Washington College

Department of Environmental Science and Studies

The Chester River as a Source of Nitrous Oxide to the Atmosphere

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Abstract

Nitrous oxide, a potent greenhouse gas, is emitted as a byproduct of nitrification and denitrification, which occurs by microbes in sediments and the water column. The Chester River is a reservoir for collecting nutrients from nearby Eastern Shore agriculture that are necessary to stimulate nitrous oxide production. River samples were taken at two depths in longitudinal transects in the river for spatial analysis. For temporal analysis, river samples were collected approximately weekly between August and December from two docks in Chestertown. Abiotic parameters were measured with a YSI probe. The samples were analyzed on Gas Chromatograph for nitrous oxide concentrations. The Chester River exhibited an increase in nitrous oxide content from summer to winter. Spatially, nitrous oxide concentrations were lower further downstream than upstream. In addition to gas solubility, microbial processes largely contributed to the production of nitrous oxide in the Chester River, which can be seen from such large background saturation percentages. The Chester River is thus considered a source of nitrous oxide to the atmosphere.

Keywords: Nitrous oxide, Chester River, nitrification, denitrification, greenhouse gas

Introduction

Nitrous oxide (N_2O), an atmospheric trace gas that has been naturally produced since before the industrial revolution, is on the rise and greatly contributing to the greenhouse effect and global warming (Dickinson & Cicerone, 1986). A common characteristic of a greenhouse gas is the bending vibrations exhibited by its linear molecular structure, enabling absorption of infrared radiation (Baird & Cann, 2012). When existent in the stratosphere, nitrous oxide absorbs infrared radiation from the sun, which produces oxygen in an excited state (Davidson, 2009; Girard, 2010). The oxygen then reacts with a nitrous oxide molecule forming two excited molecules of nitric oxide, which then reacts with ozone molecules, producing two oxygen gas molecules (Davidson, 2009; Girard, 2010; Schmeltekopf, 1977). Girard (2010) and Solomon (1999) state that “ozone absorbs UV radiation” before the harmful rays reach the troposphere. Nitrous oxide is thus an indirect ozone depleting pollutant because it yields the reagent necessary for the destruction of the ozone layer through a series of reactions (Ravishankara et al., 2009). This reaction with ozone takes place in the stratosphere; however, no sinks exist in the troposphere for collection of nitrous oxide (Davidson, 2009; Girard, 2010; Ramanathan et al., 2009). With no available tropospheric sinks and a long atmospheric lifetime of 120 years, nitrous oxide accumulates in the troposphere over time, resulting in a long-lasting supply for future stratospheric reactions (Girard, 2010). Although atmospheric carbon dioxide exists in higher concentrations, nitrous oxide has a much larger global warming potential (GWP). One emitted molecule of nitrous oxide causes the same amount of warming as 300 emitted carbon dioxide molecules (Schlesinger & Bernhardt, 2013). The large GWP and long atmospheric lifetime of nitrous oxide pose a high importance to the study of trace atmospheric greenhouse gases.

The troposphere receives nitrous oxide from both natural and anthropogenic sources (Beaulieu et al., 2011; Davidson, 2009; Schlesinger & Bernhardt, 2013). Nitrous oxide is naturally formed as an intermediate in the process of denitrification, where a nitrate ion is reduced to molecular nitrogen (Smith et al., 1991; Wrage et al., 2001). This intermediate is released when the nitrate ion is reduced (Wrage et al., 2001). Wrage et al. (2001) further explained that nitrification is the oxidation of an ammonium ion to nitrate through a series of electron transfers. Nitrous oxide forms as a byproduct of this oxidation reaction through the chemodenitrification of the intermediates (Baird & Cann, 2012; Naqvi et al., 2010; Smith et al., 1991; Wrage et al., 2001). If conditions with low oxygen exist, a different electron acceptor, such as a nitrate ion, may be used, thus releasing nitrous oxide (Smith et al., 1991; Wrage et al., 2001). These natural processes occur in environments, such as soils, sediments, and groundwater, with high moisture suitable for microbes (Girard, 2010; Schlesinger & Bernhardt, 2013). The naturally produced nitrous oxide is likely to be transferred into streams and other bodies of water through groundwater (Baird & Cann, 2012; Dillon & Chanton, 2005; Girard, 2010).

Coupled nitrification-denitrification is likely to be associated in sediments found on the bottom of streams, rivers, or estuaries (Xia et al., 2016). Wrage et al. (2001) explained that nitrification happens on the top portion of the sediment column where aerobic conditions exist; whereas, denitrification occurs in the lower sediments where anaerobic conditions are present. Therefore, the intermediates and products are exchanged, resulting in enhanced nitrous oxide production (Walter et al., 2006). Nitrous oxide is thus released into the surrounding environment (Wrage et al., 2001). Higher oxygen content can indirectly increase denitrification rates by increasing nitrification that ends up producing a greater abundance of nitrate, which is the reagent needed for denitrification (Naqvi et al., 2010).

Direct anthropogenic inputs of nitrous oxide into the troposphere include waste incineration and combustion of fossil fuels, such as biomass, coal, and petroleum (Baird & Cann, 2012; Girard, 2010; Gutierrez et al., 2005). Additionally, the natural processes releasing nitrous oxide can be disrupted by anthropogenic factors (Schlesinger & Bernhardt, 2013). Fertilizer application on agricultural land and stormwater runoff are examples of excess nutrient runoff that leaches into groundwater (Davidson, 2009; Isermann, 1994; Naqvi et al., 2010). The increased inward flux of nutrients initiates an increased rate of production of nitrous oxide by the nitrification and denitrification processes (Schlesinger & Bernhardt, 2013).

The nitrification and denitrification processes that occur in sediments release nitrous oxide into the water column (Fox et al., 2014). Similar to other gases present in the water column, nitrous oxide can diffuse out of the water and into the atmosphere dependent upon temperature and salinity conditions (Kim & Cerco, 2003; Walter et al., 2004; Walter et al., 2006). Although not immediately thought of as sources of nitrous oxide fluxes to the atmosphere, bodies of water, such as rivers, do release nitrous oxide into the air (Beaulieu et al., 2011; Walter et al., 2004). The outward flux of nitrous oxide from water may increase with increased nutrient input into the system (Girard, 2010; Smith et al., 1991). Naqvi et al. (2010) completed a study on excess nutrients resulting in hypoxic conditions in coastal waters around the world. In this system, excess nutrients created an increased flux of nitrous oxide to the atmosphere (Naqvi et al., 2010). Specifically, anaerobic conditions in conjuncture with excess nutrients enable microbes to undergo denitrification, for there is an abundance of nitrate available for reduction in the absence of oxygen (Schlesinger & Bernhardt, 2013). Therefore, bodies of water can be major sources of nitrous oxide to the atmosphere, as they act as reservoirs for the reagents needed for the production of nitrous oxide (Schlesinger & Bernhardt, 2013).

Encompassing a wide area of the East Coast of the United States, the Chesapeake Bay has been studied as a sink for nitrous oxide (Laperriere et al., 2018). Among the Bay's many tributaries is the Chester River. Unlike larger bodies of water, the Chester River, a source of tidal freshwater to the brackish Chesapeake Bay, is an understudied area in nitrous oxide fluxes to the atmosphere (Kim & Cerco, 2003). The Chester River, on the Eastern Shore of Maryland, is largely surrounded by agriculture; therefore, it receives a high input of nutrient runoff from farms, potentially enhancing the production of nitrous oxide (Delaware, n.d.; Department, 2014; Kim & Cerco, 2003). Additionally, the Chester River experiences changes in temperatures and salinity throughout the seasons experienced in Maryland (Kim & Cerco, 2003). Thus, nitrous oxide production can vary depending on climate (Luo et al., 2013).

This observational study focused on whether the Chester River is considered a source of nitrous oxide to the atmosphere. Specifically, this study involved two main measurements. The first was temporal variability of nitrous oxide at one location. Another capacity of the study was looking at the spatial variability of nitrous oxide along the length of the Chester River. It is predicted that the Chester River is a source of the greenhouse gas, nitrous oxide, to the atmosphere. Therefore, greater knowledge and awareness should be focused on bodies of water as sources of trace greenhouse gases to the atmosphere.

Materials/Methods

Area of Study

The Chester River on the Eastern Shore of Maryland is surrounded by agriculture and a coastal plain landscape. According to Google Earth, the Chester River is approximately 30 miles, or 48 km, long, as shown in figure 1, and empties into the Chesapeake Bay. On figure 1, the yellow pin indicates Chestertown, which is also where the temporal measurements were taken.

Two strategies were used to understand both temporal and spatial variability of nitrous oxide concentration in the Chester River. Temporal variability was assessed approximately weekly from two docks within ¼ mile of each other in Chestertown, which were relatively the same distance from the shoreline. The temporal data was collected from 22 August 2018 to 14 December 2018. Water samples were obtained from both 0.5m and 1m depths. Spatial variability was evaluated at 40 sites that were positioned every 1.5 miles, or 2.4 km, at both 0.5m and 1m depths. Surface and bottom measurements allowed for determination of any possible concentration gradients, both temporally and spatially, in the water column. The 0.5m depth was designated as the "surface" measurement because it was just deep enough to not be too affected by any choppy waves, but not overly deep that it would display similar results to the deeper samples. Sampling at these depths helped keep consistency through different sampling conditions. "Bottom" measurements were taken 1 meter below the surface of the river. This distance is about the greatest depth without pulling up sediment during low tide at the sampling docks in Chestertown.

Fig. 1. Chester River Spatial Analysis Locations (Map made using Google Earth)

Fig. 2. Chester River Temporal Analysis Locations (Map made with Google Earth)

Field Sampling

Both temporal and spatial analyses involved the same methods for water sample collection. Samples were pushed up from the water column using a Cole-Parmer Mini positive pressure pump (model no. 75509-50) and a 12-volt battery. Flow was controlled using a flow controller to avoid cavitation and enhanced gas exchange in the water column. Samples from each site were collected in duplicate 12-mL Labco Exetainer vials through tubing attached to the end of the larger tubing, allowing a smooth flow (Fig. 3).

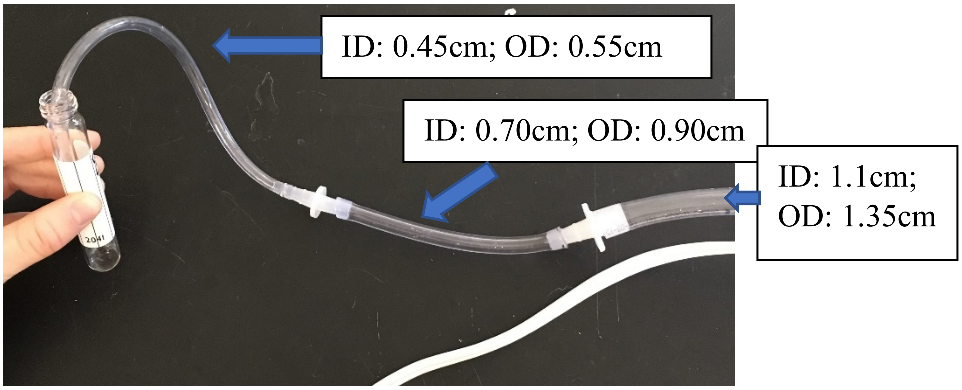


Fig. 3. Tubing diameters for sample

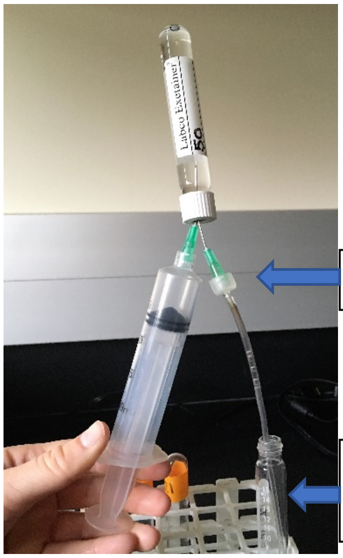
The pump was lowered to 0.5m below the surface. Then, the pump ran for several minutes until all air bubbles were cleared from the tubing and only clear water was running. The sample vials were then filled from the bottom upward by inserting the end of the pump tubing to the bottom of the vial to prevent air bubbles and avoid atmospheric contamination. The vial was overflowed, and the tubing was pulled out slowly, forming a meniscus. Then, a cap with a septum was tightened on the vial and the sample was placed in a cooler containing ice to delay microbial processes that may otherwise alter results. This process was repeated twice for both surface and bottom measurements.

Physical and chemical parameters of the river at each location were taken at each sample site for evidence of any correlation between nitrous oxide concentrations. A ProDSS YSI probe, model number 17H102026, was lowered at the same depths as the pump for the appropriate "surface" and "bottom" measurements. The readings stabilize after approximately one minute. The temperature, salinity, conductivity, pH, Total Dissolved Solids, and dissolved oxygen were recorded after taking each sample.

Laboratory Analysis

Sample Preparation and Procedure

Samples were analyzed using the same methods for both spatial and temporal evaluation. In the lab, a gas headspace was introduced into each of the vials in order to inject a volume of gas into the Gas Chromatograph. To do so, a 10-mL plastic syringe was filled with 6mL of nitrogen gas. A small BD 21G1 ¼ connected by a needle tip, with internal diameter 0.2cm/outer diameter 0.43cm tubing, was inserted a short way into the exetainer through the septum. The tubing emptied into an empty, graduated 10mL test tube. The 10-mL syringe was then inserted through the septum of the sample vial cap and the nitrogen gas was released, displacing the water.



Needle with attached tubing

Test tube collecting displaced water.

Fig. 4. Headspace formation in the sample

Approximately 6mL of water was emptied into the test tube. The volume of water that emptied into the test tube was recorded, which was equal to the volume of the nitrogen gas headspace in the sample tube. The sample vial was then over-pressurized by injecting 3mL of additional nitrogen gas with the plastic 10-mL syringe into the sample vial, without a vent needle. The sample vial was shaken for one minute to equilibrate the gas and water phases.

N_2O Standards & GC Analysis

A Shimadzu Gas Chromatograph (GC) 2014 was used to determine nitrous oxide concentration. The GC was standardized using 3 different known concentrations of nitrous oxide as standards to form a standard curve (Fox et al., 2014). In between each standard or sample, the GC was flushed with 5mL of nitrogen gas, using a 5mL Hamilton Gastight glass syringe, to clear the injection loop. Then, inserting the 5mL glass syringe into the headspace of the sample vial, 3mL of the sample vial gas was extracted and injected into the GC. The Gas Chromatograph contains an electron capture detector (ECD), which detects nitrous oxide, as well as a Flame Ion Detector (FID) that detects methane and carbon dioxide gases.

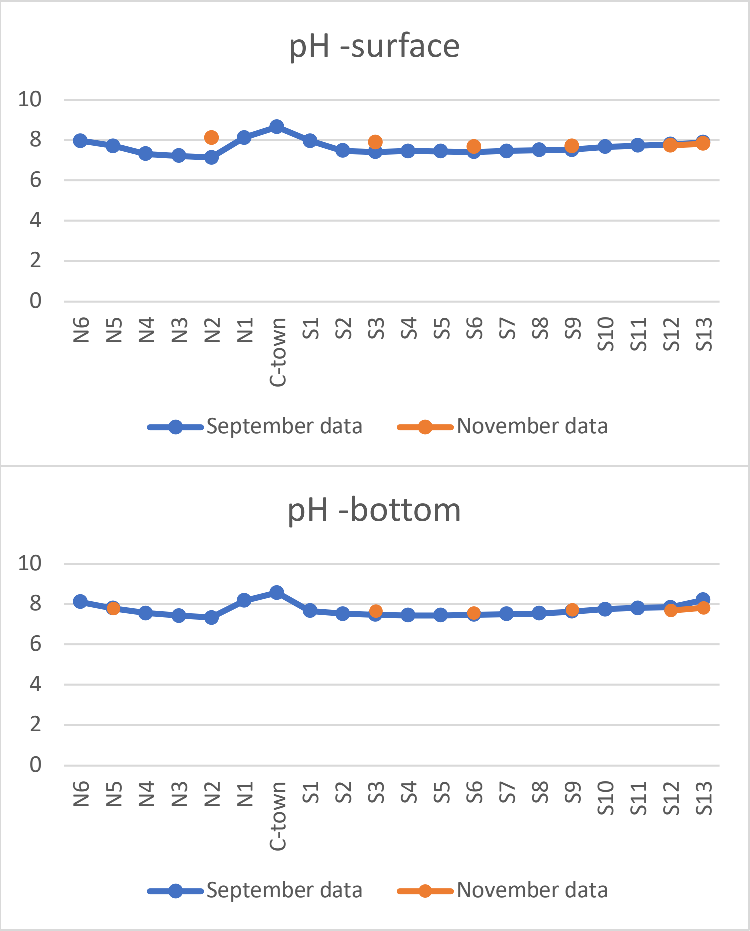
Results

Environmental Data

YSI data was measured at each sampling location for September and November longitudinal Chester River transects. The pH varied between 7.14 and 8.65 from the furthest upstream site to the mouth of the Chester in September and from 7.66 to 8.1 in November (Fig. 5). The September data showed a little more variation in pH than the November data. A spike in pH was see at Chestertown for both surface and bottom measurements in the September data.

Additionally, dissolved oxygen was measured at each September and November spatial analysis sampling location. The September surface and bottom data both had more variation than the November data. Overall, in the September data, bottom measurements of dissolved oxygen were slightly less than the surface measurements (Fig. 6). The furthest southern site had the largest percentage of dissolved oxygen in both surface and bottom measurements for both September and November data.

Salinity and conductivity were also measured at all longitudinal sites for both September and November. In the September data, salinity ranged between 0.12 and 6.15 ppt; whereas, the salinity ranged between 0.18 and 3.66ppt in the November data (Fig. 7). Conductivity ranged between 252 and 10402uS/cm in September and between 1755 and 5257uS/cm in November (Fig. 7). Both salinity and conductivity decreased in the colder months. The September and November data show that salinity and conductivity positively correlate to each other and are both high at southern points, where the Chesapeake Bay and Chester River unite.



pH -surface

pH -bottom

Fig. 5. pH along the Chester River.

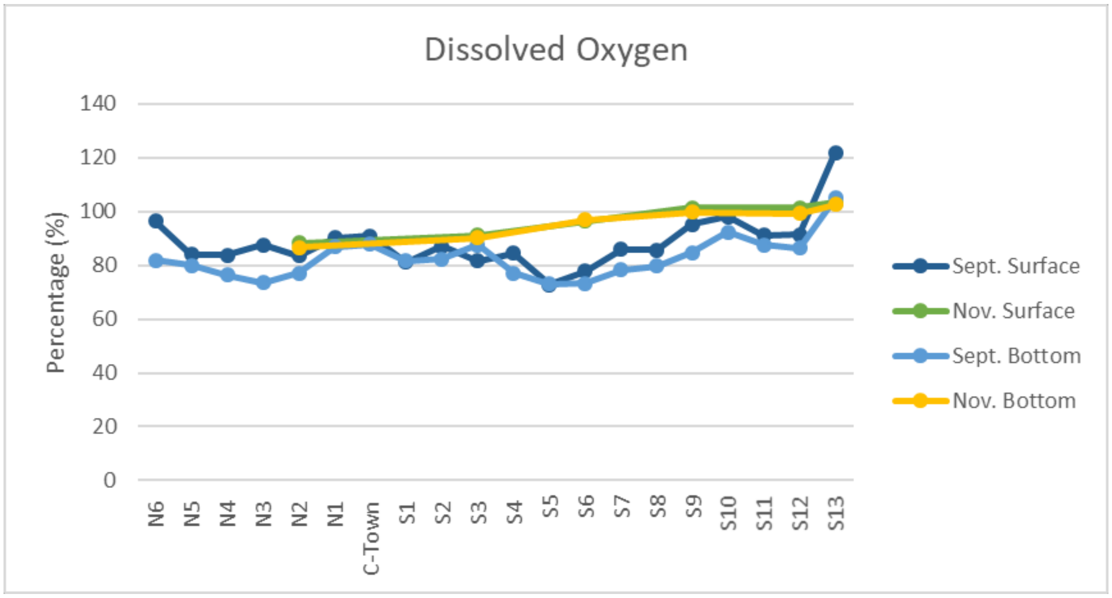


Fig. 6. Spatial analysis of dissolved oxygen at surface and bottom measurements in Sept. and Nov.

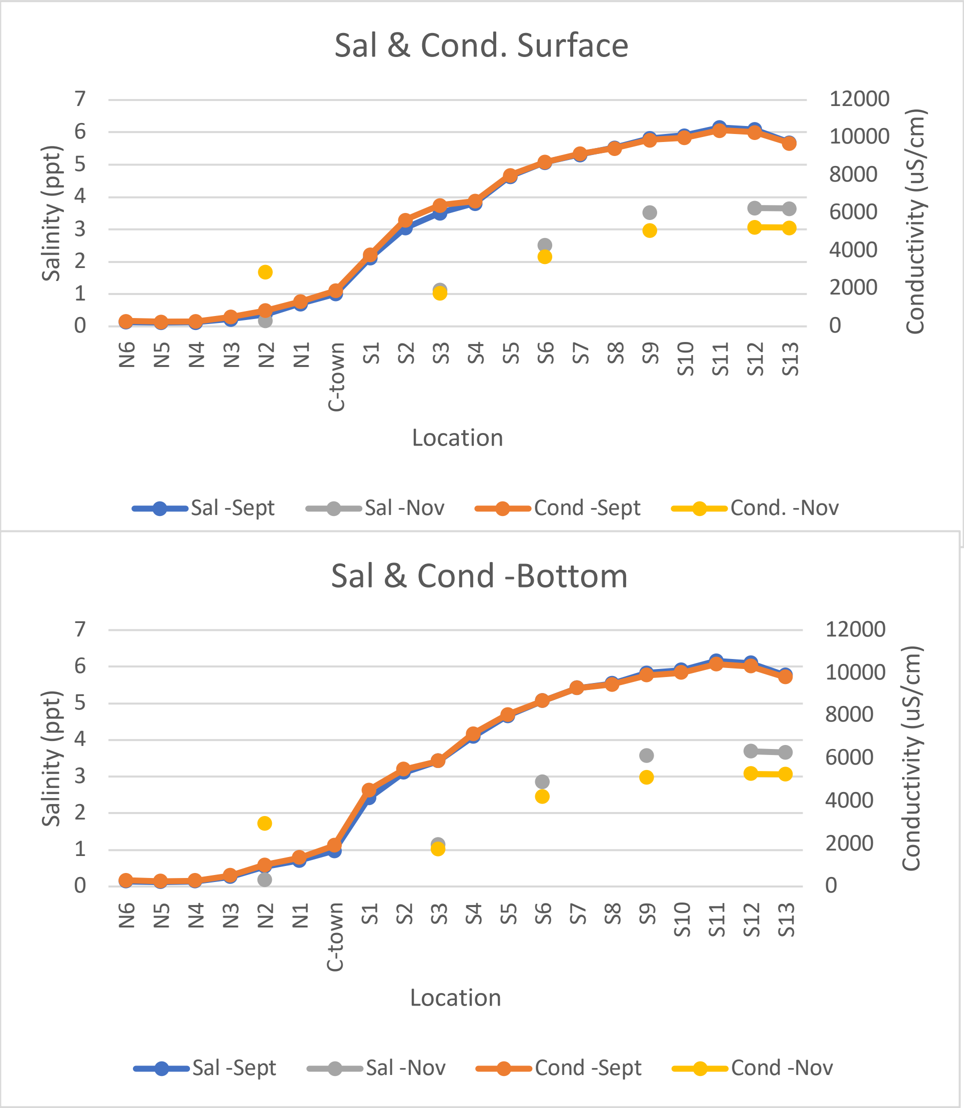


Fig. 7. Salinity and Conductivity along the Chester River.

Environmental data was also taken after each temporal sampling at the two docks in Chestertown. The pH, conductivity, salinity, and dissolved oxygen were similar between both docks.

Temporal Nitrous Oxide Concentrations

Temporal data was taken at 2 locations within ¼ mile of each other along the Chester River, which were relatively the same distance away from the shoreline. The temporal data yielded an overall increase in nitrous oxide content in both bottom and surface measurements from summer to winter. During this same time period, temperature decreased. Concentrations ranged from 18.95 to 56.49nmol N_2O/L at the Washington College dock, with the lowest concentrations recorded in August and early September (Fig. 8/9). The highest concentration was recorded on October 18, 2018. A large increase in nitrous oxide was evident on November 8. The Oros Dock portrayed the same trend. Significant variation in nitrous oxide concentrations was observed during this 4-month time period, with an average surface concentration of 33.81nmol/L and a standard deviation of 1.77. The average bottom concentration was 35.65nmol/L with a standard deviation of 1.37. There was a peak nitrous oxide concentration on October 18. Chestertown also has higher pH than its surrounding regions.

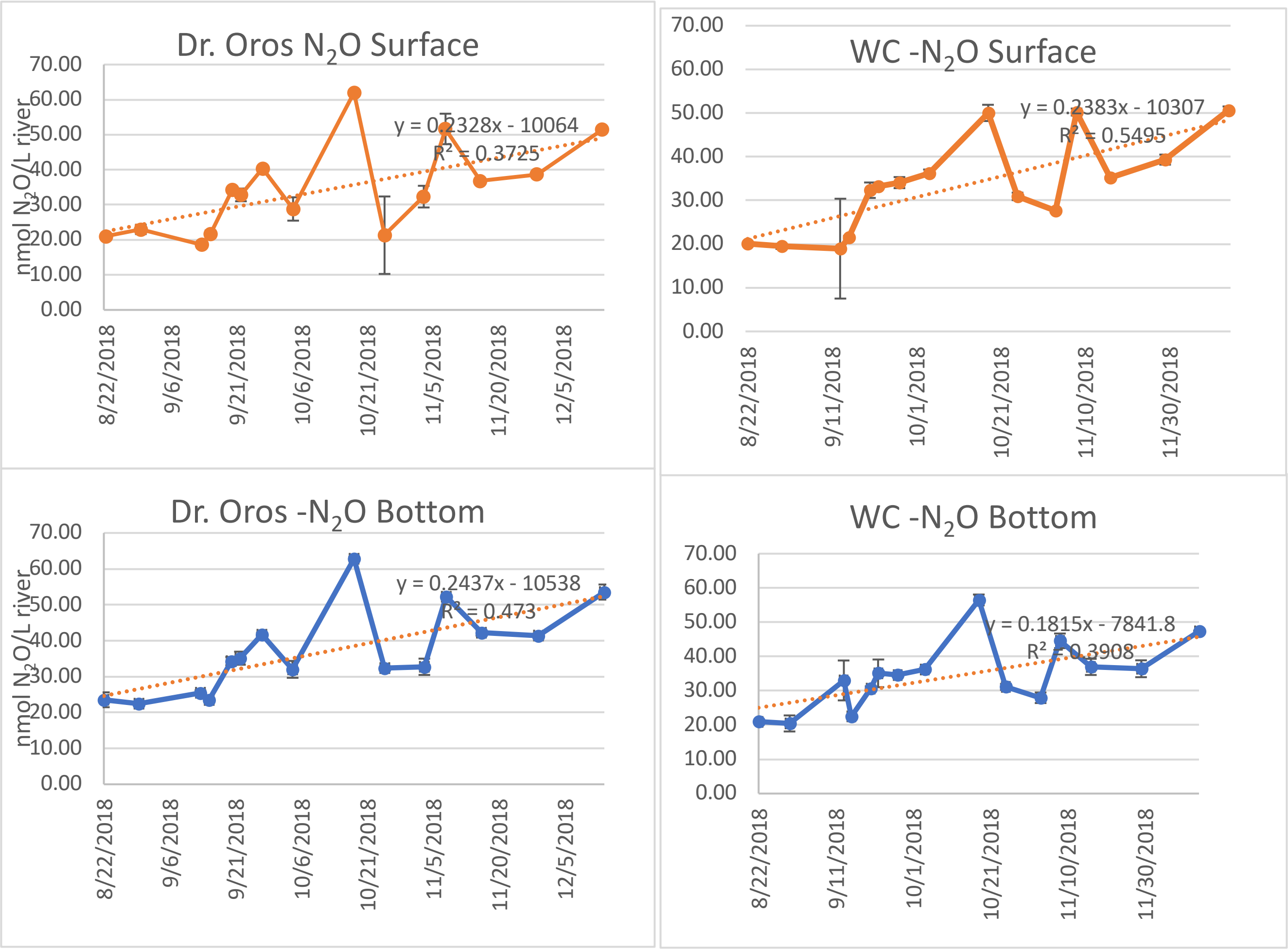


Fig. 8 + 9. Nitrous oxide measurements at two different locations over time.

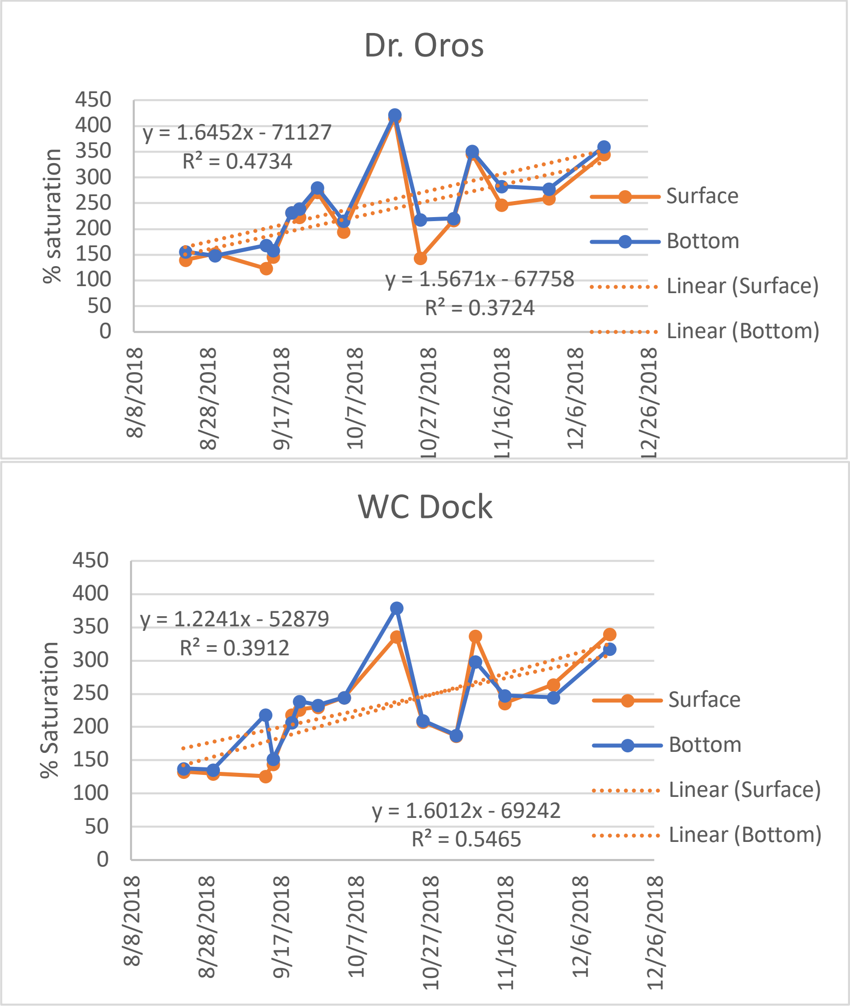


Fig. 10. Percent saturation of N_2O that is expected to be present in the river.

The expected concentrations of nitrous oxide are very large percentages, showing an increase over time as well (Fig. 10). The increasing linear trend follows the same trend displayed in the nitrous oxide measurements. This similarity and precision show that samples taken within greater distances of each other would still accurately represent the gases present in the water column.

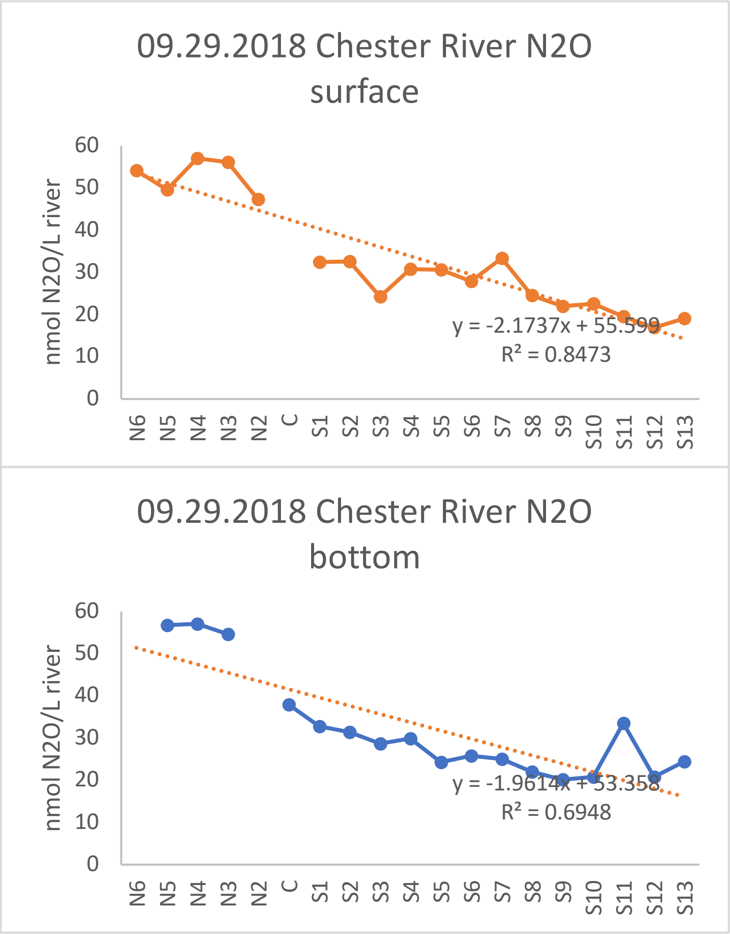


Fig. 11. Surface and bottom nitrous oxide measurements of the Chester River at 19 locations.

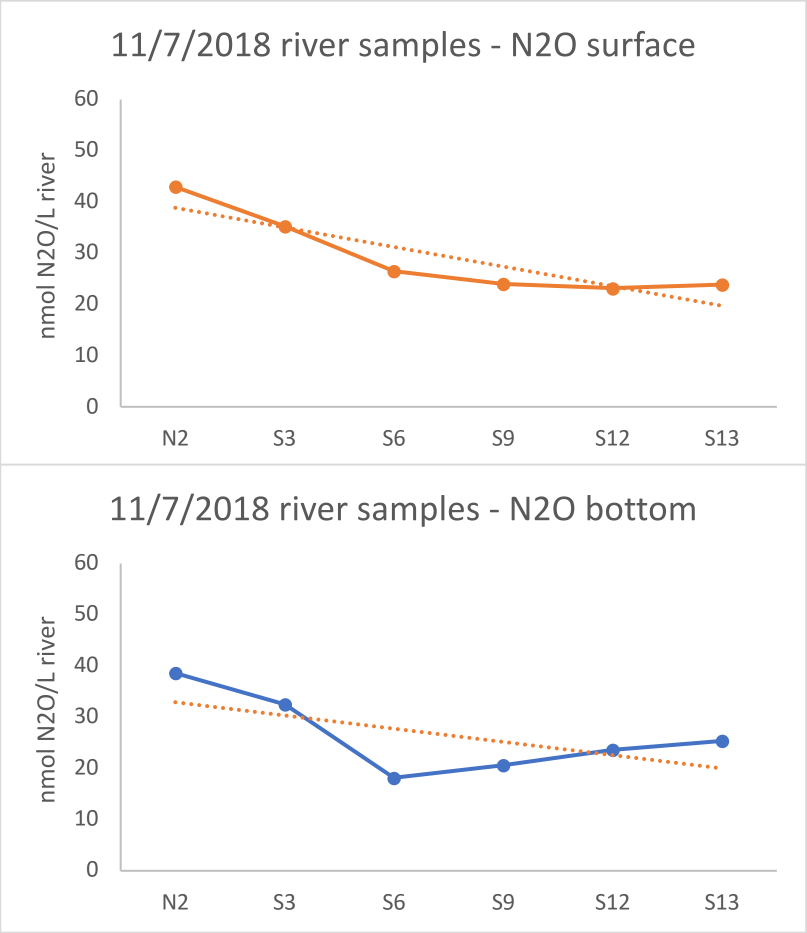


Fig. 12. Surface and bottom nitrous oxide measurements along the Chester River at 6 locations.

Spatial Nitrous Oxide Concentrations

Spatial data taken at longitudinal transects along the Chester River yielded an overall decreasing trend in nitrous oxide concentrations in both surface and bottom measurements from upriver to downriver on both sampling dates. Concentrations from the September data ranged from 16.9-57.09nmol/L (Fig.11). Concentrations ranged from 18.16 to 42.94nmol/L in November (Fig.12). The average nitrous oxide concentration was 31.50nmol/L with a standard deviation of 11.9. Surface and bottom measurements shared similar values. The bottom measurements in

November showed a low concentration at site S6, downriver from Chestertown. The September data showed a spike in the bottom measurements of nitrous oxide concentration at site S11.

An excel spreadsheet was used to calculate the nitrous oxide concentrations from the peak areas given by the GC. A standard curve was calculated from the analyzed standards, and this equation was used to calculate the concentration of nitrous oxide in the sample's headspace. To determine the remaining nitrous oxide concentration in the liquid portion of the sample, salinity, room temperature, and barometric pressure of each sampling day were recorded for each sample. The volume of air inserted into each sample vial was also recorded. The concentration of nitrous oxide in the water phase at room temperature and sampling salinity was calculated according to Weiss & Price (1980). The actual concentration of nitrous oxide dissolved in the water phase of the sampling tube was determined by multiplying the mole fraction by the solubility in nmol/mL. To determine the concentration of nitrous oxide in the river, the headspace and water phase concentrations were combined by dividing the product of the volume of air in the sample tube and the concentration of nitrous oxide in the air added to the concentration of N2O in water by the volume of water in the sample tube.

Discussion

Overall, evident trends of increasing nitrous oxide upriver and from summer to winter from collected data support the idea that the Chester River could a source of nitrous oxide to the atmosphere.

Spatial Variability of Nitrous Oxide Concentration and Environmental Data

Higher nitrous oxide measurements observed upstream in the Chester River (Fig.11/12) could be due to increased inputs of nutrients from the streams feeding into the river (Beaulieu et al., 2011). During baseflow conditions, groundwater feeds into these streams that flow into the upper part of the river (Beaulieu et al., 2011). Due to the dominant local land use of agriculture, high concentrations of nitrogen species accumulate in groundwater (Vitousek & Matson, 1993). These small streams are therefore likely to collect nutrients from surrounding agriculture and transport them downstream into the Chester. Microbial processes that transform nitrogen into nitrous oxide can provide the nitrous oxide upriver, where streams are sources of nutrients (Fox et al., 2014).

Lower nitrous oxide concentrations observed downstream (Fig. 11/12) are likely due to degassing of the nitrous oxide from the water column before reaching locations further downriver (Roland et al., 2010). The lower oxygen content downstream did not impact nitrous oxide concentrations. Low oxygen concentrations can be conducive to denitrification but does not account for it because of a greater volume to surface area ratio of the river (Peterson et al., 2001). Lower nitrous oxide concentrations downriver may also be due to higher salinity. Gas solubility decreases with increases in salinity (Weiss & Price, 1980). With more solutes in the water column, less gas molecules occupy the water column. Lemon & Lemon (1981) noted a similar trend in river junctions in the Great Lakes.

Studies in New York City and China have noticed the similar trends in higher nitrous oxide concentrations in the upstream part of rivers (Cole & Caraco, 2001; Xia et al., 2016). The rivers under study were much larger in volume; however, the Hudson River data exhibited a large percentage, greater than 100%, of background saturation (Cole & Caraco, 2001; Xia et al., 2016).

A 100% background saturation would indicate the gases present are purely due to solubility. However, with the background % saturation of nitrous oxide following the same trend as the measured nitrous oxide concentrations, biological processes must be the cause of such large percent saturation over 100. It follows closely with the nitrous oxide measurements and therefore no dependence on physical conditions is evident that would otherwise alter the saturation line. Microbial processes of nitrification and denitrification are the result of such nitrous oxide concentrations produced in either the groundwater or river (Beaulieu et al., 2011; Fox et al., 2014).

Salinity, conductivity, and pH data do not show any distinctive differences between surface and bottom measurements along the length of the river. This shows the river contains relatively consistent concentrations of nitrous oxide throughout the depth profile, although this project was limited to sampling depth based upon the pump capabilities. The higher pH in Chestertown could be a result of being directly downstream of the wastewater treatment plant.

Temporal Variability of Nitrous Oxide Concentration and Environmental Parameters

The higher nitrous oxide concentration later in the year may be due to higher stream and groundwater flow in to the river and thus increased sediment and biological processes (Fox et al., 2014). Additionally, colder temperatures result in higher solubility of gases (Laperriere et al., 2018). Therefore, the increase in nitrous oxide concentrations in the Chester River into the colder season is most likely due to its greater ability to be solubilize into the water.

The peak in nitrous oxide concentration on October 18 evident in both surface and bottom measurements could be a result of the high pressure of 30.44inHg on that day. Laperriere et al. (2018) shows that concentrations of nitrous oxide are dependent on atmospheric pressure and Weiss and Price (1980) show the positive correlation in the solubility equation between solubility of gases and atmospheric pressure. More nitrous oxide is able to stay in the water column.

The large error bars for figures 8 and 9 could be due to error in preparing the samples for the GC or the actual sampling process. Two samples were taken at surface and bottom, so there is a chance for the samples to be both very different.

Future Suggestions

In the future, nitrous oxide fluxes through air-water exchange could be measured as an extension of this study. This would require sampling the air for nitrous oxide at the surface and above the water (Lemon & Lemon, 1981). Measuring the nitrous oxide concentration in groundwater discharged into the river would narrow down the actual concentration produced strictly in the river. To further extend this study, surrounding region nitrous oxide fluxes could be calculated to get the complete nitrous oxide contribution from all potential sources, such as forests, agriculture (Cole & Caraco, 2001). Taking measurements among different rivers would help statistically by increasing the number of replicates, as Roland et al. (2010) used multiple reservoirs in a similar study. Lastly, wind affects solubility of gases and fluxes of gases to the atmosphere and thus could be recorded in addition (Laperriere et al., 2018; Walter et al., 2006).

This observational study could be further improved by choosing greater difference in depths for surface and bottom measurements. This may show more variation against the constantly changing depth of the river. Additionally, this study could be extended to measure nitrous oxide concentrations over a yearly course, to provide an accurate depiction of temporal variation of nitrous oxide.

Conclusion

Overall, nitrous oxide concentration in the Chester River appears to increase with colder temperatures and thus changes in solubility. Concentrations in nitrous oxide decrease downriver as river volume increases. Physical and chemical parameters, such as salinity, temperature, pH, and conductivity, indirectly contribute to changes in nitrous oxide concentrations both spatially and temporally. Nitrous oxide concentrations in the river are higher than expected under typical solubility conditions, evoking that microbial processes take place in the sediments and water column. The collected data therefore supports the notion that the Chester River is a source of nitrous oxide to the atmosphere.

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