Evaluation of surface runoff and road dust as sources of nitrogen using nitrate isotopic composition

Keisuke Kojima ^a, Michio Murakami ^{b, *}, Chikage Yoshimizu ^c, Ichiro Tayasu ^c, Toshi Nagata ^d
and Hiroaki Furumai ^a

^a Graduate School of Engineering, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo
113-8656, Japan

^b "Wisdom of Water" (Suntory), Corporate Sponsored Research Program Organization for
Interdisciplinary Research Projects, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku,
Tokyo 113-8656, Japan

^c Center for Ecological Research, Kyoto University, Japan, 2-509-3, Hirano, Ohtsu, Shiga
520-2113, Japan

^d Atmosphere and Ocean Research Institute, The University of Tokyo, 5-1-5, Kashiwanoha,
Kashiwa, Chiba 227-8564, Japan

* Corresponding author:

Phone +81-3-5841-6263

e-mail: michio@env.t.u-tokyo.ac.jp

Abstract

Stable nitrogen and oxygen isotope ratios of nitrate ($\delta^{15}\text{N}\text{-NO}_3$ and $\delta^{18}\text{O}\text{-NO}_3$) have recently been used to identify nitrogen sources in water environments. However, there have been no investigations designed to determine nitrate isotopes in non-point sources in urban areas for evaluating the impact of surface deposits on nitrogen in surface runoff. In this study, we collected rainwater, surface runoff and surface deposits (road dust, roof dust and soil) to evaluate the nitrogen sources in surface runoff using nitrate isotopes. There were no large differences in $\delta^{15}\text{N}\text{-NO}_3$ among rainwater (-0.3–1.5‰), surface runoff (-2.7–0.4‰), leachates from road dust (-5.8–6.2‰) and soil (-11.5–0.6‰). In contrast, the $\delta^{18}\text{O}\text{-NO}_3$ in surface runoff (28.5–47.9‰) was lower than that in rainwater (62.7–78.6‰), and higher than that in leachates from road dust (6.1–27.6‰) and soil (-1.1–6.6‰). $\delta^{18}\text{O}\text{-NO}_3$ is a useful indicator for evaluating the $\text{NO}_3\text{-N}$ sources in surface runoff. Using this indicator, $\text{NO}_3\text{-N}$ from road dust was estimated to account for more than half of the $\text{NO}_3\text{-N}$ in surface runoff. This is consistent with a result based on a comparison of their loads per unit surface between rainwater and surface runoff, which also showed that most of the nitrogen in surface runoff was derived from surface deposits.

Key words:

Atmospheric deposition; Diffuse pollution; Nitrogen isotope; Non-point pollution; Road runoff; Street dust;

1. Introduction

Urban surface runoff is contaminated by non-point pollutants such as nitrogen, heavy metals and polycyclic aromatic hydrocarbons derived from traffic activity and has been regarded as an important pathway for the delivery of pollutants to water environments (Garnaud et al., 1999; Zobrist et al., 2000; Shinya et al., 2003; Haus et al., 2003; Murakami et al., 2004; Baun et al., 2006). Non-point pollutants are widely distributed in the atmosphere and on surfaces. Since it is difficult to control these distributed pollutants, pollutant loads from non-point sources have become relatively larger than those from point sources. Consequently, effective strategies are needed to control pollutants from non-point sources.

The sources of non-point derived nitrogen in urban areas include atmospheric particles and surface deposits (e.g. road dust) (Turner et al., 2002; Shinya et al., 2003; Tsai and Cheng, 2004). It is useful to distinguish between the loads imposed by the atmosphere and surface deposits when considering source-specific countermeasures such as road sweeping. A comprehensive investigation of pollutant loads per unit surface in rainwater and surface runoff is a traditional way to distinguish between loads imposed by the atmosphere and by surface deposits (Davis et al., 2001; Sabin et al., 2005). Sabin et al. (2005) collected wet and dry deposition and stormwater within a small, highly impervious urban catchment in Los Angeles and estimated that, according to the ratio of the loads per unit surface in total deposition to that in stormwater, atmospheric deposition potentially accounted for as much as 57–100% of the total trace metal loads in stormwater within the study area. Zobrist et al. (2000) showed that NO_3 loads in wet depositions and the tile roof runoff and the runoff ratio

1 were 2.9 mgN m⁻², 3.1 mgN m⁻², and 79%, respectively, and the contribution of NO₃ from wet
2 atmospheric deposition to the runoff was therefore calculated to be 93%. However, there were
3 large uncertainties in the estimates of the loads per unit surface, because of the propagation of
4 errors associated with determining the concentration, rainfall amount, and runoff flow rate.
5 Another approach is to use nitrogen stable isotope ratios, because nitrogen stable isotope
6 ratios differ among sources, and this difference would be useful for estimating their sources
7 (Widory et al., 2005; Xue et al., 2009; Kohzu et al., 2009). Recently, it has become possible to
8 measure stable nitrogen and oxygen isotopes of nitrates ($\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$), and
9 therefore $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ have been used to identify nitrogen sources in agricultural
10 soil, rivers, groundwater, estuarine systems, and aerosols (Mengis et al., 2001; Ohte et al.,
11 2010; Kaowan et al., 2009; Wankel et al., 2009a, b). However, to our knowledge, there have
12 been no investigations to determine the nitrate isotopes in non-point sources in urban areas
13 and to evaluate the impact of surface deposits on nitrogen in surface runoff. It is now
14 necessary to investigate $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ from non-point sources in urban areas, and
15 to evaluate the impact of surface deposits on nitrogen in surface runoff using $\delta^{15}\text{N-NO}_3$ and
16 $\delta^{18}\text{O-NO}_3$.

17 In this study, we collected rainwater and surface runoff in an urban catchment served by
18 a separate sewer system to measure their nitrogen concentrations, loads per unit surface,
19 $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$. In addition, we collected surface deposits (road dust, roof dust and
20 soil from a park and planted zones) and compared the nitrogen concentration, $\delta^{15}\text{N-NO}_3$ and
21 $\delta^{18}\text{O-NO}_3$ in leachates from the surface deposits with those in surface runoff and rainwater to
22 evaluate the nitrogen sources in the surface runoff.

2. Materials and methods

2.1. Samples

The rainwater, surface runoff and surface deposits were collected in Asahimachi, Chiba City, Chiba Prefecture, Japan, as shown in Fig. 1. The catchment area is about 5.4 ha, and is served by a separate sewer system. The discharge pump station is situated at the end of the sewer system. In this study, road dust, roof dust, and soil from a park and planted zones were considered surface deposits.

The rainwater (bulk water) was collected in cylindrical containers (10 centimeters in diameter) installed 2 m above the ground. The rainwater sampler collected rainwater together with atmospheric fallout during dry weather periods. Surface runoff was collected at the end of separate sewer pipes by an automatic water sampler (ISCO Co., LTD.). The automatic water sampler went on line when 1 mm of rainfall was recorded within 2 hours. The sampling interval was 10 minutes. A water level gauge (Grant Co., Ltd.) was also employed to measure the water level of the surface runoff. The flow rate of the surface runoff was calculated with a height-quantity curve.

Table 1 shows information about the rainwater and surface runoff sampling. The rainwater samples were collected in all five events, whereas surface runoff samples were collected in Events 2 and 4. The initial 2-h samples of surface runoff were collected. The flow rate was measured in Event 4. The rainwater and surface runoff samples were filtered with a PTFE membrane filter (Advantec, H045A, pore size: 0.45 μm).

Road dust (collected at Sites A–D, Fig. 1), roof dust (A, B) and soil from a park and planted zones (A–C) were also collected in the same catchment area on March 30, 2009. The antecedent dry weather period and rainfall amount were 117 h and 4.5 mm, respectively. The

road dust samples were collected from the side of a road using a dry vacuum cleaner (Hitachi CV-100S6). The roof dust and soil samples were collected with pig-bristle brushes and plastic tubes, respectively. The road dust, roof dust and soil were air-dried at room temperature, and then homogenized after being sieved through a 2 mm mesh to remove larger particles. The amounts of road dust collected at Sites A to D were 138, 51, 1291 and 136 g m⁻², whereas the amounts of collected roof dust A and B were 3.4 and 7.8 g m⁻².

All the samples were stored in a refrigerator at 5 °C until their subsequent analysis.

2.2. Extraction tests

To get information about the compositional ratio of inorganic nitrogen and nitrate isotope values in leachates from surface deposits, extraction tests were conducted in accordance with those of previous studies (Murakami et al., 2008a, 2009). The air-dried samples and deionized water were mixed at an L/S ratio of 10 L kg⁻¹ dry material and shaken for 16 h at a speed of 200 rpm at room temperature in the dark. All of the leachates were obtained by the centrifugation (1600 G, 20 min) and filtration of the supernatant with a glass fiber filter (Whatman, GF/F, pore size: 0.7 µm) and then with a PTFE membrane filter (Advantec, H045A, pore size: 0.45 µm).

It has already been confirmed that the pH and pollutant concentration, such as the total nitrogen, dissolved organic carbon (DOC) and heavy metals, in the road dust leachates, were of the same order of magnitude as those in the dissolved phase of actual road runoff water (Murakami et al., 2008a, b, 2009).

2.3. Chemical analyses

The NO₂-N and NO₃-N concentrations were measured by ion chromatography (Metrohm, Compact IC 761) with a Shodex SI-904E column (4.0 mm i.d. × 250 mm) and a suppressed conductivity detector at an oven temperature of 40 °C and a flow rate of 1.2 mL min⁻¹ using 1.7 mM NaHCO₃ and 1.8 mM Na₂CO₃ as eluents. The NH₄-N concentration was measured using indophenol blue absorptiometry. The total inorganic nitrogen (TIN) was regarded as the sum of NO₂-N, NO₃-N and NH₄-N.

δ¹⁵N-NO₃ and δ¹⁸O-NO₃ were analyzed using the denitrifier technique (Sigman et al., 2001; Casciotti et al., 2002). In brief, a sample (NO₃⁻) was converted into nitrous oxide (N₂O) by denitrifying bacteria that lacked N₂O-reductase activity. When the NO₂-N/(NO₂-N+NO₃-N) ratio of the samples exceeded 0.05, NO₂ was removed by reaction with ascorbic acid prior to incubation (Granger et al., 2006). The N₂O was stripped from the sample vial using He as the carrier gas, purified using cryogenic trapping (Precon, ThermoFisher), separated chromatographically (GasBench, ThermoFisher), and analyzed using isotope ratio mass spectrometry (Delta^{Plus}XP, ThermoFisher).

The isotope values are reported using the usual delta notation as per mil relative to standard material. In this study, δ¹⁵N-NO₃ and δ¹⁸O-NO were calculated as the following equations.

$$\delta^{15}\text{N} = ((^{15}\text{N} / ^{14}\text{N})_{\text{sample}} / (^{15}\text{N} / ^{14}\text{N})_{\text{standard}} - 1) \times 1000$$

$$\delta^{18}\text{O} = ((^{18}\text{O} / ^{16}\text{O})_{\text{sample}} / (^{18}\text{O} / ^{16}\text{O})_{\text{standard}} - 1) \times 1000$$

Where, (¹⁵N/¹⁴N)_{sample} and (¹⁸O/¹⁶O)_{sample} are the molar ratios of the samples, and (¹⁵N/¹⁴N)_{standard} and (¹⁸O/¹⁶O)_{standard} are the molar ratios of standard materials (N; nitrogen gas

in the atmosphere ($^{14}\text{N} : ^{15}\text{N} = 99.634 : 0.366$), O; Vienna Standard Mean Ocean Water (VSMOW) ($^{16}\text{O} : ^{17}\text{O} : ^{18}\text{O} = 99.762 : 0.038 : 0.200$)).

3. Results and discussion

3.1. Nitrogen concentration in rainwater, surface runoff and leachates from surface deposits

Fig. 2 shows the temporal change in the nitrogen concentration in surface runoff in Events 2 and 4. The TIN, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ concentrations in Event 2 were 1.71–5.62, 0.10–0.13, 1.11–3.59 and 0.49–1.90 mg L^{-1} and those in Event 4 were 1.45–1.98, not detectable (<0.03), 1.24–1.71, 0.21–0.36 mg L^{-1} , respectively. First flush phenomena were typically observed in both events; i.e. their concentrations were high in early periods and then gradually decreased. All of the nitrogen concentrations in the early periods in Event 2 were higher than those in Event 4, probably due to the longer antecedent dry weather period.

Table 2 compares the concentrations of TIN, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and the ratios of the sum of $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$ ($(\text{NO}_2\text{-N} + \text{NO}_3\text{-N}) / \text{NH}_4\text{-N}$) in rainwater, surface runoff, and leachates from surface deposits. The concentrations of $\text{NO}_3\text{-N}$ in surface runoff were higher than those in rainwater for each rain event. These results highlight the fact that the nitrate in surface runoff derived from surface deposits as well as the atmosphere.

On the other hand, the $\text{NH}_4\text{-N}$ concentrations in surface runoff were similar to those in rainwater. The $(\text{NO}_2\text{-N} + \text{NO}_3\text{-N}) / \text{NH}_4\text{-N}$ ratios in surface runoff were higher than those in rainwater. This result suggested the adsorption of $\text{NH}_4\text{-N}$ onto solids and/or the preferential wash-off of $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ from surface deposits.

To evaluate the nitrogen sources, rainwater and surface runoff were compared with

leachates from surface deposits (road dust, roof dust and soil), as shown in Table 2. The TIN concentrations in leachates from road dust, roof dust and soil were in the 0.96–4.19, 0.88–10.4 and 0.09–3.54 mg L⁻¹ ranges, respectively.

The (NO₂-N+NO₃-N)/ NH₄-N ratios of leachates from road dust, roof dust and soil were in the 0.33-6.91, 0.13-0.25 and 1.94-31.7 ranges, respectively. The (NO₂-N+NO₃-N)/ NH₄-N ratios in leachates from roof dust were much lower than those in surface runoff (1.8–6.3). This is probably because roof dust was not a major source of nitrogen in surface water. This is consistent with a finding that roof dust plays a minor role in non-point pollutants in surface runoff (Murakami et al., 2004). On the other hand, the (NO₂-N+NO₃-N)/ NH₄-N ratios in leachates from road dust and soil varied widely and overlapped with those in rainwater (0.59–1.67) and surface runoff. These results indicate that there was a limitation to the apportionment of the nitrogen source using the (NO₂-N+NO₃-N)/ NH₄-N ratios as indicators of surface deposits.

3.2. Estimation of contribution of nitrogen from surface deposits based on the loads per unit surface in rainwater and surface runoff

The Sartor and Boyd model (Sartor and Boyd, 1972) was used to estimate the total load per unit surface of nitrogen in surface runoff.

$$dP(t) / dt = -kR(t)P(t)$$

$$W = P_0(1 - e^{-kQ})$$

Where, P(t) is the mass of pollutants per unit surface [mg m⁻²], k is the wash-off coefficient

[m³], R(t) is the runoff rate [m³ min⁻¹], t is time [min], W is the wash-off mass of pollutants per unit surface [mg m⁻²], P₀ is the initial mass of pollutants per unit surface at t = 0 [mg m⁻²], and Q is the accumulated runoff volume [m³].

Fig. 3 shows the relationship between the accumulated runoff volume and accumulated wash-off mass of TIN, NO₃-N and NH₄-N. As shown in Fig. 3, it is possible to express the nitrogen wash-off using the Sartor and Boyd model. The total loads per unit surface of nitrogen in surface runoff were then calculated using the Sartor and Boyd model and the total runoff volume in Event 4 (28.6 m³). Although the total rainfall amount was relatively low (2.5 mm), it is very important to determine the nitrogen loads in a weak rainfall event. In fact, weak rainfall ≤ 2.5 mm occurred frequently in this study area; e.g. 90 out of 155 events in 2008 (Japan Meteorological Agency, 2010).

Table 3 compares the total loads of nitrogen per unit surface for rainwater and surface runoff in Event 4. The NO₃-N load per unit surface in surface runoff was larger than that in rainwater, whereas the NH₄-N load per unit surface in surface runoff was lower than that in rainwater. The contribution ratio of nitrogen from surface deposits to surface water was calculated using the following equation.

$$R_{\text{Surface}} = 1 - (L_{\text{Atmosphere}} \times \text{runoff ratio}) / L_{\text{runoff}} \times 100$$

Where, R_{Surface} is the contribution ratio of nitrogen from surface deposits [%], L_{Atmosphere} is the load per unit surface in rainwater [mg m⁻²], L_{runoff} is the load per unit surface in surface runoff [mg m⁻²], and the runoff ratio is the ratio of total surface runoff volume to total rainfall

1 volume [-].

2
3 Since the total rainfall amount in Event 4 was low (2.5 mm), the runoff ratio in Event 4
4 was 0.21. This value possibly includes uncertainty originating in the measurements of the
5 rainfall amount and flow rates. Table 3 also shows the contribution ratio of nitrogen from
6 surface deposits to surface runoff. The contribution ratios of TIN, NO₃-N and NH₄-N from
7 surface deposits were 85, 89 and 65%, respectively. Since the minimum quantity of rainfall
8 measurement is 0.5 mm, values of 2.0 to 3.0 mm were used to evaluate the uncertainties. The
9 estimated contribution ratios of TIN, NO₃-N and NH₄-N from surface deposits were 81–87%,
10 86–91%, and 56–70%, respectively. These results reveal that nitrogen from surface deposits
11 had a great impact on the loads in surface runoff.

12
13 ***3.3. Evaluation of nitrate source in surface runoff using nitrate isotopes ($\delta^{15}\text{N-NO}_3$ and***
14 ***$\delta^{18}\text{O-NO}_3$)***

15 The nitrate isotopes ($\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$) in rainwater, surface runoff and
16 leachates from surface deposits are shown in Fig. 4 and Table S1. Fig. 4 includes the results
17 reported by Kendall et al. (2007). To our knowledge, this is the first study to reveal nitrate
18 isotopes in surface runoff and leachates from surface deposits. Also, the temporal changes in
19 $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ in surface runoff are shown in Fig. S1. The temporal trends of the
20 two events were inconsistent. Fig. S2 shows the relationship between NO₃ concentration and
21 the values of $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ in rainwater and surface runoff. $\delta^{15}\text{N-NO}_3$ varied little
22 over the gradient of NO₃ concentration, whereas $\delta^{18}\text{O-NO}_3$ values in rainwater (lower NO₃
23 concentrations, <1 mg L⁻¹) were higher than those in surface runoff (higher NO₃

1 concentrations, $>1 \text{ mg L}^{-1}$). These results indicate that a source (or sources) that is isotopically
2 distinct from rainwater (i.e., $\delta^{18}\text{O-NO}_3$ values lower than rainwater) contributed to NO_3 in
3 surface runoff.

4 The $\delta^{15}\text{N-NO}_3$ in rainwater and surface runoff were -0.3 – 1.5 and -2.7 – 0.4‰ ,
5 respectively. There was no large difference between the $\delta^{15}\text{N-NO}_3$ in rainwater and surface
6 runoff. The $\delta^{15}\text{N-NO}_3$ in leachates from road dust, roof dust and soil were -5.8 – 6.2 , 20.3 – 25.7
7 and -11.5 – 0.6‰ , respectively. The leachates from roof dust exhibited a particularly high
8 $\delta^{15}\text{N-NO}_3$. This result suggested that roof dust makes a negligible contribution to the $\text{NO}_3\text{-N}$
9 in surface runoff, which was consistent with the finding derived from the $(\text{NO}_2\text{-N}+\text{NO}_3\text{-N})/$
10 $\text{NH}_4\text{-N}$ ratios as shown in Section 3.1. Since the rainwater, surface runoff and leachates from
11 road dust and soil were in a similar $\delta^{15}\text{N-NO}_3$ range, $\delta^{15}\text{N-NO}_3$ is not a good indicator for
12 distinguishing between nitrate from rainwater and nitrate from road surface deposits.

13 On the other hand, the values of $\delta^{18}\text{O-NO}_3$ in rainwater, surface runoff, and leachates
14 from road dust, roof dust and soil were 62.7 – 78.6 , 28.5 – 47.9 , 6.1 – 27.6 , 65.9 – 67.0 and
15 -1.1 – 6.6‰ , respectively. There were large differences among the values in rainwater, surface
16 runoff, and leachates from road dust and soil, and that in rainwater was the highest. The
17 values of $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ in rainwater were comparable to those in rainwater
18 reported by Kendall et al. (2007) and Xue et al. (2009). The leachates from roof dust also
19 exhibited particularly high $\delta^{18}\text{O-NO}_3$. Atmospheric deposition materials are known to exhibit
20 high $\delta^{18}\text{O-NO}_3$, because photochemical reactions with ozone generate extremely high
21 $\delta^{18}\text{O-NO}_3$ when nitrogen oxide is formed in the atmosphere (Kendall et al., 2007). High
22 $\delta^{18}\text{O-NO}_3$ in rainwater and leachates from roof dust showed that their nitrates were derived
23 from the atmosphere. High $\delta^{15}\text{N-NO}_3$ in roof dust may be attributed to additional sources such

as bird droppings, which show high $\delta^{15}\text{N-NO}_3$ (Kendall et al., 2007). Low $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ in leachates from soil might result from oxidation of NH_4^+ in rainwater or fertilizer (Kendall et al., 2007). Widory (2007) reported that the values of $\delta^{15}\text{N}$ in vehicle emissions, heating sources, and waste incinerators were 3.9–5.4, -19.4–15.4 and 5.5–8.0‰, respectively. The value of $\delta^{15}\text{N-NO}_3$ in leachates from road dust was in the range of these values. NO_3 in road dust is likely to be mixture of these sources. To our knowledge, there are no investigations of $\delta^{18}\text{O-NO}_3$ in vehicle emissions: further investigations are required in order to identify the source of NO_3 in road dust.

Interestingly, the $\delta^{18}\text{O-NO}_3$ in surface runoff fell between that in rainwater and leachates from road dust and soil. The $\delta^{18}\text{O-NO}_3$ in surface runoff can be explained in terms of a mixture of atmospheric deposition materials and leaching from road dust and/or soil that have low $\delta^{18}\text{O-NO}_3$. $\delta^{18}\text{O-NO}_3$ is considered to be useful for evaluating the contributions of nitrate from rainwater and road surface deposits to surface runoff.

Since the infiltration rate in soil is reported to be 2.5–25.4 mm h⁻¹ (Horton, 1940), the runoff of nitrate leachates from soil was negligible for weak events such as Event 2 (initial 2 h rainfall: total rainfall amount, 3.3 mm; average rainfall intensity, 1.6 mm h⁻¹; maximum rainfall intensity; 3 mm h⁻¹) and Event 4 (total rainfall amount, 2.5 mm; average rain intensity, 0.6 mm h⁻¹; maximum rain intensity, 3 mm h⁻¹). Therefore, we assumed that rainwater and road dust could have a great impact on the amount of nitrate in the surface runoff in Events 2 and 4. The contribution ratio of $\text{NO}_3\text{-N}$ in the surface runoff from road dust was calculated with the following equation using $\delta^{18}\text{O-NO}_3$.

$$\delta^{18}\text{O-NO}_3_{\text{runoff}} = R_{\text{road}} \times \delta^{18}\text{O-NO}_3_{\text{road}} + (1 - R_{\text{road}}) \times \delta^{18}\text{O-NO}_3_{\text{rain}}$$

Where, $\delta^{18}\text{O-NO}_3_{\text{runoff}}$ is the $\delta^{18}\text{O-NO}_3$ in surface runoff [‰], $\delta^{18}\text{O-NO}_3_{\text{road}}$ is the $\delta^{18}\text{O-NO}_3$ in leachates from road dust [‰] (arithmetic mean; 15.6‰), $\delta^{18}\text{O-NO}_3_{\text{rain}}$ is the $\delta^{18}\text{O-NO}_3$ in rainwater [‰], and R_{road} is the contribution ratio of $\text{NO}_3\text{-N}$ in surface runoff from road dust [%].

Using this equation, the contribution ratio of $\text{NO}_3\text{-N}$ in surface runoff from road dust was estimated to be 49-75% (arithmetic mean; 62%) in Event 2 and 41-73% (52%) in Event 4. In this way, it is possible to quantify the contribution ratio of $\text{NO}_3\text{-N}$ in surface runoff from road dust by using $\delta^{18}\text{O-NO}_3$.

Two evaluations using nitrate loads per unit surface (see Section 3.2.) and $\delta^{18}\text{O-NO}_3$ showed a consistent result; i.e. the contribution ratio from the road surface accounted for more than half of the $\text{NO}_3\text{-N}$ in the surface runoff. This suggests that it is possible to reduce nitrogen loads by sweeping road surfaces. The small difference between the contribution ratios in the two evaluations was attributable to uncertainty in the calculation of the runoff ratio based on rainfall amount and flow rate.

4. Conclusion

Nitrate isotopes in surface runoff, rainwater and leachates from surface deposits (road dust, roof dust and soil) were investigated to evaluate the sources of nitrogen and their utility as indicators. Results obtained from this research were as follows.

- The concentrations of TIN , $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ in surface runoff were higher than those in

rainwater. The ratios of the sum of $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ to $\text{NH}_4\text{-N}$ in surface runoff were higher than those in rainwater. $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ were preferentially derived from surface deposits.

- A comparison of the rainwater and surface runoff in the nitrogen loads per unit surface showed that nitrogen was mainly derived from surface deposits.

- The nitrate isotopes ($\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$) in surface runoff and leachates from surface deposits were determined in this study. There was no difference among the $\delta^{15}\text{N-NO}_3$ in rainwater, surface runoff and leachates from road dust and soil. On the other hand, the $\delta^{18}\text{O-NO}_3$ in surface runoff was lower than that in rainwater, and higher than that in leachates from road dust and soil. $\delta^{18}\text{O-NO}_3$ is a useful indicator for evaluating the $\text{NO}_3\text{-N}$ sources in surface runoff. Using this indicator, $\text{NO}_3\text{-N}$ from road dust was estimated to account for more than half of the $\text{NO}_3\text{-N}$ in surface runoff.

- Two evaluations, namely the nitrogen loads per unit surface and the use of nitrate isotopes, indicated that it is important to consider nitrogen from road dust as a source of nitrogen in urban areas.

Acknowledgements

This study was partly supported by the Japan Sewage Works Association (2008FY) and the CREST project grant on ‘Development of Well-balanced Urban Water Use System Adapted for Climate Change’ provided by the Japan Science and Technology Agency (JST).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

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Table and Figure captions

Table 1 Information on rainwater and surface runoff sampling.

Table 2 Concentrations of TIN , $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, $\text{NH}_4\text{-N}$ and the $(\text{NO}_2\text{-N}+\text{NO}_3\text{-N})/\text{NH}_4\text{-N}$ ratios in rainwater, surface runoff, and leachates from road dust, roof dust, and soil.

1 Table 3 Total loads of nitrogen in rainwater and surface runoff per unit surface and their
2 contribution ratio from surface deposits to surface water in Event 4.

3
4 Fig. 1 Sampling locations.

5
6 Fig. 2 Temporal change of nitrogen concentration in surface runoff. (a) Event 2, (b) Event 4.

7
8 Fig. 3 Relationship between accumulated runoff volume and accumulated mass fluxes of
9 nitrogen in Event 4. (a) TIN, (b) NO₃-N, (c) NH₄-N.

10
11 Fig. 4 $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ in rainwater, surface runoff and leachates from road dust, roof
12 dust, and soil. Area shows the range of the $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values in Kendall et al.
13 (2007).

Table 1 Information on rainwater and surface runoff sampling.

	Date	Total rainfall amount [mm]	Rainfall duration [h]	Maximum rainfall intensity [mm 10min ⁻¹]	Antecedent dry weather period [h]	Antecedent rainfall amount [mm]
Event 1	May 12 - 14, 2008	63.5	21	2.0	31	23.0
Event 2	June 12, 2008	30.5	15	2.5	152	31.5
Event 3	June 21 - 23, 2008	103.5	47	4.0	200	30.5
Event 4	June 26, 2008	2.5	4	0.5	49	103.5
Event 5	June 29 - 30, 2008	65.0	31	8.0	54	2.5

Table 2 Concentrations of TIN, NO₂-N, NO₃-N, NH₄-N and the (NO₂-N+NO₃-N)/ NH₄-N ratios in rainwater, surface runoff, and leachates from road dust, roof dust, and soil.

	TIN [mgN L ⁻¹]	NO ₂ -N [mgN L ⁻¹]	NO ₃ -N [mgN L ⁻¹]	NH ₄ -N [mgN L ⁻¹]	(NO ₂ -N+NO ₃ -N)/NH ₄ -N
<i>Rainwater</i>					
Event 1	0.32	n.d. ^a	0.20	0.12	1.67
Event 2	2.35	n.d. ^a	0.87	1.48	0.59
Event 3	0.37	n.d. ^a	0.17	0.20	0.88
Event 4	0.31	n.d. ^a	0.18	0.13	1.44
Event 5	0.36	n.d. ^a	0.21	0.15	1.45
<i>Surface runoff</i>					
Event 2	1.71-5.62	0.10-0.13	1.11-3.59	0.49-1.90	1.8-2.5
Event 4	1.45-1.98	n.d. ^a	1.24-1.71	0.21-0.36	3.9-6.3
<i>Road dust leachates</i>					
Road dust A	1.37	n.d. ^a	0.53	0.84	0.63
Road dust B	4.19	n.d. ^a	1.04	3.15	0.33
Road dust C	0.96	0.08	0.59	0.10	6.91
Road dust D	1.24	n.d. ^a	0.40	0.85	0.47
<i>Roof dust leachates</i>					
Roof dust A	10.40	0.04	2.02	8.31	0.25
Roof dust B	0.88	n.d. ^a	0.10	0.78	0.13
<i>Soil leachates</i>					
Soil A	0.09	n.d. ^a	0.09	n.d. ^a	>3.0
Soil B	2.00	n.d. ^a	1.94	0.06	31.7
Soil C	3.54	0.03	2.31	1.20	1.94

a: not detectable (detection limit is 0.03 mgN L⁻¹).

Table 3 Total loads of nitrogen in rainwater and surface runoff per unit surface and their contribution ratio from surface deposits to surface water in Event 4.

	Rainwater [mg m ⁻²]	Surface runoff [mg m ⁻²]	Contributions from surface deposits
TIN	0.78	1.06	85% (81-87%) ^a
NO ₃ -N	0.46	0.88	89% (86-91%) ^a
NH ₄ -N	0.32	0.19	65% (56-70%) ^a

a: Uncertainties were evaluated based on minimum quantity of rainfall amount measurement.

Fig. 1 Sampling locations.

Fig. 2 Temporal change of nitrogen concentration in surface runoff. (a) Event 2, (b) Event 4.

Fig. 3 Relationship between accumulated runoff volume and accumulated mass fluxes of nitrogen in Event 4. (a)TIN, (b) NO₃-N, (c) NH₄-N.

Fig. 4 $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ in rainwater, surface runoff and leachates from road dust, roof dust, and soil. Area shows the range of the $\delta^{15}\text{N-NO}_3$ and $\delta^{18}\text{O-NO}_3$ values in Kendall et al. (2007).