THE INFLUENCE OF SOIL PHYSICOCHEMICAL PROPERTIES ON THE QUALITY AND QUANTITY OF WATER DISCHARGE IN SUBTROPICAL SMALL-ISLAND COASTAL FOREST CATCHMENT

(亜熱帯島嶼沿岸森林流域における流出水の質・量に及ぼす森林土壌の物理化学的特性の影響)

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March 2015

The influence of soil physicochemical properties on the quality and quantity of water discharge in subtropical small-island coastal forest catchment

By

W.M.C.J. Wijekoon

A dissertation submitted to the United Graduate School of Agriculture, Kagoshima University, Japan in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

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Approval of dissertation

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Abbreviations

In alphabetical order

AD	-	Acid detergent
ADF	-	Acid detergent fiber
ADL	-	Acid detergent lignin
AEM	-	Anion exchange membrane
BF	-	Baseflow
CEM	-	Cation exchange membrane
Ex	-	Exchangeable
IC	-	Ion chromatography
ICPE	-	Inductively coupled plasma – emission spectrometry
IEM	-	Ion exchange membrane
JMA	-	Japan meteorological agency
ND	-	Neutral detergent
NDF	-	Neutral detergent fiber
RF	-	Rainfall
SDM	-	Sessile drop method
SF	-	Stemflow
STF-H	-	Streamflow – High
STF-L	-	Stream flow - Low
SWR	-	Soil water repellency
TF	-	Throughfall
TOC	-	Total organic carbon
WDPT	-	Water drop penetration time

Abstract

Forests are among the main sources of water in the Ryukyu archipelago. Yet, little is known about the linkages between the physicochemical aspects of the forest soil and the properties of water being delivered. Surrounding sea and frequent typhoons also influence the hydrology. This study aims to understand those linkages by holistically studying the related processes that water is undergoing, since its entry into the forest until the discharge. Main experimental plots were located in a catchment in northern Okinawa Island.

Water quality was assessed in terms of major ions, pH and conductivity. Continuous sampling was done for one year starting from February 2013. The quality and quantity of rainfall (RF), stemflow (SF) and throughfall (TF), processes through which water enters into the soil, were studied in each plot. Influencing the water movement in the soil, soil water repellency (SWR) and soil aggregation were studied. Litter decomposition dynamics were evaluated by an incubation experiment. Potential soil solute movement was evaluated with undisturbed soil columns, soil solution extracts and ion exchange membranes. Water discharge was measured with a broad-crested weir at the catchment outlet, where the quality of baseflow and two arbitrary levels of stormflow were studied.

Findings showed that Chloride, sodium and sulfate were the dominant ions of the influx (SF+TF). Although it indicates a possible influence of sea salts, the ratio of Na^+ to Cl^- is lower than that of the seawater. The influence of vegetation on TF and SF quality is not clearly visible and so was the case of anthropogenic inputs. Further, the influx has higher K^+ and Ca^{2+} content compared to seawater. An exchange of K^+, Ca^{2+} and NO_3^- within the canopy might have occurred.

Potential SWR was found in the catchment at varying levels and is not likely to cause significant influence on the water infiltration under regular moisture regime. However, long dry

spells may induce severe SWR levels. In the soil aggregates, the highest carbon content was observed in association with clay and silt fractions. Therefore, the topsoil having clay and clay-loam texture indicates favorable conditions for soil aggregation and hence, facilitating water movement through the surface soil layers. Higher organic matter decomposition rates explain an active biochemical transformation, promoting organo-mineral interactions. Soil column evaluations confirm the near-surface and preferential pathways of water in the shallow soil. Ion exchange membranes were found to qualitatively predict the composition of the soil solution when it is about to start flowing.

Indicating a possible influence of the sea salts, the ions of the litter leachate, topsoil and subsoil are also dominated by Cl^-, Na^+ and SO_4^{2-}. Litter leachate and topsoil have comparatively higher amounts of Ca^{2+}, K^+ and Mg^{2+}; the litter decomposition products could be the main source. The efflux (discharge) has relatively high Ca^{2+} and Mg^{2+} and low K^+ and Cl^- percentage compared to the influx. Therefore, K^+ seems to be subjected to biotic retention while Ca^{2+} is being released from soil to the streamwater. The Mg^{2+} content across the other phases remains more or less constant. Inconspicuous dilution effect during storm flow also indicates higher surface runoff during storms. Overall, the quality of the streamwater delivered by small-island coastal forests was found to be determined mainly by the composition of the water influx; the contribution of soil is limited to certain ions. The river discharge response to rain events is comparatively higher in the present study area than the catchments with similar geology. The total runoff accounts for nearly 36% of the precipitation, an amount on par with the findings related to nearby catchments under similar rainfall conditions.

Chapter 1 General introduction

1.1. A glance at the research area – the life and the challenges

The Ryukyu archipelago, currently known as the Okinawa prefecture of southern Japan is well known for the richness in life *i.e.* the richness in culture and the environment. Despite its small size, for centuries, the Ryukyu kingdom has had cultural and trade ties with the neighboring countries such as China, Korea, and Taiwan. Although the battles during the Second World War nearly leveled Okinawa to the ground, the community was able to recuperate and treasure the rich cultural legacy inherited from their ancestors. Bounded by the East China Sea and the vast Pacific Ocean, subtropical islands of Okinawa are blessed with diverse marine environment. Tourists enjoy the warm and crystal-clear waters full of captivating marine life. Although the land area is limited in most of the islands of Okinawa, the forests are well known for the high species diversity in terms of plant and animal life. The richness of life is a result of a delicate balance between the culture and nature. However, due to the increasing human need for water, land and shelter, this balance is often being challenged. The present research focuses on the main island of Okinawa (*Okinawa honto*) hereinafter referred to as Okinawa.

The classification of islands based on their size has been done by various authors and various fora. The necessity for such classifications arise due to the existence of characteristic features of the islands with different sizes, which distinguish them from the rest of the land masses. The criteria for defining small islands is considered not solid due to various reasons. However, the islands with a surface area less than 2000 km^2 and width not exceeding 10 km at any point are considered as small islands in general (Falkland, 1991). Thousands of islands all around the world can be categorized into this category. In addition to the scale, various other factors such as geography are also responsible for the determination of specific characteristics of the islands. Okinawa fits well into the small island category and also belongs to the subtropical subset. Hawaii, the Bahamas and Canary Islands are some of the comparable islands in terms of size, in the subtropical region.

When the small islands environments in general are compared with the rest of the larger land masses, the needs of the population are not considerably different. However, the capacity of the small islands to cater the increasing demand is comparatively low due to the isolation, fragile natural resources and proneness to natural disasters *etc.* (Overmars & Gottlieb, 2009). In addition to the lack of capacity, small islands feel the consequences of the global climate change more than the other land masses. As examples, long dry spells, unusually heavy rains and sea level rise can be pointed out. From the socio-economic perspective, the populations of the small islands are increasing and the resource exhaustive industries such as tourism are also on the rise (Falkland, 1991). These factors exert a tremendous pressure on the natural resources of the small islands. Therefore, proper management of natural resources has become a must and a challenge.

As far as the water is concerned, most of the small islands have only few options. Almost all the natural water comes in as the precipitation. However, the capacity of retaining the water is limited in most cases due to various reasons. High permeability or conversely the impermeability of the underlying rocks which reduces water storage and, small area of the watersheds having low capacity to moderate the stream flow levels have been identified as the main causes. In addition, seawater intrusion into aquifers is also not rare in the small islands and, as a result, the stored water become unusable (Falkland, 1991; Miwa *et al.*, 1988; Overmars & Gottlieb, 2009). Often, the water supply or importation from the other areas is not an economically and technically viable solution. Desalination of seawater and purification and recycling of water still suffers from technological bottlenecks.

These common problems identified in the small island environments have been observed in Okinawa at various extents. According to Cederstrom (1947) the streams have to be dammed to store water to be used in dry periods and wells in the Shimajiri formation and the alluvium yield a small amount of water. Further, Nakagawa *et al.* (2000) state that the seawater intrusion into the groundwater occurs when the water is extensively harvested. Meanwhile, short length and fast flow rates are characteristic to the rivers of Okinawa. The mean area of a catchment in Okinawa is approximately 5.4 km^2 and this value is comparatively small in terms of water storage and hence, moderation of river water flow. Therefore, the rainwater is quickly flowing to the surrounding sea and large fluctuations of the water levels of the rivers can be seen (Miwa *et al.*, 1988; Yamashita *et al.*, 2002). Although Okinawa Main Island receives relatively high annual rainfall, these conditions cause quick loss of water making water management strategies even more challenging.

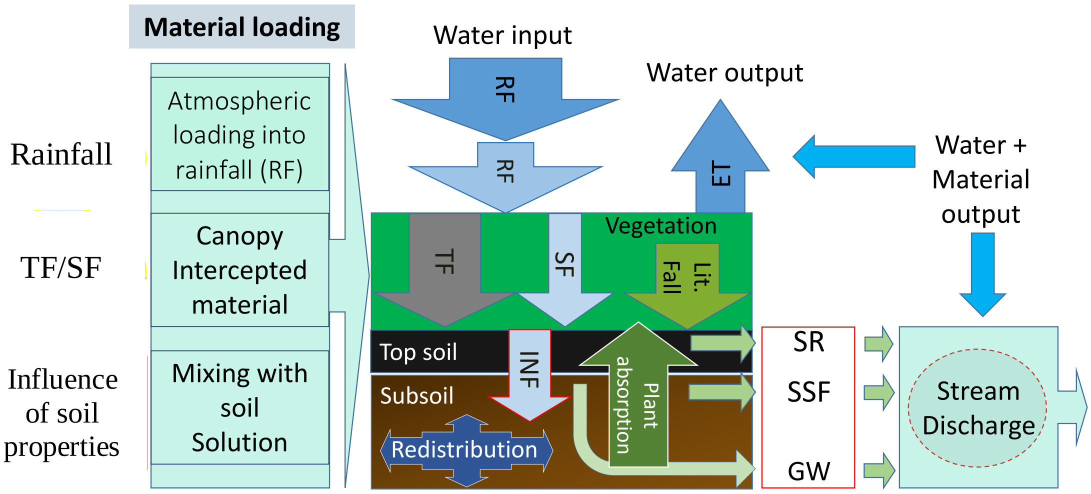
At present, most of the water sources of Okinawa are located in the mountainous areas of the northern region. The catchments are comprised mainly of natural and old secondary forests (Ito, 1997) and play a major role in the hydrologic cycle in the area. Therefore, most of the water management practices have to be conducted in these forested areas. Due to the limited availability of land and the high bio diversity, construction of dams and other structures to store water is a huge challenge to the water managing agencies. Despite the disadvantages, several dams have been constructed in the northern part of the main island of Okinawa. To keep up with the balance in the natural environment, various strategies have been deployed to offset the negative effects of the dam constructions (Yamashita *et al.*, 2002). To reduce the effects on the aboveground environment and prevent seawater intrusion into the groundwater, underground dams have also been built in various parts of Okinawa islands (Sathoshi Ishida *et al.*, 2003; Satoshi Ishida *et al.*, 2011). Therefore, management of water resources in the islands of Okinawa is of great importance, a top priority and should be precisely done. Water management can be viewed from various perspectives. The quantity and the quality of water is important in terms of human consumption perspective. In addition, the hydrological aspects such as river flow regimes and groundwater storage can be viewed from the management of infrastructure, disaster mitigation and environmental conservation perspectives. Therefore, a sound understanding of water resources is necessary for realistic and efficient management strategies.

The forests of Okinawa and its surrounding islands are worth observing from a different angle than considering them as yet another system of coastal forests. The micro-climate inside the forests changes significantly within few hundred meters when moving away from the coast and, with the increase in elevation by as little as 100 m. For instance, the forests above 100 m altitude are drenched with the clouds for a significant period of the day (Kubota *et al.*, 2005). As a result, the forest exhibits the characteristics of the cloud forests. Cloud forests are usually seen in much higher altitudes and the only low altitude region where cloud forests occur is mountain islands (Bruijnzeel & Proctor, 1995). Due to the undulating terrain, various parts of the forest are exposed to the sunlight and wind at varying levels resulting in differences in vegetation and biological processes. The monsoonal winds and the typhoons regularly influence the canopy characteristics (Kubota *et al.*, 2005). The influence of the ocean is inevitable in the island environments. As many studies have pointed out, the influence of the seawater on the chemistry of rainfall and river discharge is substantial (will be discussed in detail under the next section). Surrounded by Pacific Ocean and East China Sea, the climate of Okinawa is almost entirely depends on the ocean as there are no land masses nearby. Heavy rainfall usually can be expected in high elevation islands such as Okinawa because the mountains lift the moist air blowing from the ocean side. Furthermore, Kuroshio Current, which has been recognized as one of the warmest currents in the world, moves along the Ryukyu archipelago (Lee & Chao, 2003). As a result, the forests show the characteristics of the rainforests. Rainforest environments are rare in the subtropical regions and hence, the coastal forests of Okinawa hold a unique position in the subtropical biome. The forests of islands of Okinawa are comparable to the tropical rainforests in terms of tree species diversity (Ito, 1997). Further, the forests are mainly comprised of evergreen broad-leaved forests which are usually not found in the main island of Japan. Warm humid environment facilitates faster biochemical transformations. Therefore, litter decomposition, nutrient cycling and rock and mineral weathering are comparatively high than those of main island of Japan.

In spite of the unique features of the coastal forests of Okinawa, certain aspects of the hydrologic cycle still remain to be investigated. Present study, therefore, focuses on obtaining field level data related to the underlying processes of the hydrologic cycle in the coastal forest watersheds in Okinawa to assist effective water and forest management.

1.2. Research problem and aim of the study

The relationship between the forests and the water resources was known by the mankind for centuries; according to Nair (2004), even the people of the old civilizations that existed in India several centuries ago had been aware of it. Although it sounds simple, a glimpse into the core of this relationship reveals that it is extremely diverse due to the variability of the influential factors such as the type of vegetation, type of soil, and the topography. When the distribution of the forests across varying geographical contexts is considered, the number of combinations of the influential factors is uncountable. Therefore, plenty of information still remains to be understood. It is evident that certain components of the water continuum in the coastal forests in the islands of subtropical biome still remains to be investigated, including the linkages between the main phases of the water continuum. These main phases include the entry of water as precipitation, passage through the vegetation (throughfall and stemflow), passage though the soil, and discharge. These four main phases are summarized in Figure 1 along with the other related hydrological processes. The most fascinating fact about all these components is their interdependence. Behind this fascination, there lies the fact that they cannot be examined in isolation. Therefore, many researchers attempt to use models, especially in soil and water related studies, even though the field-level research to verify the models are scarce (Jury & Flühler, 1992). Hence, there is a huge need for field level data. A holistic approach is thus necessary to obtain the basic data to understand the effects of these factors on the water quality and quantity.



TF- Throughfall; **SF** – Stemflow; **ET** – Evapotranspiration; **INF** – Infiltration; SSF – Subsurface flow; GW - Groundwater

Figure 1: Major hydrological processes in a forest catchment

As mentioned in the previous section, islands of Okinawa possess special features compared to the other small islands in the world. Therefore focusing especially on the target area, *i.e.* Okinawa, various researchers have investigated some of the aforementioned phases at various extents. In their investigations on the chemistry of precipitation in Okinawa, Sakihama *et al.* (2008) states that a small number of studies have been conducted in Okinawa to assess the rainwater quality. The existing research include several studies on acid rains (Itomine & Hirose, 2006), chemistry of precipitation (Agata *et al.*, 2006; Vuai & Tokuyama, 2011) and the influence of typhoons on rainwater quality (Sakihama & Tokuyama, 2005). The results of these research highlight the influence of the sea salts as well as the air masses moving from the surrounding regions, on the quality of the precipitation. Studies on the second phase of the water continuum, *i.e.* the passage through the vegetation, have been conducted as throughfall and stemflow or in combination (Koki *et al.*, 1992; Sunagawa & Hirose, 2010; Xu *et al.*, 2005). Koki *et al.* (1991) has conducted a chemical assessment of the througfall along with the water quality of the stream. All these studies point out the closeness of the forests to the sea and, its influence on the water quality. They report high concentrations of the ions originated from sea salts, in the water. Studies on the streamwater include assessments of water chemistry (Ishiki *et al.*, 2008; Takashima *et al.*, 2007; Toda *et al.*, 2000) and pollutant transport (Higa *et al.*, 2001). The data used in most of the studies are based on short term or point observations and, water quality of different flow regimes are not discussed adequately. Considerable number of published and unpublished research are also found on the sediment transport in the rivers and soil erosion even though it is out of the scope of the this study.

Tokuyama & Hiroshi (1978) have conducted a study on the chemical fluxes of the rivers in Okinawa, with a discussion on possible influences of the soils and rocks. Beside the aforementioned research, studies assessing the contribution of soils on the determination of streamwater quality and quantity in Okinawa, were not found.

Various research have shown that the soil chemistry plays a major role in maintaining the water quality and quantity (Neary *et al.*, 2009). Most of the assessments of soil physicochemical properties and related processes in the forest soil have been conducted mainly to understand the nutrient dynamics. Only a limited number of research linking soil chemistry and water quality are currently available (Boy *et al.*, 2008; Burt & Pinay, 2005; Burt, 1979). The research conducted by Boy *et al.* (2008) points out that the near-surface flows, in the mountainous forests having steep slopes, play a major role in the nutrient cycling both in and out of the system. They further state that the behavior of different ions and substances in the soil solution and the water discharged from a catchment, are following their own ways rather than following a general pattern. Burt (1979) shows that different processes govern the solute removal from the soils of different parts of catchments.

The soil processes such as litter decomposition and subsequent nutrient release, nutrient and organic matter fixation (as organo-mineral linkages), encapsulation of soil mineral fraction by organic matter and plant absorption of nutrients are also capable of influencing the soil solution directly or indirectly. Soil aggregation, a physicochemical process occurring as a result of the interaction between soil and organic matter, directly influence the soil structure and hence, the movement of water in the soil. Aggregates also reduce the runoff and nutrient release and hence, nutrient movement (Belnap, 2006). Organic matter decomposition and the other related processes are complex in nature due to complex interactions between controlling factors and the existence of large number of combinations of controlling factors. Only a handful of studies can be found under the forest soil in Okinawa about the forest litter decomposition (Alhamd *et al.*, 2004).

The encapsulation of soil minerals by organic matter pave the way to the development of the soil water repellency (SWR), another physicochemical phenomenon occurring in the soil (Doerr *et al.*, 2000; Mataix-Solera *et al.*, 2007). Emergence of preferential flow paths, uneven and/or reduced water storage in the soil column, and the occurrence of Hortonian overland flow are some of the effects of SWR on hydrologic cycle (DeBano & Rice, 1973; Doerr & Moody, 2004; Doerr *et al.*, 2000; Kobayashi *et al.*, 2002; Nagahama *et al.*, 2001). Many research on the soil water repellency have been conducted in the forests of main island of Japan (Ide *et al.*, 2011; Kajiura *et al.*, 2010; Kobayashi & Matsui, 2006; Kobayashi, 2007; Kobayashi *et al.*, 1996). However, comprehensive studies on the existence of soil water repellency in the subtropical broad-leaved coastal forests are scarce.

Soil is being considered as a black box due to its ability to hide its secrets about what it is doing with the inputs to produce the output (Burt & Pinay, 2005). Despite the efforts of many researchers to open this black box, its secrets still remain hard to uncover. Therefore, one prospective approach is to keep attempting to open the black box while investigating the input and the output and examine what is occurring inside the box. The present research was planned based on this approach.

Therefore, the aim of this study is to understand the influence of shallow-soil physicochemical properties on the quality and quantity of water discharge in subtropical coastal forest catchment by investigating the interrelationship between water and soil properties from the water entry into the soil, movement throughout the soil column and water discharge.

Consequently, as the entry of water and nutrients into the forest system, the quality and quantity of the rainfall, stemflow and throughfall will be studied. Soil water repellency, soil aggregation and litter decomposition dynamics will be assessed as physicochemical properties affecting the water movement in the soil system. The properties of the moving soil solution will also be investigated to understand the direct influence of soil on the water moving though the soil column. The qualitative and quantitative characteristics of the streamwater will be assessed as the efflux of nutrients and water from the forest system.

1.3. Experimental approach

As stated above, there are three main divisions in the research. The experiments were divided accordingly (Figure 2). Various studies have pointed out the influence of surrounding sea on the determination of water quality of the research site. Therefore, an assessment of the entry of water into the soil should consider the changes in water quality since the raindrops starts to fall through the atmosphere, as indicated in Figure 1. Hence, the quantity and quality of rainfall and subsequent throughfall and stemflow were studied; the sum of the latter was considered as the influx of nutrients to the forest system. The processes related to the entry of water in to the forest floor are discussed under Chapter 2.

As the quantity of water actually entering the soil without being subjected to surface runoff is a major factor determining the quantity as well as the quality of water being discharged, the soil water repellency of the catchment was assessed as a major phenomenon which is determined by the physicochemical properties of the soil (Section 3.3).

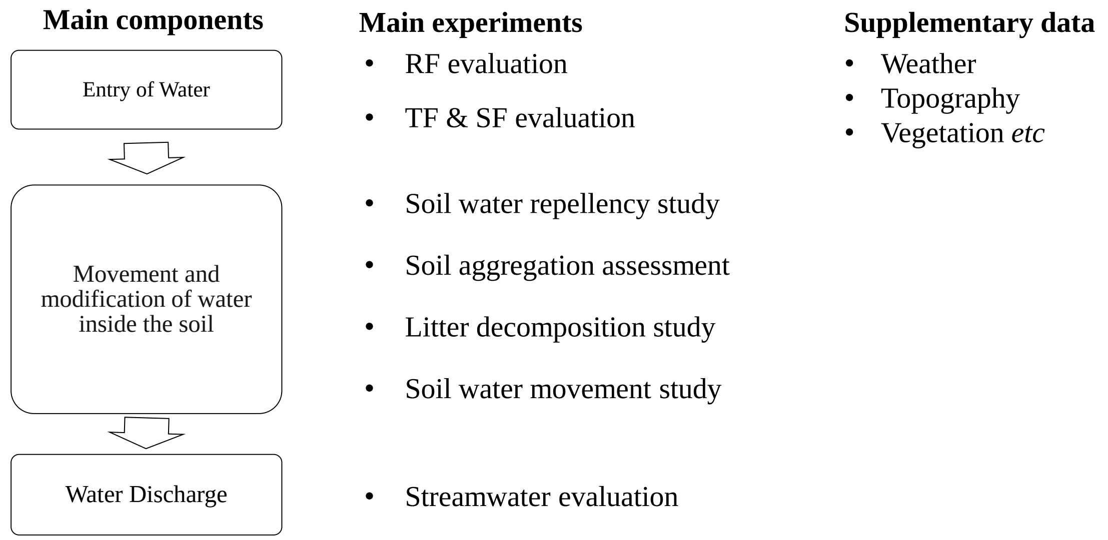


Figure 2: Experimental approach

The litter decomposition pattern was assessed by using a laboratory incubation. As the information about the litter decomposition process of the broad-leaved forests of subtropical biome are scarce, the aim of this experiment was to understand the characteristics of the litter decomposition process including decomposition pattern and the controlling factors (Section 3.5). Further, the organo-mineral interactions (mainly the aggregation), of the soil was also studied in parallel to the litter decomposition experiment. These data were compared with a nearby mangrove ecosystem to understand the carbon dynamics of the upland forest and the mangrove in the subtropical context (Section 3.4).

The study focuses mainly on soil water movement in shallow soils. Potential soil nutrient movement was assessed using conventional methods which included undisturbed column extraction and saturation extraction (J D MacDonald *et al.*, 2004; Schlotter *et al.*, 2012). In addition, Ion Exchange Membranes (IEM) were also used to assess the soil solute movement as several authors have reported that IEM technique as a convenient method for such purposes (Li *et al.*, 1993; Pampolino, 2000). Results were compared with the findings from conventional methods. Further, the soil water movement in the shallow soil was examined with modified hillslope infiltrometer (Mendoza & Steenhuis, 2002). Soil physical and chemical properties were also assessed under this experiment (Chapter 4).

The streamwater evaluation was done near the lower boundary of the catchment. The water discharge of the catchment was assessed using a broad-crested weir. The water quality of baseflow and two arbitrarily selected storm flow levels were assessed from the water samples collected upstream of the weir (Chapter 5).

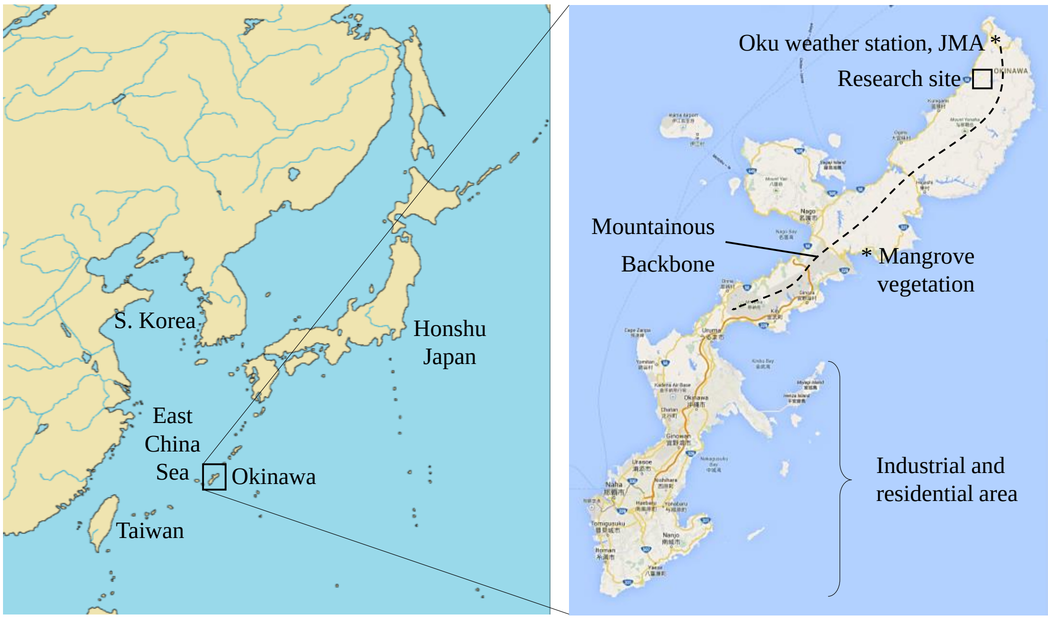
Rainfall data were obtained from onsite recorders. Long-term rainfall data and other climatic data were obtained from the meteorological stations of Japan Meteorological Agency (JMA) in the vicinity of the experimental site. Terrain analysis was done with a digital elevation model (10-m resolution) developed by the Geospatial Information Authority of Japan. Vegetation data were obtained from the secondary sources and filed surveys where necessary.

1.4. The study site

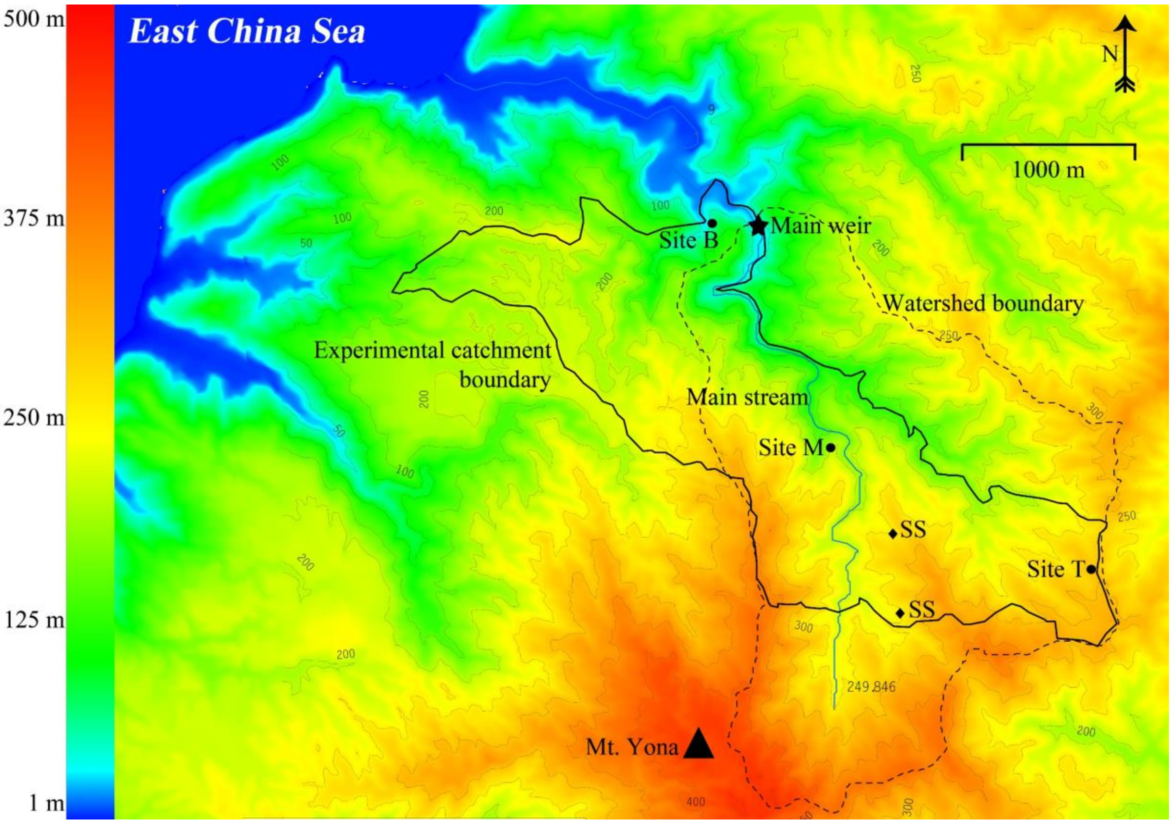
1.4.1. Geography, topography and vegetation

The site is a 318 ha experimental forest catchment of the University of the Ryukyus located in the northern part of the Okinawa main island (Figure 3). Isolated from the industrial zone of the island and the other industrial parts of Japan and other countries, this site is an ideal location for water quality related studies. Okinawa can be categorized under small-island category as its area (1200 km^2) is below the upper limit of the small island category explained by Falkland (1991). Furthermore, the northern part of the island can be categorized under high-island category while the part of the southern area is showing characteristics of low islands (Conry & Cannarella, 2010). The topography is characterized by a mountainous backbone with undulating to rolling terrain (slope range 25°-45°) where short and narrow streams extending towards the central backbone (Simonson, 1994). The highest peak in the mountain ridge is mount Yona with a height nearly 500 m above the sea level. Due to the elongated shape of the island, no location in the forest has a distance exceeding 5 km from the sea.

The northern area is considered a major source of water (Yamashita *et al.*, 2002). Most of the area of this region is covered with subtropical evergreen broad-leaved forests. These forests are considered as rainforests of the subtropical regions (Japan Wildlife Research Center, n.d.). The natural and secondary forests altogether occupy 85% of the catchment while the rest is unmanaged manmade plantations (Hirata, 1994). The present catchment possesses typical features of the forests in the northern Okinawa. Okinawan forests are mostly secondary forests and can be categorized into young and old secondary forests. Natural forests are also found as patches in certain parts of the forest. Old secondary forests are reported to be more than 50 years old (Ito, 1997). Most of the secondary forests are not subjected to management practices. Old secondary forests in the conservation areas are considered as intact forests. Relatively low species diversity has been reported in the young secondary forests and the stratification was also found to be lacking. Secondary forests are dominated with *Castanopsis sieboldii (ibid)*. Intrusions of naturally occurring plant species were clearly visible in all the plantation forests in the study area. The forests which are 100 m above sea level are often getting drenched with low-lying clouds. Therefore, forests are mostly moist and possess certain features of the cloud forests (Kubota *et al.*, 2005).



(a) Geography of Okinawa and main features of Okinawa Island along with experimental sites (Source: Google maps)

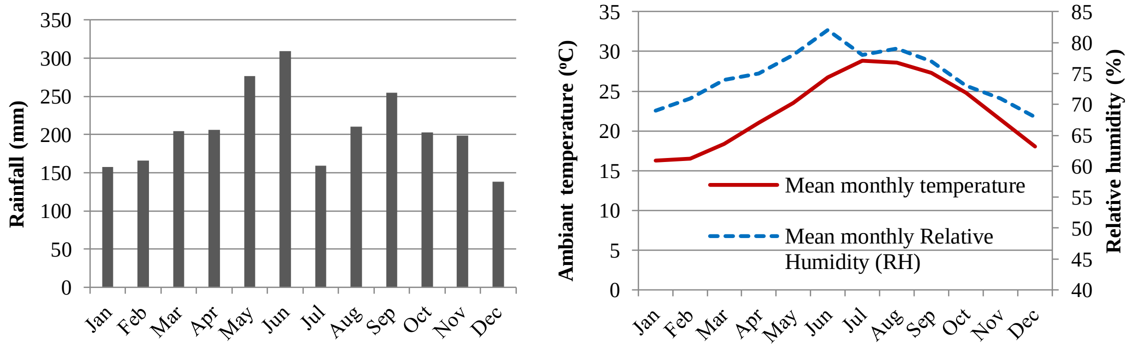


(b) Layout of the experimental plots

Figure 3: Layout of the research sites.
(SS – additional soil sampling sites)

1.4.2. Climate

Climatic parameters calculated from meteorological data from 1981 to 2010 shows that the research site receives an average rainfall of 2500 mm per year, which is comparatively higher than the 2000 mm average of Okinawa. Higher rainfall in the northern regions is a result of the occurrence of orographic rainfall. Seasonality of rainfall can be observed in Okinawa with rainy season occurring in the months of May or June. The lowest rainfall is received during the month of December with an average of 138 mm (Figure 4). The average annual temperature is 20.7°C with January being the coldest with 14.5°C while July being the warmest with 26.7°C (Data - Oku weather station of JMA located approximately 11 km north of the study site). Typhoons of various intensities strike the island several times a year during the summer. Strong winds during the typhoons cause serious damage to the forest and generally bring torrential rains. Monsoon winds in the winter has also been recognized as an influential factor in shaping the forest canopies in to a uniform layer (Fujii *et al.*, 2009). The wind circulation pattern in each season varies and, based on the direction of the wind, the material input could also vary (Lee & Chao, 2003).



(a) (b)

Figure 4: Climatic features of the area
(a) Mean monthly rainfall and (b) mean monthly air temperature and relative humidity around the study area

1.4.3. Geology and soil

The chain islands of southernmost Japan are continental islands, and were formed as a result of the formation of Okinawa trough and the tectonic shifting (Japan Wildlife Research

Center, n.d.). Nicol *et al.* (1957) described the geology of the northern Okinawa as highly deformed, metamorphosed limestone, sandstone, shale, and volcanic rock. Compared to the soils of the warm temperate parts of the main island of Japan, soils of Okinawa have higher degree of weathering. Kaolinite has been found to be the most abundant mineral.

The dominant soil groups in the area are red soils and yellow soils (Yamamori, 1994), corresponding to Udults or Udepts in the USDA soil taxonomy (Kubotera, 2006). The soil is characterized by comparatively low surface activity (Hirai *et al.*, 1991). Parent material is reported to be Paleozoic phyllites or sandstone (Hirai *et al.*, 1991; Simonson, 1994).

1.4.4. Sampling site selection

During the sampling site selection, distance from the sea and the altitude were among the major considerations. However, sites with identical features, such as maturity and forest structure, could not be selected due to limitations in the accessibility for regular sampling and the non-availability in the required areas. Three main experimental sites were selected within the catchment with elevations 295 m, 180 m and 55 m, and named as Site T, M and B respectively (Figure 3 - b). Although the vegetation of the three sites varied in maturity, none of them were subjected to management practices for over 30 years. Therefore, it was assumed that the differences could be considered minimal during the comparisons. Due to their position on exposed ridges, Site T and B are often affected by the stress from high wind, compared to site M. In each site, RF, SF, TF and soil properties were assessed. Additional soil sampling sites are marked with SS in the Figure 3-b. Stream discharge and its water quality were measured at the main weir. Mangrove soil sampling site was selected in the Oura river towards the southeast side of the main experimental site (Figure 3- a). This site is comprised of an old stand of mangroves typical to Okinawa.

Chapter 2 Entry of water and nutrients into the forest

2.1. Introduction

In the hydrologic cycle, especially in the forest environments, the entry of water in to the forest and then to the soil system is mainly due to the precipitation. Depending on the climatic zone, the forms of precipitation may differ. In the warm tropics, the liquid forms of precipitation such as rainfall accounts for almost all the precipitation while in temperate regions, liquid as well as solid forms of precipitation such as snowfall also may occur. In this study, only the rainfall is considered as the main form of precipitation. The quality of the rainwater is affected by the constituents of the atmosphere through which the water passes through (Polkowska *et al.*, 2005; Sakihama *et al.*, 2008). The constituents in the atmosphere change depending on natural and man-made phenomena such as volcanos and industrial emissions respectively. Changes in the wind circulation pattern redistribute the materials suspended in the atmosphere. Therefore, the geography and topography of the area play a major role in the determination of the rainwater quality.

It is a well-known fact that the tropical belt receives the highest amount of rainfall compared to the other parts of the world. As a subtropical island, Okinawa also receives a comparable amount of rainfall distributed throughout the year. Although the average annual rainfall of the island is around 2000 mm, the northern region receives and average of 2500 mm per annum (Data – JMA, 1980-2010). Typhoons, a common phenomenon in Okinawa has found to contribute immensely to the total rainfall as well as the material input to the ground (Sakihama & Tokuyama, 2005). The fact that Okinawa is surrounded by the ocean, is considered to be a decisive factor in the determination of the quality of the precipitation (Agata *et al.*, 2006; Sakihama & Tokuyama, 2005; Sakihama *et al.*, 2008; Xu *et al.*, 2005). In addition, the anthropogenic substances produced in the neighboring landmasses are also contributing to the quality of the precipitation (Sakihama *et al.*, 2008).

Throughfall and stemflow define the path of rainwater through the forest until it reaches the ground. Numerous research have shown that the water quality changes considerably along these paths. Several studies in Okinawa have shown that typhoons as well as surrounding sea play a major role in shaping the chemistry of throughfall and stemflow (Xu *et al.*, 2005). Previous studies suggest varying levels of throughfall and stemflow in the research site. Sunagawa and Hirose (2010) reported that throughfall and stemflow account for 45.2% and 3.7% of the precipitation respectively. However, Xu *et al.* (2005) reports a figure as high as 30.9% of stemflow. This variability could be attributed to various factors such as vegetation, influence of typhoons, characteristics of the rainfall, topography and techniques of measurement.

2.2. Specific objectives

The specific objectives of this study are to:

a. Assess the quality and quantity of the water input to the soil system

b. Understand the spatial and temporal variation of the input water quality and quantity

2.3. Materials and methods

Rainfall collection

RF collectors were comprised of 18-l polyethylene cans fitted with a funnel (20 cm in diameter) by using a 1-m long vertical PVC tube (Figure 5). A ball valve was also included to prevent evaporation. The can was covered with heat insulating sheet to reduce heating. One collector was placed in each site. The placement of the collector along with the SF and TF collectors is shown in Figure 6.

(a) Rainfall collector

(b) Throughfall collector

(c) Stemflow collector

(d) Stemflow gauge attached to a collector

Figure 5: Water samplers

Throughfall collection

TF was collected by using five PVC gutters (length-1.8 m, width-0.11 m, and cross section - semicircular) mounted on two plastic coated metal poles. Water was collected in 45 l cans and the total capturing area of each site was approximately 1 m^2 (Figure 5). The layout of the collectors is shown in Figure 6.

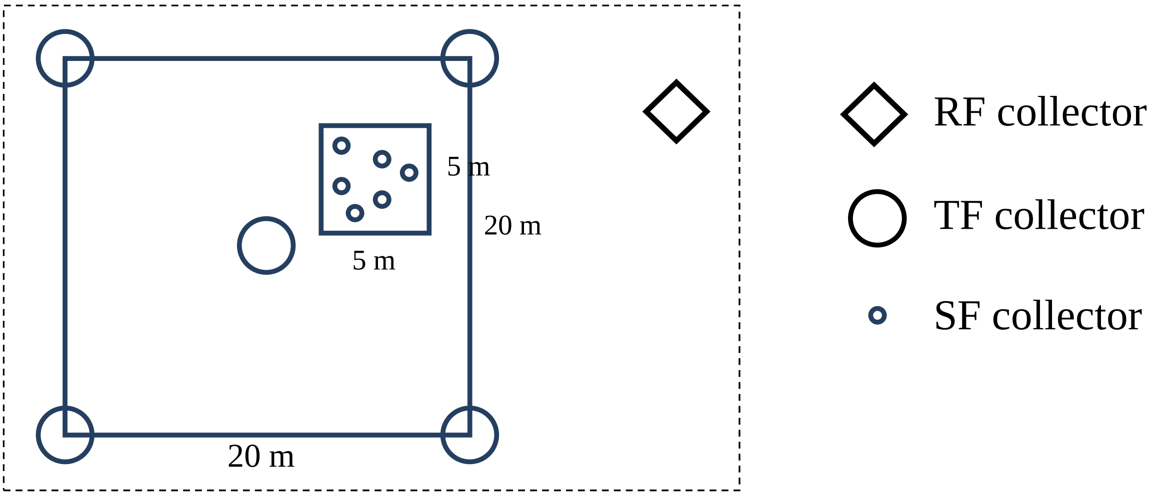


Figure 6: Layout of the Rainfall (RF), Stemflow (SF) and Throuhgflow (TF) collection setup

Stemflow collection

In each site, the SF plot was located inside the TF plot. SF was collected by using six 45 l cans connected to polyethylene collars attached to six trees. Thin felt sheet was attached to the outer edge of the collar to prevent water overflow and reduce the entry of TF. The distance from the tree bark to the edge of the collar was approximately 1 cm at the bottom (Figure 5). Trees inside the 5 × 5 m plot was divided into three categories based on the DBH (large, medium and small) excluding the trees with diameter less than 5 cm. Collars were attached to two trees from each category.

Sample collection and analysis

RF, SF and TF sampling was done from March 2013 to March 2014. Samples were collected every two-week interval. However, sampling interval changed when necessary to reduce possible overflow situations and depending on the availability. Samples were collected in polypropylene bottles and brought to the laboratory as a batch. Water was filtered, initially with qualitative filter paper. Then pH and EC was measured. Subsamples were filtered with 45 µm membrane filters to be analyzed for major ions. Cations were analyzed by using Inductively Coupled Plasma-Emission spectrophotometer (ICPE) (Shimadzu ICPE-9000) and anions were analyzed by using ion chromatography (Dionex ICS-1600).

2.4. Results and discussion

Climate characteristics of the area during the sampling period

Although the average annual rainfall of the area is 2500 mm, onsite measurements indicate a relatively low rainfall of 2030.5 mm during the sampling period. Conspicuously low rainfall figures can be seen from June to September (Figure 7). However, general wind direction resembled the normal pattern explained by (Lee & Chao, 2003). Eight influential typhoons were

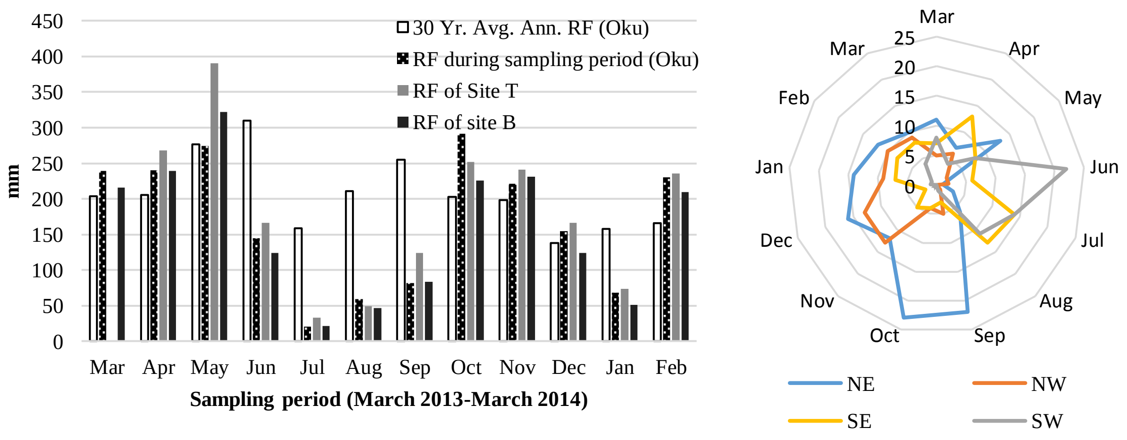


Figure 7: Rainfall (left) and wind pattern (right) during the sampling period.
The most observed wind direction in each month was expressed as a count and plotted in the diagram.

identified during the sampling period. Although typhoons usually bring heavy rains, some typhoons during the sampling period (especially during July and August) had brought markedly small amount of rainfall (Figure 8).

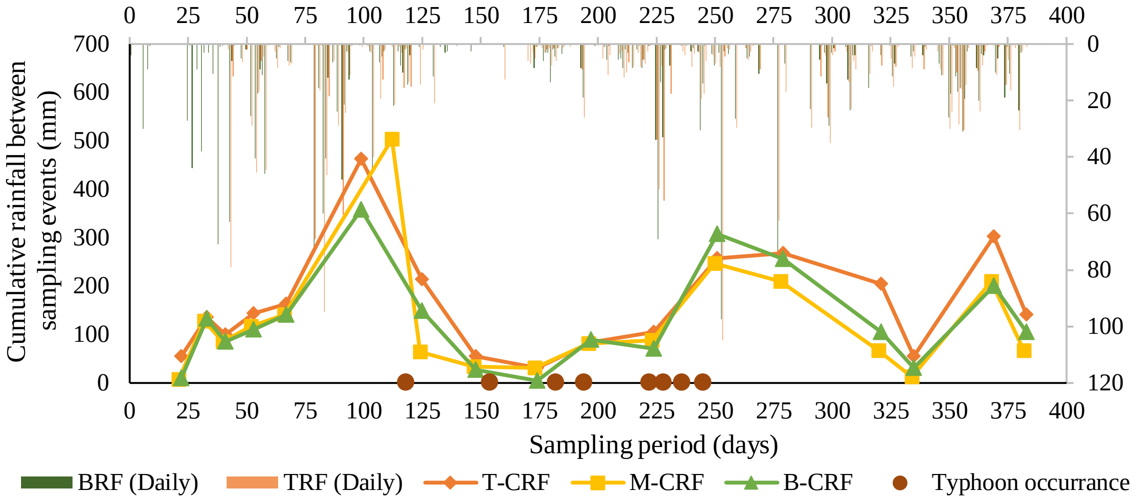


Figure 8: Daily rainfall and cumulative rainfall of each site and the occurrence of typhoons
BRF – Rainfall at site B, TRF – Rainfall at site T, CRF – Cumulative rainfall

Rainfall, stemflow and throughfall characteristics

Figure 8 summarizes the distribution of the cumulative rainfall for each sampling event, rainfall and the occurrence of typhoons during the sampling period. Slight differences in the quantity of the rainfall could be observed among the three sites. In terms of the cumulative rainfall for the sampling period, site T often had higher values compared to the other two sites that had received nearly similar amount of rainfall. However, the rainfall pattern of all the sites were similar in pattern.

Cumulative TF and SF along with cumulative rainfall of each site are summarized in Figure 9. The TF as a percentage to the rainfall in sites T, M and B are 49, 66 and 63 respectively. SF of sites T, M and B are 18.3%, 8.1% and 7.2% respectively. Similar studies conducted in the same forest had obtained varying results, especially in terms of stemflow (M. Kinjo & Terazono, 1994; Sunagawa & Hirose, 2010; Xu *et al.*, 2005). Present findings lie in between these values.

Stemflow values tend to vary depending on the wind pattern, topography and the maturity and type of vegetation, *etc*. High variation of topography and a considerable variation in canopy characteristics can be observed in the experimental catchment. The variation of the canopy shape could be a result of different exposure to wind caused by topographic variation. As the previous studies do not specify the exact locations of their experiments, further comparisons are difficult.

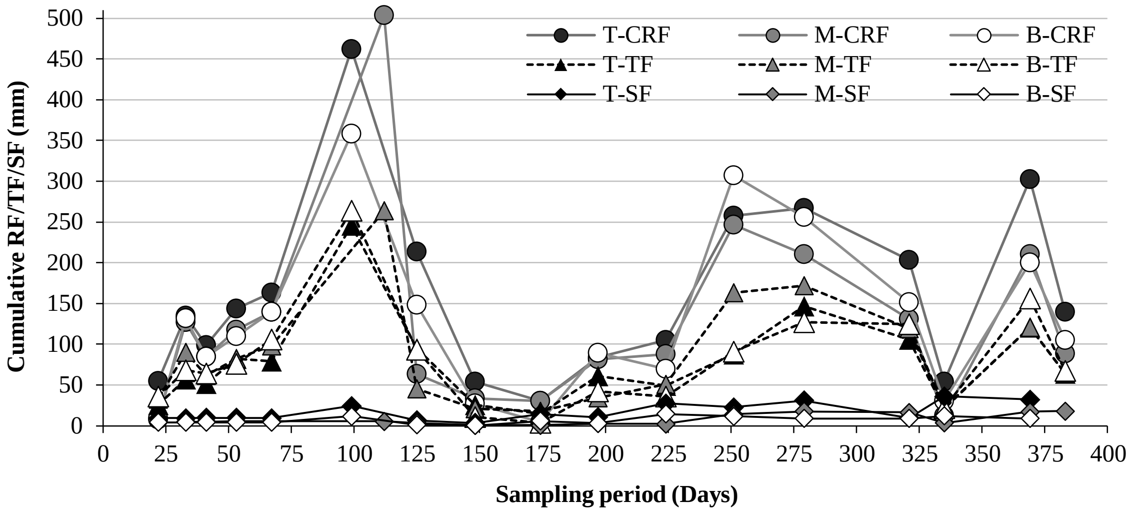


Figure 9: Cumulative throughfall and stemflow in comparison with cumulative rainfall

The composition of rainfall across the three sites was not significantly different. The pH was slightly acidic (avg. 5.75) and EC was 41.54 µS/cm. Average composition of the rainwater of sampling sites is given in Figure 10.

The variation of the stemflow composition within each site was assessed using the data for the entire sampling period. Except for K^+ in all three sites and Ca^{2+} in site B, all other ions did not show within-site variation. Although EC also did not vary in all the sites, pH of two SF collectors were significantly different in site B. Various researchers have pointed out that the composition of the stemflow and throughfall is dependent on the plant species (Levia Jr. & Frost, 2003; Reo Ikawa, 2007; Zhang *et al.*, 2007). In the present study, stemflow collectors were fixed to different tree species. No tangible difference were observed in the stemflow quality among the trees in most of the instances. However, K^+ shows some variation among the collectors. Zhang et al., (2007) have shown that canopy exchange of K^+ was several times larger than the dry deposition under a subtropical deciduous-conifer I forest in China. They also state that the canopy exchange of Ca^{2+} and Mg^{2+} was comparatively high. Findings from the present study indicate that if a variability exist between the compositions of the stemflow and throughfall collected in a particular site, it exists in relation to the above mentioned ions. On the other hand, the occurrence of K^+, Ca^{2+} and Mg^{2+} in the sea salt is comparatively low. Therefore, the variability between the stemflow and throughfall collectors is better expressed in terms of these ions.

When the SF of three sites were compared, Site T and M were not significantly different in terms of the averages of all the ions except for K^+. However, the concentration of all the ions in the SF of site B was significantly higher than those of the other sites (Figure 10).

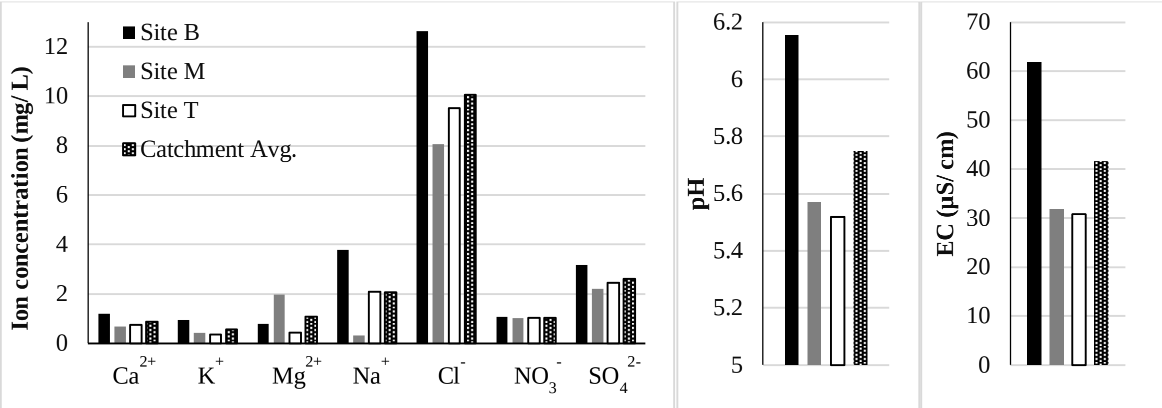
For throughfall, site T had no within site variation for any of the ions or pH and EC. Only Ca^{2+}, K^+ and EC of site M varied. Except Cl^-, SO_4^{2-}, NO_3^- and pH all other parameters of site B varied among the collectors. However, Na^+ was similar in four out of five collectors. When the three sites were compared, except pH, all other parameters of site T and site M had no significant differences. As in the case of stemflow, site B was different from the rest of the sites in most aspects (Figure 10).

Higher concentration of ions in stemflow and throughfall of site B could be attributed to the extensive deposition of sea salts due to the openness of the slope to the wind fronts and closeness to the sea. Excessive damage to site B during typhoons is an evidence for this phenomenon.

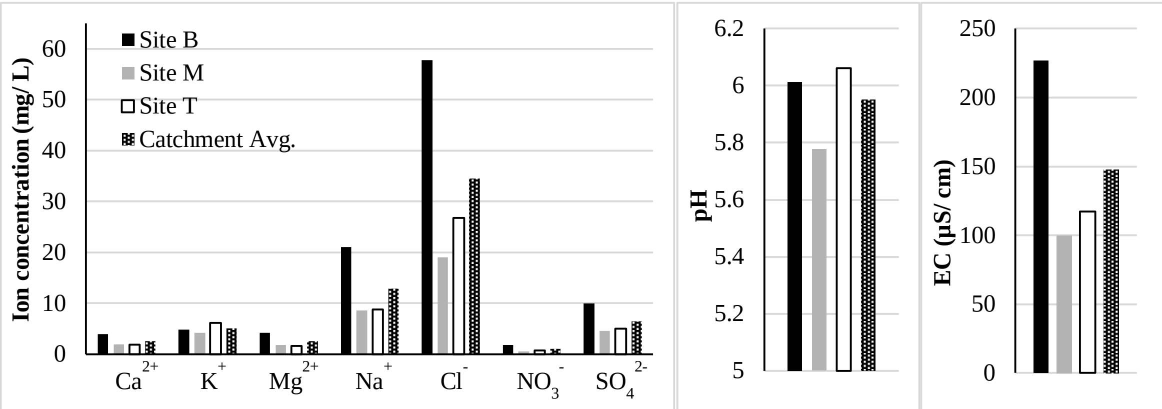
The chemistry of rainwater shows slight fluctuations during the sampling period. Prominent peaks in the ion contents can be seen in the samples collected after typhoons. Na^+

and Cl^-, SO_4^{2-} and EC appear to increase sharply during the typhoon events. The intensity at which the typhoon hit the island and the amount of rainfall were the key factors that determined the above mentioned parameters in the rainwater. As other influential factors of the rainwater quality, the direction and speed of the wind were compared with the variation of the chemistry of rainwater. However, important relationships were not observed.

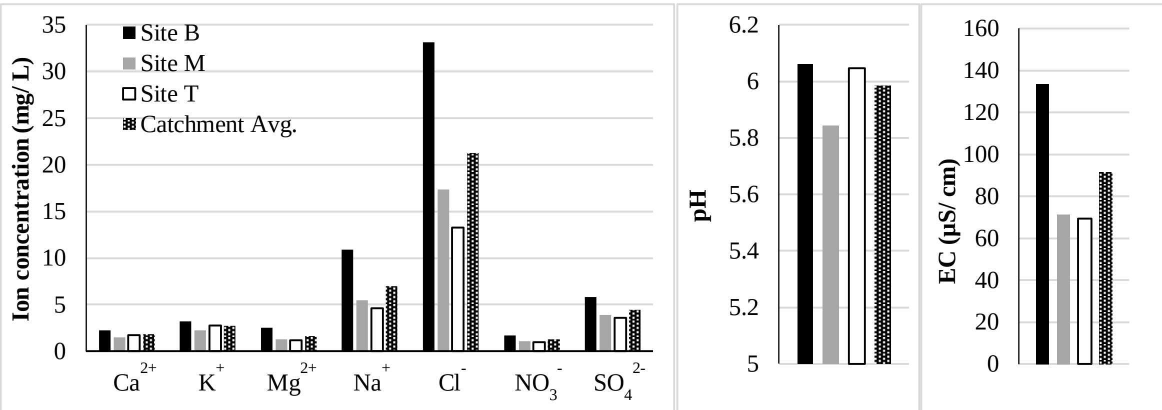
Several extensive studies on the rainwater quality, effects of typhoons on the chemistry of rainwater and the distribution of rainfall in Okinawa are found. Sakihama *et al.*, (2008) reported that typhoons have accounted for the 77% of the annual wet deposition. They also report pH values < 5.6 in more than 72% of the samples they collected. The average pH for the sampling period in the catchment (5.74) agrees well with their findings. It has been shown that the entry of the ions originating from the sea salts depends on the maximum wind speed during the typhoons (Sakihama & Tokuyama, 2005).



Rainfall (RF)



Stemflow (SF)



Throughfall (TF)

Figure 10: Mean ion concentration, pH and electrical conductivity (EC) of rainwater, stemflow and throughfall in three sites

The average influx of the ions of the three sites was calculated as kg/ha/year basis (Table 1). These values were compared with those reported by Xu *et al.* in year 2005 for the same experimental catchment. Although the distribution of the ions shows similarities, the quantity of this study is comparatively lower. As the number of typhoons occurred during the sampling and their characteristics can make a marked difference in the ion input, fluctuations of ion input can be expected. The data shows that Cl^- and Na^+ ions are the most abundant. The detection of relatively large amount of NO_3^- was an important observation and the values are comparable with the total N reported by Xu *et al.*, (2005).

Table 1: Nutrient fluxes during the sampling period (kg/ha/year)

	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
RF	17.30	10.45	13.81	68.27	276.91	22.67	7.50	62.40
TF	21.74	34.75	19.75	93.43	280.64	14.07	1.57	56.93
SF	4.47	10.10	4.46	26.20	63.40	1.29	0.19	12.17
TF+SF	26.21	44.85	24.21	119.63	344.04	15.36	1.76	69.10

As far as the RF, TF and SF are concerned, all are dominated by Cl^-, Na^+ and SO_4^{2-}. Previous studies conducted in the same catchment or similar catchments highlighted very strong correlations between the ion content of the precipitation and the sea salts (Sakihama & Tokuyama, 2005; Sakihama *et al.*, 2008; Xu *et al.*, 2005). They show that the ratio of Cl^- to Na^+ in their samples is highly correlated to that of the seawater. However, in the present study, such a strong correlation was not observed. When the concentration of ions expressed in terms of milli equivalents/l and compared with the findings of Sakihama *et al.* (2008), the order of the ion content has dissimilarities in the present study. Further, the differences in the collection site also may have contributed to these differences. When the ion concentration of the three sampling sites are concerned, site M shows similar pattern in most of the ions to the findings of Sakihama *et al.* (2008). Furthermore, the seasonal wind pattern also may affect the ion composition in the atmosphere. Especially during the winter, the wind is blowing from the direction of Asian continent where industrial zones are abundant. Therefore, the composition of the RF, SF and TF may have high spatial and temporal variation.

According to Sakihama *et al.* (2008), the estimation of the contribution of the sea salts on the ion composition of the rainwater is possible by using the ratio of a particular ion to Na^+ in the seawater. For this calculation it is assumed that the main source of Na^+ is the seawater. Furthermore, Sakihama *et al.* (2008) have also observed a strong correlation between the Na^+ and Cl^- in rainwater showing a Na^+/Cl^- ratio similar to seawater (0.85) when the ion composition is expressed as meq/l. However, data of the present study shows that the Na^+/Cl^- ratio is inconsistent during the sampling period and relatively low in terms of average (0.31). Therefore, the assumptions used in the estimation of the contribution of the sea salts for the composition of the rainwater should be further studied.

2.5. Conclusions

The rainfall of the three experimental plots varied slightly in quantity; this could be attributed to their respective locations. Plots T, M and B of the experimental catchment had throughfall of 49%, 66% and 63% respectively during the sampling period. Therefore, the catchment average was 59%. SF of sites T, M and B were 18.3%, 8.1% and 7.2% respectively and the catchment average was 11.2%. Together stemflow and throughfall accounts for nearly 70% of the rainfall. As high variability in both throughfall and stemflow were observed in the catchment, selection of more than one site for the measurements appears beneficial for the accuracy of the present study compared to previous studies. The variation of the stemflow and throughfall could be attributed the topography and the modifications which have been caused by different exposure to winds.

Although there is a slight variation in the amount of rainfall across the sampling sites, the composition has no significant difference. Further, the composition of the rainfall throughout the sampling period shows that the contamination with pollutants was minimal. Chloride, sodium and sulfate ions dominate in the rainwater. In addition, relatively large amount of nitrate can also be seen. There are evidences for the canopy exchange of nutrients during the transition of rainfall to throughfall and stemflow. The ions subjected to canopy exchange are mainly NO_3^- and K^+. Substantial quantity of material had been deposited on the canopy. Significant differences in the stemflow was not observed between the collectors in terms of most of the ions except for K^+ and Ca^{2+} in site M and B. Potassium and calcium are comparatively high in the topsoil and the exchange of these ions within the canopy may have been pronounced when the external inputs are low. As far as the overall ion influx is concerned, the ions that appear in large quantities in the seawater are dominant in all the fluxes in the current catchment. However, similar proportions were not observed. Therefore, it can be concluded that the influx is affected largely by the surrounding sea although the quantification of the degree of contribution is difficult with the present data.

Chapter 3 Main physicochemical phenomena affecting soil water movement

3.1. Background

The understanding that the soil play an important role in the hydrologic cycle may have been known to mankind for centuries although it was not seen as it is. Centuries-old manmade reservoirs should have been built by taking the soil parameters into consideration. However, until the observations of H.S. Tomson in mid-18th century, soil was considered as an inert material that did not react with water (Thompson & Goyne, 2012). Since then, interactions of soil mineral and organic matter with water have been viewed from various standpoints. However, soil has been hiding its secrets even after centuries, leaving scientists busy uncovering them. Therefore, as mentioned in chapter 1, soil is being considered as a black box. Huge diversity in the soil environment could be the reason for the soil to behave as a black box.

Close observations reveal that there are many clues to the role that soil is playing in the manipulation of water entering the soil. In their review of linkages between the forest soil and water quality and quantity, Neary *et al.* (2009) shows how the forest soils alter the quality and quantity of water being discharged from the forests. In brief, the soil is equipped with biological workforce which includes microbial community as well as higher organisms working continuously in tandem with the abiotic environment maintaining an environment for the manipulation of water.

The influence of soil on the water can be divided into two main streams. They are the physical and chemical process in the soil. However, they are interrelated and, in some instances these two streams are hard to differentiate. For example, soil water repellency and soil aggregation are two phenomena that depend on the soil chemical and physical aspects but the outcome is produced mainly in a physical form. These can be categorized as physicochemical properties of soil and are directly responsible for the determination of the quantity of discharge.

As another example, soil aggregation provides a conducive environment for the water movement within the soil while soil water repellency may hinder the water input causing preferential flow paths, uneven and/or reduced water storage in the soil column, and Hortonian overland flow. On the other hand, the same phenomenon is capable of redirecting the soil water so that it causes some changes in the chemical composition of the water coming out of the soil. For an example, due to the high porosity in topsoil resulting from soil aggregation, the moving water takes on the near-surface paths rich in nutrients and other chemicals (Neary *et al.*, 2009).

Soil organic matter is a key determinant of almost all the soil processes. The influence of organic matter on the soil starts from the soil genesis itself. Soil genesis is a result of additions, removals, transfers and transformations and, organic matter is involved in all these processes (Simonson, 1959). These processes continue as long as the soil exists. Soil aggregation and soil water repellency are two of the soil processes depend entirely on the soil organic matter dynamics. Organic matter dynamics of the soil depend on various factors. It has been reported that the climatic factors govern the organic matter dynamics in the large spatial scale. In the regional scale or the local scale however, the quality of the litter has been found to dominate the organic matter dynamics (Aerts, 1997). Large number of research is being conducted around the world in both these aspects. However, the research in the subtropical coastal forest environments such as the forests of Okinawa are scarce. A sound knowledge of the organic matter dynamics is important for various purposes such as estimating carbon sequestration in the forest soil, soil fertility management, ecosystem health assessments and understanding the secondary effects of soil organic matter in the soil such as soil water movement.

Several physicochemical phenomena were examined along with the soil chemistry. This chapter includes an assessment of the expression of soil water repellency in the experimental catchment as a factor that determines the water infiltration into the soil and hence, determining the rate of water discharge and storage. Furthermore, the characteristics of the soil aggregates of the forest soil was assessed, compared with the aggregates of a nearby mangrove soil in view of expanding the understanding of organo-mineral interactions of both mangrove and forest soil under subtropical environments. The properties of litter decomposition process were also assessed by means of a laboratory incubation of the litter.

3.2. Specific objectives

The specific objectives of this study are to:

a. Understand the properties of the soil physicochemical factors affecting water movement in the soil

b. Understand the characteristics of the litter decomposition in the subtropical coastal forest soil

3.3. Soil water repellency – a factor that hinders the water infiltration

3.3.1. Assay of the occurrence of potential soil water repellency in the catchment

3.3.1.1. Introduction

Soil water repellency (SWR) was first described in early 20th century; it can be explained as a phenomenon that reduces the affinity of soil to water (Doerr *et al.*, 2000) or inability of soil to get wet spontaneously when water is added (Leelamanie *et al.*, 2008). Due to the dipolar nature of the water molecules, cohesive forces develop in water. If there are no external forces, cohesive forces pull the water molecules on the outer boundary towards inside reducing the surface area causing the water to form droplets. This process is also known as surface tension. Solid surfaces on the other hand also have the surface forces. If the surface forces can overcome the cohesive forces of the water, water spreads on that surface (Doerr *et al.*, 2000). Same principle applies to the soil and, if the soil surface has no sufficient energy to overcome the surface tension, water will form droplets rather than wetting the surface. This is the mechanisms behind the occurrence of water repellency. Usually mineral particles of the soil have high surface free energy than water, indicating that they can be wetted. However, due to the presence of hydrophobic material on the soil mineral surfaces, wettability of the soil declines (Doerr *et al.*, 2000; Leelamanie & Karube, 2009a).

Usually organic matter acts as the main hydrophobic material (Mataix-Solera *et al.*, 2007). The features of organic matter determine the degree of hydrophobicity. The content of hydrophilic and hydrophobic substances, their chemical characteristics and physical arrangement are examples for the features of the organic matter. Soil micro-flora has also found to be responsible for SWR (DeBano, 1981; Hallett, 2008; York & Canaway, 2000) due to their secretions and structural elements such as fungal hyphae. Surface area of the soil particles is important in terms of the surface energy. Therefore, soil texture is also a major determinant of SWR (Hallett, 2008). Secondary factors that can influence SWR are mainly the soil moisture content, forest fires and soil pH. Even if the soil has the potential to be repellent, it has been found to depend on the soil moisture content (Hallett, 2008; Leelamanie & Karube, 2011). Fire support the coating process of the hydrophobic compounds on soil particles by volatilizing (DeBano, 2000; Letey, 2001). Soil pH determines the behavior polar functional groups and active sites. Therefore, the surface free energy may be affected and hence SWR (Hurraß & Schaumann, 2006). Because of the complexity of the interactions of the above factors, explaining the SWR or its effect on other processes might be difficult in certain situations (Doerr *et al.*, 2003).

Water repellency has been reported from different areas of the world at varying levels under varying environmental conditions (Barrett & Slaymaker, 1989; DeBano, 1981; York & Canaway, 2000). In some regions amelioration methods have also been considered (Hallett, 2008). Some authors have shown the significance of considering SWR in runoff modeling, though its real-time application is much complicated (Doerr *et al.*, 2003). Emergence of preferential flow paths, uneven and/or reduced water storage in the soil column, and the occurrence of Hortonian overland flow are some of the effects of SWR on hydrologic cycle (DeBano & Rice, 1973; Doerr & Moody, 2004; Doerr *et al.*, 2000; Hallett, 2008; Kobayashi *et al.*, 2002; Miyata *et al.*, 2009b; Nagahama *et al.*, 2001).

Large number of research has been conducted on the SWR in the forests of main island of Japan. Oldest research date back as far as 1950s and report an anomaly in soil moisture recharge after the rainfall (Yamaya, 1950). Since then, this research field expands in a wide range of aspects related to SWR. Fundamental aspects of SWR such as the dependence of SWR on soil organic matter and soil moisture, have been reported in the early stages of experiments (Nakaya & Yokoi, 1973; Nakaya *et al.*, 1975, 1976). Lot of effort has been made in the characterization of SWR (Kobayashi & Matsui, 2006; Kobayashi, 2007; Kobayashi *et al.*, 1996; Leelamanie & Karube, 2007, 2009a, 2009b, 2011; Leelamanie *et al.*, 2008; Nakaya *et al.*, 1977).

Apart from the fundamental aspects mentioned above, certain research were focusing on the applied aspects of SWR. Most of these were focusing on the SWR development under Japanese Cypress (*Chamaecyparis obtusa*: Cupressaceae) because these soils have shown very high level of SWR. These studies have attempted to understand the factors behind some of the hydrological processes such as surface runoff (Ide *et al.*, 2011; Kobayashi, 1999, 2008; Kobayashi *et al.*, 2000; Miyata *et al.*, 2009b). Meanwhile some studies were focusing on the other types of forests (Gomi *et al.*, 2008; Kajiura *et al.*, 2010; Kobayashi & Matsui, 2006; Kobayashi *et al.*, 2006).

The observations on the stream discharge of the present catchment indicate quick responses of stream to the rainfall even at relatively low rainfall intensities. Such behavior can be expected when the surface runoff has a large contribution to the water movement in the soil. Soil water repellency could be one of the factors behind the generation of surface flow conditions in the experimental catchment. However, SWR related research conducted under the broad-leaved evergreen forests of subtropical parts of Japan could not be found.

3.3.1.2. Specific objectives

The specific objectives of this study are to:

a. Investigate the occurrence of SWR in the experimental catchment (which also includes long unattended manmade plantation forest patches)

b. Clarify the degree of repellency and potential implications of repellency on the hydrological processes

c. Identify the major causes of repellency.

d. Investigate how sessile drop method and WDPT test results are related when applied to forest soil.

3.3.1.3. Materials and methods

Thirty six soil samples were collected from nine 15-20 m transects, each with four sampling points. Primarily, the sampling transects were selected to include the dominant stages of the forest succession: natural forest, secondary climax forests (>50 years old) and young secondary forests (<50 years old). In addition, the availability of information about the history of the forest, minimal interferences to the forest development, topography, and accessibility were also taken in to consideration.

Natural forest had two transects, NAT 1 and NAT 2 located on a ridge and a slope lying surrounded by relatively high-lying areas respectively. The transect in the secondary climax forest was identified as SCF. The transect identified as APF is a young secondary forest left unattended for about 30 years. The original plantation was a Ryukyu Pine (*Pinus luchuensis* Mayr: Pinaceae) plantation. Other young secondary forests identified by the Japanese name of initially planted trees were selected as all these plantations forests are of similar age. They have not been subjected to any management operation, and they occupy a substantial area of a small sub-catchment where parameters such as water discharge, soil moisture are continuously being monitored for other studies. Transects SUG, ISU, HIK, IJU, and EGO were selected in Sugi (*Crypromeria japonica*: Taxodiaceae), Isunoki (*Distylium racemosum*: Hamamelidaceae), Hikanzakura (*Prunus cerasoides*: Rosaceae), Iju (*Schima wallichii*: Theaceae) and Egonoki (*Styrax japonica*: Styracaceae) respectively. Total area of the plantations is approximately 5 ha and plantations were established in late 1970s and early 1980s and, have been left unattended (Figure 11).

Soil samples were taken from 0-5 cm depth (Šimkovic *et al.*, 2009) after removing the litter layer as much as possible. Three 100-cc core samples were taken for subsequent soil

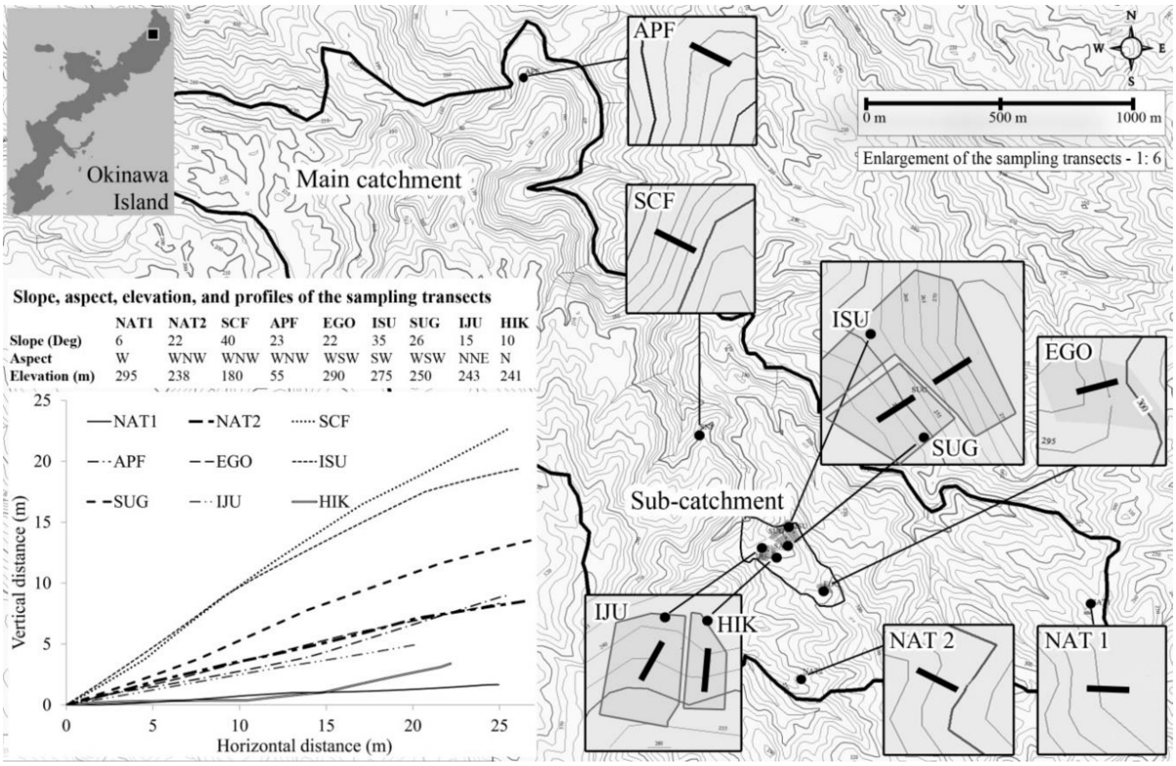


Figure 11: Layout and the slope characteristics of sampling transects.

The black straight line in each enlarged box indicates the sampling transect; Four sampling sites are located approximately 5-6 m apart along each transect; Legend - NAT-Natural forest, SCF-Secondary climax forests, APF-Abandoned plantation forest, EGO-Egonoki, ISU-Isunoki, SUG-Sugi, IJU-Iju, HIK-Hikanzakura.

evaluations. Sampling was done in December 2012 following about one week of dry spell. Initial moisture content, porosity, field capacity, bulk density and hydraulic conductivity were measured with soil cores. Soil samples were air-dried at room temperature and prepared for further analysis.

Field measurement of soil water repellency

In situ WDPT Test was done in each site by applying three 45~50 µl drops of deionized water (Figure 12). Relative humidity (RH) and the air temperature of the site were recorded (Dekker *et al.*, 2009).

Figure 12: Field measurement of soil water repellency by water drop penetration time test

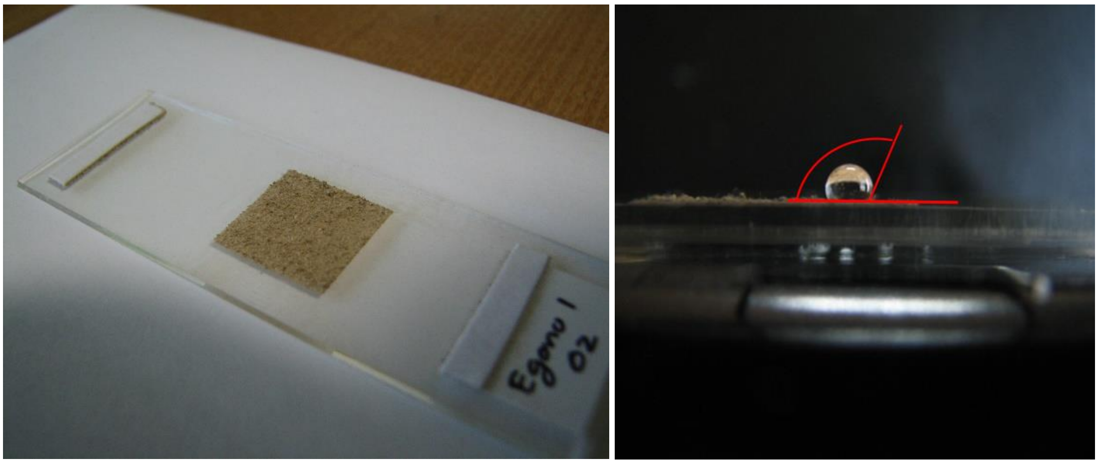
Laboratory WDPT test

Weighing bottles with 25 mm diameter and 30 mm height were filled with approximately 5 g of air dried soil samples sieved with 2 mm sieve. Three replicates of each sample were kept in a chamber with 75% RH for a week for moisture stabilization. A drop of de-ionized water (45 ± 1 µl) was added from 10 mm above the soil surface in a room with RH 75 ± 5% and constant temperature of 25°C. During the time of water drop penetration, bottle was capped to stop evaporation (Leelamanie & Karube, 2012; Leelamanie *et al.*, 2008) (Figure 13).

Figure 13: Laboratory water drop penetration time test

Laboratory sessile drop method.

Air-dried soil was sieved with 1 mm sieve. A 15 x 15 mm double sided tape was fixed to a glass slide in the middle of one side. Soil samples were sprinkled on to the double sided tape and fixed to the tape by pressing with another slide using a 100 g weight for 10 seconds. Excess soil was removed by gently tapping the slide. Procedure was repeated twice (Figure 14-a). Three replicates were prepared from each soil sample (Total 96). Samples were stored in a chamber with 75% RH for a week. 10 µl of de-ionized water was added to the soil layer with a micro-pipette in a room with 75 ± 5% RH and constant temperature of (25°C). A picture was taken within one second using a micro-camera. Contact angles were manually measured on micrographs (Figure 14-b). Average of left and right side contact angles were calculated (Leelamanie *et al.*, 2008).



(a) (b)

Figure 14: Contact angle measurement with sessile drop method
(a) Soil monolayer prepared for the sessile drop experiment (b) micrograph showing the water drop and the contact angle measurement

Soil texture was evaluated with hydrometer method. Total soil organic carbon (TOC) was evaluated by dry combustion (NC analyzer - SUMIGRAPH NC-220F). As a measure of hydrophilic material content in soil organic matter, water soluble organic carbon (WSOC) was extracted from 5 g of soil with de-ionized water with soil: water ratio of 1:10 by shaking the samples for 15 minutes at 200 rpm. Supernatant was filtered with No. 2 qualitative filter paper (Jones & Willett, 2006; X. Lu *et al.*, 2011). Carbon content was determined by TOC–L CPH.

3.3.1.4. Results and discussion

A general assessment of vegetation of sampling transects and soil characteristics are given in Table 2 and Table 3 respectively. Natural forest and the secondary climax forest have high species diversity. Young secondary forest and abandoned plantation forests are also being intruded by the plant species occurring naturally in the area.

Table 2: Tree species distribution of the sampling sites

Transect	Plant species composition			Total stem count/ 25 m² (DBH > 5 cm)	DBH range (cm)	Height (m)
	Canopy *Species* (%)	**Sub-canopy**	**Shrubs layer** Spp (No. of Bushes)			
NAT1 and NAT2	*Castanopsis sieboldii* (50) *Schima wallichii* (20) *Elaeocarpus japonicus* *Distylium racemosum* *Tutcheria virgata* *Tricalysia dubia*	*Syzygium buxifolium* *Camellia sasanqua* *Ternstroemia gymnanthera* *Ardisia quinquegona* *Dendropanax trifidus* *Cinnamomum doederleinii*	*Pleioblastus linearis* - only in NAT 1 (15)	10	3-39	5-10
SCF	*Castanopsis sieboldii* (50) *Schima wallichii* *Daphniphyllum glaucescens* *Elaeocarpus japonicas* *Ternstroemia gymnanthera* *Myrica rubra*	*Myrsine seguinii* *Damnacanthus biflorus*	*Pleioblastus linearis* (17)	11	4.5-30	3-10
APF	*Pinus luchuensis* (30) *Castanopsis sieboldii* (20) *Cinnamomum doederleinii Persea thunbergii*	*Rhaphiolepis indica* *Syzygium buxifolium* *Ternstroemia japonica*	*Dicranopteris linearis* (as a layer covering the ground) *Pleioblastus linearis* (4)	9	2-15	4-9
EGO	*Styrax japonica* (<30) *Schima wallichii* (50) *Distylium racemosum* *Castanopsis sieboldii* (20) *Elaeocarpus japonicus* *Machilus thunbergii*		*Blechnum orientale L* (15) *Pleioblastus linearis* (6)	17	4-12	6-8
HIK	*Prunus campanulata* (50) *Schefflera octophylla*	*Schefflera octophylla* *Maesa montana* *Ficus bengutensis* *Wendlandia formosana*	*Blechnum orientale L* (15)	24	4-15	9
IJU	*Schima wallichii* (60) *Diospyros morrisiana* *Styrax japonica*	*Alsophia podophylla*	*Blechnum orientale L* (19) *Pleioblastus linearis* (1)	23	3-12	3-5
ISU	*Distylium racemosum* (50) *Castanopsis sieboldii* (30)		*Pleioblastus linearis* (Numerous) *Blechnum orientale L* (15)	21 Including stems < 5 cm	2-10 (Forked trees)	3-5
SUG	*Crypromeria japonica* (100)		*Blechnum orientale L* (19)	16	7-12	11-13

Table 3: Soil characteristics of the sampling sites

	NAT1	NAT2	SCF	APF	EGO	HIK	IJU	ISU	SUG
D_b (g/cm^3)	0.69	0.93	0.78	0.80	0.71	0.98	0.64	0.74	0.99
Initial moisture (%)	69.9	44.1	57.1	51.7	78.5	49.4	77.4	57.2	42.7
SHC (cm/s)	0.006	0.008	0.009	0.043	0.002	0.008	0.033	0.018	0.012
Field capacity (%)	60	59	56	56	61	55	58	57	50
Porosity (%)	62	61	57	57	64	56	59	57	51
Soil Texture	CL	C/CL	CL	L	CL	C/CL	C/CL	C/CL	C/SCL
Soil pH	4.49	4.46	4.34	4.35	4.18	4.33	4.37	4.09	4.8
TOC (%)	8.57	14.12	6.37	5.18	5.4	4.98	5.49	4.97	5.31
WSOC (%)	0.09	N.A.	0.071	0.062	0.063	0.054	0.065	0.067	0.067
D_b - Bulk Density, SHC - Saturated Hydraulic Conductivity, C - Clay, CL - Clay loam, SCL - Sandy clay loam, L - Loam, N.A. – Data not available									

Level of SWR in the catchment and how it could affect the hydrological processes

During the field WDPT test, no repellency was observed at any sampling site. RH and temperature during the measurement was 83% and 17°C. However, results of the laboratory SDM and WDPT test done with air-dried soil to investigate the potential SWR provide evidence for the existence of potential SWR but not at extreme levels. Therefore, during the field test, highly moist soil environment may have masked the hydrophobic characteristics of the soil.

The dependence of SWR on the antecedent soil moisture has been studied by many researchers. Runoff study in Japanese cypress plantations in central Japan has shown that the overland flow was high during the precipitation following a dry spell. They have also observed seasonal changes in the infiltration characteristics in the experimental soil and suggest that SWR induced by low soil moisture content could have partially involved in changing infiltration process (Gomi *et al.*, 2008). A similar study on soil under Japanese cypress and *Castanopsis spp* (*Koji* in Japanese) in central Japan has showed that partially dry soil expressed repellency characteristics even in soil under *Castanopsis spp* plantation (Kobayashi *et al.*, 2002). Kobayashi *et al.* (2000) reported SWR as a reason for uneven infiltration pattern of stemflow under Japanese cypress trees. Studies conducted under deciduous forests and broad-leaved forests in Japan have shown the existence of potential repellency but at a lower degree (Gomi *et al.*, 2008; Kajiura *et al.*, 2010; Kobayashi & Matsui, 2006; Kobayashi *et al.*, 2006). Miyata et al. (2009) suggests that the degree of influence of SWR on hydrological processes such as overland flow may depend on other factors. These findings are comparable with our findings for the subtropical evergreen coastal forests situated on a largely different geographical and geological setting.

Unlike in the main island of Japan, seasonal differences in climate are not strong in Okinawa in terms of total monthly rainfall. Northern Okinawa, in particular, receives relatively high rainfall distributed throughout the year maintaining relatively high soil moisture levels (Figure 4). Therefore, if the normal moisture regime of the area continues to persist, water repellency may not come into effect and hence, may not interfere in hydrological processes significantly.

A separate study was conducted with different moisture levels under undisturbed and processed soils to understand how soil moisture play its role in the expression of the SWR in the catchment. The study is explained in detail under section 3.3.2.

Forest fire could also induce repellency, particularly in natural forest where soil organic matter is relatively high. But this phenomenon also needs further investigations as it may depend on the type of organic matter and the degree of burning (Obuchi *et al.*, 2009).

Characterization of SWR using SDM and WDPT test

The criteria to interpret SDM results are not well-defined. Theoretically 90° contact angle indicates the existence of repellency (DeBano, 1981). However, water repellent soils have shown wide range of contact angles (Bachmann *et al.*, 2000). Many authors have attempted to compare it with the categorization based on WDPT (Table 4). It has been shown that contact angles 70° to 88° may correspond to slight repellency and all other higher categories of repellency may fall between 88° to 93° for model sand (Leelamanie *et al.*, 2008). For sandy soils of temperate pine forest, contact angles of 90° or above, 80-90° and less than 80° have

Table 4: Repellency severity categories based on water drop penetration time

Severity category	**WDPT (s)**
Non-repellent	≤ 1
Slightly repellent	1- 60
Strongly repellent	60 – 600
Severely repellent	600 – 3600
Extremely repellent	≥ 3600

(Leelamanie *et al.*, 2008)

corresponded to severely repellent to extremely repellent, slightly to strongly repellent and non-repellent respectively (Bachmann *et al.*, 2000). According to these criteria and present findings, all sites have some level of potential repellency. However WDPT test results interpret the occurrence of SWR at different levels though some measurements are in agreement (Table 5). APF and SCF have contact angles greater than NAT1 (slightly repellent under WDPT test) even though they do not display repellency under WDPT test. Similarly ISU with a contact angle greater than IJU do not show SWR. Despite having the lowest contact angle HIK soil shows slight repellency under WDPT test. In order to understand this discrepancy, individual repellency values of each sampling site from both methods were plotted against each other (Figure 15) and partitioned into different levels of repellency based on similar previous studies (Bachmann *et al.*, 2000; Leelamanie *et al.*, 2008).

Table 5: Distribution of water repellency across transects measured by sessile drop method and water drop penetration time test

	Sessile Drop Method (*In vitro*)		**WDPT Test (*In vitro*)**		**WDPT Test (*In situ*)**
Transect	**Mean contact angle (Deg)**	**Severity of repellency**	**Mean WDPT (s)**	**Severity of repellency**	**Severity of repellency**
NAT2	100.25	SVR to ETR	175.24	STR	NR
APF	96.75	SVR to ETR	<1	NR	NR
SCF	95.75	SVR to ETR	<1	NR	NR
NAT1	94.25	SVR to ETR	3.55	SLR	NR
ISU	92.00	SVR to ETR	<1	NR	NR
IJU	90.75	SVR to ETR	1.04	SLR	NR
SUG	86.75	SLR to STR	<1	NR	NR
EGO	83.25	SLR to STR	<1	NR	NR
HIK	80.50	SLR to STR	1.04	SLR	NR

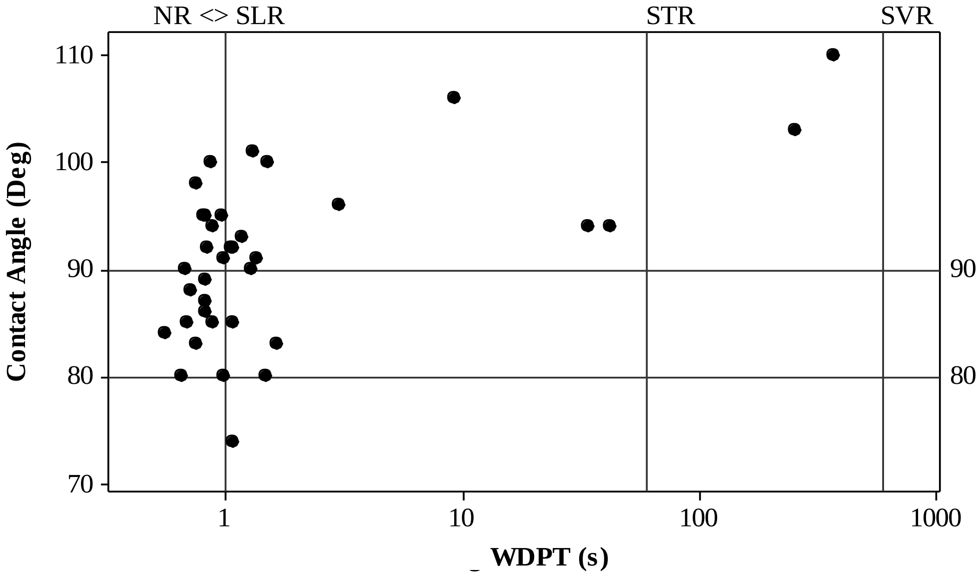


Figure 15: Relationship between contact angle (Deg) and water drop penetration time (S)

There was no observation of any particular pattern especially around the boundary of non-repellency to slightly repellency in both methods (80°/ 90° and 1 second in SDM and WDPT test respectively). The comparability of the results of the soil sample from the field may vary despite the good correlations observed under certain studies as cited earlier. For example, in an assessment of SWR by Kawamoto and Banyar (2004), in volcanic soils using WDPT test, capillary rise method, and ninety degree surface tension method, the result of the latter has deviated from the other two tests. A possible reason for this difference could be that the influence of soil structure (mainly the aggregation) on water repellency may not have been portrayed in SDM results as the soil used in the SDM was used as a monolayer in contrast to the soil passed through the 2 mm sieve in WDPT test. A close association between SWR and soil structure in aggregated soils has been reported in a previous study by Kawamoto and Nakamura (2003).

As both sets of samples were moisture-stabilized under 75% RH and 25°C the effect of moisture in expressing repellency could be assumed minimal. Therefore, it can be suggested that the SDM has revealed the potential of soil to be repellent. On the other hand WDPT test has shown how the soil may exhibit repellency in its natural form where, surface characteristics of the soil is altered by conditions such as aggregation and organic matter coating.

Factors affecting SWR

The effects of soil moisture and the structure are explained in detail under section 3.3.2. As major factors determining SWR, TOC content and the WSOC content of the samples were compared with the repellency values obtained from both methods. A strong correlation was observed between the TOC and the WDPT ($r^2=0.89$) irrespective of the site (Figure 16). A similar pattern has been observed in a study investigating the effect of organic matter on water repellency with kaolinite and silica sand hydrophobized with Stearic acid. When increasing the Stearic acid content, a sharp increase in WDPT and contact angle has been observed from the boundary of slight repellency to extreme repellency (Leelamanie *et al.*, 2010). Our results indicate that the repellency starts to increase rapidly and correlate well with TOC when TOC is approximately 7-8% or above. A similar pattern has been observed in another field study to assess the repellency under different tree species. Slight repellency has been observed in 3 out

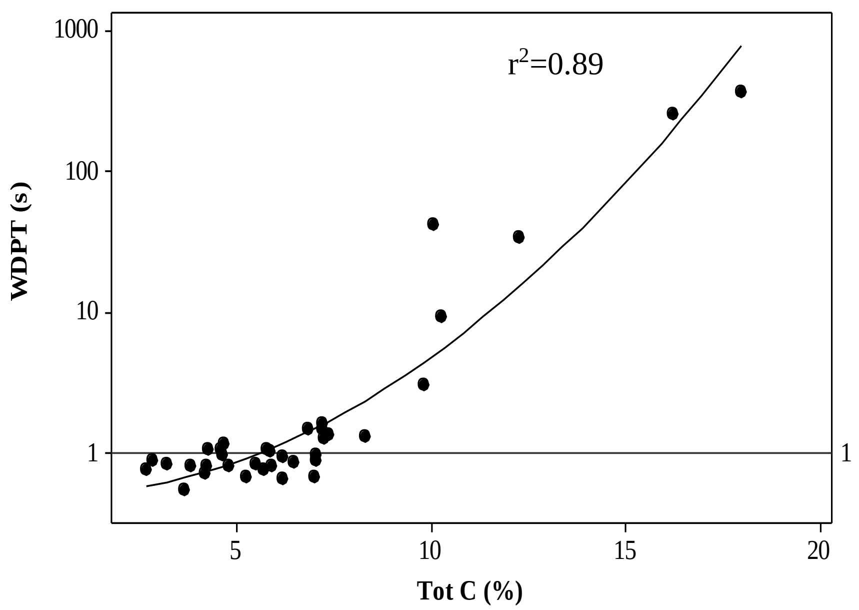


Figure 16: Relationship between water drop penetration time and total organic carbon

of 4 plant species where organic matter is above 7-8 % (Mataix-Solera *et al.*, 2007). In an investigation of the soil organic matter and initial moisture content of volcanic soil, it has been found that the extremely repellent soils have corresponded to carbon contents above 7.5% when volumetric water content was between 0.15 and 0.27 (Kawamoto & Banyar, 2004). The SWR assessed under the forests mainly with broad-leaved trees, by molarity of ethanol drop (MED) test has also shown that MED had been high for most of the observations when the total carbon content is above 7-8% (Kajiura *et al.*, 2010). Therefore, a trend is observed in the relationship between total carbon and SWR under broad-leaved forests or trees. In these cases abundant organic matter may have encapsulated the soil particles lowering surface-free energy causing repellency. The relationship between TOC and the WDPT is explained as a concave-up type exponential graph in Figure 16. Therefore, theoretically, WDPT will reach a maximum at a particular level of TOC in the soil. At this level the soil particles could be completely covered by hydrophobic organic matter. On the other hand, soil aggregates are also a result of the interaction between organic matter and the soil minerals and, they are known to cooperate with water than to repel water. With this perspective, the general understanding is that, higher the organic matter better the conditions for soil moisture storage and movement. Therefore, in real time, an equilibrium may be reached in the expression of SWR and the functions of soil aggregates. The equilibrium may be dependent on the type of organic matter, the degree and characteristics of the coating process, changes in soil moisture in the long term or beyond a critical limit *etc*. An example for this is the SWR in the soil under Japanese cypress has shown high MED values but very low correlation to the total carbon (Kobayashi & Matsui, 2006). Therefore, these aspects have to be further studied.

Contact angle measurements did not show a strong relationship to total organic matter content (r^2 = 0.31). A similar relationship (r^2 = 0.22) was also reported (Vogelmann *et al.*, 2010). In their study the SWR measured as “repellency index” has also showed very low correlation to the organic matter ($r^2 = 0.185$) and it could possibly be due to the low organic matter content (3-7.3%) in the soil.

The distribution of water soluble organic carbon across the sites is similar to the total organic carbon. Therefore, it does not significantly indicate differences in hydrophobicity of organic matter across the sites and, hence influence on repellency. Each soil textural fractions was compared with the WDPT and the contact angle and no significant relationship was observed. Organic matter encapsulation of soil particles and the aggregation could have masked the effect of texture on repellency.

Possible reasons for the spatial variability

The natural forest has been found to have very high plant diversity (Ito, 1997; Kubota *et al.*, 2005). Slight variations in the structure of the vegetation can be observed due to the degree of influence of typhoons and exposure to winds depending on the topographic variations (Kubota *et al.*, 2005). In the sampling transect NAT1, forest floor is more exposed to wind and sunlight compared to NAT2 as its location is on a relatively open ridge (Figure 11). Abundance of *Pleioblastus linearis* in the shrub layer of NAT1 is a major difference between the two transects. Based on these observations it was assumed that the relatively low organic matter content in NAT1 can be attributed to the exposure of the forest floor and, hence faster decomposition rates. The difference of organic carbon content mentioned above could be a major reason for the larger differences in the potential water repellency observed in the transects located in the natural forest.

The secondary climax forest (SCF) also has comparatively high plant diversity but not as high as that of the natural forest. Most of the plant species found in the natural forest are found in the secondary climax forest. Although the transect is in a relatively enclosed area in terms of topography, the canopy cover is more or less similar to NAT1. Furthermore, the influence of typhoons and strong winds is not clearly visible in the site. The shrub layer is occupied mainly by *Pleioblastus spp.* On the other hand, the abandoned plantation forest (young secondary forest) has relatively low plant density and canopy cover. Most parts of the forest floor are covered by *Dicranopteris linearis* (Gleicheniaceae).

Although the sampling in the sub-catchment was done in different plantation forest blocks, intrusions of naturally occurring plant species were observed in all the plantations. The shrub layer of the Isunoki plantation (ISU) is comprised mainly of *Pleioblastus spp*. Abundance of dwarf, forked and thin Isunoki trees is a prominent feature of the plantation allowing sunlight to reach the shrub layer. In addition, the plant diversity is also low in this plot. Egonoki (EGO) plantation on the other hand has relatively high species diversity and stand characteristics are more or less similar to the secondary forests. However, *Blechnum orientale* (Blechnaceae) is also abundant in the shrub layer. Sugi plantation also had *Blechnum orientale* as the shrub layer and almost no other plant species can be observed. Iju and Hikanzakura plantations also have relatively low plant diversity but intrusion of natural species can be clearly seen. *Blechnum orientale* is common in both plantations but *Pleioblastus spp* is absent in Hikanzakura plantation while very sparse in Iju plantation. Therefore, it is difficult to isolate the effects of different plant species or communities on the emergence of repellency under these conditions

3.3.1.5. Conclusions

Considering the results of both SDM and in vitro WDPT test, this study confirms that the surface of forest soil in northern Okinawa possesses potential water repellency at varying levels. The major factor that determines the severity of the potential repellency is the percentage of total carbon. High total carbon content in the soil promotes the occurrence of SWR. SWR occurrence and its severity appear to correspond well to the TOC when it is approximately 7-8% and above, in the soils of broad-leaved forests where trees are not specifically known for their role in causing SWR. High soil moisture reduces the occurrence of the repellency. In other words, SWR may not occur when the soil is sufficiently moist even if the soil is potentially repellent with high levels of total carbon. Therefore, if the regular moisture regime of the area continues to persist, the influence of repellency on water infiltration and, hence on the hydrological processes will not be significant in the catchment. The results of WDPT test and SDM were not directly comparable in the forest soil samples. A reason could be that the soil monolayer used to assess potential SWR in the SDM does not possess the actual soil structure which can influence the expression of SWR. However, the results of the two methods may correlate well under high repellency levels.

3.3.2. Effects of soil structure and moisture content on the occurrence of SWR

3.3.2.1. Introduction

As mentioned in the previous section, the WDPT test is one of the widely used method in assessing SWR. Although WDPT test can be applied in the field, SWR experiments are usually conducted in the laboratory with processed soil samples (sieved and debris free) as field measurements have several limitations. Due to the dependence of SWR on soil moisture, the field measurements have to be done when the soil moisture level has reached a level where SWR is occurring. However, finding this moisture level and waiting until it is reached is not practicable. Even if it was measured, the comparability of the results is low. Therefore, the measurements are done in the laboratory with air-dried soil under standard temperature and relative humidity for practicability and to improve comparability of the results.

Kawamoto and Nakamura (2003) and Vogelmann et al. (2010) have pointed out that the soil structure is capable of altering the soil water repellency. Therefore, it was hypothesized that the estimation of SWR by using processed soil samples will not adequately describe the occurrence of SWR in the field and hence, the implications on the hydrological processes.

3.3.2.2. Specific objectives

Specific objectives of the study are to

a. Compare the differences in the degree of SWR estimated by widely-used WDPT test on undisturbed soil samples and processed soil samples
b. Understand the effect of soil moisture on the expression of SWR

3.3.2.3. Materials and methods

The experiment was carried out by using soil samples taken from two sites (NAT 1 and NAT 2) which showed potential soil water repellency in the previous experiment. Twelve undisturbed soil samples were obtained from the topsoil of each site by 100 cm^3 core samplers. Approximately 200 g of soil was also collected from the first 2-3 cm. Both types of samples were air dried at approximately 28°C under a dehumidifier. Soil structure and moisture were considered the two treatments. Undisturbed soil and processed soil were considered as two treatments related to soil structure and moisture content at 50% field capacity and completely air-dried (until constant weight) state were used as two moisture levels.

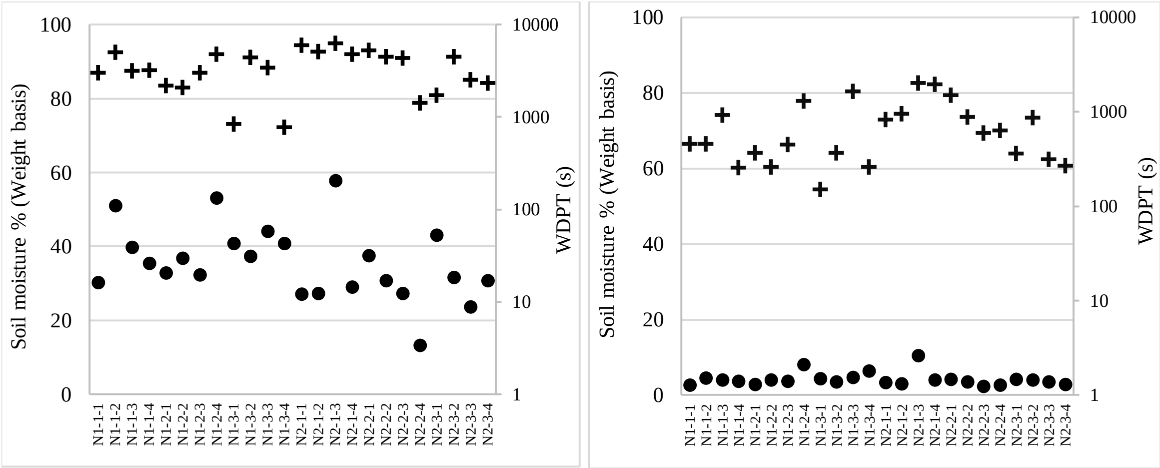
When the soil moisture reached 50% field capacity, soil cores were closed and allowed for moisture redistribution within the soil. After 48 hours, SWR was measured with WDPT test. SWR was measured again when there was no further weight loss due to air drying.

Soil was sieved (2 mm mesh) when sufficiently dry and the debris (roots and decaying leaves) were removed. SWR was assessed with WDPT test when there was no further loss of weight due to air drying. All the measurements were done at temperature 28°C ±2 and relative humidity 78% ±3. Total carbon (TC) content was measured with NC analyzer (Sumigraph NC-220F).

3.3.2.4. Results and discussion

Large differences were observed between the results of the WDPT test when applied to each treatment. After three days of air drying, most of the undisturbed core samples exhibited severe repellency (WDPT 600-3600 s) or extreme repellency (WDPT ≥3600 s) levels. However, when air-dried to a constant weight, the degree of SWR declined to the strongly-repellent level (WDPT 60-600 s) (Figure 17). Processed soil samples on the other hand, when subjected to the WDPT test showed very low level of water repellency (Figure 18).

Total carbon contents of the two sites are not significantly different (t-test $p<0.05$). A strong quadratic relationship between TC and the SWR can be observed in the processed soil samples as in the previous experiment (Figure 19). However, undisturbed soil samples do not



Site ID (NAT1 – N1 and NAT2 –N2)

Figure 17: Levels of soil water repellency observed in the undisturbed soil cores at soil moisture ≈ 50% of initial moisture (left) and after complete air drying (right).
Legend: + SWR, ● Soil moisture

show such relationships. The application of the WDPT test on undisturbed soil cores reaffirms the dependence SWR on soil moisture and demonstrates how strongly the SWR could resist the entry of water in to the soil. Extreme levels of water repellency were observed when the mean soil moisture was approximately 35% by weight. As the soil moisture of the topsoil can reach this level following a warm dry period, SWR could seriously affect the hydrological processes

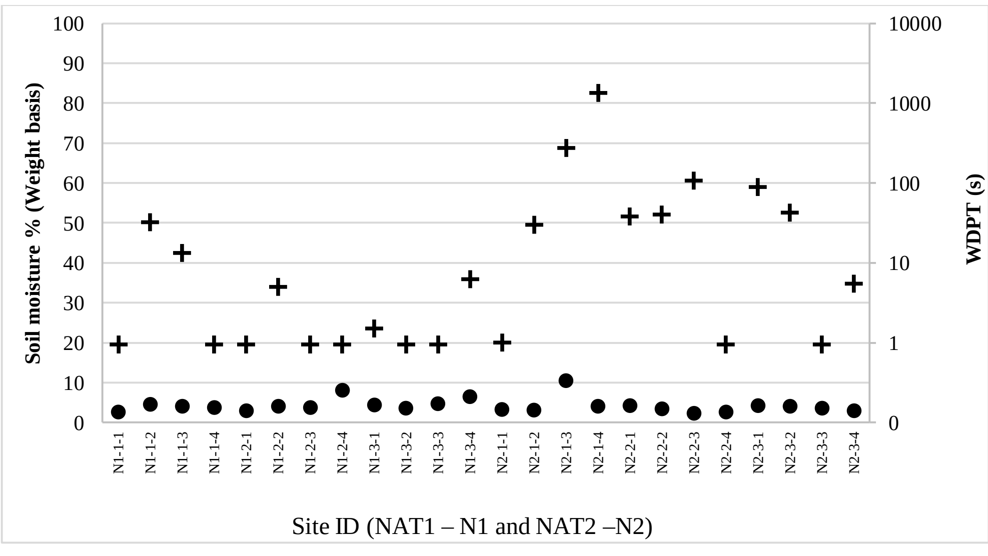


Figure 18: Levels of soil water repellency observed in processed soil after complete air drying.

such as surface runoff and soil water distribution and storage. SWR dropped significantly when the soil moisture was further reduced (although this type of situation is hardly reached in the field) to a very low level (4.2% in average), but remained relatively high. At the same moisture level, same soil showed very low level of SWR when the structure was disturbed. Assessment of the SWR is generally practiced with the processed soil samples as a standardized procedure of measuring SWR and to enhance the comparability of the results. Current results under subtropical mixed forest soil indicate that the use of the processed soil samples underestimates the level of SWR and hence, the predictions on the effects of SWR on the hydrological processes may not be accurate. However, soils under tree species which are known to cause high levels of soil water repellency, such as Japanese cypress (*Chamaecyparis obtuse*) may behave differently.

According to these results, soil structure is a major factor that determines the occurrence of SWR. Although a strong relationship cannot be observed between the WDPT and the total soil carbon in the case of undisturbed soil, it can be suggested that the pattern of organic matter

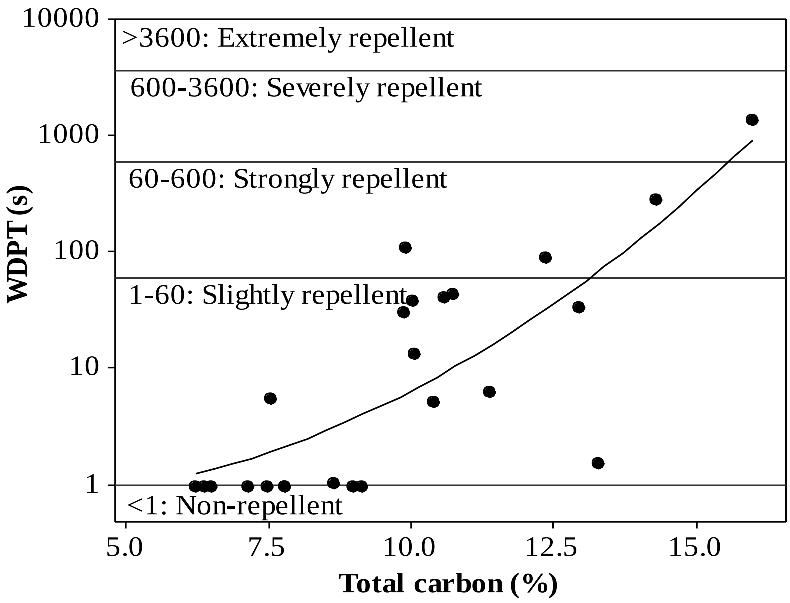


Figure 19: Relationship of water drop penetration time to soil total carbon of processed soil samples

coating, how organic matter may act as a barring film for infiltrating water and hydrophobic characteristics, may also be major determinants of the occurrence of SWR.

3.3.2.5. Conclusions

An assessment of soil water repellency in view of understanding its implications on the hydrological processes of a particular catchment should consider the effects of soil moisture and soil structure in addition to the widely considered quality and quantity of the soil organic matter and soil texture. Although undisturbed soil samples can be obtained with preserved soil structure, it is difficult to define at which soil moisture level the SWR could effectively be measured. Therefore, further studies are necessary to improve the SWR measurement procedures.

3.4. Soil aggregate properties under subtropical coastal forest environment

3.4.1. Introduction

The role of soil aggregates in the modification of soil environment is not new in the soil science context. Soil aggregates are formed mainly by the combination of soil mineral fraction with other organic and inorganic substances (Bronick & Lal, 2005). Therefore, they are composed mainly of soil textural fractions (sand, silt and clay), humic substances, fungal hyphae and plant roots (Caravaca *et al.*, 2001; Denef & Six, 2005). In addition, certain metal ions such as Al, Fe, and Ca are also involved in the formation of aggregates (Barthès *et al.*, 2008; Bronick & Lal, 2005; Egli *et al.*, 2008; Wada *et al.*, 1987). During the formation of soil aggregates, clay-sized particles have been identified as key mineral counterparts of the organic and inorganic material (Bronick & Lal, 2005). Decomposing organic matter also was found to be an important contributor to the formation of aggregates (G. Lu *et al.*, 1998). The processes that govern the formation of aggregates can be divided mainly into biological, chemical and physical. However, these processes do not occur in isolation (Bronick & Lal, 2005). Therefore, it is not wrong to identify soil aggregation as a physicochemical property of the soil.

Soil aggregates modify the soil environment both physically and chemically. Physical effects of aggregates are often being discussed because they play an immense role in the determination of soil structure. Soil structure on the other hand, play a major role in providing better environment for the occurrence of biotic and abiotic processes. Enhanced aeration, improved water storage and retention of nutrients are some of the influences on the soil biology. In the case of abiotic processes, improved water infiltration and storage, aeration and physical stability of the soil are the main functions.

The hydrology of a catchment can be directly affected by the soil structure. As mentioned earlier, good soil structure improves water infiltration and storage resulting in reduces surface runoff. Further, the changes in soil structure may determine the water flow paths within the soil *i.e.* higher volume of water will move through the porous soil layers and vice versa. These in turn, may determine the constituents of water ultimately reaching the streams. For example, a negative relationship has been observed between the sediment concentration of the stream and the stability of soil aggregates (Boix-Fayos *et al.*, 1998). On the other hand, aggregation may negatively affect the plant growth under certain conditions by reducing water storage due to excessive leaching (Franzluebbers, 2002; Nissen & Wander, 2003).

Soil aggregation and the occurrence of soil water repellency can be considered as two sides of a coin. In other words, both are products made out of the same material and under the same processes and collectively express the outcome. However, one can complement or hinder the outcome of the other depending on the context.

Carbon storage is another function of soil aggregates and it is being investigated by various researchers under various conditions. The carbon associated with the stable aggregates are a good repository of carbon and accounts for large proportion of the carbon stored in the soil (Bronick & Lal, 2005).

Studies which explore the features of soil aggregates in the forests of the current experimental area are scarce. Few studies have attempted to investigate the properties of the humic substances in upland forests and mangrove forests (K. Kinjo *et al.*, 2006; Teruya & Kinjo, 2014).

Mangroves are an important ecosystems in island environments although their existence has been recently threatened. They are well known for high biodiversity, coastal erosion protection and recreational purposes. Recently mangroves have been found important because they are able to barricade tsunami waves (Dahdouh-Guebas *et al.*, 2005; Kathiresan & Rajendran, 2005). Although it is not completely understood, the carbon storage is also being considered as a major ecosystem service of mangrove ecosystems (Donato *et al.*, 2011). Further, these authors recognize mangroves as one of the richest forest systems in terms of carbon in the tropics. They also state that 50% of the total carbon is stored in the soil. Although mangroves and upland forests are different in ecosystem characteristics, they are usually linked by the rivers or flowing water from the mountainous areas towards the sea. The linkages are based on the material (sediments) being transported with water.

Due to the complex nature of the material which are undergoing different processes in the soil, especially organic matter, grouping of materials having similar properties (eg. Origin, functionality and maturity) is common in soil and related research. Organic matter, which is the focus of this section, has wide ranges of substances with diverse properties. Therefore, the grouping or fractionation is common during the experiments. In this experiment density fractionation is used. Density fractions are capable of grouping organic matter based on their maturity and functionality (Crow *et al.*, 2007). Further the density fractionation is also capable of grouping soil mineral components into meaningful categories in the aggregate related studies.

With the understanding of the role of soil aggregates in the forest hydrology and the need to understand the characteristics of the soil aggregates, current experiment investigates the organo-mineral interactions of the forests soil. For better understanding and, to expand the knowledge, a mangrove soil will be studied in comparison as a related ecosystem.

3.4.2. Specific objectives

The specific objectives of this study are to:

a. Elucidate the properties of soil aggregates under upland forest soils and mangrove soil
b. Understand the links between carbon storage and mineralogy of both soils

3.4.3. Materials and methods

Characteristics of the sampling sites and sample collection

Upland soil was collected from the main experimental catchment and the mangrove soil was sampled from the estuary of the Oura River located in the southeast of the experimental catchment (Figure 3). The mangrove site is frequently flooded with seawater as the area was low-lying and close to the seashore. The distance to the mangrove vegetation from open sea was approximately 200 m. Data related to stand characteristics of the mangroves in this area are scarce. Nakasuga & Kobashigawa (1976) reported that the original stands located in sampling site were comprised of *Kandelia candel* and *Bruguiera conjugata* (*gymnorhyza*). Currently the dominant plant species is *Bruguiera gymnorhiza* while *Kandelia spp* was found scattered in some parts of the mangrove forest. There was no noticeable litter accumulation in the sampling sites, mainly due to the frequent flushing of falling litter with seawater. A dense root layer was observed in the sampling sites. Therefore, the main source of the organic matter is expected to be the decaying roots. In addition, deposition of river water sediments and relocated organic material could also contribute to the organic matter input.

Soils from both sites were collected from 5 points inside a 2 m × 2 m square at 1 cm depth. Five samples were pooled to prepare a composite soil sample. During the sampling point selection, places with large roots were avoided. Collected soils were ground and sieved through 2 mm mesh after removing the roots and other debris.

Assessment of soil chemical and mineralogical properties

Soil pH (soil : water = 1:2.5) and EC (soil : water = 1:5) were measured by respective electrodes (HORIBA). Carbon (C) and nitrogen (N) contents were analyzed by NC analyzer (SUMIGRAPH NC-220F). Exchangeable cations (Ex-Ca, Ex-Mg, Ex-K and Ex-Na) were extracted with ammonium chloride solution and analyzed by ICP-AES (Shimadzu ICPE-9000).

Clay, silt and sand fractions of both soils were separated by sedimentation and decantation method and expressed on weight basis. Silt and sand fractions were directly analyzed by X-ray diffraction (Rigaku, Ultima+, 2~60° (2θ), 30kV, 15mA, XCuKα) using random direction method. Clay fraction was treated with potassium acetate and magnesium acetate. Treated clay fractions were air-dried, heated at 105°C, 300°C, and 550°C for one hour, allowed to cool down and saturated with glycerol. Each treated clay fraction was analyzed by X-ray diffraction (Rigaku, Ultima+, 2~30° (2θ), 30kV, 15mA, XCuKα).

Density fractionation of samples

The physical separation of the soil organic matter and mineral particles by density fractionation technique has been used in understanding organic matter–mineral interactions. The linkages between organic matter and different soil minerals and the degree of protection within aggregates are examples for these interactions. Further, density fractionation also aid in separating different pools of organic matter based on their state of decomposition. Principally, the lighter fractions contain plant like substances and clay minerals. The denser fractions contain sand, silt and organic matter in the advanced stages of decomposition bound to soil minerals. Among the various solutions used in the density fractionation, sodium polytungstate is a less hazardous solution with densities reaching as high as 2.9 g cm^{-3} (Crow *et al.*, 2007). Therefore, the density fractionation technique was identified as the best-suited method for the present study and, sequential density fractionation was carried out by slightly modifying the methods described by Sollins et al. (2006) and Sollins et al. (2009).

Four density fractions were separated by sodium polytungstate with three density levels. During the separation, air-dried soil (<2 mm) was placed in a centrifuge tube and sodium polytungstate (d=1.6 g cm^{-3}) was added. The tube was shaken for 24 hours and allowed to stand for 30 min before centrifuging at 2000 rpm for 30 min. The supernatant was extracted as <1.6

g cm^{-3} fraction. Particles of the supernatant were extracted by a glass fiber filter (Membrane filter, pore size=0.45 μm) under a vacuum. Sodium polytungstate was washed off with distilled water and filter was dried at 30°C for 24 hours. The dried fraction on the filter was separated by a brush and weighed. After extracting the <1.6 Mg m^{-3} fraction, next sodium polytungstate solution with d=2.0 Mg m^{-3} was added to the residue left after the previous step. The supernatant was comprised of 1.6~2.0 g m^{-3} fraction and it was extracted by the same method explained above in extracting <1.6 g m^{-3} fraction. Finally, sodium polytungstate solution with 2.5 g m^{-3} density was used to separate 2.0~2.5 g m^{-3} fraction and the remainder was >2.5 g cm^{-3} fraction. Each fraction obtained by density fractionation was sieved with 0.25 mm mesh. Carbon and nitrogen of each sieved fraction were measured by NC analyzer (SUMIGRAPH NC-220F). To assess the mineralogical properties, first, the organic matter of each fraction was removed by oxidizing with 6% peroxide. After the oxidation, suspensions of each fraction were prepared by adding a little water. Suspensions were applied on glass slides and air-dried. Mineralogical properties of each fraction were analyzed by X-ray diffraction (Rigaku, Ultima+, 2~30° (2θ), 30kV, 15mA, XCuKα). Sand, silt and clay fraction of each density fraction in both types of soils were separated by sedimentation and decantation and expressed on weight basis.

Estimation of the degree of humification of humic acids

The method of humic acid extraction and subsequent estimation of the degree of humification was adopted from Kumada (1977). Density fractions were treated with a mixture of 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ solutions for 30 minutes in a hot water bath (100°C). Soluble and insoluble fractions were separated by centrifugation. The soluble fraction was mixed with concentrated sulfuric acid and resulting supernatant and the precipitate were separated. The precipitate was dissolved in the mixture of 0.1 M NaOH and 0.1 M $Na_4P_2O_7$ solutions again and the resulting soluble fraction was extracted as humic acids. The degree of humification of the humic acids was estimated by the parameters (Δ log K and RF value) derived from optical density (K) of the solution.

$$\Delta \log K = \log K_{400nm} - \log K_{600nm} \qquad \text{eq. (1)}$$

$$\text{RF value} = \frac{K_{600nm} \times 1000}{Amount\ of\ 0.1N\ KMnO_4\ (ml) consumed\ by\ 30\ ml\ of\ humic\ acid\ solution} \qquad \text{eq. (2)}$$

3.4.4. Results and discussion

Soil chemical and mineralogical properties

Table 6 shows the chemical and physical properties of both upland forest and mangrove soils. The pH of upland forest and mangrove soils were 4.3 and 7.8 respectively. Mangrove soil was rich in exchangeable cations (Ex-Ca, Ex-Mg, Ex-K and Ex-Na) and alkaline due to the salts from the seawater. Upland forest soil had high clay content while mangrove had high sand content. Sand from seaside may have washed into the mangrove area. Carbon contents of upland forest soil and mangrove soils were 33.9 and 19.3 g/ kg respectively. High carbon accumulation in the upland forest soil compared to mangrove soil, could be attributed to the comparatively high clay content in the upland soil.

Table 6: Chemical and physical properties of upland and mangrove soils

	pH (H_2O)	Organic-C (x 10^{-1} g kg^{-1})	Total-N (x 10^{-1} g kg^{-1})	Exchangeable Ca	Mg	K	Na	Clay	Silt	Sand
				------- (cmol$_c$ kg^{-1}) -------				-------- (g kg^{-1}) --------		
Upland forest soil	4.3	33.9	1.3	1.2	0.2	0.3	0.1	437	271	292
Mangrove soil	7.8	19.3	1.6	3.2	1.5	1.1	20.1	269	162	569

Figure 20 and Figure 21 shows the X-ray diffraction patterns of sand, silt and clay fractions of upland forest and mangrove soil. Quartz (0.336, 0.24, 0.22, 0.19 and 0.18 nm), monohydrate calcite (0.43 nm) and K-feldspar (0.330 nm) were identified in the sand fractions of both upland forest and mangrove soils. Quartz (0.33, 0.24, 0.22, 0.19, 0.18 and 0.16 nm), illite (1.04, 0.55 and 0.26 nm) and kaolin minerals (0.70 and 0.35 nm) were identified in the silt fractions of both soils. In the clay fractions of upland and mangrove soil, illite and kaolin minerals were identified by using the variation and shift of main peaks of each mineral (Figure 20). Vermiculite-chlorite intergrade was also identified in the clay fraction of mangrove soil and upland forest soil by the 1.17 nm and 1.47 nm peaks. Therefore, upland and mangrove soil were similar in terms of soil mineralogical properties.

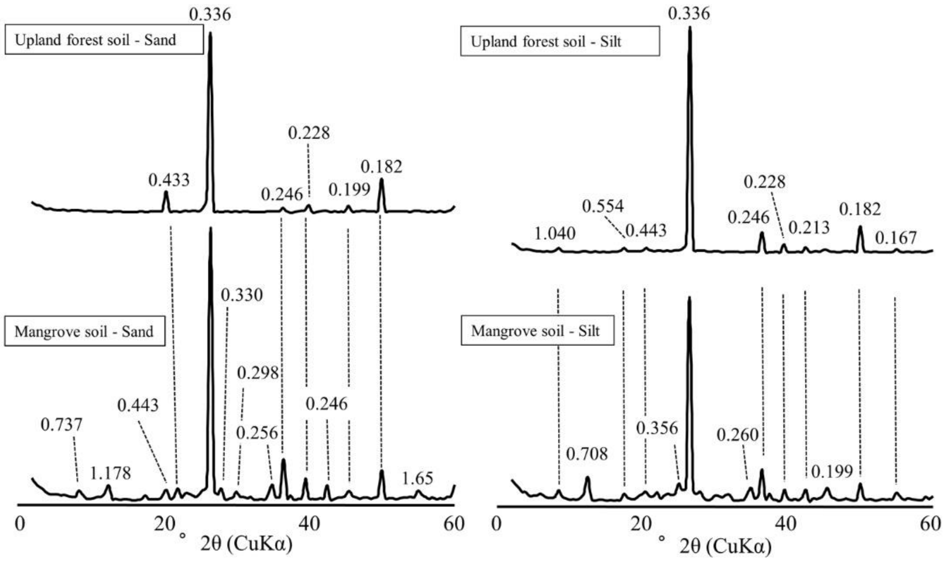


Figure 20: X-ray diffraction patterns of sand and silt fractions of upland forest and mangrove soils

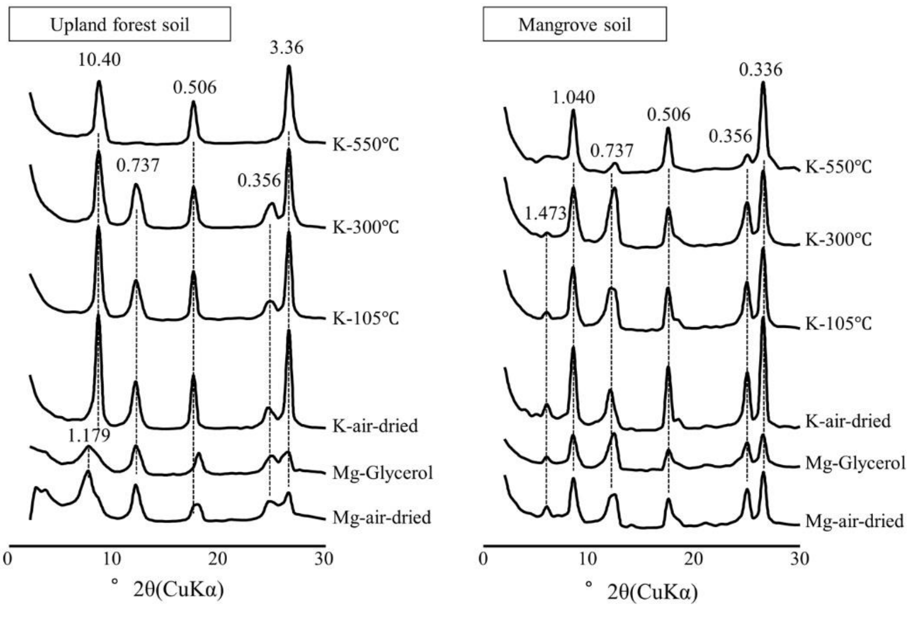


Figure 21: X-ray diffraction patterns of clay fractions of upland forest and mangrove soils

Properties of density fractions

Figure 22 shows the distribution of clay, silt and sand across the density fractions of each soil. In both soils, sand content in 2.0~2.5 and >2.5 g cm^{-3} fractions was higher than the other fractions. Clay content did not differ across four density fractions of the mangrove soil. However, clay and silt contents in 1.6~2.0 g cm^{-3} fraction were higher than that of the other density fractions in upland forest soil. As the conditions of mangrove and upland forest soil are different, particle size distribution in each fraction also may vary.

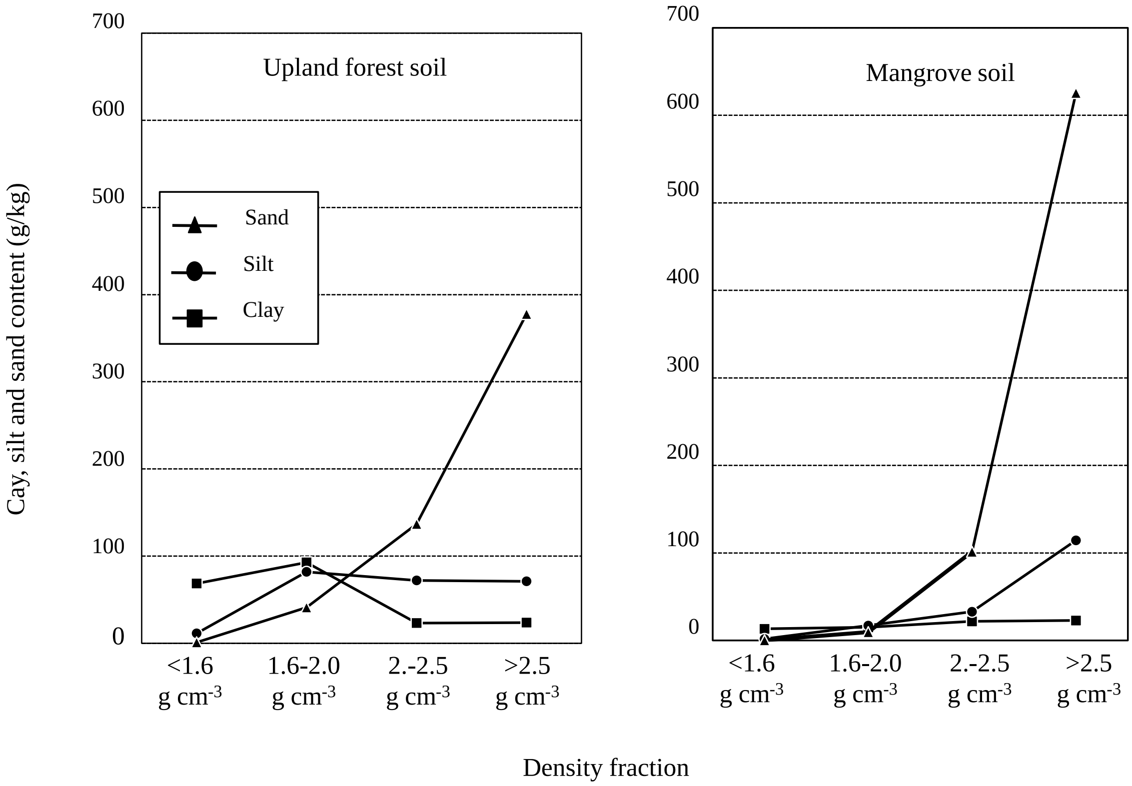


Figure 22: Clay, silt and sand content in each density fraction

Figure 23 shows the X-ray diffraction pattern of each density fraction of upland and mangrove soils. In the mangrove soil, the dominant mineral quartz (0.336, 0.246, 0.225, 0.199 and 0.185 nm) was found in 1.6~2.0, 2.0~2.5 and >2.5 g cm^{-3} fractions. As the sand and silt contents of the mangrove soil was high (Figure 22), these fractions may have contributed more to the overall quartz content. The dominant minerals of <1.6 g cm^{-3} fraction were kaolin minerals (0.737, 0.363, 0.267 nm), illite (0.104, 0.506, 0.356 and 0.256 nm), and vermiculite-chlorite intergrade (0.804 nm). From the current data, it can be said that the light-density fraction of mangrove soil is mainly comprised of clay minerals. Quartz (0.336 and 0.228, 0.182 and 0.169) was the dominant mineral in the >2.5 g cm^{-3} and 2.0~2.5 fractions of the upland forest soil. Kaolin minerals (0.737, 0.363 and 0.267) and quartz (0.336 and 0.246 0.228, 0.182 and 0.169) dominated the 1.6~2.0 g cm^{-3} fraction. Kaolin minerals (0.737 and 0.363 nm), vermiculite-chlorite intergrade (1.179 and 0.804 nm) and quartz (0.336 and 0.169 nm) were identified in <1.6 g cm^{-3} fraction. The light-density fraction of the upland forest soil had high clay mineral content compared to mangrove soil. In the X-ray diffraction pattern of the upland soil, a peak was observed at 0.535 nm in <1.6 g cm^{-3} fraction. However, the mineral corresponding to this peak could not be identified. Even though illite was identified in the clay fraction (Figure 21) of the upland soil, it was not identified in any of the four density fractions. As the main peak corresponding to illite was not observed (Figure 23), the mineral contributed to the unknown peak could have been illite. In both soils, clay minerals tended to appear with decreasing density.

Table 7 shows the percentage of each density fraction in each soil along with the percentages of carbon and nitrogen and C/N ratio in each density fraction. In the mangrove soil, the proportion of the material included in the density fractions increased with increasing density and the percentage of carbon and nitrogen in each density fraction decreased as the density increases. Therefore, compared to the other fractions, <1.6 g cm^{-3} fraction had the highest carbon and nitrogen content and C/N ratio in the mangrove forest. (Wagai *et al.*, 2008) reported that the low-density fraction, which includes plant detritus, was easily separable from soil minerals. Therefore, <1.6 g cm^{-3} fraction of the soil seems to have plant detritus and separable soil particles. The upland forest soil also follows a similar pattern. The result obtained for the

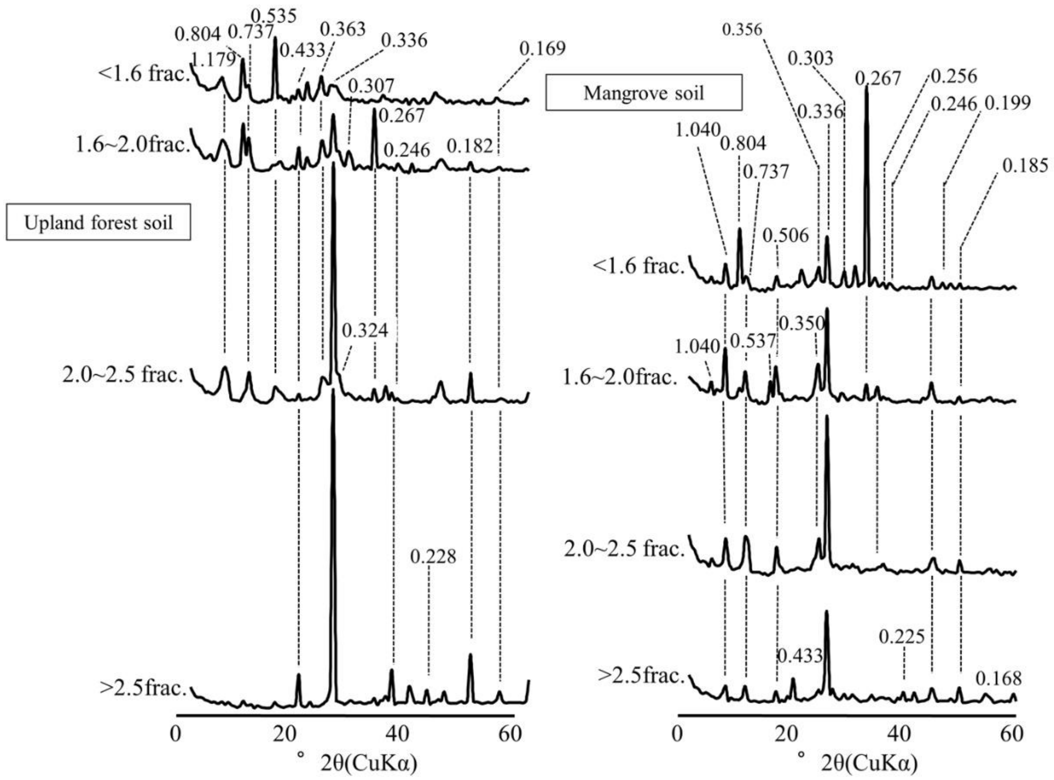


Figure 23: X-ray diffraction patterns of each density fraction of upland forest and mangrove soils

Table 7: Percentage of each density fraction in each soil type and carbon, nitrogen and C/N ratio of each density fraction

		Fraction	**C**	**N**	**C/N**
			%		
Mangrove soil	<1.6 frac.	1.5	31.7	1.1	29.6
	1.6 ~ 2.0 frac.	4.3	26.4	1.2	21.8
	2.0 ~ 2.5 frac.	16.0	5.9	0.5	12.3
	> 2.5 frac.	78.2	0.7	0.05	7.3
Upland forest soil	<1.6 frac.	8.0	32.0	1.2	26.7
	1.6 ~ 2.0 frac.	21.6	18.5	0.9	19.8
	2.0 ~ 2.5 frac.	23.2	9.3	0.6	14.8
	> 2.5 frac.	47.2	2.2	0.2	14.6

upland soil of this study are comparable with the data reported in other similar studies conducted under upland forests occupied by *Tsuga heterophylla, Thuja plicata, Taxus brevifolia, Acer circinatum, Cornus nuttallii, Vaccinium spp.* and *Polystichum munitum* (Grünewald *et al.*, 2006; Sollins *et al.*, 2006, 2009).

Figure 24 shows the distribution of total carbon content across the density fractions. Compared to the other density fractions, 1.6-2.0 g cm^{-3} fraction of both mangrove and upland soil had the highest carbon content. As 1.6~2.0 g cm^{-3} fraction was comprised of silt and clay mostly (Figure 22), it is possible that silt and clay contribute more to the formation of clay-humus complexes. However, mangrove soil had low clay and silt content compared to upland forest soil in the 1.6~2.0 g cm^{-3} fraction. Therefore, the carbon storage mechanism of both soils were different.

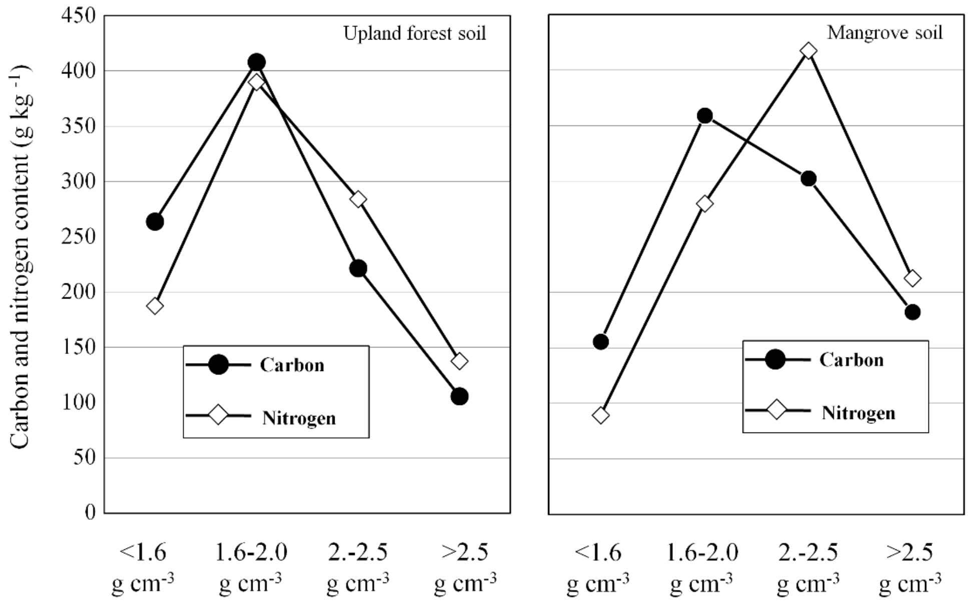


Figure 24: Distribution of the total soil carbon and nitrogen across the density fractions

Although the variation of the carbon was similar, the variation of nitrogen was dissimilar in two soils. In the mangrove soil, nitrogen content in 2.0~2.5 g cm^{-3} fraction was higher than in other fractions, whereas 1.6~2.0 g cm^{-3} fraction had the highest nitrogen content in upland soil. Available data are not sufficient to explain the reasons for the differences between the upland and mangrove soil nitrogen distribution. However, it has been reported that size and the activity of microbial populations and detritus input along with the availability of other essential nutrients may affect the nitrogen dynamics in mangrove systems (Boon & Cain, 1988).

Although the carbon distribution is similar in two soils the constituents in the carbon pools could be different and hence, the distribution of nitrogen could also differ.

The degree of humification of humic acids in each density fraction of mangrove and upland forest soils is shown in Figure 25. The categorization was based on the criteria stated by Kumada (1977). Generally, the degree of humification increases when the RF value is increasing and the Δ log K value is decreasing. Therefore, Rp region indicated in the figure has the less-humified material. Four density fractions of the mangrove soil represented type Rp. On the other hand, all the fractions of the upland forest soil were categorized into type B and therefore, the degree of humification was higher than the mangrove soil

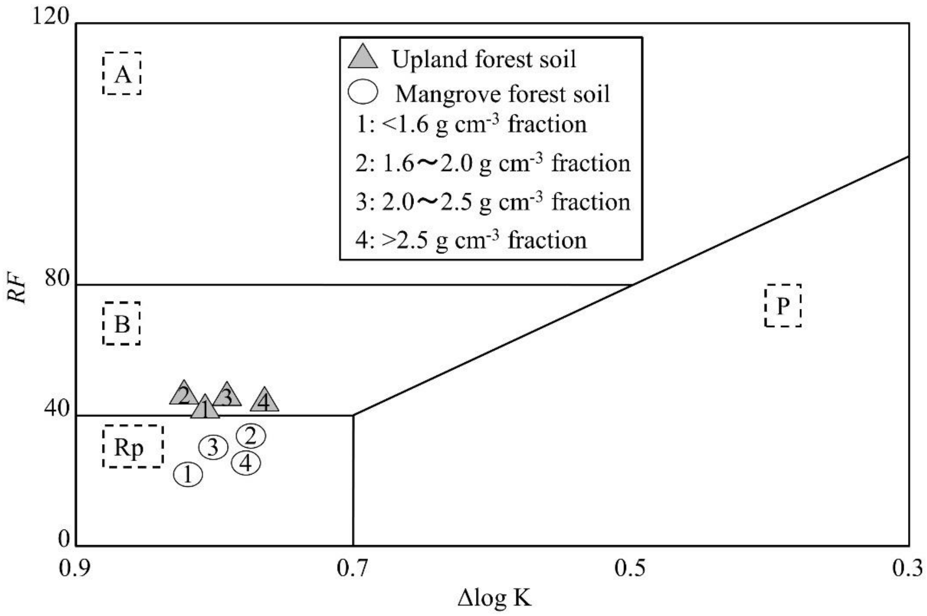


Figure 25: The degree of humification of humic acids in each density fraction of mangrove and upland soil

Although the chemical and physical properties of the organic matter, biota and the organo-mineral interactions could be decisive factors in controlling the degree of humification, the difference in the redox status of the two soil types could be a dominant factor in the overall context.

3.4.5. Conclusions

The organic matter dynamics of the two systems vary in several aspects. As the litter of the mangrove ecosystem is frequently flushed, the accumulation of litter layer is very much limited. Relatively high litter accumulation was observed in the upland soil. However, due to the presence of favorable conditions for rapid decomposition, large litter buildup cannot be observed. Furthermore, the redox status of the two sites could lead to the differences in overall biochemically-driven processes such as litter decomposition, integration of litter to the mineral fraction and organic matter storage. The assessment of soil aggregates under upland forest soil in comparison with the mangrove system, by density fractionation yielded important information about the interactions between organic matter and minerals and hence, about the characteristics of the carbon storage. Four fractions (<1.6, 1.6~2.0, 2.0~2.5 and >2.5 g cm-3 fractions) were successfully separated by sodium polytungstate solutions with three different densities. In both soils, lighter fractions had the highest carbon and nitrogen content and C/N ratio and, all of them decreased with increasing density. Clay and silt minerals and sand and silt minerals were included in low-density fractions (<1.6 and 1.6~2.0 g cm-3) and high-density fractions (2.0~2.5 and >2.5 g cm-3) respectively. In upland forest soil, highest clay and carbon percentages were observed in the 1.6~2.0 g cm-3 fraction. Mangrove soil also had the highest carbon content in the 1.6~2.0 g cm-3 fraction but had low clay content. The result of the upland soil of this study agrees with the results reported in similar studies conducted under other upland forests (Grünewald *et al.*, 2006; Sollins *et al.*, 2006, 2009). However, similar studies on mangrove soil were not found.

Therefore, the data from this study suggest that the clay minerals are necessary to stock carbon in the upland soil. However, such relationship is not visible in the mangrove soil, signifying the important differences in the organo-mineral interactions of the mangrove soil compared to the upland soils. These differences can be further clarified by assessing the other influential parameters such as litter quality, biotic and abiotic factors affecting the litter decomposition

3.5. Litter decomposition dynamics under subtropical coastal forest environment

3.5.1 Introduction

As discussed in the previous sections under chapter 3 of this thesis, soil organic matter mediates in almost all the processes in a forest soil. In most of the forest ecosystems, the origin of organic matter is the litter falling from the overlying vegetation. However, transported material also could be the origin of organic matter under low-lying ecosystems such as mangroves. Where the litter or transported material reach the soil, they undergo various processes including mechanical breakdown, biological breakdown, and chemical transformations. Collectively all these processes are called decomposition. This is a continuous process and therefore, the soil organic matter is composed of a range of material at various stages of decomposition. The whole process is dependent on the properties of original organic material, the properties of soil and the climatic parameters governing the area. On the other hand, the organic matte at various stages of decomposition influence the other soil processes such as nutrient cycling, soil aggregation, soil water repellency, soil nutrient retention and carbon storage *etc*.

Because of the importance of the organic matter for the sustenance of the soil ecosystem as well as the complexity of the organic matter related processes, large number of research are being conducted all around the globe under various research themes. As terrestrial forests are considered as one of the richest ecosystems in terms of carbon storage, various studies are being conducted on the aspects of the litter decomposition process in view of harnessing the carbon storage. Factors affecting the litter decomposition have been a focal point of most of the recent research. Due to the complexity of the factors affecting the litter decomposition, lot more information still remains to be uncovered. Swift *et al.* (1979) proposed that litter decomposition is a function of physicochemical environment (P), litter quality (Q) and organisms (O). In general, actual evaporation (AET), C:N ratio, N concentration, Lignin:N ratio, P concentraion, C:P ratio and Lignin :P ratio affect the litter decomposition process in any climatic zone (Aerts & ChapinIII, 2000). Litter quality is mainly defined in terms of the constituents of the litter and, it has been found to alter the decomposition process in the local scale. Due to the complexity of the litter decomposition process and the experiments in the field, many researchers are focusing on finding indicators of decomposition process so that they can be used to explain the decomposition process under various contexts. However, only a few studies can be found related to the litter decomposition in the subtropical coastal forests (Alhamd *et al.*, 2004; Ono *et al.*, 2011).

Generally, litter is comprised mainly of simple carbohydrates, hemi-cellulose, cellulose and lignin (phenolic compounds). The decomposability of these material decrease in the order of carbohydrate, hemi-cellulose, cellulose, and lignin (Nyle C. Brady & Weil, 2008). Due to the complexity of the litter composition, proximate fractions are often used in the litter decomposition studies. Mostly, these fractions include groups of similar compounds. Fractionation of carbon in organic material to fiber fractions is often being used in forage science and litter related studies (Goering & Van Soest, 1970; Undersander *et al.*, 1993; Van Soest, 1967). Berg & McClaugherty (2007) shows that non-fiber fraction (simple carbohydrates etc…) is easily decomposed compared to the other fractions (fiber fraction: cellulose and lignin etc…). Different decomposition patterns have been observed for different fiber fractions of the litter (Coûteaux *et al.*, 1998). Therefore, the quality and quantity of the fiber fraction of the litter has a linkage to the rate and the degree of litter decomposition. Recently, it has been reported that neutral detergent fiber, acid detergent fiber and acid detergent lignin of different types of manure can be used in explaining the decomposition process (Oyanagi et al. 2007 and 2010). Furthermore, fiber and non-fiber fractions can be separated with ND (Neutral detergent) and AD (Acid detergent) solutions using simple laboratory equipment in a relatively short time.

In the present study the organic matter decomposition patter of the subtropical coastal forests is studied by emphasizing on the composition of the litter in terms of proximate fiber fractions.

3.5.2. Specific objectives

The specific objectives of this study are to:

a. Understand the litter decomposition pattern of the mixed forest litter of subtropical coastal forests.
b. Examine the relationship of different proximate fiber fractions to the litter decomposition pattern
c. Examine the predictability of the litter decomposition process by using different fiber fractions of the litter.

3.5.3. Materials and Methods

Sampling and sample preparation

The study was conducted as a laboratory incubation using the litter collected from the main sampling sites of the experimental catchment. Litter samples comprised of leaves, fruits and branches were collected in sixteen sites. Collected samples were dried under 30°C and then sufficiently ground to pass through a 0.75 mm sieve. A bulk soil sample was collected from the B horizon of one sampling site. Soil was air-dried and sieved with 2 mm sieve.

Incubation study

Litter carbon decomposition was measured by a laboratory incubation test. Litter samples were added to the soil so that the carbon content was 5% in the soil and litter mixture. Water content of the mixture was adjusted to 60% water holding capacity and incubated in 200 mL glass bottles in the dark at 30°C. Incubation test was conducted for nine months. After 1, 2, 3, 6 and 9 months of incubation, samples were taken out as batches. Samples were air-dried and ground to pass through 0.25 mm sieve. Carbon content of treated samples were measured by NC corder (Sumigraph NC-220F).

Litter analysis

Major minerals (Ca, Mg and K) and P were assessed by ICP-AES (Shimadsu ICPE 9000) after digesting the litter by using perchloric acid and nitric acid. NDF fraction and ADF fractions were isolated by washing off the respective soluble fraction (ND soluble and AD soluble) with ND (Sodium lauryl sulfate, Ethylenediaminetetraacetic acid (EDTA), Sodium borate, Sodium phosphate and Triethylene glycol, dissolved in deionized water) and AD solutions (1N Sulfuric acid and Cetyltrimethylammonium bromide (CTAB)) (Undersander *et al.*, 1993).

ADL fraction was extracted by removing the cellulose of ADF fraction using 72% sulfuric acid (Sanger *et al.*, 1998). NDF and ADF and ADL fractions were dried at 30°C and ground to pass through a 0.25 mm sieve. Carbon of each fraction was measured by NC corder. Generally, the composition of the NDF and ADF fractions are considered as the sum of hemicellulose, cellulose and lignin and the sum of cellulose and lignin respectively.

Soil analysis

Soil pH and EC were determined by respective electrodes. Exchangeable cation extracted with ammonium chloride were measured by ICP-AES. Carbon of non-treated and incubated soils were determined by NC corder.

3.5.4. Results and discussion

Chemical composition of soil and litter

Table 8 and Table 9 shows soil and litter chemical properties respectively. Soil reaction was acidic (pH= 4.2) and the carbon content was low (0.70×10^{-1} g/kg). The ranges of carbon and nitrogen contents of thr litter were 26.22-44.87 g/kg and 0.69-1.65 g/kg respectively. C/N ratio had a wide range (24-64). Ca in litter was high compared to the other minerals. The ranges of ND soluble carbon, NDF-carbon, AD soluble carbon, ADF-carbon and ADL-carbon as percentages were 0.9~7.7, 25.3~39.5, 3.1~9.7, 23.1, 35.6 and 12.9~20.5, respectively. High ADF and ADL-C percentages indicate high cellulose and lignin content in the litter. The reason for high fiber content in the litter could be attributed to the use of whole litter which included high fiber materials such as decaying branches and fruits *etc*.

Table 8: Chemical properties of soil used for the incubation experiment

	pH (Water)	EC (mS/m)	C	N	Exchangeable Ca	Mg	K	Na
			$\times 10^{-1}$ g/kg		cmol$_c$/kg			
Soil used for the incubation	4.1	5.8	0.70	0.07	1.1	0.2	0.5	0.097

Table 9: Chemical properties of litter

Sample ID	C	N	C/N	ND soluble - C	NDF-C	AD soluble - C	ADF - C	ADL - C	Ca	Mg	K
	× 10^{-1} g/kg										
1	41.10	0.91	45	5.9	35.2	8.0	33.1	14.2	0.87	0.18	0.007
2	41.19	0.93	44	4.5	37.4	6.7	35.2	19.8	1.06	0.08	ND
3	43.35	0.96	45	3.9	39.5	7.6	35.6	18.2	1.35	0.08	ND
4	39.76	1.00	39	1.9	37.9	7.5	32.3	18.8	0.83	0.002	ND
5	43.84	1.05	42	7.2	36.6	8.7	35.1	16.8	0.90	0.12	ND
6	44.99	0.70	64	5.9	39.1	9.7	35.3	20.1	0.97	0.11	ND
7	34.12	0.69	49	2.8	31.3	5.7	28.4	16.8	0.67	0.14	0.098
8	42.18	1.58	26	7.5	34.7	7.5	34.7	18.2	0.85	0.17	ND
9	34.62	1.28	27	5.7	28.9	7.6	27.0	15.2	1.00	0.23	0.098
10	35.29	1.11	32	4.4	30.9	6.3	29.0	17.1	1.16	0.21	0.091
11	37.07	1.15	32	6.3	30.8	9.7	27.4	12.9	1.33	0.18	0.016
12	44.87	1.52	30	7.4	37.5	9.4	35.5	20.5	1.62	0.21	ND
13	40.09	1.65	24	7.7	32.4	9.4	30.7	16.0	0.19	0.002	ND
14	38.13	1.11	34	3.6	34.5	7.4	30.7	18.8	0.34	0.05	ND
15	41.70	1.10	38	5.0	36.7	7.6	34.1	19.1	0.78	0.16	ND
16	26.22	0.92	29	0.9	25.3	3.1	23.1	15.2	0.29	0.15	0.038
Avg	***39.00***	***1.1***	***37***	***5.0***	***34.3***	***7.6***	***31.7***	***17.4***	***0.89***	***0.13***	***0.06***

ND – Not detected

Decompsiton of litter carbon during the incubation

Figure 26 shows the decomposition pattern of the litter carbon during the nine month period. The litter carbon sharply decreased after the first month. Other studies conducted with different litter types have also shown a rapid rate of decomposition at the early stages (Melillo *et al.*, 1989; Wang *et al.*, 2004). At the end of this stage the remnant carbon of litter was 0.97 g/ 30 g $_{soil}$ (64% of the initial carbon content).

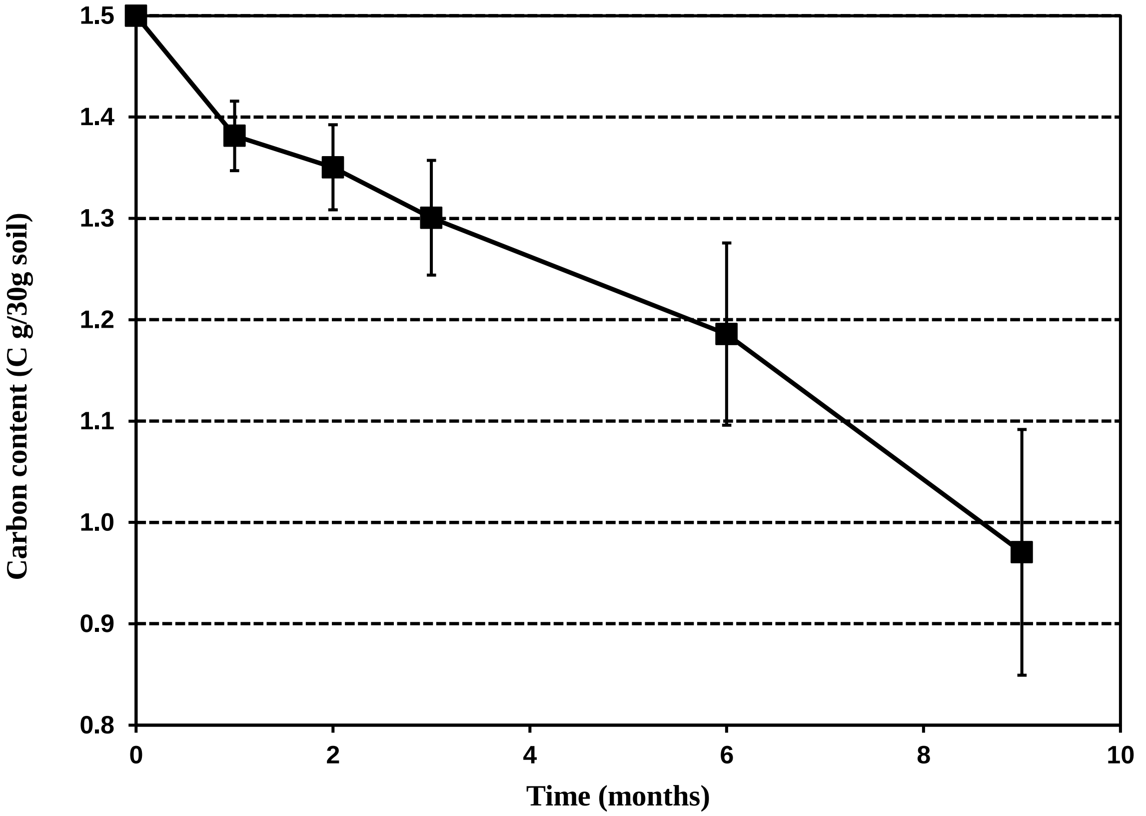


Figure 26: Changes in the litter carbon content during the 9-month incubation

Table 10 shows respective coeficients of the significant correlations between litter chemical composition and the carbon decomposed after each incubation period. There were significant relationships between ND and AD soluble carbon during first month and first two-months. In addition, AD soluble carbon had significant relationship also for 0-3 month period. C/N ratio showed significant relationships for 0-3 month and 0-6 month period. None of the factors showed significant correlations for the whole 9 month period. The highest correlation coefficient (r = 0.73) was observed for AD soluble carbon during the first 2-month period. From this relationship, it can be suggested that the non-fiber fraction and the hemicellulose were dominant in the carbon decomposed during the first two-month period.

(Aerts & ChapinIII, 2000) reported that C/N of litter as a factor dominating the litter decomposition in all climatic zones. However, Osono & Takeda (2004) proposed that the lignin/N ratio of the litter is more useful as factor determining the decomposition process.

Findings of the present study deviates from above findings and shows that factors of decomposition changes with the stages of decomposition. Further, ligning/ N ratio is not a useful indicator in the early stages of decomposition. As lignin has low decomposablity, it may not be subjected to extensive microbial decomposition in early stages.

Table 10: Correlation coefficients of the correlations between the carbon decomposed after different incubation periods and selected litter chemical properties

	0-1 month	**0-2 month**	**0-3 month**	**0-6 month**
C/N	**-**	**-**	**0.50***	**0.51***
ND soluble - C(%)	**0.52***	**0.50***	**-**	**-**
AD soluble -C(%)	**0.64****	**0.73****	**0.55***	**-**

∗∗:*p*<0.01, ∗*p*<0.05

Oyanagi *et al.* (2007) and (2010) proposed that carbon fractions extracted by detergent solutions (ND and AD solution) is useful as an indicator for manure decomposition. They have observed that AD soluble organic mater and AD soluble carbon in manure corresponded to the amount of decomposed carbon during the first 10 days and during first month of decomposition respectively. In comparison to above results, the results of the present study suggest that the carbon fractions extraced by detergent solutions is a determinant of the forest litter decomposition.

Prediction of remnant carbon of litter during the decomposition

Remnant carbon in the soil after each period of incubation was plotted against each initial carbon fractions of the litter. Figure 27 shows the best relationships observed among them *i.e.* the relationship between remnant carbon and NDF-C (r = 0.454) and remnant carbon and ADF-C (r = 0.704) after 1 and 2 months of incubation respectively. These data shows that the remnant carbon after 1 and 2 months can be predicted by using initial NDF-C and ADF-C of the litter. Two equations derived for the relationships are

$$Y = 0.235 X + 1.073 \qquad \text{eq.(1)}$$

$$Y = 0.573 X + 0.655 \qquad \text{eq.(2)}$$

When these two equations are concerned eq.(2) could be more useful than eq.(1). Oyanagi *et al.* (2007) reported that the relationship between ADF-C and remnant carbon of manure, after

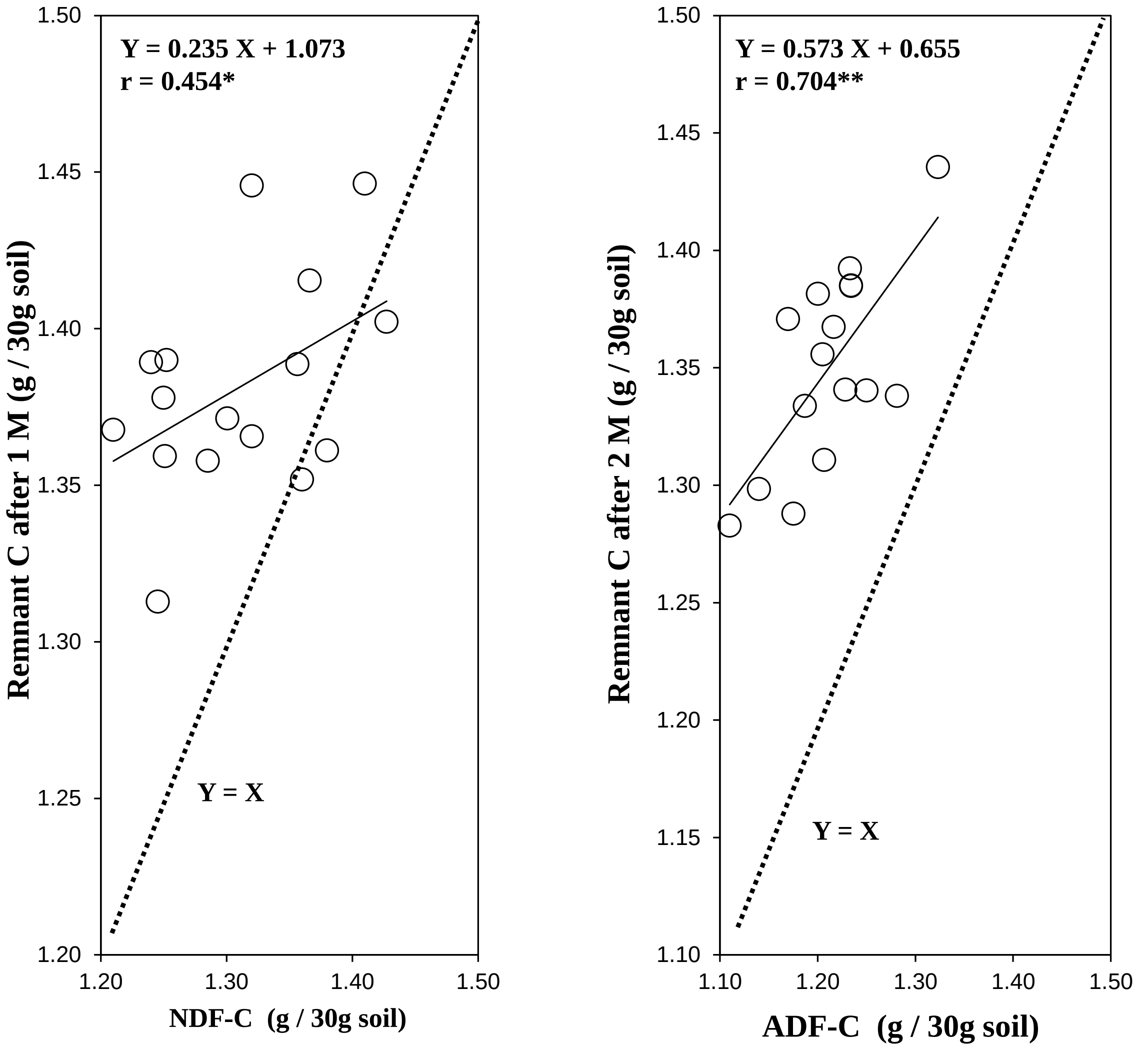


Figure 27: The relationship between remnant carbon and NDF-C and ADF-C during the incubation

three months of decomposition, resembled an identity function. The difference between the findings of Oyanagi *et al.* (2007) and the present study can be attributed to the differences in the substrates as well as the conditions under the experiments were conducted. The experiment of Oyanagi *et al.* (2007) was conducted on various types of manure in an andolsol under field conditions.

Following equations were derived by multiple linear-regression analysis of ND-soluble C, NDF-C, AD soluble C, ADF-C and ADL-C of litter to predict the litter decomposition after 1, 2, 3, 6 and 9 month periods.

$$\text{Renmant carbon after 1 M} = 1.464 + 0.258 \cdot \text{ND-soluble C} + 0.254 \cdot \text{NDF-C} - 0.267 \cdot \text{AD-soluble C} - 0.258 \cdot \text{ADF-C} + 0.007 \cdot \text{ADL-C} \quad \text{eq.(3)}$$

$$\text{Renmant carbon after 2 M} = 1.464 + 0.283 \cdot \text{ND-soluble C} + 0.275 \cdot \text{NDF-C} - 0.300 \cdot \text{AD-soluble C} - 0.276 \cdot \text{ADF-C} + 0.004 \cdot \text{ADL-C} \quad \text{eq.(4)}$$

$$\text{Renmant carbon after 3 M} = 1.351 + 0.070 \cdot \text{ND-soluble C} + 0.057 \cdot \text{NDF-C} - 0.088 \cdot \text{AD-soluble C} - 0.058 \cdot \text{ADF-C} + 0.008 \cdot \text{ADL-C} \quad \text{eq.(5)}$$

$$\text{Renmant carbon after 6 M} = 1.345 - 0.304 \cdot \text{ND-soluble C} - 0.324 \cdot \text{NDF-C} + 0.29 \cdot \text{AD-soluble C} + 0.322 \cdot \text{ADF-C} + 0.08 \cdot \text{ADL-C} \quad \text{eq.(6)}$$

$$\text{Renmant carbon after 9 M} = 1.126 - 0.254 \cdot \text{ND-soluble C} - 0.281 \cdot \text{NDF-C} + 0.225 \cdot \text{AD-soluble C} + 0.285 \cdot \text{ADF-C} + 0.001 \cdot \text{ADL-C} \quad \text{eq.(7)}$$

Figure 28 shows the relationships between the measured remnant carbon and the remnant carbon predicted by the equations after each incubation period. The highest correlation coefficient (r = 0.815) was obtained for the two month incubation. The slope (0.663) of the above relationship is the closest to the identity funtion compared to the other relationships (Figure 28). From these results, it can be suggested that equation 2 has the potential to be used in the prediction of the remnant carbon in the mixed forest litter. Field trials are necessary to verify how this relationship behaves in the forest floor.

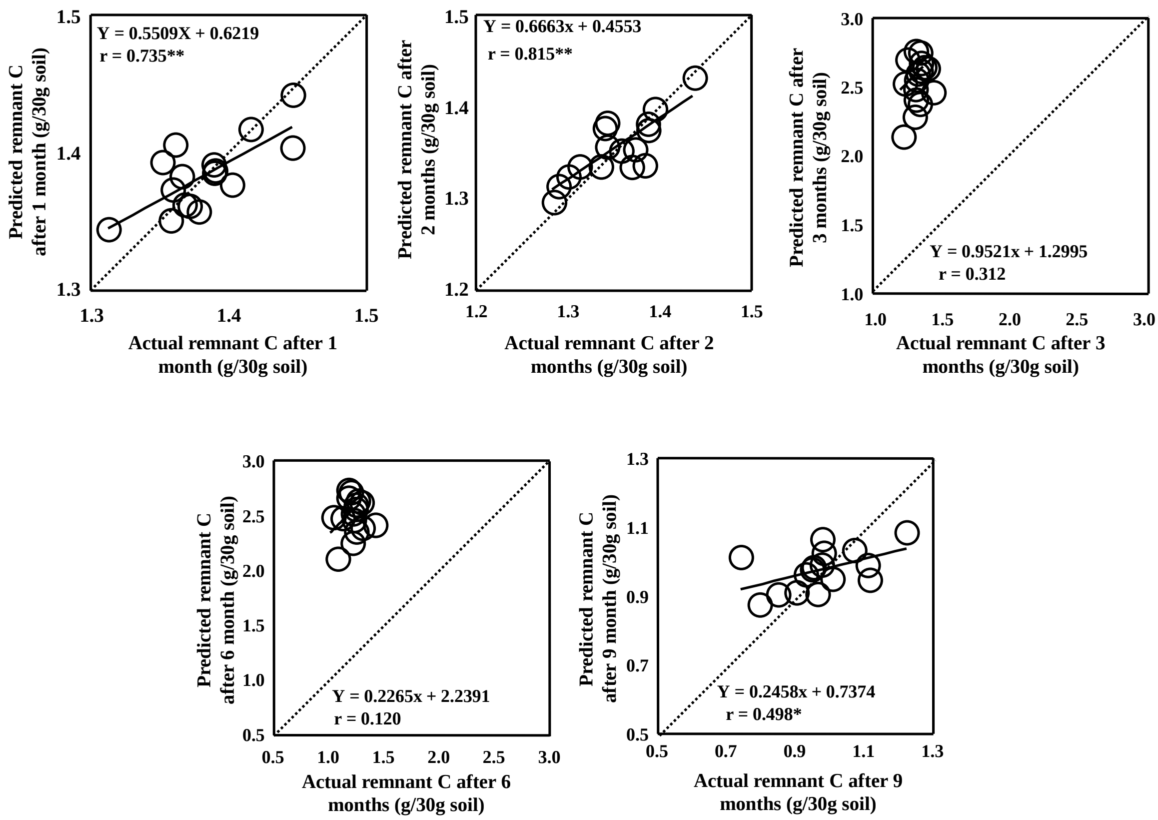


Figure 28: The relationship between the actual remnant carbon and the remnant carbon predicted by the equations after each incubation period

3.5.5. Conclusions

The carbon fractions extracted by ND and AD solutions were exmined as factors of mixed forest litter decomposition. The quantity of carbon decomposed during the first two months and the AD soluble carbon of the litter had the highest correlation. Similarly, the highest linear correlation was observed for the relationship between ADF carbon of the litter and the remnant carbon after first two months of incubation. Some of the equations derived by carrying out multiple linear regression analysis on ND-soluble C, NDF-C, AD soluble C, ADF-C and ADL-C of the litter, appear to be capable of predicting the remnant carbon at various stages during the decomposition process. Among them, the equation for two months of incubation had the highest correlation coefficient and has the highest potential to be used in the prediction of the remnant carbon. Further, it can be suggested that the quantity of decomposed carbon and the remnant carbon in early stages of decomposition were related to the AD soluble carbon and ADF carbon of the litter. From the present data it can be suggested that the degree of organic matter decomposition can be predicted for up to two months with relatively high accuracy. However, further experiments have to be done in the actual forest floor to investigate the litter decomposition pattern.

Chapter 4 Soil solute movement

4.1. Introduction

The soil solution is a key component of the soil system, and determines major soil processes such as plant nutrient supply, sustenance of soil life, and the transport of solutes through the soil system (J.D. MacDonald *et al.*, 2007). The properties of soil such as permeability, occurrence of soil water repellency, biological activities such as earthworm movement and decomposition of plant roots and soil aggregation, are capable of determining the water flow paths within the soil. For an instance, the water will take surface routes if the soil has low permeability or hydrophobic properties. The composition of the soil may vary across the depth of the soil profile due to the soil forming processes including biogeochemical activities (N.C. Brady & Weil, 2010). Therefore the water draining through different layers of soil as well as different soils exhibits different chemical properties (Stutter *et al.*, 2006). As soil is the final phase that water is passing though before it reaches the stream, the effects of soil should be related to the streamwater chemistry than any other component in a catchment. Various research has shown that the soil sections immediately above the streams (also known as riparian zones) can influence the water quality to a great extent (Burt & Pinay, 2005; Norström, 2010). Therefore, assessment of the soil solution is of crucial importance in soil diagnostics (Di Bonito *et al.*, 2008).

Hyeto-hydrographs related to the experimental catchment and literature (Yamashita *et al.*, 2002), shows that the stream responds quickly to the rainfall events. This indicates the existence of high degree of surface flows during the storm events. Furthermore, the water discharge of the streams are very low during the dry periods, indicating low water storage in the soil system after the rain. Shallow soil profiles as well as steep slopes in most of the areas of the catchment (Simonson, 1994; Yamamori, 1994) also support this hypothesis by being supportive factors for the occurrence of surface flow. Therefore, the research mainly focused on the water movement in the surface soils of the catchment. The literature on the soil solution properties related to the experimental catchment or surrounding areas are scarce. Therefore, basic data related to the properties of the soil solution are of great importance.

Various methods are used for soil solution sampling and subsequent assessments. The soil solution can be collected by using zero-tension methods such as lysimeters, buried troughs, and trenches, or it can be extracted in situ or in vitro by using methods such as miscible displacement, centrifugation, compression of soil-packed syringes, suction cups, saturation extracts, 1:2 extracts, desorption solution, equilibrium soil pore solutions, low-pressure Rhizon™ samplers, and ion exchange resins (Di Bonito *et al.*, 2008; Litaor, 1988; Pampolino, 2000; Ross & Bartlett, 1990; Schlotter *et al.*, 2012). However, no method has been qualified as universally applicable, because of the limitations regarding applicability under diverse soil environments (LITAOR 1988). Moreover, these different extraction methods may extract different portions of the soil solution rather than the overall soil solution (Lajtha *et al.*, 1999; J D MacDonald *et al.*, 2004).

The aim of the study is to obtain a soil solution similar to the mobile phase of the soil solution which contribute more to the stream flow. For the lateral water and solute flow to occur, the soil moisture should reach close to the saturated state (Weiler & McDonnell, 2006). Therefore, the techniques that extract the soil solution when the soil is saturated were mainly used during the study.

Although it is not specific to the current catchment, conventional soil solution extraction techniques are labor and time consuming. However, Ion exchange resin beads (IERBs) and ion exchange membranes (IEMs) have been used as convenient soil diagnostics techniques for several decades (Amer *et al.*, 1955; Saunders, 1964). These methods were primarily used to assess the plant nutrient supply of soils (Amer *et al.*, 1955; Huang & Schoenau, 1996; McLaughlin *et al.*, 1993; Pampolino, 2000; Qian *et al.*, 1996; Saggar *et al.*, 1990; Saunders, 1964; Schoenau & Huang, 1991). Recently, however, their use has been extended to other fields, such as assessment of atmospheric deposition of pollutants, soil microbial activity, and soil solute movement (Fenn & Poth, 2004; Fenn *et al.*, 2002; Li *et al.*, 1993; Pampolino, 2000). Data regarding the use of ion exchange material for the assessment of ion transport in the soil are scarce; however, these research have shown promising results (Li *et al.*, 1993; Pampolino, 2000). The advantages of using ion exchange materials in soil studies are convenient field application and subsequent ion extraction for analysis and reusability of material. There are two types of ion exchange material known as ion exchange membranes (IEM) and ion exchange resin beads (IERB). The planar surface of IEMs facilitates accurate quantification of charge and ensures that the entire surface of the IEM is in direct contact with the soil. Moreover, IEMs minimize soil or soil solute flow disturbances during field application (Lajtha *et al.*, 1999). Therefore, it was envisioned that there is a great potential to use IEMs in soil solute movement studies if they were used in a suitable way.

Previous research have shown that the performance of IEMs is dependent on soil moisture because the mobility of the ions in the soil solution enhances with increasing soil moisture (Pampolino, 2000). As explained earlier, soil solution starts to flow when the soil is nearly saturated. Therefore, if IEMs were used when the soil is at near-saturation state, not only they will perform better but measure the composition of the mobile phase of the soil solution.

4.2. Specific objectives

The specific objectives of this study are to:

a. Assess the composition of the soil solution when it is about to flow through the soil
b. Examine the potential of using ion exchange membranes (IEM) in assessing soil solute movement

4.3. Materials and methods

Study site

An experiment was carried out in a sub catchment inside the main catchment (Figure 29). The sites were selected randomly, and accessibility was of concern because of rocky and steep slopes. We selected three sites along one side of the central stream, at approximately equal distances from the stream. Most of the areas in the catchment are covered by plantation forests established in late 1970s and early 1980s. Since the establishment, management operations have not been carried. Currently the forest exhibits the characteristics similar to the secondary forests often found in the main catchment.

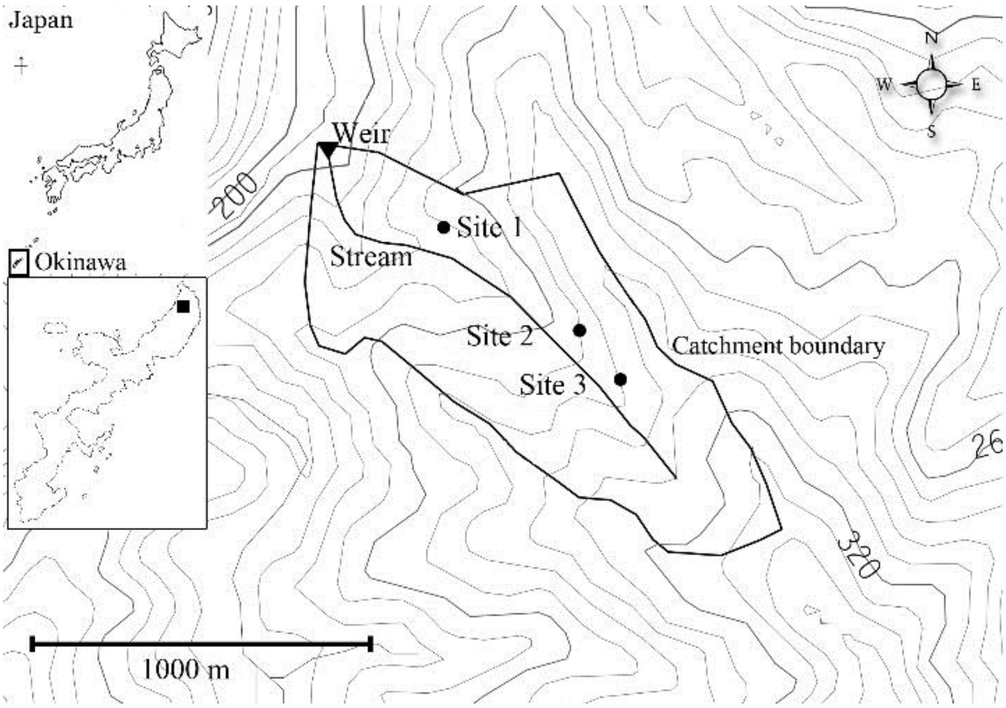


Figure 29: Experimental sites used in the soil solute movement assessment

Preliminary evaluation of soil water flow pattern in the shallow soil

Hillslope infiltrometer (Mendoza & Steenhuis, 2002) method was slightly modified and used in the three sites to evaluate the water flow paths in the shallow soil using 30, 60 and 80 mm/ h rainfall intensities (Figure 30).

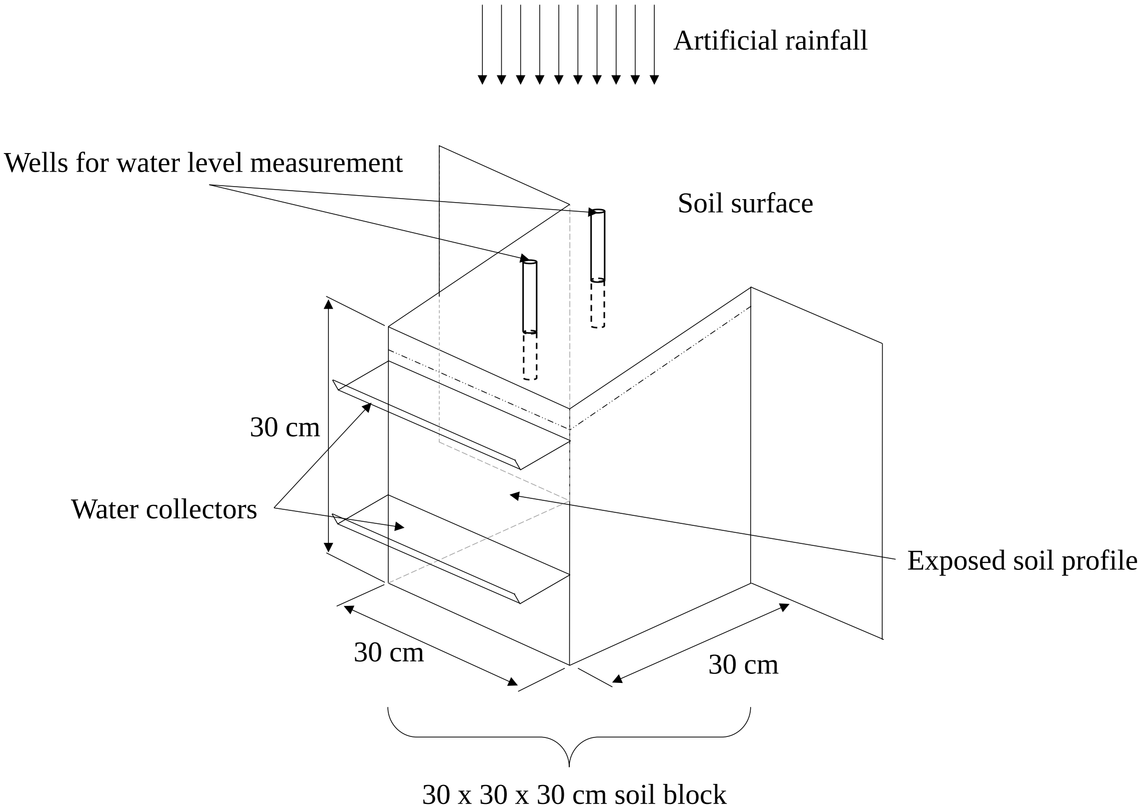


Figure 30: Hillslope infiltrometer

Soil sampling and analysis

Four and six 100-cm^3 undisturbed core samples from topsoil (0-12 cm) and subsoil (12-35 cm) respectively were collected at each site, for column extraction of the soil solution. A separate set of cores was collected to assess the soil physical properties. In addition, three topsoil and three subsoil samples were also collected at each site, to assess the soil chemical properties and texture.

Soil pH and EC was measured by using a Hanna™ combined pH/EC meter (soil:water ratios of 1:2.5 and 1:5, respectively). Exchangeable cations were extracted by using 1 M ammonium acetate (Robertson *et al.*, 1999). The soil saturation extract was collected by shaking 5 g of freshly air-dried soil with deionized water (soil:water ratio of 1:10) for 1 h at 200 rpm. Cations were analyzed by using inductively coupled plasma emission spectroscopy (ICPE) (Shimadzu ICPE-9000). Anions from the saturation extracts were measured by using ion chromatography (IC) (Dionex ICS-1600). Texture was assessed by using the hydrometer method. Saturated hydraulic conductivity (SHC) was assessed by using undisturbed soil cores. Bulk density (Db), porosity, water-holding capacity (WHC), and field capacity (FC) were gravimetrically assessed.

Extraction of soil solution by undisturbed soil column

Zero-tension lysimeters collect the mobile fraction of the soil solution. MacDonald *et al.* (2004) have shown that the column leaching extracts from packed columns are similar to the soil solution collected from zero-tension lysimeters. In the present study, undisturbed soil columns are used to collect the mobile fraction of the soil solution. Undisturbed soil samples were collected by using cleaned stainless steel cores. After saturation with deionized water, the cores were tightly fitted with polyethylene-coated paper cups on the upper side. Polypropylene funnels lined with filter paper were placed on 100-ml polypropylene vessels, and the cores were placed on the funnels. Next, 50 ml of deionized water were applied to each core (Figure 31). The obtained leachate was analyzed by using ICPE and IC.

Figure 31: Soil solution extraction from undisturbed soil column

In vitro and in situ application of IEM technique

During the *in vitro* experiment the soil cores were saturated with deionized water. Next, two slits (2 cm long and 2 cm deep) were made on the upper soil surface of the soil core, by using a thin stainless steel spatula. The CEMs and AEMs (2 × 3 cm) were inserted into each slit by using a pair of forceps, such that a small area of the IEM (1 × 2 cm) remained out of the soil for handling (Figure 32 - a). The soil was gently pressed from either side of the membrane, to ensure better contact. After 2 h, the IEM was extracted, washed, eluted, and analyzed. The size and shape of the IEMs used in these experiments were selected to facilitate insertion into the soil without a frame support.

For the in situ evaluation, fresh IEMs were transported to the field in zipper storage bags. Four CEMs and four AEMs each was inserted into the topsoil and subsoil at each site, as described above. A clean stainless steel cylinder (100 cm^3) was inserted into the soil to a depth of 1 cm, in such a way that the two IEMs were placed in the center of this cylinder (Figure 32 - b). The cylinder was then filled with deionized water. The infiltrating water was expected to lead to the development of a temporary bulb-shaped saturated area surrounding the IEM.

The IEMs were extracted 2 h later, washed thoroughly with deionized water, and packed in moist zipper storage bags. Cations were analyzed by using ICPE. The anion extract was

(a) (b)

Figure 32: *In vitro* (a) and *in situ* (b) application of ion exchange membrane technique

analyzed by using ICPE for sulfur and phosphorous, and a spectrophotometer for nitrate (Clesceri 1999). The properties of the IEM used in the experiment are summarized in Table 11.

Table 11: Properties of ion exchange membranes

	Cation Exchange Membrane	***Anion Exchange Membrane***
Manufacturer	ASAHI glass company, Japan	
Product name	CMV	AMV
Type	Standard	
Intended use	Electro dialysis	
Thickness (µm)	130	
Counter ion	Na^+	Cl^-
Regeneration/ Hydration	3% NaCl solution	
Functional group	Sulfonic acid	Quaternary ammonium
Charge * (mmol/g)	2	
Weight per unit area * (g/cm^2)	0.014 – 0.016	
Charge per unit area ($mmol/cm^2$)	0.028 – 0.032 (Calculated)	

Source: http://www.selemion.com/SELC.pdf
* Personal communication with the manufacturing company

Extraction of litter leachate

Litter from 15×15 cm area was collected from three sampling sites of the main catchment and air dried until constant weight. Litter was then spread on similar size polyethylene troughs and 10 mm rain equivalent deionized water was added to the tray as a mist by a sprayer. Water draining the litter layer was collected and analyzed for cations and anions.

4.4. Results and discussion

Water flow paths in the shallow soil

The hillslope infiltrometer experiment showed that the water in the shallow soil follows different paths depending on the conditions of the soil. Preferential flow paths occurring as a result of the fissures in the rocks and dead plant roots was observed in both topsoil and subsoil. When such paths are not available, water predominately flows through the surface soil layers.

Soil properties

The soil properties are shown in (Table 12). The forest soil was covered with a 2 to 3 cm litter layer. The brownish A-horizon was 2.5–4 cm thick, and a light brown transitional horizon was observed up to a depth of 11–12 cm. The A-horizon was occupied by ramified plant roots, especially in the uppermost layer. The B-horizon had occasional large plant roots, along with scattered disintegrating rocks. The soil reaction was acidic, with an average pH of 4.46. The nutrient content in the subsoil was relatively low.

Table 12: Soil chemical and physical parameters

		Site 1				**Site 2**				**Site 3**			
		Topsoil		**Subsoil**		**Topsoil**		**Subsoil**		**Topsoil**		**Subsoil**	
pH (H_2O)		4.55		4.53		4.45		4.48		4.41		4.39	
EC (µS/cm)		81		38		74		40		76		41	
Major Ions		Exc.	Sa.E.	Exc.	Sa.E.	Exc.	Sa.E.	Exc.	Sa.E.	Exc.	Sa.E.	Exc.	Sa.E.
(mg/ kg_{soil})	Ca^{2+}	171.0	11.0	30.0	5.0	113.0	9.0	45.0	5.0	78.0	10.0	15.0	6.0
	Mg^{2+}	123.0	7.0	19.0	2.0	61.0	4.0	40.0	2.0	70.0	8.0	15.0	2.0
	K^{+}	80.0	14. 0	34.0	10.0	54.0	11.0	31.0	9.0	43.0	9.0	15.0	14.0
	Na^{+}	-	29.0	-	-	-	19.0	-	-	-	19.0	-	26.0
	Al^{3+}	6.0	3.0	6.0	-	3.0	2.0	2.0	-	128.0	2.0	67.0	-
	Fe^{3+}	-	-	-	-	-	-	-	-	5.0	1.0	-	-
	NO_3^-		0.72		0.3		0.4		-		0.8		1.1
	SO_4^{2-}		18.3		11.1		15.5		9.3		14.3		11.9
	PO_4^{3-}		-		-		-		-		-		-
SHC (cm/s)		4.8×10^{-2}		1.5×10^{-2}		1.7×10^{-2}		1.1×10^{-2}		1.4×10^{-2}		2.1×10^{-3}	
Texture		Sandy loam		Clay loam		Loam		Clay		Loam		Loam	
Bulk density (g/cm^3)		0.78		1.29		1.11		1.29		1.09		1.28	
Porosity (%)		70		51		58		51		59		52	

Exc.: Exchangeable; Sa.E.: Saturation extract; -: Non-detected; SHC: Saturated hydraulic conductivity

Ion composition of the soil extracts

The ion concentrations in the saturation extract and the ammonium acetate extract were expressed as milligrams per kilogram of soil (mg/kg_{soil}). The ion concentration in the column extract was expressed as mg/l assuming the column extract as the mobile fraction of the soil solution. In a previous study, Pampolino (2000) assumed that the displaced water from the core represented the soil solution with flushable labile nutrients. The average porosity of the soil in the present study was approximately 56% and the soil cores were already saturated; therefore, addition of 50 ml of water would flush the entire macro-pore space. Litter leachate was also expressed as mg/l (Figure 33) comparatively shows the averaged composition of soil solution extracts by various methods.

The ion compositions of the column extracts were compared between the three sites. With the exception of K^+ in the topsoil, no significant differences were determined ($p < 0.05$) between the three sites. In addition, no significant differences were observed in the saturation extracts between the three sites. Column extract and the saturation extract showed similar ion distribution. Chloride, sodium and sulfates account for almost 80% of the ions considered. These ions were relatively high in all of the soil extracts, possibly because of the addition of the sea salts along with precipitation. Topsoil and subsoil have differences in certain ions. Sodium in the subsoil is higher than the topsoil in both extracts. However, chloride and sulfate shows no such trend. Phosphate was undetectable most of the occasions while nitrate was found in minute quantities in soil extracts. The nutrient cycles of PO_4^{3-} and NO_3^- are almost closed in forests, and therefore these nutrients may be readily being incorporated into the biomass. Ca, K and Mg is higher in the topsoil possibly because of the nutrient release from the organic matter decomposition. The composition of the litter leachate provide evidence for this phenomena. Although litter leachate has high chloride, sodium and sulfate content, Ca, Mg, and K content is also comparatively high. Litter leachate, in overall, has high amount of dissolved ions and, this is expressed as relatively high electrical conductivity. Na was barely detected in the exchangeable cation extract. However, other extracts possess Na in measurable quantities. The reason for this difference is unclear. Both saturation extract and the exchangeable cation extract were extracted in the same manner although the extraction medium was different. Exchangeable cations were extracted under a neutral pH while saturation extract was extracted under normal soil pH (4.5). Although soil is moderately acidic dissolution of iron and aluminum is not clearly visible.

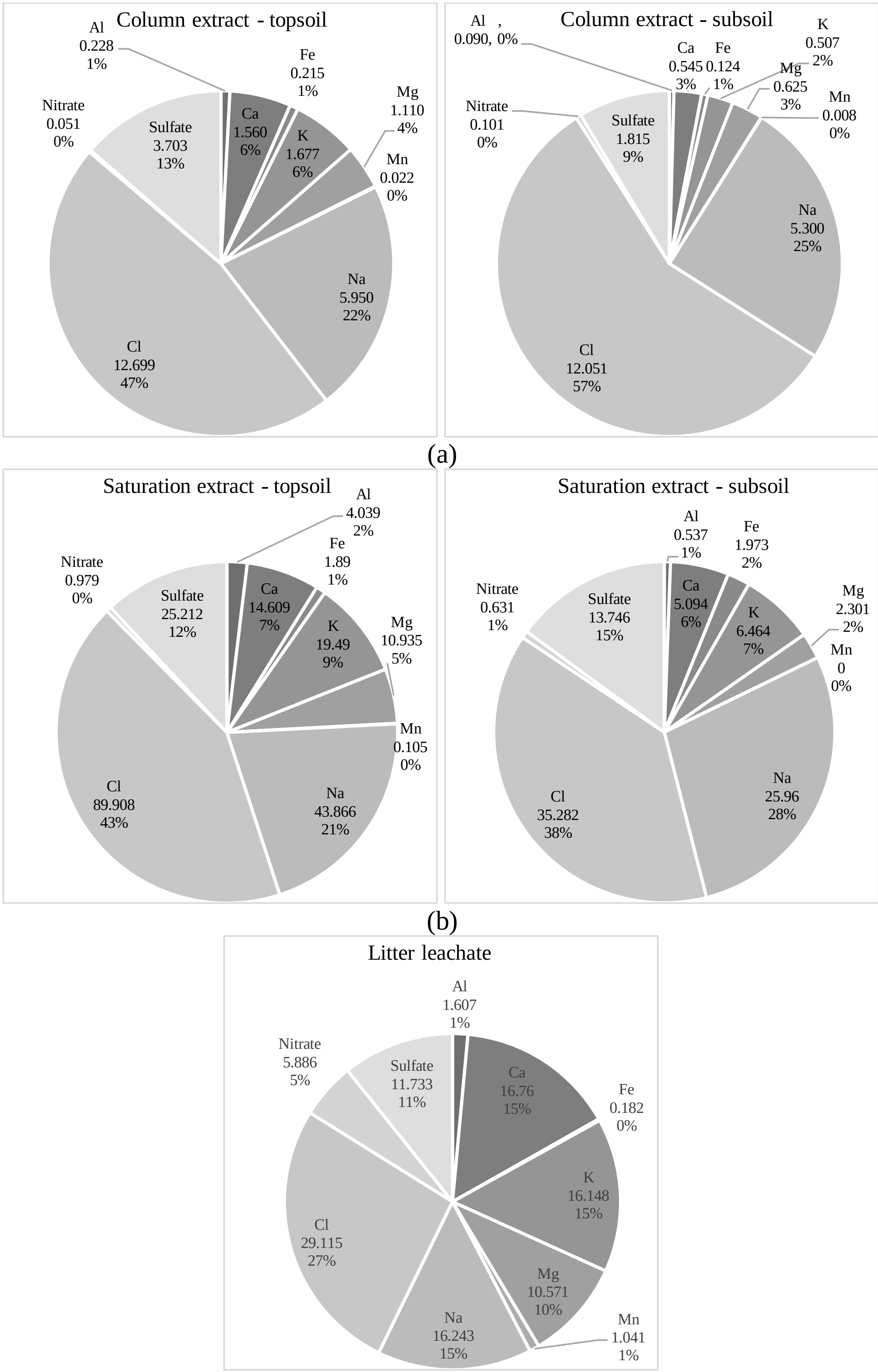


Figure 33: Composition of the soil solution and litter leachate

(a) Column extract (mg/l), (b) Saturation extract (g/kg_{soil}) and (c) Litter leachate (mg/l)

Applicability of IEM technique in soil solute movement assessment

In vitro assessment revealed that the selected size (3 × 2 cm) of IEM could easily be inserted into the soil by using a pair of forceps. Furthermore, under nutrient-limiting conditions, the IEMs captured detectable quantities of ions (especially anions) within 2 h. Therefore, the IEMs could be used in field experiments without the use of physical support such as a frame. This not only reduces the cost of the technique, but also facilitates handling and transport. Direct insertion also ensures better contact of the IEM surface with the soil. As sodium and chloride are being use as counter ions in the IEMs composition of those ions could not be investigated. In previous assessments of soil ion movement by using IEMs or IERBs, the IEMs have been used without modifying the field moisture conditions (Li *et al.*, 1993; Pampolino, 2000). This approach is appropriate for relatively long-term observations, in combination with determination of other parameters such as rainfall, to evaluate the way in which ions in the soil move during a particular period. However, during the research planning it was hypothesized that, when using IEMs to estimate the soil ion movement by assessing ion composition of the soil solution, near-saturation conditions are required, because the saturation of the soil will increase the mobility of the ions. In the present study, this hypothesis was validated by demonstrating comparable results for IEMs and column extracts under near-saturation conditions. The attainment of saturation by using the prescribed technique (*i.e.* ponding water in a cylinder) may be limited to soils with fine to moderately fine texture and sufficient moisture. However, if the soil is extremely dry, the quantity of water added may be increased, to compensate for the rapidly spreading wetting front while maintaining the core of the wetted bulb in a saturated condition.

Performance of IEM technique in vitro and in situ

Analysis of the mean quantities of ions captured during the *in vitro* and *in situ* IEM experiments for topsoil and subsoil revealed significant differences for Al^{3+} and SO_4^{2-}, but not for Ca^{2+}, K^+, or Mg^{2+} (t-test, $p < 0.05$). Mn^{2+} differed significantly only in the subsoil. Al^{3+} was higher in the field experiment than in the *in vitro* experiment, while SO_4^{2-} showed contrary results for subsoil and topsoil. We were unable to compare Fe^{3+} and NO_3^- statistically, because the number of observations available was small. The results of analysis based on the remaining Na^+ ions in the CEMs revealed that, for topsoil, the total quantity of ions captured by the CEMs did not differ significantly between the *in situ* and *in vitro* tests. However, for subsoil, the CEMs captured a significantly higher quantity of ions in the field experiment than in the laboratory experiment.

The differences in the results of our *in vitro* and *in situ* IEM tests may have been caused by a number of factors, including the difference in soil temperature during the two tests (Dobermann *et al.*, 1994). The field test was conducted during the winter, when the ambient temperature was approximately 14°C. This may have affected the dissolution of certain ions in the soil solution, rather than changes in the IEM adsorption characteristics (Qian & Schoenau, 2002). Dobermann et al. (1994) noted that the presence of plant roots may also affect the adsorption characteristics of IEMs.

IEM extraction of soil solutes versus column extract

Comparison of the IEM results with those of the column extract showed that the IEMs produced a comprehensive snapshot of the ions available in the soil solution (Figure 35). In a 4 cm^2 surface area, the quantity of ions captured by the IEMs within 2 h was comparable with the quantity of ions flushed by a quantity of water roughly equal to the pore space of the soil (50% of the total soil volume). For topsoil, with the exception of Al^{3+} in the *in vitro* experiment, the quantities of ions captured by the IEMs differed significantly from those of the column extract (*t*-test, $p < 0.05$). With regard to individual ions, relatively high variations were observed in all of the extracts. For subsoil, with the exception of NO_3^-, the quantities of ions captured by the IEMs differed significantly from those of the column extract. The quantities of ions captured by the IEMs were higher than those of the column extract for some ions (e.g. Mg^{2+} and K^+), but lower for other ions (e.g. SO_4^{2-}). Depending on the adsorption kinetics of each ion species, the quantities of ions captured by the IEMs were expected to be high or low. The saturation extract and the column extract showed similar ion profiles; however, the quantities of the ions could not be directly compared.

IEM extraction of soil solutes versus exchangeable cations

The ions that showed relatively high adsorption rates to the CEM (Al^{3+}, Ca^{2+}, Mg^{2+}, and K^+) corresponded to the most abundant ions in the exchangeable cation extract. This result indicates the behavior of the IEMs during the ion adsorption process, *i.e.* the CEMs rapidly captured readily exchangeable ions. Extremely large quantities of Al was detected in the soil one sampling site and this causes the standard deviation to behave abnormally in Figure 34.

The compositions of the soil solution extracts by using various methods may not always be in line with each other, because each method may have limitations according to the conditions under which it is applied (Wolt, 1985). Similarly, the ion profile estimated by using IEMs may not necessarily be similar to the ion profiles produced by using other extraction methods, or to the ion profile of the actual soil solution. This is one of the drawbacks of using the IEM approach in soil ion movement studies. Ion exchange substances may exhibit selectivity in ion adsorption (Skogley & Dobermann, 1996), because of various factors such as the hydrated ionic radii and pH of the solution (Sparks, 2003). Skogley and Dobermann (1996) reported the relative affinities of different ions to a selected brand of IEMs. For example, if

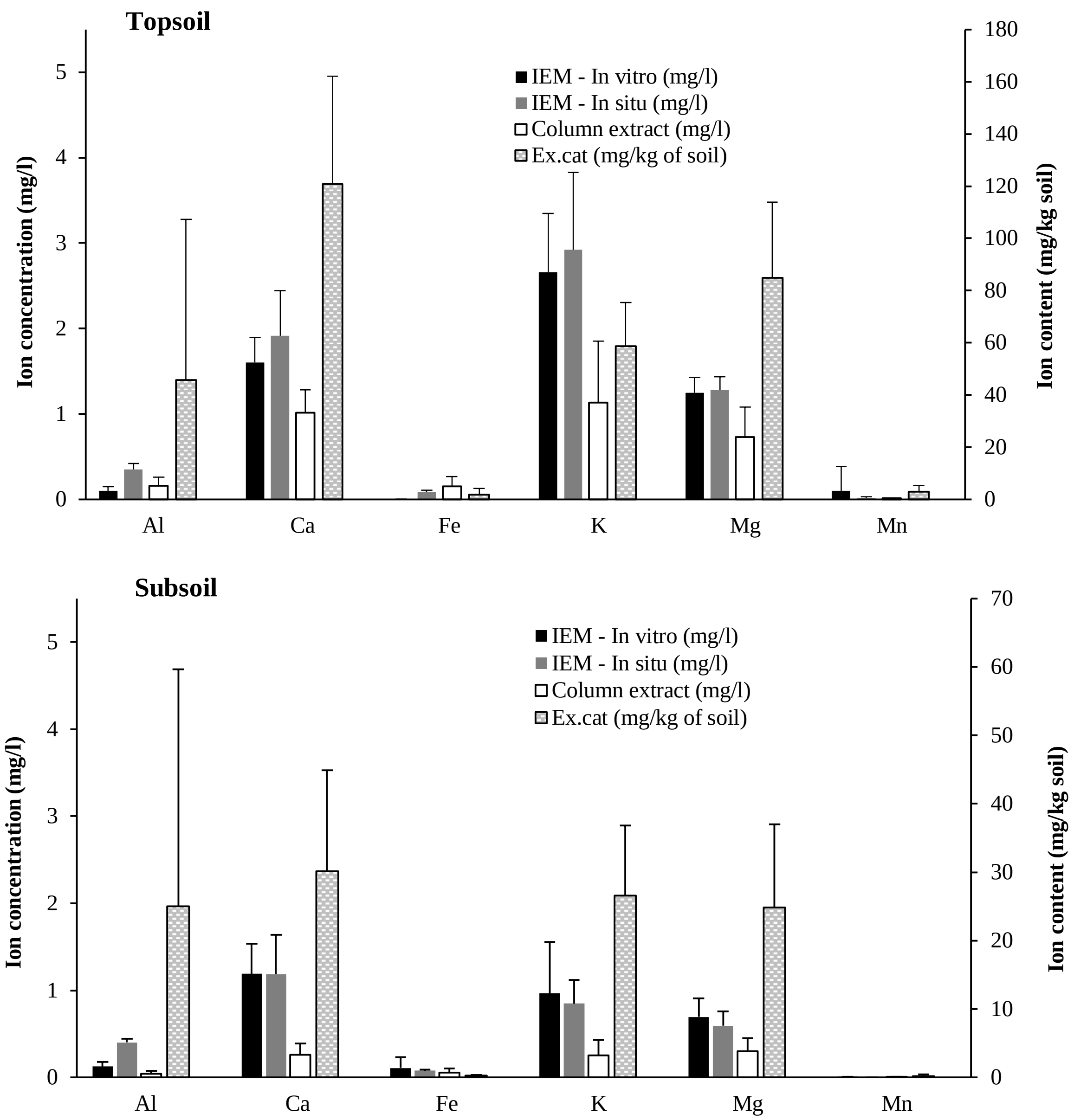


Figure 34: Ions captured by ion exchange membranes during *in-vitro* and *in-situ* experiments in comparison with undisturbed column extract and exchangeable cation extract (Ex.cat). (Error bars: standard deviation)

Ca^{2+} and Mg^{2+} are compared as ions with the same valance, Ca^{2+} has a higher affinity for the adsorbent than does Mg^{2+}. Our present findings revealed no significant difference in the quantities of exchangeable Ca^{2+} and Mg^{2+} in the subsoil. However, the IEMs captured significantly larger quantities of Ca^{2+} than Mg^{2+}. On the other hand, for topsoil, the Ca^{2+} content was higher than the Mg^{2+} content, but the quantities of ions captured by the IEMs did not reflect

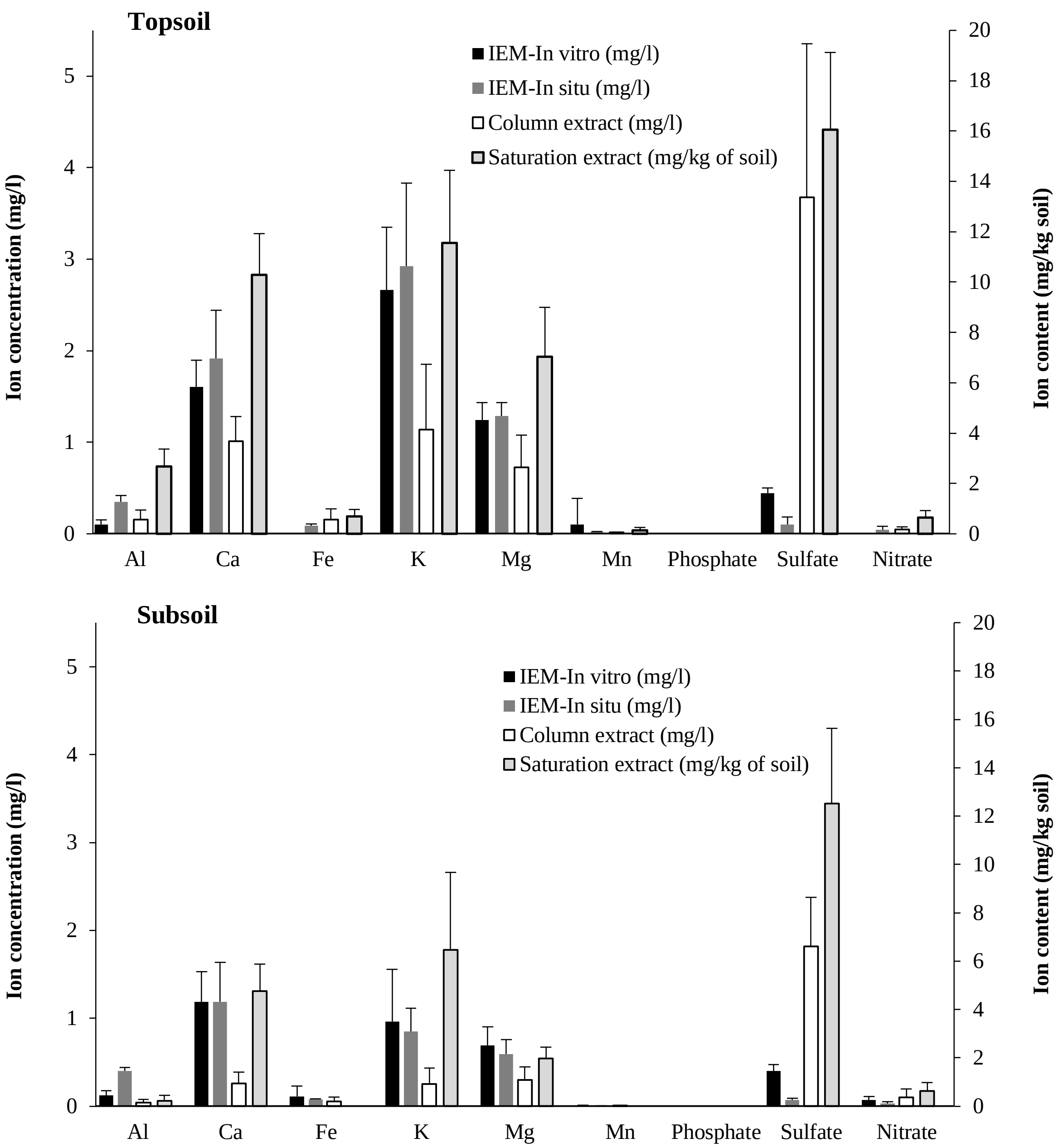


Figure 35: Ions captured by ion exchange membranes during *in-vitro* and *in-situ* experiments in comparison with undisturbed column extract and saturation extract (Error bars: standard deviation)

this difference. In both cases, the IEMs were not saturated with any type of ions, including ions other than Ca^{2+} and Mg^{2+}.

Quantification of ions captured by IEM

The correlations of the quantities of ions captured by the IEMs and the column extract was examined by using regression fitting. With the exception of K^+ in the field test (r^2 = 0.60), no significant correlations for topsoil was determined. For subsoil, no marked correlations for any of the investigated ions was observed.

Some previous investigations of the applications of IEMs in soil testing have reported good correlations between the quantities of ions captured by IEMs and the quantities of ions in the soil solution. High correlations were shown to exist between P (Saunders, 1964) and multiple metal elements (Ca, Mg, K, Mn, Al) (McLaughlin *et al.*, 1993), and between N, P, K, and S (Qian *et al.*, 1992). On the contrary, other studies did not report such good correlations (Sherrod *et al.*, 2003). The use of the IEM technique in soil studies has therefore, shown inconsistent results in terms of quantitative assessments, because of the variability of influential factors.

4.5. Conclusions

Unless there are alternative paths such as preferential flow paths, the soil water movement in the experimental catchment is mainly dominated by the near surface flows. High spatial variation can be observed in the flow paths, and extensive studies are suggested to better understand the overall water flow pattern in the catchment. Soil solution of both topsoil and subsoil is dominated by chloride, sodium and sulfate ions. However, the topsoil has relatively higher quantity of Ca, Mg and K ions compared to the subsoil. Litter leachate has the highest quantity of ions compared to column and saturation extracts. Higher percentage of Ca, Mg and K in the litter and topsoil indicate that these ions are readily being added to the topsoil.

IEM can successfully be used for the qualitative assessment of potential ion movement in the soil, by applying the proposed technique of ponding water surrounding the IEM to create a temporarily saturated area. Further studies in different soils and under different nutrient management levels will provide valuable information regarding the limitations, advantages, and adjustments required when using the proposed methodology.

Chapter 5 Quality and quantity of water discharge

5.1. Introduction

As in most parts of the world, rivers have been an integral part of the culture of Okinawa since the establishment of early settlements. Most of the settlements were along the sides of the rivers and the same trend has continued until present. In the remote subtropical islands such as Okinawa, main source of water is the rainfall and water supply from the other regions is not an option. The groundwater also play a main role in fulfilling the water demand in the islands where the geology permits the groundwater storage. Although Ryukyu limestone permit large groundwater storage, the water has found to be saline in most of the cases. Confined aquifers have found to store good quality water. In the small islands, the ryukyu limestone layer is lining the sea and, the water in these open aquifers are of limited use (Miwa *et al.*, 1988). Therefore, the quality and quantity of the river water as a surface water resource, is an important factor for the sustainability of both nature and culture.

When the rivers of Okinawa are concerned, out of 152 rivers, approximately 80% of the rivers are located in the northern region. These rivers are short in length and the catchments are small in area (mean area 5.5 km^2). Therefore, large differences have been observed in the stormflow and the flow during dry periods (Miwa *et al.*, 1988; Yamashita *et al.*, 2002). The northern area of Okinawa receives an annual rainfall exceeding 2500 mm. This is considerably larger than the national average of Japan. Yet, due to the low water storage capacity of the river basins due to their small size, steep slopes and hard bedrock, the surface water is a scarce resource. Furthermore, runoff to rainfall ratio of 0.67 has been observed in discharge related studies in northern Okinawa (Fujieda *et al.*, 1995; Kabeya *et al.*, 2014; Miwa *et al.*, 1988). When the geology is concerned, stream discharge was found to be quick when the sedimentary rocks such as sandstones underlie the catchment (Katsuyama *et al.*, 2008). Similarly, the present catchment is underlain with sandstone and shale mainly. According to Yao et al., (2009) the forest also may play a role in the reduction of stream flow especially during low-flow regimes. From the data of a subtropical/ warm temperate catchment in Japan, they have shown that evapotranspiration could drive out considerably large amount of water out of the forest causing the streams to shrink. Similar processes may also occur in the coastal forests of Okinawa.

Several studies had been conducted to investigate the water quality of the rivers in the islands of Okinawa. Some of them were conducted in the northern area where the present research was conducted. Most of these studies highlight the influence of sea salts on the water quality. Tokuyama & Hiroshi, (1978) stated that 40% of the solutes in the river water are from the sea salts and rest of the 60% is from the rocks and soil. When the rivers in the university forests of Japan were compared, the electrical conductivity of water was highest in the rivers of Okinawa (Toda *et al.*, 2000). An assessment of the water chemistry of neighboring Iriomote Island has shown that the water chemistry is mainly determined by a combination of sea salts and the products of silicate rock weathering (Ishiki *et al.*, 2008). Takashima *et al.* (2007) have reported a very low level of HCO_3^- which results from the weathering and dissolution of soil silicate minerals in the Urauchi River in Iriomote Island. This information has lead them to reach the conclusion that the contribution of weathering material is limited in the determination of water chemistry.

In the present study, one of the main rivers flowing out from the Yanbaru forsts, Yona River was studied for selected chemical properties of water and the discharge.

5.2. Specific objectives

Specific objectives of the study are to

a. Understand the river response to the precipitation
b. Examine the chemistry of water during baseflow and stormflow

5.3. Materials and Methods

The experiment was carried out at the water outlet of the main experimental catchment (Figure 3). The total area of the catchment contributing to the stream was 542 ha (marked with dotted line in Figure 3). The catchment has a form factor of approximately 0.48. Mean slope towards the main stream was estimated to be 18°.

The slope and approximate length of the stream estimated by GIS software is shown in Figure 36. The main stream has an overall slope of 19°. Stream discharge was measured by an already build structure converted to a broad-crested trapezoidal weir (Figure 37). Height of water was measured with a pressure transducer attached to a data logger (Figure 38). The equipment setup and weir calibration was done based on the data produced by WinFlume software (Version 1.06.0005) developed by the United States Department of Interior, Bureau of Reclamation. The accuracy of the flow measurements during the low flow rates was approximately 12% and 4% during the high flow rates. Therefore, actual discharge was estimated applying area-velocity method for low flow rates. The actual flow was 16% smaller than the measured flow. Due to the large range of flow observed in the selected stream the limitations of the weir were unavoidable.

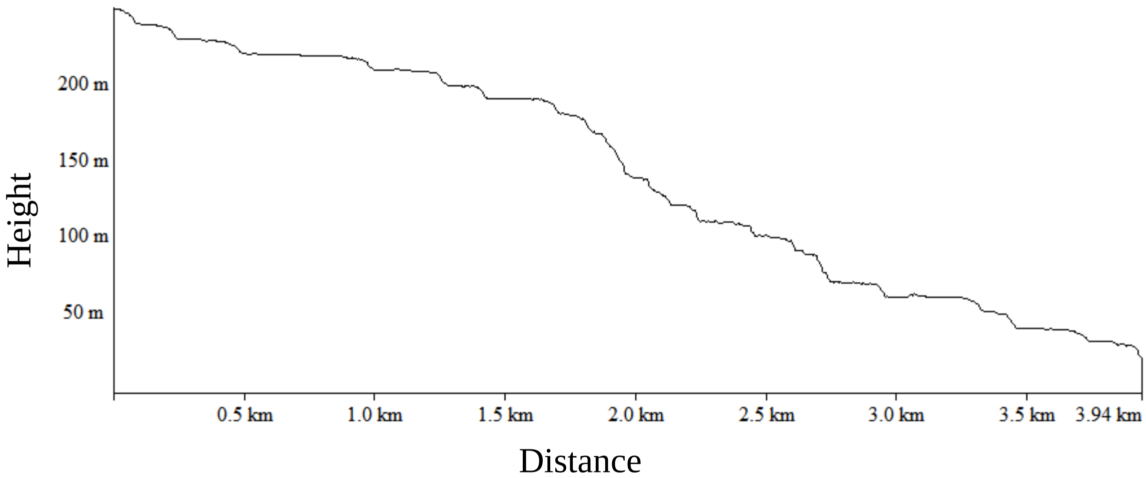


Figure 36: Profile of the stream along its length

The baseflow was sampled every two weeks or at the time where baseflow was occurring. As previous data on the discharge was not available information on the stormflow was limited. Therefore, an arbitrarily selected stormflow levels were selected for water sampling. The levels were 15 cm and 30 cm above the weir crest. These discharge levels are identified as STF – L and STF – H respectively. Sampling was done with self-closing water samplers (Figure 39) fixed upstream of the weir.

Water chemistry analysis was done in the laboratory after filtering with membrane filters. Cations and anions were analyzed with ICP-AES and Ion Chromatography. pH and EC were also measured.

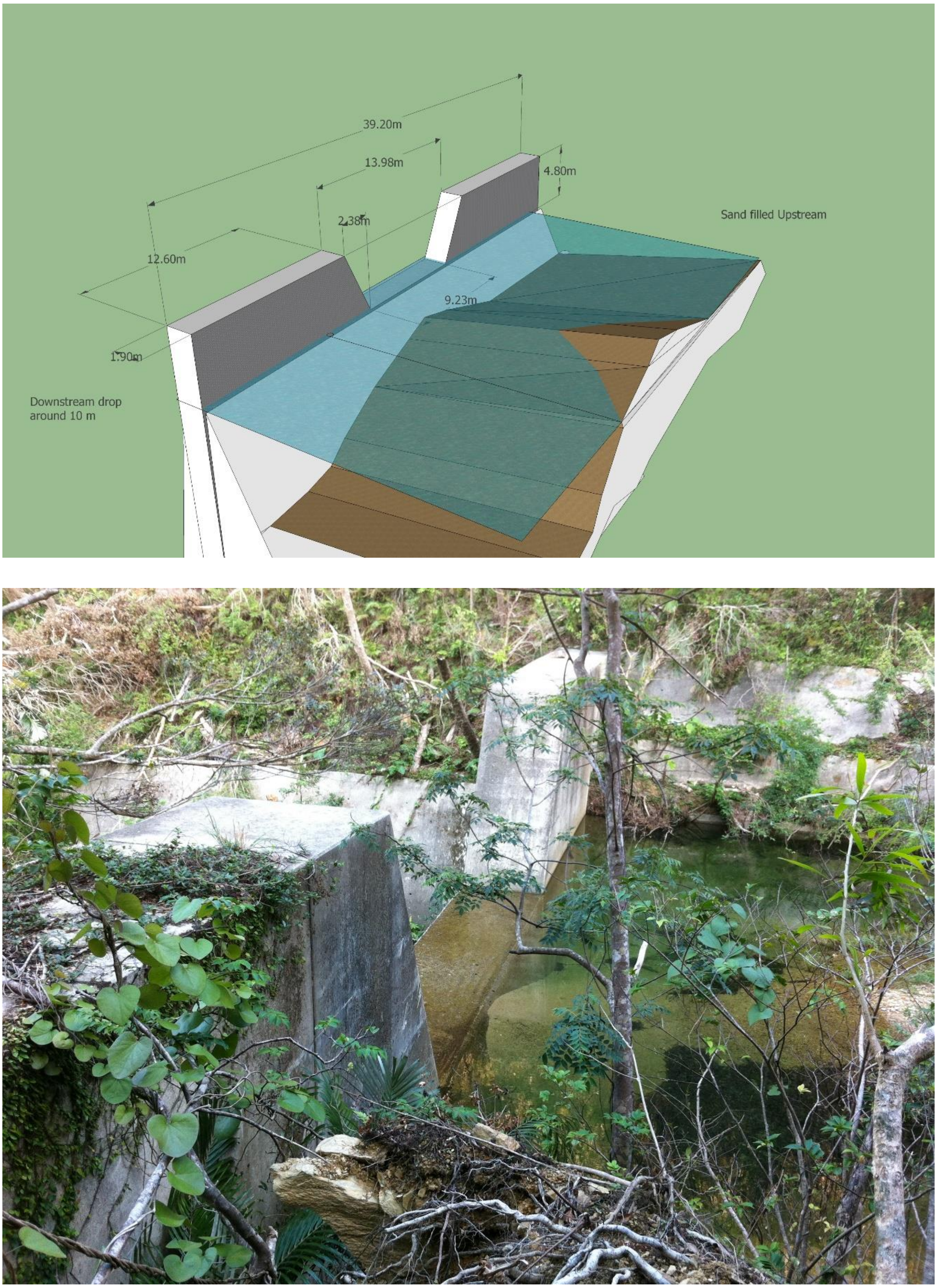


Figure 37: The broad crested weir calibrated for discharge measurement

Figure 38: Water level gauge and the data logger

Figure 39: Stormflow collectors

5.4. Results and discussion

Stream discharge

Due to various field problems such as obstructions in the weir and failure of data logger, stream discharge data could not be obtained in certain periods during the sampling period. Lower flow rates at which the weir had low accuracy were corrected from the data obtained by actual discharge measurements.

Figure 40 shows the hyeto-hydrograph for the sampling period. Quick responses of the stream to the rainfall events can be observed in the diagram indicating the occurrence of extensive surface flow or preferential flow in the control section of the soil. During the sampling period in the present catchment, stream has responded to rainfall events with peaks ranging from 3 mm/h to 34 mm/hr within 6 hours to 2 hours respectively (Lag time). Studies conducted on similar geological setting (shale and sandstone) in the main island of Japan have also shown quick stream discharge responses to the rainfall events (Katsuyama *et al.*, 2008). They also further explain that the discharge in the sedimentary rocks is faster than the granite bedrock. A separate study conducted in watersheds underlain by granite and shale in central Japan has reported that the lag time in the catchments underlain by the shale to be 10.2 h and 35 h at the antecedent precipitation index – API_{30} (15.5 mm) (Onda *et al.*, 2006).

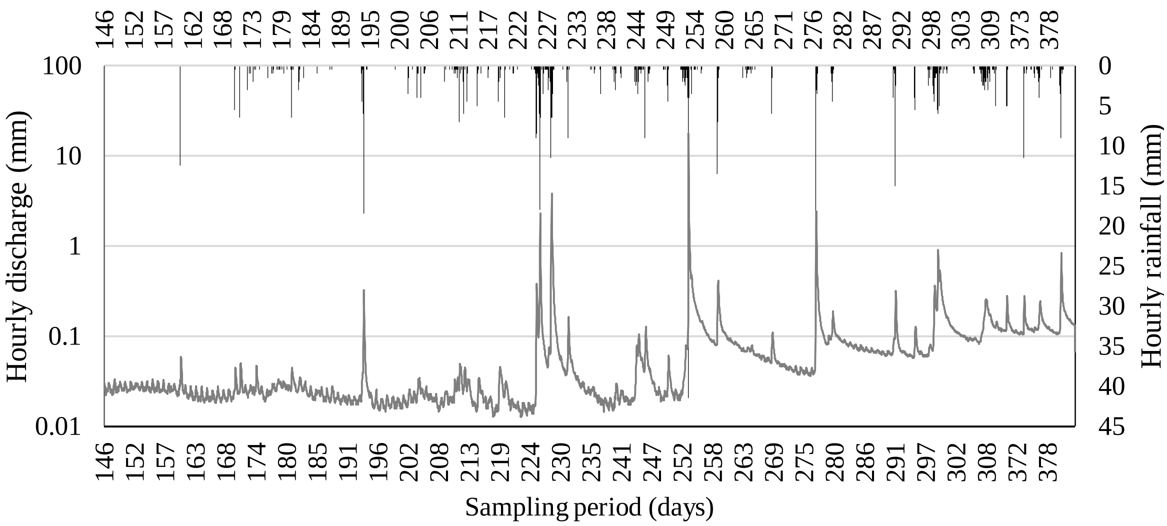


Figure 40: Hyeto-hydrograph for the catchment during sampling period
(Continuous graph was prepared by omitting the period where data was unavailable)

During the periods with low rainfall, the discharge peaks have receded quickly following the rainfall events. The stream flow has been almost constant throughout this period. As it can be expected, after heavy rainfall events (especially after typhoons) the peak recede at a comparatively slow rate. This can be seen at the discharge peaks on the observations of day 226 and 254. However, the response of the stream to the following comparatively small rainfall events has been faster and persists for a longer period compared to the dry periods. This phenomenon can be clearly observed from the heavy rainfall around 254th day and following rainfall events. From this behavior it can be suggested that intermittent heavy rains and the heavy downfall during the typhoons seem to contribute to ground water recharge significantly. Moreover, heavy rainfall events have increased the rate of water recharge in the catchment.

When the quantity of the water discharge is concerned the values show a high variation. The frequency distribution of the stream discharge is given in Figure 41. Mostly occurred discharge was 0.039 mm/hr. The maximum and minimum discharge observed were 17.74 and 0.012 mm/hr. Kabeya *et al.* (2014) have conducted a similar rainfall runoff study in a relatively smaller catchment (approximately 36 ha) neighboring the current study site. Their data also

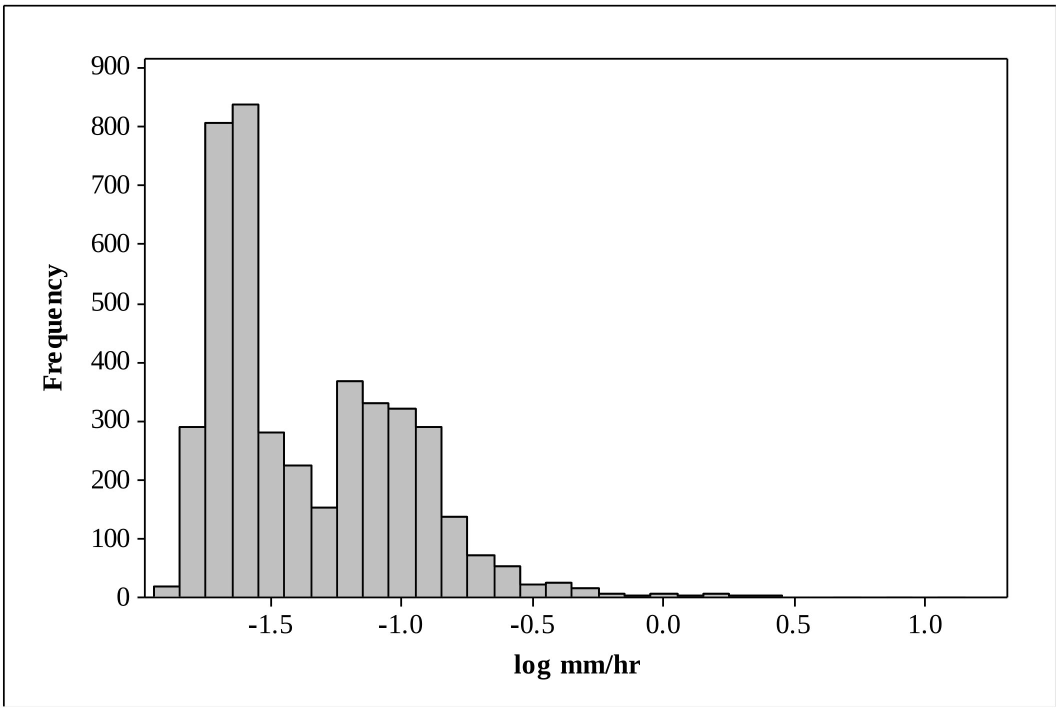


Figure 41: Frequency distribution of stream discharge
Data displayed are from July 17, 2013-December 28, 2013 and February 25, 2014-March 11, 2014

shows that the stream has responded quickly to the rainfall. However, the stream discharge has dropped to the initial level faster than the current catchment. This could be due to the difference in the scale of the catchment. The runoff (334.4 mm) as a percentage to the precipitation (930 mm) during the sampling period was 36% (total for the period were concerned). These values are less than the values observed by Kabeya *et al.* (2014). They have reported a value of 67%

for year 2010 with a total rainfall of 3400 mm. However, in a catchment of nearly similar in size (24.8 ha) to the catchment described by Kabeya *et al.* (2014), located to the south of the present catchment, the percentage of runoff has been 38.7% under a total rainfall of 1785. These values are comparable with the findings of the present study for a total rainfall of 930 mm during the sampling period. Therefore, it can be suggested that the runoff ratio may vary with amount and the characteristics of the rainfall. However, further observations are needed in the present catchment to confirm whether there is an effect of the large size of the catchment on the water storage and runoff.

Chemistry of the streamwater

The averages of the concentration of the constituents, pH and EC of each flow category are tabulated below (Table 13). The ions which were not detected consistently during the chemical analysis were omitted. Heavy metals and phosphate were not detected. In a previous assessment of river water in Okinawa, it has been reported that the concentration of the nutrients such as nitrate, ammonia and phosphate were extremely low in the rivers of northern Okinawa while the rivers in central and southern had values above the ecological threshold levels (Shilla

Table 13: Composition of the stream discharge

	Ca^{2+}	**K^{+}**	**Mg^{2+}**	**Na^{+}**	**Cl^{-}**	**NO_3^{-}**	**SO_4^{2-}**	**pH**	**EC** µS/cm
Baseflow	38.18	2.61	26.79	50.45	75.69	1.34	11.83	7.27	159.56
(SD)	*7.12*	*0.82*	*5.14*	*12.19*	*25.16*	*0.77*	*2.60*	*0.22*	*17.07*
Grouping	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*	*A*
STF-L	32.01	3.22	21.39	38.19	63.09	2.23	10.78	7.07	142.80
(SD)	*6.71*	*0.99*	*4.19*	*7.75*	*13.82*	*2.37*	*1.49*	*0.14*	*12.45*
Grouping	*A*	*A*	*B*	*B*	*A*	*A*	*A*	*AB*	*B*
STF-H	34.41	3.41	20.83	36.22	57.36	1.91	10.53	6.96	134.37
(SD)	*11.18*	*0.84*	*6.45*	*9.80*	*19.27*	*2.63*	*1.81*	*0.28*	*14.42*
Grouping	*A*	*A*	*B*	*B*	*A*	*A*	*A*	*B*	*B*

#.## The ion concentration (meq/L) × 10^{-2}
#.## SD – Standard deviation × 10^{-2}
"_" Statistical grouping – ANOVA, p=0.05, Tukey grouping

et al., 2013). When the pH and EC are concerned, these values are higher than the those reported in the main island of Japan (Toda *et al.*, 2000). However, when compared to the Urauchi River (Ishiki *et al.*, 2008) in Iriomote Island, EC is substantially high although pH is comparable. When the ion concentration was compared, values of the present study are on par with the average data for Okinawa measured by Tokuyama & Hiroshi (1978).

When the three flow levels are concerned, effects of dilution is small in the stormflow situations. Except for potassium, calcium and Nitrate all other ions and parameters dilute with when the flow increases. However, statistically different levels can be observed only in Mg^{2+}, Na^{+}, pH and EC (Table 13). Although Ca content is highest in the baseflow, STF-H had relatively higher level compared to STF-L. Mg and Na in the baseflow was significantly different from the stormflows. The data for nitrate had high degree of variation.

The fluxes of each ion was calculated by applying respective flow levels. As the baseflow occurs continuously throughout the year the flux with regards to the baseflow were calculated per year. However, as the stormflow may vary depending on the rainfall distribution within the year, the flux was calculated per hour (Figure 42). The relative ion composition of the efflux was compared with that of the seawater (Figure 43). Ishiki *et al.* (2008) argues that the source of chloride in the river water of Iriomote Island are solely from the seawater because the

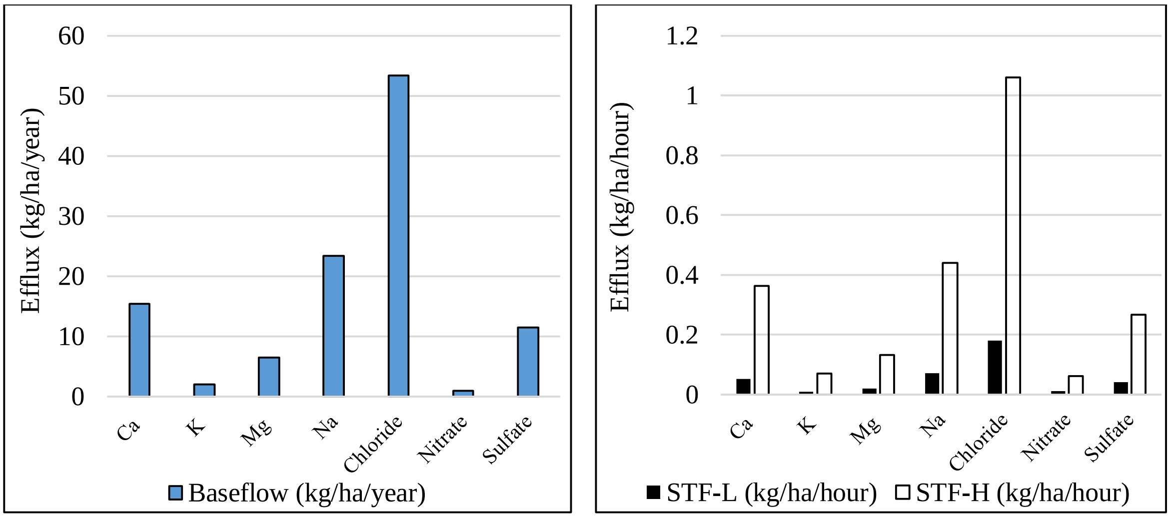


Figure 42: Catchment ion effluxes (STF-L: Stormflow – low, STF-H: Stormflow - high)

underlying rocks do not contain substantial amount of chlorine containing minerals and external sources of chloride such as industrial sources are not around. Similarly, in the present catchment, the geology is characterized by sandstone and the site is isolated from the industrial sources of chloride. Therefore, the source of chloride can be attributed to the seawater. Based on this assumption, Ishiki *et al.* (2008) have proposed two equations to separate the ions originating from the sea salts and the other sources (mainly rocks and soil). However, the wind blowing from the north, sweeping the heavily industrialized zones of Asian continent could bring extraneous material to the catchment due to the changes in wind patterns.

$$\mathrm{SS}_X = \left(\frac{[X]}{[Cl]^-}\right)_{seawater} \times [Cl]^-_{sample} \qquad \text{eq. (1)}$$

$$NSS_X = [X]_{sample} - \mathrm{SS}_{X_{sample}} \qquad \text{eq. (2)}$$

$\mathrm{SS_X}$ – Concentration of the sea salt fraction of an ion

$\mathrm{NSS_X}$ – Concentration of the non-sea salt fraction of an ion

$\left(\frac{[X]}{[Cl]^-}\right)$ - Concentration ratio in the sea salt

$[Cl]^-_{sample}$ - Concentration of Cl^- in river water

The concentrations are in equivalent values (Ishiki *et al.*, 2008)

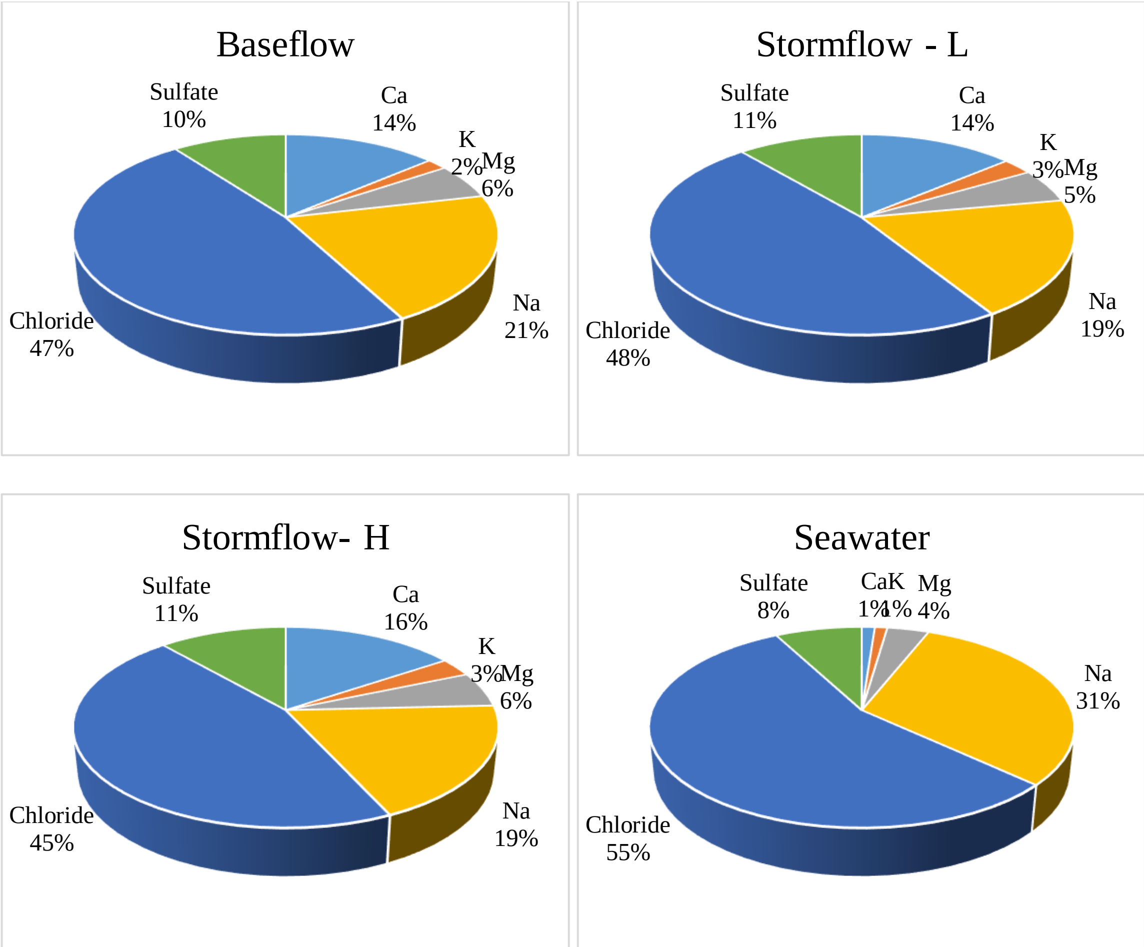


Figure 43: Comparison of relative ion composition of streamwater with the seawater

Using the above equations the contribution of sea salts for the streamwater composition was calculated for the present catchment. Nitrate was not considered because the values were very small in sea water and inconsistent in the samples. According to these results, the main source of Ca^{2+} is not the sea salts in all flow regimes. K^+ and Mg^{2+} appear to be the next least influenced ions. However, the contribution of sea salts on the K^+ content appear to decrease drastically as the flow rate increase. Other than K^+, the difference between the three flow regimes is not tangible in all the ions which were considered. In addition, Mg^{2+}, Na^+ and SO_4^{2-} of STL appear to have slightly higher values compared to both baseflow and STH. A possible explanation for this behavior could be given by considering the pattern streamwater dilution and the composition of the influx (TF+SF). When the dilution of different ions is concerned, except for

Mg^{2+} and Na^+, significant dilution was not observed in the steam water during the three flow regimes. The influx has higher amount of K^+ compared to Ca^{2+} and Mg^{2+} in the rainfall (which has lower amount of K^+ compared to Ca^{2+} and Mg^{2+}) is considered. Therefore, the addition of K^+ to the rainwater as it passes through the canopy, may have appeared as the decline in the contribution of the sea salts.

These indicate that the surface runoff has occurred in both stormflow regimes. Furthermore, the lower degree of dilution in the stormflow in general, indicates the movement of water through the nutrient rich surface soil layers as well as litter layers.

In the case of Na^+, the contribution of the sea salts shows values beyond 100%. This could be a result of a deficiency of the assumptions of the equations used in the estimation of the sea salt contribution. Moreover, as the Na/Cl ratio of the influx is less than that of the sea salts, there is a possibility that the contribution of the sea salts to go beyond 100%.

The interpretations above are based on the mean values for each flow regime. It should not be forgotten that typhoons and wind can deposit large amount of aerosols on the tree canopy and later washed away with the rainwater and contribute to the stream flow chemistry. However, the number of typhoons occurred during the study period and the amount of rainfall they brought in are insufficient for detailed analysis of the influences of such phenomena.

5.5. Conclusions

According to the observations on the stream discharge, it can be concluded that the stream respond quickly to rainfall events even with a small magnitude compared to other catchments in the other parts of Japan. The stream discharge peaks that occurred after long dry periods recedes faster than that occurring after heavy downfall. Although it is a normal phenomenon, rainfall events with relatively smaller intensities occurring after a heavy downfall are capable of not only generating high peaks but maintaining sustained runoff for a relatively longer period, even when the initial flow levels were very low. Therefore, during prolonged dry periods, the soil water infiltration may have been hindered by certain factors. Once such could be the occurrence of soil water repellency. In average nearly 36% of the precipitation exits the forest catchment as runoff. However, this is highly dependent on the rainfall characteristics. Overall, the occurrences of surface runoff situations are common in the catchment.

Stream dilution after rainfall events is not clearly visible for the selected flow regimes. This could be attributed to the water flow paths within the soil and the ion input from the influx. When the water is flowing into deeper layers of the soil *i.e.* when the baseflow is occurring, it may have sufficient time to drain through the smaller pore spaces flushing the nutrients contained in them. When the water is moving along the nutrient rich surface soil layers, the water is loaded with relatively higher amount of nutrient ions even though the water is flowing at a higher rate.

Mainly Ca^{2+} in the streamwater is supplied by the soil. In addition, Mg^{2+} and K^+ are also being supplied by the soil compared to the other ions. K^+ appear to be supplied largely by the influx when it comes to the stormflow. When the composition of the influx and efflux is compared, there are evidences that biotic retention of K^+ also occur in the catchment.

Overall discussion and conclusions

Findings from the previous studies conducted in the present experimental site and other sites with similar attributes, it was observed that the streamwater chemistry of the coastal forests of small subtropical islands could be influenced by the surrounding ocean (Ishiki *et al.*, 2008; Toda *et al.*, 2000), in addition to the soil related factors. Thus, there is a need to study the quality of the incoming water to the forest in order to isolate the influence of soil on the water quality. Furthermore, it was observed that the water discharge responds quickly to the rainfall events, indicating the occurrence of surface runoff, after the rainfall events. Therefore, this study focused on the shallow soil properties related to the water movement. In order to clarify these processes and interrelationships, the main processes of the catchment related to the hydrology, starting from the entry of water into the forest until the exit, were studied by adopting a holistic approach. It enabled the clarification of valuable information about the underlying processes of the hydrologic cycle of coastal forest catchments in small-island environment.

Many studies reported that the composition of the precipitation is directly influenced by the seawater. In the present study, major ions in the seawater (Cl^-, SO_4^{2-} and Na^+) were detected in the precipitation, stemflow and the throughfall as major ions, confirming the influence of the seawater. However, the ratio of Na^+ to Cl^- was dissimilar as opposed to the findings reported by the previous studies (Ishiki *et al.*, 2008). The rainfall composition did not vary across the main plots although the quantity varied slightly. The influence of topography on the formation of precipitation could have caused this difference. Conditions such as high winds speeds and typhoons have been found to increase the sea salts loading into the precipitation. Compared to the seawater composition, the throughfall and stemflow have relatively higher percentage of K^+ and Ca^{2+} but low in Na^+. Provided that the topsoil is rich in K^+ and Ca^{2+}, deposition of plant exudates on the canopy surface may have occurred. Furthermore, NO_3^- which occur extremely low in seawater under normal circumstances, appears high in rainfall and low in throughfall and stemflow. As nitrogen is a limited element in undisturbed forests, plants could have absorbed the nitrogen as it passes through the canopy (Bowman & Paul, 1992). These are evidences for the exchange of ions in the canopy.

As far as the composition of the influx and the efflux (stream discharge) are concerned, the percentage of Ca and Mg^{2+} in the streamwater is comparatively high and K^+ is low. This shows that the K^+ is being recycled in the forest system. Ca^{2+} is markedly high in the efflux when compared to the influx. In the analysis of the origin of the ions in all the studied streamflow regimes, it was found that Ca^{2+} is least affected by the sea salts and followed by Mg^{2+} and K^+. However, the comparatively large amount of K^+ appearing in the influx seems to influence the K^+ content in the streamwater during the stormflow levels. The SO_4^{2-} content from the non-sea salt origin is low in the stream discharge during the baseflow indicating that most of the SO_4^{2-} is coming from the sea salts. Due to the presence of relatively high sulfate content in all the phases water in the forest, the SO_4^{2-} which was estimated to be from the non-sea salt origin could be resulting from an equilibrium between the SO_4^{2-} of soil origin and sea salt origin. NO_3^- was low in the streamwater and PO_4^{3-} was mostly undetected indicating that the forests have been least subjected to human activities.

The chemistry of the streamwater during the selected flow regimes shows evidences of the water flow paths in different depths of the soil column. The water flowing through the deeper layers of the soil contributing to the baseflow carries the products of the rock and mineral weathering and therefore, the contribution from the ions from the rocks and soil can be best seen in the baseflow. During the low-stormflow levels (STL), water is moving though the surface soil layers including the litter layer where nutrients released from litter decomposition are abundant. These abundant nutrients could have been loaded to the moving water and therefore, a significant dilution of the streamwater could not be seen during the sampling period.

Although it is not statistically significant, the high-stromflow (STH) shows relatively higher degree of dilution compared to low-stormflow.

Soil water repellency and soil aggregation were studied as factors affecting the soil water movement. Both these phenomena occur as a result of the organo-mineral interactions in the soil and affect the soil water movement process physically. Soil water repellency hinders the soil water infiltration and reduces the soil water storage while soil aggregation usually facilitates water movement and storage. The initial assay of soil water repellency showed that potential soil water repellency exists in some parts of the forest. However, its effects were not observed under normal soil moisture regime in the forest soil. When the effects of soil moisture on the SWR was studied with intact soil cores, extreme levels of soil water repellency were found to occur under relatively dry soil conditions. Therefore, depending on how dry the soil becomes during intermittent dry spells observed in the catchment, extreme levels of SWR may occur. Further studies are necessary to understand the behavior of soil moisture and confirm the occurrence and persistence of SWR. A conducive environment for the litter decomposition can be seen in the forest floor. Comparatively high litter decomposition rates indicate rapid transformation of organic matter. The texture of the surface soil is mostly clay to clay loam. The soil carbon was found to be associated with the clay and silt fraction of the soil. Therefore, conditions are favorable for organo-mineral interactions leading to soil aggregation as well as the development of SWR. When the discharge pattern is observed, several clues can be found to assume that the soil water repellency exists when the soil is dry for a long period. However, during the wet periods, better water movement within the shallow soil and considerable storage of water within the soil can be observed.

The proposed technique of using ion exchange membranes was found to be suitable for the qualitative estimation of potential soil solute movement in forest soil in a short period of time with relatively low cost and labor. However, further studies need to be conducted in various soil conditions to expand the use of the technique more accurately.

In conclusion, it can be stated that the physicochemical properties of the soil play a substantial role in the determination of soil water flow characteristics and hence, the quantity of stream discharge under subtropical small-island coastal forest catchments. Although the contribution of the soil is substantially high for the determination of the composition of the stream discharge in terms of several ions, both soil and the streamwater chemistry are under the influence of the influx of ions to the forest.

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