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Measuring Rates of Atmospheric Phosphorus Deposition into a Fresh Water Wetland

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Abstract

Wetlands have recently been used to help filter out nutrients, like nitrogen and phosphorus, in water to reduce the rates of eutrophication in water bodies. Prairie Wolf Slough is a restored wetland that was used to showcase this ecosystem service; however, the wetland actually exports more phosphorus from its outlet than it takes in at its inlet. The role that atmospheric phosphorus deposition might play in this wetland’s phosphorus loading was examined in this study using a vertical collecting method and a horizontal collecting method. The spatial and temporal variation of phosphorus deposition was also examined. The methods were both found to collect particulate matter; however, the vertical collector was more efficient at collecting total solids deposition, while the horizontal collector was more efficient at collecting total phosphorus deposition. Rainfall was not found to be a significant indicator of the efficiency of either collector for total phosphorus or total solids deposition collection. This study is a start in collecting data on the influence of atmospheric phosphorus deposition in Prairie Wolf Slough, but more research over multiple years and seasons needs to be done in order to see long-term patterns.

Introduction

A problematic phenomenon in many aquatic ecosystems is eutrophication. Eutrophication causes excessive algal blooms, which reduce the amount of oxygen in the aquatic system to the point that much of the life dies off, and the area becomes a dead zone (Smith 2009). There are many processes that can contribute to eutrophication. Nonpoint exports of nutrients caused by activities like farming and fertilization are large contributors to eutrophication because they disrupt the natural of nutrients that would be found in an area. Nutrients can also be added into an aquatic system through biological mechanisms where the flora and fauna within a system add nutrients, mainly through death and decay, or through abiotic mechanisms like internal loading, where there is a shift in oxidation-reduction processes within the system (Smith 2009). Oxidation occurs when a molecule receives an oxygen atom and loses a hydrogen atom. The opposite, when an oxygen atom is released and a hydrogen atom is received, is called reduction. (Mitsch and Gosselink 2007). Run-off can be a large contributor to eutrophication because nutrients that are caught in overland water flows run directly into wetlands, streams, lakes, or other bodies of water. In addition, geological weathering, where erosion of the Earth’s crust naturally inputs nutrients into the water,
contributes to eutrophication (Smith 2009, Schoumans et al. 2014). Atmospheric deposition can also be a contributor where particulate or gaseous nutrients are deposited or dissolved into aquatic systems (Smith 2009).

Many research studies have looked at remediating ecosystems and preventing eutrophication from damaging water bodies around the globe. One of the most implemented methods recently has involved the restoration or protection of wetlands (Fischer and Acreman 2004, Verhoeven et al. 2006). Wetlands are known for their ability to purify water and store nutrients. A relatively long-term sink within the wetland for both phosphorus and nitrogen is through plant uptake and storage of the nutrients. Phosphorus can be absorbed by wetlands through the process of sedimentation, where the phosphorus particles get confined in new rock by attaching to clay particles or other cations, like iron or aluminum, in the soil that eventually get compressed into rock. The process of adsorption, where the phosphorus gets attached to other molecules, therefore plays a large part in the uptake of phosphorus in wetlands. Phosphorus can also become interned in organic litter and peat as a result of its ability to adsorb onto other molecules (Mitsch and Gosselink 2007). These processes can help to reduce phosphorus in the water flowing through the wetland, but they tend to vary in their effectiveness (Verhoeven et al. 2006). A diagram of the phosphorus cycle can be seen in Figure 1.

As a result of a wetland’s ability to reduce nutrient loadings, many people have looked towards rehabilitating or preserving wetlands in order to use them to purify waste water or runoff from agriculture or other businesses that produce waste water with high levels of phosphorus and nitrogen (Hoffman et al. 2012, Fischer and Acreman 2004, Verhoeven et al. 2006). One Chicagoland example of a wetland restoration to help purify water flowing through it is Prairie Wolf Slough, which is located in Lake County in Highland Park, Illinois, USA. Prairie Wolf Slough was originally drained in order to use the land for agriculture. Eventually, it was abandoned and left barren for years. When the area was drained, and after it was left barren, the amount of water that was being discharged into the Chicago River from that area increased (Hill 2000). This phenomenon can be attributed to population increase, which caused more development within the watershed, increasing the amount of impervious ground. This then increased eutrophication and flooding problems downstream because the volume of water not only increased the potential for excessive water levels, but it also brought more nutrients with it due to run-off, which spurred algal blooms (Hill 2000). As a result, Chicago officials faced high levels of nitrogen and phosphorus being ejected from surrounding areas into the Chicago River, and one of the culprits helping to contribute high amounts of phosphorus and nitrogen into the river was a storm water detention area near Prairie Wolf Slough. Re-establishing Prairie Wolf Slough as a wetland offered an opportunity to show a wetland’s ability to purify water by reducing the amount of nitrogen and phosphorus in the water that flows through the wetland, in addition to demonstrating the other ecosystem benefits of wetlands like flood prevention and wildlife refuge. Prairie Wolf Slough was then rehabilitated starting in 1996 by removing the drainage tiles that had been put in place and restoring the hydrology of the area by building a dyke at the southern end of the site to redirect the flow out and towards the wetland (Hill 2000). This was all done in an effort to limit the nitrogen and phosphorous going into the Chicago River from that area and to help reduce flooding downstream (Hill 2000). The restored marsh can be seen in Figure 2.

In many cases, wetlands are very efficient at retaining nitrogen, but how they retain phosphorous is largely variable (Hoffman et al. 2012, Fischer and Acreman 2004). Some wetlands will retain phosphorous, while others can expel more phosphorous than originally came into the wetland through their inlets. The latter phenomenon is what is
Figure 1: Phosphorus Cycle Diagram

Currently happening in Prairie Wolf Slough. Prairie Wolf Slough was monitored before and after it was restored in order to see how it was retaining the nutrients flowing through it. It was found that the area is removing nitrogen effectively, but it is expelling more phosphorous than is coming in from the water detention pond (Montgomery and Eames 2008).

There are many reasons why Prairie Wolf Slough may expel more phosphorous through its outlet than comes in through the wetland’s inlet. How this may happen touches upon the factors that control eutrophication: human agricultural activities, geological weathering, run-off, waste disposal, biotic mechanisms, internal-loading and atmospheric deposition (Smith 2009). Any one of these processes could be adding the excess nutrients into the wetland.

Recently, the influence of the atmosphere on certain ecosystems, through atmospheric deposition, has been examined more extensively. Atmospheric phosphorus deposition occurs when phosphorus particles get into the atmosphere through mechanisms like natural erosion and anthropogenic processes, such as the incineration of organic wastes and during the plowing of farmland, and then the particles fall to the ground (Migon et al. 2001). Atmospheric phosphorus deposition occurs through either wet or dry deposition (Mignon et al. 2001, Pollman et al. 2002). Dry deposition occurs when phosphorus particles are carried and deposited on surfaces by wind, and wet deposition occurs during a rainstorm when the atmosphere is cleansed and the phosphorus particles attach to rain droplets. To collect and analyze the atmospheric phosphorus, many studies will use low or high-volume pumps to actively pump air through a filter that will catch the dust particles. Deposition can also be studied through passively collecting dust from a collector with a known surface area after a defined period of time. A study by Christodoulaki et al. (2013) found that the phosphorus and nitrogen deposition they observed in an area in the eastern Mediterranean could be correlated with increased production and biomass accumulation in monitored phytoplankton and bacteria in the region. In a study conducted by Eisenreich et al. (1977) in and around Lake Michigan, the phosphorus loadings in the lake were studied by collecting bulk precipitation on a monthly basis. It was found that atmospheric phosphorus deposition constituted about sixteen percent of the total phosphorus budget for Lake Michigan. The southern basin of the lake received as much as 62 percent of its phosphorus budget from atmospheric phosphorus deposition. It was believed that wind-blown soil and re-entrained dust were the major sources of atmospheric...
phosphorus to Lake Michigan. From these studies, it can be assumed that there are strong cases for the fact that atmospheric phosphorus deposition could in fact influence the amount of nutrients that are within a body of water.

There is a gap in information on how much atmospheric phosphorus is deposited in Prairie Wolf Slough during any season, how much deposition is needed to influence a wetland ecosystem in the first place, and whether atmospheric deposition is responsible for the export of phosphorus out of Prairie Wolf Slough. The goals of this study were to: (1) to test the efficacy of different atmospheric dust samplers for measuring atmospheric phosphorus deposition and (2) to measure spatial and temporal variation in phosphorus deposition into PWS.

**METHODS**

**Sample Site**

Prairie Wolf Slough is located in Lake County in Northeastern Illinois (Lat 42°11’51.53”N; Long 87°51’13.77” W). The site covers 14 hectares and of those 14, 10 hectares were restored from farmland back to wetland in 1996. The remaining 4 hectares were left as a woodland area. Of the ecological communities restored, there is savanna, mesic prairie, wet prairie, and a shallow marsh (Figure 2) (Montgomery and Eames 2008).

Six sampling sites were established: three sites for vertical collectors and three sites for horizontal collectors. Each collector was identified using its type, vertical or horizontal, and the site in which it was placed. The vertical collector VP was located in the prairie, VM was located in the marsh, and VC was located in a fringe of cattails (*Typha x glauca*) surrounding the marsh. The horizontal collector HP was located in the prairie next to VP, HPR was located in the prairie close to the road, and HPW was located in the prairie closer to the woodland.

**Collectors**

Two different methods were tested: one vertical collector that was meant to capture dust from all angles and to capture rainfall, which was adapted from the marble dust collector method (Gossen and Rajot, 2007).

The vertical collector (Figure 3) consisted of an inflexible mesh bag (diameter 11.43 cm; height 45.72 cm) filled with 1000 marbles (diameter 1.27 cm) which was attached to a funnel (diameter 19.05 cm) using steel wire that led into a one liter bottle. It was hung on a shepherd’s hook that was planted into the ground at each site.

The horizontal collector (Figure 4) consisted of a funnel (diameter 19.05 cm) attached to a 500 ml bottle. The funnel had a layer of mesh wire secured to the inside of the funnel and covered with marbles. The collector was then buried into the ground to secure the device and so that only the funnel could be seen.

**Collection and Analysis**

Two collectors were made for each designated sample site. All three vertical collectors and one horizontal collector were placed in PWS on July 8, 2014. Only one horizontal collector could be placed in the designated spot because the marsh was inundated from recent rainfall. On the next collection date, July 16, 2014, each of the collectors placed out previously were collected and replaced, and sites that would not easily flood were found for the last two horizontal collectors. The two horizontal collectors were then placed in the ground. Collections occurred from July to November for a total of ten collections. To collect the vertical collectors, the device was removed from the shepherd’s hook, the bottle and funnel were disconnected from the mesh bag and the bottle was capped. The mesh bag was placed in a PVC tube that was capped at each end so as to help with transportation. To collect the horizontal collectors, the marbles were transferred into a labeled plastic bag to help with transfer back to the lab, and the bottle was secured with a cap or Parafilm when a cap could not be found. If any collector was found to be compromised, which would be indicated by such things like a loss of marbles or a toppled collector, the data for that collector was discarded.
Figure 2: Aerial Map of Prairie Wolf Slough
In the lab, each collector was washed using deionized (DI) water. Each vertical collector was washed in its respective PVC tube where it was filled with enough water to cover the collection bag. The bag was then pumped up and down inside of the PVC to force the water to cover and wash all the marbles. That water was then transferred to a 3000 ml Erlenmeyer flask. The funnel was rinsed and the rinse was added to the flask. Any water collected in the bottle was added to the flask as well. The flask was placed on a large hot plate, and the wash was boiled down to a little under 500 ml.

For each horizontal collector, the marbles were washed with DI water. The wash was transferred to a 2000 ml Erlenmeyer flask. The funnel was washed and the rinse was added to the flask as well. Any water collected in the bottle was added to the flask as well. The flask was then placed on a hot plate and allowed to boil down to under 500 ml.

Each boiled sample was then transferred into 500 ml bottles, and the bottle was filled to a complete 500 ml level to create a baseline volume for each of the samples. The boiled samples then underwent a total solids (TS) and total phosphorus (TP) analysis following standard procedures of the American Public Health Association, American Water Works Association and Water Environment Federation (1995). To conduct the total solids analysis, 25 ml of each sample was pipetted into a labeled and pre-massed aluminum weight boat and dried in an oven for 48 hours. The boat with dried sample was then massed, and the mass of the dried sample was calculated. This was done in duplicate for each sample. The total phosphorus test was conducted using the Hach™ method 536 on the DR5000 UV-Vis spectrophotometer for total phosphorus. This test was performed in duplicate for each sample. The total solids analysis and total phosphorus analysis were then used to quantify the amount of total phosphorus each collector captured and the total mass of solids captured by each collector per the 500 mL boiled down sample.

To understand if there is a difference in efficiency of TP deposition collection between the horizontal and vertical collectors, a one-way ANOVA was performed on the pooled data for the vertical and the pooled data for the horizontal collectors using Microsoft Office Excel (2010). The data used for the ANOVA was log-transformed in order to make it more normal, and each collection was treated as an independent sample because a new collection apparatus was put out each time and, although
the samples are repeated over time, it is not likely that the samples influence each other. If no statistical difference is found, there is no difference in efficiency of TP deposition collection between the collectors. If a statistical difference is found, then the collector with the higher pooled average is more efficient at capturing atmospheric phosphorus. A similar statistical method was used for TS deposition.

To understand whether or not rainfall has an effect on the collection efficiency of either collector, the interaction term between TP and TS for both collectors as it was related to rainfall was found using JMP Pro from SAS (2007). The rainfall data for the entire period between sampling dates was obtained from the Lake County (IL) Stormwater Management Agency’s rain gage in the village of Riverwoods, IL (Table 1).

Table 1: Rainfall data for between each collection date

<table>
<thead>
<tr>
<th>Date of Collection</th>
<th>Rainfall (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7/8/2014</td>
<td>12.57</td>
</tr>
<tr>
<td>7/16/2014</td>
<td>2.768</td>
</tr>
<tr>
<td>7/22/2014</td>
<td><strong>0.1016</strong></td>
</tr>
<tr>
<td>8/5/2014</td>
<td>3.505</td>
</tr>
<tr>
<td>8/27/2014</td>
<td>9.169</td>
</tr>
<tr>
<td>9/19/2014</td>
<td>7.036</td>
</tr>
<tr>
<td>9/26/2014</td>
<td>0.3048</td>
</tr>
<tr>
<td>10/17/2014</td>
<td>9.347</td>
</tr>
<tr>
<td>10/31/2014</td>
<td><strong>0.4318</strong></td>
</tr>
<tr>
<td>11/14/2014</td>
<td>0.3048</td>
</tr>
</tbody>
</table>

The dates and data that are bolded indicate dates where no rainwater was found in the collectors.

**RESULTS**

Summer 2014 was uncharacteristically wet and, therefore, only two collection times, 7/22/14 and 10/31/14 resulted in collecting only dry deposition. The dry collections resulted in values for TP and TS deposition (Figures 5 and 6). For the other collections, the bottles used to collect any rain water falling off the collectors were usually halfway or completely filled. They were not only filled with dust and other small particles, but many times they were also filled with insects that became trapped in the water and other debris. All of these solids were considered in the TP and TS analyses because it was assumed that if they were captured, they would have contributed to the total phosphorus entering the system from the atmosphere.

**Total Phosphorus Deposition Rate**

Phosphorus deposition varied through time and across sample site. Mean TP deposition rates for each collector over the sampling period are shown in Figure 5. The highest TP deposition rates throughout the entire collection period were gathered by HPW on Oct. 17, 4.357 mg m$^{-2}$ day$^{-1}$, and HPR on Oct. 31, 1.673 mg m$^{-2}$ day$^{-1}$. Every other sample was below 1.5 mg m$^{-2}$ day$^{-1}$.

The one-way ANOVA performed on the log-transformed TP deposition rates of the pooled vertical data and pooled horizontal data indicated a significant difference in mean TP deposition rates between collectors (p=0.004785).

The interaction term for TP deposition for each collector as it relates to rainfall indicates that rainfall is not a significant predictor of either collectors’ efficiency (p=0.7672).

**Total Solids Deposition Rate**

Total solid deposition also varied throughout time and over each sample site. Figure 6 shows mean TS deposition rates for each collector over the entire sampling period. The highest TS deposition rates were captured by VM on Aug 5, 47.42 mg day$^{-1}$, by VC on July 8, 28.80 mg day$^{-1}$, and by HPR, 17.5 mg day$^{-1}$, on July 22. Every other sample’s rates were below 15 mg day$^{-1}$.

The one-way ANOVA performed on the TS deposition rates of the pooled vertical data and pooled horizontal data indicated a significant difference in mean TS deposition rates between each collector type (p=0.02165).

The interaction term for TS deposition for each collector as it relates to rainfall indicates that rainfall is not a significant indicator of either collectors’ efficiency (p=0.6930).
Only one VC sample was lost in a lab accident. There was a lack of data for the horizontal collectors in certain cases. On July 8, only HP was placed out, on July 22 HP was toppled and data was lost, on Aug. 5 HPR was toppled and data was lost, and on Oct 31. HPW was toppled and data was lost.

In lab, materials clogged the pipette bore during TS analysis, resulting only in the TS analysis of materials that could fit in the pipette.

**DISCUSSION**

To understand the relationship between TS and TP collection for each collector, the ratios of TS and TP for vertical collectors and horizontal collectors were analyzed separately on each sampling date. On four of the ten sampling dates, the decrease in the concentration of both TP and TS occurred in the same collector sequence. For example, on July 8, the concentration of both TP and TS decreased in the same sequence of vertical collectors; VC > VM > VP. On the other six sampling dates, the TP and TS deposition rates decreased in different collector orders. The horizontal collectors only had the same decreasing sequence on five sampling dates. This lack of association between the TS and TP deposition rates for both of the collectors suggests that the phosphorus collected was not always physically bound to atmospheric particles that were collected as dust. It may be the other non-particulate sources of phosphorus that were caught in the collectors like insects, leaves, or even soluble phosphorus that was dissolved in rainwater that contributed to the differing TS and TP deposition levels.

The high levels of TP deposition captured by the HPW on Oct. 17 may be caused by the number of small leaves that were caught in the pipette of the TP sample. This is not completely indicative of the phosphorus deposition in this area because the leaves are from plants already within the system, but their presence may have influenced the phosphorus levels in this sample. All other samples on that day were relatively free of leaves except for the samples for HPW. The level of TP deposition for HPR on Oct. 31 is harder to explain because it was a relatively clear sample compared to the other samples from that day. It may just be that HPR captured more atmospheric P than the other samplers that day.

The high levels of TS deposition captured by VM on Aug. 5 can be explained by the fact that the liquid collected that day was a very dark brown with a lot of small particles. Bird poop, algae, and some other organic matter may have gotten into the sample to make it change such a drastic color and have so many particles in the captured rainwater. VC on July 8 had a lot of little particles that were captured in the sampler, which could explain the high level of TS. HPR did not have as high of a TS deposition level, but it was still higher than the levels most samples caught. This sample also had a lot of small, visible particles in it, which may explain the level of TS.

For mean TP deposition, the ANOVA showed there was a significant difference between the collection rates for each collector type. Since the average for the horizontal pooled data, 0.1817 mg m$^{-2}$ day$^{-1}$, was higher than the average for the vertical pooled data, 0.0759 mg m$^{-2}$ day$^{-1}$, the horizontal collector was able to collect more TP deposition. This may be a consequence of the smaller surface area of the collector because it was a smaller collector and had less marbles in comparison to the vertical collector; in comparison to surface area it seems like it collected more TP. It could also be that more dust and atmospheric particles settle vertically and the collector is not as affected by wind, which could blow some dust away, because the collectors were surrounded by plants that block the wind for most of the collection period.

The ANOVA performed on the pooled TS deposition data for each collector indicated a significant difference between collectors as well. The average for the vertical collector, 0.1177 mg day$^{-1}$, was higher than the average for the horizontal collector, 0.1106 mg day$^{-1}$, which suggests that the vertical collector was more efficient at collecting TS deposition. This may
Figure 5: Mean TP deposition per day for collector x collection day throughout collection period

Figure 6: Mean TS for each collector x collection day throughout collection period
be skewed by the large number of cattail seeds that the VC collector gathered in the last four sampling periods. It may also be skewed because the bottles that were used to collect rainwater did not have a screen or anything to prevent material other than rainwater from getting into them. This may have allowed for an increased amount of insects, seeds, and other material to get caught in the bottles as compared to the horizontal collectors where the layer of marbles acted like a barrier to those materials.

The lack of significance for the interaction term for TP/TS for either collector type indicates that rainfall is not a significant indicator of collector efficiency for either TS or TP deposition collection. This may be because the rainfall data was acquired from a different town than the one Prairie Wolf Slough is in because Prairie Wolf Slough’s town did not have rain gauge data available and the onsite rain gauge at Prairie Wolf Slough was malfunctioning during the experiment period. It may also be attributed to the collectors’ bottles overflowing during rain storms, which would result in skewed TS and TP deposition rates.

CONCLUSIONS

The results for this study indicate that these two collection methods (e.g. vertical and horizontal) may be appropriate for passively sampling the atmospheric phosphorus deposition over an area because TP and TS deposition rates were collected on days when there was no rainwater in the collectors. Therefore, dust was actually being captured by the marbles used in each of the collectors. The collectors do not actively (e.g. via a pump) draw air, which may help to create a more accurate idea of the natural deposition that occurs in and around an area like Prairie Wolf Slough. In terms of ability to collect TP/TS deposition, the ANOVA showed that the vertical collector was more effective at collecting TS deposition, while the horizontal collector was more effective at capturing TP deposition. In terms of reliability through field observations, the vertical collectors seemed to be the most reliable collectors because they were not toppled or otherwise compromised during the sampling periods. In all, more data is needed to see whether or not one collector is a better method for capturing atmospheric dust, but there is a clear idea of which is more resilient in the field.

In terms of improvements in the lab, a larger bore pipette should be used in future TS analysis because the pipette would get clogged very frequently. The samples could also get filtered so that all large materials are not considered in sample analysis, for either TP or TS. These methodological changes could improve the accuracy of the TS analysis.

The collection period for this experiment was not long enough to establish clear spatiotemporal deposition trends throughout the wetland; however, this study is a strong start to better understanding how the atmosphere may interact with this wetland’s phosphorus cycle. It is now understood that phosphorus does enter the wetland from the atmosphere as indicated by the dust captured on the two dry deposition collections, but more research over multiple years and multiple seasons will need to be performed in order to better understand how atmospheric dust may actually be impacting this wetland’s phosphorus levels. It may be useful during future sampling periods to filter out large materials so as to focus on the impact of atmospheric phosphorus particles rather than atmospheric material. The impact of the cattails and how they capture dust and sediment from the atmosphere may also be useful to research with respect to atmospheric phosphorus deposition. For example, the cattail fringe at PWS is a mass of tightly packed, tall plants with a tremendous leaf canopy surface area. Further research must be conducted to address this hypothesis: The cattail leaf canopy constitutes an intermediate surface between the atmosphere and the marsh that intercepts atmospheric dust before slowly releasing it to the marsh via canopy drip. The literature is sparse on the influence of canopy drip from cattails as a source of phosphorus into wetlands.
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REFERENCES


