## AN ABSTRACT OF THE DISSERTATION OF

Marc G. Kramer for the degree of Doctor of Philosophy in Forest Science presented on May 11, 2001. Title: Maritime Windstorm Influence on Soil Process in a Temperate Rainforest

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Maritime cyclonic windstorms cause widespread disturbance to forested ecosystems in southeast Alaska. The consequence of this disturbance process on the movement, storage, and quality of soil carbon, forest hydrology and streamwater chemistry was studied along a windthrow disturbance sequence. Soil profiles were described and the thickness of the major organic and mineral horizons were measured every 5 m along transects in 3 catchments with contrasting disturbance histories. A subset of these horizons were randomly selected and sampled to determine the quantity and quality of carbon present. Mineral soil samples were physically fractionated based on particle density. Total C and N, natural abundance $\delta^{15}N$, $\delta^{13}C$ isotopes, and solid state $^{13}C$ NMR were used to compare soil organic carbon pools in catchments with contrasting disturbance histories. An event-based sampling scheme was then used to compare hydrochemical properties of each catchment. Six storms were sampled over 14 months, representing a range of rainfall and soil moisture conditions. Streamflow was measured, and water samples were collected every 4 hours during storm events from each catchment. Evidence for two distinct pathways for mineral soil carbon accumulation was found; 1) mineral and organic particle mixing by windthrow, 2) soil water transport of mobile organic carbon (MOC) to mineral soil horizons. MOC accumulated in mineral horizons principally through adsorption to mineral particles, and the extent of strong chemical association (adsorption) with mineral particles increased in older, thicker illuvial horizons. Forested catchments which experienced more intense soil mixing from windthrow were depleted in strongly humified soil carbon pools, and an overall increase in quality of soil carbon toward a partially decomposed particulate form was observed. Streamflow on more-disturbed catchments peaked 4 to 12 hours later than in less-disturbed catchments. During summer months, streamwater temperatures in more disturbed watersheds were cooler than air temperatures and less-disturbed catchments. Streams in more-disturbed catchments had higher pH, alkalinity and base cation concentrations than streams in less-disturbed catchments. These results suggest that catastrophic windthrow disturbance smoothes hydrograph response to storms, and increases the chemical interaction of rainwater with mineral soil horizons by increasing rainwater infiltration and storage in deeper soil profiles. The changes in concentration and characteristics of organic carbon in mineral soil which result from soil mixing disturbances (windthrow, landslides) can strongly influence the hydrology, chemical properties of catchments, and the rate of nutrient cycling.

# Maritime Windstorm Influence on Soil Process in a Temperate Rainforest
by

Marc G. Kramer

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Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

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Marc G. Kramer, Author

# Acknowledgments

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I first arrived in southeast Alaska in 1995. Ross Keister was instrumental in getting me started in Alaska, by providing funding through Andy Hansen. Toward the end of 1997, upon completion of my masters degree, Everette Kissinger, Gene Degayner, Greg Nowacki and Bill Pawuk were instrumental in providing funding for my regional windthrow assessment work, and funding for my graduate work. My collaboration with an NSF funded windthrow project lead by Bernard Bormann comprised a considerable portion of my dissertation work. The PI's on this project were a tremendous value.

Bernard Bormann provided me with office and lab space while at OSU. Mark Nay was instrumental in the construction and maintenance of a float house, which was used throughout the duration of this project. I am thankful for assistance from Phillip Sollins, Ron Sletten and Kermit Cromack all of whom served well both as mentors colleagues and friends. Phil not only taught where and how to use commas, but also suggested I try density fractionation as a way to study soil carbon. Ron Sletten taught me how to do analytic chemistry (lots of coffee and late nights), and encouraged me to study soil carbon with 13C NMR. From ICP to DOC analysis! Thanks Ron. Peter Swart provided lab facilities and encouragement in doing natural abundance stable isotope work with carbon and nitrogen. Geoffrey Ellis, Amel Saiid, and Rene Price provided additional assistance in running samples. Philip and Patricia Kramer not only helped with fieldwork in Alaska, but also let me stay on their boat while working at RSMAS. Thanks Phil and Trish.

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Dedicated to my father, Gerald H. Kramer.

# Maritime Windstorm Influence on Soil Process in a Temperate Rainforest

## 1. Introduction

Maritime cyclonic windstorms cause widespread disturbance to the natural forested ecosystem of southeast Alaska. These forests occur in the hyperhumid maritime climatic zone, which is dominated by exogenous (offshore) influence from moisture bearing maritime air masses, and strong windstorm activity. While most forests of the world are influenced by multiple natural disturbance processes, including, in many cases, strong influence by human activity (landuse conversion, timber harvest), the forests of southeast Alaska are particularly well suited to study the long-term effects of a single natural disturbance agent, windthrow, on the forested landscape. The limited logging and fire are not sufficient to have confounded or erased beyond recognition the windthrow history reflected in present day forests. Recent studies suggest many large catastrophic windstorms have affected significant portions of southeast Alaska over the last 400 years (Kramer et al. In Press).

At large spatial and temporal scales, topographic, edaphic conditions and prevailing storm direction appear to constrain the intensity of maritime windstorm effects on some portions of the landscape, that results in a gradient of long-term storm effects across the landscape (Kramer et al. In Press). This gradient can be made spatially explicit and predicted on a broadscale using multiple logistic regression (Kramer et al. In Press). The implications of this research is that past and present maritime windstorms strongly influence the present-day forested ecosystem of southeast Alaska and that forests most susceptible to windthrow may never reach a late-seral stage. The return interval of catastrophic storms appears to be sufficiently short to cycle these forests back to an early-seral, even-aged stand before the longest-lived trees die (approximately 350–950 yr; Lertzman et al. 1996). By contrast, the wide range of ages and lack of a single identifiable cohort found in storm-protected forests suggest that at least one turnover cycle since the last stand-replacement event may occur in many of windstorm protected forests.

In addition to influencing forest stand dynamics across the landscape, windthrow disturbance over long periods of time may have important consequences for ecosystem function and process (Shulze and Mooney 1994, Ulanova 2001). Ecosystem properties (productivity, diversity and resiliency) may vary spatially and temporally across the landscape as a result of windthrow. Forests that are susceptible to chronic maritime windstorm effects may develop considerably different soil and nutrient conditions than those that are more protected from these storms.

The goal of my dissertation work is to investigate the question: How do chronic maritime windstorms influence long-term ecosystem properties? I focused my research on understanding how maritime windstorms might influence soil processes. The consequence of long-term maritime windstorm activity on the movement, storage, and quality of soil carbon, forest hydrology, and streamwater chemistry was studied along a windthrow disturbance sequence on High Island, a small 500-ha island in the middle of the Alexander Archipelago. High Island was struck most recently by a windstorm which occurred approximately 95 years ago. The western portion of the island experienced intense windstorm damage, while the northern portion experienced less intense, partial disturbance effects. On some portions of the island, no evidence of windthrow damage from this storm could be found. Four catchments, located throughout the island, with contrasting disturbance from past windthrow were studied. Soil profiles were described and the thickness of the major organic and mineral horizons were measured every 5 m along transects in 3 of these catchments with contrasting disturbance histories. A randomly selected subset of these horizons were sampled to determine the quantity and quality of carbon present. Mineral soil samples were physically fractionated based on particle density. Total C and N, natural abundance $\delta^{15}N$, $\delta^{13}C$ isotopes, and solid state $^{13}C$NMR were used to compare soil organic carbon pools in catchments. An event-based sampling scheme was then used to compare hydrochemical properties of each the 4 catchments. Six storms were sampled over 14 months period, representing a range of soil moisture and rainfall conditions. Stream flow was measured and solution samples were collected every 4 hours from each catchment.

# CHAPTER 2

## 2. Hydrochemical Properties of Small Spodosol-Dominated Catchments with Contrasting Disturbance from Windthrow in a Temperate Rainforest, Southeast Alaska.

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## 2.1 Abstract

We examined the influence of windthrow on the hydrochemistry of small Spodosol-dominated catchments on a 200-ha forested island located in the panhandle of southeast Alaska. Four watersheds (0.3 to 0.8 ha) with contrasting disturbance histories were selected and sampled using an event-based sampling scheme. Baseflow conditions and 6 rainstorms were sampled over 14 months, representing a range of antecedent and rainfall intensity conditions. During rainstorms, stream flow was measured and water samples were collected on average every 4 hours from each catchment. Stream flow peaked 4 to 12 hours earlier on more-disturbed catchments than on the less-disturbed catchments. During rainstorm events, streamwater temperatures were more equilibrated to ambient air temperatures in the more-disturbed catchments than in the less-disturbed catchments. Water discharged from more-disturbed catchments had greater concentrations of Si and lower dissolved organic carbon (DOC) than water from less-disturbed catchments. Hydrograph-separation analysis of rainstorm events suggests more of the water flowed through or originated from deeper mineral soil horizons in the more-disturbed catchments. We conclude that catastrophic windthrow disturbance can smooth hydrograph response to rainstorm events, and increase the chemical interaction of rainwater with mineral soil horizons, by increasing rainwater infiltration and storage in deeper mineral soil.

## 2.2 Introduction

In the absence of disturbance, thick spodic soil horizons may impede water infiltration (Savill 1976, Wang et al. 1978, McKeague and Sprout 1975) and increase lateral flow of rainwater through near-surface soil horizons. In some extreme cases, such as the formation of a duripan (or orstein) horizon, these alterations in soil water movement may lead to saturated, anoxic soil conditions and the development of bogs (Ugolini and Mann 1979, Banner et al. 1983, Lapen and Wang 1999). While the disruption of soil horizons by windthrow (termed regressive podzolization by Saetczhel et al. 1990) on Spodosols has been a topic of much research (Lutz 1940, Denny and Goodlett 1956, Lyford and Maclean 1966, Brown 1977, Laffan 1979, Beke and McKeague 1984, Bormann et al. 1995, Vesenev and Targul'yan 1995, Ulinova 2001), hydrochemical changes resulting from windthrow in forested catchments where Spodosols occur have not been studied. The objective of this study was to examine the influence of windthrow on the hydrochemistry of small, forested catchments dominated by Spodosols. The study was conducted in the temperate rainforests of southeast Alaska, where Spodosols predominate (Ugolini and Mann 1979, Alexander et al. 1980) and windthrow is common (Kramer et al. In press).

In southeast Alaska, spodic horizons form rapidly and can exert strong control on ecosystem properties. Through podzolization, clearly visible illuvial soil horizons can develop in less than 100 years and thick spodic horizons can form in as little as 200 years after glacial retreat or windthrow on a variety of parent materials (Chandler 1946, Ugolini 1968, Heilman and Gass 1974, Bormann et al. 1995, Alexander and Burt 1996). The rapid formation of spodic horizons and associated changes in soil-water dynamics both have major implications for ecosystem development and the role of disturbance in this region (Ugolini and Mann 1979). In the absence of disturbance, Spodosols may develop into highly organic hydric soils that support only scrub forest. In some cases paludification may result in the formation of bogs (Ugolini and Mann 1979). Spruce stumps and logs buried under upland bogs, common in this region (Dachnowski-Stokes 1941), led Zach (1950) to conclude that bogs were the climax vegetation for this region.

However other factors are likely to result in bog formation such as landform position and slope (Banner et al. 1983, Lapen and Wang 1999).

## 2.3 Methods

### *2.3.1 Overview*

Four small zero-order basins (0.3 to 0.8 ha in size) with contrasting windthrow histories were selected for the study. An event-based sampling scheme was then used to compare hydrochemical properties (stream flow, temperature, DOC, DIC, pH, major cations and anions) of each catchment. Baseflow conditions along with 6 rainstorms were sampled over a 14-month period, representing a range of antecedent and intensity precipitation conditions. Streamflow was measured and solution samples were collected every 4 hours from each catchment during each sampled storm.

This work was conducted in the Tongass National Forest, a vast area of mostly pristine coastal temperate rainforest in southeast Alaska. Forests are distributed throughout the Alexander Archipelago on 7 million ha on over 1000 islands with diverse geology and topography (Alaback 1996). Soils are characteristically shallow, because of Wisconsin glaciation. Podzolization is common, largely as a result of year-round precipitation and a cool maritime climate (Heilman and Gass 1974, Alaback 1986).

Six conifer species dominate the region (Pawuk and Kissinger 1989). On well-drained sites, productive western hemlock (Tsuga heterophylla (Raf.) Sarg.) and Sitka spruce forests (Picea sitchensis (Bong.) Carr.) are common. On less well-drained sites, hemlock and spruce still dominate, but are mixed with Alaska yellow cedar (Chamaecyparis nootkatensis (D. Don) Spach) and western red cedar (Thuja plicata Donn ex D. Don). At higher elevations (above 400 m), mountain hemlock (Tsuga martensiana (Bong.) Carr.) typically replaces western hemlock. Low productivity mixed conifer-scrub forests, often dominated by lodgepole pine (Pinus contorta Dougl. ex Loud. var.

contorta), occur extensively on the landscape, along with muskeg plant communities on low productivity hydric soils or wetlands (Pojar and MacKinnon 1994, Alaback 1996).

Rainstorms and windthrow in southeast Alaska are driven by the passage of extratropical cyclones, that pass as frequently as every four or five days during late fall and winter (Shumacher and Wilson 1986). Associated with these storms are winds up to, and occasionally in excess of, 40 $ms^{-1}$, persistent cloud cover, and up to 13 m of annual precipitation in the coastal mountains. Trajectories for these low-pressure systems are largely determined by the location and strength of three semi-permanent atmospheric features: the Aleutian low and Siberian high pressure systems in autumn, winter, and spring, giving way to the east Pacific high pressure system in summer. Large interannual changes in storm frequency, intensity, and size, and moisture delivery may be expected as a consequence of El Niño, which can penetrate poleward into the Gulf of Alaska (Schumacher and Wilson 1986).

### *2.3.2 Study site*

High Island (approx. 500 ha) is located in the middle of the Alexander Archipelago, in the Tongass National Forest, approximately 160 km from the mainland and 20 km south of the town of Kake (Figure 2.1). Maximum elevation on the island is 150 m. The parent material is fractured basalt. Average annual precipitation is 1.9 m, with the wettest months during fall and winter. Extreme temperature fluctuations are infrequent due to the maritime influence. Cloud cover, precipitation, cool ambient air temperatures (4-10 °C), and high relatively humidity (>80%) are characteristic throughout the year.

The island was struck by a strong cyclonic storm approximately 95 years ago. Forests on the south and west portion of the island show evidence of greater damage from the storm than north to northeast portions of the island. Four watersheds that span a range of windstorm damage effects were selected for the study (Figure 2.2). Most of the overstory trees in Watershed 1 (WS1), located on the west side, appear to have been blown down by the storm. We did find 20 stumps from selective logging that most likely predated the storm. Storm effects include large windthrow mounds and pits distributed throughout the watershed as well as a predominantly young even-aged forest that regenerated after the storm. Watershed 2 (WS2), adjacent to WS1, experienced near complete overstory stand damage, but contained more standing residual trees, some portions of the watershed were little disturbed and 6 cut stumps were found. Watershed 3 (WS3), located on the north portion of the island, shows evidence of partial disturbance to the overstory from the storm. Watershed 4 (WS4), located on the northeast portion, shows very little evidence of recent storm damage such as downed stems or pit and mound microtopography. The catchments are in close proximity, have identical parent material, and relatively similar slopes and sizes. Catchment size and shape was determined by hand surveying the topographic boundary. The major axis length of WS1 (0.6 ha), WS2 (0.8 ha) and WS3 (0.4 ha) is about 120 m, with 50 m of elevation gain. The smaller WS4 (0.3 ha) has a 60 m major axis length with 20 m of elevation gain. Slope profile is relatively constant and steep in WS1 (40-45%). The slope of the major axis in WS2 is steep (40-45%), but flattens somewhat toward the bottom of the catchment. Slope in WS3 (40-45%) is initially flat then is constantly steep to the bottom of the catchment. The less-steep slope profile in WS4 (33-38%) is relatively constant. Elevation ranges from 3-60 m above sea level. Only western hemlock and Sitka spruce are found in the 4 catchments. The basin shapes of each catchment are shown in Figure 2.2.

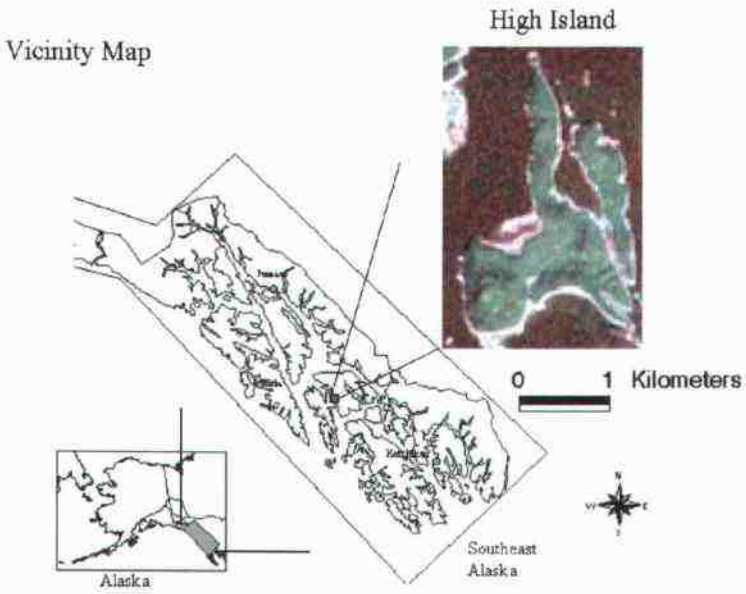


Figure 2. 1. Vicinity map of high island.

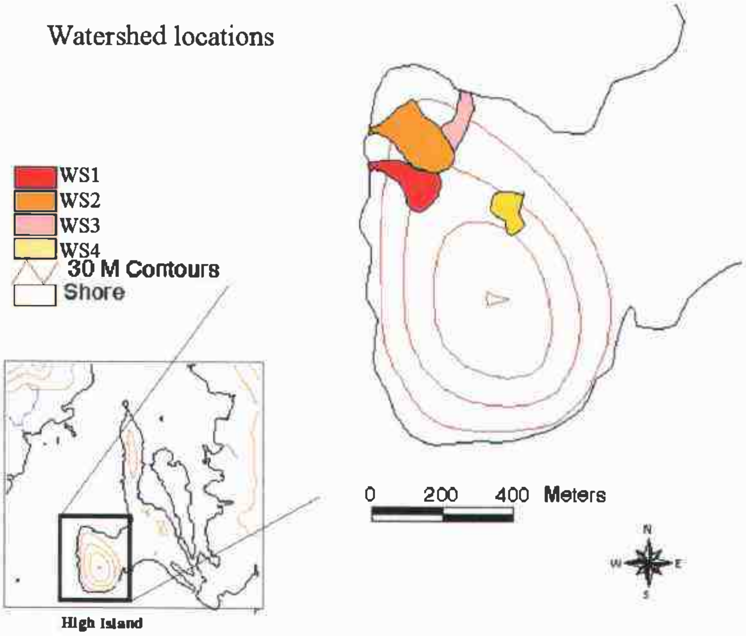


Figure 2. 2. The location and shape of watersheds.

### *2.3.3 Damage from past windstorms*

The extent of windstorm damage in each catchment was determining by aging trees, measuring stem size, and quantifying the aerial extent of prominent pit and mound topography. The ages of tress in each catchment were determined by coring a random sample (more then 50% of the trees) of overstory trees in each catchment and counting annual growth rings, with a dissecting microscope. Cores that were difficult to count were mounted, sanded, then counted.

### *2.3.4 Water chemistry*

An event-based sampling scheme was used to compare hydrochemical properties (stream flow, temperature, dissolved organic carbon (DOC), $HCO_3$-, dissolved inorganic carbon (DIC), pH, and major cations and anions) of drainages from each catchment. Baseflow conditions and six rainstorms were sampled over a 14-month period, representing a range of antecedent precipitation and rainfall intensity conditions. During rainstorms, streamflow was measured and water samples were collected on average every 4 hours from each catchment.

Streamflow was measured with PVC outflow pipes installed in concrete weirs in WS1, WS2, WS3. In WS4, 3 PVC outflow pipes were installed along a wide trench dug across the bottom of the catchment. An additional PVC pipe was installed at the top of the catchment, where water draining from an undefined contributing area entered the catchment. Flow was determined by measuring the time required to fill a bucket of known volume. In WS4, total flow was determined by adding all outflow pipes draining out of the bottom of the catchment and subtracting out measured inputs at the top of the catchment.

During rainstorms, organic horizon soil solutions were collected using zero tension lysimeters. Throughfall was collected using PVC rain gutters installed above the forest floor and funneled into 1-L polyethylene bottles. Solution samples were collected upstream from the weirs at designated sampling sites. A 500 ml polyethylene bottle was rinsed 5 times, then filled to minimize air bubbles. Stream temperature and pH were measured onsite using a waterproof pH/temperature meter (Thermo Orion Model 265A, Bevereley, MA, USA).

Samples were filtered within 4 hours of collection through 0.45 $\mu$m glass fiber filters (Whatman G45). Solution samples were then split in 3 acid-washed 120 ml polyethylene bottles and stored at 2° C. One of the samples, designated for cation determination, was acidified to pH 2 with HCl. Samples were then shipped to the University of Washington Quaternary Research Center for chemical analysis within 4 weeks.

Solution samples were analyzed for major cations, anions, DIC and DOC. Cations were determined with a Jarrel Ash 955 Inductively Coupled Plasma Emission Spectrometer (Thermo Elemental, Franklin, MA, USA). Dissolved inorganic and organic carbon content was determined by persulfate and $CO_2$ measured oxidation using an OI 700 Carbon Analyzer (OI Analytical, College Station, TX, USA). Anions were determined by ion chromatography (Dionex, Sunnyvale, USA). Daily precipitation and air temperature were measured at a weather station installed on the south side of the island, equipped with a tipping bucket, air temperature, and relative humidity sensor (Campbell Scientific).

Total alkalinity was measured by titration to a pH 4.5 endpoint within 1 hour of collection. For the pH range of these natural streamwaters (4.5-6.5), it can be assumed that most of what is determined as total alkalinity is dissolved HCO3- and DOC (Stumm and Morgan 1996, Mather 1997). For samples in which total alkalinity was not measured, DIC was used to calculate $HC0_3^-$. A one-to one plot of DIC and alkalinity was linear ($R^2=0.85$, $p<.01$). The strong relationship between DIC and total alkalinity confirmed that most of what was measured as total alkalinity was $HC0_3^-$.

### *2.3.5 Mass Balance Hydrograph Separation Approach*

Hydrograph separation was used to infer flowpath differences between catchments (Brown et al. 1999). In this study, 2 non-conservative solutes were chosen for hydrograph separation to differentiate between mineral soil and O-horizon water contributions to streamflow. We used 3 two-component models and a single two-solute, three-component model to compare O-horizon and mineral-soil water contributions to streamflow. The extent to which each solute differentiated the source of water and the biogeochemical process influencing solute concentrations, were considered in solute selection. The end members evaluated were throughfall, O-horizon soil water, and deep mineral soil water. We used baseflow (pre-event) streamwater, most likely derived from old, deeper soil water contributions, to represent our mineral soil water end member (Pinder and Jones 1976, Hooper and Shoemaker 1986, Ribolzi et al. 2000). Two component hydrograph separations (Pinder and Jones 1969) are solved through substitution by using the 2 following equations, which reflect water and solute mass balance:

i.) $Q_{strm} = Q_{m\text{-}hor} + Q_{o\text{-}hor}$

ii.) $C_{strm}\ Q_{strm} = (Q_{o\text{-}hor}\ C_{o\text{-}hor} + Q_{m\text{-}hor}\ C_{m\text{-}hor})$

Where :

$C_{strm}\ Q_{strm}$ are storm event discharge. $C_{o\text{-}hor}\ Q_{o\text{-}hor}$ are O-horizon soil water contributions, and $C_{m\text{-}hor}\ Q_{m\text{-}hor}$ are deep mineral soil water contributions.

Substituting eq. i) into equation ii.) $Q_{m\text{-}hor}$ is calculated:

iii) $Q_{sw} = Q_{strm*} (C_{strm} - C_{o\text{-}hor}) / (C_{m\text{-}hor} - C_{o\text{-}hor})$

A two-solute, three-component hydrograph separation (DeWalle et al. 1988) using throughfall, O-horizon and soil water endmembers was constructed. The water balance can be written as:

iv) $Q_{strm} = Q_{tf} + Q_{o\text{-}hor} + Q_{m\text{-}hor}$

v) $C_{strm}\ Q_{strm} = (Q_{o\text{-}hor}\ C_{o\text{-}hor} + Q_{m\text{-}hor}\ C_{m\text{-}hor} + Q_{tf} C_{tf}$

where the subscript tf refers to contributions from throughfall. Equations for each component can be derived through substitution of v) into iv) then solving for the terms $Q_{o\text{-}hor}$, $Q_{sw}$, and $Q_{tf}$. For example $Q_{o\text{-}hor}$ is given by:

vi) $Q_{o\text{-}hor} = ([\,(C_{strm} - C_{sw}) / (C_{strm} - C_{sw})] - Q_{tf} / Q_{strm}\,[\,(C_{tf} - C_{sw}) / (C_{o\text{-}hor} - C_{sw})]\,) * Q_{strm}$

### *2.3.6 Rainstorm analysis*

For the rainstorms sampled, a summary table describing each precipitation event (intensity, duration), antecedent conditions, and season was constructed. A summary table of stream water response from each catchment to these precipitation events was then constructed. Hydrometric results (timing of peak flow), total water discharge during storm flow period, and fluxes of select solutes are included in the table. Results from the hydrograph separation (two-component and three-component models) are included as well. Bivariate plots were created to evaluate the hydrograph separations and compare hydrochemical differences between catchments. Discharge concentration graphs for select solutes for each rainstorm were used to evaluate chemical behavior in streams during rainstorm response.

## 2.4 Results

### *2.4.1 Past damage from windstorms*

The extent of soil disturbance from windthrow and associated downslope movement of soil from hillslope processes is likely to be greater than is reflected by the pronounced pit and mound topography (Schaetzl and Follmer 1990, Norman et al. 1995). We used the extent of prominent pit and mound topography in each catchment to rank tree uprooting damage from recent (<100 yr) windstorms, not to quantify soil disturbance. The extent of recent (<100 yr) prominent pit and mound topography was greatest in WS1, which appeared to have experienced the most stand damage from a storm that occurred 90 years ago (Table 2.1, Figure 2.3) (11%). WS2 had fewer pits and mounds (8 % of the area) and trees were older, but WS2 nonetheless showed strong evidence of widespread stand damage and a distinct pulse of tree recruitment that occurred shortly after the storm struck. WS3 had fewer pits and mounds than WS2 (5% of the area) and evidence that at least some portion of the WS3 was not disturbed by the storm was found. WS4 had a wide range of tree sizes and ages and no evidence (0 %) of recent pits and mounds and fallen logs were highly decomposed (class IV). Trees in WS1 were smaller and more numerous, and most (78%) established after or near the time the storm struck (Table 2.1) In WS2 and WS3, trees were older and more variable in but still contained many (>45%) trees which regenerated after the storm struck (Figure 2.3). WS4 showed evidence of gap-phase forest development, and no distinct pulse (<10%) of recruitment or recent (<100 yr) soil disturbance could be detected. Small-scale, low intensity disturbances likely explain the present WS4 stand attributes (age, size and density). These results are summarized in Table 2.1.

Table 2. 1. Tree size and age characteristics of catchments

| | Stand Density (trees/ha) | Mean Stem Size (cm) | Mean Tree Age (years) | Pronounced Pit and Mound Topography (%) |
|---|---|---|---|---|
| WS1 | 663 | 31.43 (0.81) | 68 (2) | 11 |
| WS2 | 505 | 33.88 (1.01) | 102 (7) | 8 |
| WS3 | 408 | 31.58 (1.39) | 128 (5) | 5 |
| WS4 | 360 | 48.36 (7.17) | 218 (29) | 0 |

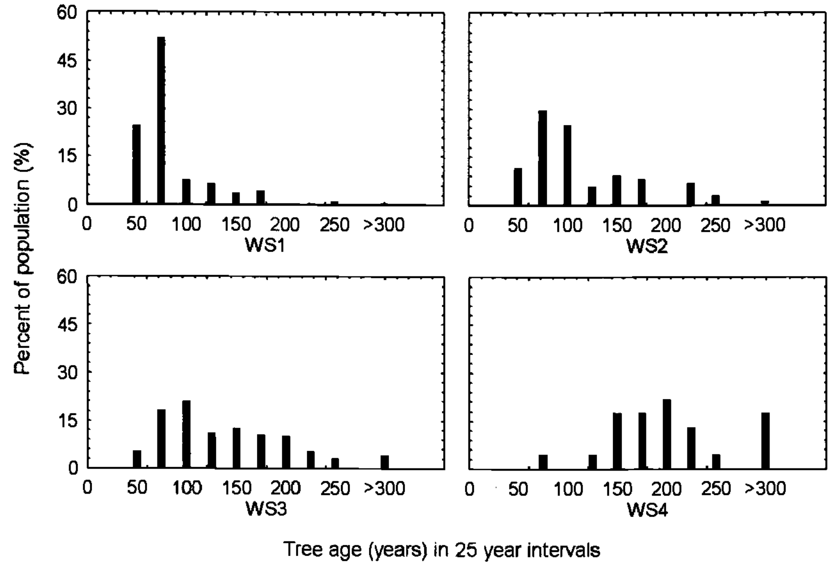


Figure 2. 3. Stand age characteristics of WS1-WS4.

### 2.4.2 *Climate of High Island*

From 1997-2000, the annual maximum and minimum air temperature average between 4 to 10 °C. Mean daily temperatures are shown in Figure 2.4. Relative humidity averaged >80% year round (Figure 2.5) Total annual precipitation averaged 1.9 m/yr and was greatest during October (Figure 2.6). Maritime rainstorms delivered the majority of the precipitation (>70%) during high intensity rains (>2cm/day) that occurred most frequently during the late summer and fall (Figure 2.7).

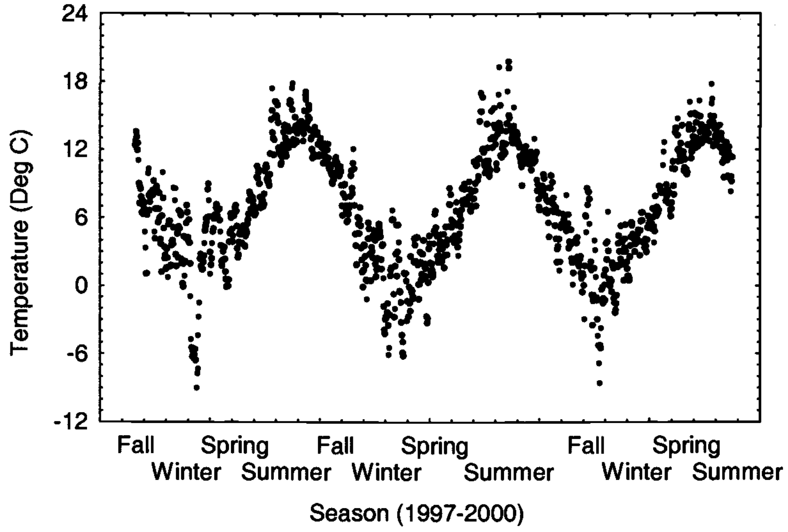


Figure 2. 4. Mean daily air temperature between 1997-2000.

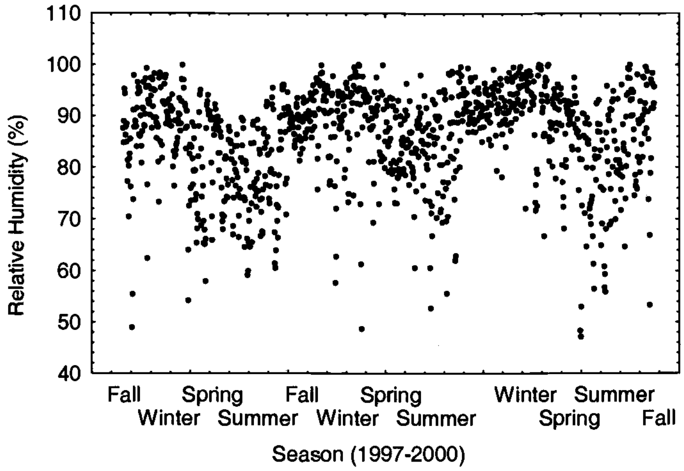


Figure 2. 5. Mean daily relative humidity between 1997-2000.

During the winter months, WS1 and WS2 streamwater was warmer than WS3 and WS4. And during summer months, WS1 and WS2 were cooler than WS3 and WS4. (Figure 2.8). Stream water temperatures in the more-disturbed watersheds were less equilibrated to ambient air temperatures. Streams in WS3 and WS4, which showed less evidence of recent windthrow disturbance, were more equilibrated to ambient air temperatures.

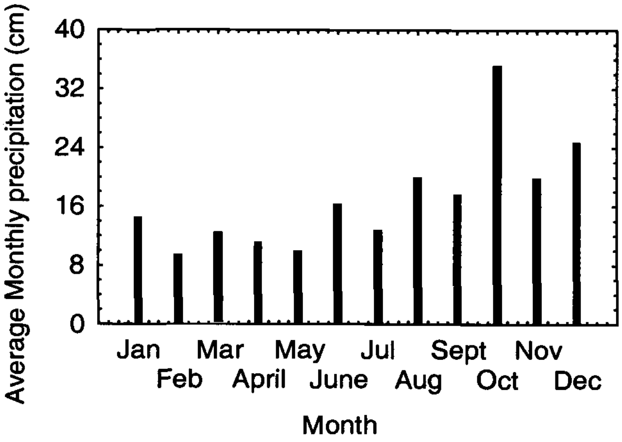


Figure 2. 6. Average monthly precipitation on High Island 1997-2000.

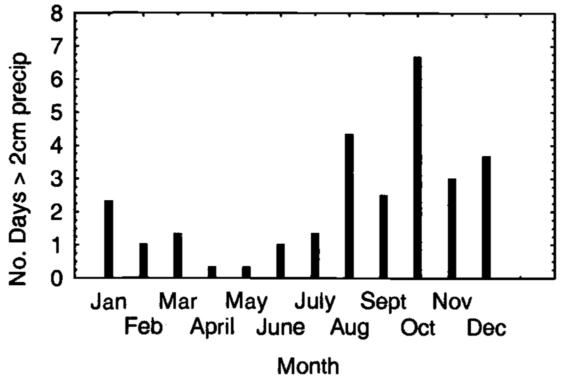


Figure 2. 7. Number of high precipitation (>2mm) days per month 1997-2000.

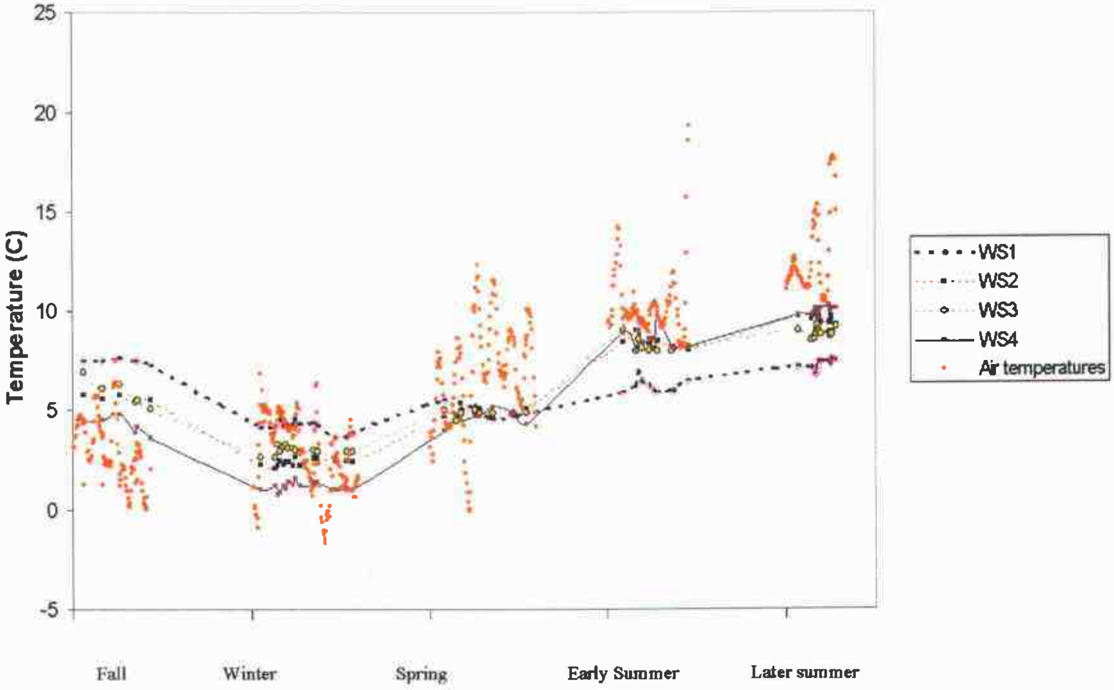


Figure 2. 8. Ambient air and streamwater temperatures by season.

Table 2. 2. Mean (standard error in parentheses) of Si, DOC and DIC in rainfall, throughfall and O-horizon water sampled by season.

| Sample | Season | Si (ppm) | DOC (ppm) | DIC (ppm) |
|---|---|---|---|---|
| Rainfall | Fall | 0.00 (0.00) | 0.55 (0.10) | 0.89 (0.08) |
| | Winter | 0.01 (0.01) | 6.67 (3.42) | 0.86 (0.05) |
| | Spring | 0.00 (0.00) | 3.05 (1.4) | 0.35 (0.03) |
| | Early summer | 0.00 (-----) | 2.60 (----) | 0.45 (-----) |
| | Mid summer | 0.12 (0.01) | 0.91 (0.04) | 0.76 (0.03) |
| | Late summer | 0.00 (0.38) | 2.79 (0.10) | 0.82 (0.00) |
| Throughfall | Fall | -- | -- | -- |
| | Winter | 0.07 (0.02) | 6.73 (1.19) | 0.95 (0.07) |
| | Spring | 0.04 (0.01) | 10.86 (2.19) | 0.43 (0.04) |
| | Early summer | 0.04 (0.02) | 19.9 (2.50) | 0.99 (0.18) |
| | Mid summer | -- | -- | -- |
| | Late summer | 0.01 (0.01) | 12.25 (1.38) | 1.10 (0.05) |
| O-horizon | Fall | 0.07 (0.01) | 23.92 (3.76) | 1.50 (0.13) |
| | Winter | 0.07 (0.02) | 19.16 (2.80) | 1.00 (0.05) |
| | Spring | 0.08 (0.03) | 26.04 (3.97) | 0.54 (0.03) |
| | Early summer | 0.15 (0.04) | 56.26 (6.35) | 1.22 (0.11) |
| | Mid summer | 0.38 (0.06) | 51.72 (8.39) | 1.04 (0.07) |
| | Late summer | 0.19 (0.95) | 40.8 (11.06) | 0.19 (0.03) |

### *2.4.3 Mass Balance Hydrograph Separation Approach*

To perform hydrograph separations, we began by using the solute Si, which only becomes strongly enriched (>0.5 ppm) through contact with mineral soil. Although Si increases through weathering processes (Mather 1997), other non-conservative exchange/sorption mechanisms occur as well, such as irreversible adsorption to Fe-oxides (Jone and Hendrick 1963, Hingston et al. 1972). High rates of Si precipitation can occur at high concentrations in alkaline systems (Casey and Neal 1986). In spite of its quasi-conservative behavior in solution (Richey et al. 1998), Si has been used in past studies for hydrograph separations and has compared well with known conservative tracers, such as

$^{18}O$, when rates of precipitation and absorption of Si are low (Hooper and Shoemaker 1986, Pionke et al. 1993, Turner and Barnes 1997). The other solute selected, DOC showed strong end member differentiation. DOC is highly non-conservative and was found to be strongly enriched after rainwater percolated through O-horizons (Table 2.2). DOC is immobilized during contact of water with mineral soil horizons (McDowell and Likens 1988, Qualls and Haines 1992). Throughfall and O–horizon DOC declined noticeably during late fall and early spring, and increased during summer (Table 2.2).

### *2.4.4 Rainstorm events*

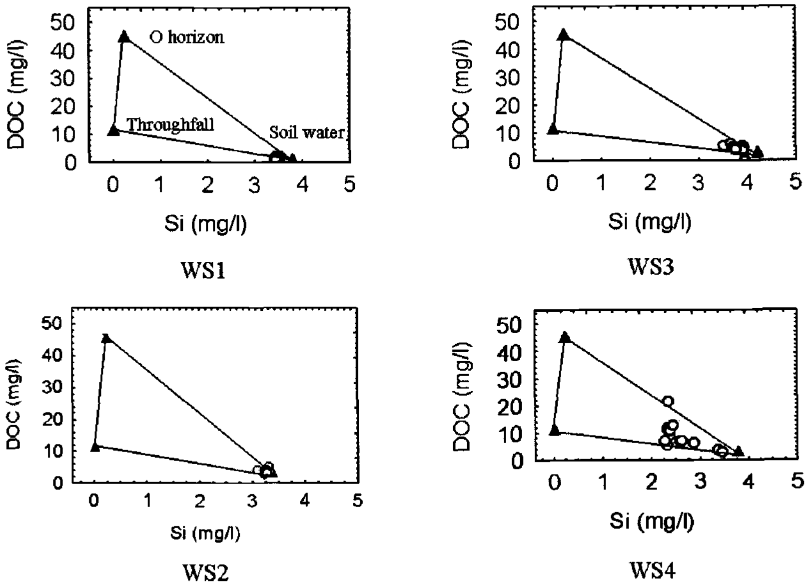
The time storms were sampled is measured in days since the study began, Jan 1. 1998. Six rainstorms were sampled through a 14-month period. Four of which occurred during the late summer to early fall. Antecedent conditions and characteristics of each storm are summarized in Table 2.3. Three storms sampled during the late-summer early-fall all had wet antecedent conditions (>22 mm accumulation 72 hrs prior to the rainstorm event) and high intensity (>30 mm/24 hrs) precipitation. Storm #1 occurred during early summer, antecedent conditions were comparatively dry, and rainstorm intensity was low. Storm #3 occurred during the winter months; snow was present at the time of sampling. Initially temperatures were sub-freezing, then rain fell on snow, and air temperatures rose during the storm. The rainfall intensity was moderate.

Table 2. 3. Summary characteristics of 6 storms sampled; Storms are ordered non-sequentially.

| Storm# | Date | 72 HR Antececedant Precip (mm) | Storm period Precip (mm) | Storm duration (hr) | Max Precip. Intensity (mm/hr) | Ave Precip. Intensity (mm/hr) | Total precip. during storm period (mm) |
|---|---|---|---|---|---|---|---|
| 1 | June 28, 99 | 12 | 12 | 19 | 2 | 1 | 12 |
| 2 | July 30, 99 | 5 | 30 | 22 | 10 | 1 | 30 |
| 3 | March 07, 99 | 27 | 22 | 90 | 5 | 0 | 22 |
| 4 | August 25, 98 | 22 | 55 | 15 | 9 | 4 | 64 |
| 5 | August 28,98 | 30 | 34 | 32 | 6 | 1 | 34 |
| 6 | Sept. 1,98 | 35 | 31 | 24 | 6 | 1 | 31 |

### *2.4.5 Storm #1, June 28th 1999*

A low intensity (<12 mm/19 hrs) storm with relatively dry (<12 mm/72 hr) antecedent conditions occurred in June 1999. This storm had the lowest maximum intensity of any sampled (2mm/hr). Bivariate plots of Si and DOC suggest that most of the discharged water originated from mineral soil horizons (Figure 2.9). Peak flow in WS4 occurred shortly after rainfall ceased (Figure 2.10). Peak flow in WS2 and WS3 occurred 1.3 hours later.



WS1

WS3

WS2

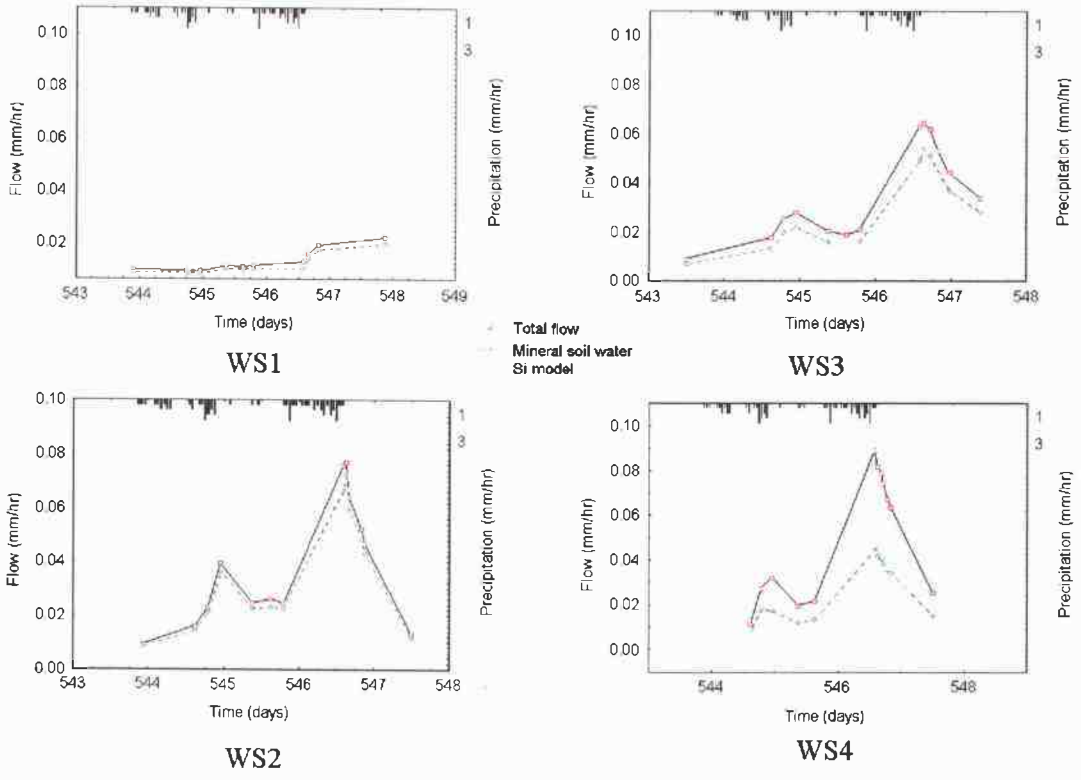
WS4

Figure 2. 9. June storm bivariate plots of Si and DOC with endmembers.

Table 2. 4. Summary table of streamflow response to 6 rainstorms.

|  |  |  |  |  |  | 2 component separation |  | 3-component separation |
|---|---|---|---|---|---|---|---|---|
| Watershed | Peak flow lag (hr) | DOC flux (kg/ha) | Si flux (kg/ha) | Storm runoff coefficient (%) | Total storm discharge (mm) | Si-model mineral soil contribution | DOC-model mineral soil contribution | O-horizon contribution |
| June 29, 99 |  |  |  |  |  |  |  |  |
| WS1 | 27.3 | 0.02 | 0.05 | 11% | 1.3 | 83% | 98% | 0% |
| WS2 | 1.2 | 0.12 | 0.09 | 25% | 3.0 | 87% | 100% | 1% |
| WS3 | 1.3 | 0.16 | 0.12 | 26% | 3.1 | 78% | 87% | 0% |
| WS4 | 0.0 | 1.39 | 0.22 | 77% | 9.2 | 61% | 82% | 10% |
| July 30, 99 |  |  |  |  |  |  |  |  |
| WS1 | 4.4 | 0.11 | 0.17 | 16% | 4.7 | 96% | 96% | 0% |
| WS2 | 1.1 | 1.19 | 0.40 | 41% | 12.2 | 89% | 84% | 20% |
| WS3 | 0.8 | 1.78 | 0.46 | 46% | 13.8 | 67% | 63% | 22% |
| WS4 | 0.0 | 4.14 | 0.58 | 90% | 27.1 | 66% | 60% | 28% |
| March 07,99 |  |  |  |  |  |  |  |  |
| WS1 | 3.36 | 0.14 | 0.31 | 50% | 10.6 | 95% | 98% | 0% |
| WS2 | 47.04 | 0.54 | 0.46 | 83% | 17.7 | 86% | 98% | 0% |
| WS3 | 0.48 | 0.32 | 0.39 | 55% | 11.7 | 94% | 95% | 1% |
| WS4 | 0.00 | 1.69 | 0.40 | 93% | 19.8 | 86% | 62% | 25% |
| Aug. 25 98 |  |  |  |  |  |  |  |  |
| WS1 | 4.0 | 0.2 | 0.81 | 41% | 26.0 | 75% | 38% | 0% |
| WS2 | 3.8 | 5.7 | 1.32 | 75% | 48.0 | 76% | 70% | 21% |
| WS3 | 3.4 | 7.6 | 1.54 | 77% | 49.0 | 65% | 59% | 25% |
| WS4 | 0.0 | 14.7 | 1.49 | 83% | 53.0 | 57% | 50% | 47% |
| Aug. 28 98 |  |  |  |  |  |  |  |  |
| WS1 | 5.3 | 0.2 | 0.31 | 29% | 10.0 | 88% | 82% | 0% |
| WS2 | 3.4 | 0.8 | 0.50 | 53% | 18.0 | 87% | 40% | 4% |
| WS3 | 1.7 | 0.7 | 0.54 | 53% | 18.0 | 76% | 35% | 3% |
| WS4 | 0.0 | 3.4 | 0.42 | 65% | 22.0 | 68% | 74% | 21% |
| Sept. 1 98 |  |  |  |  |  |  |  |  |
| WS1 | 6.7 | 0.2 | 0.51 | 47% | 16.0 | 86% | 74% | 0% |
| WS2 | 4.5 | 0.9 | 0.57 | 59% | 20.0 | 88% | 70% | 5% |
| WS3 | 4.1 | 0.8 | 0.79 | 65% | 22.0 | 77% | 75% | 3% |
| WS4 | 0.0 | 3.5 | 0.50 | 59% | 20.0 | 69% | 66% | 30% |

By strong contrast WS1 streamflow increased during this time, did not peak until 27 hours after initial precipitation (Table 2.4), and showed only a weak hydrograph response to precipitation (Figure 2.10.) Total storm discharge was highest for WS4 (77% of storm-period precipitation), lower for WS2 and WS3 (25% and 26%), and lowest for WS1 (<12%) (Table 2.4). All hydrograph separation models suggested mineral soil water contributions were greatest in WS1, and, while still high, were lower in W2-WS4 (Table 2.4). O-horizon flow contributions to storm flow were very low in all catchments, although highest in WS4. Relative to other storms sampled, the rising limb duration was long (>20 hours) in all catchments. Stream discharge solute relationships in all catchments were not strong for this storm (Figures 2.10-2.11).



WS1 WS3

WS2 WS4

Figure 2. 10. June storm hydrograph separations.

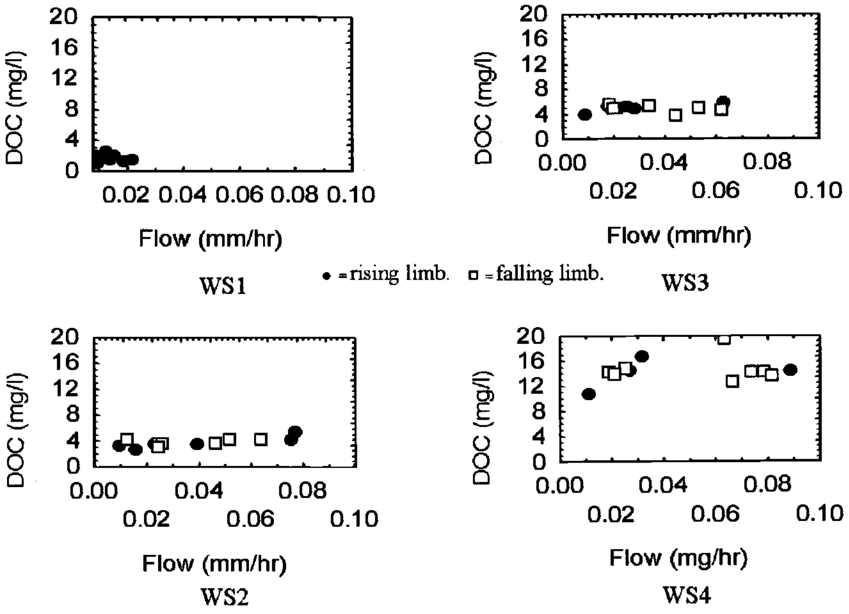


Figure 2. 11. June storm DOC stream vs discharge.

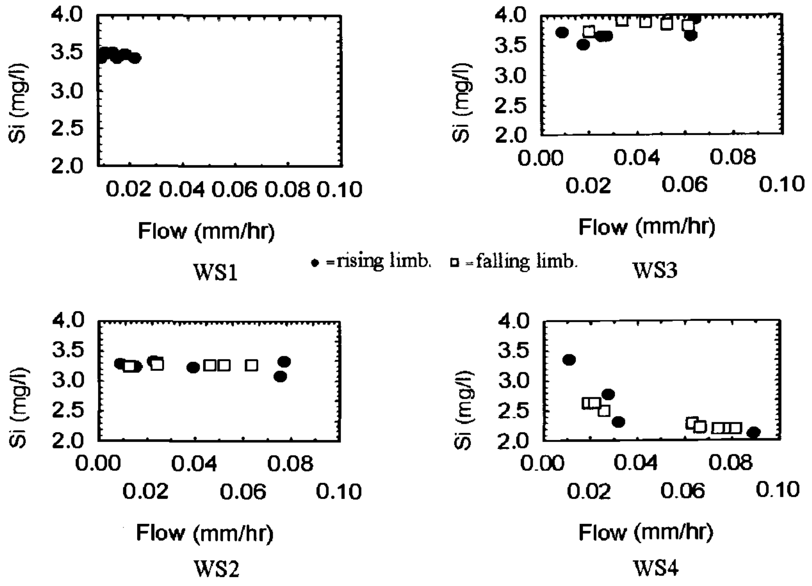
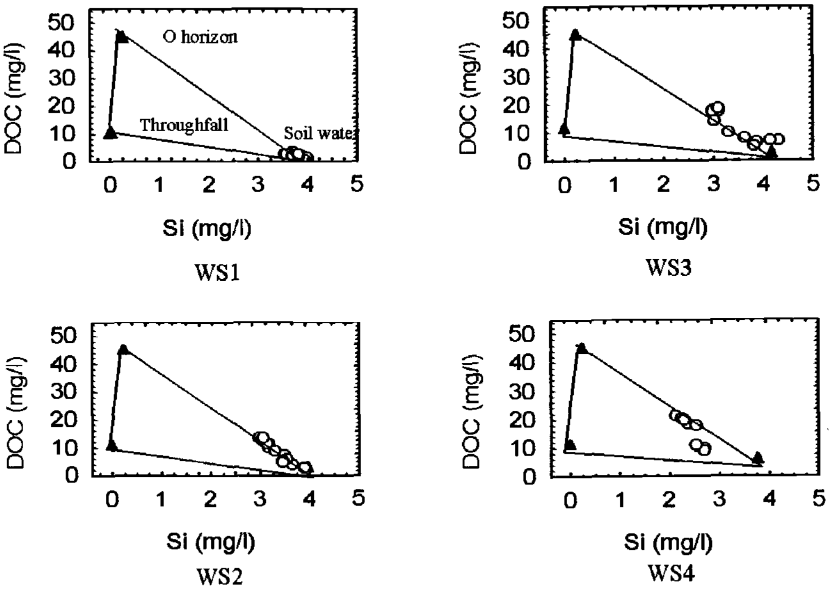


Figure 2. 12. June storm Si vs stream discharge.

### *2.4.6 Storm #2, July 30th 1999*

A high-intensity late-summer rainstorm (30mm/22hrs) occurred following dry antecedent conditions (5mm/72hr) (Table 2.3). This storm had the highest maximum intensity of any sampled (10mm/hr) and lasted 22 hours. Bivariate plots of Si and DOC suggest streamwater composition was a mix of both O-horizon and mineral-soil water in WS2 through WS4 (Figure 2.13). Rainfall ended abruptly before streamflow response began (Figure 2.14). During this rainstorm, more pronounced hydrograph shapes with increasingly sharp rising and falling limbs occurred in the least disturbed catchment (WS4) (Figure 2.14), corresponding to a quicker peak flow timing. The WS4 hydrograph peaked first, and the more smoothed less pronounced hydrograph for WS1 peaked 4.4 hours later. A stronger difference in total storm discharge occurred in response to storm#2, ranging from 11% of storm-period precipitation in WS1 to 90% in WS4 (Table 2.4). All separation models suggest mineral soil water contributions were greatest in WS1, and, while still high, were lower in WS2-WS4 (Table 2.4). O-horizon water contributions to streamflow were greater during storm#2 than in storm#1 for all catchments except WS1, contributing from 0 to 28% of discharge in WS1-WS4 respectively (Table 2.4). Si decreased with higher streamflow rates, while DOC increased (Figures 2.15-2.16). DOC was considerably greater during the rising limb than in the falling limb of the hydrograph in all catchments (Figure 2.15).



WS1

WS3

WS2

WS4

Figure 2. 13. July storm. Bivariate plots of Si and DOC with endmembers.

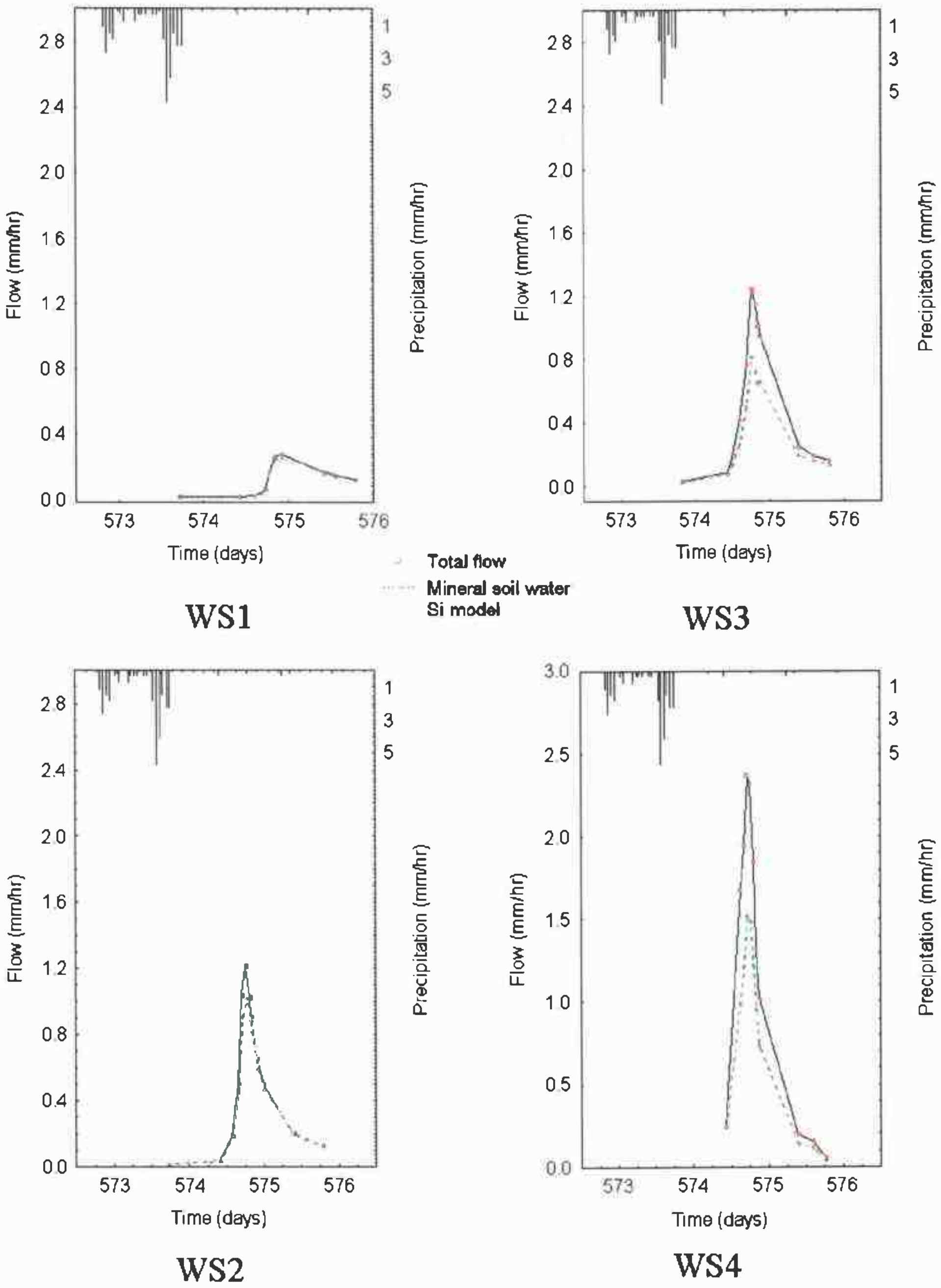


Figure 2. 14. July storm hydrograph separations.

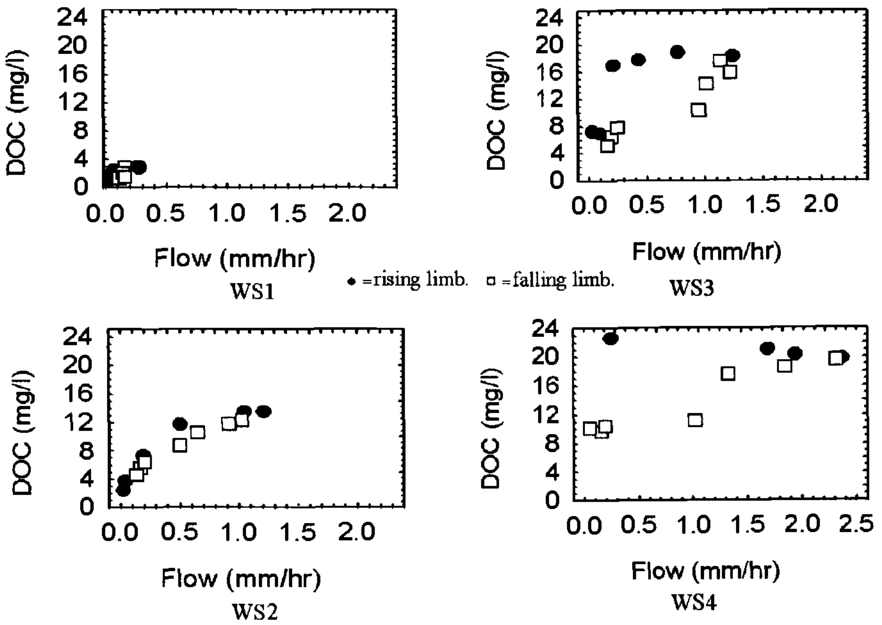


Figure 2. 15. July storm. DOC vs stream discharge.

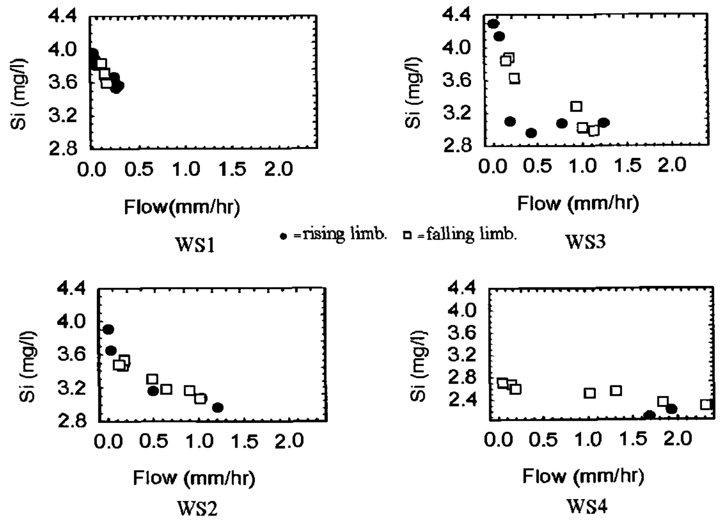


Figure 2. 16. July storm. Si vs stream discharge.

### *2.4.7 Storm #3, March 07th 1999*

A rain on snow event, accompanied by thawing, was sampled in late winter 1999. The precipitation intensity was moderate to low (22 mm/90 hours), and maximum intensity was 5 mm/hr. Antecedent conditions were wet (27mm/72hours) and cold (below freezing). During the rain event, considerable warming occurred, and all snow cover (estimated at 20 cm snow depth) melted. Unlike storm #1, the falling limb in all catchments lasted days longer than the rising limb. A streamflow response to precipitation inputs could be detected within hours in WS2, WS3, and WS4, but lagged by 47 hours in WS1 (Table 2.4). WS1 showed no early streamflow response to precipitation (Figure 2.18). Total storm discharge was substantially greater from all catchments for storm #3 than for the other storms sampled (from 50% in WS1 to 93% in WS4) (Table 2.4), most likely due to meltwater from the thawing snow pack. Bivariate plots of Si and DOC suggest that most of the discharged water originated from mineral soil horizons (Figure 2.17). All hydrograph separation models suggest mineral soil water contributions were greatest in WS1, and, while still high, were lower in WS2 through WS4. O-horizon water contributions were lowest in WS1 (0%), greatest in WS4 (25%) (Table 2.4). Solute concentrations during stream discharge was greatest (Figures 2.19-2.20) in WS1, then lower in WS2 through WS4. Si and DOC changed the most with flow in WS4. Si and DOC for all catchments and flow conditions were noticeably lower during this winter rainstorm than during the summer rainstorms.

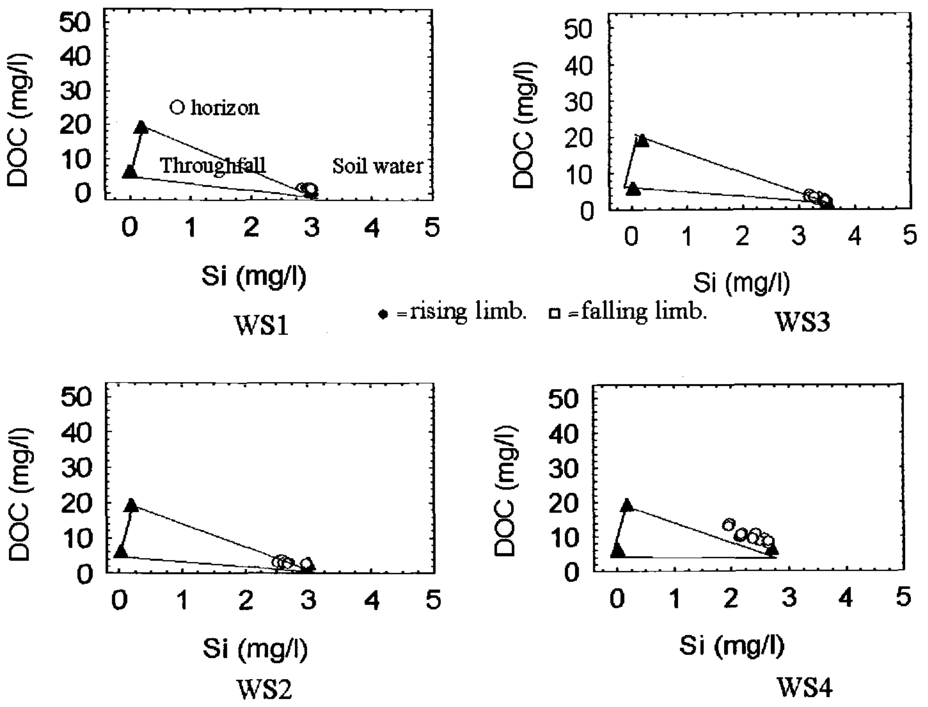
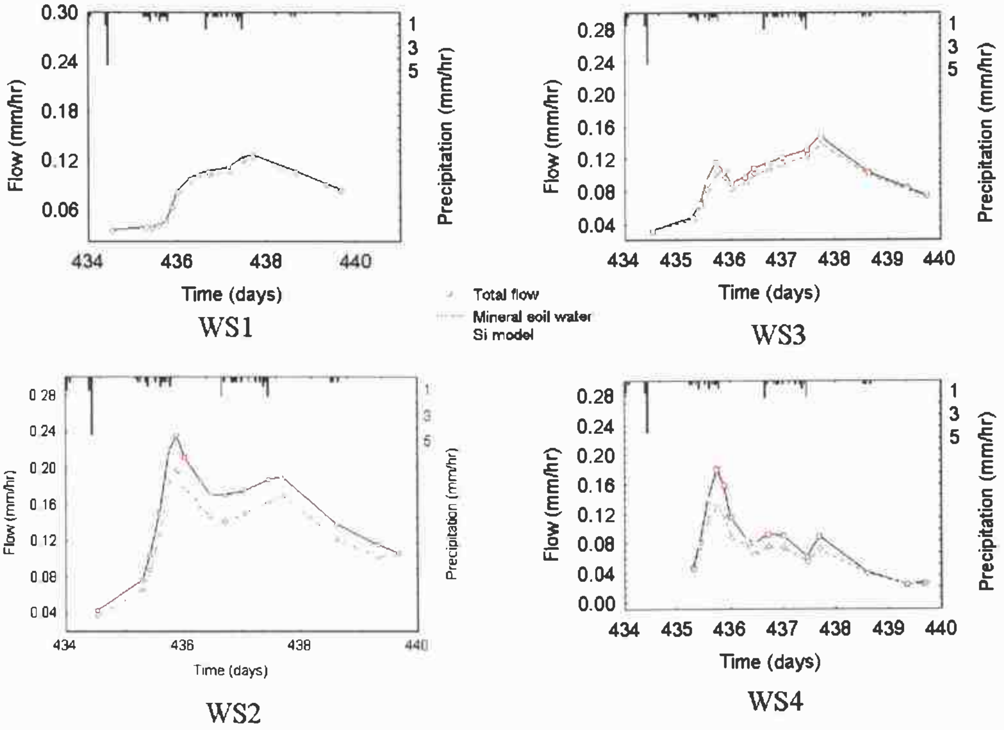


Figure 2. 17. March storm. Bivariate plots of Si and DOC with endmembers.



WS1

WS3

WS2

WS4

Figure 2. 18. March storm hydrograph separations.

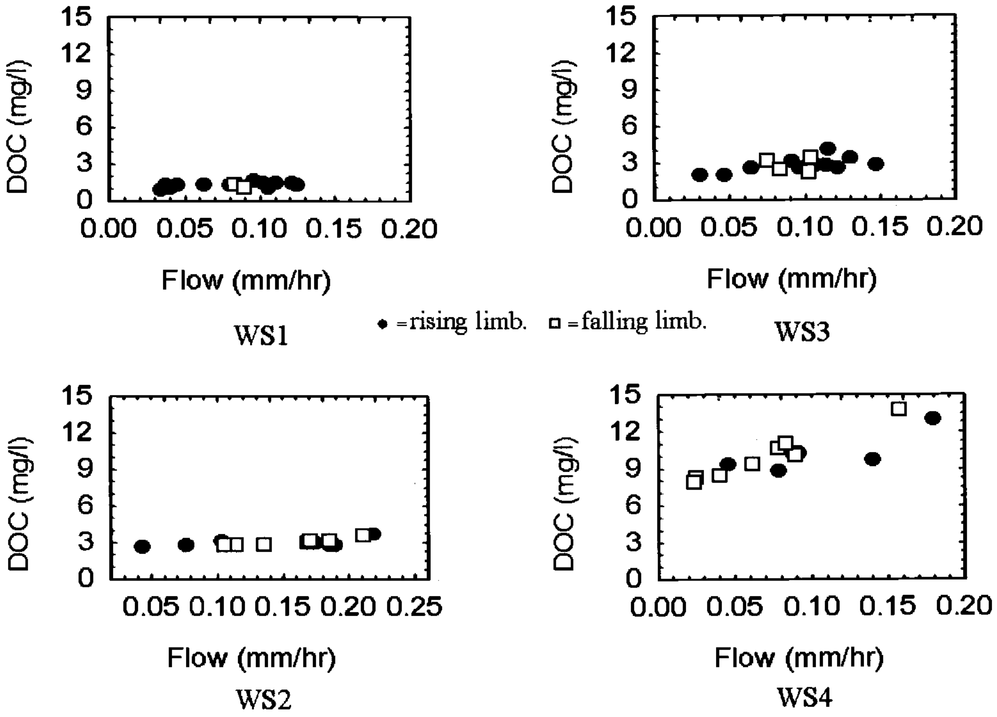


Figure 2. 19. March storm. DOC vs stream discharge.

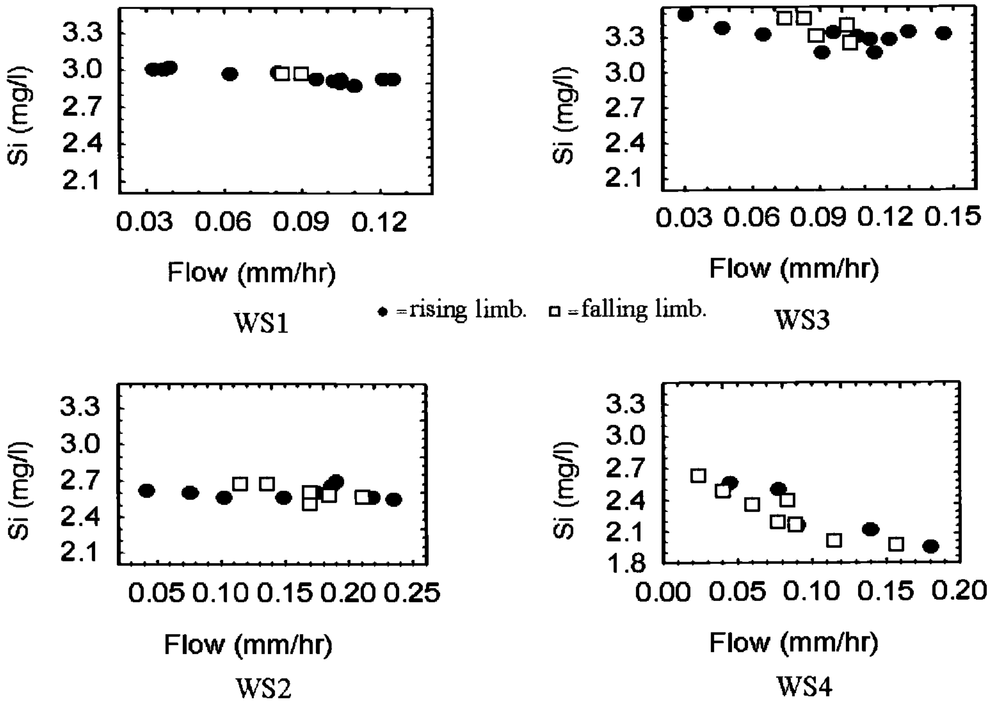


Figure 2. 20. March storm. Si vs stream discharge.

### *2.4.8 Storms #4-6, September 1998*

In September 1998 three rainstorms occurred within a period of 7 days. Antecedent conditions were wet (>22 mm/72 hrs). Precipitation intensity for storm #4 was very high (55mm/15 hrs), with a maximum intensity of 9 mm/hr, and was considerably higher than for any of the other rainstorms sampled. Mineral soil water contributions to streamflow were lower than for all other storms sampled (between 57-75% in WS1 through WS4 respectively)(Table 2.4). O-horizon water contributions to streamflow ranged from 0% in WS1 to 47% in WS4 (Table 2.4). Solute fluxes were largest for this storm event (from 14.7 kg/ha DOC for WS4 to 0.2 kg/ha DOC for WS1). Total storm discharge ranged between 41% for WS1 to 83% for WS4. Following storm #4, two more high intensity (>34mm/32 hrs) rainstorms occurred. Mineral soil water contributions to streamflow were greater during storms #5 and #6 than during storm # 4 (Figure 2.22)(Table 2.4). By contrast O-horizon water contributions to hydrograph response were lower, and ranged from 0% in WS1 to 21% in WS4. (Table 2.4). Bivariate Si and DOC plots suggest both mineral soil water and O-horizon contributions contributed to total flow during the three storms. (Figure 2.21). DOC increased considerably with flow (Figure 2.27), but the rate of increase was highest for WS4 and least for WS1. Si decreased with increasing flow for all watersheds (Figure 2.28).

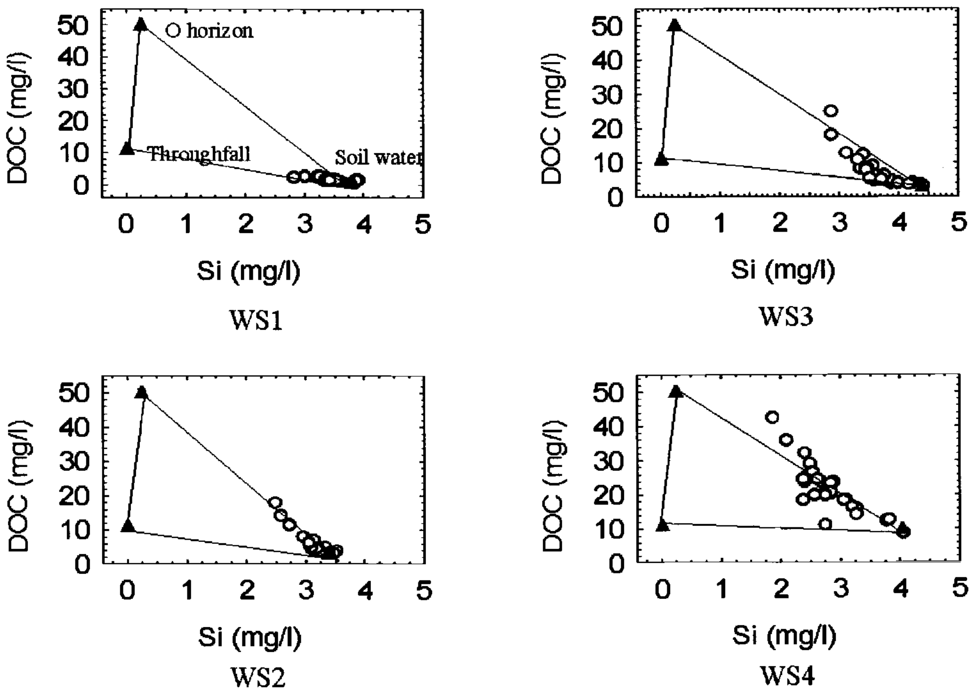


Figure 2. 21. September storm bivariate diagram of Si and DOC.

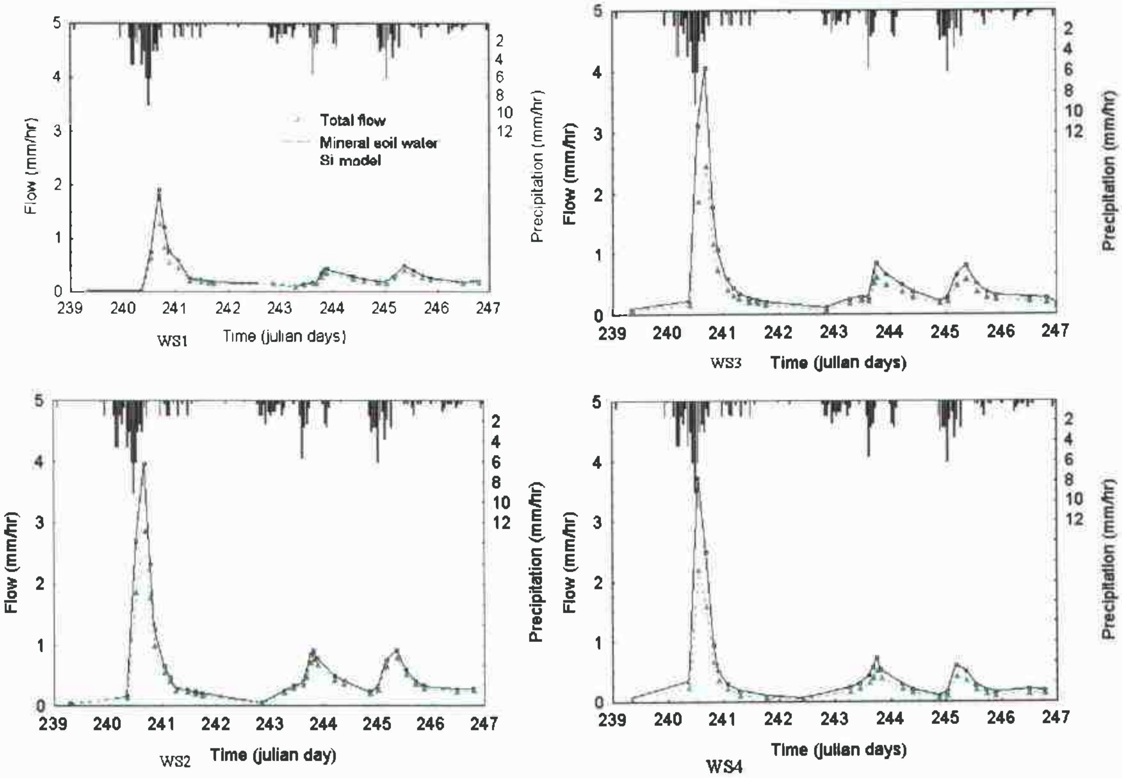
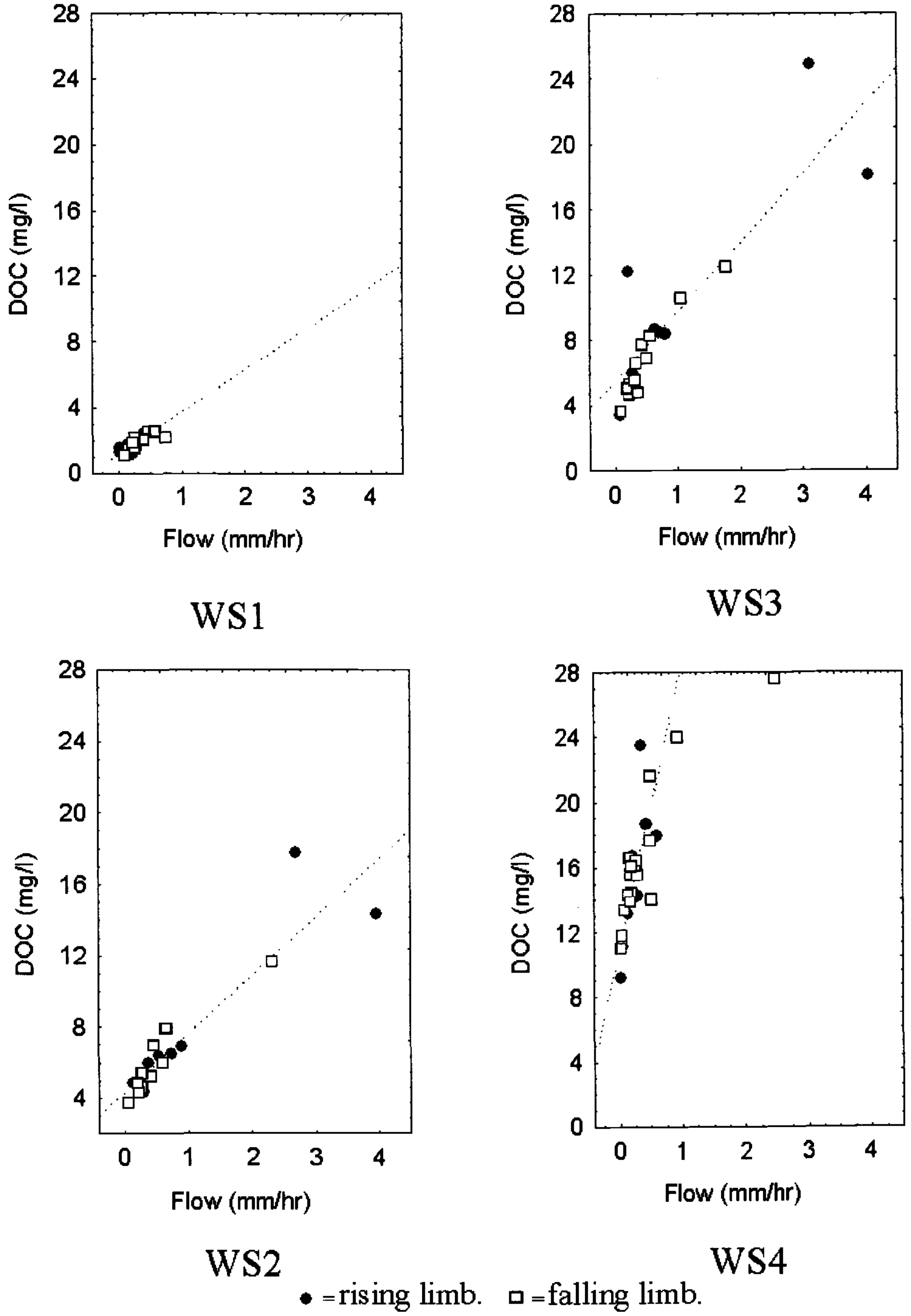


Figure 2. 22. September storm hydrograph separations.



WS1

WS3

WS2

WS4

Figure 2. 23. September storm DOC vs stream discharge.

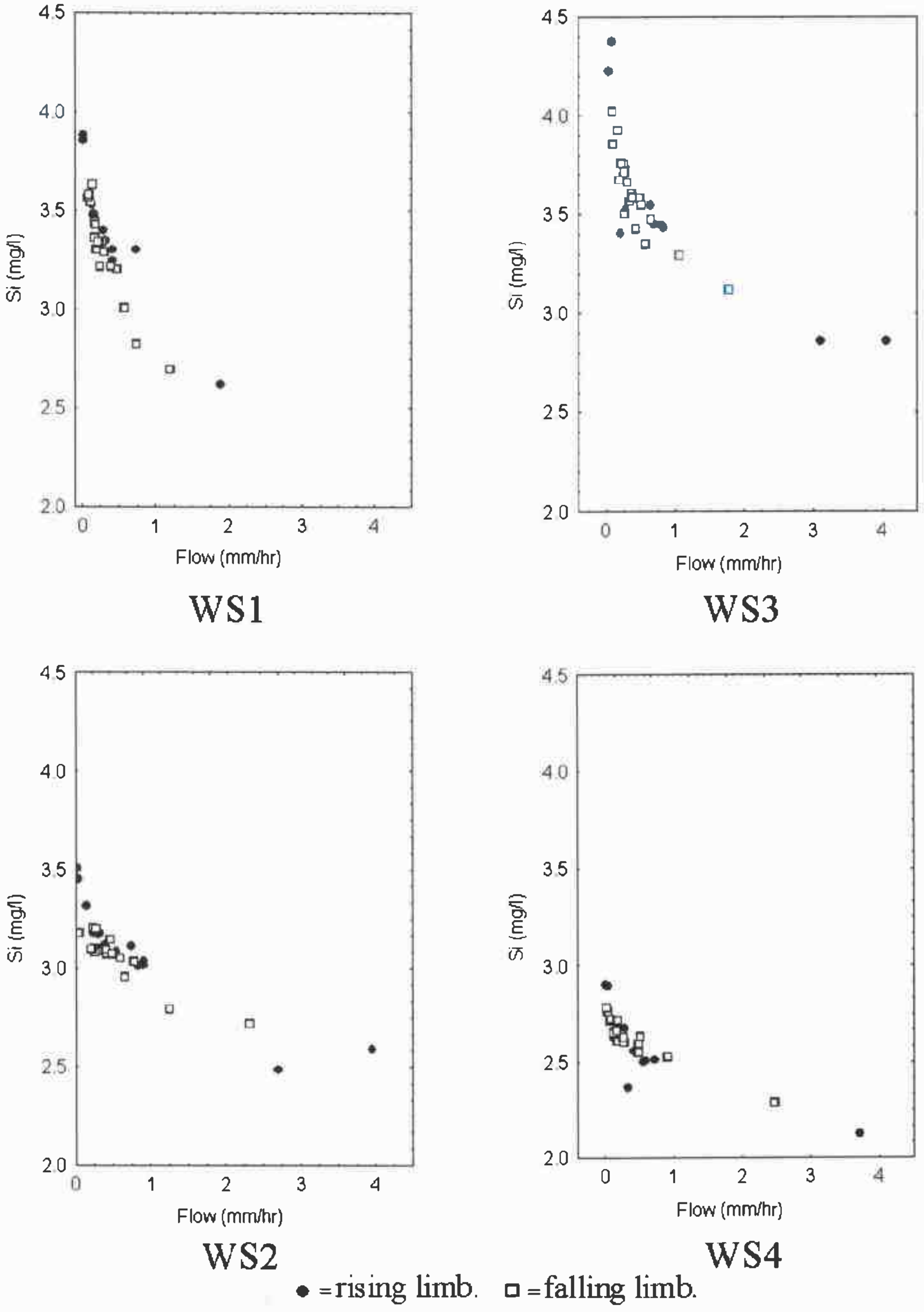


Figure 2. 24. September storm Si vs stream discharge.

## 2.5 Discussion

### *2.5.1 Hydrochemical response to rainstorm events*

Hydrochemical differences were found between the 4 catchments studied. A trend in stream water behavior (hydrometric, hydrothermal, hydrochemical properties), which corresponded to the trend in windthrow disturbance across the catchments, was apparent during all rainstorms sampled. Strongest differentiation between catchments occurred during high intensity rainstorms with wet antecedent conditions. These types of storms are the most common during the late-summer early-winter months, but can occur throughout the year (Figures 2.5 and 2.6). Hydrometric data and hydrograph separation modeling suggest the differences may be due to flow path differences between catchments. The data strongly suggests that rainwater in more windthrown catchments experiences greater interaction and storage in mineral horizons prior to discharging in streams. By contrast water originating from shallow O-horizon sources contributes more to runoff during rainstorms in less disturbed watersheds. These trends varied by season, rainstorm intensity and antecedent conditions, but were consistent across all 6 rainstorms.

Our focus in this study was on comparing hydrologic and hydrochemical properties of these watersheds over a range of rainstorm conditions, and not the specific flow paths in a catchment during a given storm. The specific flowpath which rainwater takes prior to discharge in the stream, and the corresponding processes which influence solution chemistry, are unclear and complex (Buttle 1994). Our understanding of the precise routing is limited because hydrograph separation can only provide insight into the relative contributions of shallow O-horizon or deeper mineral soil horizon water to total stream discharge. For example, WS4 exhibited a quicker hydrograph response to rainstorm events and evidence of greater O-horizon water contribution. However, rainwater which percolates through the O-horizon may travel through deeper mineral soil for at least part of the total flow path length to the stream. While the flow path appears to be somewhat more homogenous for WS1 than for less disturbed catchments, the precise routing of water prior to stream discharge is difficult to infer. The streamwater in WS1 was always enriched in Si and strongly depleted in DOC. These results suggest that, whatever the specific flow path, more rainwater contacts mineral soil prior to discharge.

Late-winter, early-summer and early-fall rainstorms each exhibited unique hydrologic and hydrochemical responses. Late fall rainstorms were characterized by steep rising and falling hydrograph limbs and a strong change in streamwater chemistry during the storm period. By contrast, antecedent dry conditions and moderate intensity rainfall produced hydrographs with a gradually rising limb and steeply falling limb. In the single winter rainstorm sampled, a prolonged falling limb (on the order of days) was observed in all the catchments. Solute concentrations were noticeably lower than during storms sampled in other seasons. Lower DOC fluxes are likely due to decreased microbial activity during winter months. Lower Si in streams may have been due to dilution from the snowmelt and saturated antecedent conditions.

### *2.5.2 Hydrothermal differences*

Hydrothermal differences between these catchments changed with season. During summer and fall, the more disturbed watersheds had cooler streamwater, suggesting that streamwater originated from deeper soil water sources that were more insulated from ambient air. Although not shown, these temperature differences were maintained during increased streamflow during rainstorm inputs. During the fall months, as air temperatures cooled, contrast between streamwater temperatures decreased. During winter and early spring months, waters from more disturbed catchments were warmer than less disturbed catchment or ambient air, again suggesting a deeper, insulated water source (Suzuki 1960, Tsuboyama et al. 2000). Finally, during spring, as air temperatures began to rise, virtually no difference in streamwater temperatures between catchments could be observed. The fact that streams in more disturbed watersheds were less equilibrated to ambient air temperatures and cooler than streams in less disturbed watersheds during the summer/early fall storms sampled, suggests that streamwater originated from an older deeper source in more disturbed catchments.

### *2.5.3 Hydrograph separation*

Hydrograph separation models must be interpreted with caution, especially when using non-conservative solutes (Buttle 1994, Turner and Barnes 1997). We focused on the relative mineral soil and O-horizon water contributions to streamflow between catchments. The results were interpreted in conjunction with hydrometric and other hydrochemical measures. Since the solute concentrations for mineral soil water were based on low-flow pre-event stream samples, our estimate of mineral soil water contributions likely reflect soil water that has percolated through deeper (Bs) horizons, rather than upper Bh horizons. A trend of greater mineral soil water contributions with increasing windthrow disturbance was observed for all hydrograph separation models used. However, hydrograph separations using Si and DOC solutes were quite different from one another. Each solute reflects unique biogeochemical processes. Si and DOC solutes were used in 3 component hydrograph separation to differentiate O-horizon water contributions from mineral soil water contributions. Rainwater was observed to be highly enriched in DOC after it passed through the O-horizon, but still very low in Si. As this water comes into contact and travels deeper into mineral soil, DOC may be expected to decline through adsorption, while a net increase in Si may be expected from weathering and any immobilization reactions. Even short contact time (on the order of hours) of rainwater with mineral soil can result in increased Si (Turner and Barnes 1997, Hoeg et al. 2000).

Our data suggest streamwater discharge in all catchments was dominated by mineral soil water contributions. The maximum O-horizon contribution to streamflow was always found in WS4. During storm#4 a maximum O-horizon contribution of 47% was observed. Rainfall intensity was extremely high during this storm (55 cm/15 hours), and throughflow in the O-horizon was observed during sampling. During other storms O-horizon water contributed at most up to 30% of the streamwater in WS4. Our finding that mineral soil water dominated streamflow for all catchments during all the storms sampled has been widely reported in the literature (Turner and Barnes 1997). These conclusions reached from hydrograph separation modeling are consistent with those reached based on the hydrothermal, hydrochemical, and hydrometric results.

### *2.5.4 Solute-discharge relationships*

DOC was always higher in the less disturbed watersheds. Due likely to the greater contribution from O-horizon water to stream flow in these catchments. Late-summer early-fall rainstorm activity, in which antecedent conditions were wet and rainstorm intensity was high, resulted in the strongest increase in DOC as stream flow increased. DOC increased during hydrograph response in the late winter storm as well. The rate of increase, however, was greatest in less disturbed catchments (Figures 2.11, 2.15, 2.19, 2.23). Strongest hysteresis was observed during Storm #2, the July storm (Figure 2.15). During this storm, DOC was higher on the rising limb than in the falling limb. These results suggest that, during this high intensity rainstorm, O-horizon water entered into the stream early, and outflow became increasingly dominated by mineral soil water contributions during the later response to rainstorm inputs.

Si in streamwater was greatest in the most disturbed watersheds. During rainstorm activity Si declined in all watersheds. The rate of change in concentration was greatest in less disturbed watersheds. Hysterisis was not as apparent with Si as it was with DOC. Some of the storms showed evidence of slight Si decline with falling hydrograph limbs (Figure 2.24). September storms (#4-6) showed strong silica concentration decline during high flow conditions (Figure 2.24), which suggest all catchments experienced a dilution effect from O-horizon water which was low in Si. This event-water dilution effect was more pronounced in less disturbed watersheds.

### *2.5.5 Flux differences*

Total discharge of solutes during storm discharge response varied considerably between catchments. DOC flux differed more between catchments than did other solutes. Discharge of DOC ranged from 3 kg/ha for WS4 to .2 kg / ha for WS1. The difference was due both to the higher total stream discharge and higher DOC in streamwater for WS4. Si discharge varied less between catchments. Between .3 and .5 kg/ha in all watersheds was discharged during high intensity (2.5 mm/day) rainstorm events. These results suggest greater retention of DOC in catchments more disturbed from windthrow.

### *2.5.6 Hydrometric differences*

Timing of peak flow varied by storm, season and catchment. The sequence of peak flow timing in catchments was consistently in the sequence WS4 to WS1. The increase (in hours) between peak flow response times across these catchments can be explained by increased residence time and movement through mineral soil in more disturbed catchments. A difference of even 1 hour of peak flow lag time due solely to catchment size, would require a difference of orders of magnitude (ie.. 1 vs 100 ha) in size. This is because water travels quickly when it travels through upper surface horizons (1 cm/s) (Dunn 1970, Brown et al. 1999).

Total discharge / ha during storm events was greatest in WS4 and lowest in WS1. Near 100% of the input in WS4 was discharged during high intensity storm events. Our estimate of catchment size in WS4 is conservative (the upper limit). However, we are uncertain of the precise size because the topographic boundaries of the catchment are not well-defined. The topographic boundaries in catchments WS1-WS3 are better defined. Less then 50% of inputs discharged during hydrograph response in WS1. This may be due either to longer residence time and storage in WS1, or more percolation and flow through fractured bedrock. For either storage in mineral soil or leakage through bedrock to occur, rainwater would have to percolate to greater soil depths in WS1.

### *2.5.7 Concluding remarks*

The idea put forth that podzolization can reduce soil water drainage in the absence of soil mixing disturbance was evaluated at the catchment scale along a natural windthrow disturbance sequence. Our results support the conclusion that catchment wide shifts in hydrologic behavior may result from podzolization, and that soil mixing from windthrow may reverse these effects. Supporting evidence includes hydrothermal, hydrochemical and hydrometric results. Because these data, in addition to hydrograph-separation modeling results, are consistent with one another, our conclusion is that rainwater contact and interaction with mineral soil materials increased with watershed disturbance. By using a sequence of four catchments with varying disturbance from windthrow, our inference is strengthened. The trend observed between these four catchments corresponds to the trend of windthrow disturbance between them. We cannot, however, assign cause and effect in this natural disturbance sequence study. The results are suggestive, and must be evaluated in the context of laboratory and pedon scale research or long-term watershed-scale experimental studies.

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# CHAPTER 3

# 3. Soil Carbon Dynamics Along a Windthrow Disturbance Sequence in a Montane Temperate Rainforest, Southeast Alaska.

Marc G. Kramer, Phillip Sollins, Ronald S. Sletten

## 3.1 Abstract

Soil carbon dynamics were examined along a windthrow disturbance sequence in a mountainous temperate rainforest in southeast Alaska. Our objectives were to 1) examine the influence of windthrow and illuviation on the accumulation of soil organic carbon (SOC) in mineral horizons and 2) examine the forms of SOC that have accumulated. Soils were described and the thickness of the major organic and mineral horizons was measured every 5 meters along transects in three catchments with contrasting windthrow histories. A subset of soil description sites was randomly selected and sampled to determine the quantity and quality of carbon. Mineral soil samples were physically fractionated based on particle density. Total C and N, natural $^{15}N$ and $^{13}C$ abundance, micromorphologic analysis (using scanning electron microscopy), and solid state $^{13}C$-NMR were used to compare soil organic carbon pools in catchments. Evidence was found that both illuviation and soil mixing from windthrow strongly influenced soil organic matter accumulation in mineral soil. Mobile organic carbon (MOC) transported in soil water accumulated in mineral horizons principally through adsorption to mineral particles and the extent of strong association (adsorption) with mineral particles increased in older, thicker illuvial horizons. In some of the older, thicker illuvial horizons, light (<1.65 g/ml) illuvial-like material found suggests that immobilization of MOC may have occurred through flocculation of metal bearing organic acids. The extent of humification (carbon-compound alteration) ranged from partial to strong in both organic and mineral soil horizons, and the degree of humification was correlated with increasing $^{15}N$ abundance, but not with changes in $^{13}C$ abundance. Forested catchments that experienced more intense soil mixing from windthrow had lower levels of strongly humified soil organic matter, and more in a partially decomposed particulate form. Processes leading to the formation of, and consequent concentrations and characteristics of, organic carbon in mineral soil strongly influences the hydrology, chemical properties of catchments, and the rate of nutrient cycling. The large and diverse stores of mineral soil C observed in these shallow mountain forest soils may be attributed to the unique, chronic wet cool conditions. Most temperate forest soils, even at higher latitudes, experience a longer

warm, dry season, in which microbial activity is favored, and considerable soil carbon can be lost.

Keywords: podzolization, $^{13}$C Solid State NMR, natural $^{15}$N, $^{13}$C abundance, scanning electron microscopy (SEM), DOC immobilization, windthrow, decomposition, humification, illuviation, flocculation, precipitation, density fractionation, mineral soil carbon, temperate rainforest soil, lateral flow, southeast Alaska, soil mixing, tree uprooting.

## 3.2 Introduction

The global significance of soil organic carbon (SOC) and its profound influence on environmental processes and ecosystem functioning have been appreciated for some time (Lal et al. 1998). More recently, interest and concern over how global warming will affect SOC decomposition has generated considerable debate and new research (Mac Donald et al. 1999). There is evidence to suggest that global SOC pools may be sensitive to increasing air temperatures and will release more $CO_2$ (Perruchoud et al. 2000, Davidson et al. 2000). Regionally, the quantity and quality of organic carbon present in forest soil may exert strong control on ecosystem properties such as nutrient availability, soil drainage, and consequently the rate of forest growth.

In spite of our appreciation for their edaphic, ecological and global biogeochemical importance, soil organic carbon dynamics remain poorly understood. For example, while SOC is thought to possibly represent the missing 'sink' in the global carbon cycle, our uncertainty in changes in the SOC pool size is too high for us to know (Armentano and Ralston 1980, Schindler 1999, White et al. 2000). Better estimates of changes in SOC stocks throughout the world are needed (Eswaran et al. 1993, Chadwick et al. 1994, Perruchoud et al. 2000). Even fewer studies have examined the processes and forms of SOC accumulation in forest soils, or the linkages between these pools and other ecosystem processes (Richter et al. 1999). Investigations into the quantity and quality of SOC will contribute not only to our understanding of the global carbon cycle, but to ecosystem scale questions as well. This study examines processes of SOC formation and forms of SOC across a windthrow disturbance sequence of temperate rainforest mountain soils in southeast Alaska.

In southeast Alaska, soil organic carbon (SOC) accumulations are among the highest in the world (Alexander et al. 1989, Van Cleve and Powers 1995). Illuviation, the accumulation of translocated carbon, iron and aluminum, is recognized as a major process for carbon accumulation in mineral soil (Ugolini and Mann 1979, Lundstrom et al. 2000*a*). Maritime cyclonic windstorms cause widespread disturbance to forested ecosystems in southeast Alaska. (Kramer et al. in press). One noticeable feature of these blowdown events is the redistribution and mixing of mineral and organic soil horizons.

Organic particles (root, wood and litter fragments) become mixed with mineral particles (Figure 3.1).

Figure 3. 1. Large windthrow mounds with organic and mineral particles mixed together.

The illuviation of soil carbon in southeast Alaska occurs as the consequence of chemical/physical interactions between SOC, soil water, and mineral soil, known collectively as podzolization. Podzolization typically occurs when thick organic horizons (Oi,Oe,Oa) accumulate in wet cool climates. The passage of soil water through organic horizons results in leaching of large amounts of organic acids. Highly reactive fulvic and humic acids chelate iron and aluminum from upper mineral horizons, resulting in the formation of a white leached horizon (E) at the surface of the mineral soil. Percolating with soil water, metal bearing organic acids are then transported to greater soil depths, where they eventually accumulate or decompose. While it has been widely observed that illuviation can occur through podzolization (Ugolini and Dahlgren 1987), the mechanisms of immobilization remain unclear, especially for aluminum, and are still the subject of considerable research (Farmer 1999). For mobile organic carbon in soil water, proposed mechanisms of immobilization include 1) flocculation through organo-mineral interactions, 2) microbial degradation and polymerization of organics, and 3) physical adsorption—principally to mineral particles (Lundstrum et al. 2000*a*). Other interactions between organics and metals associated with the process of immobilization include ligand exchange, van der Walls bonding, H bonding, and cation bridging (Dalgren and Marrett 1991). Immobilization results in the illuviation of mobile organic carbon, iron and aluminum to various mineral horizons below (Bh,Bs) (Ugolini and Dalgren 1987). Illuvial carbon in mineral soil may decompose over time (Lundstrom et al. 2000*b*), but its turnover rate is much slower in illuvial horizons and it may persist in the soil for more than 6000 years (Theng et al. 1992).

While the general processes of illuviation and windthrow are relatively well understood, their influence on SOC dynamics in forested catchments has not been studied. In southeast Alaska, forest soils commonly occurs on mountainous terrain (Kramer, *unpublished data, SCS survey of the area*) where illuviation may occur as a result of both lateral and vertical flow of water (Ranville and Macalady 1997, Hornberger et al. 1994, Sommer et al. 2000). On forested hillslopes, soil disturbance is common on steeper slopes and often in association with windthrow (Schaetzl and Follmer 1990, Normal et al. 1995, Kramer et al. In press). The redistribution of material from soil mixing can lead to a loss of mineral soil carbon, as well as the addition of SOC to mineral horizons (Beatty and Stone 1986, Cremeans and Kalisz 1988). While hilllslope processes influencing SOC accumulation have not been well studied, they are known to strongly influence temporal and spatial distributions of SOC across watersheds (Hammer et al. 1995). Fine root turnover may also input both dissolved organic carbon and particulate organic matter (POM) directly into mineral horizons (Brewer 1994, Joslin and Henerson 1987). Macrofauna are not likely to be a major source of SOC in mineral soil since they are relatively scarce in these acid (mor) soils (Schaefer and Schauermann 1990) and confined largely to surface organic horizons.

The first objective in this study was to examine the influence of windthrow and illuviation on the accumulation of SOC in mineral horizons of mountain forest soils. Previous workers (e.g. Sollins et al. 1983) have separated two distinct pools of SOC in mineral soil: a heavy and light fraction, with different composition and function. SOC in the heavy fraction is more stable and recalcitrant due to strong adsorption on mineral particles, while the light fraction SOC has retained more of its initial biological structure, is in particulate form, and is less associated with mineral matter. Few studies have investigated factors controlling light vs heavy fraction SOC accumulation in forest soils (Sollins et al. 1983). Heavy fraction SOC in illuvial (black) horizons might result from chelation of mobile organic carbon (MOC) with iron and aluminum, and its subsequent precipitation or adsorption onto mineral soil particles (Zunino and Martin 1977). Conversely, light fraction SOC accumulation could result from mineral and organic particle mixing or root inputs since it is in particulate form and it has weaker chemical and physical association with mineral particles.

The second objective was to examine the forms in which SOC accumulates in major organic and mineral horizons in watersheds with contrasting disturbance histories. While the composition of organic matter in surface layers of forest soils has been extensively researched, the forms of carbon in mineral soil remain poorly understood (Zech 1996). Total C and N, natural $^{15}$N and $^{13}$C abundance, solid state $^{13}$C NMR, and scanning electron microscopy were used to compare total quantity, extent of humification, and chemical composition of SOC in major organic and mineral soil horizons.

## 3.3 Methods

Three forested catchments with apparently contrasting disturbance histories were selected for the study. Soil profiles were described and the thickness of the major organic and mineral horizons was measured every 5 meters along a transect in each catchment. A subset of these horizons was randomly selected and sampled to determine the quantity and quality of carbon present. Carbon enriched (Bh) illuvial samples were physically fractionated based on particle density. Some of the samples were dispersed using an ultrasonic probe prior to fractionation to determine if aggregation influenced particle density. Total C and N, natural $^{15}$N and $^{13}$C abundance, solid state $^{13}$C NMR, and scanning electron microscopy were used to compare soil organic carbon pools in each catchment.

### *3.3.1 Study site*

This work was conducted in the Tongass National Forest, a vast region of pristine coastal temperate rainforest in southeast Alaska. The forests are distributed throughout the Alexander Archiplago on 7 million ha located on over 1000 islands with diverse geology and topography (Alaback 1996). Soils are characteristically shallow, due to recent glaciation. Podzolization (Ugolini and Mann 1979) is common largely as a result of year-round precipitation and cool maritime climate (Alaback 1986).

Six conifer species dominate the region (Pawuk and Kissinger 1989). On well-drained sites, productive western hemlock (*Tsuga heterophylla* (Raf.) Sarg.) and Sitka spruce forests (*Picea sitchensis* (Bong.) Carr.) are common. On less well-drained but still productive sites, hemlock and spruce still dominate with some mixtures of less productive Alaska yellow cedar (*Chamaecyparis nootkatensis* (D. Don) Spach) and western red cedar (*Thuja plicata* Donn ex D. Don). At higher elevations (above 400 m), less productive mountain hemlock (*Tsuga martensiana* (Bong.) Carr.) typically replaces western hemlock. Low productivity mixed conifer-scrub forests often dominated by lodgepole pine (*Pinus contorta* Dougl. ex Loud. var. contorta) occur extensively on the landscape, along with muskeg plant communities on lower site hydric soils or wetlands (Pojar and MacKinnon 1994, Alaback 1996).

In southeast Alaska, extratropical cyclones pass through every four or five days during winter (Shumacher and Wilson 1986). Associated with these storms are winds up to and occasionally in excess of 40 m s, persistent cloud cover, and up to 13 m of precipitation annually in the coastal mountains. Trajectories for these low pressure systems, referred to as the North Pacific Storm Track, are largely determined by the location and strength of three semi-permanent atmospheric features: the Aleutian low and Siberian high pressure systems in autumn, winter, and spring, giving way to the east Pacific high pressure system in summer. Large interannual changes in storm frequency, intensity, and size may be expected as a consequence of El Niño, which can penetrate poleward into the Gulf of Alaska (Schumacher and Wilson 1986).

High Island (approx. 500 ha) is located in the middle of the Alexander Archipelago in the Tongass National Forest, approximately 160 km from the mainland and 20 km south of the town of Kake (Figure 3.2). Maximum elevation on the island is 150 m. The parent material is fractured basalt. Average annual precipitation is 1.9 m, with the wettest months occurring during fall and winter. Cloud cover, precipitation, cool ambient air temperatures (4-10 °C ), and high relatively humidity (>80%) are characteristic throughout the year (Kramer et al. *unpublished data*). Extreme high and low temperatures are infrequent due to the maritime influence. Limited logging (16 trees/ha) occurred in WS1 during the early 1900s.

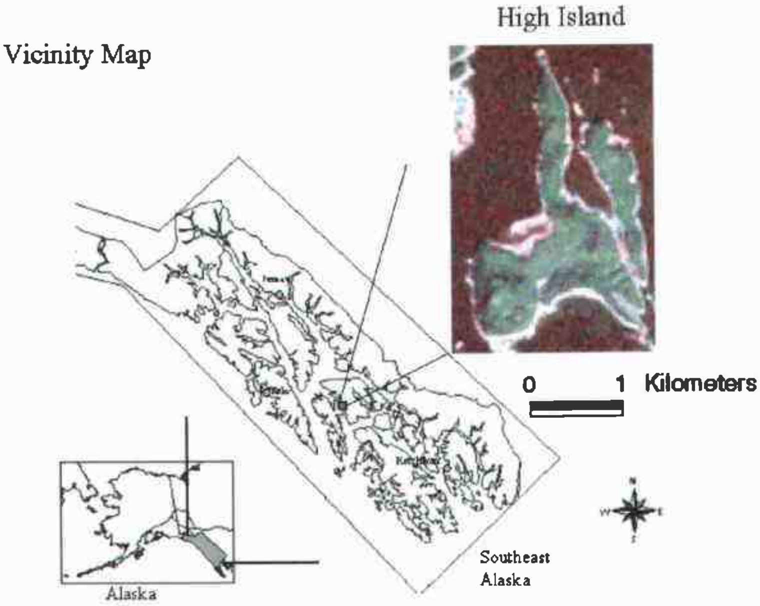

Figure 3.2 Vicinity map of High Island.

The island was struck by a strong cyclonic storm approximately 95 years ago. Forests on the south and west portion of the island show evidence of greater damage from the storm than north to northeast portions (Figure 3.3). Three watersheds (WS1,WS3,WS4) were selected were selected for this study. WS1, located on the west side, experienced complete catastrophic stand damage from the storm. Storm effects include many large windthrow mounds and pits throughout the watershed as well as an even-aged forest that regenerated after the storm. WS3, located on the north portion of the island, shows evidence of partial disturbance from the storm. WS4, located on the northeast portion, shows very little evidence of recent storm damage such as downed stems or pit and mound microtopography. The forest in WS4 is older and shows evidence of a gap-phase stage of forest development. The catchments are located in close proximity, have identical parent material, and similar slope profiles. Elevation ranges from 3-60 m above sea level. Only western hemlock and Sitka spruce are found in the catchments.

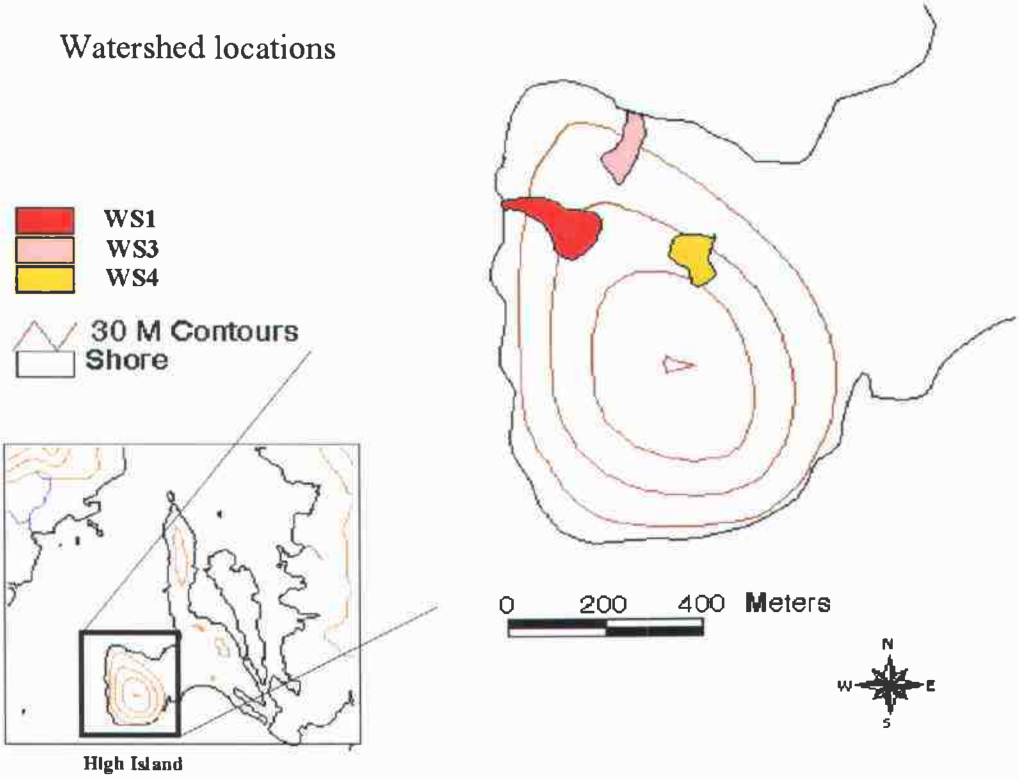

Figure 3.3. Watershed locations map.

### *3.3.2 Damage from past windstorm activity*

The extent of windstorm damage in each catchment was determining by aging trees, measuring stem size, and quantifying the extent of area occupied by prominent pit and mound topography. The ages of tress in each catchment were determined by coring a random sample (>50%) of overstory trees in each catchment and counting annual growth rings, using a dissecting microscope. Cores that were difficult to count were mounted, sanded, then counted.

### *3.3.3 Field measurements and sampling*

Each catchment was divided into a grid consisting of 25 $m^2$ cells. Soils were profiled every 5 meters at survey sites located in the center of each cell across the entire watershed. The thicknesses of major organic and mineral horizons (> 1cm) were measured at each site (Oiea, A, E, Bh, Bhs, Bs). Horizons were identified based on color and field estimation of organic vs mineral content (by measuring the grittiness of the soil) (Soil Survey Staff 1998). Depth to bedrock was determined at the same location by probing with a 2-meter steel rod. Samples of major mineral and organic soil horizons were collected from randomly selected survey sites with a 200 ml, 10 cm diameter corer. Soils were weighed, dried for 48 hours at 60° C then weighed again to determine wet and dry bulk density. Oven dried samples were sieved (2-mm mesh) to remove large organic and mineral particles, and estimate stone content. A 1-mm sieve was used to further pick out large organic particles including roots, bark, and other identifiable plant parts. The samples were then shipped to Oregon State University (OSU) for physical and chemical characterization.

### *3.3.4 Density fractionation*

For Bs and Bh mineral horizons, a 10 g dry sample of the < 2mm fraction was physically separated based on particle density. Samples of dry mineral soil were ground with a mortar and pestle to pass through a 0.425 mm sieve. The density fractionation was made by placing 10 g of soil in a 110 ml centrifuge tube and suspended in 30 ml of sodium-polytungstate (NaPT) at a density of 1.65 g/ml using a modification of Strickland et al. (1987) procedure. After mixing for 12 hours using a low speed shaker, the sample was centrifuged at 300 rpm for 1 minute, and allowed to settle for 48 hours. The suspended light fraction was removed by gentle aspiration through a Tygon hose. The light and heavy fractions were placed on a a 52 Whatman paper filter [Whatman Incorporated, Clifton New Jersey]and rinsed 5 times with 300 ml of deionized water. Heavy and light fraction were oven dried overnight (60 deg C), then weighed. Fraction weights are reported as percent of dry soil sample weight.

Ultrasonic dispersion (1050 J/ml (Christiansen 1992)) was performed on 10 samples to estimate the influence that remaining aggregates (<425 mm) had on particle density. Dispersion should free light organic particles that may be trapped in aggregates (and possibly microaggregates) in the heavy fraction (Christensen 1992). After ultrasonication, the same density fractionation procedure was applied. Loss-on-ignition (LOI) was measured on a subset of the coarse (>2mm) fraction from light and heavy Bh samples.

### *3.3.5 Elemental analysis*

Dry samples (<2mm) were ground finely with a zirconium mortar and pestle, and loaded into tin boats. Each sample was analyzed for total C, and N and $\delta^{15}N$, $\delta^{13}C$ using a Europa 20/20 ANCA GSL continuous-flow isotope-ratio mass spectrometer (PDZ, Eurpoa, Cheshire, UK) at the Rosenthial School of Marine Science, University of Miami. The analytical protocol included analysis of a standard for every 10 unknowns, and 2 blanks and standards at the beginning and end of each run. Analysis of internal standards indicated an analytical error of <5% for N and <2% for C.

Natural Isotope Ratios were reported as:

$$\delta_{\text{sample}} = \frac{R_{\text{sample}} - R_{\text{standard}} \times 1000\,‰}{R_{\text{standard}}}$$

Where $R_{\text{sample}}$ and $R_{\text{standard}}$ are the heavy and light isotope ratios of sample and standard.

Pool size of light and heavy fraction SOC in soil profiles was calculated for each 25 $m^2$ cell across the watersheds by estimating soil horizon thickness from soil pits examined in each cell, along with the average quantity and type SOC found in soil samples to quantify light and heavy SOC present for each 25 $m^2$ cell.

**SOC ($g/m^3$) = horizon thickness(m) x 25$m^2$ x bulk density($g/m^3$) x organic carbon present(%) x <2mm fraction present (%).**

The quantity of heavy and light carbon in the Bh mineral horizon across each watershed was calculated and compared.

### *3.3.6 Solid state $^{13}$C NMR spectroscopy and microscopy*

Fresh litter material (needles, wood, and fungal mat), light and heavy fraction Bh samples, and samples from Oie and Oa organic horizons were characterized for functional groups using nuclear magnetic resonance (NMR) with a Bruker AF-300 solid-state Pulse NMR spectrometer with cross polarization and magic angle spinning (CP/MAS), equipped with a double tuned, single coil probe with an external lock and an Andrew-Beams type spinning apparatus at 1 sec recycle time and a cross polarization time of 1 ms at the University of Washington. The magnetic field was 300 MHz (7.0 T) giving a $^{13}$C resonance frequency of 75.46 MHz. Typical parameters were : proton 90 deg pulse, 5 $\mu$S; contact time, 1ms; recycle delay, 1 sec; spinning speed, 3.5 KHz; number of scans, 3600-5000. Due to the formation of sidebands, which is greater on 300 Mhz than 100 MHz NMRs, there is more oxygen substituted alkyl carbon (carbohydrates) and less aromatic carbon. However, this problem did not affect significantly the internal comparison between samples. Select samples were also examined under a scanning electron microscope (AMRAY Oregon State University, Department of Botany) to visually differentiate organic detritus from unidentifiable organic-mineral matter.

## 3.4 Results

### *3.4.1 Damage from past windstorms*

The extent of soil disturbance from windthrow and associated downslope movement of soil from hillslope processes is likely to be greater then is reflected by the pronounced pit and mound topography (Schaetzl and Follmer 1990, Norman et al. 1995). We used the extent of prominent pit and mound topography in each catchment to rank tree uprooting damage from recent (<100 yr) windstorms, not to quantify soil disturbance. The extent of recent (<100 yr) prominent pit and mound topography was greatest in WS1, which appeared to have experienced the most damage from a storm that occurred 95 years ago. Eleven percent of the soil surface had pronounced pit and mound topography. WS3 had fewer pits and mounds (5% of the area) and trees were older, but WS3 nonetheless showed evidence of partial damage and a distinct pulse of tree recruitment from this storm. WS4 had a wide range of trees and no evidence of recent (<100 yr) pits and mounds. Fallen logs were highly decomposed (Class IV). Trees in WS1 were smaller, higher in density, and most established after or near the time the storm struck (Table 3.1) In WS3, trees were older more variable in age and comprised at least two distinct age classes (Figure 3.4). WS4 showed evidence of gap phase forest development, and no distinct pulse of recruitment could be detected. Small-scale, low intensity disturbances likely explain the present WS4 stand attributes (age, size and density).

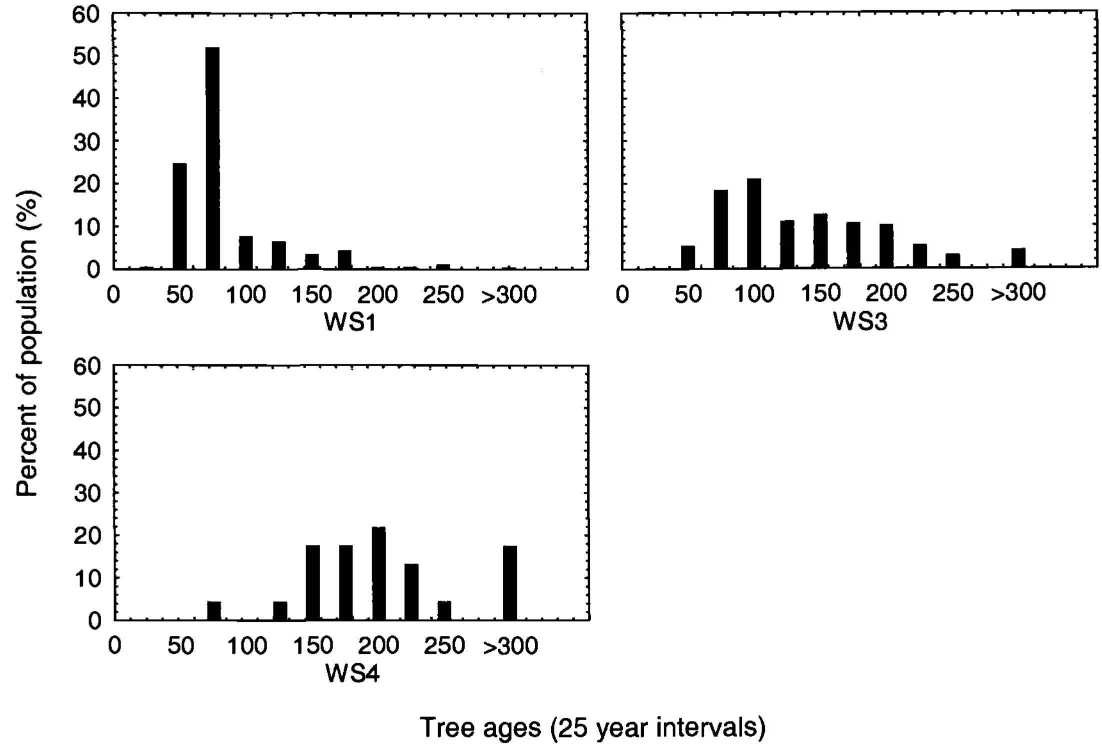

Figure 3.4. Tree age characteristics in watersheds.

Table 3.1. Tree age and size characteristics.

| | Stand Density (TPHA) | Stand Size (cm) | STD Stand Size | Stand Age | STD Stand Age | Pronounced Pit and Mound Topography (%) |
|---|---|---|---|---|---|---|
| WS1 | 663 | 31.43<br>(0.81) | 16.21 | 68.75<br>(2.33) | 37.87 | 11 |
| WS3 | 408 | 31.58<br>(1.39) | 19.8 | 127.99<br>(5.06) | 70.17 | 5 |
| WS4 | 360 | 48.36<br>(7.17) | 43.04 | 218.53<br>(28.6) | 171.59 | 0 |

### *3.4.2 Field measurements and sampling*

The number of survey point locations where pits were dug and soils were profiled was 251, 147, and 36 for WS1,WS3 and WS4 respectively. Frequency distributions of the thickness of major soil horizons from each watershed are shown in Figures 3.5, 3.6. Mean horizon thickness was not reported because horizons were not found at all survey point locations, and many of the horizon thickness frequency distributions were non-normal (negative exponential or uniform) (Figures 3.5,3.6). Presence/absence of horizon thickness >1 cm for each horizon, and the number of soil samples collected from each horizon in each watershed is reported in Table 3.2. This table also reports total soil volume ($m^3$/ha), <2mm fraction, and uncorrected bulk density (wet and dry) which were used to calculate whole soil carbon content. Stone content was corrected for by multiplying the uncorrected bulk density by <2mm fraction. Stone content is likely underestimated with the small core used to collect samples. Bulk densities of major horizons were comparable across all catchments. Bh > 2mm particle abundance increased in more disturbed catchments.

### *3.4.3 Density fractionation/Elemental analysis*

Results from the density fractionation, C, N, and isotope analysis are summarized in Table 2.3. Nitrogen isotopes showed greater discrimination than carbon between fresh organic source material and deep soil Bs samples. $\delta^{13}C$ values were low (-29.3‰ to –26.3‰) in fresh organic material and forest litter (-27.5‰), and only slightly enriched in $^{13}C$ in deep mineral soil horizons (-25.63‰). $\delta^{15}N$ values were low in fresh organic material(-5.7‰ to –5.1‰), and highly enriched $^{15}N$ in (5‰ to 8.71‰) in mineral soil samples. Forest litter (Oie) $\delta^{15}N$ values were considerably lower in WS4 than in either WS1 or WS3. Lower major soil horizons were on average slightly lower in $\delta^{15}N$ in WS4 then in WS1 or WS3. The C/N ratio of forest litter (Oie) in WS1 was significantly lower than in WS3 or WS4 ($P<0.01$). On average, $\delta^{13}C$ and $\delta^{15}N$ and C/N values decreased with depth across all catchments (Table 3.3). The correlation between N and C increased with depth (Figure 3.7).

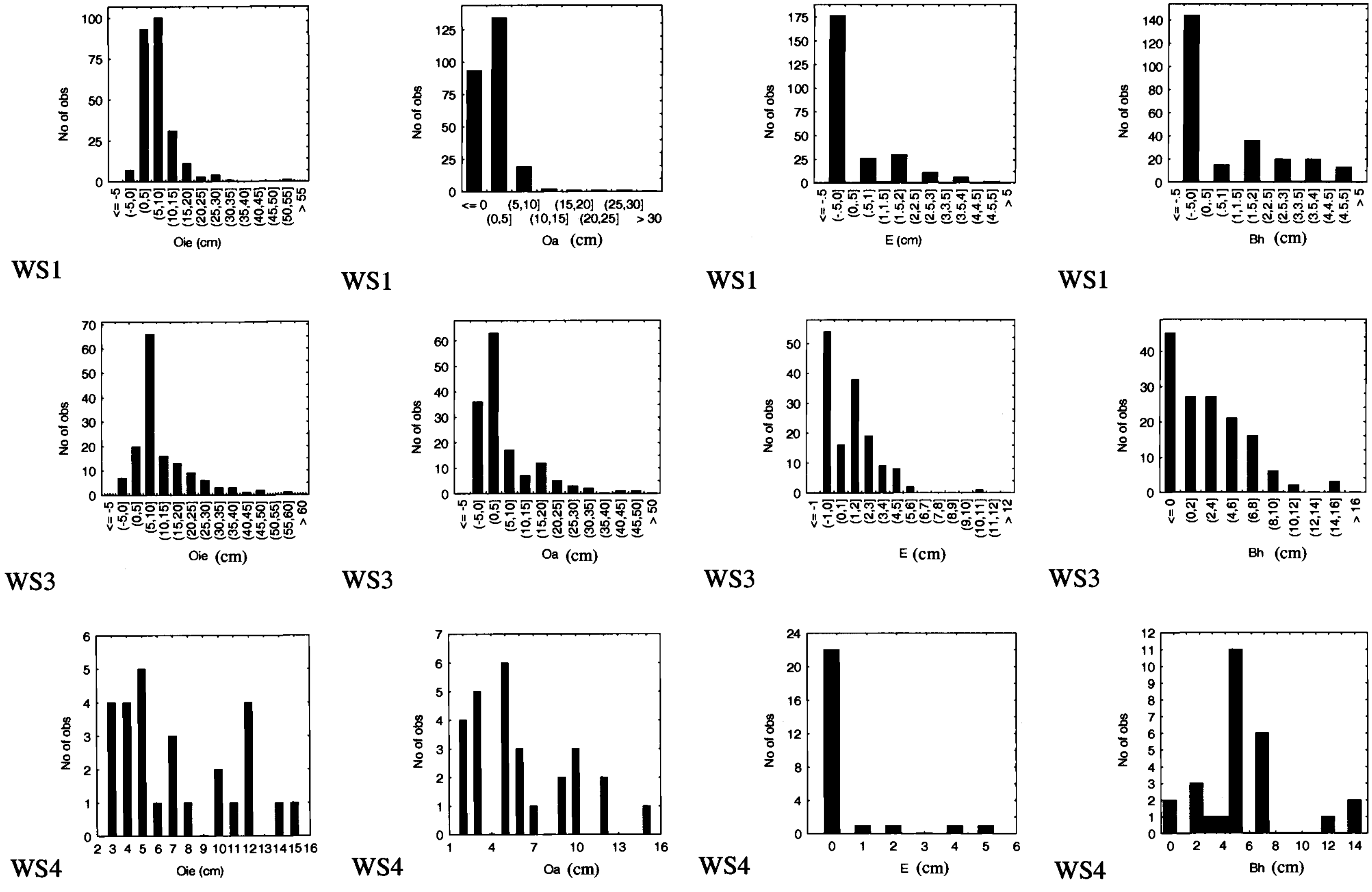

Figure 3.5. Frequency distributions of diagnostic horizon thickness in each catchment.

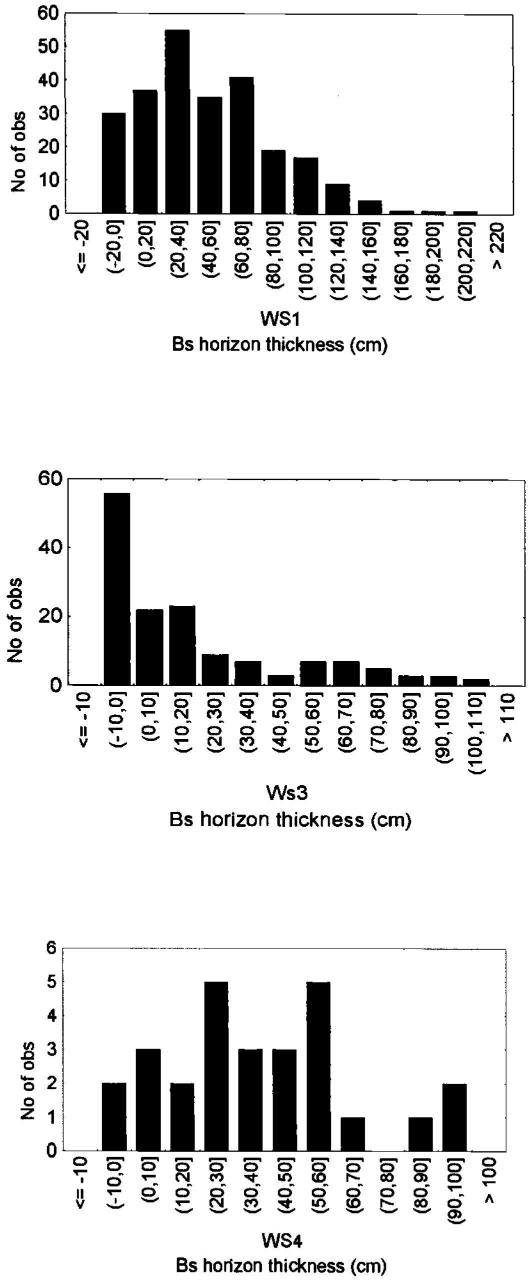

Figure 3.6. Frequency distributions of diagnostic horizon thickness in each catchment.

Table 3. 2. Bulk density and <2mm fraction from samples collected. Standard error is reported in ().

| | | N | Dry Bulk density g/cm3 | Water content g/cm3 | < 2mm fraction (%) |
|---|---|---|---|---|---|
| WS1 | Oe | 34 | 0.10 (0.01) | 0.29 (0.02) | -- |
| | Oa | 40 | 0.17 (0.01) | 0.50 (0.02) | -- |
| | Bh | 32 | 0.39 (0.02) | 0.45 (0.02) | 67 (5) |
| | Bs | 125 | 0.43 (0.01) | 0.31 (0.01) | 49 (2) |
| WS3 | Oe | 29 | 0.10 (0.01) | 0.35 (0.02) | -- |
| | Oa | 69 | 0.16 (0.01) | 0.63 (0.07) | -- |
| | Bh | 55 | 0.37 (0.02) | 0.75 (0.15) | 79 (2) |
| | Bs | 46 | 0.39 (0.02) | 0.39 (0.02) | 62 (3) |
| WS4 | Oe | 12 | 0.08 (0.00) | 0.40 (0.02) | -- |
| | Oa | 27 | 0.12 (0.00) | 0.55 (0.02) | -- |
| | Bh | 38 | 0.35 (0.03) | 0.70 (0.03) | 84 (4) |
| | Bs | 21 | 0.38 (0.04) | 0.55 (0.02) | 82 (3) |

Table 3. 3. Summary of CN, natural abundance isotope results, and density fractionation.

| | | n | C | δ13C | N | δ15N | C/N |
|---|---|---|---|---|---|---|---|
| | | | (%) | | (%) | | |
| Fresh organic matter | | 32 | 49.58 (0.27) | -29.01 (0.22) | 0.99 (0.04) | -3.92 (0.29) | 53.93 (3.79) |
| Hemlock Needles | | 25 | 49.36 (0.01) | -29.24 (0.23) | 1.02 (0.01) | -3.83 (0.27) | 49.47 (1.39) |
| Hemlock Wood | | 2 | 51.59 | -28.96 | 0.41 | -5.75 | 128.28 |
| Spruce Needles | | 1 | 48.55 | -26.30 | 1.10 | -0.51 | 43.97 |
| Spruce Wood | | 1 | 50.82 | -27.30 | 1.09 | -1.97 | 46.62 |
| Fungal Mat | | 1 | 50.35 | -29.30 | 0.48 | -6.19 | 104.35 |
| Ws1 | Oie | 14 | 44.01 (0.74) | -27.22 (0.12) | 1.41 (0.06) | 2.07 (0.28) | 31.79 (1.06) |
| | Oa | 21 | 39.96 (1.11) | -26.29 (0.10) | 1.34 (0.07) | 2.13 (0.48) | 31.91 (2.25) |
| | Bh Lf | 32 | 34.77 (0.67) | -26.31 (0.09) | 1.39 (0.05) | 5.01 (0.27) | 26.17 (1.13) |
| | Bh Hf | 29 | 16.43 (1.07) | -26.05 (0.08) | 0.75 (0.05) | 5.68 (0.16) | 22.43 (0.81) |
| | Bs | 57 | 12.68 (0.60) | -25.31 (0.07) | 0.61 (0.03) | 5.04 (0.30) | 21.33 (0.73) |
| Ws3 | Oie | 13 | 47.93 (0.51) | -27.5 (0.2) | 1.14 (0.09) | 1.98 (0.29) | 47.4 (5.73) |
| | Oa | 48 | 40.99 (1.09) | -26.91 (0.12) | 1.04 (0.06) | 5.05 (0.24) | 49.88 (4.64) |
| | Bh Lf | 52 | 31.08 (0.81) | -27.06 (0.10) | 1.06 (0.04) | 6.58 (0.25) | 31.08 (1.37) |
| | Bh Hf | 52 | 14.58 (0.79) | -26.44 (0.06) | 0.63 (0.04) | 7.18 (0.29) | 25.52 (1.21) |
| | Bs | 44 | 14.23 (0.89) | -25.63 (0.10) | 0.55 (0.04) | 8.71 (0.39) | 28.24 (2.48) |
| Ws4 | Oie | 14 | 44.18 (0.82) | -27.34 (0.14) | 1.21 (0.09) | -1.18 (0.76) | 38.65 (2.35) |
| | Oa | 23 | 43.06 (0.75) | -26.55 (0.12) | 1.45 (0.06) | 1.89 (0.48) | 31.01 (1.54) |
| | Bh Lf | 7 | 31.63 (1.35) | -26.71 (0.30) | 1.49 (0.10) | 2.8 (1.73) | 22.03 (2.28) |
| | Bh Hf | 37 | 16.2 (0.80) | -26.12 (0.05) | 0.87 (0.05) | 6.65 (0.22) | 19.08 (0.50) |
| | Bs | 10 | 12.96 (1.42) | -25.77 (0.09) | 0.6 (0.04) | 7.32 (0.55) | 21.28 (1.24) |

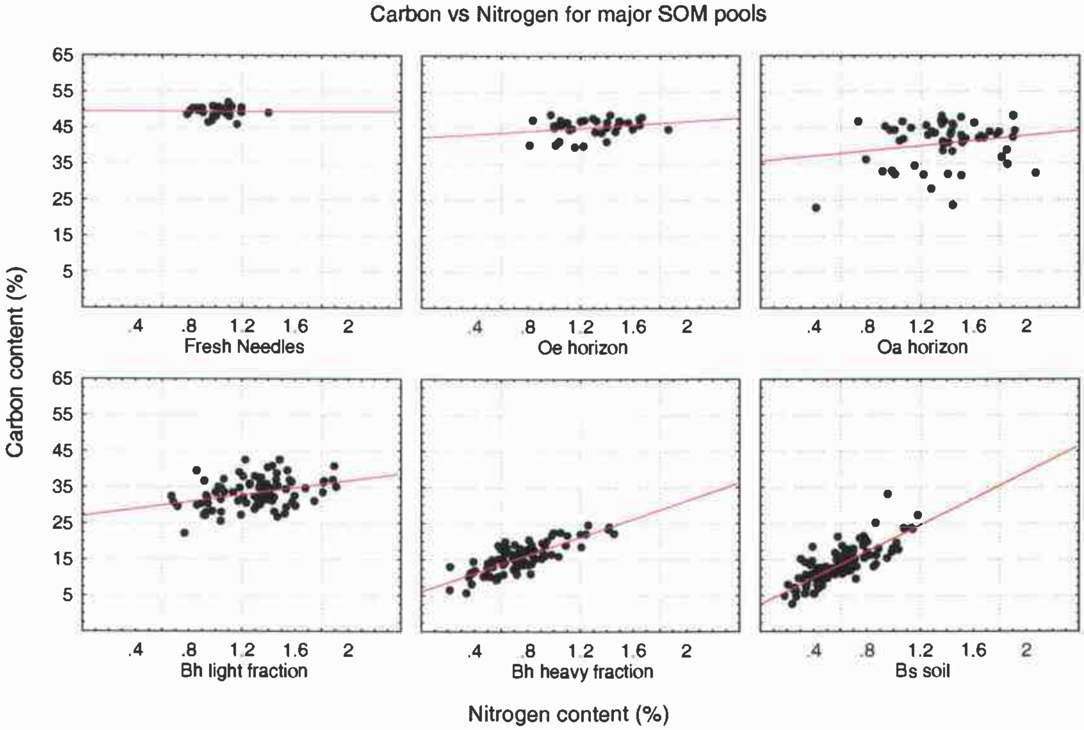

Figure 3.7. Observed shifts of N and C in major SOM pools from samples collected across all watersheds

The concentration of whole soil carbon in heavy fraction Bh samples was higher in older less disturbed watersheds while light fraction Bh soil carbon concentrations were lower (Figure 3.8). The total quantity of carbon in the light and heavy fractions are shown in Figure 3.9. Catchment-wide total SOC pools were slightly higher (160 to 200 Mg/ha) in less disturbed watersheds (Figure 3.10). However the quantity of SOC in a given horizon differed considerably among watersheds. Bh SOC pools ranged from 7 Mg/ha in WS1 (most disturbed) to 38 Mg/ha in WS4 (least disturbed). SOC in the Oa horizon was lowest in the most disturbed watershed (17 Mg/ha vs 63 Mg/ha). Ultrasonication prior to density fractionation of Bh samples resulted in recovery (+/- 3%) similar to that from samples fractionated without ultrasonication (> 15%). Mass loss on ignition of >2mm fraction samples was less then 1% (se 0.2%).

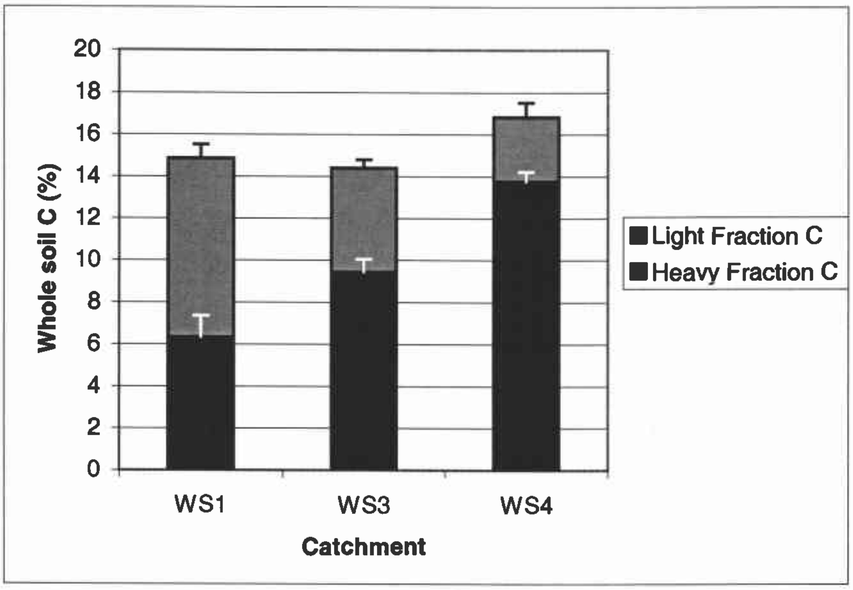

Figure 3.8. Concentration (with s.e. bars) of carbon in LF and HF Bh horizon carbon in watersheds with contrasting windthrow disturbance.

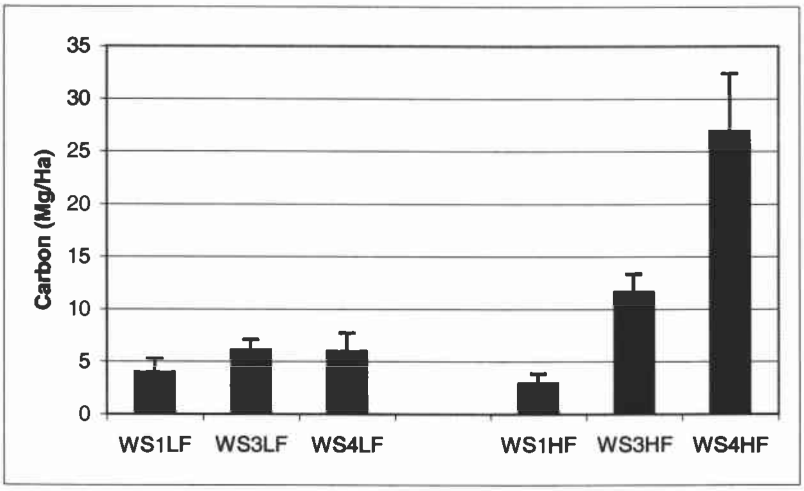

Figure 3.9. Carbon pools in light and heavy fractions from illuvial horizons from each watershed. Error bars are 95% confidence intervals.

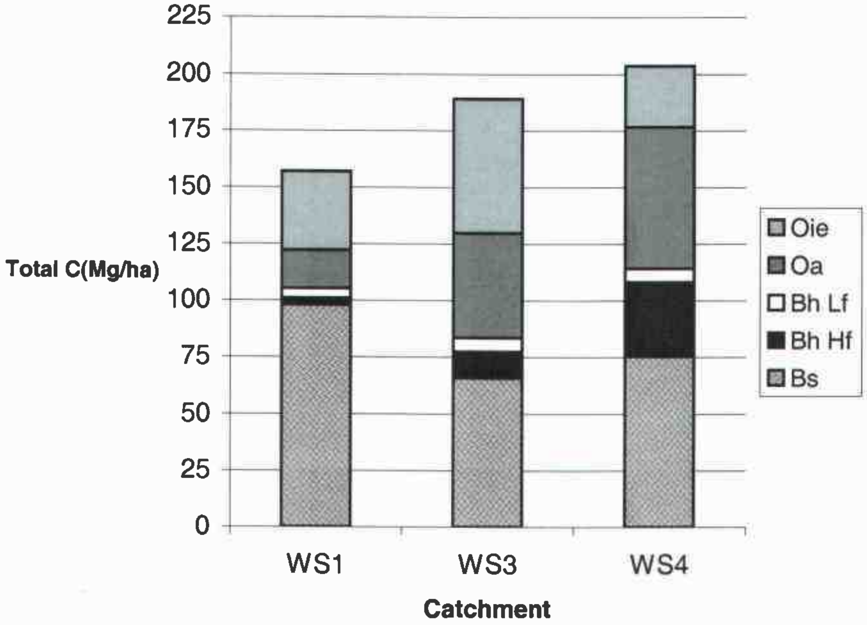

Figure 3.10. Distribution of total C in major SOM pools in catchments with contrasting disturbance from windthrow.

### *3.4.4 Solid state $^{13}C$ NMR spectroscopy*

Chemical shifts for major carbon types are shown in Table 3.4. NMR spectra from select samples across horizons and fresh litter (Oie, needles and fungal mats) were clustered based on O-alkyl, aliphatic, aromatic and carboxyl content using a Chebychev distance metric (Figure 3.11)(Michalski et al. 1981). The O-alkyl group decreased, while aliphatic, carboxyl and aromatic groups increased with depth (Figure 3.12). Heavy fraction Bh samples across all catchments and 4 light fraction Bh samples from WS3 were richest in aliphatic, carbonyl, and aromatic groups.

Table 3. 4. Peaks used for NMR groups.

| ppm | Assignment |
|---|---|
| 0-45 | Alkyl-C |
| 45-110 | O-Alkyl-C |
| 110-160 | Aromatic-C |
| 160-220 | Carbonylic-C/ carboxylic-C |

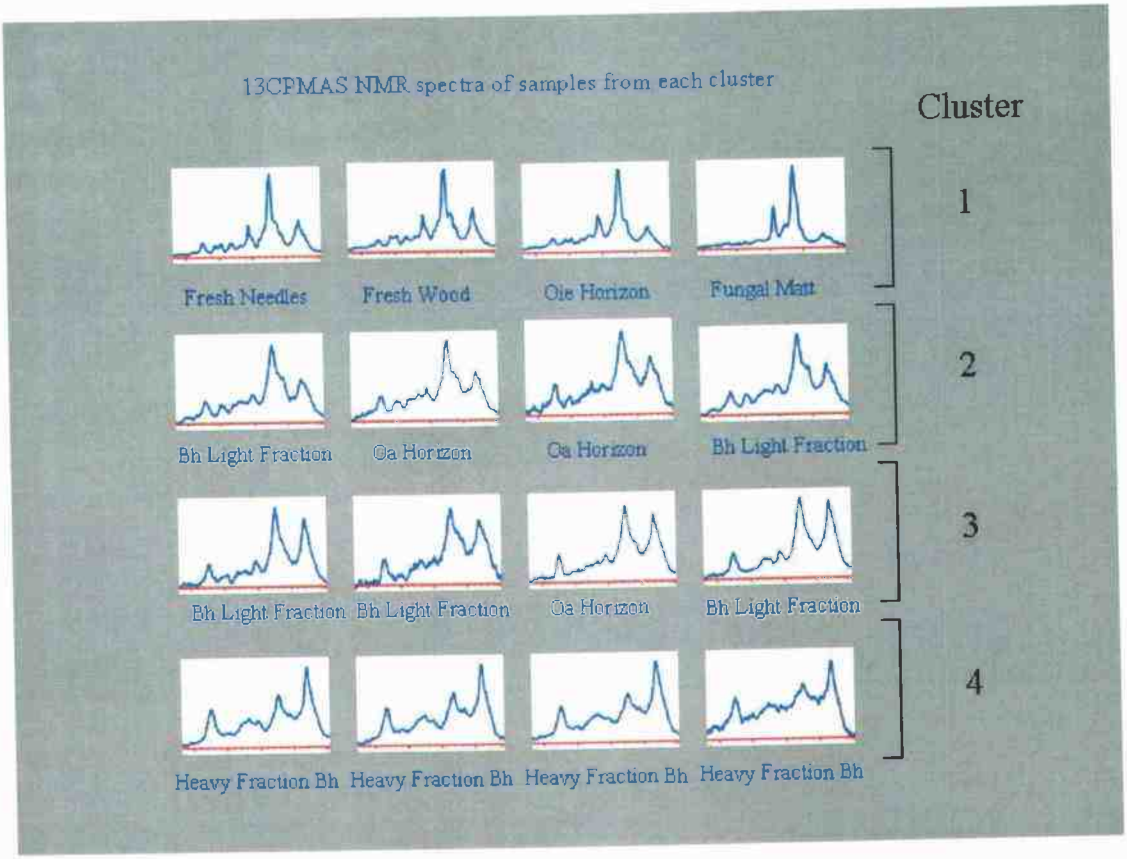

Figure 3.11. Clustering of NMR data based on aliphatic, o-alkyl, aromatic, and carboxyl groups. Clustering resulted in 4 distinct clusters which varied in the extent of decomposition, and generally reflected distinct soil horizons.

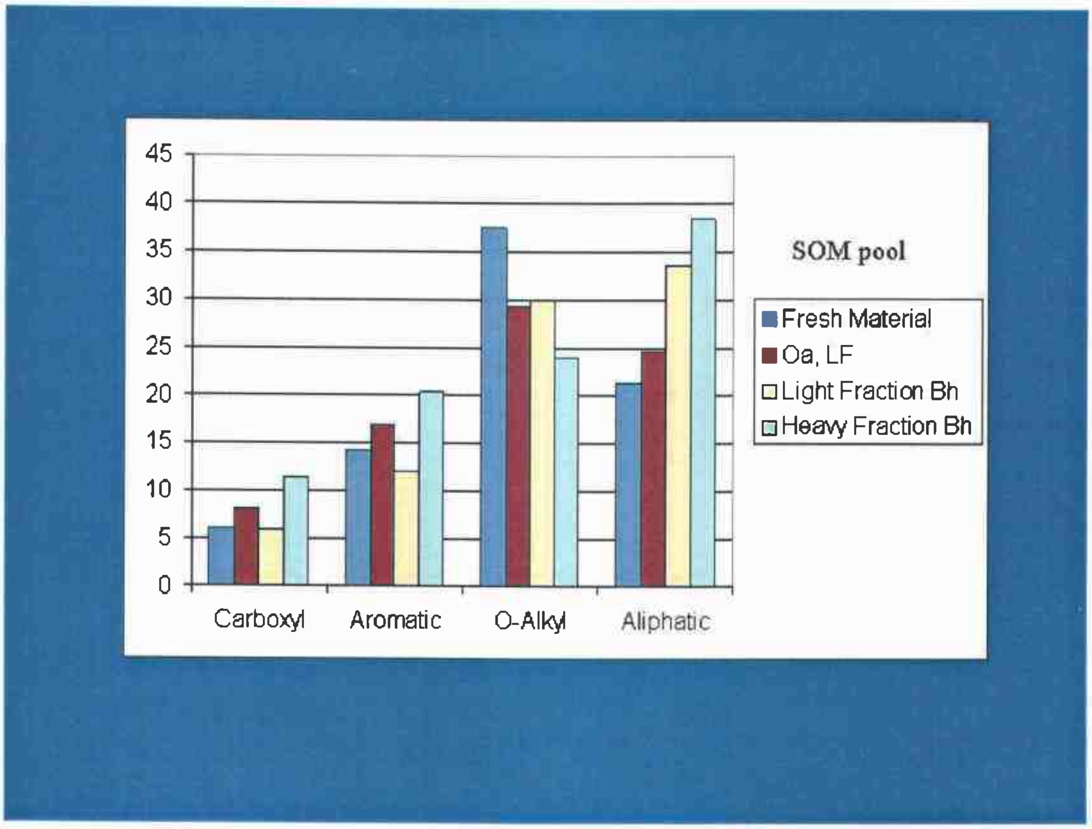

Figure 3.12. Qualitative summary of the distribution of C types from major SOM pools.

### *3.4.5 Naturally occurring isotope ratios, C/N, and NMR*

Aromatic and carboxyl groups are poorly quantified using CP-MAS NMR due to the nature of protonation and the associated resonance of these groups. Aromatic and carboxyl signals can be dampened in some cases up to 30%, although the extent of signal dampening is unpredictable (Dai and Johnson 1999, Smernik and Oades 2000). I performed repeated runs on a light fraction Bh sample and found a 6% difference in the quantity of aromatic carbon detected. The ratio of aliphatic/O-alkyl groups was compared with $\delta^{15}N$, $\delta^{13}C$ values and C/N ratios using 38 samples. Quantitation of these two groups using $^{13}C$ solid state NMR has shown good agreement with direct polarization (DP) NMR and Fourier Transformation Infra-Red Spectroscopy quantitation (Kinchesh et al. 1995, Conte et al. 1997, Smernik and Oades 2000). Both $\delta^{13}C$ values and C/N ratios show a parabolic pattern of change with increasing aliphatic/O-alkyl ratios (Figure 3.13, 3.14). $\delta^{15}N$ values increased with increasing aliphatic/O-alkyl values (P<.01, R2 =.6823,Fstat xxx) (Figure 3.15). The relationship between aliphatic/O-alkyl ratios and carbon and nitrogen content is shown in Figures 3.16,3.17.

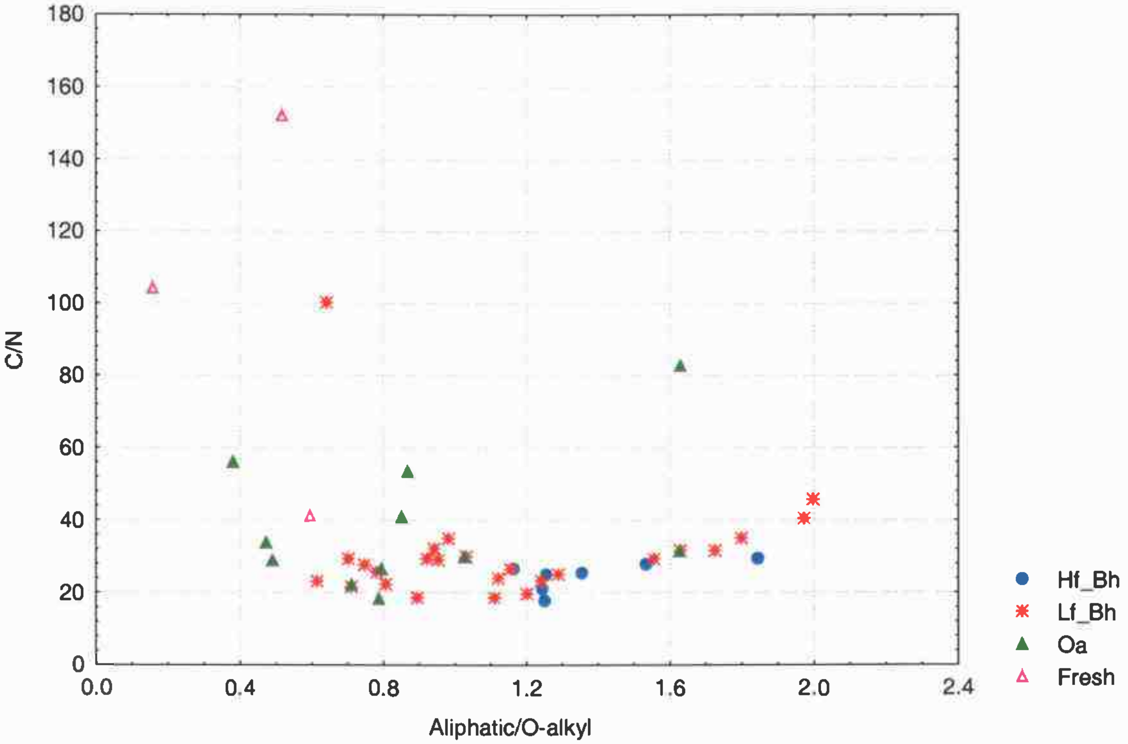

Figure 3.13. C/N plotted against aliphatic/O-alkyl ratios.

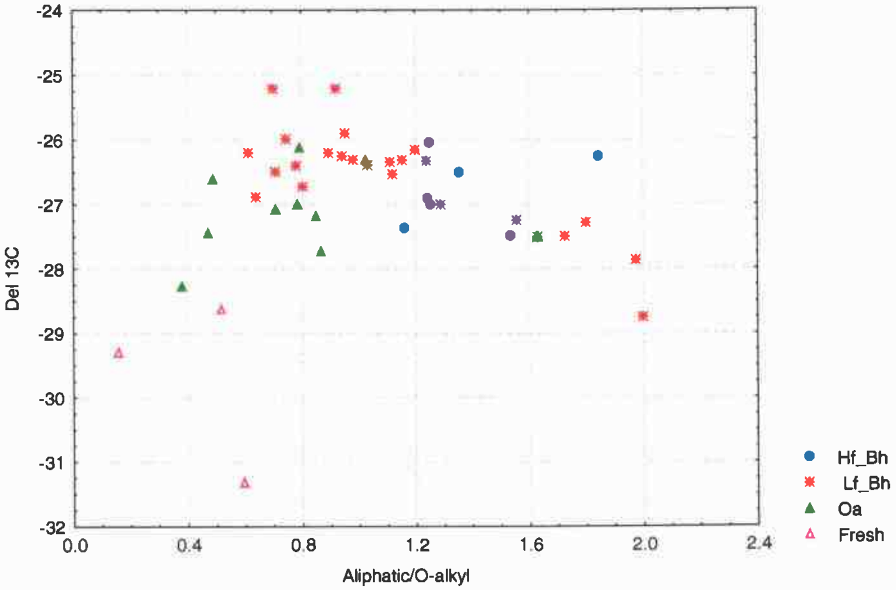

Figure 3.14. Del 13C plotted against aliphatic/O-alkyl ratios.

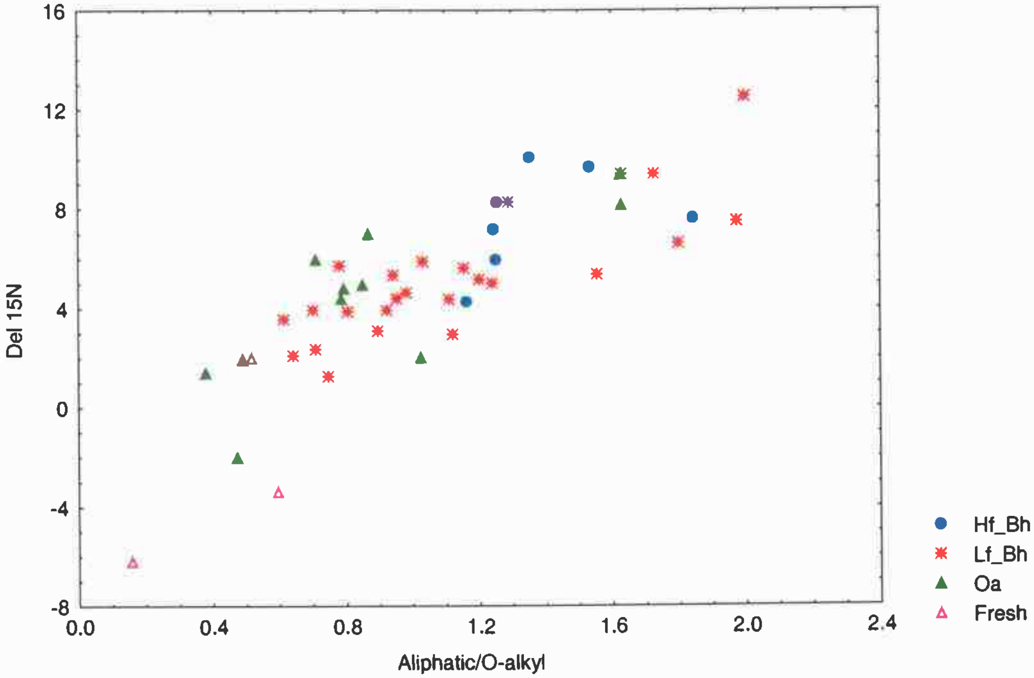

Figure 3.15. Del 15N plotted against aliphatic/O-alkyl ratios.

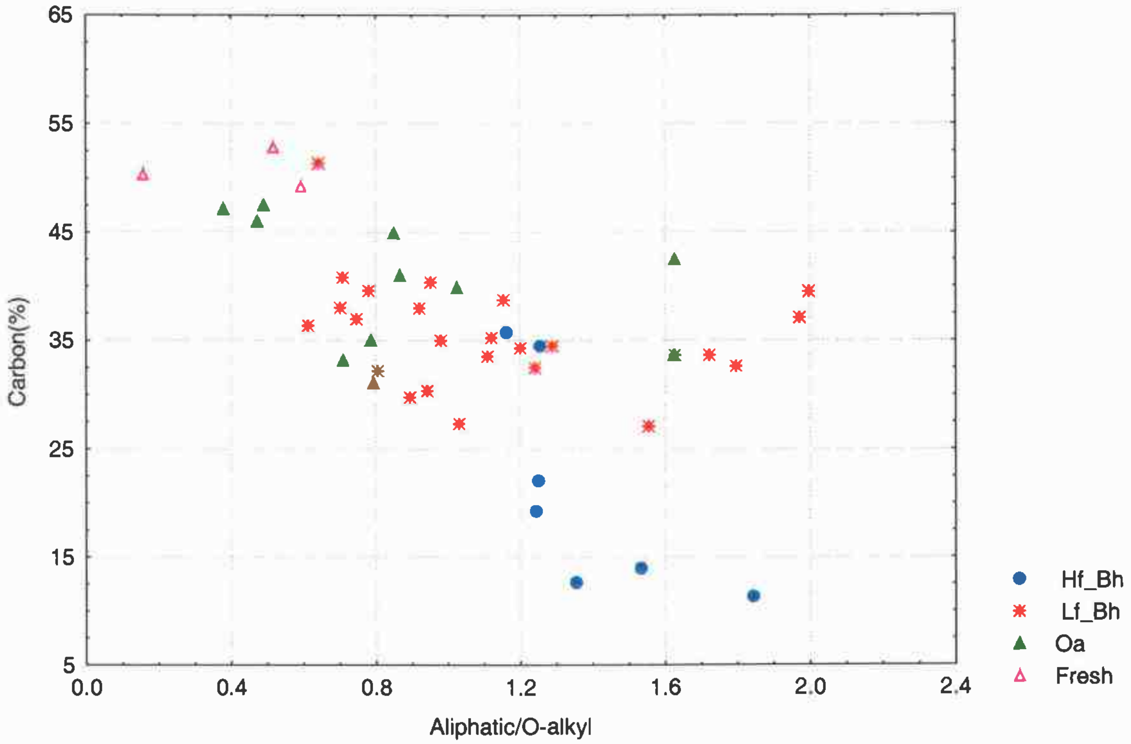

Figure 3.16. Aliphatic/O-alkyl ratios plotted against carbon content (%).

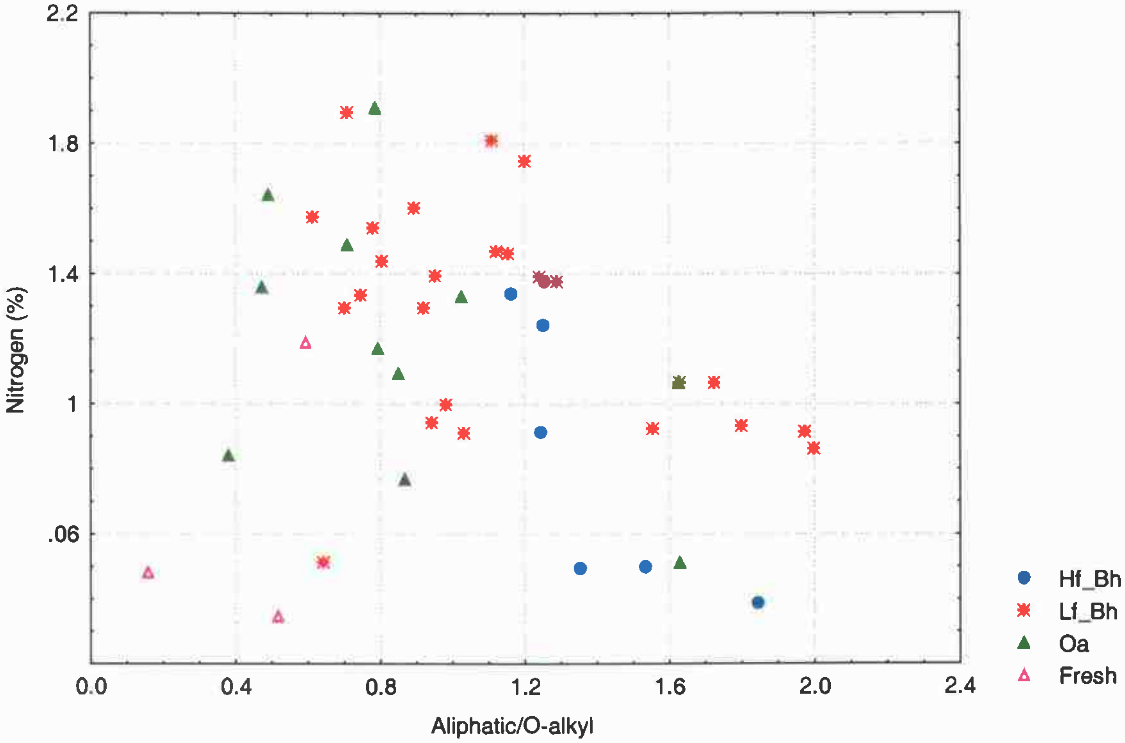

Figure 3.17. Nitrogen content (%) plotted against aliphatic/O-alkyl ratios.

### *3.4.6 Scanning Electron Microscopy*

SEM images of select samples show identifiable plant remains in Oie, Oa, and light fraction Bh samples (Figures 3.18, 3.20). In contrast, I could not discern recognizable plant remains in most of the material in the four light fraction Bh samples which had high aromaticity and carboxyl groups, or in any of the heavy fraction Bh samples examined and from SEM (Figures 3.19, 3.21). SEM images of precipitated humic acid (Figure 3.22) and these same samples showed micromorphologic similarities. Both were amorphous with smooth surfaces and distinct fracturing and cracked coatings.

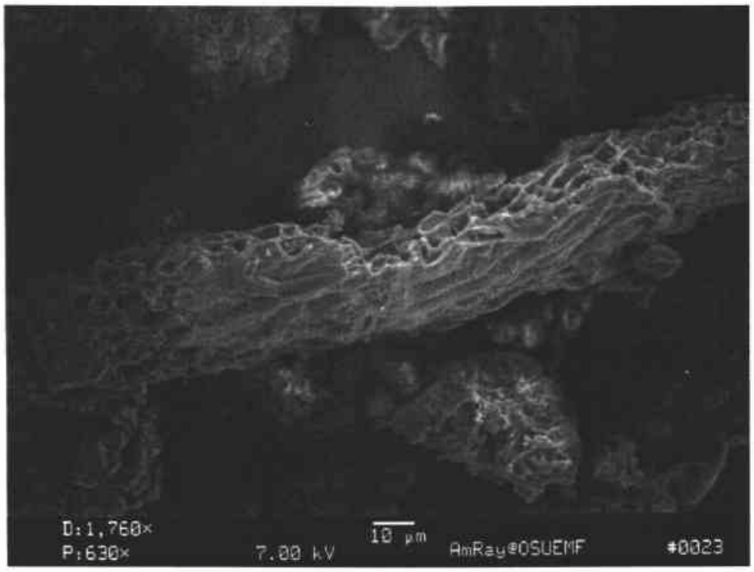

Figure 3.18. Scanning electron images of light fraction Bh with partially humified organic particles.

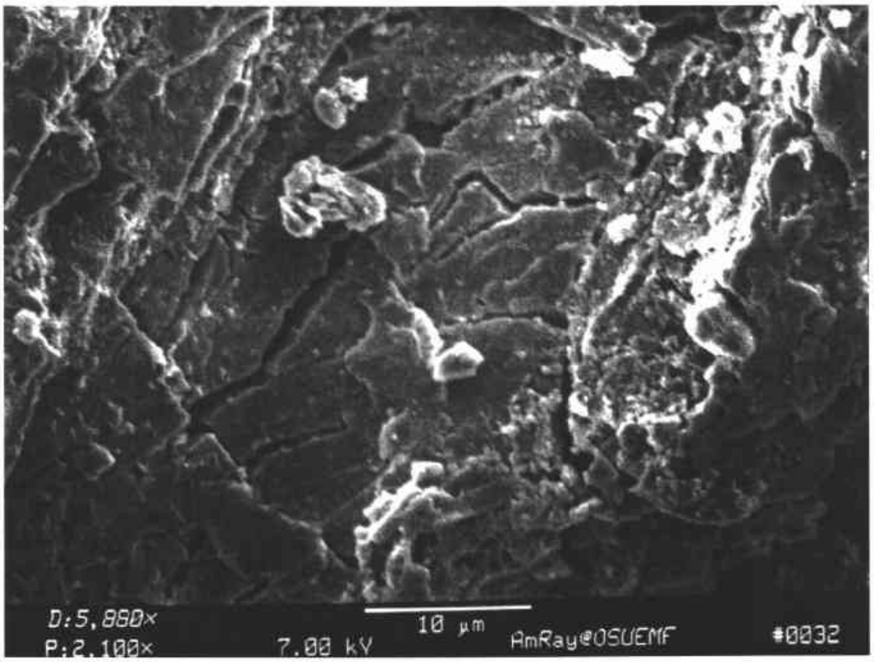

Figure 3.19. Scanning electron microscope images of heavy fraction Bh with evidence of cracked coatings.

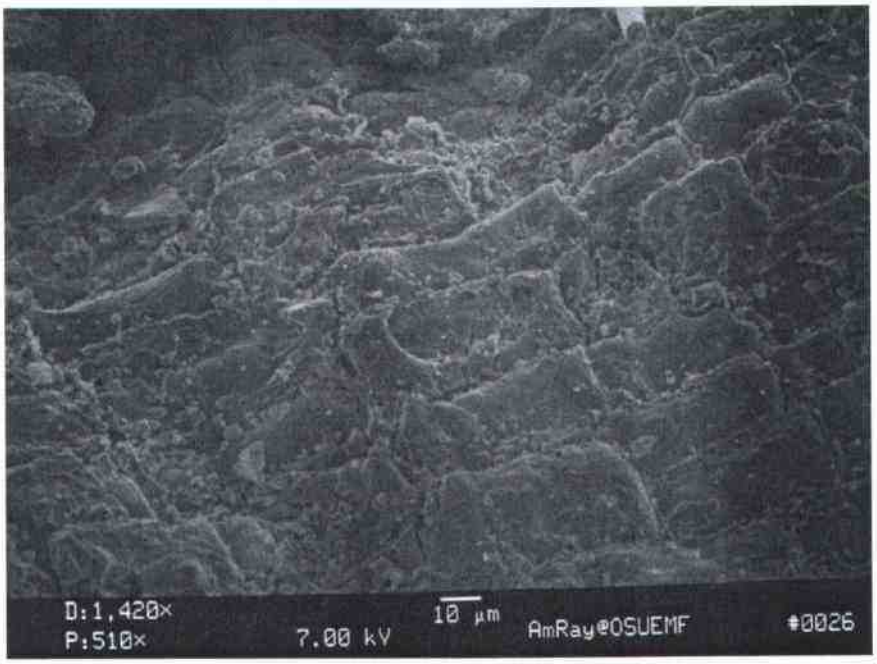

Figure 3.20. Light fraction Bh sample with evidence of particulate partially humified organic matter.

Figure 3.21. Light fraction Bh sample with evidence of extensive cracked coatings.

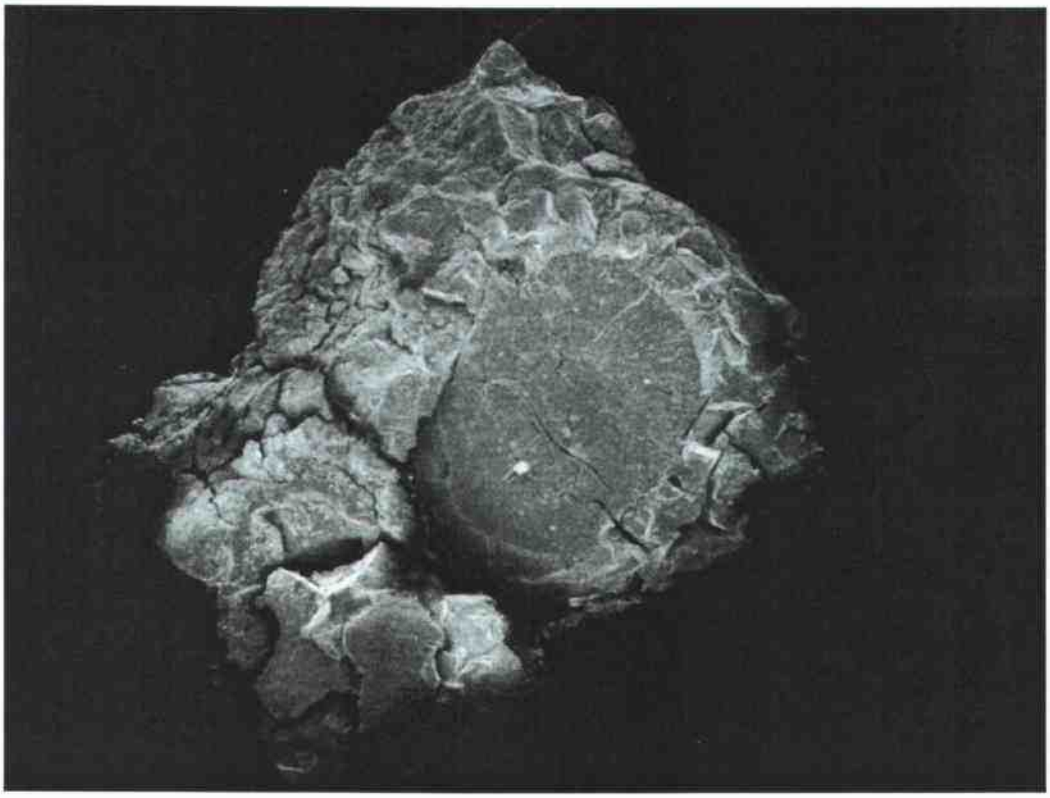

Figure 3. 22 Laboratory isolated humic acid with evidence of cracked structure from dehydration of the hydrated organo-mineral complex.

## 3.5 Discussion

Our results suggest that both windthrow and illuviation strongly influence the accumulation of carbon in these mineral horizons. Both processes and the interactions between the two are discussed in subsequent sections. The chemical and physical mechanisms for stabilization and immobilization of SOC and the forms of SOC that have accumulated are then discussed.

### *3.5.1 Redistribution of SOC from windthrow*

Partially decomposed organic particles were found in all black C-rich mineral horizons sampled, but the proportion of total C in this form declined with increasing horizon thickness (Figure 3.9). These thicker black mineral horizons are probably older since they were found in watersheds with older trees and less evidence of recent soil disturbance. Soil mixing and soil creep due to hillslope processes was observed in all catchments because they occur on steep slopes. The light fraction particulate organic matter, with identifiable plant remains, found in black mineral horizons was likely the result of tree uprooting during windthrow and subsequent slope redistribution processes (Schaetzl and Follmer 1990, Norman et al. 1995). In the most disturbed watershed (WS1), pronounced pit and mound topography occupied 10% of the soil surface. However, the extent of soil disturbance was greater than that reflected by pronounced pit and mound topography (estimated to be in excess of 40% of the catchment area). Many pits were filled, and mounds were smoothed from slope movement and redistribution of materials.

*In situ* decomposition of root fragments, fungal mats, and microbial biomass (biotic deposition processes) are alternative mechanisms that can lead to the presence of particulate organic matter in mineral soil horizons. Macrofauna, such as earthworms, are not likely to be a major source of SOC in this mineral soil since they are relatively scarce and inactive in acid (mor) podzol soils (Schaefer and Schauermann 1990, Beyer and Irmller 1991), and were never observed in the field. Spiers et al. (1986) did find earthworms in mor humus of the coastal temperate rainforests of North America, but activity was restricted to organic horizons. *In situ* root mortality may contribute a considerable amount of carbon to deeper mineral soil horizons (Nepstad et al. 1994).

Relative to soil mixing from windthrow and subsequent hillslope redistribution processes, earthworms and root death alone are not likely to have resulted in the large accumulations of particulate organic matter (POM) in black mineral horizons and observed in bare Bs mineral soil horizons exposed from recent windthrow (pit and mound topography) or recently uprooted trees. Live root density was often low in the horizons where samples were collected. I rarely observed large discernable root fragments that appeared to be the result of in-situ mortality in the black mineral horizons sampled. Thus the contribution of root derived C was neither studied nor well estimated in the calculation of soil C pool size.

In addition to redistributing and mixing organic and mineral soil horizon materials, windthrow can cause warmer soil temperatures, increased microbial activity, and pronounced pit and mound topography, which leads to increased litter accumulation, soil moisture in pits (accelerated podzolization), and well-drained drier mounds with higher rates of decomposition (Schaetzl and Lansing 1990). Our results suggest that soil mixing from windthrow resulted in the redistribution and increase in the quality of soil carbon across entire watersheds. The low litter (Oie) C/N ratio in WS1 suggests that the quality of litter increased after windthrow (Table 3.3), perhaps due to increased decomposition rates of litter inputs due to increased aeration and warmer soil temperatures. Total SOC stocks were lower (by 50 Mg/ha) in more disturbed watersheds, likely due to SOC destabilization from mixing. The quality of whole soil OC in more windthrown watersheds was considerably higher than in older, less disturbed watersheds. SOC occurred principally in particulate (Oie) or deep soil (Bs) horizons in more disturbed watersheds, likely due to destabilization of the recalcitrant pools (heavy Bh, and Oa) and redistribution of this material to upper and lower horizons during mixing (Figure 3.10). The difference in total SOC stocks (50 Mg/ha) between catchments can be attributed to reduced Bh and Oa horizon SOC pools in the most disturbed watershed. Overall the total C stocks found in each catchment (150-190 Mg/ha) are very close to those reported in the literature (Alexander et al. 1986, Van Cleve and Powers 1995). The light fraction Bh pool (~5 Mg/ha) was similar in size across all three catchments (Figure

3.9). This suggests that particulate carbon in these illuvial horizons is relatively constant and neither accumulates nor declines as forest soils age.

### *3.5.2 Illuviation from lateral/vertical soil water transport*

SEM images and NMR characterization suggest heavy fraction carbon accumulated through illuviation. Scanning electron micrograph images of heavy fraction carbon found in black carbon-rich mineral-soil horizons show cracked coatings on the surface of large particles (Figures 3.19, 3.23). Cracking of these coatings has been shown to be the result of dehydration of gelatinous, hydrated organo-mineral complexes which were transported in soil water to mineral horizons from overlying organic horizons (Deconnick 1980, Pustovoitov and Targulian 1996). Our NMR analysis of heavy fraction C shows a high proportion of the carbon is comprised of carboxyl and carbonyl groups, characteristic of dissolved fulvic and humic acids (Beyer 1996, Parfitt et al. 1999). In the less disturbed, older catchments, three changes in illuvial (black) mineral horizons were observed: 1) horizon thickness increased (Figure 3.5), 2) the concentration of carbon in the heavy fraction increased (Figure 3.8). and 3) amount of heavy fraction increased. All of these increases occurred most likely as the result of illuvial processes.

Chronosequence studies of podzolization and soil solution studies of mechanisms of podzolization have purposely chosen flat, well-drained surfaces where vertical water flow results in distinct elluvial and illuvial soil horizons. Such a model has been essential toward elucidating mechanisms of podzolization. By holding the state factors of topography, vegetation, climate and parent material constant, these chronosequence studies have substituted space for time, providing insight into rates of podzolization, mechanisms of carbon, iron, and aluminum translocation, subsequent immobilization, and consequent soil horizon development.

Bullock and Claydon (1980) pointed out that podzols occur over a tremendously wide range of climatic, lithic, topographic, temporal and biotic state conditions –all of which may strongly influence the rate of illuviation and possibly mechanisms for precipitation and accumulation of carbon, iron and aluminum in mineral soils. From this research, many anomalous podzols, which do not fit conventional soil classification schemes or the 'typical' model of podzolization, have been reported (e.g. Watters and Price 1988, Pavlov et al. 1997, Van Ranst et al. 1997,Sommer et al. 2000, Beyer 2000). This discrepancy between theory and observation may be attributed, in part, to an assumption that soil water moves predominantly in the vertical direction under normal or typical conditions.

In contrast to research on flat, well-drained soils, there is increasing research to suggest that lateral flow causes movement of soluble, mobile materials, and consequent illuviation in mountain forest soils (Scatena and Lugo 1995, Newmann et al. 1998, Sommer et al. 2000 paper, Hagedorn et al. 2000). In our study, the thicker black soil horizons observed could not be explained by vertical translocation (illuvial) processes alone: 1) white, elluvial soil horizons were thinner and often altogether absent above underlying black horizons 2) the elluvial horizons found were concentrated in the upper, outer reaches of the catchment, often in the absence of an underlying black horizons (not shown), and 3) lateral flow out of mineral soil horizons could be observed regularly in soil pits under wet conditions. While both lateral and vertical soil water movement may lead to translocation of carbon to mineral horizons, their relative contributions remain unclear. Translocation of materials via lateral flow may deplete or enrich entire mineral soil profiles down to bedrock, or deposit translocated material in surface organic horizons, depending on factors such as hillslope position, fractured vs unfractured bedrock, and soil permeability. Many of the older, wetter Oa (black muck) horizons contained high concentrations of inorganic material (20-50%). The source of this inorganic material may be mobile organo-mineral complexes, which may become immobilized when they are transported through highly decomposed organic horizons.

### *3.5.3 Interactions between windthrow and illuviation*

Tree uprooting from windthrow, as a pedogenic process, has been recognized, studied, and discussed for over a century, and its global importance is widely recognized today (Schaetzl et al. 1989, Schaetzl 1996, Ulanova 2000). Soil mixing resulting from tree uprooting (termed pedoturbation) and podzolization may be viewed as opposing processes, as has been suggested by numerous authors (Johnson et al. 1987). In fact many studies have referred to soil mixing as a process of regressive podzolization (Schaetzl et al. 1990). In this view, a succession of soil development processes beginning with podzolization may develop an ecosystem toward a climax condition, unless soil disturbance resets this sequence (Ugolini and Mann 1979, Bormann et al. 1995). This view of the interaction between disturbance and soil development is similar to plant succession in which community succession is reset after catastrophic disturbance – a punctuated equilibrium view of ecosystem change (Pickett and White 1985). Many studies in New Zealand have reported the presence of brown Inceptisols where Spodosols are expected to prevail (Campbell and Mew 1986, Schaetzel et al. 1990, Stewart et al. 1993, Mew and Ross 1994) and attributed the presence of these younger soils to soil mixing from windthrow. On a catchment scale, we found that watersheds that experienced greater damage from windthrow contained younger (Inceptisol) soils with less evidence of soil development (horizonation).

In addition to disrupting and reinitiating soil horizon development, our results suggest illuvial horizon carbon was the result of both windthrow disturbance and subsequent podzolization. In thin, poorly developed illuvial horizons, most carbon was light, particulate and likely originated from windthrow which occurred 90 years ago (Figures 3.4, 3.10, Table 3.1.). In WS3, which experienced partial or less recent windthrow, particulate organic carbon still comprised 33% of the total carbon present. In the oldest watershed, in which we found no evidence of recent (<200 yr) windthrow, most carbon in the older thicker illuvial horizons was in heavy fraction, and likely originated predominantly from immobilization of mobile, organic carbon (Figure 3.10). Soil mixing influences not only the OM quantity and quality in the illuvial horizons, but likely subsequent processes (rates, mechanisms) of illuvation as well. Our results provide evidence for windthrow as both a regressive and progressive pedogenic process (Johnson et al. 1987). More research to discern mechanisms of immobilization, stabilization and destabilization of carbon added to mineral soil through soil mixing is needed.

Windthrow may add considerable C, amorphous Fe, and Al to mineral horizons. Carbon added by soil mixing may persist and become stabilized in mineral soil either in particulate form or through adsorption to mineral particles. Bh fragments deposited in Bs horizons may lead to decomposition of metal-bound precipitated fulvic and humic acids (Lundstrom et al. 1995), and subsequent release of $Fe^{3+}$ and $Al^{3+}$. Deposition of organo-mineral particles, followed by decomposition of the organics, may be responsible, in part, for the formation of imogolite in Bs horizons (Lundstrom et al. 2000). The high carbon content found in these volcanically-derived Bs soils (Table 3.3) suggests imogolite may be present. Carbonic acid weathering may be involved in imogolite formation in Bs horizons as well (Dahlgren and Ugolini 1989). Our results suggest soil turnover from treethrow/hillslope processes may be a pathway of carbon accumulation (and possibly amorphous Fe, and Al ), in mineral soil horizons.

The quantity of C accumulating in mineral soil as a result of windthrow and illuviation likely depends on factors such as the quality and quantity of forest litter, precipitation, temperature, and soil mineralogy. The forms of carbon that accumulate may be altered through humification or lost through destabilization of mineral soil C (through microbial $CO_2$ evolution and leaching). The quantity and forms of mineral soil C are determined then, by the relative rates of these two mechanisms (stabilization and destabilization). Southeast Alaska soils are unusual in that large quantities of C are transported to mineral soil layers, and the environmental factors favor stabilization of this C over destabilization. The large and diverse stores of mineral soil C observed in these shallow mountain forest soils may be attributed to the unique, chronic wet cool conditions. Most temperate forest soils, even at high latitudes, experience a longer warm, dry season, in which microbial activity is favored and considerable soil carbon can be lost.

### *3.5.4 Mechanisms of carbon stabilization and immobilization in mineral soil*

In weakly developed thin illuvial horizons, light (<1.65 g/ml) particulate carbon, with discernible plant fragments, was the dominant form present (Figures 3.8, 3.18, 3.20). When such a form of carbon exists in mineral soil, the dominant association with mineral particles is thought to be microbially mediated, principally through microbial secreted binding agents (Golchin et al. 1998). Smaller clay and mineral particles encrust the larger degrading organic particles. This form of organo-mineral association (principally physical) can be observed in the scanning electron microscopic images of light fraction illuvial horizon samples (Figures. 3.18, 3.20, 3.24). Overall, these carbon pools have weak chemical association with mineral particles, are particulate, and contain identifiable plant and microbial matter.

In older, less disturbed watersheds, the concentration of carbon in the heavy fraction increased. SEM and optical images of these samples show cracked coatings which have been shown elsewhere to be a result of deposition of organo-mineral carbon on mineral particles through illuviation (Deconnick 1980). Jardine et al. 1989 have surmised that physical adsorption from hydrophobic interactions is the dominant mechanism for immobilization of DOC in mineral soil. However, chemical adsorption (ligand exchange) could play a strong role in heavy fraction carbon. NMR analysis shows abundant carboxyl and carbonyl groups in heavy fraction carbon (Figure 3.12) which can complex with hydrated mineral surfaces. Cation bridging, anion exchange (outer sphere), and van der Walls force are likely to be involved as well, although these bonds are weak.

In some of the oldest and thickest illuvial soil horizons, light (< 1.65 g/ml), heavily processed (based on $\delta^{15}N$ values and NMR analysis) carbon was found (Figure 3.15). Identifiable plant and microbial fragments could not be discerned in this light fraction from either optical or SEM images (Figs 3.21). NMR, isotopic, and SEM analysis suggest strong resemblance of this material to organo-mineral coatings found in the heavy fraction of illuvial horizons. It also showed strong micromorphologic resemblance and similar density characteristics (<1.65 g/ml) to a laboratory-isolated precipitated humic acid (through NaOH extraction) which we examined under SEM and suspended in a 1.65 g/ml solution (Figures 3.21, 3.22). The origin of this light material is unclear. Its density, composition and distinct micromorphologic features (fracturing and cracks) suggest that it has originated by flocculation or precipitation. This light material was found only in those illuvial horizons which were well developed (older, less disturbed watersheds). In these illuvial horizons, the concentration of heavy fraction carbon is high (Figure 3.8). Other environmental factors, which would increase the likelihood of flocculation such as lower pH, high aluminum and iron concentrations in solution (or quasi solution), and a high C/metal ratio, are likely present in these older, thick illuvial horizons.

### *3.5.5 Forms of soil organic carbon: accumulation and humification*

The source materials examined (needles, wood and a fungal mat) each had distinct C/N ratios, functional groups present, and isotopic signatures (Table 3.3). The chemical, physical and micromorphologic properties of samples collected from each horizon show they each contained distinct SOC types (Table 3.3, Figures 3.12, 3.18, 3.19), and all were enriched with heavy isotopes relative to source materials. This may be due to the degradation of these source materials in the forest floor. The lower $\delta^{15}N$ values for litter and deeper soil in WS4 than in other watersheds may reflect greater contributions from fungal mat material, which had a very low $\delta^{15}N$ value (-6.19 ‰)(Table 3.3). During field sampling more fungal material was observed in the Oie of WS4 than in other watersheds.

The increase in aliphatic/O-alkyl ratio and heavy isotope enrichment, and decrease in C/N with depth, all suggest humification of SOC forest litter increased with soil depth in each catchment (Figure 3.15, Table 3.3) (see also Baldock and Preston 1995, Webster et al. 2000). Heavy fraction Bh and Bs horizon carbon was comprised largely of aliphatics and was heavily enriched in $^{15}N$ (Table 3.3.), suggesting that deeper mineral soil carbon was more humified then other SOM pools. These results suggest that the forms of carbon in soil reflect not only the addition of new materials and subsequent processes that influence their accumulation throughout the soil profile, but also the on-going alteration of these materials through humification.

The observed trend of increasing $^{15}N$ abundance with the increase in aliphaticity of carbon (Figure 3.15) suggests that $\delta^{15}N$ values may serve as a potentially useful measure of SOM humification. $^{15}N$ has not been widely used to understand soil organic matter humification (Tiessen et al. 1984, Ehleringer et al. 1992) because of potentially high rates and consequent considerable variation in $^{15}N$ fractionation from many processes operating in the N cycle (i.e. N mineralization Nitrification, Ammoniafication, N assimilation) (Hogberg 1997). It has been suggested that $\delta^{15}N$ values may not correspond with increased humification of SOM at all in forests that cycle nitrogen rapidly (open N systems) if decomposition is complete (Change and Handley 2000). The strong trend of $^{15}N$ enrichment we observed in deeper soil horizons relative to surface layers is likely because these temperate rainforests are very closed N systems (Hedin et al. 1995), with long N residence times (Martinelli et al. 1999) and few processes which strongly influence the fractionation of $^{15}N$. In deeper soils, gradual $^{15}N$ enrichment might result from gradual loss through DON leaching (Hogberg 1997), of a $^{15}N$ pool. While N loss in temperate rainforests is thought to be controlled largely through DON leaching (Lars et al. 1995) other mechanisms of N loss including denitrification, and plant uptake of isotopically light inorganic N ($NO_3^{2-}$,$NH^{4+}$) could be involved as well. More research on the processes controlling $^{15}N$ fractionation and N loss in temperate rainforest soils, in particular in hydric soils, is needed.

Why $^{15}N$ abundance increased with the aliphaticity of carbon in these soils is unclear. An obvious and plausible explanation is the concurrent humificiation (alteration) of the C and N pool through microbial activity. However, illuviation of DOM may be involved as well. Many soil solution studies (both field and laboratory) have shown a strong correlation (or coupling) between dissolved organic carbon and nitrogen (DOC and DON) in DOM over a range of concentration values in temperate forest ecosystems (Andersson et al. 1999, Michalzik et al. 2001). We observed a strong correlation between C and N in deeper soil horizons (Figure 3.7) which likely resulted from retention of DOM through illuviation. Below the B horizon, studies have found that DOC concentrations declined, and DOC and DON concentrations were poorly correlated (Andersson et al. 1999). It is unclear why DOC and DON concentrations are well correlated in DOM above the Bs horizon, and the chemical and physical associations of DOC and DON in solution are poorly understood. There is evidence to suggest that highly aliphatic soluble carbon becomes physically associated with proteinaceous nitrogen, although chemical association with other DON is likely to be involved (Zang et al. 2000).

A less clear trend of $^{13}C$ depletion, when plotted against increasing aliphatic/o-alkyl ratios (Figure 3.14) was observed than with $^{15}N$. $\delta^{13}C$ values decreased then increased somewhat with increasing aliphatic/o-alkyl ratios. The less clear trend of decrease in $\delta^{13}C$ followed an in increase, may be due to two distinct processes: humification and illuviation. We could find no other studies that examined isotope natural abundance ($\delta^{13}C$ and $\delta^{15}N$) or trends in C/N in relation to aliphatic/O-alkyl C ratios. However, the depletion of $^{13}C$ in mineral soil carbon has been reported (Volkoff and Cerri, 1987) and is attributed to the process of illuviation while enrichment of $^{13}C$ is thought to occur during loss and alteration of SOM in soil (Garten et al. 2000, Nadelhoffer and Fry 1988).

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# 4. Conclusion

In chapter 2, the idea put forth that podzolization can reduce soil water drainage in the absence of soil mixing disturbance was evaluated at the catchment scale along a natural windthrow disturbance sequence. Our results support the conclusion that catchment wide shifts in hydrologic behavior may result from podzolization, and that soil mixing from windthrow may reverse these effects. Supporting evidence includes hydrothermal, hydrochemical and hydrometric results. Because these data, in addition to hydrograph-separation modeling results, are consistent with one another, our conclusion is that rainwater contact and interaction with mineral soil materials increased with watershed disturbance. By using a sequence of four catchments with varying disturbance from windthrow, our inference is strengthened. The trend observed between these four catchments corresponds to the trend of windthrow disturbance between them. We cannot, however, assign cause and effect in this natural disturbance sequence study. The results are suggestive, and must be evaluated in the context of laboratory and pedon scale research or long-term watershed-scale experimental studies.

In Chapter 3, soil carbon dynamics were examined along a windthrow disturbance sequence in a mountainous temperate rainforest in southeast Alaska. Evidence was found that both illuviation and soil mixing from windthrow strongly influenced soil organic matter accumulation in mineral soil. Mobile organic carbon (MOC) transported in soil water accumulated in mineral horizons principally through adsorption to mineral particles and the extent of strong association (adsorption) with mineral particles increased in older, thicker illuvial horizons. In some of the older, thicker illuvial horizons, light (<1.65 g/ml) illuvial-like material found suggests that immobilization of MOC may have occurred through flocculation of metal bearing organic acids. The extent of humification (carbon-compound alteration) ranged from partial to strong in both organic and mineral soil horizons, and the degree of humification was correlated with increasing $^{15}N$ abundance, but not with changes in $^{13}C$ abundance. Forested catchments that experienced more intense soil mixing from windthrow had lower levels of strongly humified soil organic matter, and more in a partially decomposed particulate form. Processes leading to the formation of, and consequent concentrations and characteristics of, organic carbon in mineral soil strongly influences the hydrology, chemical properties of catchments, and the rate of nutrient cycling. The large and diverse stores of mineral soil C observed in these shallow mountain forest soils may be attributed to the unique, chronic wet cool conditions. Most temperate forest soils, even at high latitudes, experience a longer warm, dry season, in which microbial activity is favored, and considerable soil carbon can be lost.

Perhaps one of the most challenging yet often lacking aspects in ecological research is a discussion on the scope of inference of one's work. Under what range of conditions are the findings from a study applicable? High Island is a small 500 ha island in the middle of the Alexander Archipelago. How representative is this island of the Tongass National Forests –which spans 17 million ha on over 1000 islands? And, how representative is southeast Alaska of forest ecosystems in general? The body of literature on podzolization and windthrow is vast, and both processes are of global importance to forest ecosystems. Yet these processes occur under a range of climates, lithologies, and floral assemblages. In other forest ecosystems, the rate of decomposition or faunal soil mixing may be higher. Conversely, the rate of windthrow and illuviation may be lower in other places. So how applicable are these research findings to temperate forests in general?

The temperate rainforests biome of southeast Alaska is unique when compared with other forests in the world. Only two other regions have a somewhat similar climatic and forested ecosystem: Chile and New Zealand. Windthrow and illuviation occur at a very high rate in all these regions, owing to very strong recurrent windstorms, high rates of precipitation, productive forests, and the maritime climate. Southern Hemisphere coastal temperate rainforests contain a suite of biogeographically distinct flora and have a considerably different glacial and tectonic history to southeast Alaska. The region was not subject to glaciations during the last ice age (Alaback 1996). Earthquakes, volcanic eruptions and intense maritime windstorm activity are believed to play a more active role in temperate rainforests dynamics of south America (Alaback 1996).

The basalt parent material found on High Island is not the most common in the region of southeast Alaska (Alexander et al. 1993). Therefore it would be misleading to suggest that High Island is typical or representative of islands found in southeast Alaska. The influence of windthrow and illuviation on soil properties may be quite different on other lithologies. For example, soils developed from granitic parent material may have a more pronounced elluvial horizon formation, owing to the lower Al and Fe content in the rock. And bulk density of the weathered Si-rich material may be higher. Therefore soil carbon, and hydrologic differences may not be as apparent after windthrow on these parent materials. Limestone, such as that found on Prince of Whales may maintain a higher soil pH during illuviation, which could significantly reduce the quantity of carbon stored in Bh horizons during the illuvial process. Therefore the contrast between recently windthrown and undisturbed forests may be less apparent.

Also limiting, is our understanding of the role earthworms play in soil mixing. Many studies state that earthworm activity in mor humus is minimal, due to the acidity of the humus (Schaefer and Shaurmann 1990). The few earthworm studies which have been conducted in mor humus, such as Spiers et al (1980), report that mixing was restricted to upper, surface organic horizons. Another aspect of High Island research which must be considered, is the hydrologic response on zero order basins. The small catchment hydrology of High Island may be more sensitive to soil mixing processes. In larger watersheds, I would expect less of a measurable effect from windthrow, because of many more processes which become integrated at larger catchment scales, and stronger edaphic gradients with more complex hydrology. For example, groundwater flow dynamics likely plays a stronger role in larger catchments.

The reader should not be discouraged by these assessments and study limitations. Ecological complexity is not easily unraveled, or solved. And it is difficult to imagine how much we could expect to learn by studying a single plot of forest, or a small forested island when forests are distributed across so many lithic and climatic gradients. In short my conclusions are two fold 1) The findings from this study are most applicable to the coastal temperate rainforest biomes of the world, which are, by virtue of their climates, all windy, wet and productive ecosystems, and 2) The extent to which High Island findings might be applicable to forests developed on other parent materials is unknown. I would expect somewhat less of a contrast between windthrown and undisturbed forests on other lithologies, owing to higher bulk densities of those soils.

A number of exciting avenues are open for future research on windthrow and illuviation. These processes could be investigated at larger spatial scales, and on a range of parent materials. Methods to characterize, fractionate, and describe carbon pools could be considerably revised, and include direct polarization (DP) nuclear magnetic resonance (NMR), Fourier transformed infra red spectroscopy (FTIR), and Analytical pyrolysis techniques. Chemical and physical fractionation procedures could be combined to further describe the diverse carbon forms and their processes in southeast Alaska. Sequential density fractionations (Young and Spycher 1979) could provide further SOM separation, and help identify new carbon forms, and possibly provide insight into the processes that led to their formation. Nitrogen accumulations should be studied in these soils. Because nitrogen and carbon soil processes are closely related, it may only be possible to understand one by researching both.

Southeast Alaskan soils play an important role in the sequestration and storage of carbon from the atmosphere. More accurate annual fluxes, and total soil carbon pool sizes are needed. From a nutrient cycling standpoint, more research on processes governing tree growth in southeast Alaska is needed. While nitrogen is believed to be most limiting, effects of soil pH and soil saturation are unknown. In short, more research on basic biogeochemical processes of the temperate rainforest ecosystem is needed.

Research in southeast Alaska has been scant over the last 100 years, owing largely to its remoteness. This is not an easy environment in which to conduct research. However, this region is also one of the most intact natural productive forest ecosystems remaining on the planet. As such it should be valued and researched for the wealth of information contained in present day forests and soils.

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