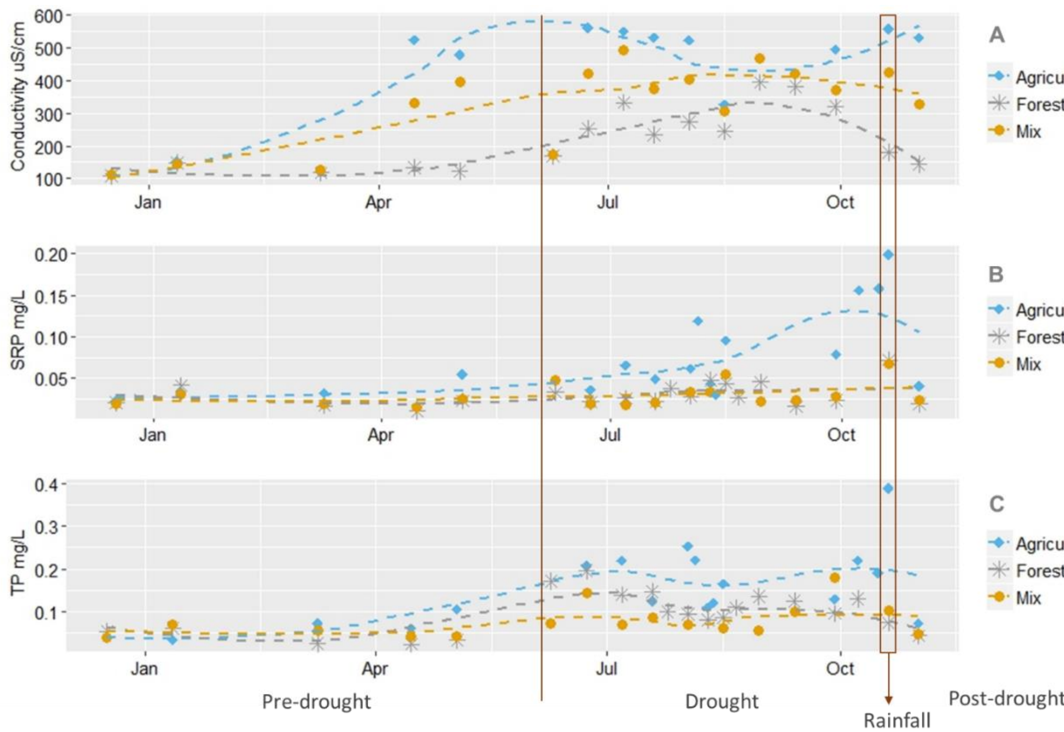

Figure 6. 2016 conductivity (A) and phosphorus concentrations (B&C) per sampled date averaged by land use type. The points indicate the mean averaged per sampled date by land use type. The line represents the smooth moving average between the values.

For the rest of the water quality parameters, land uses also play an important role. For conductivity, ANOVA results also showed a strong interaction effect of land use and seasons. Post-hoc comparisons showed that conductivity was significantly higher in agricultural areas during spring, summer and fall (p value <0.01). In a different manner, when we analyze conductivity time series, the drought does not seem to play a key role (Figure 6A). The differences observed among land uses is likely driven by manure application during the whole growing season in agricultural areas, which is correlated with higher conductivity values (Ju et al., 2007; Roberts and Clanton, 2000). Conversely, ANOVA results for TSS show no effect of seasons and/or land uses, yielding similar TSS concentrations and loads in agricultural and forested areas along the year. It is not clear why agricultural and forested areas had similar TSS levels, but previous research in the region has shown that steep land correlates to agricultural abandonment (Flinn et al., 2005). Steep watersheds will result in high-kinetic energy streams which foster higher erosion rates than low-topography watersheds. In our study, agricultural sub-catchments slopes ranged in between 0 to 20 degrees, while forested areas slopes ranged between 10 to 60 degrees.

The combined drought and post-drought effect on nutrient export patterns from different land uses have been captured in several other studies. Mosley et al. (2015), observed that as runoff decreased during dry periods, the catchment influence on stream water also decreased, suggesting that the processes dominating stream water quality differs between low and high flow scenarios, as the relative importance of water sources varies according to hydroclimatic conditions. Elsdon et al., (2009) reported no differences in nutrients parameters between urban and rural estuaries in South Australia during drought conditions, showing that, as the proportion of sampled water coming from runoff decreased, the influence of land use in nutrient parameters decreased as well.

In addition, there are several studies evaluating the effect of drought events on different water quality parameters with a focus on water conductivity and main ions' concentrations (e.g., chloride, sodium, and sulfate), as an approximate measure of total dissolved ions (Burt et al., 2015; Caruso, 2002, 2001; Foster and Walling, 1978; Hellwig et al., 2017; Mosley et al., 2012; Muchmore and Dziegielewski, 2007; Nosrati, 2011; van Vliet and Zwolsman, 2008). Such studies have shown a deterioration of water quality during drought events as solute concentrations increase and suggest that the concentration effect is a result of low flows and evaporation, as opposed to the dilution effect that will usually prevail during high flows. Our results agreed with these studies, as we also observed increased conductivity during summer and fall (drought period).

Nutrient dynamics seem to be less consistent in their response to drought and highly related to the nutrient source involved. Some authors reported a decrease in stream nutrient concentration in drought to pre-drought comparisons, mainly as a result of reduced runoff during dry periods in areas dominated by non-point sources (Baurès et al., 2013; Boar et al., 1995; Caruso, 2002, 2001; Golladay and Battle, 2002; Morecroft et al., 2000; Mosley et al., 2012; Oelsner et al., 2007). On the other hand, several studies, in areas where point sources of pollution are the most important, have reported an increase in nutrient concentrations during drought periods (Andersen et al., 2004; Boar et al., 1995; Caruso, 2002, 2001; Davies, 1978; Macintosh et al., 2011; Oborne et al., 1980; Sprague, 2005; van Vliet and Zwolsman, 2008). Moreover, studies in areas where the relative importance of water sources (surface vs. groundwater) change seasonally or which may have changed over time due to fluctuations in hydrometeorological conditions, showed no significant changes in nutrient concentrations between drought periods and reference years (García-Prieto et al., 2012; Hellwig et al., 2017; Wilbers et al., 2009). Several authors have emphasized the role of biological activity on nutrient concentrations during drought events. As temperature increases, biological uptake increases, which contributes to lower nutrient concentrations during droughts (Caruso, 2001; Hellwig et al., 2017). Our results for these parameters were ambiguous, with TP and SRP showing a slight increase in concentration from agricultural lands during the drought but sustained low concentrations for the other two land uses (Figure 6), which emphasizes the importance of the land use-season interaction.

The effect of rain events occurring immediately post-drought rain deserves special attention. In particular, high intensity or magnitude rain events are already increasing in frequency throughout the NE US and elsewhere (Horton et al., 2014). Studies of a prolonged drought in SW England between May 1975 and August 1976 (Burt et al., 2015; Foster and Walling, 1978; Worrall and Burt, 2008), concluded that solutes and/or nitrate concentrations increased dramatically during the first rain event after the drought. Burt et al., (2015) analyzed conductivity, major cations, and pH during the first few storms after a drought period for one small catchment. Their results showed a significant concentration increase during the first rain event after the drought, with conductivity peaking drastically, and total dissolved solids concentrations doubling when compared to pre-storm levels. The second rain event also showed a concentration increase, but much more subdued than the first one, while stream response to the third storm, returning to a more typical dilution effect process, suggested that the supply of readily available soluble loads had been exhausted during the first two events. Our results showed a similar concentration increase for P following the first storm event after a prolonged drought period for small sub-catchments. Foster and Walling, (1978) studied the effect of the first post-drought rain event in conductivity and nitrate concentrations, suggesting that the source of high solute levels was the solution of soluble residues that accumulated and concentrated in the soil during the drought period as a result of evaporation of soil moisture and capillary rise. In addition, Worrall and Burt, (2008) suggested that drought events might change the delivery pattern of water quality constituents, retaining them in catchments during dry conditions and releasing during wet conditions.

We therefore suggest that the first rain event of fall 2016 had a large influence on stream water quality, by mobilizing accumulated pools of TP and, to a lesser degree, SRP. We hypothesize that the lack of storm runoff for weeks to months allowed P to accumulate in the watershed. The first storm event after the drought, which also coincided with the most intense precipitation event of the year (Figure 1), resulted in a flushing effect that drastically increased the concentration of P in the streams. Contrary to the effect of the drought, which masked the effect of land uses on nutrient export, the first rain event after the drought exacerbated the differences among land uses, with significantly larger concentrations and loads observed in agricultural areas. There are several biogeochemical processes that could be involved in nutrients and dissolved solids release to streams after dry periods, but the details of the mechanics are not well understood, particularly for P. However, in our study, this first post-drought rain event occurred in late October, after fields had been harvested and before any cover crops could become established. As such, the agricultural landscape was most vulnerable to runoff processes. Our results, together with previous studies on the effect of the first rainfall after a drought on water quality (Burt et al., 2015; Foster and Walling, 1978; Worrall and Burt, 2008) provide evidence towards recognizing the first few storm events after a drought period as hot moments (Mcclain et al., 2003) for nutrient export in areas where NPSs dominate over point sources. We speculate that the large storm in October saturated parts of the landscape and then continuous rain connected many of these saturated areas to the stream, generating a network of saturation excess flow paths (e.g., Dunne and Black, 1970), which provided conduits for P to be transported from the landscape to the stream.

These findings contribute to our management approach for lake water quality in the context of rapid climate change, as projections for the NE US suggest that, although total precipitation will remain relatively stable, summer rains are likely to become concentrated in fewer events of higher intensities, interspaced with more prolonged dry periods (Hayhoe et al., 2007; Horton et al., 2014). Landscapes covered with forests and other vegetation clearly provide greater protection during large storm events, by reducing both peak flows in the streams and P transport. On the other hand, agricultural landscapes are most vulnerable to climate extremes. Hence, it will be critical to include management practices that help reduce environmental impacts. Greater implementation of BMPs such as cover crops, riparian buffers and cattle fencing along streams and roadside ditches, and water and sediments control basins will all help to reduce P and sediment transport, as it has already been demonstrated in other watersheds in the region (Herendeen and Glazier, 2009; Makarewicz et al., 2009; Zollweg and Makarewicz, 2009), and at farm scale in the OWL watershed (Georgakakos et al., 2018). More specifically, managing the timing of fertilizer and/or manure application relative to runoff producing storm events, is already a critical component of many nutrient management programs (e.g, USDA-4R) (King et al., 2018). Our results showed the importance of the first rain event after a dry period for P export, hence fertilizer application timing will be a critical management practice under the current climate projections for the NE US. Following a dry growing season, it would be prudent to stall manure application until past the first rains, as a way to decrease P export to water bodies.

The main findings of this paper help to better understand the interaction between land uses and hydroclimatic conditions in the context of climate extremes, and its impact on nutrient runoff. Still, many pieces and interactions of the complex P dynamic need to be revealed in order to understand the fate of P loads, and its role in aquatic ecosystems. Our results showed the highest P load from agricultural areas to the lake at the end of October. However, toxic algal blooms in general occur during late summer, when lake water temperature reach ideal values for cyanobacteria to grow, among other conditions i.e: wind, species interactions, etc. In particular, during 2016, Owasco Lake experienced a highly toxic algal bloom during the first days of September (dry period), resulting in high concentrations of toxins in the lake water, and to a lesser extent into the drinking water supply (NYS DEC, 2018). This event highlights the complexity of the system, and the necessity for further studies and better understanding of the mechanisms underlying nutrient dynamic and fate, and its resulting ecological impact.

5. CONCLUSIONS

We expected spring and summer P concentrations and loads to be higher compared to other seasons, due to the intensity of recreational and agricultural activities during the growing season. However, the highest P load in 2016 occurred during the fall, presumably due to a prolonged summer drought followed by one large storm event in October. The first storm event after the drought exposed differences in NPS loads among land uses, with highest P concentrations from agriculture. Both the hydroclimatic conditions and anthropic activities seem to be controlling factors of P dynamics in this situation. Since dry years do not occur on a regular basis in the NE US, the observations, preliminary conclusions, and inferences drawn from this study could prove useful for management purposes in the context of climate change. One outstanding question is the ecological implications of the unusual P-loading patterns in the receiving lake or reservoir, i.e., does a seasonal shift in P loading to later in the most biologically active period reduce eutrophication risks?

6. APPENDICES

Appendix 1: Water quality parameters comparison to guidelines and statistic summary

All pH values were in the range that the USEPA established for aquatic life in freshwater (6.5 to 9.0). No obvious patterns were observed between land uses and the values were fairly constant over the year (Table 4, Figure 4A). Similarly, dissolved oxygen values were never below the limit of 4mg/L that the USEPA established for aquatic life (Table 4). We did observe a seasonal fluctuation, with dissolved oxygen decreasing as temperature increases. The lowest oxygen concentrations were observed during the summer followed by the fall, spring and winter.

Regarding P and TSS, in New York State regulations use qualitative standards. For example, the current standard for P and N is: “None in amounts that result in the growths of algae, weeds and slimes that will impair the waters for their best usages” (NYS DEC, 2011). Additionally, there is a quantitative guide for TP (0.02 mg/L), which is in place for most lakes and reservoirs. However, there is no quantitative guidance for rivers or other waters flowing into lakes or reservoirs. Since the majority of the streams monitored here are direct tributaries to Owasco Lake, we are going to apply the lake and reservoir guidance as a general evaluation criterion. The mean and median TP concentrations exceeded the guidance criteria in all cases except for sites M2 and M3, both dominated by mix use. Sites A4, A2 and A3 exceed the criterion by a wide margin. Sites A2 and A3 yielded the highest medians, as well as the maximums individual values during storm events, while site A4 yield concentration higher than the guidance criterion in every single sampling event (Table 4). These results suggest that watersheds A2, A3, and A4 may be where NPS mitigation management should be targeted. Note, however, that Prestigiacomo et al., (2016) challenge the use of TP as a critical freshwater quality analyte because it is generally much less biologically available than SRP. Unfortunately, there is no quantitative criteria established for SRP and TSS. Although the correlation between TP and SRP is not very strong, in general, sites exceeding the guidance limit for TP also had the highest SRP concentrations (Table 4). TSS was different; while sites A2 and A3 also yielded the highest TSS values, site A4 had TSS concentrations around median values of the rest of the sites. Interestingly, the forested sites F1, F2, and F3 had the highest mean and median values for TSS (Table 4).

Table 4. pH, Conductivity (µS/cm), DO, TP, SRP and TSS (mg/L), (minimum, maximum, mean, standard deviation and median), for each sampling site, season and land use.

Parameter	LU	Forest								Mix										Agriculture								
	Summary	Per Site			Per Season				Annual	Per Site					Per Season				Annual	Per Site				Per Season				Annual
	Site	F1	F2	F3	Winter	Spring	Summer	Fall		M1	M2	M3	M4	M5	Winter	Spring	Summer	Fall		A1	A2	A3	A4	Winter	Spring	Summer	Fall	
pH	Mean	7.98	7.88	7.99	8.08	8.20	7.93	7.68	7.94	8.11	8.02	8.14	7.95	8.08	8.00	8.16	7.96	8.04	8.04	7.94	8.00	7.81	8.00	7.97	8.09	7.85	7.94	7.95
	SD	0.25	0.29	0.35	0.26	0.21	0.25	0.22	0.29	0.20	0.16	0.35	0.23	0.14	0.30	0.18	0.22	0.12	0.22	0.15	0.27	0.22	0.34	0.21	0.18	0.29	0.32	0.27
	Median	8.10	7.80	8.05	8.15	8.20	8.05	7.70	8.10	8.20	8.10	8.10	8.00	8.10	8.00	8.20	8.00	8.10	8.10	7.90	8.10	7.80	8.10	7.90	8.10	7.80	8.00	8.00
	Min	7.60	7.40	7.40	7.70	7.90	7.40	7.40	7.40	7.70	7.80	7.80	7.50	7.70	7.60	7.80	7.50	7.80	7.50	7.80	7.60	7.40	7.40	7.80	7.80	7.40	7.40	7.40
	Max	8.30	8.20	8.60	8.30	8.60	8.20	8.10	8.60	8.30	8.20	8.50	8.30	8.30	8.50	8.50	8.30	8.20	8.50	8.10	8.30	8.10	8.40	8.30	8.40	8.30	8.30	8.40
Conductivity uS/cm	Mean	189.2	275.9	142.9	138.5	128.4	254.7	226.8	212.1	304.3	250.9	129.6	257.3	466.3	128.9	256.3	392.1	383.3	305.0	420.2	468.4	344.7	483.5	132.7	450.5	509.4	539.6	438.4
	SD	52.6	110.9	18.4	20.4	17.2	90.3	107.4	95.4	164.4	172.0	14.7	73.3	120.4	18.9	148.6	140.3	115.9	156.1	228.0	206.8	197.1	127.1	21.2	172.2	122.5	86.9	184.6
	Median	192.0	335.0	149.0	147.5	123.0	238.0	189.5	157.0	396.0	144.0	130.0	274.0	489.0	130.7	178.5	350.0	447.5	305.0	521.5	567.0	454.0	496.0	130.0	486.5	542.0	537.0	496.0
	Min	108.0	118.0	112.0	108.0	112.0	153.0	132.0	108.0	117.3	116.7	106.0	107.0	130.0	106.0	117.0	174.0	130.0	106.0	116.0	109.0	117.0	125.0	109.0	125.0	137.0	394.0	109.0
	Max	265.0	395.0	168.0	151.0	156.0	395.0	391.0	395.0	460.0	455.0	145.0	350.0	588.0	151.0	448.0	588.0	535.0	588.0	659.0	644.0	544.0	644.0	158.0	644.0	615.0	659.0	659.0
DO mg/L	Mean	10.82	9.30	9.92	13.43	11.95	8.21	10.17	9.99	11.60	11.57	11.93	9.82	8.06	12.88	11.39	7.94	9.58	9.97	11.32	9.64	10.46	8.89	11.95	11.54	8.01	9.59	9.90
	SD	2.30	2.59	2.68	1.34	1.13	1.98	1.66	2.52	1.48	1.91	0.93	2.14	1.65	0.87	0.96	1.80	1.52	2.24	1.68	1.98	2.44	1.97	1.10	0.74	1.99	1.44	2.10
	Median	11.70	8.80	10.50	14.00	12.10	7.80	10.00	10.65	11.20	11.30	11.75	9.70	8.10	13.20	11.40	7.55	9.80	10.30	11.70	10.30	10.80	9.40	11.90	11.50	7.20	9.50	10.40
	Min	7.20	5.20	5.40	11.90	10.50	5.20	8.50	5.20	10.30	9.80	11.00	7.20	5.60	11.90	10.30	5.60	7.00	5.60	8.20	6.00	6.90	6.00	10.80	10.40	6.00	6.90	6.00
	Max	14.00	14.40	13.30	14.40	13.30	11.20	12.30	14.40	13.70	13.60	13.20	13.20	10.40	13.70	13.20	12.10	12.10	13.70	13.20	11.60	12.80	11.20	13.20	12.80	11.90	11.20	13.20
TP mg/L	Mean	0.094	0.100	0.080	0.059	0.026	0.135	0.080	0.092	0.074	0.064	0.039	0.085	0.072	0.055	0.048	0.083	0.092	0.072	0.072	0.152	0.201	0.172	0.036	0.070	0.187	0.231	0.155
	SD	0.090	0.056	0.051	0.021	0.007	0.074	0.042	0.068	0.039	0.040	0.016	0.056	0.051	0.032	0.028	0.057	0.051	0.047	0.073	0.126	0.297	0.067	0.022	0.038	0.056	0.225	0.145
	Median	0.078	0.091	0.069	0.054	0.025	0.113	0.073	0.076	0.066	0.060	0.047	0.075	0.065	0.046	0.041	0.070	0.082	0.061	0.036	0.098	0.052	0.165	0.045	0.068	0.196	0.164	0.129
	Min	0.024	0.014	0.020	0.040	0.014	0.066	0.037	0.014	0.034	0.022	0.022	0.028	0.015	0.022	0.015	0.040	0.041	0.015	0.000	0.020	0.041	0.061	0.000	0.020	0.090	0.036	0.000
	Max	0.382	0.191	0.159	0.090	0.033	0.382	0.155	0.382	0.138	0.121	0.057	0.249	0.206	0.102	0.094	0.249	0.206	0.249	0.203	0.425	0.858	0.288	0.056	0.135	0.288	0.858	0.858
SRP mg/L	Mean	0.028	0.032	0.030	0.035	0.015	0.031	0.038	0.030	0.028	0.027	0.022	0.034	0.024	0.024	0.018	0.029	0.037	0.028	0.028	0.035	0.085	0.099	0.028	0.027	0.059	0.129	0.069

Parameter	LU	Forest								Mix										Agriculture								
	Summary	Per Site			Per Season				Annual	Per Site					Per Season				Annual	Per Site				Per Season				Annual
	Site	F1	F2	F3	Winter	Spring	Summer	Fall		M1	M2	M3	M4	M5	Winter	Spring	Summer	Fall		A1	A2	A3	A4	Winter	Spring	Summer	Fall	
	SD	0.018	0.015	0.020	0.012	0.005	0.010	0.026	0.017	0.018	0.013	0.007	0.019	0.015	0.007	0.006	0.013	0.022	0.016	0.032	0.041	0.134	0.051	0.008	0.022	0.044	0.100	0.073
	Median	0.022	0.029	0.023	0.041	0.016	0.029	0.023	0.025	0.023	0.023	0.021	0.030	0.021	0.023	0.018	0.029	0.027	0.025	0.019	0.023	0.027	0.100	0.026	0.021	0.044	0.119	0.040
	Min	0.010	0.014	0.009	0.021	0.009	0.014	0.016	0.009	0.015	0.014	0.015	0.006	0.008	0.014	0.006	0.008	0.019	0.006	0.002	0.001	0.018	0.024	0.019	0.002	0.001	0.019	0.001
	Max	0.074	0.065	0.078	0.042	0.023	0.048	0.078	0.078	0.066	0.051	0.033	0.086	0.066	0.033	0.027	0.055	0.086	0.086	0.096	0.142	0.384	0.196	0.040	0.058	0.119	0.384	0.384
TSS mg/L	Mean	34.5	33.6	28.7	12.2	3.3	55.0	23.2	32.6	46.1	23.7	10.1	6.4	10.1	19.9	19.9	5.2	22.0	16.3	21.3	97.5	31.9	18.6	47.1	12.8	42.4	53.4	40.6
	SD	51.4	35.0	41.5	11.4	3.0	51.4	26.3	42.2	55.5	42.8	21.6	9.7	6.5	33.7	37.4	3.5	36.1	30.2	38.6	112.7	52.5	17.7	50.4	20.9	75.0	88.2	68.7
	Median	22.3	16.3	5.5	9.1	2.2	39.0	14.3	16.3	5.0	3.9	0.8	3.2	9.3	2.8	3.6	4.0	10.0	4.0	9.2	50.9	5.2	13.0	25.2	4.9	13.2	18.5	13.0
	Min	1.2	1.2	0.4	2.6	0.4	1.2	1.2	0.4	0.4	1.8	0.0	0.0	0.8	0.0	0.2	0.0	0.0	0.0	0.2	2.2	0.6	0.6	5.2	0.8	1.4	0.2	0.2
	Max	203.0	111.2	115.0	28.2	8.8	203.0	79.6	203.0	124.4	110.0	48.8	36.8	21.0	96.8	124.4	10.0	110.0	124.4	108.0	301.8	146.4	63.2	112.8	63.2	287.4	301.8	301.8

Appendix 2: Nitrogen concentrations and loads data summary

Table 5. Nitrate (mg/L) (minimum, maximum, mean, standard deviation and median), for each sampling site, season and land use.

Parameter	Land use	Forest							
	Summary	Per Site			Per Season				Annual
	Site	F1-10	F2-13	F3-14	Winter	Spring	Summer	Fall	
Nitrate	Mean	1.33	0.54	0.54	0.13	0.44	1.32	0.35	0.79
	SD	1.69	0.35	0.95	0.14	0.65	1.44	0.30	1.12
	Median	0.58	0.50	0.19	0.11	0.20	0.77	0.35	0.47
	Min	0.05	0.00	0.00	0.76	0.30	0.09	0.35	0.00
	Max	5.21	1.21	3.11	5.25	5.25	5.25	5.25	5.21

Parameter	Land use	Mix									
	Summary	Per Site					Per Season				Annual
	Site	M1-1	M2-2	M3-3	M4-6	M5-11	Winter	Spring	Summer	Fall	
Nitrate	Mean	1.43	1.74	0.25	1.26	1.44	1.13	1.20	1.28	1.45	1.29
	SD	0.75	0.34	0.09	0.68	0.88	0.72	0.77	0.82	0.81	0.77
	Median	1.51	1.73	0.29	1.04	1.18	1.18	1.43	0.91	1.17	1.17
	Min	0.23	1.43	0.14	0.55	0.51	0.00	0.07	0.27	0.00	0.14
	Max	2.71	2.35	0.34	2.50	2.77	0.87	1.87	5.21	0.28	2.77

Parameter	Land use	Agriculture								
	Summary	Per Site				Per Season				Annual
	Site	A1-4	A2-7	A3-9	A4-12	Winter	Spring	Summer	Fall	
Nitrate	Mean	2.35	3.95	1.35	2.26	2.38	2.62	2.43	2.69	2.54
	SD	1.22	1.68	1.79	0.56	1.82	1.63	1.48	1.51	1.52
	Median	2.47	4.65	1.07	2.23	2.20	2.32	2.29	2.29	2.29
	Min	0.76	0.30	0.09	1.38	0.34	0.23	0.52	0.14	0.09
	Max	4.36	5.25	5.25	3.57	2.77	2.43	2.66	1.78	5.25

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