*Pol. J. Environ. Stud. Vol. 21, No. 6 (2012), 1621-1627*

*Original Research*

# Nitrogen and Phosphorous in Atmospheric Deposition and Roof Runoff

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*Received: 3 March 2012*
*Accepted: 9 August 2012*

## Abstract

Nitrogen (N) and phosphorus (P) were measured in atmospheric deposition and roof runoff in Beijing, China from May to October 2009. Serious N pollution caused by summer rainfall was found in Beijing. N was mainly transported in dissolved from, while P was predominantly found in its particle form. Bulk deposition potentially accounted for as much as 70%, 71%, 97%, and 45% of total nitrogen (TN), dissolved nitrogen (DN), total phosphorus (TP), and dissolved phosphorous (DP) loads in roof runoff, respectively, indicating that atmospheric deposition predominantly contributes to roof runoff pollution in Beijing. Moreover, wet deposition was an important source of TN, DN, and DP, while dry deposition was the main source of TP. N and P concentrations in roof runoff decreased as the amount of rainfall increased. The monthly loads of N and P in roof runoff were linearly and positively correlated with the amount of rainfall, indicating that the amount of rain is an important factor that influences the N and P loads in roof runoff. The positive relationship between N and P fluxes (load divided by the dry weather period; mg/m$^2$d) and the mean daily rainfall intensity (amount of rainfall divided by the dry weather period; mm/d) suggest that N and P loads in roof runoff can be estimated by measuring the amount of rainfall and the antecedent dry weather period.

**Keywords:** nitrogen, phosphorus, wet deposition, dry deposition, bulk deposition, roof runoff

## Introduction

Urban nonpoint pollution has been identified as a major contributor to the degradation of urban water bodies [1]. Roof runoff is known as a potential source of nonpoint pollution because roofs typically make up a significant proportion of the impervious surfaces of urban catchments and because the compounds contained in roofing materials and those that are deposited onto roof surfaces can leach into the runoff [2]. Most studies report that roof runoff has a high concentration of pollutants [3, 4]. Therefore, it is essential to identify the sources of these pollutants and the factors that influence the water quality of roof runoff.

Roof runoff is affected by air quality (dry deposition), rainwater quality (wet deposition), and the materials used on the roof surface [5]. In urban areas, anthropogenic activities generate atmospheric emissions that mostly consist of submicron-sized particles and aerosols. These particles and aerosols are then deposited by fallout or washed out in the atmosphere by precipitation. Atmospheric deposition may be an important source of pollutants that end up in stormwater runoff, especially in urban areas. Previous research has mostly focused on the effect of roofing materials on the water quality of roof runoff [6-9]. There are a few studies about the contribution of atmospheric deposition to roof runoff [10, 11].

By measuring nitrogen (N) and phosphorus (P) pollution in wet deposition, dry deposition, bulk deposition (wet + dry), and asphalt roof runoff, this study aims to:

(1) characterize the concentrations and forms of N and P present in atmospheric deposition and roof runoff in Beijing

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(2) quantify the contributions of N and P load in atmospheric deposition to roof runoff
(3) determine the crucial factors that influence the water quality of roof runoff
(4) estimate nutrient loads in roof runoff

## Materials and Methods

### Site Description

This study was carried out at the Research Center for Eco-Environmental Sciences (RCEES) in northern Beijing. The campus is surrounded by residential and educational areas without any industrial activities around. The climate of Beijing is classified as Asian monsoon. The average annual rainfall is 600 mm, approximately 80% of which occurs in the summer and fall. Thus, sampling was conducted from May to October 2009.

### Sample Collection

Wet deposition was sampled using an automated wet deposition sampler that was installed on a rooftop (16 m in height) at RCEES. The automated sampler was equipped with two polyethylene boxes (60 cm × 40 cm × 50 cm) under a moveable cover triggered by a rainfall sensor. On dry days, the two boxes were covered. Rainfall activates the motor, opening the boxes and allowing wet deposition to be collected. Immediately after rainfall, the samples were brought to the laboratory for analysis and the dirty boxes were replaced.

Bulk depositions were collected using a funnel (211.15 $cm^2$) connected to a 2.5-L polyethylene bottle. The funnel and bottle were installed 150 cm above the rooftop of the RCEES building. Samples were collected approximately twice per month by rinsing the funnel and bottle with 250 mL of ultra-pure water in order to wash any N and P that had been adsorbed by or deposited onto the funnel.

Roof runoff was sampled by diverting part of the flow from the final point of the roof's draining pipes into a 120-L polyethylene container. The roof was made of asphalt. Three sampling sites were installed around the building.

Rainfall was measured at the Beijing urban ecosystem research station that had been installed on the rooftop of a building (16 m in height) at RCEES. Samples were only analyzed if the rainfall was significant enough to yield enough roof runoff. Twenty-eight rainfall events were collected in total in the RCEES campus during May 9, 2009 to October 30, 2009.

### Sample Analysis

All samples were filtrated using a 0.45-μm Millipore filter before measuring dissolved nitrogen (DN) and dissolved phosphorus (DP). Total nitrogen (TN) and DN were measured using the alkaline potassium persulfate digestion-UV spectrophotometric method. Total phosphorus (TP) and DP were measured using the persulfate digestion spectrophotometric method [12].

### Data Analysis

TN, DN, TP, and DP loads ($mg/m^2$) in bulk deposition were calculated as follows:

$$L_b = \frac{\sum_{i=1}^{n} C_i \times V_i}{S} \quad (1)$$

...where: $L_b$ is the bulk deposition load ($mg/m^2$), $C_i$ is the *i*th sampling concentration of the bulk deposition (mg/L), $V_i$ is the *i*th sampling volume of the bulk deposition (L), S is the surface area of the funnel ($m^2$), n is the number of samples.

TN, DN, TP, and DP concentrations ($mg/m^2$) in wet deposition or roof runoff were calculated as follows:

$$L_{w/r} = \sum_{i=1}^{n} C_i \times h_i \quad (2)$$

...where: $L_{w/r}$ is the wet deposition or roof runoff load ($mg/m^2$), $C_i$ is the *i*th sampling concentration of the wet deposition or roof runoff (mg/L), $h_i$ is the ith rainfall amount (mm), and n is the numbers of rainfalls recorded.

Note that evaporation, infiltration, and detention of roof runoff were unaccounted for when estimating the roof runoff load because these data were lacking.

The dry deposition load ($L_d$) was defined as the bulk deposition load ($L_b$) minus the wet deposition load ($L_w$) over the same sampling period.

The fluxes of TN, DN, TP, and DP in roof runoff were calculated by dividing the N or P loads ($mg/m^2$) per rainfall by the antecedent dry weather period (d).

Mean daily rain intensity (MDRI, mm/d) was defined as the amount of rainfall (mm) divided by the antecedent dry weather period (d).

Logarithmic and linear regression analyses were used to test the relationship between nutrient concentration (load or fluxes) and amount of rainfall (MDRI). All statistical analyses were performed using SPSS 13.0 (SPSS Inc., USA) and Excel 2003 (Microsoft, USA).

## Results

Total rainfall measured from May to October 2009 was 406.16 mm, which accounted for 84.51% of the total annual rainfall (480.6 mm) in Beijing in 2009. Rainfall ranged from 0.52-83.6 mm per event. The rain mainly fell in July and August

From May to October 2009 the mean concentrations of TN, DN, TP, and DP in wet deposition were 7.69±4.99, 6.54±4.13, 0.044±0.034, and 0.016±0.014 mg/L (n = 28), respectively. The mean concentrations of TN, DN, TP, and DP in bulk deposition were 10.87±7.08, 7.46±3.54, 0.285±0.395, and 0.029±0.034 mg/L (n = 10), respectively. The mean concentrations of TN, DN, TP, and DP in the roof runoff were 13.86±10.56, 12.12±9.94, 0.122±0.085, and 0.042±0.041 mg/L (n = 28), respectively (Table 1).

Table 1. Summary of N and P concentrations in atmospheric deposition and roof runoff during the 2009 wet season.

| Type | | Samples | Mean | Standard deviation | Median | Maximum | Minimum | National Standard |
|---|---|---|---|---|---|---|---|---|
| Wet deposition (mg/L) | TN | 28 | 7.69 | 4.99 | 7.27 | 18.51 | 0.84 | 2 |
| | DN | 28 | 6.54 | 4.13 | 6.4 | 15.71 | 0.83 | 2 |
| | TP | 28 | 0.044 | 0.034 | 0.035 | 0.165 | 0.008 | 0.4 |
| | DP | 28 | 0.016 | 0.014 | 0.011 | 0.055 | 0.001 | 0.4 |
| Bulk deposition (mg/L) | TN | 10 | 10.87 | 7.08 | 8.92 | 23.84 | 2.58 | 2 |
| | DN | 10 | 7.46 | 3.54 | 6.9 | 13.25 | 2.42 | 2 |
| | TP | 10 | 0.285 | 0.395 | 0.073 | 1.106 | 0.01 | 0.4 |
| | DP | 10 | 0.029 | 0.034 | 0.015 | 0.104 | 0.002 | 0.4 |
| Roof Runoff (mg/L) | TN | 28 | 13.86 | 10.56 | 11.9 | 58.38 | 2.56 | 2 |
| | DN | 28 | 12.12 | 9.94 | 9.96 | 55.23 | 2.37 | 2 |
| | TP | 28 | 0.122 | 0.085 | 0.108 | 0.39 | 0.036 | 0.4 |
| | DP | 28 | 0.042 | 0.041 | 0.026 | 0.164 | 0.011 | 0.4 |

National Standard corresponds to Class V of the National Standard for Surface Water Quality (GB 3838-2002) [13] issued by State Environmental Protection Agency of China.

DN concentration accounted for 85%, 67%, and 88% of TN concentration in wet deposition, bulk deposition, and roof runoff, respectively, while DP concentration accounted for only 36%, 10%, and 34% of TP concentration in wet deposition, bulk deposition, and roof runoff, respectively. This indicates that N was predominantly available in dissolved form, but P was predominantly available in particulate form (TP minus DP) (Fig. 1).

From May to October 2009, the bulk deposition loads of TN, DN, TP, and DP were 2614.17, 2138.77, 32.745 and 4.587 mg/m$^2$, respectively, accounting for as much as 70%, 71%, 97%, and 45% of TN, DN, TP, and DP loads in roof runoff, respectively (Table 2). The wet deposition loads of TN, DN, and DP were 2095.28, 1738.57, and 4.583 mg/m$^2$, accounting for as much as 56%, 58%, and 45% of the TN, DN, and DP loads in the roof runoff, respectively (Table 2). However, TP content of the dry deposition was an important source of roof runoff and accounted for as much as 63% of the TP load in roof runoff.

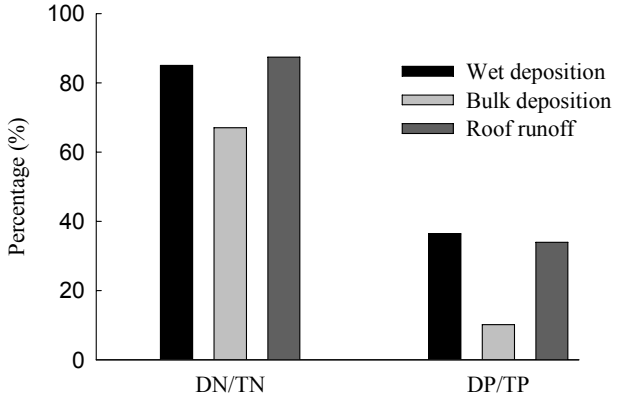


Fig. 1. Percentage of dissolved substance (DN and DP) in total substance (TN and TP).

In July and August TN, TP, DN, and DP concentrations were much lower than those measured in April, June, September, and October (Fig. 2a and 2b). A negative logarithmic relationship between mean TN, TP, DN, and DP concentrations and rainfall was noted (Fig. 3).

Monthly loads of TN, TP, DN, and DP in July and August were higher than that those measured in April, June, September, and October, except for DP in June (Fig. 2c and 2d). A linear positive relationship between the monthly nutrient loads and amount of rainfall was observed (Fig. 4).

The fluxes of TN, TP, DN, and DP increased significantly along with MDRI in a linear fashion ($p < 0.001$) (Fig. 5).

## Discussion

### N and P Levels in Atmospheric Deposition and Roof Runoff

In our study, the mean N concentrations in wet deposition, bulk deposition, and roof runoff were 3-7 times greater than those allowed by the Class V surface water standards developed by China [13] (Table 1). In addition, the mean N concentrations reported in this study are much higher compared with other study areas, such as Singapore (wet deposition: 1.05 mg/L TN) [14], Connecticut, USA (bulk deposition: 1.2 mg/L TN) [15], and Wuhan, China (roof runoff: 6.4-10.4 mg/L TN, 3.07-4.39 mg/L DN) [16]. The high concentration of N in atmospheric deposition and roof runoff in Beijing may be due to large $NH_x$ and $NO_x$ emissions that result from the use of fertilizers in suburban and rural areas, and fossil fuel combustion in urban areas. Beijing is surrounded by the North China Plain, which is

Table 2. N and P loads in atmospheric deposition and roof runoff during the 2009 wet season.

| | TN | DN | TP | DP |
|---|---|---|---|---|
| Wet deposition (mg/m$^2$) | 2095.28 | 1738.57 | 11.433 | 4.583 |
| Dry deposition (mg/m$^2$) | 518.89 | 400.2 | 21.312 | 0.004 |
| Bulk deposition (mg/m$^2$) | 2614.17 | 2138.77 | 32.745 | 4.587 |
| Roof runoff (mg/m$^2$) | 3746.3 | 2993.29 | 33.536 | 10.235 |
| Wet deposition/roof runoff | 0.56 | 0.58 | 0.34 | 0.45 |
| Dry deposition/roof runoff | 0.14 | 0.13 | 0.63 | 0.00 |
| Bulk deposition/roof runoff | 0.70 | 0.71 | 0.97 | 0.45 |

one of the most agriculturally intensive and rapidly developing regions in China. The excessive use of N fertilizer is very common, which results in a large amount of atmospheric N emission and deposition. Liu et al. [17] and Zhang et al. [18] found the annual bulk deposition (27-30 kg/ha N) of $NH_4^+$-N and $NO_3^-$-N in the North China Plain is 3-4 times that of Rothamsted Experimental Station, UK (9 kg/ha N) and central New York, USA (7.7 kg/ha N). In addition, local anthropogenic activities (e.g., traffic exhaust, incineration of domestic waste, industrial activities, etc.) in urban microclimates may be other important sources that contribute to the high rates of N deposition in Beijing. A previous study [19] found that there was a relatively larger amount of N deposition around traffic arteries and power plants than other areas in urban Beijing, and the authors have suggested that the main sources of N are vehicles and power plants *via* the combustion of oil or coal. However, the mean concentration of P measured in wet deposition, bulk deposition, and roof runoff were within Class V surface water standards [13]. The mean concentrations of P measured in atmospheric deposition and roof runoff in the present study are comparable to the values measured in Lake Taihu, China (wet deposition: 0.044 mg/L TP) [20], Singapore (wet deposition: 0.025-0.027 mg/L TP) [21], and Estonia (roof runoff: 0.102-0.104 mg/L TP) [22]. These results indicate that atmospheric deposition and roof runoff are seriously polluted by N in Beijing, and protective measures should be taken such as reducing N emissions from vehicles, power plants, and the use of fertilizers.

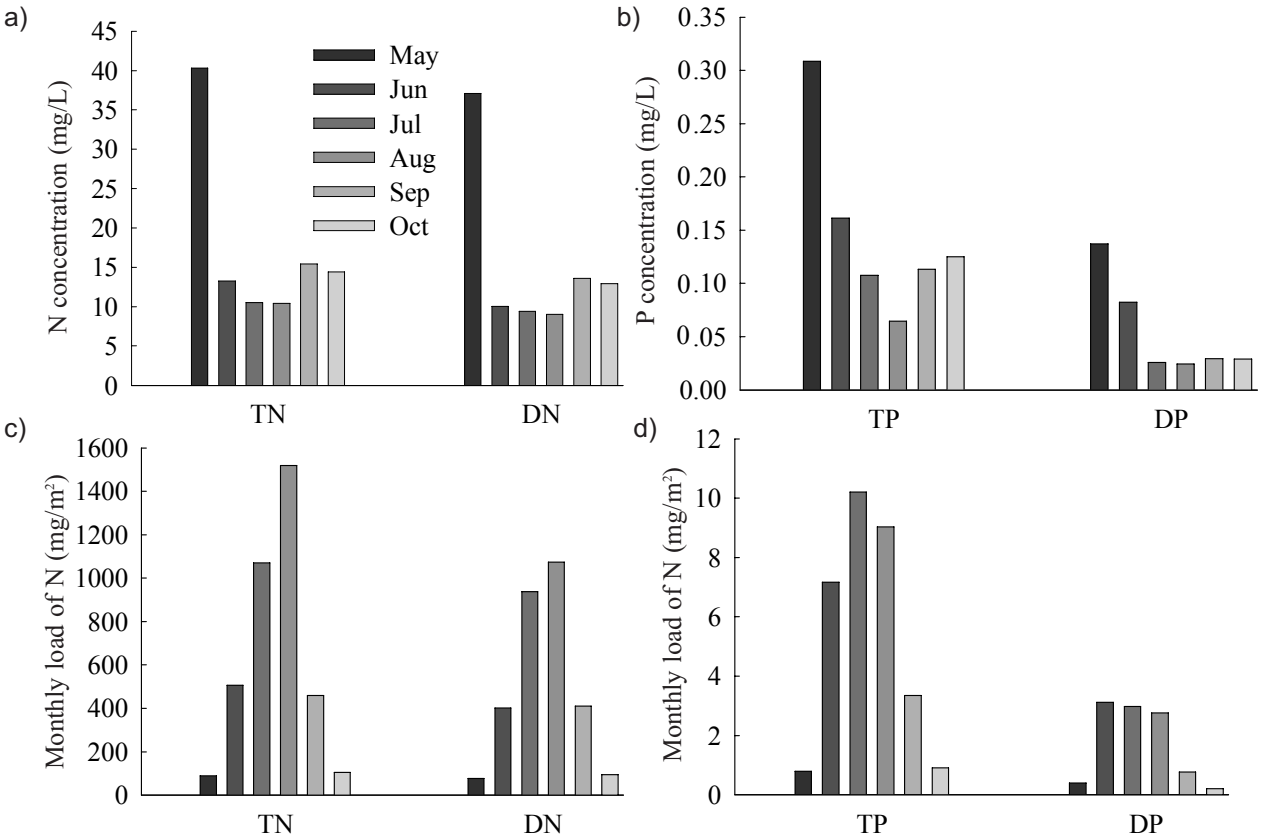


Fig. 2. Monthly mean concentrations (a and b) and loads (c and d) of N and P in roof runoff, respectively.

## Contributions of Atmospheric N and P to Roof Runoff

Assuming that the total quantity of the deposition onto the rooftop was available for removal via rainfall runoff, bulk deposition potentially accounts for as much as 45-97% of the nutrient load in roof runoff, which indicates that bulk deposition is an important contributor to roof runoff in Beijing. Furthermore, TN, DN, and DP loads in wet deposition were much higher than dry deposition from May to October 2009 in the present study (Table 2), suggesting the dominance of wet deposition in Beijing. However, the TP

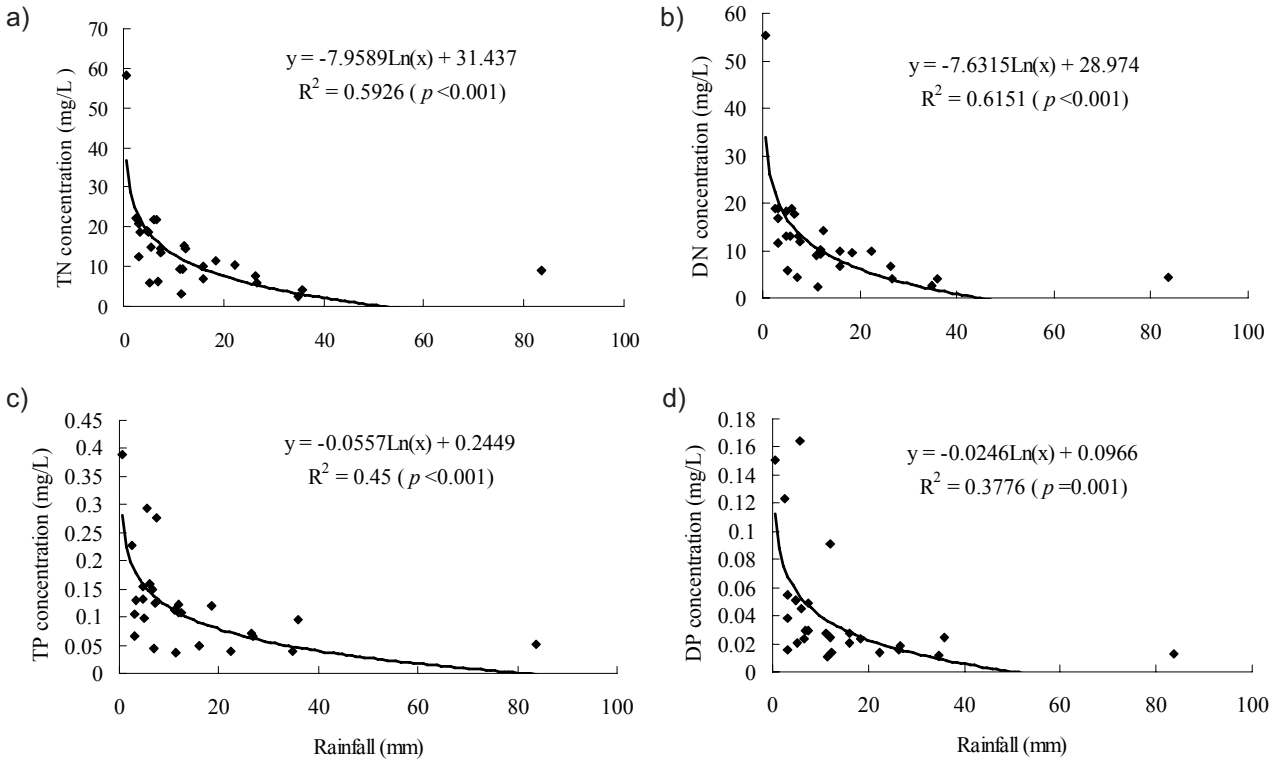


Fig. 3. Relationships between TN (a), DN (b), TP (c) and DP (d) concentrations and rainfall amount in roof runoff.

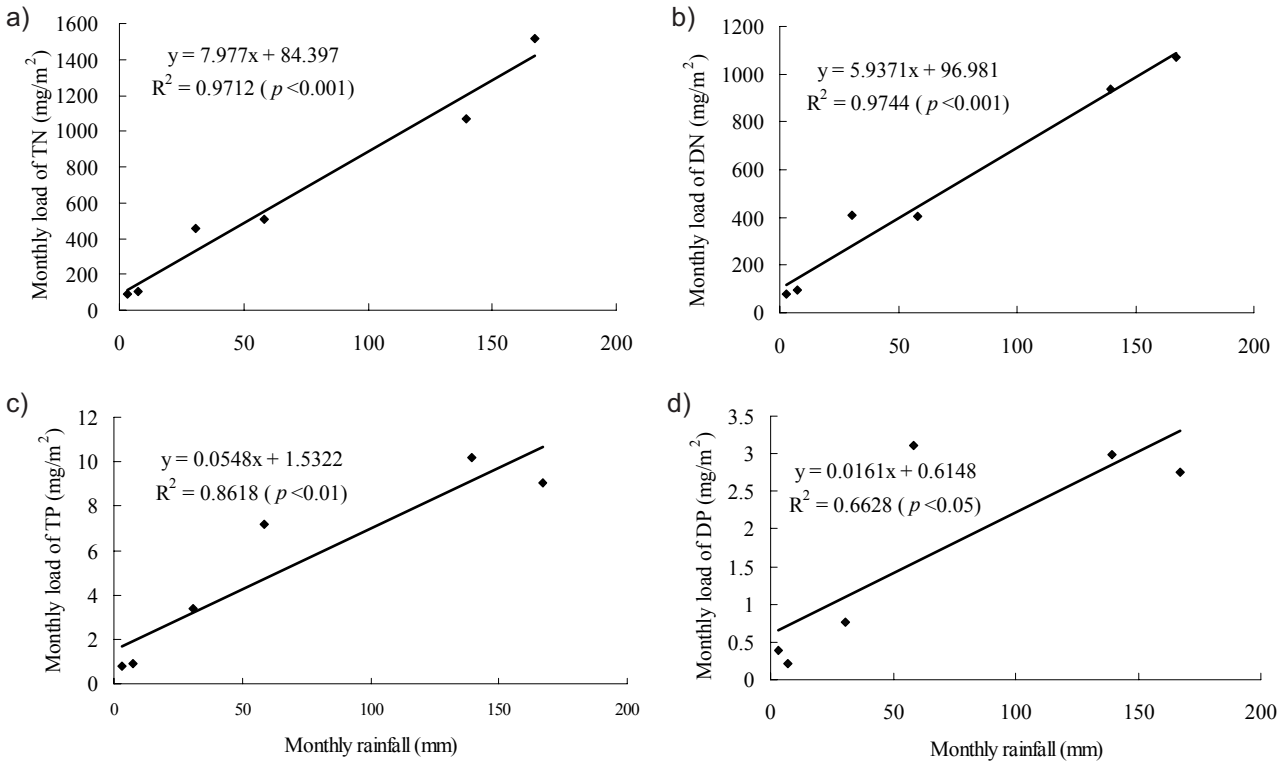


Fig. 4. Relationships between monthly loads of TN (a), DN (b), TP (c) and DP (d) and monthly amount of rainfall in roof runoff.

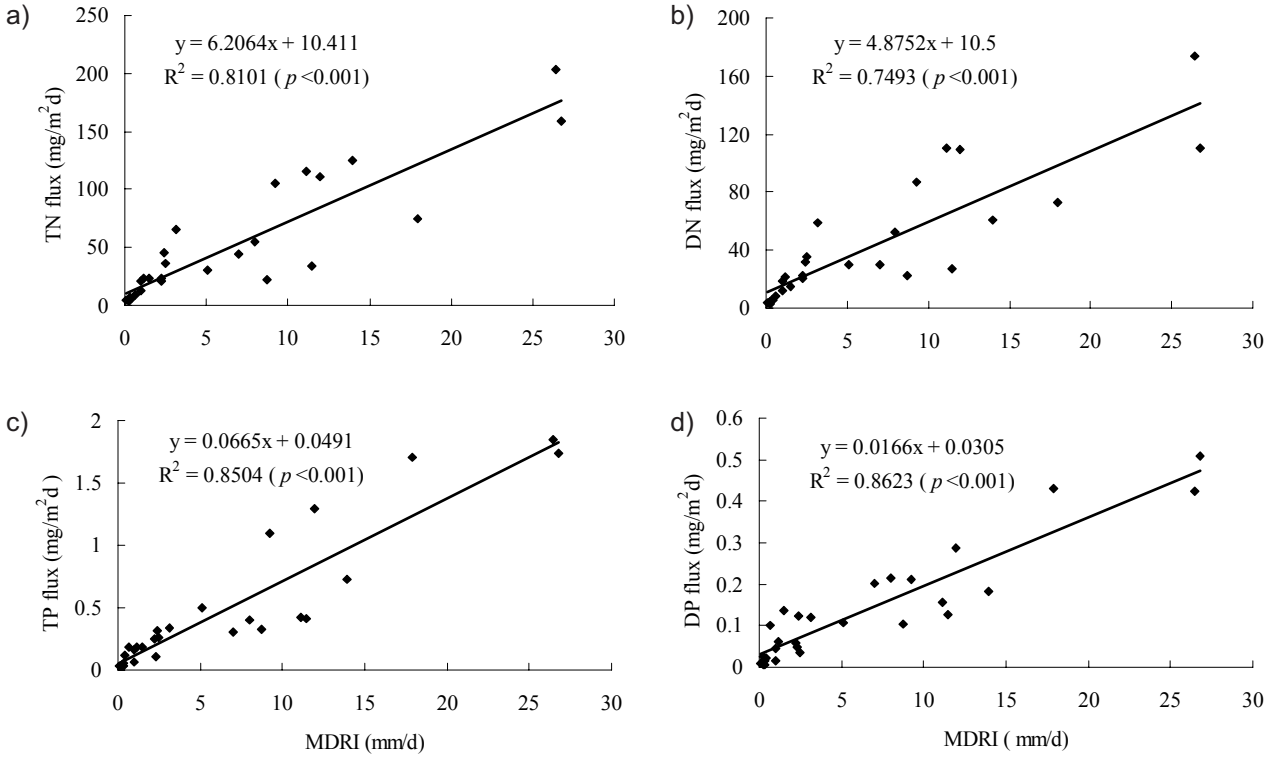


Fig. 5. Relationships between TN (a), DN (b), TP (c) and DP (d) fluxes and mean daily rain intensities (MDRI) in roof runoff.

load in dry deposition was higher than in wet deposition (Table 2). Several studies also support the finding that dry deposition of TP is higher than wet deposition [23, 24]. The different distributions of wet and dry depositions may be related to the form and origin of N and P pollutants. Generally, N was available in the dissolved form in rainwater, which washes out the gaseous and aerosol forms of $NO_x$ and $NH_3$ components before it falls to the ground [25]. However, P was mainly available in its particle form, and P that originates from the soil or impervious surfaces is not incorporated into rainfall [24]. These results indicate that atmospheric deposition should not be ignored when assessing the sources of nutrient pollution that contaminate waterbodies in urban areas.

## Factors Influencing N and P Pollution in Roof Runoff

There are many factors that influence urban stormwater runoff pollution, such as duration and intensity of the rainfall event, amount of rainfall, and the antecedent dry weather period. In the present study, a negative logarithmic correlation between rainfall and N and P concentrations in roof runoff was observed (Fig. 3), indicating that significant nutrient concentrations are diluted in rainwater. A previous study also found the dilution effect and they suggested that the initial rainfall washes out most pollutants that had adsorbed or deposited onto rooftops or roads and any additional rainwater further dilutes the pollutants that have already been washed out [11, 26]. The lower concentrations of N and P that were measured in July and August (Figs. 2a and 2b) further confirms this dilution effect on rainwater, as the rainfall and frequency were high in these 2 months. However, the monthly loads of nutrients in the roof runoff increased with the monthly amount of rainfall (Figs. 2c and 2d), and the positive relationship between monthly N and P loads and rainfall (Fig. 4) suggest that the amount of rainfall is an important factor that influences the N and P loads in roof runoff.

## Estimating the Nutrient Load in Roof Runoff

To estimate nutrient loads in roof runoff, the relationship between N and P fluxes and MRDI were further investigated. Rocher et al. [10] also estimated the loads of hydrocarbons and metals using the relationship between fluxes and MRDI. In the present study, the nutrient fluxes correlated well with MDRI (Fig. 5). The equations used could provide a new approach for estimating the N and P loads in urban areas of Beijing with similar roof runoffs by measuring the amount of rainfall and the antecedent dry weather period.

## Conclusion

Atmospheric deposition and roof runoff were seriously polluted by N in Beijing. N was predominantly available in its dissolved form in atmospheric deposition and roof runoff, while P was mainly available in its particle form. TN, DN, and DP were mainly present at high levels in wet deposition, while TP was mostly present at high levels in dry deposition. Bulk deposition was an important contributor to roof runoff. The concentrations and loads of N and P in roof runoff were predominantly dependent on the

amount of rainfall. In Beijing, nutrient load in roof runoff can be estimated by measuring the amount of rainfall and the antecedent dry weather period.

## Acknowledgements

This research was funded by the National Natural Science Foundation of China (No. 41030744, 40901265, and 41230633) and the Chinese Academy of Sciences (KZCX2-EW-310).

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