Contrasting patterns of nutrient dynamics during different storm events in a semi-arid catchment of northern China

Xinzhong Du, Xuyong Li, Shaonan Hao, Huiliang Wang and Xiao Shen

ABSTRACT

Nutrient discharge during storm events is a critical pathway for nutrient export in semi-arid catchments. We investigated nutrient dynamics during three summer storms characterized by different rainfall magnitude in 2012 in a semi-arid catchment of northern China. The results showed that, in response to storm events, nutrient dynamics displayed big variation in temporal trends of nutrient concentration and in nutrient concentration–flow discharge relationships. Nutrient concentrations had broader fluctuations during an extreme storm than during lesser storms, whereas the concentration ranges of the a moderate storm were no broader than those of a smaller one. The different concentration fluctuations were caused by storm magnitude and intensity coupled with the antecedent rainfall amount and cumulative nutrients. Correlation coefficients between nutrient concentrations and flow discharge varied from positive to negative for the three different events. There were no consistent hysteresis effects for the three different events, and no hysteresis effects were observed for any of the variables during the moderate storm (E2). Our findings provide useful information for better understanding nutrient loss mechanisms during storm events in semi-arid areas of a monsoon climate region.

Key words | nitrogen, nutrient dynamics, phosphorus, semi-arid catchment, storm event

INTRODUCTION

Nutrients from different sources can be exported to receiving waters by storm events, which can wash out large amounts of debris, sediments and nutrients, and might even induce eutrophication, a major environmental problem in many river ecosystems. The monitoring of nutrient concentrations in the Liu River catchment in Hebei province of northern China have been limited to monthly sampling (Wang et al. 2011), or in some cases bimonthly; thus, storm events that discharge large amounts of nutrients into the river would be much less likely to be observed. For instance, it has been observed that most of the annual nutrient load can enter the receiving waters following a small number of storm events (Johnes 2007). Thus, understanding nutrient dynamics during storm events could provide important information that would be less likely to be observed by infrequent sampling and would reduce the uncertainties in estimations of nutrient load.

Previous studies have demonstrated a high degree of complexity and variability of nutrient dynamics during storm events, due to the temporal and spatial variations in a variety of factors, such as meteorological conditions, hydrological conditions, land use, soil properties, nutrient source conditions, and anthropological disturbances (Alvarez-Cobelas et al. 2008). Because of the effects of different factors, nutrient dynamics display different patterns in respect of the temporal variation of nutrient concentration, the nutrient concentration–flow discharge relationships, and the discharge responses of different nutrient species to storm events, etc. With regard to the temporal variation of nutrient concentration, little is known about the fluctuation variation in nutrient concentration associated with different rainfall magnitude and hydrological conditions during storm events, especially in the semi-arid area of a monsoon region where discharge flush in a few summer storm events is a predominant cause of nutrient loss.

The hysteresis effect and correlation between nutrient concentration and flow discharge are commonly used to
describe the nutrient concentration–stream discharge relationships. There have been strong arguments about the correlation relationships between nutrient concentration and flow discharge in previous studies. Some studies found negative correlations (Ahearn et al. 2004), while others found positive correlations (Arheimer et al. 1996). In some cases (Chen et al. 2012), both negative and positive correlations were found for different storm events and nutrient species at the same monitoring site. Moreover, both clockwise and anti-clockwise hysteresis effects were observed among different nutrient species and storm events (Evans & Davies 1998), but no definitive pattern has been confirmed. For instance, hysteresis effects of nutrient concentrations determined from storm events in the River Frome, UK, showed contrasting patterns among the events and nutrient species (Bowes et al. 2009). Moreover, Luz Rodriguez-Blanco et al. (2009) found that there were contrasting patterns for hysteresis effects of nutrient concentrations among the events and nutrient species during four storms in an agroforestry catchment in Spain. In a semi-arid area with a monsoon climate in northern China where the nutrient loss is dominated by a few storm events, little is known about nutrient concentration–discharge relationships during those storm events. The Liu River catchment is located in a semi-arid area with the typical ‘monsoonal’ climate of northern China. In the study catchment, nutrients are mainly discharged through runoff and erosion processes driven by storm events in the summer season. In this study, the following questions were addressed: (a) what is the variation of fluctuations in nutrient concentration during storm events associated with different rainfall magnitude and intensities? (b) what is the concentration–flow discharge correlations and hysteresis effect during storm events?

MATERIALS AND METHODS

Description of study area

The study area, upstream of the Liu River catchment, is situated in the northeast of Hebei province, China (Figure 1) and is a typical sub-basin of the Luan River catchment. The catchment is a semi-arid region with an annual mean temperature of 8.4 °C and annual mean precipitation of 650 mm. The study catchment is a mountainous area, which covers an area of about 626 km² (the area above the LiYing hydrometric station). The average slope of the catchment is 14% with the highest elevation of 1,941 m and the lowest elevation of 745 m. The dominant land use type is forest, which accounts for 55% of the catchment area; other land uses are agricultural land (7%), orchards (14%), grassland (17%) and settlements (7%). The major soil type in this catchment is brown earth soil which covers about 44% of the watershed area. The brown earth has low permeability making it easier for surface runoff generation, and the soil texture is sandy loam and clay loam.

Sampling and water quality analysis

Stream discharge and water samples for chemical analysis were measured and collected manually at the LiYing hydrometric station during three storm events. Instantaneous water discharge during these storm events was measured by the workers of the LiYing hydrometric station through the velocity-area method, i.e. instantaneous discharge was computed by multiplying water flow velocities by the cross-sectional area. The rainfall during storm events was
measured by a tipping bucket rain gauge deployed at the hydrometric station. In addition, rainfall data from eight rain gauges throughout the catchment were collected from the Chengde Branch of Hebei Provincial Survey Bureau of Hydrology & Water Resources. Total catchment rainfall was calculated based on the nine rainfall gauges through the Theissen polygon method. The water samples were collected in 1-L polyethylene bottles that were pre-rinsed with river water. The samples were analyzed for the following parameters: total nitrogen (TN), total phosphorus (TP), total dissolved nitrogen (DN), total dissolved phosphorus (DP), nitrate (NO₃⁻), ammonia (NH₄⁺) and nitrite (NO₂⁻). A portion of each water sample collected in the bottles was filtered (0.45 μm) and taken as the filtered sample, and the remainder was stored as the unfiltered sample. The water samples were stored at 4°C and the analysis was completed within 24 h of collection. Filtered samples of the runoff were analyzed for NO₃⁻, NH₄⁺, NO₂⁻, DP and DN, and the unfiltered water samples were analyzed for TN and TP. The concentrations of TN, NO₃⁻, NH₄⁺, NO₂⁻ and TP were analyzed according to Hach methods 100,071, 8,039, 8,038, 8,507 and 8,190, respectively, with a Hach DR2800 spectrophotometer (Loveland Co., USA). Quality assurance programs including blanks, spiked samples (5% of samples), duplicates (10% of samples) and instrument calibration were conducted throughout each batch analysis and adhered to the QA/QC procedures detailed in sampling and analysis methods (APHA 2005).

Data analysis

River discharge and nutrient concentrations during storm events were the main data used for the analysis in this study. Correlations between nutrient concentrations and discharge were analyzed using Pearson correlation at a significance level of 0.05. In addition, the hysteresis effects of concentration–discharge relationships through the three events were used to analyze the concentration–discharge patterns. Clockwise nutrient hysteresis patterns are produced when a particular nutrient has a higher concentration during the rising stage of a hydrograph compared with the falling stage. An anti-clockwise hysteresis pattern is produced when the concentration peak occurs on the falling limb of the hydrograph.

Antecedent soil moisture is one of the most important factors for the hydrological response of a catchment to rainfall. Several researchers have used different antecedent precipitation index (API) values (Perrone & Madramootoo 1998) to compare soil moisture among pre-storm conditions. The API index was calculated for the three storm events in our study and is defined as

\[
API = \sum_{i=1}^{n} k^i \cdot Pi
\]

where \(Pi\) are the precipitation depths (mm) 1, 2…\(i\) \((i = 12)\) days prior to the storm events and \(k\) is a constant defined as 0.85.

RESULTS AND DISCUSSION

Storm characteristics and hydrological conditions

Data for the three storm events on July 21 (E1, extreme), July 28 (E2, small) and August 1 (E3, moderate) during the monitoring period in 2012 were collected successfully. The general characteristics of the three events are shown in Table 1 and the rainfall in E1 was more extreme and shorter in duration than during E2 and E3, and was accompanied by different hydrological responses in terms of runoff process. A single peak discharge was observed for E1 and E3, whereas two peaks were observed during E2. Peak discharge of E1 was 16 times that of E2 and 7 times that of E3. The soil antecedent moisture conditions were compared according to the computed API values. The lowest soil antecedent moisture condition was in E1 with an API value of only 10.20; there were nine days without rainfall prior to E1. The soil antecedent moisture condition of E3 was the highest with an API value of 67.75. E2 had moderate

<table>
<thead>
<tr>
<th>Strom event</th>
<th>Date</th>
<th>Rainfall</th>
<th>Discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total (mm)</td>
<td>Max (mm h⁻¹)</td>
<td>Rainfall duration (h)</td>
</tr>
<tr>
<td>E1</td>
<td>21/7/12–26/7/12</td>
<td>177.4</td>
<td>53</td>
</tr>
<tr>
<td>E2</td>
<td>28/7/12–29/7/12</td>
<td>20.9</td>
<td>18.8</td>
</tr>
<tr>
<td>E3</td>
<td>1/8/12–6/8/128</td>
<td>32.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>
antecedent moisture conditions and the only storm event prior to it was E1. The characteristics of the storm events presented here were useful information for analyzing the effects of the storms on nutrient dynamics.

The variation of fluctuations in nutrient concentration during different events

Temporal changes in nutrient concentrations and discharge during three events are showed in Figure 2, and discharge and nutrient concentration ranges in response to the three storm events are presented in Table 2. In general, nutrient concentrations exhibited broader fluctuations in E1 with heavy rainfall and a higher peak discharge than in the moderate and small events. The broader fluctuation of concentrations of E1 suggested that the extreme hydrological conditions associated with an intense storm, i.e. high peak discharge and broad discharge range, resulted in the highly dynamic nature of riverine nutrient concentration change. The broader fluctuation of concentrations also implied that storm intensity and discharge characteristics, which reflect the storm characteristics and hydrological conditions, played a key role in the nutrient concentration change.

However, the concentrations of E3 (moderate) did not show a broader fluctuation than E2 (small). The concentration ranges of E3 were narrower or equivalent compared with those of E2, which indicated that nutrient concentration change may be controlled by other factors coupled with storm magnitude. The other factors that influence the concentration change during storm events are the antecedent moisture conditions and the levels of accumulated nutrients that can be potentially washed off by these events. There had already been the extreme storm (E1) and several other events, including E2, which had washed off large amounts of nutrients stored in the catchment prior to E3. This difference in the antecedent conditions resulted in the concentration ranges of E3 being no broader

![Figure 2](https://iwaponline.com/wst/article-pdf/69/12/2533/470891/2533.pdf)
than those of E2. Therefore, nutrient concentration change is influenced by the characteristics of storm magnitude and intensity, coupled with the antecedent rainfall amount and accumulated nutrients prior to a storm event.

Concentration–stream discharge relationships for different storm events

Table 3 shows the Pearson correlation coefficients of nutrient concentrations and discharge. Most of the correlation coefficients were positive and only four were negative. TN, DN, NO₃⁻, NO₂⁻ in E3, and DN in E2 all showed negative correlations with discharge. Moreover, TN and DN in E3 displayed strong negative correlations (statistically significant). In general, nutrient concentrations in E1 displayed stronger correlations than those in E2 and E3. The higher correlations of most nutrient concentrations in E1 indicated that the storm intensity and broad discharge change were the main factors controlling the concentration–discharge relationships of the extreme storm events compared with other factors. Furthermore, the negative correlations of TN, DN, NO₃⁻ and NO₂⁻ in E3 were consistent with the fact that these concentrations displayed a dilution effect, and the dilution effect of TN, DN and NO₃⁻ during the event following a heavy storm was also reported by Blanco et al. (2010). This dilution effect can be attributed to the dilution of nitrogen solutes in the background flow by storm runoff caused by this event.

The concentrations and discharge data throughout the events were plotted and examined visually for the presence of hysteresis effects (Figure 3). For E1, most variables, including TN, PN, NH₄⁺, TP, and PP, displayed clockwise hysteresis with higher concentrations on the rising limb of the hydrographs, whereas NO₃⁻ displayed anti-clockwise hysteresis with higher concentrations on the falling limb; no obvious hysteresis effects were found for DP and DN. For E2, no obvious hysteresis effects were observed for any of the variables. For E3, TN, DN, PN and NH₄⁺ all displayed clockwise hysteresis with higher concentrations on the rising limb of the hydrographs, whereas NO₃⁻ displayed anti-clockwise hysteresis with higher concentrations on the falling limb; no obvious hysteresis effects were found for the concentrations of TP, DP and PP. Previous work demonstrated that concentration–discharge patterns varied on the basis of a number of factors (hydrograph component volume and timing, antecedent conditions and rainfall characteristics) related to storm variability (Chanat et al. 2002). Our results showed that there were no consistent hysteresis effects for different nutrient species and different storm events. For instance, TP and PP displayed clockwise hysteresis during E1, whereas no hysteresis effect was displayed during E3. However, some nutrient species including TN, PN, NH₄⁺ and NO₃⁻ displayed consistent hysteresis effects during E1 and E3. For instance, TN, PN and NH₄⁺ all displayed clockwise hysteresis, whereas NO₃⁻ displayed anti-clockwise hysteresis. This anti-clockwise hysteresis for NO₃⁻ was also observed in the other catchments (Kato et al. 2009), whereas some authors (Houser et al. 2006) have observed that NO₃⁻ concentrations were higher on the rising limb of the hydrograph. The anti-clockwise trajectories suggested that NO₃⁻ was transported to the stream mainly by the subsurface flow and

### Table 2 | Discharge and nutrient concentration ranges in response to the storm events

<table>
<thead>
<tr>
<th>Event</th>
<th>Q (m³/s)</th>
<th>TN (mg/L)</th>
<th>DN (mg/L)</th>
<th>PN (mg/L)</th>
<th>TP (mg/L)</th>
<th>DP (mg/L)</th>
<th>PP (mg/L)</th>
<th>NO₃ (mg/L)</th>
<th>NH₄ (mg/L)</th>
<th>NO₂ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>0.9–418</td>
<td>4.6–72.6</td>
<td>2.5–58.8</td>
<td>2.1–22</td>
<td>0.2–2.9</td>
<td>0.07–2.6</td>
<td>0.013–0.151</td>
<td>0.2–15.6</td>
<td>0.19–2.4</td>
<td>0.02–14.3</td>
</tr>
<tr>
<td>E2</td>
<td>17.9–25.3</td>
<td>9.6–12.7</td>
<td>8.6–9.5</td>
<td>0.6–4.1</td>
<td>0.2–11</td>
<td>0.58–1.28</td>
<td>0.07–0.51</td>
<td>0.27–0.71</td>
<td>0.07–0.37</td>
<td>0.09–0.41</td>
</tr>
<tr>
<td>E3</td>
<td>17.3–61.8</td>
<td>7–10.1</td>
<td>7–9.6</td>
<td>0.5–1.6</td>
<td>0.1–3.4</td>
<td>0.17–0.65</td>
<td>0.19–0.53</td>
<td>0.26–1.05</td>
<td>0.19–0.41</td>
<td>0.01–0.79</td>
</tr>
</tbody>
</table>

### Table 3 | Pearson correlation coefficients between nutrient concentrations and discharge

<table>
<thead>
<tr>
<th>Event</th>
<th>TN</th>
<th>DN</th>
<th>PN</th>
<th>TP</th>
<th>DP</th>
<th>PP</th>
<th>NO₃-N</th>
<th>NH₄-N</th>
<th>NO₂-N</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>0.74</td>
<td>0.70</td>
<td>0.60</td>
<td>0.91</td>
<td>0.43</td>
<td>0.89</td>
<td>0.23</td>
<td>0.96</td>
<td>0.08</td>
</tr>
<tr>
<td>E2</td>
<td>0.29</td>
<td>-0.52</td>
<td>0.42</td>
<td>0.40</td>
<td>0.41</td>
<td>0.19</td>
<td>0.25</td>
<td>0.57</td>
<td>0.04</td>
</tr>
<tr>
<td>E3</td>
<td>-0.71</td>
<td>-0.81</td>
<td>0.27</td>
<td>0.40</td>
<td>0.45</td>
<td>0.27</td>
<td>-0.32</td>
<td>0.46</td>
<td>-0.42</td>
</tr>
</tbody>
</table>

Values in bold are statistically significant ($p < 0.05$).
thus had a high export during the falling limb of the hydrographs in this catchment. However, NH$_4$ concentration was almost synchronized with the discharge change and displayed mainly a clockwise trajectory, and this pattern was also reported by Chen et al. (2012). This implies that the majority of NH$_4$ in the storm runoff might

Figure 3 | Example for hysteresis patterns of nutrient concentrations and discharge during E1 and E3; the arrows indicate the time course.
have been delivered from surface sources, and mainly washed off and transported by surface runoff during the storm events.

CONCLUSIONS

Contrasting patterns of nutrient dynamics were investigated during three storm events associated with different rainfall characteristics in a semi-arid catchment with a typical monsoon climate in northern China. The results show that nutrient concentrations had broader fluctuations in the extreme storm than the moderate and small events, whereas the concentration fluctuation ranges during the moderate storm were no broader than those during the small storm. Correlation coefficients between nutrient concentrations and flow discharges varied from positive to negative for the different storm events, and the hysteresis effects showed no consistent patterns among the three events. These findings provide useful information for better understanding of the nutrient dynamics during storm events that would be much less likely to be observed by infrequent sampling investigations in this semi-arid area of a monsoon climate region. Infrequent sampling (e.g. monthly) can lead to severe underestimation of annual nutrient load because our results demonstrate that nutrient concentration will increase dramatically during storm events. It can thus be suggested that the monitoring and modeling of watershed nutrient discharge need to be conducted in high temporal resolution on a continuous basis to better understand nutrient dynamics. Moreover, the high contribution of storm events to annual nutrient load indicates that control measures should be implemented to reduce nutrient discharge to receiving water bodies during storm events, and structural best management practices, such as detention ponds and swales have been demonstrated as effective measures (Chang et al. 2007). However, the number of storm events collected in this study was limited and more event-based observations are needed to investigate nutrient dynamics for various combinations of different hydrological and antecedent conditions.

ACKNOWLEDGEMENTS

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REFERENCES


APHA 2005 Standard Methods for the Examination of Water and Wastewater, 21st edn, American Public Health Association, Washington, DC.


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