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Advancing Understanding of the Surface Water Quality Regime of Contemporary Mixed-Land-Use Watersheds: An Application of the Experimental Watershed Method

Elliott Kellner [1,2,*] and Jason A. Hubbart [2]

1 School of Natural Resources, University of Missouri, 203-T ABNR Building, Columbia, MO 65211, USA
2 Institute of Water Security and Science, Davis College, Schools of Agriculture and Food, and Natural Resources, West Virginia University, Agricultural Sciences Building, Morgantown, WV 26506, USA; Jason.Hubbart@mail.wvu.edu
* Correspondence: elliott.kellner@mail.wvu.edu; Tel.: +1-304-293-3797

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Abstract: A representative watershed was instrumented with five gauging sites ($n = 5$), partitioning the catchment into five nested-scale sub-watersheds. Four physiochemical variables were monitored: water temperature, pH, total dissolved solids (TDS), and dissolved oxygen (DO). Data were collected four days per week from October 2010–May 2014 at each gauging site. Statistical analyses indicated significant differences ($p < 0.05$) between nearly every monitoring site pairing for each physiochemical variable. The water temperature regime displayed a threshold/step-change condition, with an upshifted and more variable regime attributable to the impacts of urban land uses. TDS, pH, and DO displayed similar spatiotemporal trends, with increasing median concentrations from site #1 (agriculture) to #3 (mixed-use urban) and decreasing median concentrations from site #3 to #5 (suburban). Decreasing concentrations and increasing streamflow volume with stream distance, suggest the contribution of dilution processes to the physiochemical regime of the creek below urban site #3. DO concentrations exceeded water quality standards on an average of 31% of observation days. Results showed seasonal trends for each physiochemical parameter, with higher TDS, pH, and DO during the cold season (November–April) relative to the warm season (May–October). Multivariate modeling results emphasize the importance of the pH/DO relationship in these systems, and demonstrate the potential utility of a simple two factor model (water temperature and pH) in accurately predicting DO. Collectively, results highlight the interacting influences of natural (autotrophic photosynthesis, organic detritus loading) and anthropogenic (road salt application) factors on the physiochemical regime of mixed-land-use watersheds.

Keywords: surface water quality; dissolved oxygen; pH; total dissolved solids; land use impacts; experimental watershed method

1. Introduction

1.1. Background

Land use/land cover change (e.g., forest removal, agricultural conversion, urbanization) has repeatedly and conclusively been shown to alter rates of mass (e.g., sedimentation of waterways, increased nutrient loadings) and energy flux (e.g., urban heat island, water temperature regime change) [1–4]. Such alterations impact water quality (e.g., chemical composition, pathogen presence and persistence) and quantity regimes (e.g., low flows, peak flows, flooding) [5–8], and can ultimately result in ecosystem degradation. However, water quality and quantity regimes are variably impacted by natural and anthropogenic factors, and are consequently difficult to quantify and manage in contemporary watersheds [6,9], where a mosaic of land use types confounds attributing causative mechanisms to observed alterations of hydrologic regimes.

Previous studies noted contributions of landscape alteration to stream water quality degradation. For example, Ometo et al. [10] found statistically significant correlations between land use and water quality parameters (i.e., conductivity, major cations, and major anions) in two Brazilian streams. Lenat and Crawford [11] reported higher total dissolved solids and specific conductance in an urban stream, relative to a forested reference stream; and noted urban stream biological parameters indicated a stressed environment. Rhodes et al. [12] showed positive correlations between streamwater nutrient concentrations (i.e., NO_3^-, SO_4^{2-}, and Cl^-) and anthropogenic land uses (e.g., agriculture, urban, road density) in the Mill River Watershed, Massachusetts. Li et al. [13] noted water temperature and nutrient concentration were significantly ($p < 0.05$) related to vegetative coverage at the sub-watershed-scale in the Han River Basin, China. Bolstad and Swank [14] identified downstream, cumulative increases in water quality variables (e.g., temperature, dissolved oxygen, pH, and conductivity) associated with land use/land cover changes (e.g., urbanization) in Coweeta Creek Watershed, North Carolina.

Among many important stream physiochemical parameters, in-stream oxygen availability is a particularly important variable [15] impacting community composition and species distribution in aquatic ecosystems [16], and has thus been used broadly as a proxy for water quality status [17]. For example, Rutledge and Beitinger [18] identified negative impacts of hypoxia on critical thermal maxima of fish. Connolly et al. [16] reported lethal effects of low dissolved oxygen concentrations (i.e., <20% saturation) on a variety of macroinvertebrate species from an Australian stream. However, counter to hypoxia, super-saturation can also adversely impact aquatic biota, suggesting an "ecological envelope" for organisms such as fish [15]. Dissolved oxygen (DO) concentrations are influenced by a variety of natural and anthropogenic factors, including atmospheric diffusion, streamflow (e.g., turbulence/reaeration), stream geomorphology, water temperature and pressure, aquatic organism respiration (e.g., algae and bacteria), autotrophic photosynthesis, chemical oxidation, and land use/land cover alterations [14,16,19,20]. For example, Wilcock et al. [20] noted chronically low DO concentrations in a New Zealand stream were attributable to terrestrial nutrient and organic matter loading and subsequent in-stream respiration processes. Mulholland et al. [21] showed that the catchment disturbance level (%) explained 80% of the variation in observed maximum DO deficit in ten 2nd order streams in Fort Benning, Georgia.

Given the importance of water quality constituents (including DO and others) to aquatic ecosystem health and considering the capacity of a watershed to provide ecosystem services to local and regional communities, resource managers need methods capable of investigating physiochemical stream regimes in complex, contemporary settings. The nested-scale experimental watershed study design has been demonstrated an effective approach for quantitatively characterizing hydrologic and water quality perturbations in mixed-land-use watersheds [4,22–24]. Nested watershed study designs partition a series of sub-basins inside a larger watershed to study environmental variables. Sub-basins are often delineated based on dominant land use and hydrologic characteristics. The design enables isolation and quantification of contributing processes at each monitoring location [25], and thus identification of dominant land use influences on the response variable(s) of interest (e.g., streamflow variability, suspended sediment concentration). By applying an experimental watershed approach, contributing factors (e.g., land use, hydroclimate) can be more effectively disentangled, providing applicable science-based information for land and water resource managers.

Improving understanding of stream physiochemical regimes in contemporary watersheds is vital to the accurate prediction and evaluation of water quality degradation resulting from anthropogenic landscape alteration [26]. However, despite progress, many previous studies utilized brief, episodic sampling regimes [10,11,13,14,26], likely incapable of quantitatively characterizing the full range of hydrological and environmental variability. These issues, coupled to the ongoing need for work that will help unravel the complex, competing interactions of multiple contributing factors present in contemporary mixed-land-use watersheds [6], provided the impetus for the current work.

1.2. Objectives

The overarching objective of the current work was to investigate spatiotemporal variation of in-stream physiochemical parameters, including total dissolved solids (TDS), water temperature, pH, and dissolved oxygen (DO), in a contemporary developing watershed. A sub-objective was to use observed physiochemical data to generate multivariate predictive DO models. As opposed to a more traditional experimental approach, the purpose of the study was to utilize high-frequency water quality monitoring to quantitatively describe the longitudinal and seasonal variability of water quality in a mixed-land-use watershed, thus providing critical baseline information that is currently and urgently needed.

2. Study Sites and Methods

2.1. Study Site Description

Hinkson Creek Watershed (HCW) is a rapidly urbanizing, mixed-land-use watershed located in central Missouri (Table 1, Figure 1). Land use in HCW is approximately 34% forest, 38% agriculture, and 25% urban [27], making it a regionally (if not globally) representative watershed for studying the effects of mixed-land-use types on water quality [28]. The drainage area of HCW is approximately 230 km^2, with elevations ranging from 274 m above mean sea level (AMSL) in the headwaters to 177 m AMSL near the watershed outlet. Approximately 28 km^2 of impervious surfaces in HCW (e.g., roads, parking areas, sidewalks, etc.) [29] were located within the municipal boundary of the city of Columbia (population 116,000) [30] at the time of the study. HCW contains a drainage network of 1st to 3rd order streams. Poff et al. [6] noted the importance of 1st–4th order streams, which represent approximately 97% of US stream-length. Such small streams are key regulators of watershed-scale water quality, and are most likely to reflect land use impacts, thereby providing greater inferences regarding hydrologic-geomorphic-ecological interactions [6].

Hinkson Creek, the main channel of HCW, was placed on the Clean Water Act Section 303(d) list of impaired waters in 1998. After more than a decade and more than $100 million invested, the creek remained listed. A collaborative adaptive management (CAM) program was implemented in 2011 to improve water quality management in HCW, and achieve eventual de-listing. The need to improve understanding of land use impacts on stream chemistry at nested-scales, in order to better target mitigation strategies, provided the impetus for the current work.

According to a 64-year climate record of Columbia, Missouri (station ID #231790, 231791), average annual temperature and precipitation within the watershed are 12.5 °C and 991 mm year^{-1}, respectively [31,32]. The annual wet season occurs between March and June [3,22]. Hinkson Creek is primarily stormflow-dominated with a base flow index ranging from 0.17 in the headwaters to 0.27 near the watershed outlet [33]. Soils in HCW are underlain by Pennsylvanian sandstone and Burlington formation Mississippian series limestone [28,34]. Soils in the upper reaches of the watershed are predominately glacial till overlain by a loess surface layer, while soils in the middle and lower watershed are silty and sandy clay residuum [35]. Hinkson Creek was instrumented with a nested-scale experimental watershed study design in 2008, with five gauging sites ($n = 5$) partitioning the catchment into five sub-watersheds, characterized by different dominant land use types (Table 1) [22]. Site #5 is located near the watershed outlet, and sites #1 to #4 are nested within (Figure 1). Site #4 is a U.S. Geological Survey site (USGS #06910230) where stage and discharge have been monitored since 1967. Land use/land cover in HCW spans a representative gradient of predominately agriculture in the upper watershed (i.e., site #1), to mixed-use urban in the middle watershed (i.e., site #3), to predominately suburban residential in the lower watershed (i.e., site #5) [36].

Table 1. Sub-watershed land use/land cover (%) and drainage area (km^2) for each sub-watershed located in Hinkson Creek Watershed (HCW), MO, USA.

Sub-Watershed#	Urban	Residential	Forest	Agriculture	Drainage Area
1	0.1	4.5	36.0	55.9	79.0
2	3.6	7.6	37.8	46.7	23.9
3	26.4	36.8	27.3	9.0	13.3
4	12.2	21.3	32.9	30.9	65.8
5	18.6	50.8	23.0	4.2	25.5

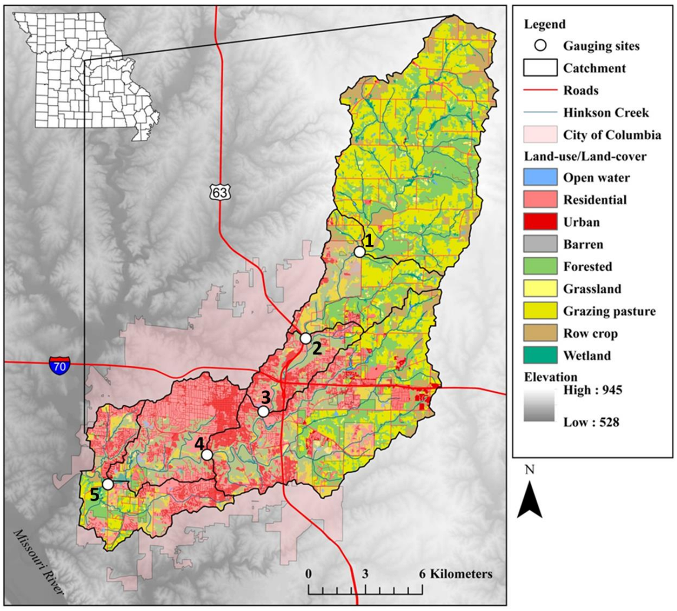

Figure 1. Nested-scale experimental watershed study design including five gauging sites/sub-watersheds in Hinkson Creek Watershed, MO, USA (Map by Sean Zeiger).

2.2. Hydroclimate Monitoring

Hydroclimate stations at each gauging site were used to monitor air temperature, precipitation, and stream stage at 30-min. intervals during the study (October 2010–May 2014). Vaisala HMP45C probes were used to sense air temperature, Texas Instruments TE525WS tipping bucket rain gauges were used to sense precipitation, and Sutron Accubar® constant flow bubblers were used to monitor stage at each gauging site. FLO-MATE™ Marsh McBirney flow meters and wading rods were used to measure flow when stage was less than 1 m deep. A U.S. Geological Survey Bridge Board was used to facilitate flow measurements during storm flows. The incremental cross section method was used to generate stage-discharge rating curves [37], in order to estimate streamflow. Land use/land cover data were generated using Arc GIS hydrology and zonal statistics tools, and the National Land Cover Dataset from 2011 [36].

2.3. Stream Chemistry Data Collection

Four physiochemical variables were selected for the current work including water temperature (Tw), pH, total dissolved solids (TDS), and dissolved oxygen (DO). Stream chemistry data were collected on Monday, Wednesday, Friday, and Saturday for the duration of the study period (October 2010–May 2014) at each gauging site (n = 5) (Figure 1), using a handheld multi-parameter sonde fitted with an Ion Selective Electrode (ISE) probe (YSI, Inc., Yellow Springs, OH, USA) [21]. Data were always collected between 12:00 (site #1) and 14:30 (site #5) at each gauging site, in numerical order of sites. The ISE probe senses water temperatures ranging from −5 to 100 °C, with an accuracy of ±0.15 °C; pH with an accuracy of ±0.2 units; TDS ranging from 0 to 100 g L^{-1}, with an accuracy of ±0.5% of reading; and DO ranging from 0 to 50 mg L^{-1}, with an accuracy of ±2% (for readings 0–20 mg L^{-1}) or ±6% (for readings 20–50 mg L^{-1}). The data collection method comprised insertion of the sonde into the stream, upstream of the operator, at 60% depth to characterize a representative water sample. The ISE probe was calibrated weekly according to standard protocol using manufacturer-supplied, EPA certified, calibration standards. In addition to this work, separate concurrent research conducted in HCW [23] resulted in daily sampling of the same physiochemical parameters at each study site from February 2011–April 2012. Daily data were utilized in the current work to maximize sampling frequency/data resolution.

Data quality issues encountered during the course of the study resulted in data gaps for stream physiochemical parameter time series. As opposed to applying a gap-fill method (e.g., linear interpolation, regression modeling, etc.) and potentially introducing error into the data, large gaps were left unfilled. As a result, time series for the four physiochemical variables were not identical. Table 2 contains a description of the time series for each parameter.

Table 2. Time series and sample size (n) for stream physiochemical parameters measured during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA.

Parameter	Time Series	n
Tw	10/1/2009–5/31/2014	1135
TDS	10/1/2009–8/18/2010; 5/19/2011–5/31/2014	949
pH	4/10/2010–9/10/2010; 9/29/2010–1/8/2011; 2/2/2011–5/31/2014	1004
DO	11/11/2009–12/31/2010; 4/24/2011–5/31/2014	1028

Tw = Water Temperature; TDS = Total Dissolved Solids; DO = Dissolved Oxygen.

2.4. Data Analyses

Hydroclimatic and stream chemistry data from each site were reduced by averaging (i.e., monthly and annual time scales), and descriptive statistics were calculated. Considering hydroclimate data are often non-normally distributed [38], the Wilcoxon signed-rank test and Mann-Whitney U test were used for statistical comparison of stream chemistry data between monitoring sites (i.e., full time series). Both tests are an appropriate non-parametric choice for paired (e.g., temporally) non-normal data sets [39]. The non-parametric Spearman's correlation was also used to test for significant relationships between physiochemical parameters and land use characteristics ($\alpha = 0.05$) [40]. Partial Least Squares Method [41] was used to generate dissolved oxygen predictive models for each site based on observed physiochemical data (i.e., water temperature, pH, TDS, and streamflow). Model performance was evaluated using goodness-of-fit measures, including coefficient of determination (R^2) and root mean of squared residual errors (RMSE), normalized using the mean of observed DO for the given site (NRMSE) and expressed as a percentage [42]. A stepwise routine was utilized for adding and removing variables in the model optimization process. Considering contrasting time series for the four parameters (Table 2), multivariate modeling and correlation analyses utilized an abbreviated, concurrent time series (i.e., 5/19/2011–5/31/2014) (n = 766).

2.5. Hydroclimate During Study

Average air temperature (i.e., five-site-average) during the study was 11.8 °C, approximately 6% below the 64-year average of 12.5 °C [31,32] (Table 3, Figure 2). Although observed air temperature time series from the five monitoring sites tracked one another closely, study period air temperature averages differed by as much as 10% [43]. Given the land use/land cover (LULC) characteristics of the delineated sub-basins (Table 1, Figure 1), the observed air temperature patterns (e.g., highest average, maximum, and minimum temperatures at site 3) suggest an urban heat island (UHI) condition in HCW [3].

Table 3. Descriptive statistics for 30-min. precipitation (mm), streamflow (m^3 sec^{-1}), and air temperature (°C) at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA [43].

	Site #1	Site #2	Site #3	Site #4	Site #5
Air Temperature					
Average	11.08	11.86	12.15	11.88	11.86
Min.	–30.64	–30.22	–26.23	–26.29	–28.70
Max.	40.60	41.28	41.85	41.31	41.09
Std. Dev.	11.86	11.95	11.81	11.73	11.92
Precipitation					
Total	3824	4590	4677	4644	4568
Min.	0.0	0.0	0.0	0.0	0.0
Max.	26	23	26	40	27
Std. Dev.	0.5	0.5	0.5	0.5	0.5
Streamflow					
Average	0.57	0.79	1.34	2.16	3.21
Min.	0.01	0.01	<0.01	<0.01	0.04
Max.	130.64	163.45	170.41	323.55	357.70
Std. Dev.	4.54	5.88	6.66	11.38	15.54

Avg. = Average; Max. = Maximum; Min. = Minimum; Std. Dev. = Standard Deviation.

Five-site-average annual precipitation was 956 mm $year^{-1}$ [43], similar to the 64-year average of 991. mm $year^{-1}$ [31,32]. Maximum annual (i.e., five-site-average) precipitation occurred during the 2010 water year (1485 mm), which was 50% greater than the 64-year average. Minimum annual precipitation was received during the 2012 water year (727 mm), followed closely by the 2011 water year (765 mm). 2012 was a drought year in the Midwest. Specifically, the period June 2012–August 2012, was characterized by extreme (D3) to exceptional (D4) drought conditions (USDM Drought Severity Classification) [44], and was ranked one of the hottest and driest on record for the region [45].

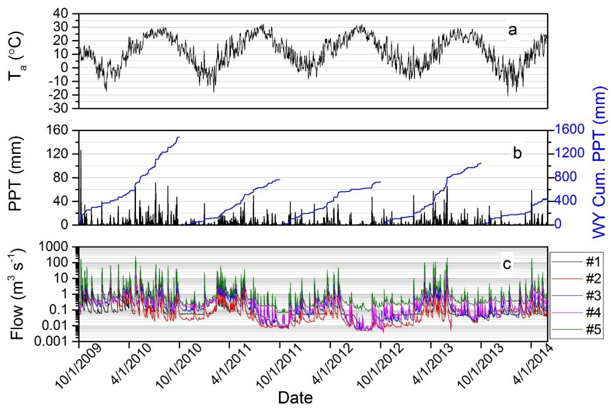

Figure 2. Five-site-average air temperature (Ta; °C) (panel a), five-site-average daily precipitation (PPT; mm), cumulative water year precipitation (WY Cum. PPT; mm) (panel b), and average daily streamflow (m^3 s^{-1}) (panel c) at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA.

Cumulative streamflow statistics for Hinkson Creek indicated high variability and increasing flow volume with increasing stream distance (i.e., in the downstream direction) (Table 3) [43]. The scale of hydrologic regime variability is illustrated by differences between low flows and high flows at all gauging sites comprising approximately five orders of magnitude (i.e., 0.001–100.00 m^3 s^{-1}). Maximum flows were observed at all sites following large spring season precipitation events. Conversely, minimum flows occurred during late summer and fall seasons of climatically dry years (e.g., 2011 and 2012 water years). The variability of hydrologic conditions during the study period afforded the opportunity to investigate stream physiochemical regime under a wide range of environmental conditions [43]. For additional information regarding constituent transport and streamflow dynamics in HCW during the study period, please see Zeiger and Hubbart [24] and Kellner and Hubbart [46], respectively.

3. Results and Discussion

3.1. Stream Physiochemical Parameters

Wilcoxon signed rank results showed significant differences ($p < 0.01$) between water temperatures for every site pairing. Although air temperature was greatest at site #3 (e.g., highest average, maximum, and minimum) (Table 3), site #2 displayed the highest average, median, maximum (i.e., with site #3), and standard deviation of water temperature, relative to the other monitoring sites (Table 4). Conversely, the lowest average, median, maximum, and standard deviation of water temperature were observed at site #1. Water temperatures tracked air temperatures (Figures 2 and 3), with highs and lows observed during the summers and winters, respectively. Notably, maximum temperatures at sites #2 and #3 exceeded the maximum allowable water temperature (32.2 °C) established by the Missouri Department of Natural Resources for "warm water habitats" [47], a threshold for potential fish mortality [33]. As opposed to a consistent spatial trend (e.g., increasing or decreasing), or the absence of a definable spatial trend (e.g., statistical similarity), water temperature regimes in HCW are apparently characterized by a threshold/step-change condition, with an upshifted (e.g., higher average, median, and maximum temperatures) and more variable (e.g., greater standard deviation) regime incident at site #2, relative to site #1, which is propagated downstream through the watershed. Given sub-watershed #2 contains the upper portions of the city of Columbia, and is characterized by a 100% increase in urban and developed land uses compared to sub-watershed #1 (Table 1), it is possible that urbanization and the removal of riparian canopy are primary drivers of water temperature regime in HCW, a hypothesis supported by the findings of Zeiger et al. [33].

Table 4. Descriptive statistics for water temperature (Tw) (°C), total dissolved solids (TDS) (mg L^{-1}), pH, and dissolved oxygen (DO, % of saturation) at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA.

	Site #1	Site #2	Site #3	Site #4	Site #5
Tw					
Avg.	12.5	13.7	13.6	13.6	13.5
Med.	12.1	13.5	13.4	13.2	13.2
Max.	29.9	32.3	32.3	31.9	31.6
Min.	–0.1	–0.1	–0.1	–0.1	–0.1
Std. Dev.	8.7	9.5	9.4	9.3	9.4
TDS					
Avg.	309.1	430.0	484.2	440.2	411.6
Med.	298.3	429.0	429.0	422.5	383.5
Max.	728.0	1144.0	3750.5	1950.0	1482.0
Min.	28.6	15.0	53.3	11.1	2.0
Std. Dev.	116.5	165.8	285.3	194.0	184.9
pH					
Avg.	7.9	8.0	8.0	7.9	7.8
Med.	7.9	8.0	8.1	7.9	7.8
Max.	9.6	9.4	9.3	9.2	9.3
Min.	6.5	6.4	6.8	6.5	6.5
Std. Dev.	0.4	0.3	0.3	0.2	0.3
DO					
Avg.	96.0	109.1	111.1	103.6	92.4
Med.	99.6	109.0	110.6	102.7	93.9
Max.	194.0	182.6	190.8	177.0	169.6
Min.	1.2	0.7	0.1	0.6	0.8
Std. Dev.	34.3	28.2	32.0	25.9	28.1

Avg. = Average; Med. = Median; Max. = Maximum; Min. = Minimum; Std. Dev. = Standard Deviation.

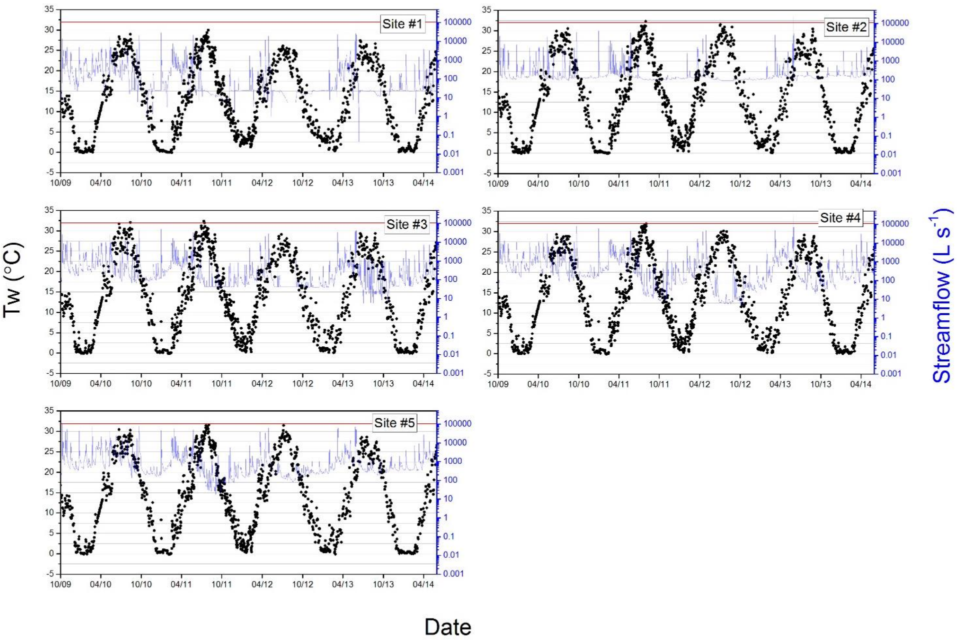

Figure 3. Stream water temperature (Tw) (°C) and streamflow (L s^{-1}) at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA. Red lines depict maximum threshold established by Missouri Department of Natural Resources.

Statistical test results showed significant differences ($p < 0.01$) between total dissolved solids (TDS) for every site pairing, except sites #2 and #4 ($p > 0.5$). TDS regimes at all sites displayed seasonality (see below), with maximum concentrations observed during winter months (i.e., 12/8/2012 for sites #1 and #2, 1/29/2014, 2/1/2014, and 1/7/2013 for sites #3, #4, and #5, respectively), and minimum concentrations observed following low-intensity summer precipitation events (i.e., 8/6/2011 for sites #1, #2, and #3, and 8/8/2011 and 8/7/2011 for sites #4 and #5, respectively) (Figure 4). Highest average, median (i.e., with site #2), maximum, minimum, and standard deviation of TDS were observed at site #3 (i.e., mixed-use urban). Whereas lowest average, median, maximum, and standard deviation of TDS were observed at site #1, the lowest minimum was observed at site #5 (Table 4). Given watershed land use characteristics, increasing TDS from site #1 (agriculture) to #3 (mixed-use urban) could be related to an increase in urban land cover (Table 1). Interestingly, the general spatial rend of TDS (i.e., increasing from site #1 to #3, and decreasing from site #3 to #5), contrasts with that reported by Zeiger and Hubbart [24], who noted an opposite spatial trend (i.e., *decreasing* from site #1 to #3, and *increasing* from site #3 to #5) for suspended sediment concentrations in Hinkson Creek. The decrease in TDS concentration from site #3 (mixed-use urban) to #5 (suburban), also contrasts with results of works from separate mixed-land-use watersheds [10,14], which reported increasing solute concentrations in the downstream direction. The decreasing spatial trend coupled with streamflow results (Table 3), may suggest the contribution of dilution processes to the physiochemical regime of Hinkson Creek below site #3. While dilution processes may only be “masking” water quality degradation in the lower watershed (e.g., increased loading despite decreased concentration), results nonetheless indicate attenuation of relatively high TDS observed at site #3.

Statistical analyses indicated significant differences ($p < 0.01$) between pH for every site pairing. Highest average, median, and minimum pH were observed at site #3, while the highest maximum value was observed at site #1 (Table 4). Average, median, and maximum values indicate alkaline water at each monitoring site. However, minimum values indicate the irregular occurrence of slightly acidic conditions. Importantly, pH maximums at each site exceeded the water quality standard of 9.0 established by the Missouri Department of Natural Resources [47]. Likewise, pH minimums at sites #1 and #2 exceeded the recommended minimum of 6.5, a threshold also approached by sites #4 and #5 [47]. However, maximum and minimum pH thresholds were only exceeded a few times during the study (Figure 5). Similar to TDS, pH regimes displayed seasonality at each site, with higher values during the winter, and lowest values observed during late summer/early fall. Moreover, the spatial trend of average and median pH was similar to that of TDS, with increasing values from site #1 to #3, and decreasing values from site #3 to #5.

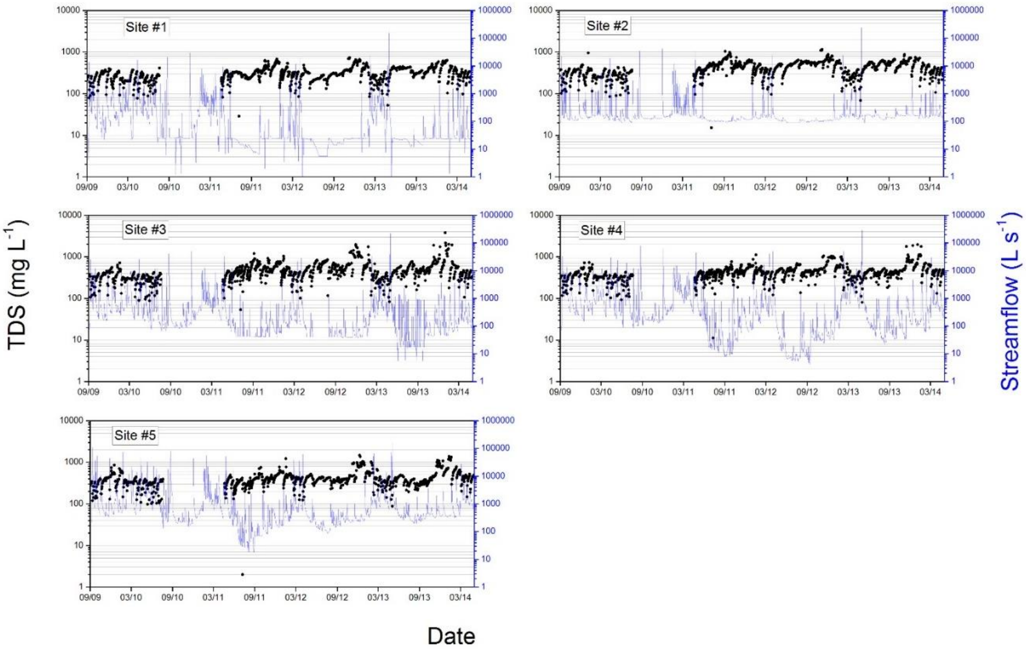

Figure 4. Total dissolved solids (TDS) (mg L^{-1}) and streamflow (L s^{-1}) at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA.

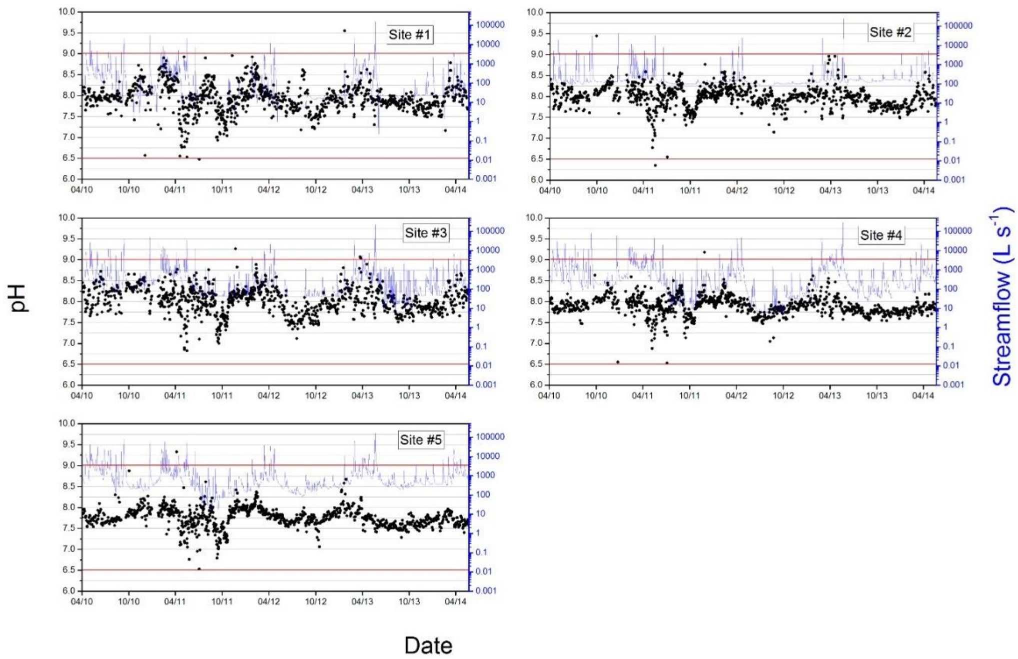

Figure 5. pH and streamflow (L s^{-1}) at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA. Red lines depict minimum and maximum thresholds established by Missouri Department of Natural Resources.

Statistical test results showed significant differences ($p < 0.01$) between dissolved oxygen (DO) for every site pairing. Highest average, and median DO were observed at site #3, as was lowest minimum. However, maximum DO was observed at site #1 (Table 4). DO descriptive statistics displayed a similar spatial trend as TDS and pH, with average and median values increasing from site #1 to #3, and decreasing from site #3 to #5 (Figures 6 and 7). Furthermore, DO displayed a similar seasonality at each site, with higher values during the winter, and lower values during late summer/early fall. Notably, DO measurements at all monitoring sites frequently exceeded water quality standards (i.e., minimum = 60% of saturation, maximum = 125% of saturation) established by the Missouri Department of Natural Resources [47,48]. DO observations were below the recommended minimum a total of 153, 46, 65, 51, and 121 times at sites #1–5, respectively. Likewise, DO observations exceeded the recommended maximum a total of 204, 290, 331, 221, and 137 times at sites #1–5, respectively. Therefore, over the course of the study, stream conditions were observed in excess of established DO-related water quality standards on 35, 33, 38, 26, and 25% of days at sites #1–5, respectively, or 31% on average. Thus, results suggest the potential for DO-related stress on aquatic biota in Hinkson Creek. Specifically, results indicate a high frequency of hypoxic conditions at sites #1 and #5, and a high frequency of super-saturated conditions at sites #2–4. It is notable that site #1 displayed such a high frequency of DO standard exceedance, given less development in sub-watershed #1 relative to other sites (Table 1). However, the sub-watershed includes 36% forested land cover and approximately 60% agricultural land uses. Agricultural land uses have previously been shown to negatively impact DO regimes and alter stream metabolism via nutrient loading, hydrological alteration, and riparian canopy reduction [20,49,50]. A previous work conducted in HCW [50] reported significantly ($p < 0.01$) higher nutrient concentrations (i.e., nitrate, ammonia, total inorganic nitrogen, and total phosphorus) at site #1 relative to all other sites. Thus, given observed DO trends, results of the current work suggest that agriculture-induced water quality degradation in the headwaters catchment are propagating downstream in Hinkson Creek. Given the spatial extent of DO issues in Hinkson Creek, results should challenge common expectations regarding the success of de-listing efforts in this and similar systems, and investments aimed at restoring contemporary mixed-use watersheds to fully-supportive aquatic ecosystems.

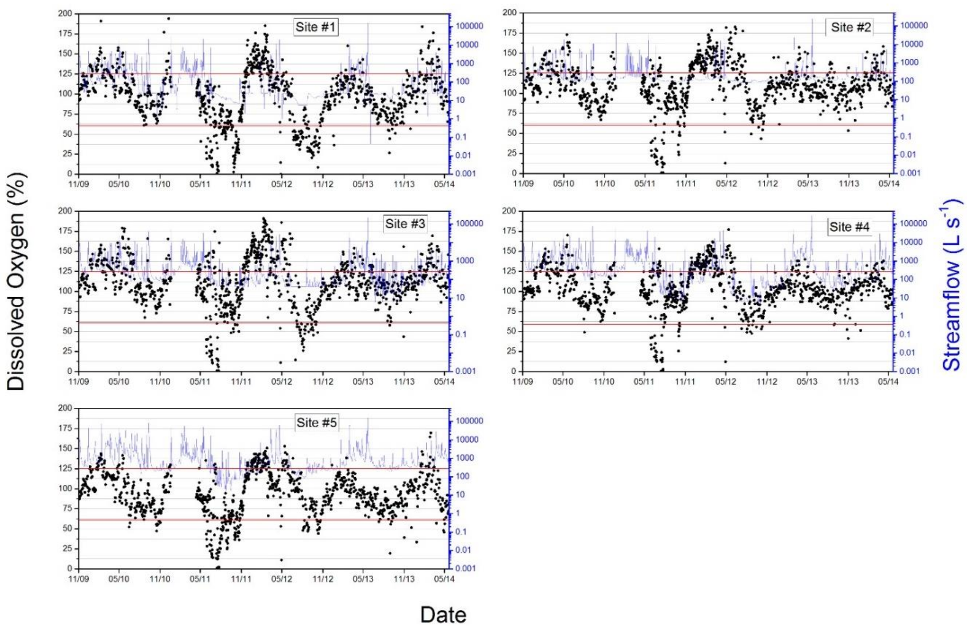

Figure 6. Dissolved oxygen (% of saturation) and streamflow (L s^{-1}) at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA. Red lines depict minimum and maximum thresholds established by Missouri Department of Natural Resources.

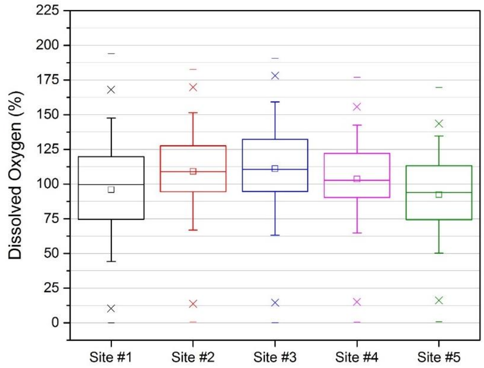

Figure 7. Box and whisker plot of dissolved oxygen (% of saturation) at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA. Boxes delineate 25–75 percentiles. Whiskers delineate standard deviation. Squares within boxes indicate means, lines show medians. X's indicate 99th percentile when above, 1st when below. Minus symbols indicate maximum when above, minimum when below.

3.2. Physiochemical Parameter Seasonality and Correlation Results

Among the four parameters studied, correlations were strongest between DO and water temperature, an expected result given the established functional relationship of the two variables [51]. Spearman correlation coefficient (SCC) values were –0.77, –0.78, –0.78, –0.82, and –0.78 for sites #1–5, respectively; and each site displayed a statistically significant ($p < 0.05$) relationship. Results for DO and TDS were more varied, with statistically significant ($p < 0.05$) positive relationships identified at sites #1 (SCC = 0.35), #3 (SCC = 0.17), #4 (SCC = 0.38), and #5 (SCC = 0.54). Statistically significant ($p < 0.05$) positive relationships were found between DO and pH at all sites, with SCC values equal to 0.40, 0.32, 0.45, 0.45, and 0.60, for sites #1–5, respectively. Negative relationships between TDS and water temperature were significant ($p < 0.05$) at all sites, with SCC values equal to –0.37, –0.24, –0.37, –0.45, and –0.54, for sites #1–5, respectively.

Physiochemical parameters displayed contrasting relationships with streamflow (Table 5). For example, statistically significant correlations ($p < 0.05$) were identified between DO and streamflow at every site, with SCC values equal to 0.54, 0.27, 0.30, 0.31, and 0.19, for sites #1–5, respectively. Likewise, Tw and TDS showed significant relationships with streamflow at every site. However, SCC values were lower than 0.6 for every pairing, indicating relatively weak relationships. Significant relationships were only observed between pH and streamflow at sites #1 and #4. Collectively, the weakness of SCC values suggests streamflow has a limited influence on physiochemical temporal variability.

Table 5. Spearman correlation coefficients for relationships between stream physiochemical parameters and daily average streamflow at each gauging site (n = 5) during study period (October 2010–May 2014) in Hinkson Creek Watershed, MO, USA.

Site #	Tw	TDS	pH	DO
1	–0.29 *	–0.09 *	0.24 *	0.54 *
2	–0.24 *	–0.51 *	0.02	0.27 *
3	–0.12 *	–0.45 *	–0.05	0.30 *
4	–0.23 *	–0.41 *	0.25 *	0.31 *
5	–0.15 *	–0.17 *	0.01	0.19 *

Tw = water temperature; TDS = total dissolved solids; DO = dissolved oxygen; * = statistically significant ($p < 0.05$).

Results indicated seasonal trends for each of the four physiochemical parameters studied (Figure 8). For example, when comparing observations from the cold (i.e., November–April) and warm (i.e., May–October) seasons, five-site-median TDS was 9% greater during the cold season. Similarly, five-site-median pH was 2% greater and five-site-median DO was 75% greater during the cold season than the warm season. The most obvious factor likely contributing to physiochemical parameter seasonality, both directly and indirectly, is air temperature, which displays the same sinusoidal annual trend as water temperature [52] (Figures 2 and 3). Given DO saturation is an inverse function of water temperature [51], the influence of air temperature can be understood to extend to DO regime. However, as illustrated by Figure 8, the DO temporal trend in Hinkson Creek does not cleanly follow that of water temperature. For example, while peak monthly median water temperature (e.g., median of all water temperature measurements conducted in every January of the study) was observed at all sites in July, DO monthly median minimums were not observed until September or October, suggesting a time lag of 2–3 months. Instead, the general DO temporal trend appears to track that of pH more closely.

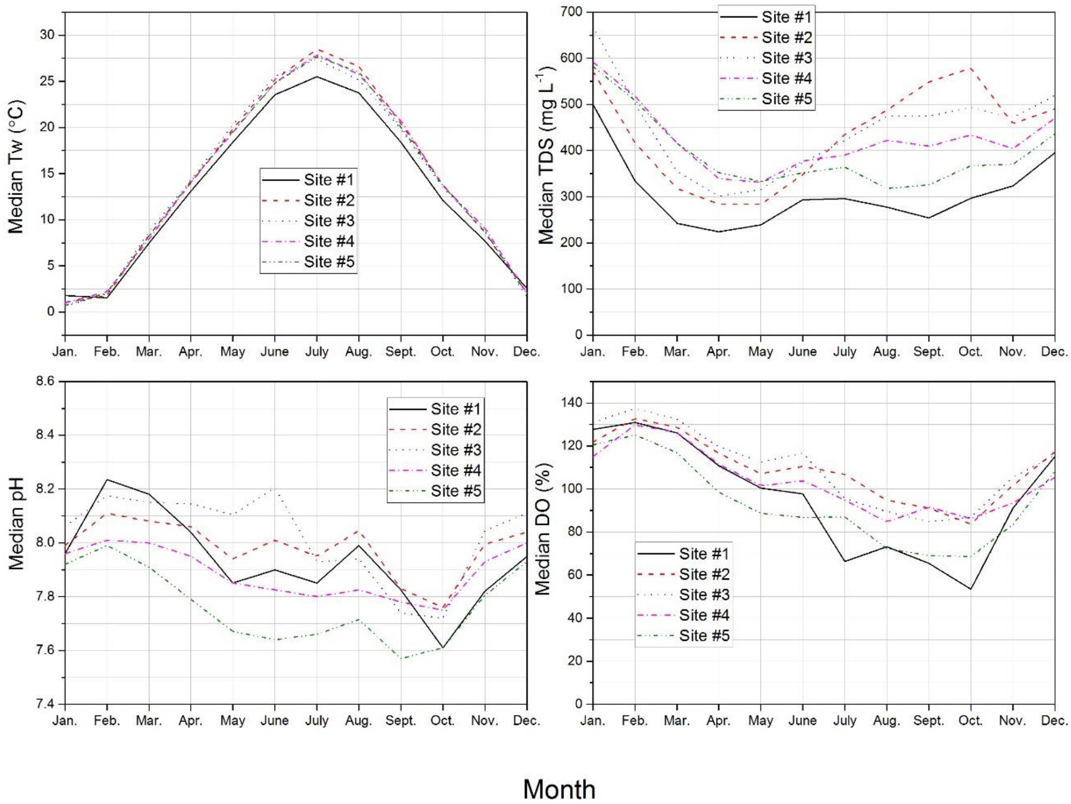

Figure 8. Median monthly water temperature (Tw) (°C), total dissolved solids (TDS) (mg L^{-1}), pH, and dissolved oxygen (%) at each gauging site (n = 5) during study period (October. 2010–May 2014) in Hinkson Creek Watershed, MO, USA.

Higher pH and TDS during the cold season is reasonable given the widespread practice of road salt application in HCW during the cold season. Hubbart et al. [43] reported acutely (i.e., >860 mg L^{-1}) and chronically (i.e., > 230 mg L^{-1}) toxic chloride concentrations in Hinkson Creek, positively related to urban land use, with seasonal peaks during late winter/early spring melting periods, attributable to road salt application. However, the practice does not explain subsequent peaks in summer and fall for pH and TDS, respectively, or the decrease in pH observed at all sites during October (Figure 8). Rather, pH, TDS, and DO appear to variably track the growing season, which extends from April to October in central Missouri. Several mechanisms could explain such observed trends. For example, terrestrial and aquatic primary productivity could contribute to increasing TDS during the growing season (Figure 8) via continuous loading of detritus, which could compose a substantial fraction of TDS. Likewise, leaf-off typically occurs during October and November, and the mineralization of organic matter is understood to lower in-stream pH by contributing acidic compounds to the water column [53], thus positively influence TDS and negatively influence DO concentrations. Furthermore, in-stream autotrophic photosynthesis is known to positively impact both DO and pH; the former through addition of oxygen to the water column, and the latter via consumption of CO_2, which in turn can lead to dissociation of bicarbonate molecules to fulfill in-stream carbon equilibrium [54]. Autotrophic photosynthesis has been cited previously as a factor contributing to DO and pH diel cycles [15,54,55], but results of the current work suggest the influence of the process on seasonal cycles as well.

Correlation results supply additional evidence regarding mechanisms potentially contributing to observed physiochemical regime. For example, the significant, negative relationships between TDS and water temperature at each site is likely attributable to the processes discussed above, namely road salt application [43] and organic detritus loading (e.g., mineralization of leaf litter), that contribute to consistently higher TDS during the cold season. However, variable TDS/DO relationships are likely the result of covariation with water temperature. Given the practice of road salt application, the same could be true of pH/DO relationships. To investigate whether significant, positive relationships between pH and DO were merely a result of covariation with water temperature, pH observations corresponding (i.e., sampling date/time) to observations of DO super-saturation (i.e., >125%) were compared to those corresponding to hypoxic conditions (DO < 60%). Mann Whitney test results indicated significant differences ($p < 0.05$) at each monitoring site, with median super-saturation pH measurements (avg. = 8.1) higher than median hypoxia pH measurements (avg. = 7.8). However, more importantly, results of seasonal analyses indicated super-saturation and hypoxia observations occurred during both the warm and cold seasons (Figure 6), thus suggesting the influence of a factor other than water temperature. As previously discussed, a likely explanation is in-stream vegetation processes (e.g., autotrophic photosynthesis), which could help explain covariation of DO and pH. Furthermore, recent studies have noted that autotrophic photosynthesis can continue throughout the warm and cold seasons in temperate streams [56–60], thus contributing to super-saturation observations in both seasons. The current work did not include investigation of stream metabolic processes, thereby providing direction for future mechanistic studies. Collectively, results highlight the interacting and competing influences of natural (e.g., climate, vegetation) and anthropogenic (e.g., road salt application) factors on the physiochemical regime of Hinkson Creek.

Correlation results did not indicate statistically significant relationships between physiochemical parameters and LULC metrics (e.g., percentage agriculture, urban, or forest cover). However, the result is to be expected given only five monitoring sites (i.e., five pairs of correlation data points) were included in the study design. Regardless, relationships merit reporting. For example, study median pH displayed a relatively strong, positive relationship (SCC = 0.70) with cumulative watershed (i.e., upstream) percentage forest cover, a reasonable result given the negative impact of leaf litter on stream pH [53]. However, DO displayed poor relationships (i.e., $R^2 \leq 0.5$) with all LULC metrics, illustrating the complicated set of factors influencing DO regimes.

3.3. Multivariate DO Modeling

Given statistically significant ($p < 0.05$) correlation results, physiochemical parameter data were used to construct multivariate DO models for each monitoring site (Table 6). Models produced generally good DO estimates, with R^2 (i.e., actual vs. predicted DO) values of approximately 0.7 and Normalized Root Mean Squared Error (NRMSE) values ranging from 21–28%. Model fit was optimized by including all four potentially contributing factors (i.e., water temperature, pH, TDS, and flow) for sites #2, #3, and #5. The optimal model for site #1 did not include flow, while the optimal model for site #4 did not include TDS. However, it is important to note that for all sites, including TDS and/or flow in models only marginally improved R^2 and NRMSE values. For example, R^2 values for DO models utilizing just water temperature and pH as independent variables were 0.71, 0.70, 0.74, 0.71, and 0.73 for sites #1–5, respectively, nearly equal to optimized model values reported in Table 6. Similarly, NRMSE values for the two factor models were 28, 21, 22, 21, and 24% for sites #1–5, respectively, equal to those for the four factor models. Notably, inclusion of pH improved model performance, as compared to a one factor water temperature model. R^2 values for DO models utilizing only water temperature were 0.60, 0.60, 0.61, 0.66, and 0.65 for sites #1–5, respectively; and NRMSE values were 33, 24, 27, 22, and 27% for sites #1–5, respectively. Therefore, despite improvements of model performance by inclusion of TDS and/or flow, results indicate a simplified two factor model (i.e., water temperature and pH) is capable of producing similarly accurate DO estimates.

Table 6. Predictive dissolved oxygen (DO) (mg L^{-1}) models and performance statistics (n = 766) for each gauging site in Hinkson Creek Watershed, MO, USA.

Site #	y-Int.	Tw	pH	TDS	Flow	R^2	NRMSE (%)
1	–28.36	–0.44	5.48	3.87	n/a	0.72	28
2	–23.97	–0.37	5.22	–1.31	3.66×10^{-6}	0.70	21
3	–27.35	–0.41	5.66	–0.32	6.47×10^{-6}	0.74	22
4	–17.46	–0.34	4.24	n/a	-2.82×10^{-6}	0.71	21
5	–30.53	–0.31	5.66	2.62×10^{-3}	1.21×10^{-5}	0.74	24

3.4. Study Implications

Collectively, results highlight the interacting and competing influences of natural and anthropogenic factors on the physiochemical regime of contemporary mixed-land-use watersheds. For example, observed TDS, pH, and DO regimes suggest road salt application, seasonal detritus loading, and in-stream autotrophic photosynthesis as likely driving forces. Considering high TDS, pH, and water temperature, and the highest frequency of DO criteria exceedance, results indicate sub-watershed #3 (mixed-use urban) is specifically prone to poor water quality (Table 4). Spatial trends of water quality and streamflow data suggest site #3 is a problematic location (i.e., stream reach/sub-watershed), where water quality issues (e.g., TDS) are accumulating from upstream, but where streamflow is insufficient to attenuate land use impacts, as is likely the case for sub-watersheds #4 and #5 (suburban). Results complement those of Hubbart et al. [43], who reported a high frequency of observed acute and chronic chloride toxicity in sub-watershed #3, attributable to road salt application. Moreover, DO spatial trends suggest the possibility that agriculture-driven water quality degradation in the headwaters catchment is propagating downstream. When considered in the context of findings from the current work, results pose serious questions regarding the feasibility of urban stream restoration. For example, barring a complete reorganization of the HCW landscape, and the discontinuation of public safety practices (e.g., road salt application), work such as that presented here should bring to question whether mid-watershed reaches of Hinkson Creek (or other physiographically similar watersheds) can be restored to a fully-supportive aquatic ecosystem, given the complex set of interacting natural and anthropogenic factors influencing the water quality regime. Furthermore, results illustrate the complicated nature of water quality regimes in mixed-land-use watersheds and illustrate the number of natural and anthropogenic factors that must be accounted for in order to maximize efficacy of management and restoration efforts. Such questions and issues must be duly considered by managers, stakeholders, and regulatory agencies in order to realistically improve the 303(d) listing process and more effectively steward natural and financial resources.

The experimental watershed method is a globally transferrable model that can be adopted by urban communities to guide current and future resource management practices, better target locations for remediation efforts, and evaluate the long-term efficacy and outcomes of management strategies. For example, in the current work, application of the method effectively identified problematic regions within the watershed (e.g., sub-watershed #3) that should be targeted for subsequent mitigation efforts, or barring the ability to successfully restore the reach, should be considered for 303(d) de- or re-listing. Bracketing stream reaches during assessment can enable managers and stakeholders to more effectively target water quality remediation investments within the watershed, thereby improving outcome success of ongoing management efforts.

Results of the current work indicate that in a contemporary, urbanizing watershed of the temperate U.S., a simple two factor model utilizing water temperature and pH can generate reliable DO estimates. While previous studies have established that DO regimes are variably influenced by additional physiochemical (e.g., TDS, streamflow, solar radiation budgets) and biochemical (e.g., in-stream photosynthesis/respiration) parameters, direct measurement of such factors can be expensive and time intensive. Thus, a more simplified approach incorporating fewer observed data, could provide scientists and practitioners with a useful site-specific option to improve the prediction, and thereby the management, of DO regimes versus traditional water temperature models. However, evaluation of the transferability of the modeling method will require similar work to be conducted in physiographically contrasting regions.

4. Summary and Conclusions

Improving understanding of stream physiochemical regimes in contemporary watersheds is vital in order to accurately predict and evaluate water quality degradation resulting from anthropogenic pressures [26]. A nested-scale experimental watershed study was implemented in the central U.S. to quantitatively describe spatiotemporal variation of in-stream physiochemical parameters, including total dissolved solids (TDS), water temperature, pH, and dissolved oxygen (DO), in a contemporary developed watershed. Hinkson Creek Watershed (HCW) (233 km^2) was instrumented with five gauging sites ($n = 5$), partitioning the catchment into five sub-watersheds, characterized by different dominant land use types. Data were collected four days per week for the duration of the study period (October 2010–May 2014) at each gauging site, using a handheld multi-parameter sonde. Predictive dissolved oxygen models were generated for each site based on observed physiochemical data (i.e., water temperature, pH, TDS, and streamflow).

Hydroclimate statistics for Hinkson Creek Watershed during the study period described a highly variable regime, as illustrated by differences between low flows and high flows at all gauging sites comprising approximately five orders of magnitude (i.e., 0.001–100.00 $m^3\ s^{-1}$). Statistical test results indicated significant differences ($p < 0.05$) between nearly every monitoring site pairing for each physiochemical parameter. Water temperatures tracked air temperatures, with highs and lows observed during the summers and winters, respectively. Notably, maximum temperatures at sites #2 and #3 exceeded the recommended regional (32.2 °C). As opposed to a consistent spatial trend (e.g., increasing or decreasing), water temperature regimes in HCW are apparently characterized by a threshold/step-change condition, with an upshifted and more variable regime incident at site #2, likely attributable to the impacts of urban land uses. TDS, pH, and DO displayed similar spatiotemporal trends, with increasing median concentrations from the predominately agricultural upper watershed to the mixed-use urban middle watershed, and decreasing median concentrations from the middle watershed to the predominately suburban lower watershed. The decreasing average concentration trend coupled with increasing volumetric streamflow, suggests the contribution of dilution processes to the physiochemical regime in the lower watershed. Over the course of the study, DO concentrations exceeded established water quality standards on an average of 31% of observation days, suggesting DO-related stress on aquatic biota in Hinkson Creek. Results showed seasonal trends for each physiochemical parameter, with higher TDS, pH, and DO during the cold season (i.e., November–April) than the warm season (i.e., May–October). Modeling results emphasize the importance of pH to DO regime in temperate multiple-use watersheds, and demonstrate the utility of a simple two factor model (i.e., water temperature and pH) in accurately predicting DO.

Collectively, results highlight the interacting and competing influences of natural and anthropogenic factors on the physiochemical regime of multiple-use watersheds. The experimental watershed method facilitated the isolation of critical areas of the watershed (e.g., site #3), and identified potential mechanisms (e.g., autotrophic photosynthesis, organic detritus loading, road salt application) contributing to the observed physiochemical regime. The results hold important information and suggest useful tools for land and water resource managers working to mitigate the impact of anthropogenic landscape pressures on water quality regimes of contemporary, mixed-land-use watersheds.

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