

Impacts of Changed Stream flow on Selected Water Quality Parameters in the Upper Esopus Creek Watershed of New York, USA

Huicheng Chien¹ & Kieran Pierce²

Abstract

Water is essential to human life and the health of the environment. Physical and chemical properties of water quality vary in response to climate, soils, geology, land use and land cover. In addition, pollutants and nutrients carried by surface runoff could be flushed into stream flow to disturb water quality. The objectives of this research are to sample water quality during and after storm events and examine the impacts of changed stream flow on water quality parameters including water temperature, conductivity, pH, dissolved oxygen, nitrate and total orthophosphate. The study site was located in the Upper Esopus Creek Watershed (Ulster and Greene Counties, NY) which is dominated by forest. The results show there were nonlinear relationships between stream flow and water quality. With increased stream flow, dissolved oxygen and nitrate increased, but pH, temperature, conductivity decreased. Within the forested watershed, surface runoff is not the dominant stream flow generation process, which leads to less nutrient pollution being flushed into streams. The increased stream flow from storm events may have a diluting influence on water quality and shorter residence time of pollution and changed water quality parameters, which mitigates the impacts of water quality disturbance on aquatic ecosystem.

Keywords: stream flow, water quality, forested watershed, surface runoff.

1. Introduction

Clean water is essential for ecosystems and for societies. The importance of water quality has been a top priority for environmental health, especially in aquatic ecosystems. In response to differences of climate, soils, geology, land use and land cover, natural water quality varies spatially and temporally. Pollution from point sources and nonpoint sources due to human activities are other disturbances to water quality (Carpenter et al., 1998). Most point source pollution is from industrial and sewage treatment plants. Nonpoint source pollution occurs when surface runoff, as a proxy for the energy associated with soil erosion and sediment transport, moves over land, picks up natural or human-made pollutions, and eventually flushes the pollution into water bodies (EPA, 1996; Kalkhoff et al., 2016). Surface runoff was recognized as the most critical energy factor for transports of sediment and sediment-attached nutrients such phosphorus and nitrogen according to empirical observations at field scales (Sharpley, 1982; Sharpley and Syers, 1979; Vadas et al., 2004; Williams, 1975). When the surface runoff generated from storm events combines with base flow, the water quality of stream flow can be disturbed by surface pollutants.

In addition, physical and chemical properties of water can be influenced by changed stream flow. Physical properties of water quality include temperature and turbidity. Chemical characteristics involve parameters such as conductivity, pH, and dissolved oxygen (DO). Previous studies have shown that water quality including sediment, nutrients, microorganisms, and physical and chemical properties can change significantly during storm events (Chen and Chang, 2014; Göransson et al., 2013; McCarthy et al., 2012; Rostami et al., 2018).

¹ Department of Geography, State University of New York at New Paltz, 1 Hawk Drive, New Paltz, NY 12561, USA, E-mail: chienh@newpaltz.edu, TEL: 845-295-2997

² Environmental Geochemical Science, State University of New York at New Paltz, 1 Hawk Drive, New Paltz, NY 12561, USA

To elucidate the impacts of changed stream flow on variations and changes in water quality, water quality sampling is necessary. Although the relationships between stream flow and water quality have been investigated in the literature, due to the fact of the geography and site-specific nature of water quality the objectives of this research were therefore to 1) sample water quality during or after storm events and 2) examine the impacts of changed stream flow on water quality. Water quality parameters focused on in this paper include water temperature, conductivity, pH, DO, nitrate and total orthophosphate (TP_{ortho}).

2. Methods

2.1 Study site

Our study area is located in the upper Esopus Creek Watershed (UECW) and its sub-watershed, the Stony Clove Creek (SC) watershed. The UECW is located in the Catskill Mountains of New York. The upper Esopus Creek (EC) is the main stream flowing into the Ashokan Reservoir, which provides 40% of the water supply to New York City. The confluence of SC and EC is located at Phoenicia, NY. The outlet of the upper Esopus Creek Watershed is located at USGS gauging station #01362500 with a drainage area of 497 km². Water quality samples were collected at USGS gauge station 01362370 at SC, Chichester, NY and 01362200 at EC, Allaben, NY, with drainage areas of 80.03 km² and 164.98 km², respectively (Figure 1). The Geology of the UECW is composed of sedimentary bedrock including sandstones, shales and conglomerate. The broken sedimentary rock is the source of stream sediment, which was deposited by glaciers during the most recent glaciation of 12,000 – 25,000 years ago (CCEUC, 2007). Analysis of climate data shows the mean average temperature for the area to be approximately 8 °C and mean annual total precipitation for the area to be approximately 1200 mm at Ashokan reservoir and 1600 mm higher in the mountains. The main land use and land cover is forest covering over 95% of the watershed. Development associated residences, businesses, and town centers are concentrated along Route 28 and roads along the tributaries.

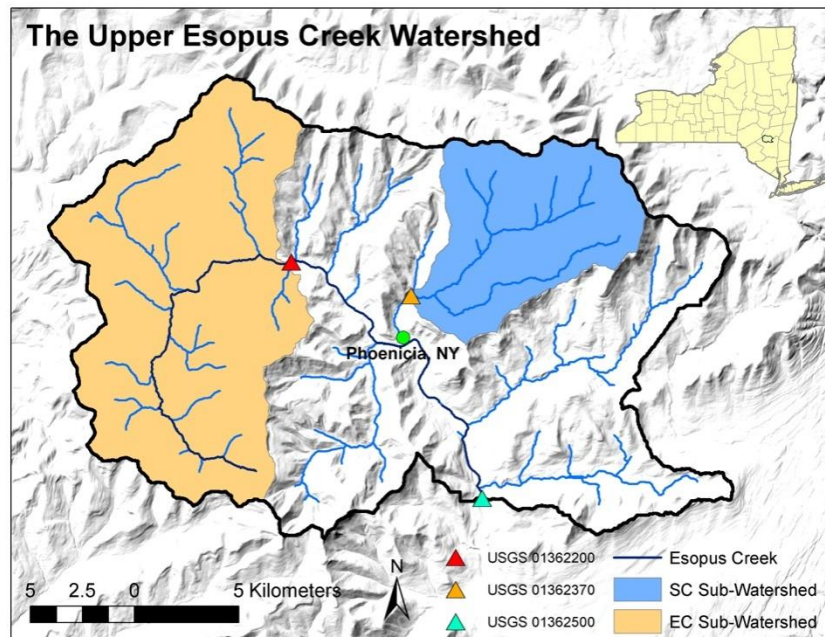


Figure 1: Map of the study site.

2.2 Water quality samplings and analysis

Water quality samples were collected once a week at the USGS gauge stations. Daily stream flow data is available at these two USGS gauge stations for the study period. When storm events were expected, water quality was sampled during or after storm events. Water quality variables including water temperature (°C), DO (mg/L), pH (range 1-14), and conductivity (μS/cm) were measured in situ using a YSI Pro2030 with a temperature/DO/pH/conductivity combined meter. At each site visit, 3 samples of water quality were collected and brought back to the laboratory to analyze TP_{ortho} and nitrate (NO_3^-) (both in mg/L). TP_{ortho} and Nitrate were measured using automated colorimetry according to EPA Method 365.1 and EPA Method 353.2, respectively (O'Dell 1993a; O'Dell 1993b). The mean data from three samples was used for our analysis.

Figure 2 shows the time of water samples at streamflow hydrographs at SC and EC from 06/01/2016 to 08/23/2016. There were 18 water quality samples at SC and 19 water quality samples at EC during the study period. The first and last water quality samples were on June 9 and August 8, 2016, respectively at both SC and EC. There were four major storm events from June 1 to August 23, 2016. The first and last water quality samples were collected after the first and third storm event, respectively. Most of water samples were collected at discharge decline.

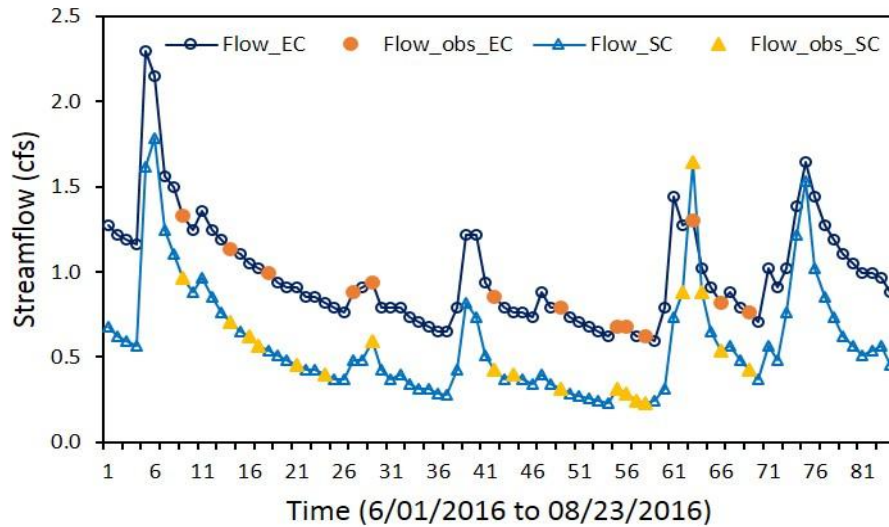


Figure 2: The time of water quality samples in streamflow hydrograph from 06/01/2016 to 08/23/2016.

Coefficient of determination (R^2) was used to represent the proportion of the total variability in water quality parameters that is explained by the regression. The value of R^2 varies from 0 to 1. A value of zero would indicate that no variability has been explained. A value of 1 would imply that all of the residuals are zero and the regression line fits perfectly through all of the observed points.

3. Results

3.1 Statistics of flow and water quality variables

Table 1 shows the summary statistics for streamflow and water quality variables. The mean streamflow was 0.51 and 0.89 (m^3/s) at SC and EC, respectively. The mean pH was 7.46 at SC and 7.29 at EC. EC had higher mean conductivity as 84.91 ($\mu S/cm$) in comparison to 74.53 ($\mu S/cm$) at SC. The mean, maximum, and minimum water temperature were 19.26, 25.20, 11.80 ($^{\circ}C$) at SC and 19.37, 24.30, and 12.00 ($^{\circ}C$) at EC. The mean DO was 7.38 (mg/L) at SC and 7.35 (mg/L) at EC. The mean Nitrate and TP_{ortho} were 0.93 and 0.04 (mg/L) at SC, respectively and 1.75 and 0.12 (mg/L) at EC, respectively. To understand the difference of water quality at SC and EC, the null hypothesis that there was no mean difference between water quality variables at SC and EC was tested with paired-samples t test. Since the significance value of streamflow, pH, and conductivity is less than 0.05, the null hypothesis cannot be supported. Thus, SC and EC are significantly different at the 95% confidence level for difference in streamflow, pH, and conductivity (Table 2). The significance values were greater than 0.05 for temperature, DO, Nitrate, and TP_{ortho} so the null hypothesis cannot be rejected. We conclude that at the 95% confidence level there is no significant difference in temperature, DO, Nitrate, and TP between SC and EC (Table 2).

Table1: Statistics of flow and water quality variables

	Stony Clove Creek				Esopus Creek		
	Units	Mean	Maximum	Minimum	Mean	Maximum	Minimum
Streamflow	m^3/s	0.51	0.96	0.23	0.89	1.30	0.62
pH	1-14	7.46	8.20	6.80	7.29	7.90	6.70
Conductivity	$\mu S/cm$	74.53	98.20	41.80	84.91	107.30	41.50
Temperature	$^{\circ}C$	19.26	25.20	11.80	19.37	24.30	12.00
DO	mg/L	7.38	9.29	6.13	7.35	9.18	6.07
NO3	mg/L	0.93	2.03	0.07	0.71	1.75	0.07
PO4	mg/L	0.04	0.10	0.00	0.04	0.12	0.00

Table 2: t statistic using paired-samples t test between water quality variables at Stony Clove Creek (SC) and Esopus Creek (EC).

		t	df	Sig. (2-tailed)
Pair 1	Streamflow_SC - Streamflow_EC	-42.196	17	.000
Pair 2	pH_SC - pH_EC	3.318	17	.004
Pair 3	Conductivity_SC - Conductivity_EC	-2.404	17	.028
Pair 4	Temperature_SC - Temperature_EC	1.408	17	.177
Pair 5	DO_SC - DO_EC	-.887	17	.387
Pair 6	Nitrate_SC - Nitrate_EC	1.381	16	.186
Pair 7	TP_SC - TP_EC	-1.422	16	.174

3.2 The response of water quality variables in response to changed streamflow

Figure 3 shows the relationships between streamflow and water quality variables including pH, conductivity, water temperature, DO, Nitrate, and TP_{ortho} at SC and EC. Generally the responses of all water quality variables in this study to changed streamflow were nonlinear. Streamflow has an inverse relationship with pH, conductivity, and temperature. When streamflow increases due to rainstorm runoff, pH, conductivity, and temperature decrease at both SC and EC sites (fig. 3). Nonlinear regressions were developed between streamflow and water quality variables; the R² was 0.4264 and 0.4348 for regression between streamflow and pH at SC and EC, respectively. For conductivity, the R² was 0.3659 at SC and 0.5415 at EC. For the regression line between streamflow and temperature, the R² is 0.5105 at S, decreasing to 0.4251 at EC. Streamflow and water quality variables including DO and Nitrite have positive relationships, in which increased streamflow caused higher DO and Nitrate concentration in mg/L. R² of nonlinear regression between streamflow and DO were 0.4683 and 0.4797 at SC and EC, respectively. For Nitrate, R² was 0.6494 at SC and 0.5148 at EC. Figure 3f shows the weak regression relationship between streamflow and TP_{ortho}. R² of nonlinear regression was 0.0401 at SC and 0.2042 at EC.

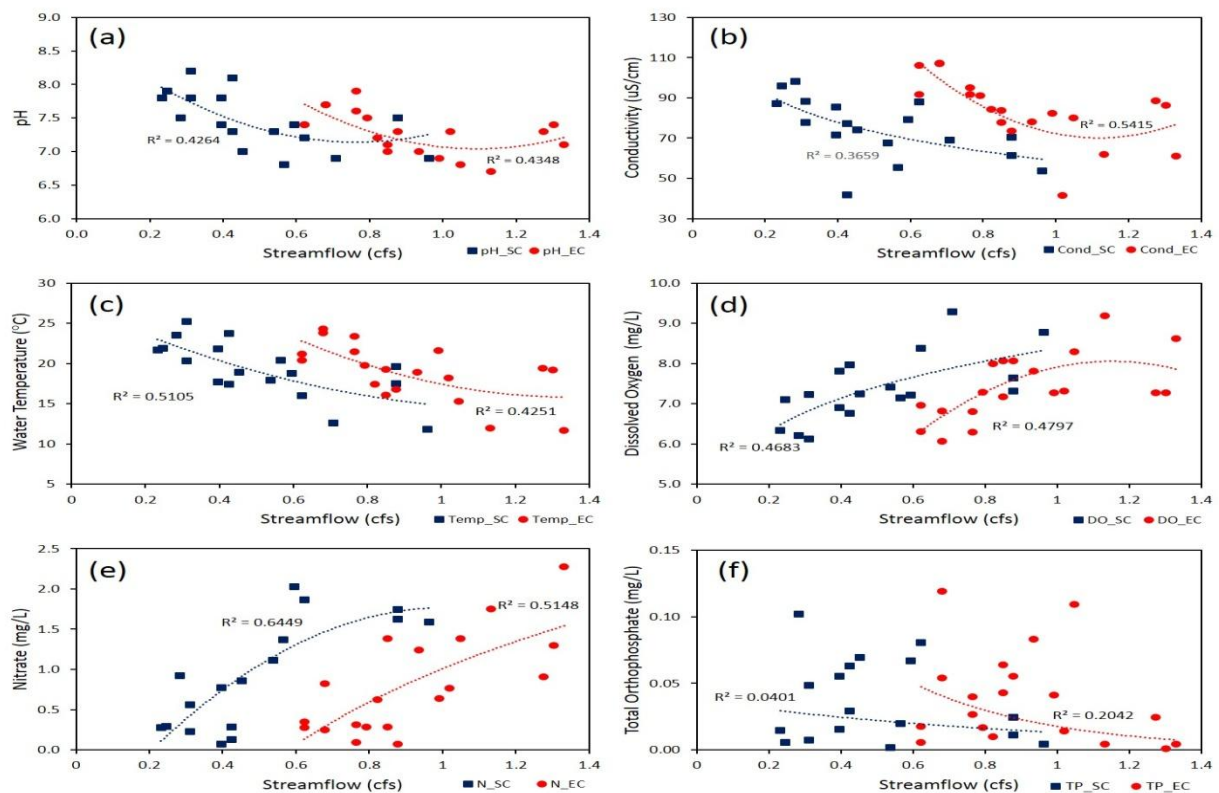


Figure 3: The relationships between streamflow and different water quality variables including (a) pH, (b) conductivity, (c) temperature, (d) dissolved oxygen, (e) nitrate, and (f) total orthophosphate at Stony Clove Creek (blue) and Esopus Creek (red).

4. Discussion

Our results show that streamflow had positive nonlinear regression relationships with DO and nitrate but negative nonlinear regression relationships with pH, conductivity, water temperature, and TP at both SC and EC. Water temperature had inverse nonlinear regression relationships with temperature but positive nonlinear regression relationship with pH at SC and EC.

4.1 pH and streamflow

Orographic lifting brings the UECW in the southeastern Catskills the highest annual rainfall in the New York State (CCEUC, 2007). The decreased pH with increased streamflow likely results from the acid rain. The Northeastern United States suffers the greatest acidity in rain because of cities, power and industrial plants, and accumulation of air pollution brought by the prevailing westerlies (USGS, 2018). Rain is naturally acidic with an average pH of about 5.6, which is caused by carbonic acid from the dissolving of atmospheric CO₂ in water. Additionally sulfur dioxide (SO₂) from burning of fossil fuels causes the rain to be more acidic (Chen and Driscoll, 2004). Our sampling results show the streamflow is relatively neutral with mean pH 7.46 at SC and 7.29 at EC, which is consistent with previous work (Stoddard, 1991), but pH in streamflow decreased in high streamflow conditions. The results suggest acid rain is still an environmental issue especially in Catskills.

4.2 Conductivity and streamflow

Conductivity is an indicator of changed water quality due to pollution. Discharge from sewage systems raises conductivity because of the presence of chloride, phosphate, and nitrate. Since 1997 New York City Department of Environmental Protection (DEP) has replaced poorly performing septic systems in areas of the West of Hudson Watershed including UECW to protect New York City's high-quality drinking water supply (NYCDEP, 2016). In addition, 95% of the land use and land cover of the UECW is forest, which suggests the influence of discharge from sewage system is limited. Previous studies showed that water quality variations could be caused by the dilution influence of storm events especially in the forested watershed (Pike et al., 2010; Whitfield et al., 1993). The dilution influence may explain the decreased conductivity with increased streamflow in the UECW dominated by land use and land cover of forest.

4.3 Water temperature and streamflow

Water temperature is an important regulator of water quality and the health of aquatic ecosystems (Caissie, 2006; Coutant, 1999; Webb et al., 2008). Most aquatic organisms have distinct tolerable water temperature ranges, so any changes in water temperature may influence the distribution, abundance and growth rate of aquatic organisms (FWPCA, 1967). Water temperature is highly correlated with air temperature (Mohseni and Stefan, 1999; Mohseni et al., 1998; Stefan and Preud'homme, 1993; Webb et al., 2003; Webb et al., 2008). Additionally streamflow, surface runoff, snowmelt, and groundwater inflow may influence water temperature (Blaen et al., 2013; Ficklin et al., 2012; Garner et al., 2014; Lowney, 2000; van Vliet et al., 2011; Webb et al., 2003; Webb and Walling, 1997). The results suggest that increased streamflow from storm events could decrease water temperature in the UECW. However, the changed streamflow can only explain 51% and 43% of variability of water temperature at SC and EC, respectively. The results suggest there should be other factors such as air temperature to explain the remaining variability in water temperature.

4.4 DO and streamflow

For DO at SC and EC sampling sites, there was a positive relationship between streamflow and DO. The result was consistent with previous studies in which low flow conditions may lead to low DO levels (Bosch et al., 2002). Our results suggest increased streamflow with higher moving velocity tends to contain more DO than stagnant water because oxygen from the air has more opportunities to mix into water. Only 47% and 48% variability of DO could be explained by changed streamflow at SC and EC, respectively, which implies other variables contributing to DO variability. Previous study shows a rainfall and nonlinear soil water storage were relatively more important than other environmental variables to control a hydrological response including streamflow, suspended sediment, and particulate phosphorus (Chien and Mackay, 2014). Figure 4 shows the response of DO to changed water temperature. With increased water temperature, DO decreases. Water temperature can well explain the variation of DO. R² were 0.9038 and 0.8518 for nonlinear inverse regression between water temperature and DO at SC and EC, respectively.

The results suggest increased streamflow causes lower water temperature and the subsequent increase in DO. in the UECW.

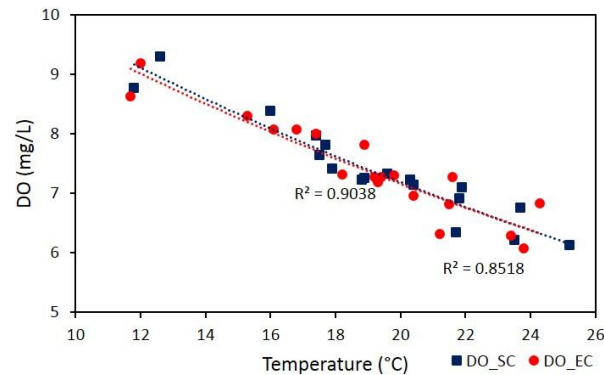


Figure 4: The regression relationship between temperature and DO at SC and EC .

4.5 Nitrate, TP_{ortho}, and streamflow

Nitrate is a compound containing nitrogen and oxygen. TP_{ortho} is known as reactive phosphorus in water. The overuse of fertilizers rich in nitrogen and phosphorus can accumulate in soils and eventually be flushed into water bodies through surface runoff, which is the main reason for eutrophication. Instead of surface runoff, subsurface flow appears to be the dominant hydrological process contributing to streamflow in forested watersheds because of the large infiltration capacities of forest soils (Hewlett et al., 1977; Mosley, 1979). In addition, forested riparian buffers located along streams benefit water quality by providing nutrient retention and promoting the settling of sediment (Anbumozhi et al., 2005). Previous research indicates that most phosphorus moves in particulate form attached to sediment (Bottcher et al., 1981; David and Gentry, 2000; Hart et al., 2004; Haygarth and Sharpley, 2000; Prairie and Kalff, 1986; Sonzogni et al., 1982). More than 95% of the land use and land cover of the UECW is forest, suggesting little nitrogen and phosphorus were flushed into streamflow via surface runoff within the UECW, which results in weak correlations between stream flow and TP_{ortho}.

5. Conclusions

This research examined the impacts of changed streamflow on water quality parameters including pH, conductivity, water temperature, DO, nitrate, and TP_{ortho}. The streamflow and water quality parameters could have either positive or negative nonlinear regression relationships, but the percentage of variability of water quality parameters explained by changed streamflow varied. The results suggest that two or more variables could influence the variability of water quality, which highlights the complexity of environmental systems even in a forest dominant watershed.

The question of whether water quality suffers most at low or high streamflow depends on the water quality parameters in question, as well as the characteristics of the watershed. High streamflow may decrease water quality through increased sediment from bank erosion, disturbed streambed sediment, nutrients released from sediments, and disturbance of the physical and chemical properties of water quality. In a forested watershed, the increased streamflow from storm events may have a diluting influence on water quality and shorter residence time of pollution and changed water quality parameters, which mitigates the impacts of water quality disturbance on aquatic ecosystem.

Acknowledgements

Primary funding for this research was provided by The SUNY New Paltz Summer Undergraduate Research Experience (SURE) and SUNY New Paltz Provost Challenge Grant.

References

- Anbumozhi, V., Radhakrishnan, J. and Yamaji, E., 2005. Impact of riparian buffer zones on water quality and associated management considerations. *Ecological Engineering*, 24(5): 517-523.
- Blaen, P.J., Hannah, D.M., Brown, L.E. and Milner, A.M., 2013. Water temperature dynamics in High Arctic river basins. *Hydrological Processes*, 27(20): 2958-2972.
- Bosch, D., Lowrance, R., Vellidis, G., Sheridan, J. and Williams, R., 2002. Dissolved Oxygen and Stream Flow Rates: Implications for TMDL's, Pp. 92-92 in *Total Maximum Daily Load (TMDL) Environmental Regulations: Proceedings of the March 11-13, 2002 Conference*, (Fort Worth, Texas, USA). ASABE, St. Joseph, MI.
- Bottcher, A.B., Monke, E.J. and Huggins, L.F., 1981. Nutrient and Sediment Loadings from a Subsurface Drainage System. *Transactions of the Asae*, 24(5): 1221-1226.
- Caissie, D., 2006. The thermal regime of rivers: a review. *Freshwater Biology*, 51(8): 1389-1406.
- Carpenter, S.R. et al., 1998. NONPOINT POLLUTION OF SURFACE WATERS WITH PHOSPHORUS AND NITROGEN. *Ecological Applications*, 8(3): 559-568.
- CCEUC, 2007. Upper Esopus Creek management Plan. Volume 1: Summary of Findings and Recommendations. Cornell Cooperative Extension – Ulster County, New York City Department of Environmental Protection, U.S. Army Engineer Research Development Center.
- Chen, H.J. and Chang, H., 2014. Response of discharge, TSS, and E. coli to rainfall events in urban, suburban, and rural watersheds. *Environmental Science: Processes & Impacts*, 16(10): 2313-2324.
- Chen, L. and Driscoll, C.T., 2004. An evaluation of processes regulating spatial and temporal patterns in lake sulfate in the Adirondack region of New York. *Global Biogeochemical Cycles*, 18(3).
- Chien, H. and Mackay, D.S., 2014. How much complexity is needed to simulate watershed streamflow and water quality? A test combining time series and hydrological models. *Hydrological Processes*, 28(22): 5624-5636.
- Coutant, C.C., 1999. Perspectives on Temperature in the Pacific Northwest's Fresh Waters. United States. doi:10.2172/9042, <https://www.osti.gov/servlets/purl/9042>.
- David, M.B. and Gentry, L.E., 2000. Anthropogenic inputs of nitrogen and phosphorus and riverine export for Illinois, USA. *Journal of Environmental Quality*, 29(2): 494-508.
- EPA, 1996. Nonpoint Pointers. EPA-841-F-96-004A, U.S. Environmental Protection Agency, <https://nepis.epa.gov/Exe/ZyPDF.cgi/20004PZG.PDF?Dockey=20004PZG.PDF>.
- Ficklin, D.L., Luo, Y., Stewart, I.T. and Maurer, E.P., 2012. Development and application of a hydroclimatological stream temperature model within the Soil and Water Assessment Tool. *Water Resources Research*, 48(1): W01511, doi:10.1029/2011WR011256.
- FWPCA, 1967. Temperature and aquatic life. Laboratory Investigations - Number 6, Technical Advisory and Investigations Branch, Federal Water Pollution Control Administration, United States Department of The Interior, <https://nepis.epa.gov/Exe/ZyPDF.cgi/93001A04.PDF?Dockey=93001A04.PDF>.
- Garner, G., Hannah, D.M., Sadler, J.P. and Orr, H.G., 2014. River temperature regimes of England and Wales: spatial patterns, inter-annual variability and climatic sensitivity. *Hydrological Processes*, 28(22): 5583-5598.
- Göransson, G., Larson, M. and Bendz, D., 2013. Variation in turbidity with precipitation and flow in a regulated river system – river Göta Älv, SW Sweden. *Hydrol. Earth Syst. Sci.*, 17(7): 2529-2542.
- Hart, M.R., Quin, B.F. and Nguyen, M.L., 2004. Phosphorus runoff from agricultural land and direct fertilizer effects: A review. *Journal of Environmental Quality*, 33(6): 1954-1972.
- Haygarth, P.M. and Sharpley, A.N., 2000. Terminology for phosphorus transfer. *Journal of Environmental Quality*, 29(1): 10-15.
- Hewlett, J.D., Fortson, J.C. and Cunningham, G.B., 1977. The effect of rainfall intensity on storm flow and peak discharge from forest land. *Water Resources Research*, 13(2): 259-266, doi: 10.1029/WR013i002p00259.
- Kalkhoff, S.J., Hubbard, L.E., Tomer, M.D. and James, D.E., 2016. Effect of variable annual precipitation and nutrient input on nitrogen and phosphorus transport from two Midwestern agricultural watersheds. *Science of The Total Environment*, 559: 53-62.
- Lowney, C.L., 2000. Stream temperature variation in regulated rivers: Evidence for a spatial pattern in daily minimum and maximum magnitudes. *Water Resources Research*, 36(10): 2947-2955.
- McCarthy, D.T., Hathaway, J.M., Hunt, W.F. and Deletic, A., 2012. Intra-event variability of Escherichia coli and total suspended solids in urban stormwater runoff. *Water Research*, 46(20): 6661-6670.
- Mohseni, O. and Stefan, H.G., 1999. Stream temperature/air temperature relationship: a physical interpretation. *Journal of Hydrology*, 218(3): 128-141.

- Mohseni, O., Stefan, H.G. and Erickson, T.R., 1998. A nonlinear regression model for weekly stream temperatures. *Water Resources Research*, 34(10): 2685-2692.
- Mosley, M.P., 1979. Streamflow generation in a forested watershed, New Zealand. *Water Resources Research*, 15(4): 795-806, doi: 10.1029/WR015i004p00795.
- NYCDEP, 2016. 5,000 Septic Systems Upgraded in New York City's West of Hudson Watershed. http://www.nyc.gov/html/dep/html/press_releases/16-092pr.shtml#.Wxq6ACOZP-Y, 09/19/2016.
- NYCDEP, 2018. Septic System, http://www.nyc.gov/html/dep/html/watershed_protection/septic_systems.shtml.
- O'Dell, J.W., 1993a. Method 353.2, Revision 2.0: Determination of Nitrate-Nitrite Nitrogen by Automated Colorimetry Environmental Monitoring System Laboratory, Office of Research and Development, US EPA, Cincinnati, Ohio 45268, https://www.epa.gov/sites/production/files/2015-08/documents/method_353-2_1993.pdf.
- O'Dell, J.W., 1993b. Method 365.1, Revision 2.0: Determination of Phosphorus by Semi-Automated Colorimetry Environmental Monitoring System Laboratory, Office of Research and Development, US EPA, Cincinnati, Ohio 45268, https://www.epa.gov/sites/production/files/2015-08/documents/method_365-1_1993.pdf.
- Pike, R.G., Feller, M.C., Stednick, J.D., Rieberger, K.J. and Carver, M., 2010. Water Quality and Forest Management (Chapter 12). In: R.G. Pike, T.E. Redding, R.D. Moore, R.D. Winker and K.D. Bladon (Editor), *Compendium of forest hydrology and geomorphology in British Columbia*. B.C. Min. For. Range, For. Sci. Prog., Victoria, B.C. and FORREX Forum for Research and Extension in Natural Resources, Kamloops, B.C. Land Manag. Handb. 66. https://www.for.gov.bc.ca/hfd/pubs/docs/lmh/Lmh66/Lmh66_ch12.pdf.
- Prairie, Y.T. and Kalff, J., 1986. Effect of catchment size on phosphorus export. *Water Resources Bulletin*, 22(3): 465-470.
- Rostami, S., He, J. and Hassan, Q.K., 2018. Riverine Water Quality Response to Precipitation and Its Change. *Environments*, 5(8): <http://doi.org/10.3390/environments5010008>.
- Sharpley, A.N., 1982. Prediction of water-extractable phosphorus content of soil following a phosphorus addition. *Journal of Environmental Quality*, 11(2): 166-170.
- Sharpley, A.N. and Syers, J.K., 1979. Phosphorus inputs into a stream draining an agricultural watershed. *Water, Air, and Soil Pollution*, 11(4): 417-428.
- Sonzogni, W.C., Chapra, S.C., Armstrong, D.E. and Logan, T.J., 1982. Bioavailability of Phosphorus Inputs to Lakes. *Journal of Environmental Quality*, 11(4): 555-563.
- Stefan, H.G. and Preud'homme, E.B., 1993. STREAM TEMPERATURE ESTIMATION FROM AIR TEMPERATURE1. *JAWRA Journal of the American Water Resources Association*, 29(1): 27-45.
- Stoddard, J.L., 1991. Trends in Catskill Stream Water Quality: Evidence From Historical Data. *Water Resources Research*, 27(11): 2855-2864, doi: 10.1029/91WR02009.
- USGS, 2018. Acid Rain: Do you need to start wearing a rain hat? The USGS Water Science School, U.S. Department of the Interior, U.S. Geological Survey, <http://water.usgs.gov/edu/acidrain.html>: (access May 10, 2018).
- Vadas, P.A., Kleinman, P.J.A. and Sharpley, A.N., 2004. A simple method to predict dissolved phosphorus in runoff from surface-applied Manures. *Journal of Environmental Quality*, 33(2): 749-756.
- van Vliet, M.T.H., Ludwig, F., Zwolsman, J.J.G., Weedon, G.P. and Kabat, P., 2011. Global river temperatures and sensitivity to atmospheric warming and changes in river flow. *Water Resources Research*, 47(2): W02544, doi:10.1029/2010WR009198.
- Webb, B.W., Clack, P.D. and Walling, D.E., 2003. Water-air temperature relationships in a Devon river system and the role of flow. *Hydrological Processes*, 17(15): 3069-3084.
- Webb, B.W., Hannah, D.M., Moore, R.D., Brown, L.E. and Nobilis, F., 2008. Recent advances in stream and river temperature research. *Hydrological Processes*, 22(7): 902-918.
- Webb, B.W. and Walling, D.E., 1997. Complex summer water temperature behaviour below a UK regulating reservoir. *Regulated Rivers: Research & Management*, 13(5): 463-477.
- Whitfield, P.H., Rousseau, N. and Michnowsky, E., 1993. Rainfall induced changes in chemistry of a British Columbia coastal stream. *Northwest Science*, 67(1).
- Williams, J.R., 1975. Sediment-yield prediction with universal equation using runoff energy factor. In *Present and prospective technology for prediction sediment yield and sources: Proceedings of the sediment yield workshop*, USDA Sedimentation Lab, Oxford, MS, November 28-30, 1972. ARS-S-40, pp. 244-252.