SEPARATION OF SOURCES AND QUANTIFICATION OF DISSOLVED NUTRIENTS IN THE THROUGHFALL

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ABSTRACT
In order to understand the fate of nutrients in a forest ecosystem, it is necessary to know the formation processes of water quality in throughfall. The purpose of this study is to clarify the effect of the rain property on the water quality in throughfall and to separate the sources (atmospheric deposition or washout of the leaching matter from internal of leaf) of nutrient in throughfall. We proposed a physically-based model on the washout of the leaching nutrients from a leaf based on Fick's first law of diffusion, in addition we separated the sources of the nutrients in throughfall by combining the model with a lab-scale experiments and field investigations. The washout model of leaching matter was sufficiently robust to estimate the amount of washout of matter during rainfall event. From the observation result, sources of NO_3^- and NH_4^+ were mainly atmospheric deposition, especially dry deposition was larger than wet deposition. On the other hand, the source of DOC was the leaching matter from internal of leaf in throughfall. Based on the model with lab-scale experiments and field measurements, the leaching DOC were possibly classified into two categories, quickly diffusing matter and slowly diffusing matter.

Keywords DOC, nitrogen, throughfall, wet deposition, dry deposition, leaching

INTRODUCTION
Nutrients diffusing from forested area, such as Japan where 70% of land is covered with forest, are important factor for eutrophication of rivers and lakes. Especially, the diffusion of nutrient with rainfall is important judging from the concentration of nutrients in stream water during high-flow period with rain is over 100 times larger than during base-flow period (Kunimatsu, 2000). Therefore it is necessary to know nutrients input, storage and outflow through the forest ecosystem as the diffuse source for controlling the eutrophication. Especially, clarification of the input process of nutrients is the most important because the input is related to the atmospheric condition, which is directly reflected on human activities. The nutrients input mainly depends on hydrological and biochemical processes through the tree leaves. The water quality of throughfall is determined by washout matter on the surface of leaves, which deposited from atmosphere (wet/dry deposition) and leached from leaves (leaching matter). In other words, it is key for understanding the nutrients input to clarify the effect of the rain property on the water quality in throughfall and to identify the sources (atmosphere or internal part of leaf) of nutrients in throughfall.

Previous studies about the effects of rain properties on the water quality in throughfall pointed out the importance of rainwater pH and reaction time for the quality of throughfall using lab-scale washout experiment (Puckett,1990) and the close relationship between rainfall and the quality of throughfall based on the field observation (Lovett *et al*., 1984). However, these previous studies do not consider the washout processes during the rainfall event and the detailed sources of matters in throughfall.

The purpose of our study is the development of the physically-based model on the washout of the matter from leaves during rain and the separation of sources of matters in throughfall. The details are (1) applying the Fick's first law of diffusion to the washout of the leaching matter from leaves, (2) examination of the washout using lab-scale experiment, and (3) separation of sources of matters in throughfall observed at a field using the model reflected the result of the washout experiment.

MODELS
Matters on surface leaf washed out by rainfall consist of dry deposition and leaching matter. It is assumed that the dry deposition is easily washed out at just a initial stage of rainfall event. On the other hand, the leaching matter is not easily taken up by rainwater. Here, we propose a model on washout the leaching matter based on the diffusion theory of matters from a solid layer. The fundamental equation is Fick's first law of diffusion:

$$\frac{dm}{dt} = -DS\frac{\Delta C}{f} \quad \ldots\ldots\ldots\ldots \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where *m* is the amount of the leaching matter on a leaf surface, *t* is the time, *S* is the area of a diffusing layer (cm^2), ä is the thickness of a diffusing layer (cm), *D* is the diffusion coefficient, and C is the difference in the concentration between the leaching matter and rainwater (mg/cm^3). In addition, the equation (1) is converted in follows:

$$\frac{dC}{dt} = -\frac{DS}{V\ddot{a}}(C0 - C) \ldots\ldots\ldots\ldots \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where C is the concentration of rainwater, $C0$ is the concentration of the leaching matter at t=0 (mg/cm^3), and V is the volume of rainwater(cm^3), into which the leaching matter diffuses.

The combination of equation (2) and $\frac{DS}{W\ddot{a}} = k$ gives equation (3):

$$C = C0(1 - e^{(-kt)}) \ldots\ldots\ldots\ldots \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

where k is a constant.

This study focuses on formation processes of the quality of throughfall. Equation (3) means that the water quality related to the washout of the leaching matter is determined by $C0$ and k.

METHODS

Site

Observation was conducted in the Forests of Yamanashi Institute of Environmental Sciences at the north foot of Mt. Fuji in Japan (Figure 1). The height above the sea level is 1030m. This area is classified as a cool temperate zone; the monthly mean temperature in 2002 ranges from 0.4^{o}C (January) to 23.5^{o}C (July). The annual precipitation is 1403mm in 2002. These meteorological data was observed at Kawaguchiko AMeDAS station (automated meteorological data acquisition system by Japan Meteorological Agency), which is nearby this study site. The dominant tree species are Japanese red pine (*Pinus Densiflora*), which is evergreen conifer and occupies the forest overstory, and Japanese holly (*Ilex pedunculosa's*) occupying the understory. The mean canopy height and the diameter of the red pine trees are approximately 19m and 0.3m, respectively. The slope of this area is 3.5^o and the bedrock is volcaniclastic rock. At the centre of this forest a tower (19m in height) for access to the forest canopy is located.

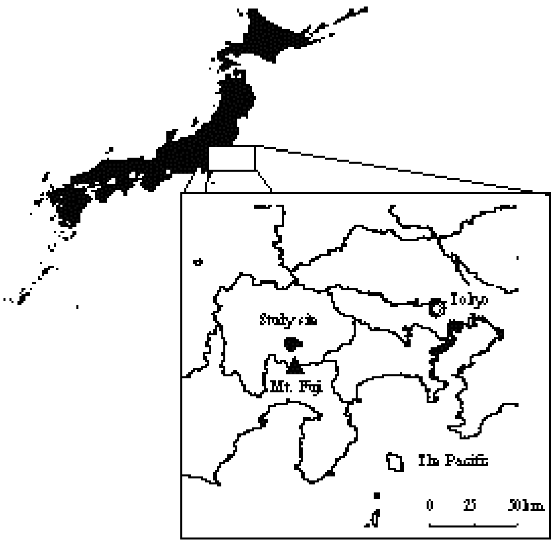


Figure 1 The location of study site

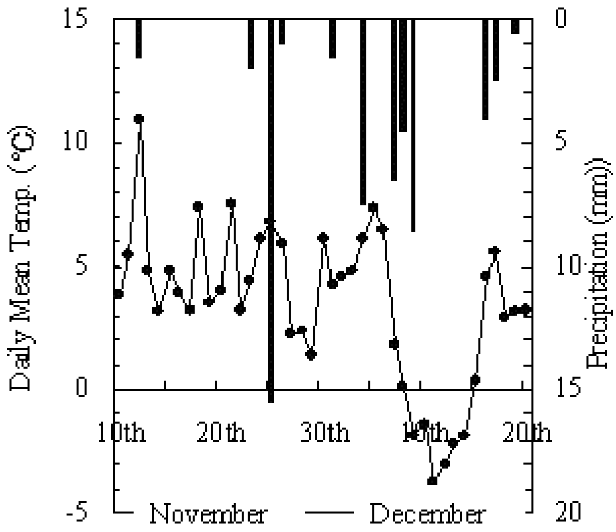


Figure 2 The daily mean temperature and precipitation in the study site during the investigation period

Observation and experiment plan and weather conditions

The observation and experiment were planned at two terms; 1st term is 12 to 25 November 2002 and 2nd term is 10 to 17 December 2002. Each term included the collection of wet deposition, dry deposition and throughfall in the study and a washout experiment in laboratory. At the 1st term, dry deposition was collected for 8 days and rainfall event was at 25 November. At the 2nd term, dry deposition was collected for 6 days and rainfall event was at 16 December. Figure 2 shows the daily mean temperature and precipitation during the investigation period. The precipitation of the 1st and the 2nd term were 16.5mm and 6.5mm, respectively. The duration of rainfall at 1st and the 2nd term ware 15hours and 5hours, respectively. The temperature of the 2nd term was colder than the 1st term and under 0 degrees during almost the period collecting dry deposition.

Wet and dry deposition and throughfall

Throughfall collected at three places in the forest and wet deposition collected at one place at the top of the tower. Throughfall and wet deposition were colleted by polyethylene funnels (30cm in diameter). Matsumoto (2001) explains the detail of instruments of throughfall and wet deposition. Dry deposition was collected using six sets of glass petri dishes

(9cm in diameter) at the same places as the study site of the wet deposition. The surfaces of the dishes were extracted with 10ml of ultrapure water. Three dishes were gathered as one sample to ensure enough amounts of dry deposition for analysis, which the concentration of dry deposition in one dish is quite low, and then nutrients in the sample were measured. The amount of dry deposition in each term was estimated; at first, the daily amount of dry deposition is calculated by dividing the measured amount of dry deposition by the number of days of the observation period, and then the daily amount of dry deposition multiplies the number of days without rainfall. NO_3^- and NH_4^+ were measured by ion chromatograph method and DOC was measured by oxidation/NDIR method.

Washout experiment

Leaves exposed to atmosphere were sampled from the canopy at the top of the tower and were put into a plastic bag and brought to the laboratory. Leaves were experimented within 24 hours after sampling of leaves. Dipping 50 to 100 leaves in the experimental solution, which was changed after 1, 2, 3, 5 and 7 hours in the 1st term and 0.5, 1, 2, 3 and 5 hours in the 2nd term. The four types of experimental solution were used, which are ultrapure water and acidified to pH 3.8, 4.8 and 5.8 with reagent grade H_2SO_4. The concentrations of NO_3^-, NH_4^+ and DOC in the each experimental solution were measured.

RESULTS

***Wet deposition, dry deposition and throughfall* – Field observation**

Figure 4 shows comparison with the amount of nutrients of wet deposition (WD), dry deposition (DD) and throughfall (TF). The amount of each nutrient during 1st term was greater than 2nd term in response to the number of days without rainfall, i.e. the duration of deposition period and the amount of rainfall for washout. Although on NO_3^- and NH_4^+ there is no constant magnitude relation between TF and WD and DD, on DOC there is a notable feature that TF is remarkably greater than WD and DD.

***Washout of leaves* – laboratory experiment**

Figure 5 shows the results of the washout experiment of NO_3^-, NH_4^+ and DOC, which pH of the experimental solution changes. The amount of each constituent at the 1st time is the largest at other times. The amount of NO_3^- and NH_4^+ after the 2nd time was less than the detection limit or very low to compare with the 1st time. The amount of DOC after the 2nd time did not fluctuate very much. The coefficient of variation of DOC at the 1st to 4th time was less than 30 %.

DISCUSSION

Comparison with the amount of leaching matter between NO_3^-, NH_4^+ and DOC

The amount of leaching matter was estimated by subtracting wet and dry deposition from throughfall, TF-(WD+DD), on the basis of field observation data. The amounts of leaching NO_3^- at the 1st and the 2nd term are 0.3eq/ha and -0.1eq/ha, respectively. The amounts of leaching NH_4^+ at the 1st and the 2nd term are -2.1eq/ha and -0.4eq/ha, respectively. The minus values mean absorption of matter into leaves. We do not intend to discuss mechanisms of the absorption because this study focuses on the leaching from leaves. On the contrary, the amount of leaching DOC at the 1st and 2nd term are very high, 2100g-C/ha and 430g-C/ha, respectively. The leaching DOC occupies the main part of throughfall, 91% in the 1st term and 74% in the 2nd term. From the estimation of and the results of the washout experiment (Figure 6), DOC differs completely from NO_3^- and NH_4^+ in leaching property, which NO_3^- and NH_4^+ hardly leach from leaves. It is implied that the washout process of leaching DOC is key to understand DOC input into forest floor as throughfall.

Parameters and verification of the model on washout of leaching DOC

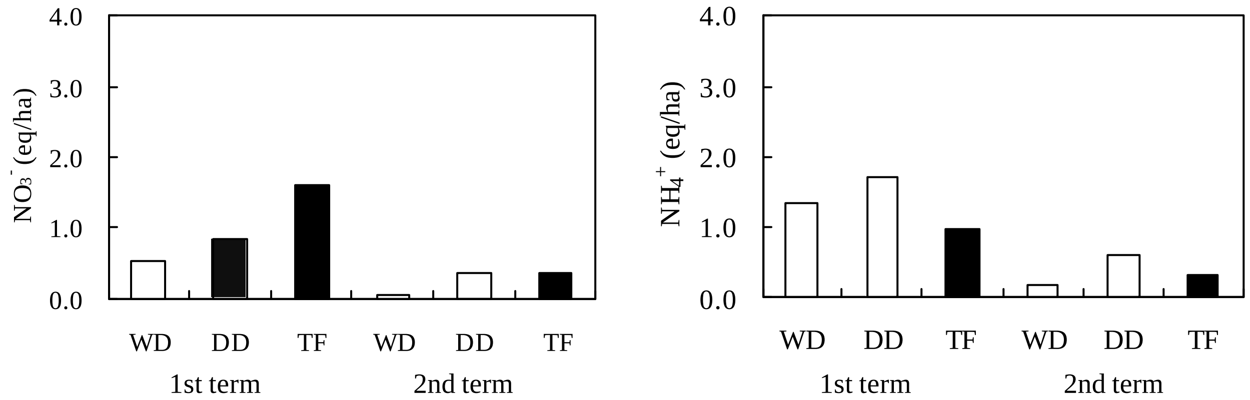
As NO_3^- and NH_4^+ seem to hardly leach from leaves, we apply the washout model to only leaching DOC. The leaching matter accumulated on the leaf surface decreases with diffusion into the experimental solution every time the solution is changed in the washout experiment (Figure 6). The concentration of the leaching DOC at *n*th manipulation in the experiment is expressed based on equation (3) as follows:

$$\begin{cases} C_{(n)} = C0_{(n-1)}(1-e^{(-kt)}) \\ C0_{(n-1)} = (C0 - \sum_{n=1}^{n} C_{(n-1)}) \end{cases} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

where $C_{(n)}$ and $C0_{(n)}$ are the concentration of the leaching matter at $t=t$ and $t=0$ at nth manipulation, respectively. Substituting n=1 and 2 gives $C0$:

$$C0 = \frac{C_{(2)}}{e^{(-kt)}(1-e^{(-kt)})} \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Here, k is given the general diffusion coefficient value 1×10^{-5}, S in the 1st term and the 2nd term are 212cm^2 and 463cm^2, respectively, V is 80cm^3 in both terms, *ä* is provided 1×10^{-3}cm, and then, $C0$ is estimated to be 45.3mg-C/l in the 1st term and 51.8 mg-C/l in the 2nd term. Figure 6 shows the comparison between DOC concentration calculated by the model and measured in the washout experiment. Although the difference of DOC concentration between the model and the measurement is large at 1st time, the difference is very small after 2nd time. Assuming that the dry deposition is easily washed out at just a initial stage of rainfall event, this result seems reasonable. Therefore, the model is sufficiently robust to estimate the amount of washout of DOC during rainfall event.



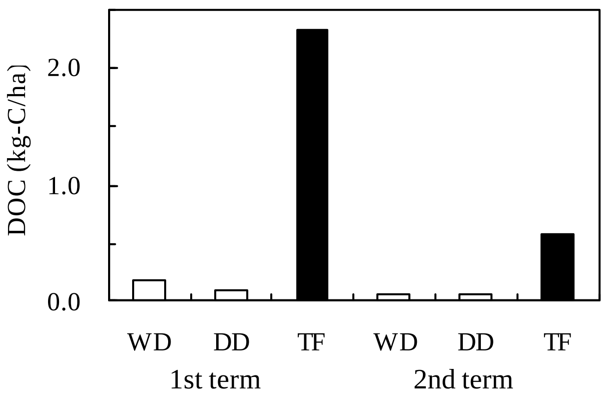
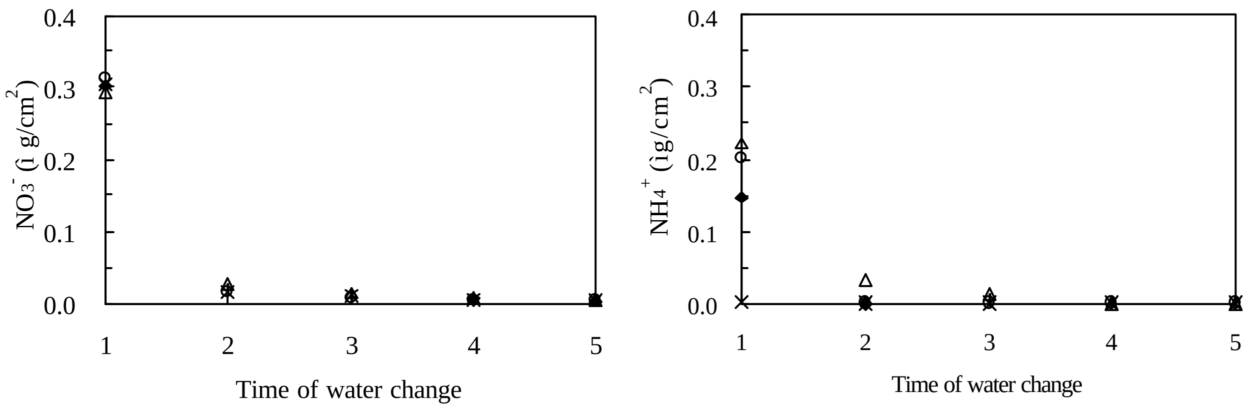


Figure 4 NO_3^-, NH_4^+ and DOC in wet deposition, dry deposition and throughfall in both terms.



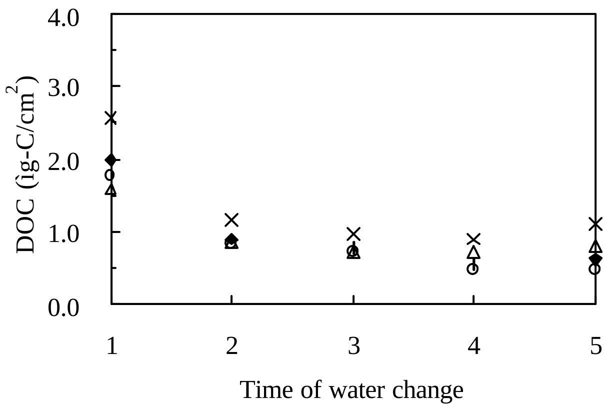


Figure 5 The washout experiment of NO_3^-, NH_4^+ and DOC which solution pH changed (3.8, 4.8, 5.8) and ultrapure solution.

l :ultrapure water O:pH 5.8

Ä:pH 4.8 ×:pH 3.8

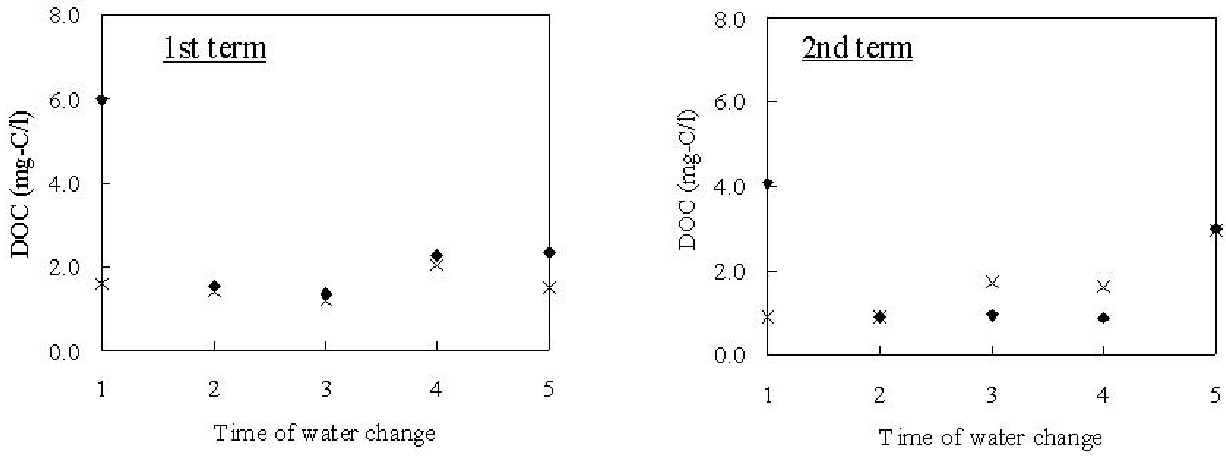


Figure 6 Comparison with the DOC concentration in the washout experiment and the model calculation in the diffusion model ◆□ measurement ×:model

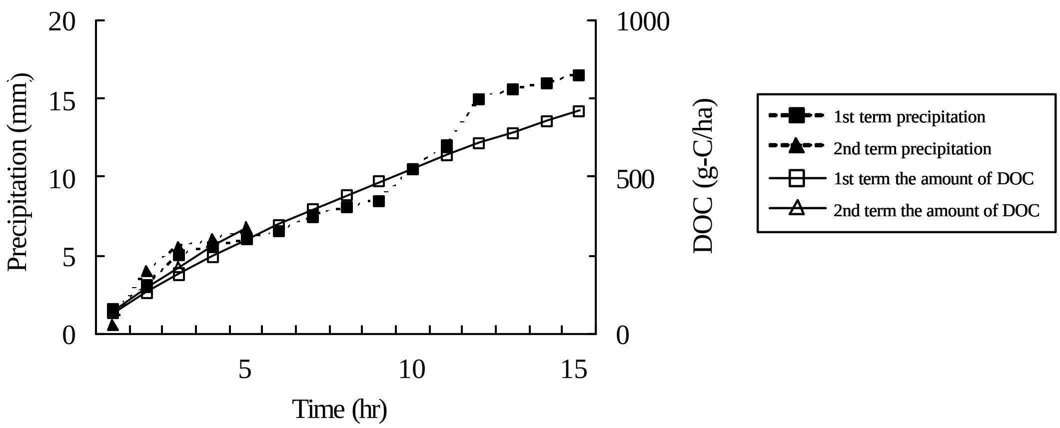


Figure 7 Precipitation and of accumulated DOC calculated by the diffusion model

Estimation of washout of the leaching DOC during rainfall event

Figure 7 shows precipitation and the accumulated DOC calculated by the washout model. The time step for calculation is one hour. *S* is given 3.0 $\times 10^{8}$cm^{2} according to the forest condition in this study site and *V* is hourly precipitation data multiplied the area of leaves. *ä* is provided 1×10^{-3}cm. For simplification, we presume that the rainwater stays for 30 minutes out of one hour on the leaf surface. In spite of irregularity of rainfall intensity, the accumulated DOC in throughfall increases at an approximately constant rate.

Sources of DOC in throughfall

Although we expected that the value subtracted C0 estimated by the model from concentration of solution at 1st time in the washout experiment was equal to the DD concentration observed, the difference, 4.04mg-C/l in the 1st term and 2.40mg-C/l in the 2nd term, was not negligible. The difference implies the existence of other sources. The organic matter in throughfall consists of various organics in molecular weight, for example organic acid is low weight and carbohydrate and terpeonoid are high molecular weight (Fahey, 1987). Hence, there would be quickly diffusing matter (QDM) and slowly diffusing matter (SDM) in throughfall. The model calculations of DOC concentration might have conducted by using smaller diffusion coefficient because of overestimation of DD at the 1st time in the washout experiment. Figure 8 shows sources of DOC in TF using the diffusion model and the mass balance of TF. The leaching from leaves occupied, 89 % and 74 % of TF at the 1st term and the 2nd term, respectively. QDM occupied 50 % in TF at the 1st term and 11 % at the 2nd term. SDM occupied 39 % at the 1st term and 63 % in the 2nd term. The difference of QDM between the 1st term and 2nd term might be caused by the difference of temperature (Figure 2) related to tree physiology.

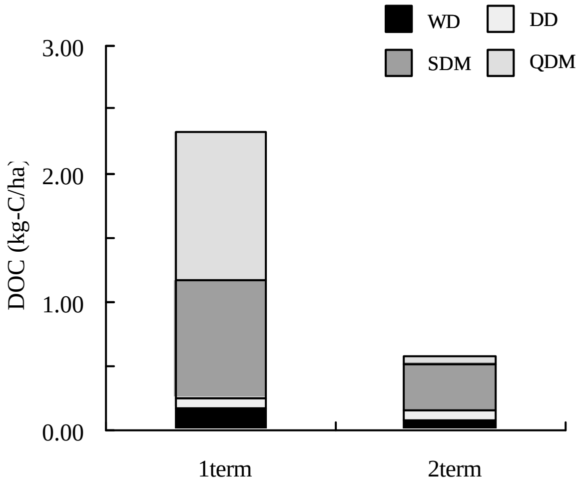


Figure 8 Sources separation of DOC in throughfall WD: Wet Deposition DD: Dry Deposition SDM: Slowly Diffusion Matter QDM: Quickly Diffusion Matter

CONCLUSIONS

In this study we proposed the physically-based model on washout of leaching matter from a leaf and separated sources of dissolved matter in the throughfall using a washout experiment, a field observation and the model. The discussion leads to the following conclusions:

1. NO_3^- and NH_4^+ are mostly not leached from leaves.
2. Leaching DOC occupies a large part of throughfall.
3. The washout model of leaching DOC is sufficiently robust to estimate the amount of washout of DOC during rainfall event.
4. The leaching DOC are possibly classified into two categories, quickly diffusing matter and slowly diffusing matter.

From our study which focused on the input process of nutrients in the forest ecosystem, it was provided that the sources of DOC was mainly in the forest canopy and the sources of NO_3^- and NH_4^+ were mainly from atmosphere.

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