Subsurface Flow and Dissolve Organic Carbon (DOC) Pathways in a Forested Headwater Catchment

Aliran Air Bawah Permukaan dan Jalur Aliran Karbon Organik Terlarut (KOT) di Kawasan Hulu DAS Berhutan

K. SUBAGYONO[1] AND T. TANAKA[2]

ABSTRACT

Soils under forested catchment are generally rich in organic matter, yet the role of organic soil layers in flow governing hydrochemical processes has rarely studied. Understanding the subsurface process and the role of rich organic matter at A horizon has been studied in Kawakami forested headwater catchment in Nagano prefecture, Central Japan from August 2000 to August 2001. The catchment is dominated by Inceptisols with 0.2-0.3 m of peat covering the soil in the riparian zone. Oak (*Quercus mongolica* Fisch) and bamboo grass (*Sasa nipponica*) are dominant vegetation in the catchment. The study is aimed to elucidate (a) can dissolved organic carbon (DOC) pathways be an indicator for tracing subsurface flow in a forested headwater catchment?, and (b) how does flushing effect the dynamic of DOC concentration?. Hydrometric and dynamic behavior of DOC as well as its variation were recorded in a transect across hillslope and riparian zone. The results showed that DOC has a specific trend across the riparian and the hillslope areas. During baseflow condition, DOC decreased with depth and away from the stream channel. The change in DOC concentration was clearly controlled by the flow pattern. In the near surface riparian, where the lateral flow was relatively steady and sustained in the direction of the stream, may facilitate the flushing high concentration of DOC. In the riparian zone, DOC concentration at the surface horizons of 0.3 and 0.6 m depth tend to decrease near the peak storm, which attributed to flushing of its high concentration. Under the three components mixing model involving the near surface riparian, the deep riparian groundwater, and the hillslope soil water contributing to storm runoff, DOC was in concave clockwise rotation with positive trend correspond to Evans and Davies (1998) case in which $C_{NSR} > C_{HSW} > C_{DRG}$ (C2 model). This was well confirmed with (a) the hydrochemistry data in which the concentration of DOC was higher in the near surface riparian zones, and (b) the hydrometric data in which the highest contributor to the storm runoff was the near surface riparian. The C2 model is the highest level of flushing in the sequence proposed by Evans and Davies (1998) confirming the highest control of the near surface riparian zone on the stream DOC concentrations.

Keywords : Subsurface flow, DOC pathways, DOC concentration, Storm runoff, Forested headwater catchment

ABSTRAK

Tanah-tanah di daerah tangkapan yang berhutan umumnya kaya kandungan bahan organik, namun demikian peranan lapisan tanah yang kaya organik ini dalam aliran air yang mempengaruhi proses hidrokimia belum diteliti. Pemahaman terhadap proses aliran air dalam tanah dan peranan horizon A yang kaya organic telah diteliti di Daerah Tangkapan Kawakami, Nagano, Jepang Tengah dari bulan Agustus 2000 sampai dengan Agustus 2001. Daerah tangkapan tersebut didominasi tanah Inceptisols dan pada zona riparian tanahnya dilapisi gambut setebal 0.2-0.3 m. Oak (*Quercus mongolica* Fisch) dan rumput bambu (*Sasa nipponica*) merupakan vegetasi yang dominan. Penelitian bertujuan untuk mempelajari (a) dapatkah jalur aliran karbon organic terlarut (KOT) digunakan sebagai indicator untuk menandai jalur aliran air di bawah permukaan tanah pada daerah tangkapan yang berhutan?, dan (b) bagaimana proses pencucian mempengaruhi dinamika konsentrasi KOT?. Data hidrometri dan karakteristik dinamika KOT serta variabilitasnya diukur pada suatu transek yang memanjang dari kawasan perbukitan hingga zona riparian. Hasil penelitian menunjukkan bahwa konsentrasi KOT memiliki variabilitas yang spesifik dari kawasan perbukitan hingga zona riparian. Pada kondisi aliran dasar, konsentrasi KOT menurun menurut kedalaman tanah dan menurun dari daerah yang dekat sungai ke yang jauh dari sungai. Perubahan konsentrasi KOT sangat dipengaruhi oleh pola aliran air. Pada lapisan tanah atas zona riparian, dimana aliran air horizontal relatif stabil menuju arah sungai, memberikan kontribusi terhadap pencucian KOT. Pada zona riparian, konsentrasi KOT pada tanah lapisan atas kedalaman 0.3 dan 0.6 m cenderung menurun pada saat mendekati puncak hujan, yang menyebabkan tercucinya KOT dalam jumlah banyak. Di bawah pengaruh tiga komponen model campuran yaitu zona riparian permukaan (NSR), zona riparian air bumi (groundwater) dalam (DRG), dan air tanah perbukitan (HSW) yang mempengaruhi runoff, dinamika KOT menunjukkan model cekung yang memutar searah jarum jam dengan tren positif sesuai dengan model Evans dan Davies (1998) dimana $C_{NSR} > C_{HSW} > C_{DRG}$ (model C2). Fenomena ini sangat sesuai dengan (a) data hidrokimia dimana konsentrasi KOT lebih tinggi di zona riparian permukaan, dan (b) data hidrometri dimana zona riparian permukaan merupakan kontributor terbesar terhadap runoff. Model C2 merupakan model yang menunjukkan level tertinggi proses pencucian sebagaimana dilaporkan oleh Evans dan Davies (1998) yang menunjukkan control tertinggi dari zone riparian permukaan terhadap konsentrasi KOT di sungai.

Kata kunci : Aliran bawah permukaan, Jalur aliran KOT, Konsentrasi KOT, Runoff, Daerah tangkapan berhutan

INTRODUCTION

Dissolved Organic Carbon (DOC) is not only an indicator for soil fertility status, which is highly concentrated in the top soil, but also be possibly used as a tracer. The use of chemical tracers for

---

[1] Central Java Assessment Institute for Agriculture Technology (Central Java AIAT), Ungaran, Semarang, Indonesia.

[2] Graduate School of Live and Environmental Sciences, University of Tsukuba, Japan.

defining hydrological flow path has come up with criticism due to environment pollution. Many authors have risen up conservative chemical compounds to use as a tracer, yet the accuracy and validity of those compounds varies from site to site.

Total Organic Carbon (TOC) is usually divided into particulate (POC) and Dissolved Organic Carbon (DOC) by filtration through < 0.45 μm, which means that particles < 0.45 μm are included in the soluble fraction (Stumm and Morgan *in* Temnerud, 2005). Studies from the Nordic at coniferous forest showed that more than 95% of TOC in streams and lakes are dissolved (Kohler *et al*., 2002; Mattson *et al*., 2003). Lobbes *et al.* (2000) reported that concentrations of DOC are on average eight times higher than particulate organic carbon (POC).

In term of water holding capacity, organic matter has very important role. A reason why the water loses a lot from the soil through percolation and evaporation is that the water holding capacity of the soil is low. Spatial distribution of organic matter in the soil quantitatively determines the ability of soil to hold water. However, since the organic material diminishes due to decomposition and mineralization as well as lost through flow processes, the ability of soil to hold water is also depleted unless organic matter is incorporated in the soil.

Several studies that have dealt with DOC flux (Benner *et al*., 2001; Royer and David, 2005; Raymond *et al*., 2007) explaining its transport through river to the sea. The relationship between DOC concentration and runoff has also been studied by Cooper *et al*. (2005), which found out that DOC concentrations were correlated with runoff fraction. Subagyono (2003) has reported that in the riparian zone, most of the solutes tend to increase near the peak storm with an exception of DOC concentration at the surface horizons of 0.3 and 0.6 m. In hillslope area where the slope steepness has a key role in flow generation, the lateral flow during peak storm also governed the DOC transport.

Investigations designed to study the linkages between site-specific hydrologic flowpath and biogeochemical pathway in the near stream zone is somewhat rare (Hill, 1993; Eshelman *et al*., 1994). Determining the change of water chemistry as a time-dependent function of flow pathways during runoff generation is critical to understand chemical variability and to conceptualize properly solute transport through a catchment. However, much attention has been paid to hydrograph separation methods in identifying source areas that contributing to stream flow and chemistry. In addition, many studies on the chemical-hydrologic interaction have been directed to the riparian zone (Pionke *et al*., 1988; Hill, 1993; Eshelman *et al*., 1994; Cirmo and McDonnel, 1997; McGlynn *et al*., 1999), yet the interaction of the flow process with the change in hydrochemistry across the hillslope segment and the interaction of the riparian and hillslope processes were poorly understood. Those were also observed in the linkage between dynamic of DOC concentration in function of flow processes.

This study is aimed to elucidate several phenomena and processes which could answer the questions of (a) can DOC pathways be an indicator for tracing subsurface flow in a forested headwater catchments?, and (b) how does flushing effect the dynamic of DOC concentration?.

MATERIALS AND METHODS

Site description

The study was conducted from August 2000 to August 2001 in Kawakami Experimental Basin (KEB), Nagano Prefecture, Central Japan. This is a first order basin of 5.2 ha from the total area of 14 ha. The altitude of the catchment ranges from 1,500 m to 1,680 m above sea level with slightly steep slopes (about 20%) over the riparian zone and very steep slopes (>60%) over the hillslope area.

This area underlied by late Neogene of the Meshimoriyama volcanic rocks, which consists of lavas and pyroclass of olivine-hornblende-pyroxene andesites (Kawachi, 1977). The upper soil mantle primarily consists of inceptisols with very narrow area of the riparian zone covered by 20 cm to 30 cm of peat. The A-horizon is rich in organic matter with rapid hydraulic conductivity (Ks = 21.6-93.6 cm h^{-1}), while the B-horizon which has more clay has a very slow hydraulic conductivity (Ks = 0.007 - 0.9 cm h^{-1}). The top 15 to 35 cm of soil profile in hillslope side is reach in organic matter. Average DOC concentrations in water at the riparian zone are 3.51; 1.75; 2.00; and 2.51 mg L^{-1} respectively at 30, 60, 100, and 200 cm depths, while those at hillslope side are 1.72; 1.00; and 1.03 mg L^{-1} respectively at 40, 100, and 200 cm depths. Mean annual precipitation is about 1,500-1,600 mm, producing 853 mm of runoff (Matsutani *et al.*, 1993). A natural deciduous forest of oak (*Quercus mongolica* Fisch), larch plantation (*Larix leptolepis* Gordon), and the bamboo grass (*Sasa nipponica*) are very common in this area.

Methods

To study the dynamic behavior of flow pattern and DOC concentration, a transect across hillslope and riparian zone approximately along the flow line was nested with piezometers, tensiometers and suction samplers with various depths to monitor the dynamic of subsurface flow and chemical pathways (Figure 1).

Hydrometric measurements

Discharge was continuously recorded with 30°V-notch gauging weir installed at upstream tributary of the northern valley of the catchment. Water level at weir was automatically recorded using a data logger that was set for every 10 min interval recording. Rainfall was measured using a tipping bucket (recording) rain gauge placed at the climate station located near the main weir (about 150 m from the experimental site).

A partly perforated piezometer was used, which is a PVC tube with an inner diameter of 4 cm and the outer diameter of 4.8 cm and bottom perforation length of 10 cm. In order to be easily installed, a PVC cup was complemented at the top of piezometer for hammering. The rest of about 20 to 30 cm remains above the surface to avoid overland flow water (if any) from entering the piezometer. Since the groundwater samples are taken from the piezometer, it was covered by a PVC cup to avoid contamination from rain water. Soil water potential was measured using a mercury manometric tensiometer connected to a water column inside. A PVC tube with inner diameter of 1.5 cm and outer diameter of 1.7 cm and the porous cup at the bottom of the tube.

Flow line was determined across hillslope and riparian zone to define the spatial variation of sub-surface flow based on this equipotential line. The equipotential line was defined using piezometer and tensiometer data. Monthly variation of vertical and lateral sub-surface flows were defined by determining vertical and lateral heads gradient of groundwater between two points at different depths in the riparian zone. The vertical head gradient ($\partial H/\partial z$) was determined as follows :

$$\partial H/\partial z = (H_2-H_1)/(z_2-z_1) \quad \text{.................................} \quad (1)$$

where : H_1 and H_2 are hydraulic head at the shallowest (0.2 m) and deepest (2 m) depths respectively, and z_1 and z_2 are the elevation of the observation points.

The lateral head gradient ($\partial H/\partial z$) was determined as follows :

$$\partial H/\partial z = (H_b-H_a)/(z_b-z_a) \quad \text{..................................} \quad (2)$$

where H_a and H_b are hydraulic heads at the nest 4 and the nest 5 respectively, and z_a and z_b are elevation at the nest 4 and 5 respectively.

DOC measurements

Suction samplers were used for sampling soil water. These samplers were PVC tubes with diameter of 1.8 cm complemented with porous cups at the bottom, which were connected to 100 ml flasks. To collect soil water, the flasks were

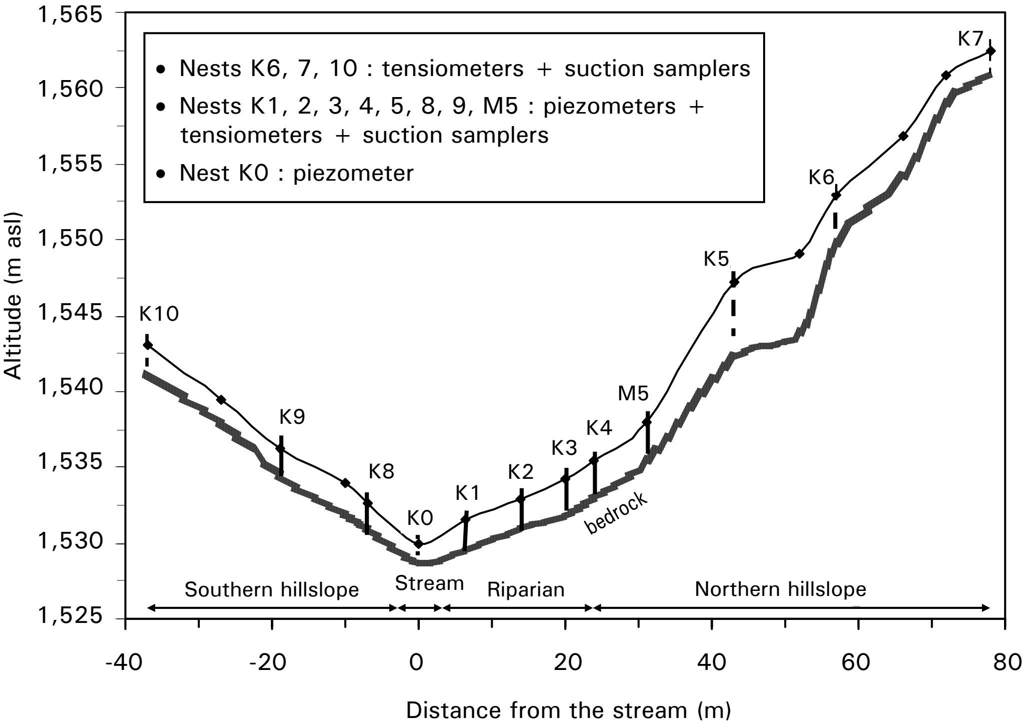

Figure 1. **The transect showing the nest of piezometers, tensiometers, and suction samplers**

Gambar 1. Transek piezometer, tensiometer, dan alat pengambil contoh air tanah

vacuumed using a hand pump at a suction of about 80 bars. Depending upon the depths of bedrock, the thickness of soil mantle and the stratification of the soil horizon, samples were taken at various depths of 0.3; 0.4; 0.5; 0.6; 1.0; 1.1; 1.5; 2.0; 3.0; and 4.0 m.

Groundwater, soil water, and stream water samples were collected monthly. Groundwater samples were taken from the piezometers (perforated at the bottom of 10 cm),whereas soil water samples were collected from suction samplers installed at the same site with piezometers and tensiometers nests at depths of 0,3; 0.4; 0.5; 0.6; 1.0; 1.1; 1.5; 2.0; 3.0; and 4.0 m. The stream water samples were taken at the upstream, middle, transect site, and at near the weir. Samples were collected using 100 ml polyethylene bottles. Before collecting the samples, the bottles were rinsed with the groundwater, soil water, or stream water depending upon the sampling sites.

The water samples were filtered through 0.22 µm millipore membrane filters to remove any suspended matters. Filtered solutions were, then, analyzed for Dissolve Organic Carbon (DOC). DOC was measured using TOC analyzer at the National Institute for Agro-Environmental Sciences (NIAES), Tsukuba.

DOC concentration-discharge (C-Q) diagram analysis

To quantify the linked hydrological and hydrochemical processes that take place during storm event, the C-Q diagram that was demonstrated by Evans and Davies (1998) and Evans *et al*. (1999) was applied in the present study. Solute concentration against discharge was plotted for DOC. These plots were combined with the time series of observed discharge and variation of corresponding solute as it has been done by

Scanlon *et al.* (2000) to study transport of dissolved silica for defining the hydrochemical response of observed flow pathways in a forested headwater catchment.

The hysteresis model of Evans and Davies (1998) was used to examine the relationships between component mixing (the three component mixing model) and C-Q hysteresis and to characterize the magnitude of flushing. Three criteria were used in the model to characterize the various hysteresis types included: (a) rotational pattern (clockwise/anticlockwise), (b) curvature (convex/concave), and (c) trend (positive/negative) to determine component rankings (Table 1). They used three components runoff of surface event water (SE), soil water (SO) and groundwater (G) to apply in the model. Since the surface component is less important than the subsurface component, the near surface riparian water was applied for the present study instead of the SE.

Statistical analysis

To evaluate spatial variation of DOC concentration amongst the sources area of runoff including Deep Riparian Groundwater, Near Surface Riparian and Hillslope Soil Water (Subagyono, 2003), one-way analysis of variance (ANOVA) at $P \leq 0.0001$ was performed. The difference of DOC concentrations between the different sources of runoff was analyzed by calculating mean values of DOC concentration using Tukey multiple comparison tests at $\alpha = 0.05$.

RESULTS AND DISCUSSION

Sub-surface flow and DOC flux

Figure 2 shows changes in potential distribution and flow direction across hillslope and riparian zone. At base flow condition (pre-onset rain) and at the storm started, the flow was considerably vertical. The flow was progressively developed into lateral flow due to increase of rainfall amount and antecedent wetness following storm runoff. Different flow patterns were observed across the riparian and the hillslope segment during the onset rain. Those flow patterns included (a) vertical flow at the near ridge, (b) the progressively change of flow direction at the mid-slope (between M5 and K5 nests), (c) variable flows at the border between the hillslope and the riparian (between K4 and M5 nests), (d) lateral flow at near surface riparian zone in the near stream channel, and (e) considerably downward flow of deep riparian groundwater combined with the lateral flow at the soil-bedrock interface.

Table 1. Diagnostic features used to determine component ranking for three components model

Tabel 1. Diagnosis penetapan komponen ranking untuk tiga komponen model

Type	Rotational direction	Curvature	Trend	Component rankings
C1	Clockwise	Convex	N/A	$C_{NSR} > C_{DRG} > C_{HSW}$
C2	Clockwise	Concave	Positive	$C_{NSR} > C_{HSW} > C_{DRG}$
C3	Clockwise	Concave	Negative	$C_{DRG} > C_{NSR} > C_{HSW}$
A1	Anticlockwise	Convex	N/A	$C_{HSW} > C_{DRG} > C_{NSR}$
A2	Anticlockwise	Concave	Positive	$C_{HSW} > C_{NSR} > C_{DRG}$
A3	Anticlockwise	Concave	negative	$C_{DRG} > C_{HSW} > C_{NSR}$

Source : Evans and Davies (1998) with modification

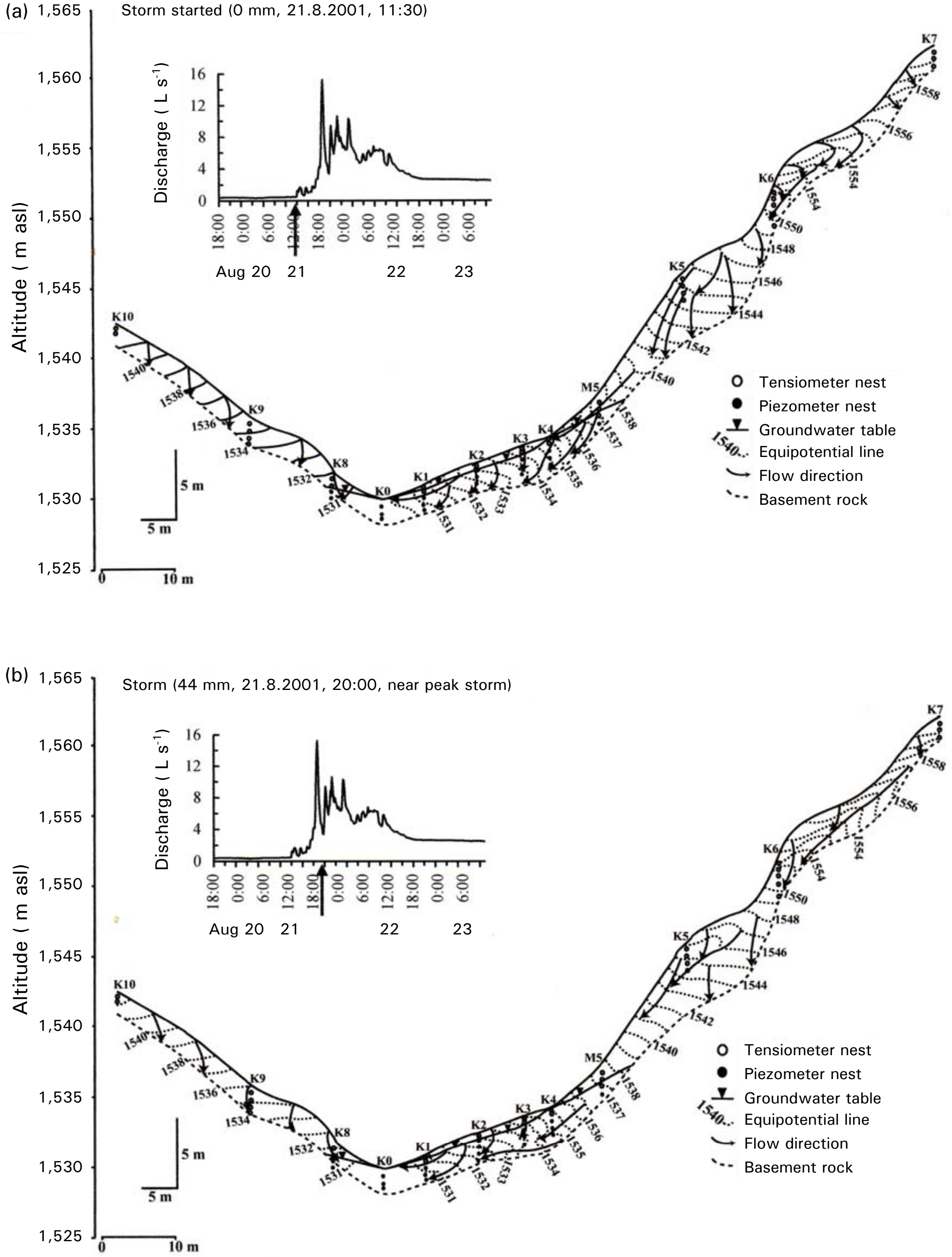

Figure 2. Changes of flow direction during storm started to the near peak storm and the spatial variation of flow directions along hillslope and riparian zone

Gambar 2. Perubahan arah aliran air selama awal sampai puncak hujan dan variabilitas spasial arah aliran air di lereng atas dan zona riparian

At hillslope side, the water was rapidly infiltrated into the soil followed by the increase of the wetness in shallow sub-surface zone. This evidence proved as well that there was no “Hortonian” overland flow observed in this hillslope segment. This water was distributed in the soil profile and part of it moves down slope through the average depth of 1 m and it was identified to be the subsurface storm flow. This evidence was observed at near peak storm (Figure 2b, between nest M5-K5 and K5-K6). This flow was similar with that defined by Freeze (1972) as a shallow perched saturated flow above the main groundwater level. Robinson and Sivapalan (1996) found that the flow in the storm flow zone is entirely down slope. The flow direction changed abruptly into more vertical when the rain became less until the end of storm.

As it has been described by Subagyono (2003), the hydrograph rises sharply (see hydrograph inserted in Figure 2), the time to peak was 7 hours and the recession time was about three times longer, during which the transient saturated zone developed in the riparian zone. This coincided with the increase in matric potential and the change of flow from vertical to lateral toward the stream in the upper 1 m of the subsurface hillslope. The development of the transient saturated zone, which is caused by the increase in potential values (Tanaka and Ono, 1998), creates a threshold response of the delivery mechanism of hillslope soil water to reach the stream channel. Despite the rainfall amount and the antecedent wetness were the important factors, the change of the hillslope soil water flow direction were also controlled by the thickness of the soil mantle and the slope features. In the mid-concave slope with a deep soil mantle (4 to 5 m deep) the flow developed at the near surface, whereas in the upper-convex slope where the soil was shallower (1.5 to 2 m deep) it was developed at the soil-bedrock interface. The flow was gradually changed into vertical downward flow during the falling limb of the hydrograph. The water was drained slowly to the stream channel during the falling limb as indicated by the gradual decrease in the hydrograph. Looking at more specific into the riparian zone, three distinct flowpaths were spatially identified including (a) lateral flow at the near surface riparian, (b) downward flow in the deep riparian groundwater and (c) variable flowpaths in the border between the riparian and the hillslope zones. During consecutive periods of storm, the flows in the near surface riparian at the near stream channel remain laterally toward the stream channel. Unlike the near surface riparian flowpaths, the deep riparian groundwater flowpaths and the flowpaths at the border changed arbitrary. The flow at the soil-bedrock interface developed laterally in the deep riparian groundwater zone as the storm was developed. However, it did not give a quick response to the stream because it was reset by the downward flow of the deep riparian groundwater. These flow patterns were somewhat different with that found by Pionke *et al*. (1988). They found that the groundwater flow direction changed prominently in the shallow depth resulting in a development of the seep zone, but did not so in the deep groundwater when the storm developed. In addition, the lateral flow at the soil-bedrock interface was not observed. In the present study the direction of the near surface riparian flow did not change considerably.

The upward gradient was developed at the border during the on-set rain providing an increase in groundwater level in this zone. The flowpaths varied in this zone, which was due to the interaction between the hillslope and the riparian flow process. The flows were predominantly upward. This finding is similar with that found by McGlynn *et al*. (1999). They reported a variable gradient existed at the break in slope, which suggested that the flow was variable. The influence of down slope flux of water from the hillslope on the sustained high water table has been documented.

The spatial variability in flow pattern has given various responses to the runoff generation process. The steady lateral flow of the near surface riparian may account for this zone to quickly response to the stream flow as the hydrograph separation data has shown that this zone was the most dominant contributor (Subagyono, 2003). The dominant downward flow in the deep riparian groundwater through out the storm could perform a delay response to the stream flow generation.

Evidence of resetting the hillslope flowpaths and chemical pathways in the riparian zone has been initiated in the research done by Robson *et al.* (1992) in the Hafren catchment Plynlimon, mid-Wales. This finding is in conflict with that found in the present study and to be not valid for the Kawakami headwater catchment, where the near surface riparian flowpaths linked with that of shallow subsurface hillslope and may not reset the chemical pathways. However, it was so for the case of deep riparian groundwater. Hillslope stormflow was hampered by deep riparian groundwater providing an increase in groundwater level at the break in slope side. Part of the hillslope water was discharged to and not well mix with the near surface riparian groundwater before reaching the stream channel. Since the deep groundwater flows remain downward, these flowpaths hamper the hillslope water to reach the stream. This evidence caused a delay response of the deep riparian groundwater to the stream flow and chemistry.

The development of flow direction was consistence with the increase in the rainfall amount and antecedent wetness of the soil profile and strongly controlled by the slope steepness (Subagyono, 2003). Evidence that topography is the dominant physical driver of flow and is a primary determinant of catchment response was presented by Baven and Kirby, (1979), O'Loughlin (1986) and more detail reported by Tsukamoto and Ohta (1988).

Dynamic of DOC concentrations at the different sources area of runoff (deep riparian groundwater, near surface riparian and hillslope soil water) were determined by the fluxes, as it has shown by the relationship between DOC concentration and fluxes (Figure 3). In general, the DOC concentration decreased with increased the DOC fluxes, which suggests that DOC will move when the water moves. This provides insight that DOC may act as a tracer, as it has been characterized by most conservative elements. The relationships between DOC concentration and fluxes were in power equations of relationship except for that occurred in the near surface riparian zone, which was more polynomial relationship.

It has been reported by many authors that DOC concentration in the stream increases with runoff (Benner *et al*., 2001; Cooper *et al*., 2005; Royer and David, 2005; Raymond *et al*., 2007). The movement of DOC in all sources area of runoff across hillslope and riparian zone stimulated flushing of DOC into the stream channel thus the concentration of DOC in the stream increases.

DOC flushing

Lost of DOC along the hillslope and riparian zone through flushing process is more clearly explain using the concentration (C)-Discharge (Q) diagram (C-Q diagram) as it has been simulated by Evans and Davies (1998). Temporal variation of measured discharge and concentration of DOC in combined with the DOC C-Q diagrams for storm event on August 21-22, 2001 explained well the phenomenon in which the DOC concentrations are changed across the hydrograph and the DOC hysteresis was occurred under various discharge rates attributing to DOC flushing process (Figure 4). DOC concentration tends to increase at the near peak of storm. Under the three components sources area involving the near surface riparian, the deep riparian groundwater, and the hillslope soil water contributing to storm runoff, DOC was in concave clockwise rotation with positive trend correspond to Evans and Davies (1998) case in which $C_{NSR} > C_{HSW} > C_{DRG}$ (C2 model). This was well confirmed with (a) the concentration of DOC was higher in the near surface riparian zones, and (b) the hydrometric data in which the highest contributor to the storm runoff was the near surface riparian. The C2 model is the highest level of flushing in the sequence proposed by Evans and Davies (1998) confirming the highest control of the near surface riparian zone on the stream DOC concentrations.

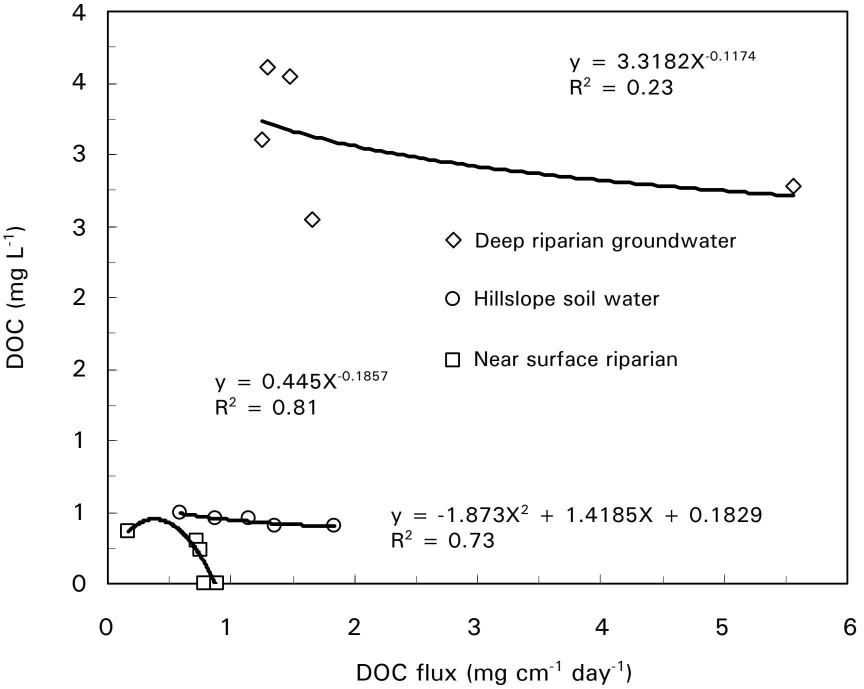

Figure 3. **Relationship between DOC flux and DOC concentrations in different sources area of runoff across hillslope and riparian zone**

Gambar 3. Hubungan antara aliran dan konsentrasi karbon organik terlarut pada sumber aliran yang berbeda di lereng atas dan zona riparian

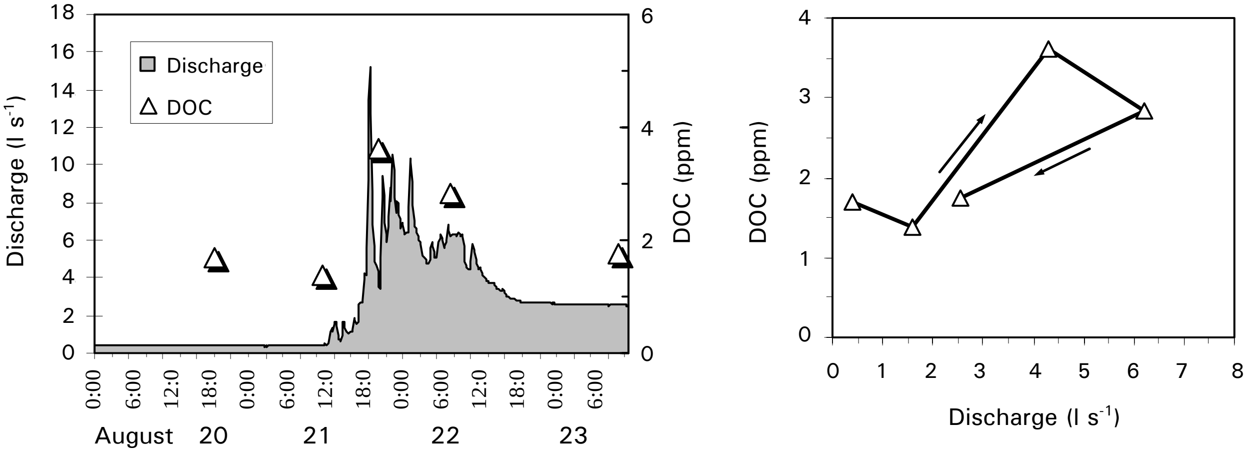

Figure 4. **Temporal variation of DOC across hydrograph (left) and DOC concentration-discharge diagram (right) during storm event 21-22 August 2001**

Gambar 4. Variasi antar waktu konsentrasi karbon organik terlarut menurut hidrograf (kiri) dan hubungan aliran air dan konsentrasi karbon organik terlarut (kanan) selama hujan tanggal 21-22 Agustus 2001

Relationship between DOC concentrations in the stream water and discharge rate during storm event on August 21-22, 2001 is depicted in Figure 5. The relationship was exponential with coefficient of determination of 0.67. It was little bit difference with that found by Raymond *et al.* (2007) as the relationship was rather linear as it was observed in all watersheds studied that a marked increase in DOC concentration with flow. This indicates that the dynamic of DOC concentrations is controlled by flow.

DOC as in many catchments used for effective indicator of flowpaths during storm runoff (McDowell and Fisher, 1976; Moore, 1989; Fiebig *et al.*, 1990) is proven to be the one of conservative element in this catchment and seems to be reasonable for a tracer.

Spatial variation of DOC concentration

Spatial variation of DOC concentrations in the sources area of runoff was clearly observed (Table 2). One-way ANOVA and multiple comparison tests showed that solutes concentration in the hillslope soil water was significantly difference with those of the riparian zone. The variability of DOC concentration of each source component was defined by the standard deviation of the observed concentration. At baseflow condition, as a common soil, where organic matter content is often high in the surface horizons of soil profiles, DOC was dominance in the near surface riparian.

A significant distinct in the distribution of DOC concentration across the hillslope and the riparian zone near the peak storm is depicted in Figure 6.

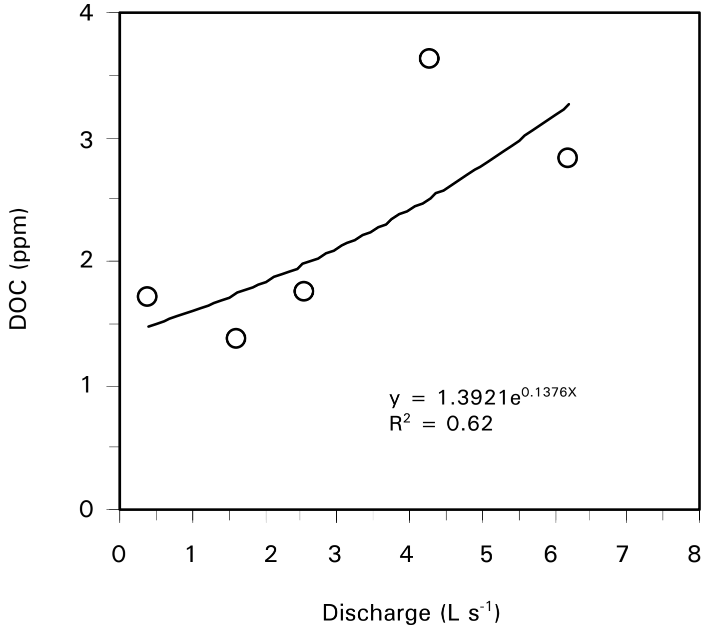

Figure 5. Relationship between discharge rate and DOC concentration in the stream water during storm event on August 21-22, 2001

Gambar 5. Hubungan antara debit aliran sungai dengan konsentrasi karbon organik terlarut selama hujan tanggal 21-22 Agustus 2001

Table 2. Spatial variability of DOC concentration in sources of runoff at different time during the storm of August 21-22, 2001

Tabel 2. Variabilitas spasial konsentrasi karbon organik terlarut pada sumber aliran pada waktu yang berbeda selama hujan tanggal 21-22 Agustus 2001

Sources of runoff	DOC (mg L^{-1}) Mean ± SD(n)
Baseflow condition	
1. Near surface riparian	2.55 ± 2.94 (8) a
2. Deep riparian groundwater	1.92 ± 0.80 (12) a
3. Hillslope soil water	1.46 ± 0.94 (3) a
2 hours after storm started	
1. Near surface riparian	2.32 ± 1.87 (6) a
2. Deep riparian groundwater	nd
3. Hillslope soil water	1.78 ± 0.85 (4) a
1 hour after peak storm	
1. Near surface riparian	3.04 ± 2.55 (8) a
2. Deep riparian groundwater	2.81 ± 1.41 (11) a
3. Hillslope soil water	1.58 ± 1.01 (7) a
Storm end	
1. Near surface riparian	2.61 ± 2.79 (8) a
2. Deep riparian groundwater	nd
3. Hillslope soil water	1.20 ± 0.56 (17) a
Post storm	
1. Near surface riparian	3.02 ± 2.83 (8) a
2. Deep riparian groundwater	2.41 ± 0.65 (7) ab
3. Hillslope soil water	1.27 ± 0.50 (21) b

Mean values in the same column with the same letter are not significantly different based on one-way ANOVA ($P \leq 0.0001$) and multiple comparison tests ($\alpha = 0.05$, Tukey)

In each observation nest within the riparian, solutes concentration was much higher than those within the hilslope areas. The reason is that the water flow direction in the riparian zone especially in the deep riparian groundwater zone was dominantly downward (Figure 2) with relatively higher DOC flux (Figure 3) leading to accumulate DOC concentration in this zone. Amongst the major solutes component DOC has a specific trend across the riparian and the hillslope areas especially in a depth of 1 m. Variation of DOC concentration was also observed in the soil profile, where DOC concentrations was higher in the surface soil layer compared to that in the sub surface layers (Figure 7).

The change in the DOC concentration was clearly controlled by the flow pattern. In the near surface riparian, where the lateral flow was relatively steady and relatively stabile in the direction of the stream may facilitate the flushing high concentration of DOC. During baseflow condition, DOC decreased with depth and away from the stream channel.

The implication of the present study for the tropics is that several steps have to be considered as the study has been conducted in the temperate region. Since the rainfall is much higher in the tropics, it can be a magnitude of two to three times higher, and in many cases occurred in short period and erosion processes is often happened, the methodology to record the hydrological and hydrochemical processes should considered several steps as follow :

1. Recording of event basis hydrological and hydrochemical processes should be more intensive under various storm events.
2. The present study did not consider erosion process, since it was negligible in the present study. In the tropics where erosion process is always happened, the amount of sediment and it chemical content should be determined beside water chemistry characterization.
3. Automatic recording nests to record groundwater and soil water flow across hillslope and riparian zone is recommended. It means that automatic piezometers and tensiometers recorders are helpful.
4. Since rainfall variability is high in the tropics as climate change has occurred, the methodology may be tested under different rainfall zones.

Principally the methodology used in the present study is possible to test and the model of End Member Mixing Analysis (EMMA) can also be used and developed.

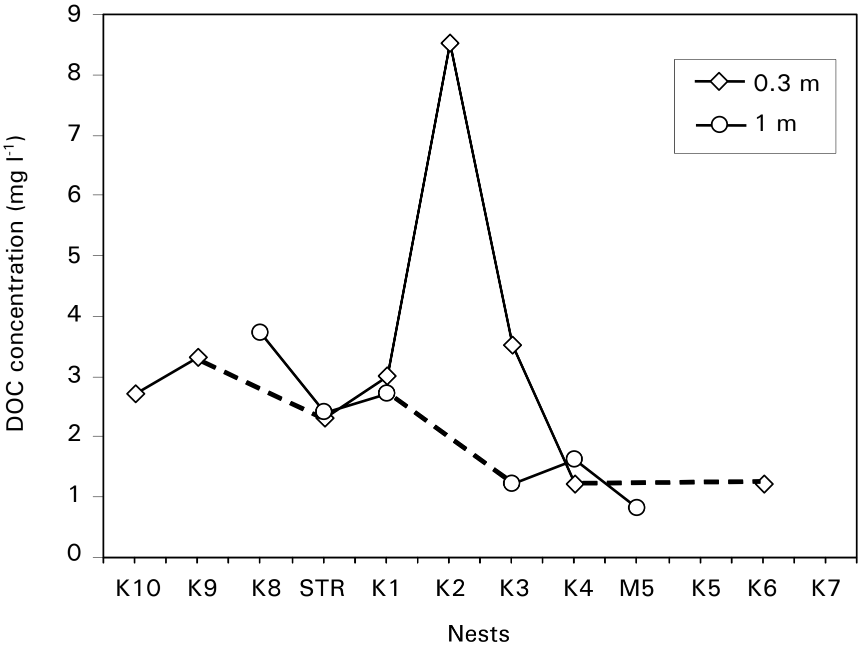

Figure 6. **Spatial variation of DOC concentration across hillslope and riparian zone**

Gambar 6. Variasi spasial konsentrasi karbon organik terlarut pada lereng atas dan zona riparian

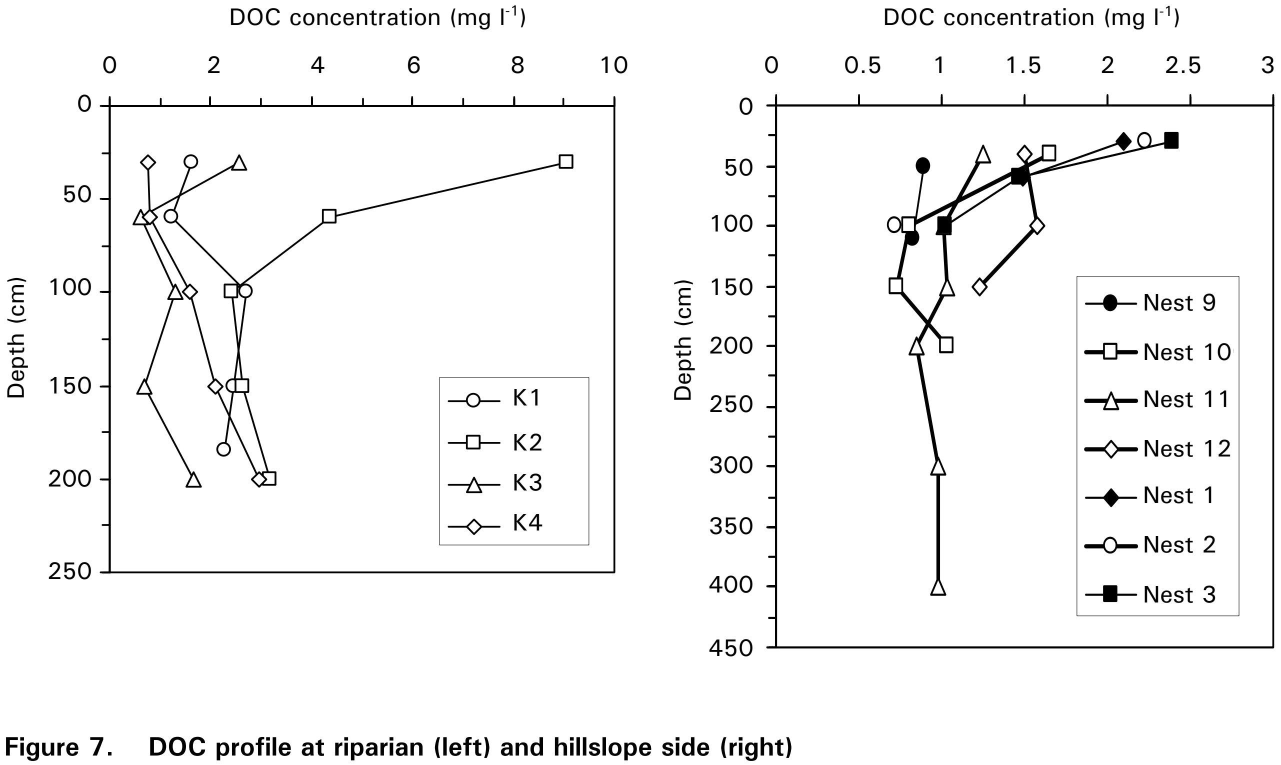

Figure 7. **DOC profile at riparian (left) and hillslope side (right)**

Gambar 7. Profil konsentrasi karbon organik terlarut di zona riparian (kiri) dan di lereng atas (kanan)

CONCLUSIONS

1. Dynamic behavior of subsurface flow in the Kawakami Forested Headwater Catchment has a great influence on the DOC pathway. The magnitude of DOC transport through different sources area of runoff (deep riparian groundwater, near surface riparian and hillslope soil water) is in line with the fluxes, which mean that DOC moves when water moves. This provides insight that DOC may potentially be used as a tracer.
2. DOC flushing is high in Kawakami Forested Headwater catchment. Based on Evans and Davies (1998) model, DOC is in concave clockwise rotation with positive trend, where its concentration in the near surface riparian is the biggest compared with those in the deep riparian groundwater and the hillslope soil water ($C_{NSR} > C_{HSW} > C_{DRG}$), which belongs to C2 model. The C2 model is the highest level of flushing confirming the highest control of the near surface riparian zone on the stream DOC concentrations.
3. Subsurface flow has significantly effect on spatial variation of DOC concentration across hillslope and riparian zone. As three sources areas of runoff of near surface riparian, deep riparian groundwater and hillslope soil water have different characteristics in flow and potential flushing of DOC, variation of DOC concentration is a large.

Acknowledgement

The authors thank to Dr. Yohei Hamada, Dr. Shin'ichi Iida and Miyuki Mori, MSc. for their unlimited help during field experiment. This is part of the study on linking runoff process and spatial and temporal variation of water chemistry in a forested headwater catchment funded by the Ministry of Education, Science, Sport and Culture of Japan (MONBUSHO).

REFERENCES

Baven, K.L. and M.J. Kirkby. 1979. A physical based variable contributing area model of basin hydrology. Hydrol. Sci. Bull. 24:43-69.

Benner, R., B.B. Nelson, K. Kaiser, and R.M.W. Amon. 2001. Export of young terrigenous dissolved organic carbon from rivers to the Arctic Ocean. Geophysical Research Letters, Vol. 31, L05305, doi:10.1029/2003GL019251, 2004.

Cirmo, C.P. and J.J. McDonnell. 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchment: a review. J. Hydrol. 199:88-120.

Cooper, L.W., R. Benner, J.W. McClelland, B.J. Peterson, R.M. Holmes, P.A. Raymond, D.A. Hansell, J.M. Grebmeier, and L.A. Codispoti. 2005. Linkages among runoff, dissolved organic carbon, and the stable oxygen isotope composition of seawater and other water mass indicators in the Arctic Ocean. J. Geophys. Res. 110, G02013, doi:10.1029/2005JG000031.

Eshleman, K.N., Pollard, J. S. and O'Brient, A.K. 1994. Interaction between groundwater and surface water in Virginia coastal plain watershed. 1. Hydrological flowpaths. Hydrol. Process. 8:389-410.

Evans, C. and T.D. Davies. 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry. Water Resour. Res. 3:129-137.

Evans, C., T.D. Davies, and P.S. Murdoch. 1999. Component flow processes at four streams in the Catskill Mountains, New York, analysed using episodic concentration/discharge relationships. Hydrol. Process. 13: 563-575.

Fiebig, D.M., M.A. Lock, and C. Neal. 1990. Soil water in the riparian zone as a source of carbon for a headwater stream. J. Hydrol. 116:217-237.

Freeze, R.A. 1972. Role of subsurface flow in generating surface runoff, 2, Upstream source areas. Water Resour. Res. 8:1273-1283.

Hill, A.R. 1993. Base cation chemistry of storm runoff in a forested headwater wetland. Water Resour. Res. 29:2663-2673.

Kawachi, S. 1977. Geology of the Yatsugatake District. Regional Geological Report. Geological Survey of Japan 89-91 (in Japanese with English abstract).

Kohler, S, I. Buffam, A. Jonsson, and K. Bishop. 2002. Photochemical and microbial processing of stream and soil water dissolved organic matter in a boreal forested catchment in northern Sweden. Aquatic Sciences 64(3):269-281.

Lobbes, J.M., H.P. Fitznar, and G. Kattner. 2000. Biogeochemical characteristics of dissolved and particulate organic matter in Russian rivers entering the Arctic Ocean, Geochim. Cosmochim. Acta 64(17):2973-2983.

McDowell, W.H. and S.G. Fisher. 1976. Autumnal processing of dissolved organic matter in a small woodland stream ecosystem. Ecology 57:561-569.

McGlynn, B.L., J.J. McDonnell, J.B. Shanley, and C. Kendall. 1999. Riparian zone flowpath dynamics during snowmelt in a small headwater catchment. J. Hydrol. 222:75-92.

Matsutani, J., T. Tanaka, and M. Tsujimura. 1993. Residence times of soil, ground, and discharge waters in a mountaineous headwater basin, central Japan, traced by tritium. *In* N.E. Peters, E. Hoehn, Ch. Liebundgut, N. Tase, and D.E. Walling (*Eds*.). Tracers in Hydrology. IAHS Publ. 215:57-63.

Mattsson, T., L. Finer, P. Kortelainen, and T. Sallantaus. 2003. Brook water quality and background leaching from unmanaged forested catchment in Findland. Water, Air and Soil Pollution 147(1-4):275-297.

Moore, R.D. 1989. Tracing runoff sources with deuterium and oxygen-18 during spring melt in a headwater catchment, southern Laurentans, Quebec. J. Hydrol. 112:135-148.

O'Loughlin, E.M. 1986. Prediction of subsurface saturation zones in natural catchments by topographic analysis. Water Resour. Res. 7: 425-448.

Pionke, H.B., J.R. Hoover, R.R. Schnabel, W.J. Gburek, J.B. Urban, and A.S. Rogowaski. 1988. Chemical-hydrologic interaction in the near-stream zone. Water Resour. Res. 24:1101-1110.

Royer, T.V. and M.B. David. 2005. Export of dissolved organic carbon from agricultural streams in Illinois, USA. Aquat. Sci. 67 (2005) 465-471, 1015-1621/05/040465-7, DOI 10.1007/s00027-005-0781-6.

Raymond, P.A., J.W. McClelland, R.M. Holmes, A.V. Zhulidov, K. Mull, B.J. Peterson, R.G. Striegl, G.R. Aiken, and T.Y. Gurtovaya. 2007. Flux and age of dissolved organic carbon exported to the Arctic Ocean: A carbon isotopic study of the five largest arctic rivers. Global Biogeochemical Cycles, Vol. 21, GB4011, doi:10.1029/2007GB002 934.

Robinson, J.S. and M. Sivapalan. 1996. Instantaneous response functions of overland flow and subsurface stormflow for catchment models. Hydrol. Process.10:845-862.

Robson, A.R., K. Beven, and C. Neal. 1992. Towards identifying sources of subsurface flow: a comparison of components identified by a physical based runoff model and those determined by chemical moxing techniques. Hydrol. Process. 6:199-214.

Scanlon, T.M., J.P. Raffensperger, and G.M. Hornberger. 2000. Shallow subsurface storm flow in a forested headwater catchment: Observations and modeling using a modified TOPMODEL. Water Resour. Res. 36:2575-2586.

Subagyono, K. 2003. Linking Runoff Process and Spatial and Temporal variation of Water Chemistry in a Forested Headwater Catchment. PhD Dissertation. Doctoral Program in Geoscience. University of Tsukuba. Japan.

Tanaka, T. and T. Ono. 1998. Contribution of soil water and its flow path to stormflow generation in a forested headwater catchment in central Japan. *In* K. Kovar, U. Tappeiner, N.E. Peters, R.G. Craig (*Eds*.). Hydrology, Water Resources and Ecology in Headwater. IAHS Publ. 248:181-188.

Temnerud, J. 2005. Spatial Variation of Dissolved Organic Carbon along Streams in Swedish Boreal Catchments. Thesis-Orebro University, University Library. Sweden. 41pp.

Tsukamoto, Y. and T. Ohta. 1988. Runoff process on a steep forested slope. J. Hydrol. 102: 165-178.