

THE DIURNAL PATTERN OF DISSOLVED OXYGEN CONTENT IN NATURAL VS. ALTERED STREAMS IN THE DOG RIVER WATERSHED

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The quantity of dissolved oxygen (DO) within a stream oscillates throughout the day due to diurnal photosynthetic and evaporative processes. Although studies involving the diurnal pattern of DO have been performed, there are very few that approach the issue from the perspective of an urban watershed. By examining the diurnal pattern of DO, it is possible to discern whether DO levels ever reach a critically low value such that asphyxiation of aquatic life occurs. In this paper, I quantitatively measure DO levels every two hours from three different types of streams found within the Dog River Watershed (an unaltered stream, an altered non-spring-fed stream, and an altered spring-fed stream) in order to determine the daily deviation of DO due to diurnal effects. Dissolved oxygen samples were taken on a mostly sunny, warm day in early April within a few days of a decent rainfall (>0.5 inches). Nonparametric statistical tests applied to the data show that the average level of DO differs between the altered and non-altered streams, but not between the spring-fed and non-spring-fed streams. The results of the statistical tests also show that there is a statistically significant difference in the daytime average DO level and the nighttime average DO level in all three streams. In addition, the data confirm that DO levels temporarily fall below that which is required for life in both altered streams during the late morning hours due to diurnal effects, but not in the unaltered stream.

Keyword: dissolved oxygen, diurnal pattern, nonparametric statistics

Introduction

Continuing urbanization in the Dog River watershed brings a plethora of negative effects to the watershed. One of the most critical, but often most overlooked, effects is that on water quality itself. In particular, aquatic life finds it increasingly difficult to survive within the streams of a watershed that is undergoing rapid and ongoing urban development. The survivability of aquatic life in such a stream depends, among other factors such as pH and temperature, on the dissolved oxygen available in the water. It is a well-known fact that urbanization and development of a watershed affects the amount of dissolved oxygen available in the streams flowing through it (Kaushal et al. 2008; Alabaster 1959; Mitchell 2009; Mallin 2006). Many of the studies of urban stream development tend to focus on the denitrification within the streams, rather than on the effects of the dissolved oxygen (Kaushal et al. 2008; Boyer et al. 2006). In addition, most of the studies concerning the dissolved oxygen in a stream focus on rural, upland streams, rather than on low-lying urban streams (Schurr, Ruchti 1977; Laurie 1942).

Finally, there is a shortage of studies that relate the dissolved oxygen in a stream to a diurnal cycle. Only one such study was found, which studied both dissolved oxygen and carbon dioxide in alpine streams in central Europe (Schurr, Ruchti 1977). As such, the effects of the diurnal cycle coupled with urban pressure on the dissolved oxygen in a stream are not well-known.

Although daily, weekly, or monthly averages may show that there is a sufficient amount of dissolved oxygen in the streams of the Dog River watershed to support aquatic life, it is unknown whether the diurnal cycle causes sufficient change in the dissolved oxygen levels to temporarily cripple the survivability of aquatic life. In order to determine the extent to which this might be an issue, the study considers a natural (or nearly natural) stream, an altered spring-fed stream, and an altered non-spring-fed stream. The results of the study help to determine whether engineering methods need to be employed to improve the quantity of dissolved oxygen to a level which is adequate for the sustenance of aquatic life.

Study Area

The observations took place within the Dog River watershed, which drains most of metropolitan Mobile, Alabama. Specifically, observations were taken at three locations along US Highway 90 (Government St.); one at Hall's Mill Creek, one at Spring Creek, and one at Moore Creek. These locations are shown below on the map (Figure 1), with the study area locations marked by white circles.

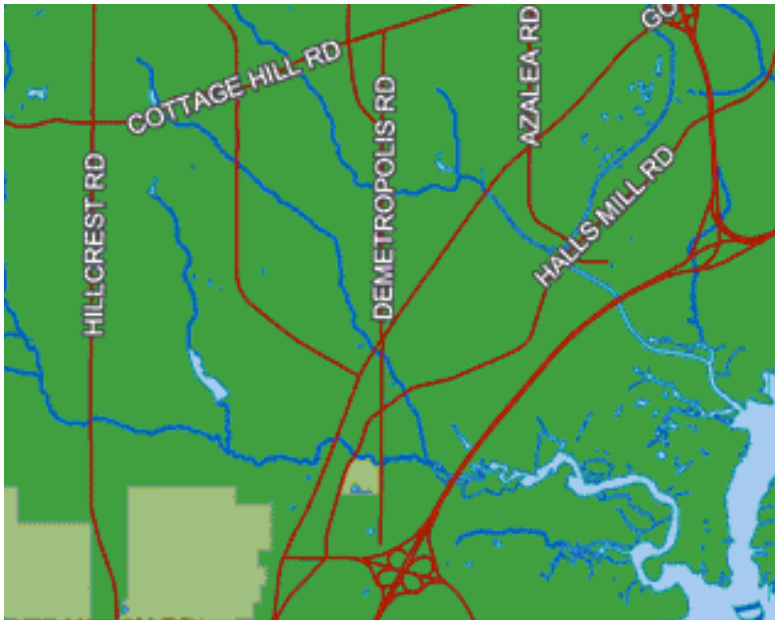


Figure 1: Map of the study area with the sampling locations shown by the white circles (Pritchard 2010).

Research Question

To what extent does the diurnal cycle affect the level of dissolved oxygen in the various types of streams found in the Dog River Watershed? Are there statistically significant differences among averages for various times of day for a particular stream? Are there statistically significant differences among averages for different types of streams?

Method

Water samples were collected from three different streams in the Dog River watershed. Halls Mill Creek is used as an example of a near-natural stream; Spring Creek is used as an example of an altered, spring-fed stream; and Moore Creek is used as an example of an altered, non-spring-fed stream. Water samples were collected at a single location from each of the three above streams; however, the sample was collected such that the portions of their respective watersheds upstream from the sampling site are not only ideally representative of the type of stream being tested (natural, altered, etc.), but also are of similar areal coverage so that statistical tests provide the greatest degree of confidence.

Water quality samples were fixed and tested for dissolved oxygen content per Alabama Water Watch Association Protocol. This involved collecting two samples simultaneously from a given stream. A LaMotte water sampler was lowered into the center of the stream so that it was submerged completely. When full, the sampler was closed off and withdrawn from the stream. A rubber hose from the sampler was inserted into an open sample bottle, which was then allowed to fill to overflowing while slowly removing the rubber tube, so that no air bubbles would be present in the sample. The sample bottles were then capped. Eight (8) drops of Manganous Sulfate were added to each of the two samples, followed immediately by eight (8) drops of Alkaline Potassium Iodide Azide. The bottles were then recapped and inverted 8 times to allow a solid, tan precipitate to form. After allowing the precipitate to settle slightly (below shoulder level of the bottle), 8 drops of concentrated sulfuric acid were added. This fixed the oxygen in the sample and dissolves the tan solid, although the mixture in the bottle maintains a color from deep amber to pale yellow, depending on the amount of dissolved oxygen

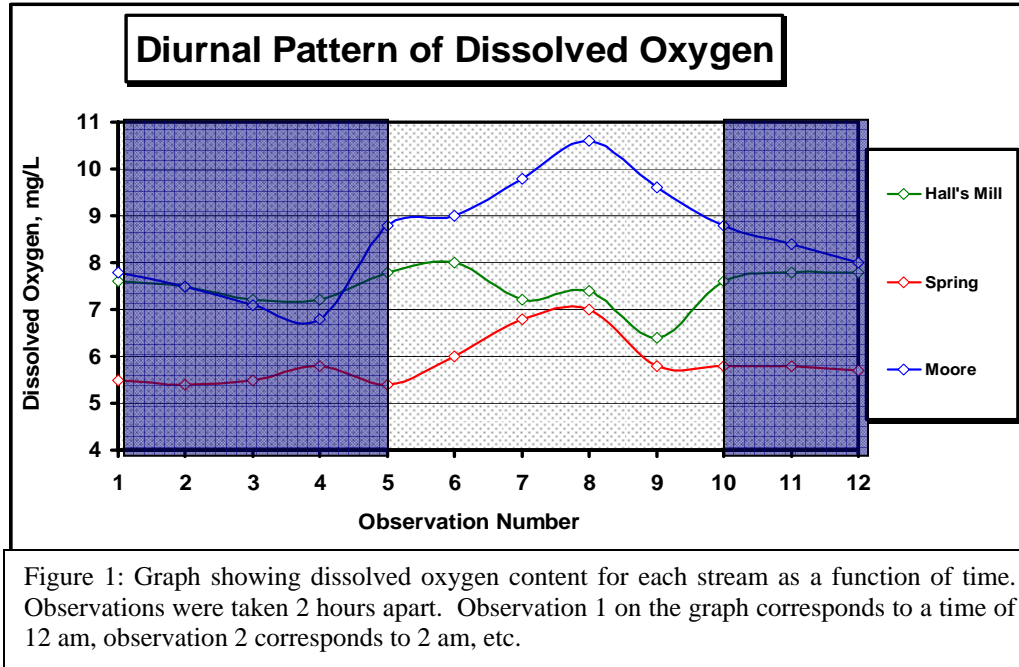
present. Next, twenty (20) mL of the sample were poured into a titration container, to which eight (8) drops of starch were added, which turned the mixture an opaque, dark blue color. The resulting mixture was then titrated with a solution of sodium thiosulfate. Once titration was complete, the mixture in the titration container became clear and colorless, at which point the titration was complete. The amount of dissolved oxygen in the sample was determined by the amount of sodium thiosulfate required to completely titrate the water sample. The process was repeated with the other sample, and the resulting levels of dissolved oxygen had to be within 0.6 units of one another in order for the result to be valid.

Water samples were obtained from each of the three streams once every two hours, for a continuous 24-hour period, which ensured an adequate representation of the diurnal cycle. Due to safety concerns, Geography major Matt Lewis and University of South Alabama senior Mindy Lepre were present overnight and assisted in the measurements of air temperature and water temperature for various observation times.

Once the data had been collected, the concentrations of dissolved oxygen were plotted on graphs with dissolved oxygen as the ordinate and time of day on the abscissa in order to determine the diurnal cycle of dissolved oxygen. Finally, non-parametric statistical tests were applied to the data to statistically test for differences in dissolved oxygen concentrations both for differing streams and for times of day.

Results

Analysis of the dissolved oxygen amounts in the streams showed that the amount of dissolved oxygen changes throughout the day. The graph of dissolved oxygen content for each of the streams throughout the day is shown in Figure 2. An interesting feature of the graph on the preceding page is that the amount of dissolved oxygen in both Moore Creek and Spring Creek (both altered streams) peaked at the same time during the day—2 pm. At this time, not only is photosynthetic activity at its peak, but so is water temperature due to daily heating. The implications of this will be discussed shortly. On the other hand, Hall's Mill Creek shows an interesting bimodal or nearly trimodal peak in dissolved oxygen amount, with peaks occurring at 10 am and 8 pm, with a lesser peak at 2 pm. The cause of this bimodal peak is unknown.



A graph of the total dissolved oxygen saturation, which is dependent on water temperature, essentially is a copy of the graph in Figure 1. However, results reveal that the dissolved oxygen saturation amount did not drop below 60% for any of the streams tested during this 24-hour period. Dissolved oxygen saturation amounts ranged from 60% to 95% for both Hall's Mill Creek and Spring Creek during the 24-hour period, with higher saturation percentages occurring during the early and middle parts of the afternoon. On the contrary, Moore Creek was frequently supersaturated with respect to dissolved oxygen; the data reveal that Moore Creek was supersaturated from 8 am until shortly before 10 pm. This result was surprising, given that at the observation location Moore Creek occupies a concrete stream bed with no visible vegetation. Possible explanations include the fact that the water just upstream was tumbling over a break in the concrete stream bed, producing small amounts of turbulent flow and splashing that might have mixed more oxygen into the water; a higher water temperature overall, due to the fact that the water at the location was only approximately 15 cm deep and was easily heated due to the concrete stream bed; and lack of aquatic life that may have otherwise been consuming the available dissolved oxygen for respiratory processes.

Two-sample t-tests were applied to the data to test statistically for any differences in the daily mean dissolved oxygen concentrations among the three streams, as well as

differences for each stream between day and night. The Minitab output of each comparison is shown below in Figure 3.

	Halls vs Spring	Halls vs Moore	Spring vs Moore
Estimate of Difference (mg/L)	1.583	-1.058	-2.642
95% Confidence Interval (mg/L)	(1.181, 1.985)	(-1.813, -0.304)	(-3.412, -1.871)
p-value	<0.0005	0.009	<0.0005
	Halls(D) vs Halls(N)	Spring(D) vs Spring(N)	Moore(D) vs Moore(N)
Estimate of Difference (mg/L)	-0.117	0.517	1.833
95% Confidence Interval (mg/L)	(-0.722, 0.489)	(-0.167, 1.200)	(0.982, 2.685)
p-value	0.663	0.11	0.001

Figure 3: Minitab output showing the results of t-tests, testing for differences in the mean dissolved oxygen concentration of each stream and for day/night differences for each stream.

These results show that the mean dissolved oxygen concentrations of each stream are significantly different from one another at the 95% confidence level. This is shown by the value of the p-value test statistic. All values of this test statistic are less than the critical value of $p=.05$ for the 95% confidence level. Thus, one can conclude that the amount of dissolved oxygen differs depending on stream type. The greatest difference occurred, surprisingly, between Spring Creek and Moore Creek, where the dissolved oxygen concentrations of each stream are estimated to differ by approximately 2.64 mg/L. The result is surprising because Spring Creek and Moore Creek are both altered streams, and the difference in their means is greater than the individual differences between their means and the mean dissolved oxygen concentration of Hall's Mill Creek, the unaltered stream. The results in the figure above show that there is no statistically significant difference (at the 95% confidence level) between the daytime and nighttime average dissolved oxygen concentrations in either Hall's Mill Creek or Spring Creek. However, the test shows that the daytime and nighttime mean dissolved oxygen concentrations in Moore Creek are significantly different at the 95% confidence level,

with the estimate for the difference being 1.833 mg/L. These conclusions are again drawn from the value of the test statistic, p . Since the tests are performed at the 95% confidence level, the critical value of p is once again 0.05. If the p -value is less than 0.05, then the data support the conclusion that the means are significantly different.

Finally, by measuring both the amount of dissolved oxygen and the water temperature, an estimate of the dissolved oxygen saturation percentage of the water was able to be calculated. The results were obtained by using a nomogram, which requires the use of a straight-edge to match water temperature and dissolved oxygen content to a bar representing the dissolved oxygen saturation percentage. The results are given in the graph in Figure 4 below.

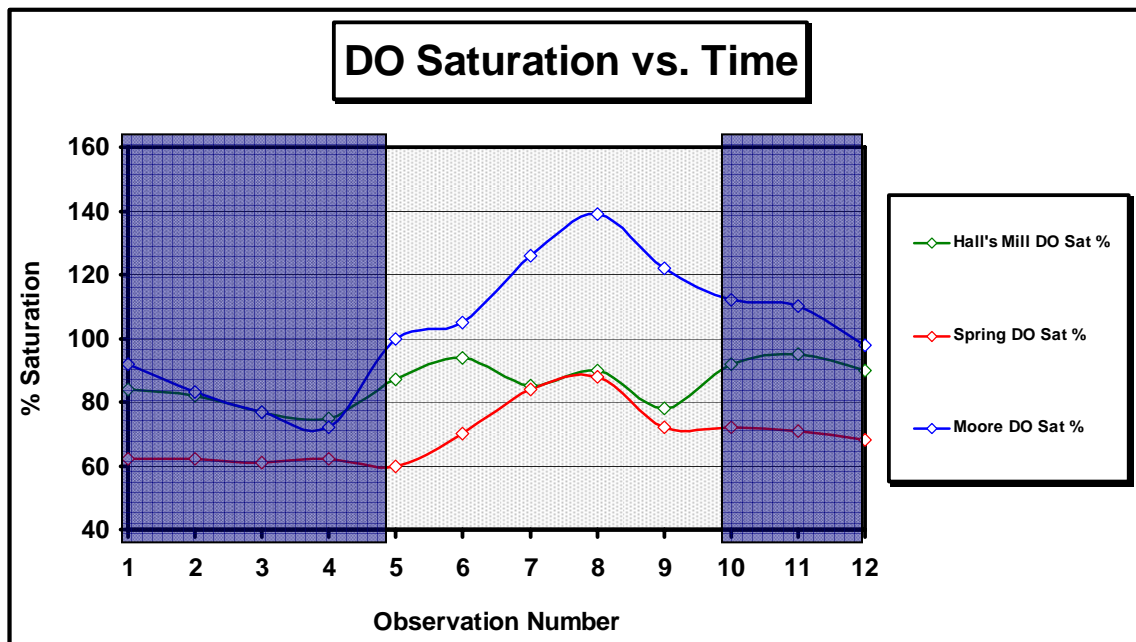


Figure 4: Excel chart showing how the dissolved oxygen saturation percentage changes with time of day for each of the three different streams.

Figure 4 shows that all of the streams were at least 60% saturated with oxygen during the entire day. The two interesting features of this graph are the afternoon/late evening dip in dissolved oxygen saturation for Hall's Mill Creek, and in the afternoon supersaturated values approaching 140% measured in Moore Creek. These features will be discussed and explained in the next section.

Discussion and Conclusion

The results of the study showed that there is some variation in dissolved oxygen levels among the three different streams that also depends on water temperature. The interpretation of the dissolved oxygen saturation results are little murkier, however. Research shows that a dissolved oxygen content of 5 mg/L is a critical point below which fish begin to die from oxygen starvation (Meck 1996). Although the dissolved oxygen saturation levels in Spring Creek exceed 60% for every observation, the actual quantity of dissolved oxygen approaches the critically low value of 5 mg/L in the early morning hours. The likely reason for this drop is that Spring Creek is fed by groundwater, which naturally has a very low amount of dissolved oxygen. Spring Creek is also a very slow-moving, stagnant stream, so there is minimal oxygen forcing into the water.

Also deserving mention are the supersaturated dissolved oxygen values recorded during the afternoon and early evening at Moore Creek. At this location, the stream was only approximately 8 cm deep, and the channel was concrete, which allowed for rapid heating of the water and hence a greater capacity for holding oxygen. Furthermore, an algal bloom was underway, which would sharply increase the dissolved oxygen values. Another possible factor is the fact that, upstream from the sampling location, Moore Creek spills over a couple of small dams and a waterfall, where oxygen from the air is forced into solution by hydraulic pressure. All of these factors likely contributed in part to the higher dissolved oxygen concentrations and supersaturated values in Moore Creek.

Finally, the drop in dissolved oxygen concentration in Hall's Mill during the afternoon merits brief discussion, as well. Unbeknownst to the author, a shower passed over the Hall's Mill watershed upstream of the sampling site during the late morning/early afternoon. This was verified by examining archived NOAA Doppler radar imagery from Mobile National Weather Service. Following a period of rainfall, dissolved oxygen levels temporarily drop. This drop is evident on the graphs showing the dissolved oxygen concentration and the dissolved oxygen saturation during the afternoon and early evening hours, as runoff enters the stream and travels downstream to the sampling site.

One of the shortcomings with the project is that only one run of data was completed. Due to a lack of ideal weather conditions (moderate drought), a second

sampling of data was impossible. A few afternoon observations were taken on a separate day at Moore Creek, but the results were discarded because the water level in Moore Creek was so shallow that the LaMotte water sampler could not be fully submerged. A second attempt at garnering a second set of data was attempted, but this was shortly after the heavy rain event on May 2, and the current was too swift in Hall's Mill to allow the LaMotte sampler to remain stationary long enough to fill and be withdrawn.

Further research needs to be performed to determine whether there is a seasonal change in the amount of dissolved oxygen, and if so, what extent that seasonal change has. It is also necessary to obtain data from two 24-hour periods that are within a week or so of each other, preferably after very similar weather conditions. This would help to minimize error, highlight true variations while masking false variations in data, and provide more solid results overall. Also, it is unknown whether the water temperatures cool sufficiently enough in the winter to drive the amount of dissolved oxygen to a critically low point at which aquatic life suffocates. Further research needs to be performed during the cooler months to determine the amount of dissolved oxygen in the three streams during that time of the year. It is important also to test different streams within the Dog River Watershed (Eslava Creek, Bolton Branch, etc.) to ascertain whether the dissolved oxygen levels are consistent across the watershed.

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