

Effects of salinization on DOC and NO₃ in an urban stream

Elizabeth G Erwin ¹

¹Affiliation not available

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Abstract

Salinization has become a widespread problem in freshwater sciences over the past decade in the United States. A rise in salt use from various anthropogenic sources, such as pot ash, road deicers, and fertilizer wastes, has caused an increase in salinity and alkalization levels of freshwater streams. Hydrologists commonly use salt tracers to determine discharge. Additionally, salt tracers can be added to other components to measure a variety of parameter responses. An example of this used in this study is the use of a salt tracer with a carbon slug composed of malt. By using a salt tracer scientists can utilize handheld conductivity probes to determine discharge, or trace a slug other wise invisible to the eye (i.e. carbon malt). However, little research has been done to determine the effects of salt tracers on stream water chemistry. The aim of this study was to determine if salt tracers have an impact on Dissolved Organic Carbon(DOC), Nitrate (NO₃) and/or if there is an effect on DOC:NO₃ ratios. This study took place in Stroubles Creek, an urban stream in Southwest Virginia.

Scientific Significance Statement

Salinization has become an increasingly large problem in aquatic sciences over the past decade due to enormous increases in salt amounts being used. Over use of salt has increased conductivity and alkalization in freshwater systems, which may have significant ecosystem impacts. However, little research has been conducted to determine the effects of increase salinization on stream water chemistry, specifically how increased conductivity affects DOC, NO₃, and DOC:NO₃ ratios. This study found evidence to suggest that increased conductivity in combination with increased carbon may have a statistically significant effect on DOC concentrations, which may suggest that DOC uptake in freshwater systems is increased with increased salinity.

Introduction

Salinization of freshwater streams is a growing phenomenon and concern in the majority of the U.S. Salinization occurs when an excess amount of salt is introduced into a stream. These introductions are primarily induced by anthropogenic activities such as, using road salts as deicers, brine waste from hydro fracturing, pot ash, and agricultural wastes. These are all known to cause prolonged unnaturally high levels of salinity when exposed to freshwater streams. These sources of the salinization are most often transported into stream networks by rain and snow melt.

To further add to the problem, a common technique to gauge discharge and measure other parameters responses, is by using a salt tracer. Using a salt tracer is a fairly easy and an accessible method for

many scientists to use and is well accepted in the academic world. However, there has been very little research on the effects of salinization in stream water chemistry from using this technique, and much less in relation with Dissolved Organic Carbon (DOC) and Nitrate (NO_3). DOC and NO_3 concentrations within a flowing network may have an impact on geochemical reactions, productivity of food webs, and microbial activity (including nutrient uptake and nutrient cycling)(Kaplan and Cory. 2016). Salinization can mobilize bioreactive elements including carbon and nitrogen due to ion exchange and through the influences of microbial activity (Duan and Kaushal 2015). Duan and Kaushal's results suggest that short term increases of salinization may cause an increase in DOC and nitrogen in urban watersheds (Duan and Kaushal 2015). When the stream was introduced with unnaturally occurring levels of salt, there was an increase in the release of DOC and sediment transformations of NO_3 (Duan and Kaushal 2015). However, the mechanisms that drive interactions between nitrogen uptake and Dissolved Organic Matter (DOM) are not well understood especially in surface waters (Rodríguez-cardona et al. 2015). DOC is a constituent of DOM and was the main parameter studied. Previous research has shown that ambient uptake velocity has a positive correlation with increasing DOC and DOC: NO_3 ratios (Rodríguez-cardona et al. 2015). In the study conducted by Rodríguez- Cardona et al., ambient NO_3 was unrelated to pH, light, temperature, dissolved oxygen, and specific ultraviolet absorbance at 254 nm. However, nothing in relation to specific conductivity was mentioned (Rodríguez-cardona et al. 2015). NO_3 uptake is mostly affected by DOC concentrations as opposed to NO_3 concentrations (Rodríguez-cardona et al. 2015). For nitrate, it is known that NO_3 concentrations increase with stream temperature and specific discharge while decreasing with catchment area (Jacobs et al. 2017). However, DOC concentrations increase with catchment area and precipitation and decrease with specific discharge (Jacobs et al. 2017).

The goal of this study was to assess how salinization affects DOC and NO_3 in urban streams. I predict that after injecting an urban stream with a salt tracer, DOC and NO_3 ratios will increase due to an increase in conductivity and mobilization of ions within the stream water. I predict to see an increase in DOC with an increase in specific conductance based what the data suggests from Duan and Kaushal, 2015. These predictions were informed by Duan and Kaushal (2015). Duan and Kaushal found evidence to suggest that salinization can mobilize bioreactive elements such as DOC and NO_3 (2015). Their results were indicative of increased sediment release of DOC into stream water with an increase in specific conductance (SC), and sediment transformations of NO_3 (Duan and Kaushal, 2015). In general, they found that increased SC resulted in a decrease of DOC in soils. This may suggest that the release of DOC is exported into the stream network, causing an increase in DOC levels in stream water. However, further research is necessary to identify DOC and NO_3 responses to SC in surface water. This question and hypotheses were addressed by: 1) collecting baseline conductive measurements at a specific site in Stroubles creek, Blacksburg, VA. 2) Performing 4salt slugs in Stroubles creek while collecting high resolution conductivity measurements, DOC and NO_3 measurements. 3) Analyzing data for changes in DOC and NO_3 levels during and shortly after the salt slug. In order to meet these objectives, the following methodology was used.

Methods

The sample sites were selected based on stream length, regular flow discharge, minimal possible upstream interactions, and accessibility. Stroubles Creek was the closest and most accessible urban stream in relation to Virginia Tech and served well for the purpose of this study. Stroubles creek is a urban stream that flows through the middle of Virginia Techs campus, with sections channelized underground. The specific study reach was picked to be below the Duck pond, which often helps to catch any influences from upstream urban activities. A total of four salt slugs were performed, two of which also included a carbon slug of malt extract. The first slug, conducted on February 21st, 2018 took place at Bridge 2 of the Stream Lab. The other three slugs took place approximately 500 meters below Bridge 2. This reach was more ideal as there were less pools for the tracers to settle in, and consisted of mostly riffles. Baseline conductivity levels were collected in two locations downstream from the slugging station prior to the addition of the salt slug. The background

conductivity data was collected using a conductivity probe, while background DOC and NO₃ levels were collected using a spectrolyser called the S::CAN. After background information was collected, we used the salt slug gauging method to collect DOC and NO₃ concentrations as a means to analyze any possible changes in result of the salt injection.

For the salt slug, stream water was collected in a 5 gallon bucket and 5 kg of salt was mixed thoroughly (Two slugs used 5 kg and two used 1 kgs of NaCl). While two people is mixed the salt, one person was stationed at the closest site, 25 m away from the slugging station. The next site was measured out 75 meters from the slugging station and this is where the S::CAN was located. The scan was set to record in 1 minute intervals during the entire study time and the conductivity loggers were set to record every second. Additionally grab samples were collected before the slug, and every 20 seconds after the slug arrived, and one was collected after the slug had passed so that a local calibration on the S::CAN could me made at a future date. After the samples had been collected, they were immediately transported to the Hotchkiss lab for filtering and storing.

A paired t test was used to determine statistical significant differences in the before and after salt injection data. R statistical software was used to preform the t tests. Further, the t test was set to have an alpha of 0.05, and a 95% confidence interval. Each day had it is own t test analysis, and one was for DOC differences before and after, and a second was run for NO₃ differences before and after injection (reference table 1).

Results

From the first slugging event on Feb 21st, there is a large variation in DOC and NO₃ values(figures 1 and 2). After running a paired t-test on the DOC and NO₃ values, the results were not significant, meaning the p-value was greater than .05 (table 1).

DATE	PARAMETERS	P VALUE	SIGNIFICANT
2018-02-21	DOC	0.57	
2018-03-23	DOC	0.48	
2018-03-28	DOC	0.0	Yes
2018-03-30	DOC	1.22e-06	Yes
2018-02-21	NO3	0.11	
2018-03-23	NO3	1.45e-09	Yes
2018-03-28	NO3	0.78	
2018-03-30	NO3	7.2e-08	Yes

Table 1: This is a summary of the p-values from a paired t test using R. The significance level was set at 0.05,. Any p-values less than 0.05 was considered significant.

March 23rd however, had more consistent DOC and NO₃ concentrations, but the NO₃ concentrations were decreasing before the salt injection. Further, the p-value for DOC was greater than .05, while the p-value for NO₃ was less than .05 (table 1). On March 28th, there was more consistency with the DOC and NO₃ values than on February 21st, however observed trends were not consistent across all three days. On March 28th, there appears to be a drop in DOC concentrations after the salt and malt injection. Further, the NO₃ concentrations remain relatively consistent before, during, and after the tracer (figure 2) . On the last day of testing, March 30th, there was a decrease in DOC values after the addition of the salt and malt tracer (figure 1). Additionally, the NO₃ values appeared to drop in concentration after the injection, but began to return to base conditions by the end of the experiment (figure 2). March 30th was the only day where the p-values were significant for both DOC and NO₃ concentrations (table 1). For the DOC:NO₃ ratios, no

pattern was observed, but there was more variation in the values on February 21st and March 23rd than the later two dates of experimenting (figure 3).

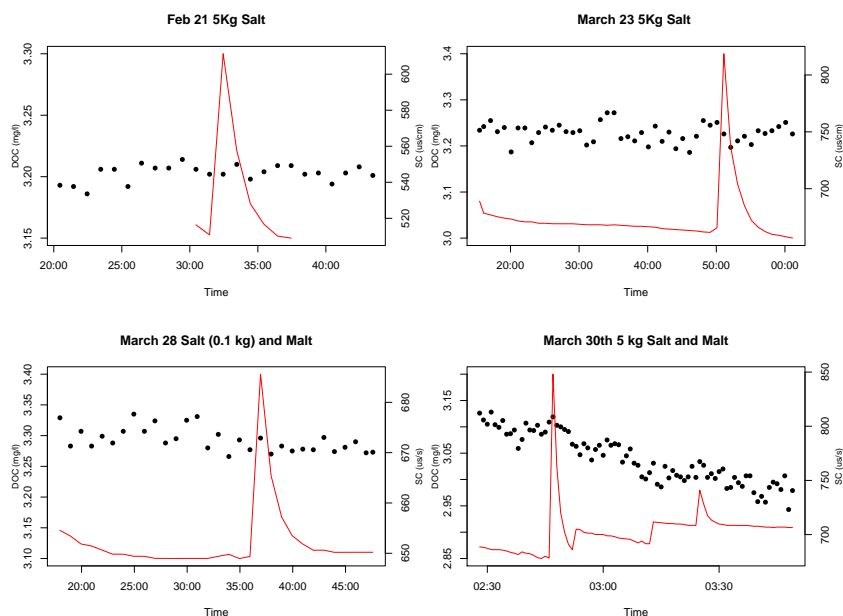


Figure 1: Time series of DOC values over the course of a salt slug. Red lines indicate Specific Conductance (SC) and black points indicate DOC values. Note: on February 24th, this slug was conducted in a different reach of Stroubles creek. It was located approximately 500 meters upstream from the site of the others. Additionally, two slugs were performed on March 30th, the first consisted of 5 kg of salt and malt, and the second was 0.01 kg of salt and malt.

Discussion

An important variable that may have affected the DOC and NO_3 concentrations observed during the time frame of this study was the time of year it took place. Blacksburg, VA was regularly receiving small amounts of snow through out February and March. Because of this, road deicers were often used, which resulted in a very high base conductivity of Stroubles creek, and may have contributed to the variable DOC and NO_3 concentrations observed on February 21st. Additionally, March 30th was the only day that had a clear impact on DOC and NO_3 concentrations, thus this injection should be repeated. This could be due to the addition of malt extract as a carbon slug, but this response was not seen on March 28th, which also had the same injection tracer of salt and malt. Malt was used as a carbon slug on March 28th and March 30th to see if the carbon slug would increase DOC concentrations. However, this was not observed, in fact, there appears to be a slight decrease in DOC concentrations as a result of the carbon slug.

Other possible reasons for this response could be other lurking variables occurring in the system, thus further investigation is required. DOC and NO_3 ratios were consistent, meaning that as DOC concentrations increased, NO_3 concentrations stayed relatively the same. This suggests that DOC concentrations do not affect or control for NO_3 concentrations. The paired t test of DOC and NO_3 concentrations showed that

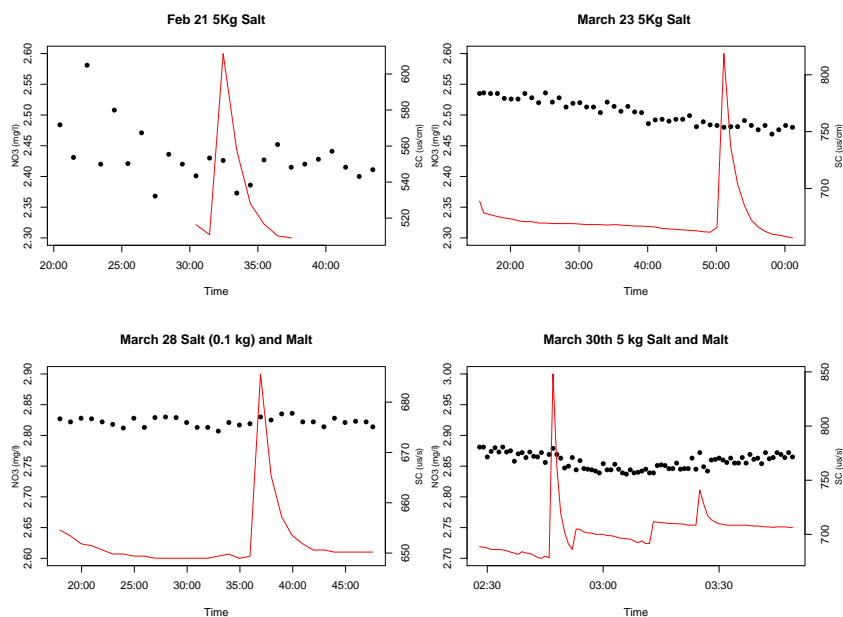


Figure 2: Time series of NO_3 concentrations during salt slugs. Red lines indicate conductivity, and black points indicated NO_3 concentrations. Amounts of salt and if the slug contained carbon is mentioned above each plot. Note that two slugs were conducted on March 30th, the first with 5 kg of salt and malt and the second with 0.1 kg of salt added. Additionally on February 21 the stream reach was approximately 500 meters upstream of the stream reach where other slugs took place.

the only day where NO_3 and DOC concentrations were significantly different was on March 30th. Both DOC and NO_3 resulted in a p-value of less than 0.05, which means we reject our null hypothesis and accept the alternative hypothesis of the means before and after salt injection were significantly different. Further, on March 28th, DOC values were found to be significantly different before and after injection. On March 23 NO_3 values were found to be significantly different before and after injection. This suggests that increased conductivity may be having an impact on DOC and NO_3 concentrations.

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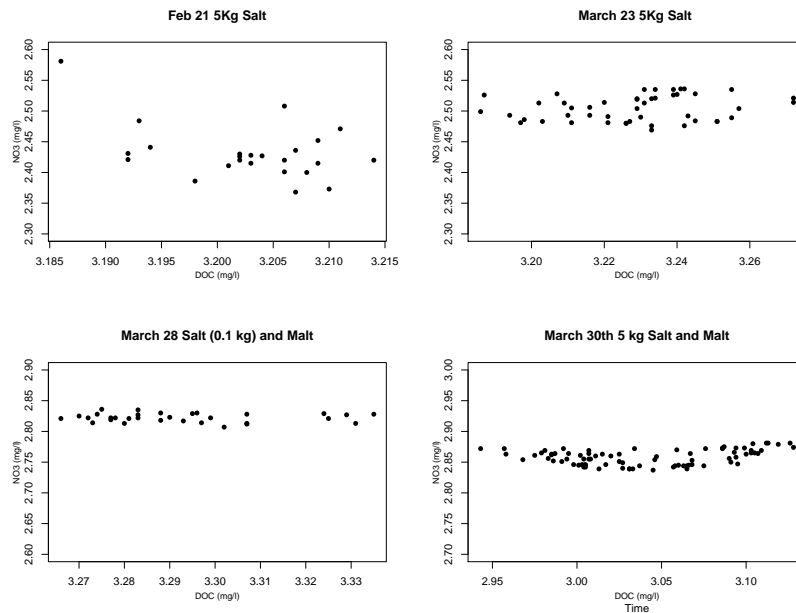


Figure 3: DOC and NO₃ ratios plotted for all four days .

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