Effects of Internal and External Processes on Water Quality and the Composition of Bottom Sediments in a Reservoir under Monsoon Climate

Dissertation

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Summary

Lately a large number of artificial reservoirs have been constructed worldwide which lead to growing interest in understanding reservoir watershed systems. This study focuses on the role of in-reservoir and external watershed processes on water quality and bottom sediment geochemistry in a reservoir (Soyang Reservoir), which is located in a monsoon climate area and is strongly affected by nutrient loads from agriculturally used catchments.

In the first study non-point source (NPS) exports under monsoonal climate of nutrients, organic matter, and suspended solids from the agriculturally used Haean catchment, a sub-catchment in the Soyang watershed, were quantified. NPS pollution from Haean catchment is the main driver for water quality in the Soyang Reservoir. Stream water samples were collected at the outlet of Haean catchment and analyzed of nutrients (nitrogen and phosphorus), organic matter, and suspended solids from the study catchment for 2 years (2009–2010). The stream water samples were taken separately in the dry and rainy seasons for evaluating the effect of monsoonal rainfall on pollutant export into the streams. Discharge was estimated using a stage/discharge rating curve at each study site. Concentrations of total phosphorus (TP), suspended solid (SS), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) showed peaks during intense rainfall conditions. The annual TP and SS loadings decreased in the streams in 2010 (3,601,173 kg km^{-2} y^{-1} and 3,676 kgP km^{-2} y^{-1}, respectively) compared to the loadings in 2009 (24,380,657 kg km^{-2} y^{-1} and 10,741 kgP km^{-2} y^{-1}, respectively). The result implies that the decreased intensity of rainfall in 2010, reducing soil erosion processes, is the main reason for the decreased SS and TP loadings. It proves that monsoon rainfalls are the main drivers for export of nutrients into the streams. We also found that government driven measures to prevent soil erosion from the catchment (including dramatic change of land uses) contributed to reducing TP and SS exports into the streams.

Sediment processes and their effect on water quality of the Soyang Reservoir were studied in the second study. The reservoir water, the main inflowing stream (Soyang River), bottom sediment, and pore water of the lake sediments were studied for 2 years (2012–2013). After intensive monsoon rain events, particulate organic carbon (POC), TP, and turbid material were abundant in the inflowing water and in the metalimnion as well as iron (Fe) and manganese (Mn). A turbid metalimnetic layer with high concentrations of suspended particles established during the summer monsoon season. During the summer stratification period, the hypolimnion and sediment became anoxic. Diffusion leads to substantial release of dissolved inorganic P and ammonia from the sediment to the hypolimnion. Sulfate and reduced sulfur concentrations were higher in the pore water of the top sediment layers compared to the deeper layers of the sediment core suggesting that substantial amounts of inorganic nutrients and minerals were supplied to the lake in the last years.

The third study deals with the effects of changes in land use on reservoir water quality under monsoon climate. To these ends the chemical composition of sediments (C, N, P, Fe, Mn, S, and isotopes of C and N) was studied and water quality parameters (suspended solid, chlorophyll *a*, and Secchi disk depth) were monitored. Sediment cores were taken along a transect from the inlet to the dam in the Soyang Reservoir and water samples were collected in the deepest part of the reservoir. Additionally, water quality data from previous studies were used to track historical water quality changes of the reservoir water. The changes of the trophic state and of activities in the watershed were well preserved in the bottom sediments in the Soyang Reservoir. C and N deposition was mainly autochthonous along with eutrophication driven by fish farming in 1990s. The terrestrial input has clearly increased after fish-farm business was terminated as indicated by an increase in soil-borne elements (Fe, Mn, S, and P) as well as terrestrial C. Such increase coincides with an increase in loads of nutrients and suspended solids following changes in land use (agricultural expansion) in the watershed.

Recently, the increased agricultural activity has the most impact on the water quality of Soyang Reservoir under monsoon climate and the effect was well recorded in the bottom sediment of the reservoir.

Zusammenfassung

Seit vielen Jahren wird weltweit eine große Anzahl an Stauseen gebaut. Dies führt zu einem wachsenden Interesse an der Entwicklung von Stauseen im Hinblick auf ihre Wasserqualität. Von besonderer Bedeutung ist hierbei die Wechselwirkung mit den Einzugsgebieten. Diese Studie konzentriert sich auf geochemische Prozesse bei der Wasserqualität und der Sedimente, welche im Stausee und im umliegenden Wassereinzugsgebiet, des Soyang Stausees untersucht wurden. Der Stausee liegt in Südkorea in einer Gegend, die vom Monsunklima geprägt ist und stark von Nährstofffrachten aus dem Haean-Einzugsgebiet, einem stark landwirtschaftlich geprägten Gebiet, beeinflusst wird.

In der ersten Studie wurden Einträge aus diffusen Quellen in das Soyang Reservoir quantifiziert wie z.B. Nährstoffe, organisches Material und Schwebstoffe. Zu diesem Zweck wurden Wasserproben in den Zuflüssen in den Jahre 2009 und 2010 untersucht um die Frachten für Nährstoffe (Stickstoff und Phosphor), organischem Material und Schwebstoffe von dem Einzugsgebiet (Haean Einzugsgebiet) abzuschätzen. Die Zuflüsse wurden sowohl in der Trockenzeit als auch während der Monsunzeit beprobt um den Monsunregeneffekt für die Schadstoffzufuhr in die Zuflüsse auszuwerten. Der Abfluss wurde an jeder Messstelle anhand einer Flusswasserpegels/ Abfluss- Bewertungskurve abgeschätzt. Die Konzentrationen von Gesamtphosphor, Schwebstoffen, biologischem Sauerstoffverbrauch und dem chemischem Sauerstoffverbrauch zeigten erhöhte Werte während der intensiven Regenzeit. Die jährlichen Gesamtphosphor- und Schwebstofffrachten nahmen in 2010 (3,601,173 kg km^{-2} y^{-1} und 3,676 kgP km^{-2} y^{-1} in 2010) im Vergleich zu den Frachten in 2009 ab (24,380,657 kg km^{-2} y^{-1} und 10,741 kgP km^{-2} y^{-1} in 2009). Diese Ergebnisse weisen darauf hin, dass im Jahr 2010 die geringere Intensität der Regenfälle der Hauptgrund für die Reduzierung der Bodenerosionsprozesse war. Dies wiederum ist der Grund für die Verringerung der Schwebstoff- und Gesamtphosphorfrachten. Monsunregenfälle sind demnach die

Hauptursache für die Auswaschung von Nährstoffen in die Zuflüsse. Ein weiterer Grund für die Verringerung von Gesamtphosphor- und Schwebstofffrachten ist in den Maßnahmen der Regierung zur Prävention von Bodenerosion in dem Einzugsgebiet zusehen sowie dem starken Landnutzugswechsel innerhalb des Beobachtungszeitraum.

Bei der zweiten Studie wurden die Prozesse im Sediment und deren Auswirkung auf die Wasserqualität des Soyang Stausees untersucht. Zwei Jahre lang (2012-2013) wurde das Wasser im Stausee, das Wasser des Hauptzuflusses (Soyang Fluss), die Seesedimente und das Porenwasser der Seesedimente untersucht. Nach intensiven Monsunregenereignissen wurde besonders viel partikulärer organischer Kohlenstoff, Gesamtphosphor, Trübstoffe, sowie Eisen und Mangan, in den zuströmenden Flüssen als auch im Metalimnion vorgefunden. Während der Zeit des Sommermonsuns bildete sich eine trübe metalimnische Schicht, welche eine hohe Konzentration an Schwebstoffen hatte. Das Hypolimnion und die Sedimente waren während der Sommerschichtung anoxisch. Aufgrund dessen kam es zu einer erhöhten Freisetzung von gelöstem anorganischem Phosphor und Ammoniak vom Sediment ins Hypolimnion. Sulfat und reduzierte Schwefelkonzentrationen wurden in größeren Mengen in den Porenwassern der oberen Sedimentkerne im Vergleich zu dem Porenwasser der unteren Teile der Sedimentkerne gefunden. Dies zeigt, dass bedeutende Mengen von anorganischen Nährstoffen und Mineralien dem Stausee bei starkem Regenabfluss während des Monsuns der letzten Jahre beigefügt wurden.

Bei der dritten Studie geht es um die Auswirkungen der Wechsel der Landnutzung auf die Wasserqualität des Stausees in dem Monsun geprägtem Klima. Dabei wurden die chemische Zusammensetzung von Sedimentkernen (C, N, P, Fe, Mn, S, und Isotope von C und N) und Wasserqualitätsparameter (Schwebstoffe, Chlorophyll *a*, and Secchi-Tiefe) untersucht. Die Sedimentkerne wurden entlang eines Transekts vom Hauptzufluss bis zur Stauseemauer des Soyang Stausees entnommen. Wasserproben wurde an der tiefsten Stelle im Stausee entnommen. Zusätzlich wurden Wasserqualitätsdaten von früheren Untersuchungen benutzt um die Veränderungen in der Wasserqualität in vergangenen Jahren nachvollziehen zu können. Die Veränderungen des trophischen Zustandes des Stausees und die Veränderungen innerhalb des Einzugsgebietes sind in den Sedimenten des Soyang Stausees gut erhalten.

Während der 1990er Jahre wurden im Stausee intensive Fischfarmen betrieben. Dabei kam es zu einer Ablagerung von Kohlenstoff und Stickstoff, welche die Eutrophierung im See ankurbelte. Der Eintrag an bodenbürtigen Elementen (Fe, Mn, S, and P) sowie auch an terrestrischem Kohlenstoff in den Stausee nahm deutlich zu nachdem die Fischfarmen aufgelöst wurden. Dies geht einher mit einem erhöhten Eintrag von Nährstoffen und Schwebstoffen, welche auf die Ausdehnung der landwirtschaftlichen Nutzflächen im Einzugsgebiet zurückzuführen sind. Seit kurzem hat die erhöhte landwirtschaftliche Aktivität den größten Einfluss auf die Sedimentzusammensetzung und Wasserqualität des Stausees im Monsun geprägten Klima.

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List of Abbreviations

P	phosphorus
TP	total phosphorus
DTP	dissolved total phosphorus
DIP	dissolved inorganic phosphorus
PO_4^{3-}	phosphate
N	nitrogen
NO_3^-	nitrate
NH_4^+	ammonium
C	carbon
TOC	total organic carbon
DOC	dissolved organic carbon
POC	particulate organic carbon
S	sulfur
SO_4^{2-}	sulfate
TRIS	total reduced inorganic sulfur
Fe	iron
Mn	manganese
Al	aluminum
Ca	calcium
K	potassium
Cl^-	chloride ion
OM	organic matter
SS	suspended solid
Chl *a*	chlorophyll *a*
SD	Secchi disk
DO	dissolved oxygen
BOD	biochemical oxygen demand
NTU	Nephelometric turbidity unit
NPS	non-point source
PS	point source
EMC	event mean concentration
BMP	best management practice
SRB	sulfate reducing bacteria
ORP	oxidation redox potential
ICP-OES	inductively coupled plasma optical emission spectrometry
XRF	X-ray fluorescence
PCA	principal component analysis
s.d.	standard deviation
d	day
yr	year
hr	hour
t	ton

Chapter 1 GENERAL INTRODUCTION

1.1 INTRODUCTION AND RESEARCH SUMMARIES

1.1.1 *The concept of watershed process linkages between upland areas and receiving water bodies*

Many studies have investigated a variety of inland waters, such as streams, natural lakes, artificial reservoirs, and wetlands in regard to water quality management, water resource preservation, and ecological views (Wetzel 2001, Allan and Castillo 2007). However, many of these studies examined individual water resource components separately rather than looking into them as closely linked, although these components are interlinked with each other. Therefore, these studies underestimated the importance of understanding the entire watershed system concurrently and holistically. This oversight dismisses the realization that streams, lakes, reservoirs, and watershed activities (i.e. agriculture type, land use changes and other anthropogenic activities) are closely interrelated as pollutant sources and reactive environments. Therefore, an integrated watershed evaluation is required to depict the systematic interactions within a watershed. For instance, land use/cover changes in upper watersheds that control soil erosion and pollutant exports from the watershed to streams can alter not only stream water quality within the upper watersheds but can also significantly impact downstream water quality of reservoirs and lakes (Huang et al. 2013, Yesuf et al. 2015). Specifically, the identification of the interactions governing water quality at the watershed scale is required to precisely characterize water quality degradation processes and to construct an integrated water quality management plan at the watershed scale. To better understand lake and reservoir system processes and the effect of bottom sediments on water bodies, analysis of historical watershed modifications and management activities are necessary since watershed processes are intricately linked and integrated across scales.

1.1.2 *Non-point source (NPS) pollution in agricultural areas under a monsoon climate*

Sources of pollutants are derived from diverse sources in watershed systems, mostly originated from non-point sources (NPS) compared to point sources (PS) (Hu and Huang 2014). For decades, agricultural NPS pollution has been the primary challenge in order to preserve water quality in many developing countries and also in South Korea (Cruz et al. 2012, Sun et al. 2012). Nutrients and eroded sediment from agricultural fields cause deterioration of water quality in agricultural watersheds (Heathcote et al. 2013).

Phosphorus (P) and Nitrogen (N), which are primary nutrients for algal growth, result in algal abundance and high growth rates depending on the amounts (Wetzel 2001). The algal overgrowth can harmfully cause undesirable symptoms in freshwater systems such as algal toxin release, oxygen depletion, and negative economic impacts (Smith 2003). The nutrients easily enter into water bodies through surface runoff on agricultural fields either in a dissolved form or particulates attached to sediment (Bartley et al. 2003). P and N are common constituents of fertilizers applied in agricultural croplands (Vitousek et al. 2009). The excess P and N not used during plant growth processes on the agricultural fields is flushed from the landscape during rainfall dominated seasons after fertilizers are applied on the fields (Gao et al. 2014). The increasing fertilizer overuse beyond crop uptake influences water quality by transporting nutrients from the croplands to water bodies (Kim et al. 2011, Thorburn et al. 2013, Guo et al. 2014).

Eroded sediments are transported from agricultural and forested areas into streams through frequent soil disturbances and land use changes (Miller et al. 2011, Glendell and Brazier 2014, Smith et al. 2015). The transported sediments to inland waters have been considered a major problem for the management of water quality, causing severe economic implications (Chaiechi et al. 2016). In particular, disturbed soils are susceptible to erosion in mountainous areas with high elevation gradients under a variety of circumstances including: deforestation and high-elevation cultivation vulnerable to agricultural expansion (Vezina et al. 2006, Otero et al. 2011). Construction activities can also cause significant sediment loss (Jahantigh and Pessarakli 2011, Shangguan et al. 2014). Sediments eroded from terrestrial watersheds and transported into water systems deteriorates water quality in a number of ways, including: destroying aquatic organisms by disordering feeding and degrading habitat (Zehrer et al. 2015), undermining recreational uses, limiting light penetration (Tamayo-Zafaralla et al. 2002), transporting heavy metal loads and toxic materials (Bibi et al. 2007, Begy et al. 2016) and attached P (Yuan et al. 2013), and also increasing drinking water purification processes (Mueller-Warrant et al. 2012).

Organic matter (OM) is also an important parameter controlling NPS pollution and water quality management (Molinero and Burke 2009). Human agricultural practices impact the OM content in soils; for example, repetitive tillage and burning of vegetation affect microorganism activity in the OM decomposition process, which results in the change of the OM decomposition rates in soil (Beare et al. 1994, Mills and Fey 2003). Residual OM in soil is eventually introduced to water bodies by flushing through runoff events (Dalzell et al. 2007).

Most of the NPS pollutants from agricultural fields are directly transported to stream reaches through surface runoff during rainfall events and the amount of pollutants increases with rainfall amount and intensity (Fig. 1.1).

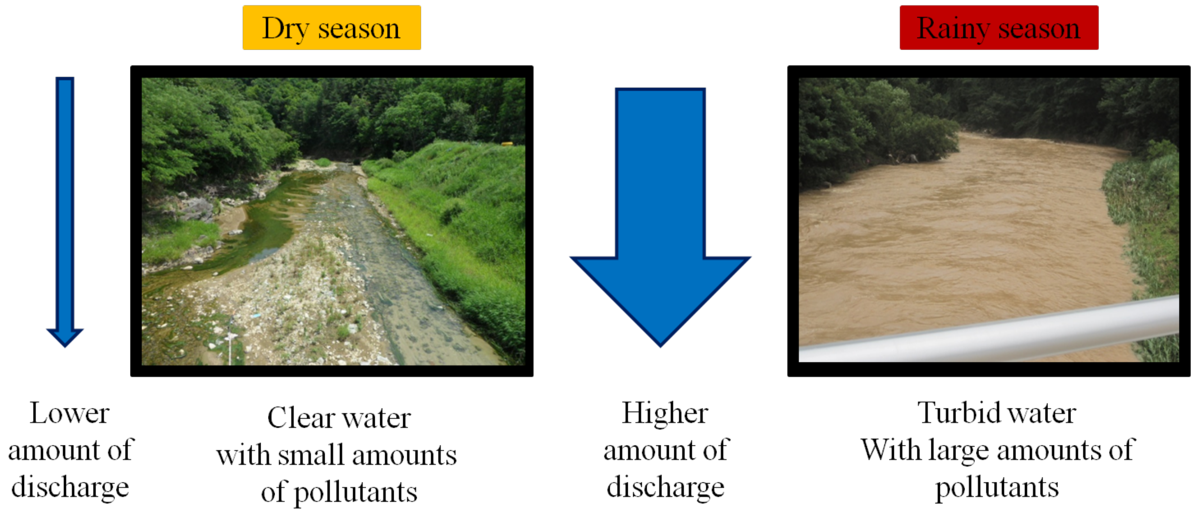

Figure 1.1 Differences of discharge and pollutants in a stream between dry and rainy seasons (photos were taken in an outlet of the study catchment)

In the Asian monsoon climate region, rainfall intensity and precipitation volume is severe and is concentrated over short time periods in the summer season. In extreme cases, the rainfall intensity is as high as 100 mm d^{-1} or 20 mm hr^{-1} causing significant runoff, transporting increased nutrients (Gao et al. 2012), OM, and sediment loads, during the summer monsoonal season. Recently, increased rainfall frequency and intensity as an effect of global climate change are becoming a critical factor to be considered for NPS pollution control.

Recent studies have focused on finding practical and efficient agricultural practices that reduce agricultural NPS pollutant yields under the guise of best management practices (BMPs) (Chiang et al. 2012, Dechim and Skhiri 2013). Among the BMP methods, land use/cover changes have been considered one of the most effective ways to improve NPS pollution problems in agricultural lands because land use changes clearly influence stream discharge and pollutant exports (Liu et al. 2013). Crop changes can also impact water quality by altering management practices such as, the amount of fertilizer used, varying harvest periods, and alternating crops (perennial or annual) (Cosentino et al. 2015).

1.1.3 *The influence of released materials from bottom sediments on water quality in a reservoir*

Reservoirs have long been considered as depositional storage locations that contain pollutants and sediment from upland watersheds that settle to the bottom of the reservoir. Therefore, reservoirs have been regarded as environmentally friendly and the construction of artificial reservoirs thereby has increased around the world for multiple purposes (WCD 2000). However, studies have recently revealed the role of bottom sediments as internal sources of pollutants and nutrients in reservoirs (Linnik and Zubenko 2000, Komatsu et al. 2006). Studies have also proved that sediments directly impact water quality by releasing internal nutrients at the interface between bottom sediments and the hypolimnion in reservoirs (Istvanovics 1994, Beutel 2003). The fate of these internal pollutants to water bodies depends on the physical water movement within reservoirs (Nowlin et al. 2005). Internal diffusion of nutrients occurs under conditions in which the dissolved oxygen content is depleted and simultaneously a large amount of organic matter is available in the bottom sediments. Under these anaerobic conditions, various substances act as electron acceptors in an OM decomposition process. Normally the anaerobic decomposition process take places in a sequence with reduction of nitrate, manganese, iron, sulfate, and carbon dioxide as the final process utilizing organic substrates in methanogenesis process (Fig. 1.2).

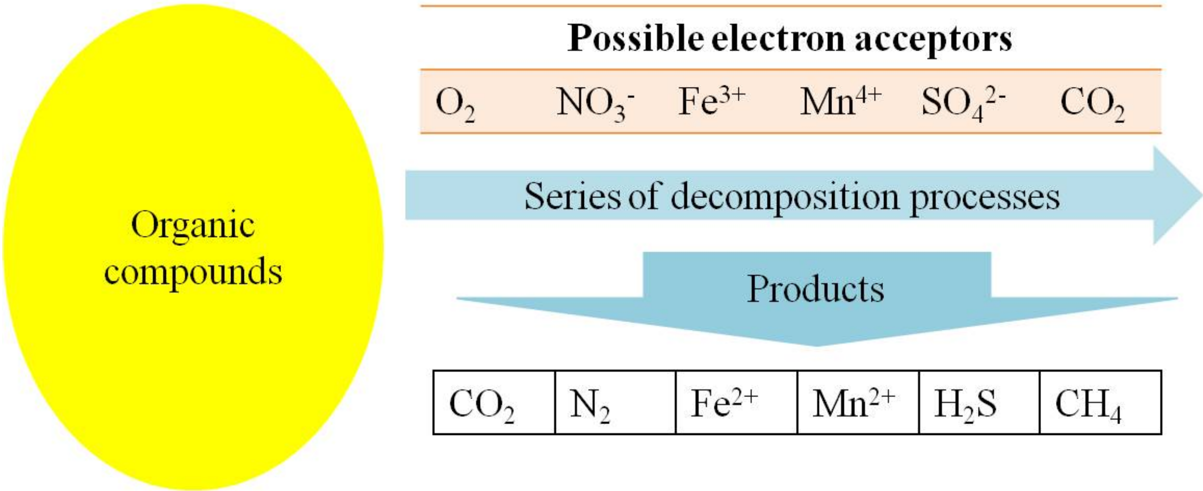

Figure 1.2 Processes of sequential decompositions under anaerobic conditions (structured based on texts in Wetzel 2001)

In the case of N, particulate organic N is mineralized to ammonium (NH_4^+) in both the oxic and anoxic states in the bottom sediments. NH_4^+ can then be oxidized under oxic conditions in the sediment through assimilation processes by benthic organisms; otherwise it diffuses into the water column from the sediments. Nitrate can be reduced by nitrification to NH_4^+ by bacteria in the sediment and can be released from sediment to the water.

Certain interests have focused on the internal supply of P from sediments to the water column due to the clear importance of P as a limiting nutrient in most lacustrine systems (Søndergaad et al. 2003). Under anaerobic conditions, inorganic exchange between the bottom sediment and hypolimnion water is strongly influenced by redox conditions. Diffusion of phosphate from Fe (III) oxides in the sediment to the overlying water column occurred as the compounds are reduced under anoxic conditions in sediments and the overlying water (Perkins and Underwood 2001). Iron sulfide formation coupled to sulfate reduction under anoxic conditions can also suppress the abundance of Fe compounds that can retain the phosphate ion and eventually initiate release of phosphate into water. The transformation of Fe compounds to iron sulfides by sulfate reducing bacteria (SRB) is a main pathway that releases Fe-associated phosphate.

Sulfate reduction in the process of OM decomposition by bacteria can produce H_2S, which is toxic for aquatic organisms (Fig. 1. 3).

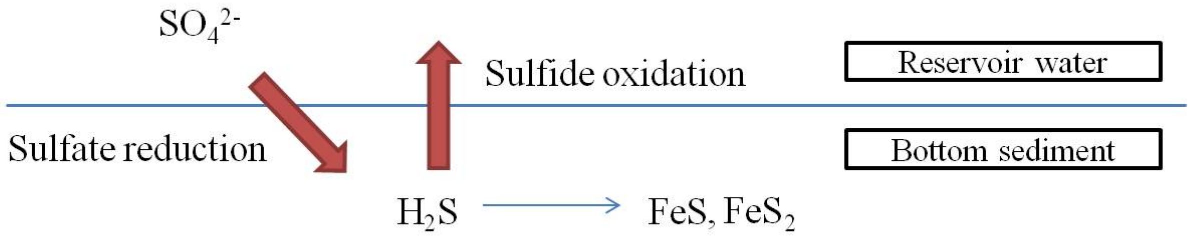

Figure 1.3 Sulfur cycle n an interface between reservoir water and bottom sediment (modified from Holmer and Storkholm 2001)

1.1.4 *The use of sediment cores as archives of changes in water quality and watershed activity*

Climate change and anthropogenic activities play an important role in aquatic system changes both ecologically and hydrologically. These changes have altered conditions of the drainage basins, water budgets, nutrients loadings, and water quality in streams and receiving water bodies. For many decades, reservoirs and lakes have been considered as storage locations, which capture sediments, nutrients, and organic matter after the materials are deposited in the bottom sediments from the watershed. Due to sedimentation of external and internal materials, chronologic records of climate change and the history of watershed changes within a watershed are stored in the bottom sediments of lakes and reservoirs (Szarlowicz and Kubica 2014). Generally, reservoirs incorporate a relatively short history in the equivalent sediment depths compared to natural lakes due to faster sedimentation rate in many cases. The record in the sediments ultimately can help us to obtain insight into the history of past water quality conditions, productivity, and human activity effects. The record also provides information about the main causes that governed the water quality in a watershed during certain periods. In addition, the information from the sediment record can be used for prediction of environmental changes in a watershed and can contribute to making efficient plans and policies for expected future problems in watersheds (Navas et al. 2009). Reservoir sediments are composed of both internal and external sources. Autochthonous materials deposit to the bottom sediment through a sedimentation process after it is generated within the reservoirs while allochthonous materials are transported mostly from the watershed. Rainfall, which generates runoff and transported pollutants in watersheds, is the main factor to govern the amount of allochthonous materials to lacustrine systems. Evaluation of historical changes in a watershed system through sediment studies requires an accurate determination of sedimentation rates. Sediment dating techniques are a useful tool to reconstruct the historical changes within bottom sediment cores. Several methods have been used and tested to determine the precise age of sediment for decades. Recently, many studies have been conducted to date the sediment cores by analyses of lead-210 (^{210}Pb) (Aranud et al. 2006, Tošić et al. 2012). Cautious interpretations are certainly required because different accumulation rates and resuspension of sediments can alter the contents of lead in the sediments. Stable isotope analyses have been considered as useful tools to determine sources of materials in lakes and reservoirs. Carbon (C) isotopes have been used for distinguishing OM sources since each source has different proportionated C isotopes (Kendall et al. 2001, Ogrinc et al. 2005). C isotopes show distinctive concentrations for the various sources, plankton, macrophyte, soil OM, and terrestrial plants (Kendall et al. 2001). N isotopes are also considered as a good indicator to show watershed activity (Filstrup et al. 2010). C/N ratios are one of the most powerful tools available and show clear differences between terrestrial soils and lacustrine sediments (Usui et al. 2006, Tue et al. 2011, Zhao et al. 2015).

1.1.5 *Research hypotheses and objectives*

The goal of the studies performed for this dissertation is to elaborate on flow and transport processes of a reservoir watershed system in South Korea under the Asian monsoon climate. Specifically, we divided the system into two sections: (1) a catchment in an upper part of the watershed and (2) a reservoir body in a lower part of the watershed. The studies focus on understanding how components interact among each other within the watershed and how they are related in terms of change in water quality in streams and in the reservoir. The three studies were conducted in the upland streams of the watershed, the reservoir, and the bottom sediments of the reservoir in order to understand processes affecting the whole watershed system. From these considerations, the following hypotheses were derived, which will be studied in each chapter of this thesis:

1) The nutrients, turbid materials, and organic matters (OM) from non-point sources (NPS) cause water quality problem of streams in an agricultural catchment under monsoon climate.
2) Under anoxic conditions at the sediment-water interface, substantial release of dissolved phosphorus (P), nitrogen (N), and sulfur (S) occurs depending on the amounts of P, N, S, iron (Fe), manganese (Mn), and organic matter (OM) in the bottom sediment.
3) The changes of trophic state and activities in the watershed are well preserved in the bottom sediment and the chronological changes can be reconstructed by analyzing sediment features and elements of the sediment.

Based on the hypotheses the following objectives of each chapter in this thesis arise:

1) To understand the effect of agricultural NPS pollution on stream water quality in a catchment under monsoon climate.
2) To understand the sediment process in a reservoir in regard to influence on water quality by internal loads.
3) To reconstruct history of trophic state changes and watershed activities based on analyses of the bottom sediments in a reservoir.

With these hypotheses and objectives, the following three studies were conducted in this thesis.

Chapter 1 (Study 1):

The agricultural NPS pollution, affecting on the water quality of streams in a catchment, was evaluated as the primary contributing source of pollutant materials into streams and eventually into reservoir water. In the Asian monsoon climate area, agricultural NPS pollution levels are enhanced by monsoonal rainfalls. In this context, intensive field work during rainy and dry seasons was conducted to identify the scale of the NPS pollution in a small agricultural catchment. The impact of land use changes on pollutant exports into streams was also assessed as a way to mitigate the water quality deterioration from NPS pollution.

Chapter 2 (Study 2):

The importance of studies on bottom sediments in reservoir systems has increased with an increase in internal sources of pollutants into reservoirs. The increased pollutants transported by heavy runoff from agricultural watersheds enter receiving water bodies and settle to the bottom. Nutrient ions such as PO_4^{3-}, NH_4^+, and S^{2-} then diffuse into the water column under anoxic conditions, which is dependent on the amount of P, N, S, OM, and other elements in the bottom sediments. In this study, the effects of intensive rainfall events on lake water quality were assessed during the monsoon season and the potential effects of sediment processes to water quality were evaluated by determining the distribution of elements in the bottom sediments and pore-water of the reservoir.

Chapter 3 (Study 3):

Sediment cores are considered as a powerful tool to reconstruct the chronological history of water quality and management activity changes in a watershed. Sediment incorporates materials from the watershed and the water body implying the potential possibility of delineating the change of activities in a watershed (such as agricultural activity, land use changes, construction events) and the history of reservoir water quality. The bottom sediment cores were evaluated as a tool that reflects the change in trophic state and watershed activities in the Soyang Reservoir. Parameters of water quality including Fe, Mn, S, P, Chlorophyll- *a* (Chl. *a*), Secchi depth (SD), and suspended solids (SS) were investigated. C and N concentration and sedimentation rates and sediment age were estimated. Stable isotopes were analysed. Finally, grain size variability in sediment cores was analysed for the historical reconstruction in the Soyang watershed.

1.2 Materials and methods

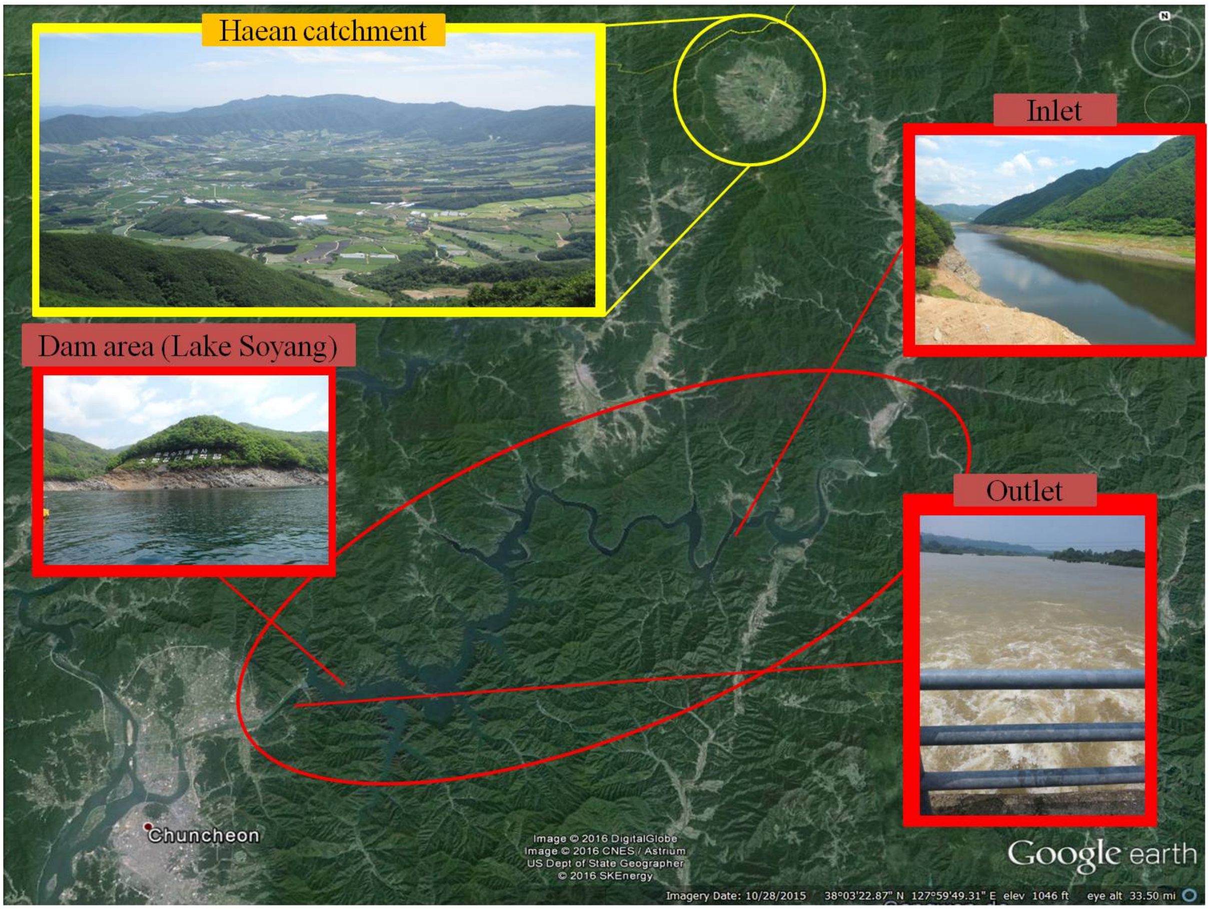

Figure 1.4 Photos at study sites and a satellite image of Soyang watershed (Map data: Google, DigitalGlobe)

Soyang watershed was chosen for studies in this thesis (Fig. 1.4)

1.2.1 *Study sites*

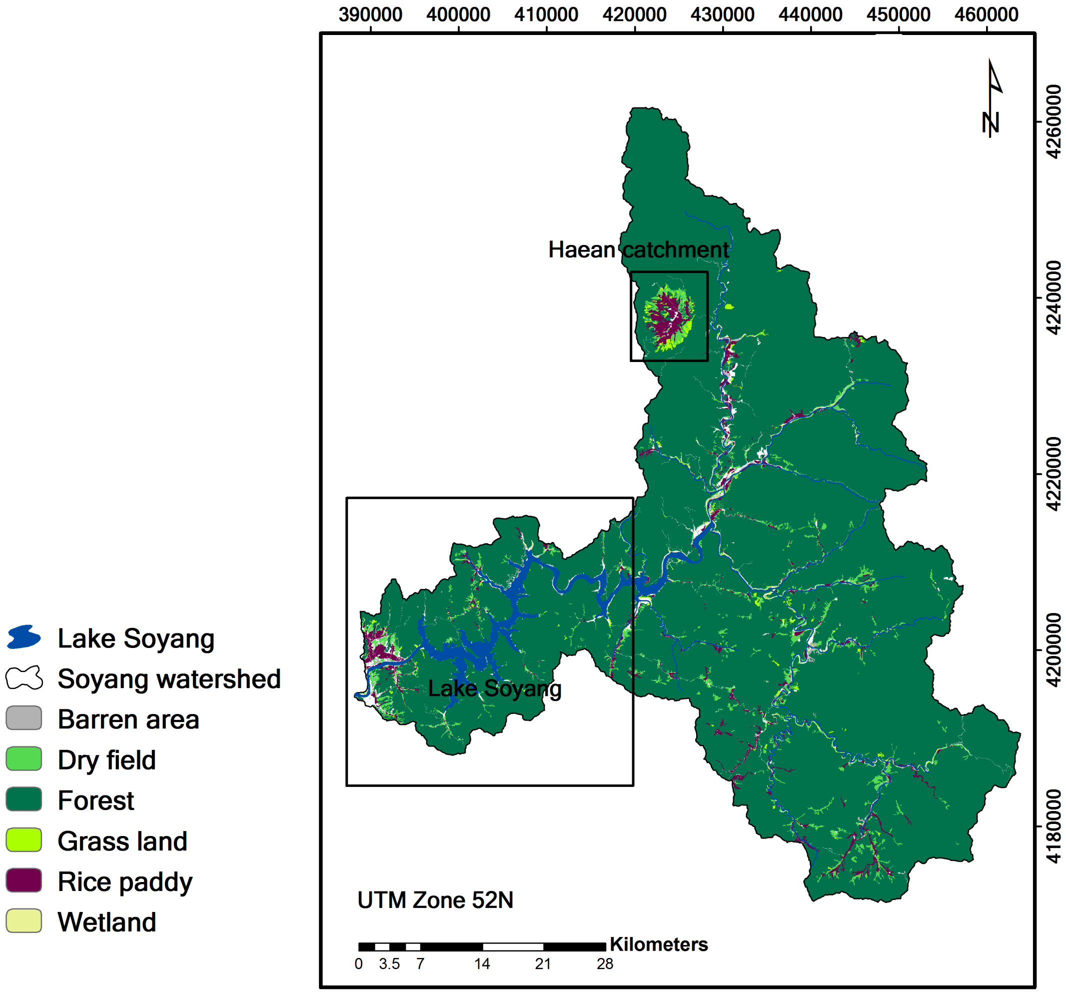

Figure 1.5 A land use map of Soyang Reservoir watershed

Soyang Reservoir watershed The Soyang Reservoir watershed is located in northeastern part of South Korea. The average annual air temperature is approximately 10 °C, with the temperature ranging between approximately –30 °C and 40 °C. The average annual precipitation is 1,300 mm with more than half of the annual precipitation falling during the summer monsoon period (June – Sep.) (Water Resources Management Information System; www.wamis.go.kr). The total area of the watershed is 2,675 km^2. Most of the Soyang watershed area is covered by forest (over 85 %) and urban areas have steadily increased around Chuncheon-si (Fig. 1.5). Agricultural lands have decreased due to urbanization within the watershed, while the highland agricultural areas have been increased with local government support, inducing agricultural land expansion in the watershed since the 1990s. Despite the relatively small area compared to forested land use, the agricultural area (especially highland farming area) accounts for the most abundant pollutant contribution to the Soyang Reservoir. Governmental policies and management directives have attempted to diminish turbidity levels in streams of South Korea. Since 2004, the Ministry of Environment of South Korea has established comprehensive NPS pollution management measures for the four major rivers: the Han, the Nakdong, the Geum, and the Yeongsan/Sumjin Rivers and has designated the Lake Soyang watershed as a special management area (Jun 2015).

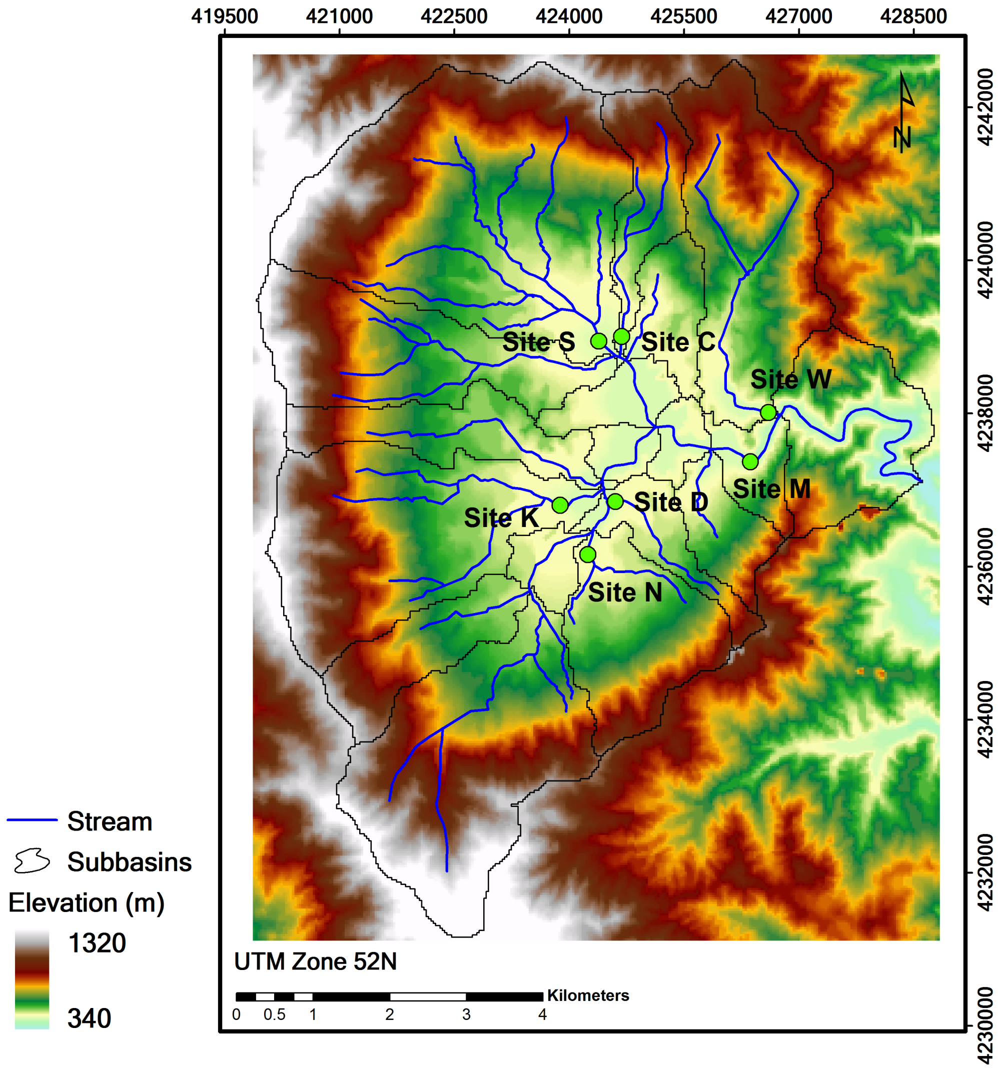

Figure 1.6 A contour map of the Haean catchment (with study sites indicated in the first study)

Haean catchment The Haean catchment is located in Yanggu Province, northeastern South Korea in the upper elevation headwater area of the Soyang Reservoir watershed along the demilitarized zone (DMZ) between North and South Korea (Shope et al. 2013). An important land use in the region is highland agriculture. The elevation of the catchment ranges from approximately 400 to 1,300 m with an average slope of 28.4 % and maximum slope of 84 % (Fig. 1.6, Jung et al. 2012, Shope et al. 2013). The punchbowl shaped catchment is composed of Precambrian gneiss at higher elevations with Jurassic biotite granite intrusions, which eroded and deposited in the central part of the catchment (Kwon et al. 1990). The catchment is divided into six regions including; Oyu-Ri, Hyun-Ri, Yihyun-Ri, Hu-Ri, Wolsan-Ri, and Mandae-Ri administrative districts. The area is surrounded by forested mountains including Mt. Daeam and the summit of Gachil. The climate has an annual average air temperature around 9 °C with winter temperatures often below 0 °C (Kettering et al. 2012, Shope et al. 2013). The average annual precipitation determined by the Korea Meteorological Administration (KMA) is approximately 1,400 mm. The area of the Haean catchment is approximately 61.52 km^2 supporting a population of 1,454. The population has decreased since the 1980s. The catchment is largely forested, covering about 36.0 km^2 of the total catchment area. The forest consists of a diverse species of trees but is dominated by oak. The remaining area is comprised mostly of dry field, rice field, and other agriculture crops. Potato, radish, and cabbage are the main dry field crops and recently, ginseng and orchard fields have increased under local government encouragement. Several streams, including the Naedong, the Dunjunggol, the Kunjigol, and the Sunghwang streams flow through the Haean catchment contributing to the Mandae stream (an outlet of Haean catchment), which continues toward Inbuk stream. Inbuk stream is a tributary to the Soyang River flowing into the Soyang Reservoir, which is the primary drinking water source for the metropolitan area of Seoul (Bartsch et al. 2014). The dominant nutrient sources in the Haean catchment are fertilizers and livestock manure applications to cropland. The catchment is considered to be a nutrient hot-spot, accounting for high levels of NPS export (especially, nutrients and sediment) into the Soyang Reservoir.

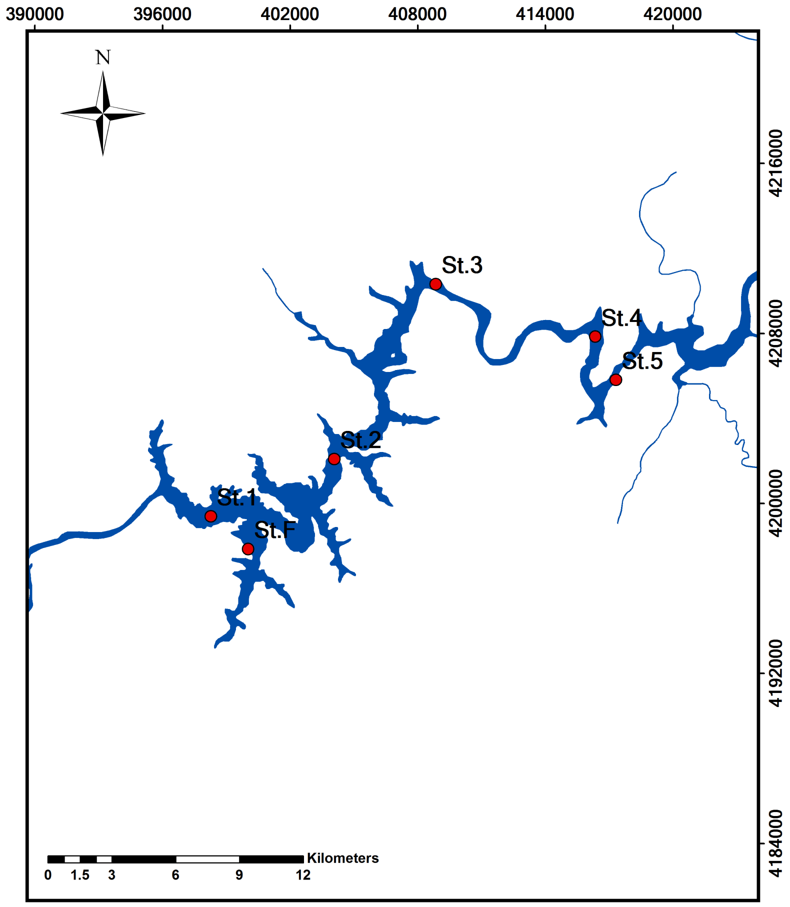

Figure 1.7 A map of Soyang Reservoir (with study sites for the second and the third study)

Soyang Reservoir The Soyang Reservoir (also known as Lake Soyang) was constructed on the North Han River system in 1973 for the purposes of electricity production, drinking water supply, and flood control (Kim and Kim 2006). The reservoir is located in the upper part of the Bukhan River, which is a major tributary of the Han River, in the central area of the Korean Peninsula. The reservoir is the largest reservoir with a volume of 2.9 billion m^3, which has stimulated a large body of work on water quality and monitoring research (Water Resources Management Information System; www.wamis.go.kr). The maximum depth of the reservoir is 120 m at the outlet and its average width is approximately 0.5 km. The reservoir mean depth and average residence time are 42 m and 0.7 yr, respectively. The reservoir is a warm monomictic lake with a mixing period in winter seasons. Ice cover only forms around the inlet area in the winter seasons due to the relatively shallow depth in the area. The reservoir has a dendrictic shape as surrounded by mountainous areas, which suppresses the wind mixing effect (Fig 1.7). The Soyang Reservoir receives most of its pollutants through the Soyang River, which is the main contributing stream. Most nutrient and organic matter loads are derived from the agricultural areas of the watershed during the summer monsoon season (usually May to Aug.) (Kim et al. 2000). More than half of the annual precipitation falls during the summer monsoon season with occasionally intensive rain events (> 100 mm d^{-1}) every year.

1.2.2 *Sampling and analyses methods*

Stream Water quality and discharge at study sites throughout the Haean catchment were regularly monitored. Water samples were collected at seven stream sites (Site N, D, C, K, W, S, and M; Fig. 1.6) during rainfall periods and dry conditions from June to December in 2009 and in the whole twelve months of 2010. During eleven storm events, with total precipitation exceeding 100 mm, at least 10 water samples were collected during individual events. Surface discharge was also measured at each of the sites. Precipitation data were obtained from the KMA.

Collected water samples were kept cool during transport to the laboratory and preserved by acidifying (with HCl or H_2SO_4) or refrigerated. Water samples were filtered through Whatman GF/C glass fiber filters (pore size 1.0 µm) to measure the concentration of suspended solids (SS) and dissolved N and P. Unfiltered water samples for total phosphorus (TP), total nitrogen (TN) were preserved by acidifying with H_2SO_4 to pH<2. TP was analyzed using the ascorbic acid method after persulfate digestion. TN was measured using the cadmium reduction method after digestion with potassium persulfate. Biochemical oxygen demand (BOD) and dissolved oxygen (DO) concentration of the first bottle was determined. The second bottle was incubated under 20℃ for 5 days and the BOD value was calculated as the difference between the initial and final DO values. The $KMnO_4$ method was used for Chemical Oxygen Demand (COD). All of analysis methods for water samples were referred from Standard Methods 20th Ed. (APHA 2012).

To estimate discharge at each of the studied sites, the velocity-area method was used with an electronic flow meter (Shope et al. 2013). Stream discharge during both wet and dry conditions was measured at each of the stream monitoring sites and rating curves were developed to describe the relationship between discharge and water level for each stream. The discharges were estimated with measured water levels in the sites on the basis of the stage/discharge rating curve.

Lake water One sampling point was chosen for water samples in order to characterize the reservoir water quality. The deepest part of the reservoir adjacent to the dam site was hypothesized to reflect the mean water quality in the reservoir as well as the outflow water quality and therefore chosen for the monitoring site. Water samples were collected bi-monthly to monthly during the study period from a boat. Sampling was performed at 10 m depth intervals to the maximum depth, and at 0, 2, and 5 m below the water surface using a water sampler. Basic limnological in-situ parameters (pH, temperature, and DO) were determined during each sampling campaign with a portable multi-parameter sensor (Hydrolab Quanta, provided by CLMR-KNU). Collected samples were stored below 4℃ before each analysis. Secchi disk (SD) depth was measured monthly from the boat with a 30 cm SD round slide.

Water samples were filtered through glass fiber filters (Whatmann GF/F) for dissolved total phosphorus (DTP), dissolved inorganic phosphorus (DIP), organic carbon (OC), nitrate (NO_3^-), sulfate (SO_4^{2-}), and other major and trace elements. Before filtration, TP of water samples was analyzed by the ascorbic method after persulfate digestion (APHA 2012). Filtered water samples were used for the measurement of dissolved organic carbon (DOC) with a total organic carbon (TOC) analyzer (Shimadzu TOC 5000, Kyoto, Japan). Particulate organic carbon (POC) measurements were conducted by combusting the dried glass fiber filters using a Yanoco MT-5 CHN analyzer. NO_3^-, SO_4^{2-}, and Chloride ion (Cl^-) concentrations of all water samples were measured by ion chromatography (Metrohm modular IC system 762, Herisau, Switzerland). Iron (Fe) and manganese (Mn) concentrations in water samples were measured through inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 3200XL, Perkin Elmer, Waltham, USA). Chlorophyll *a* (Chl. *a*) concentrations in water samples were measured by the Lorenzen method (APHA 2012). SS amount in water samples was calculated by measuring the differences in weight of GF/F filter paper before filtration and the dried filter paper (1hr, 105℃) after filtration of samples (APHA 2012).

Sediment Sediment core samples were collected with a gravity core (UWITEC, Mondsee, Austria) along the distance from a dam site to an inlet area of an inflow. Five sampling sites (St. 1 to 5) were selected for the sediment samples in 2012 and 2013 and additional sediment samples were collected in a former fish farm area (St. F) in 2013 (Fig. 1.7). Pore-water samples were extracted by centrifuge from the sliced sediment core samples. Sediment traps were deployed 5 times from July to October in 2013 and were installed at three depths (20, 50, and 80 m) at the dam site. Trap samplers were made of stainless material to prevent physical damage. The sediment samples in the trap were collected to calculate the distributed sedimentation rate of C and N in the water column of the reservoir.

Sediment core samples were sliced with a customized core cutting device at 1, 2, or 5 cm intervals according to visual identification of the structured layering. From these sliced samples, we measured TP, Fe, total reduced inorganic sulfur (TRIS), and other elements (Aluminum (Al), Calcium (Ca), Potassium (K), and S) after freeze-drying. Fe was measured after HCL extraction using the Phenantroline assay (Tamura et al. 1974) to differentiate ferric (Fe^{3+}) and ferrous (Fe^{2+}) iron in the sediment samples. TRIS species were extracted (S_2^{2-}, S^{2-}, and S^0) from freeze-dried and sectioned sediment core samples following chromium reduction (Canfield et al. 1986), trapped as H_2S in NaOH. Reduced sulfur species were measured by the methylene blue assay (Williams 1979) and using an UV-VIS-photometer. Further elements in the sediment samples were measured by ICP-OES method after 1 N HCl extraction. Sediment grain size was analyzed using Mastersizer 2000 (Malvern, UK) after sonication. C, N, $\delta^{13}C$, and $\delta^{15}N$ were analyzed with sliced sediment samples after freeze-drying. Relative C and N isotope abundances of sectioned sediment samples were measured with an elemental analyzer in a dual-element analysis mode (Carlo Erba 1108, Milano, Italy) for Dumas combustion followed by gas chromatographic separation of the gaseous combustion products. The other elemental compositions (P, S, Fe, Mn, Ca, Cd, Cu, and Pb) were detected by energy-dispersive X-ray fluorescence (XRF) spectrometry (Rigaku, Japan). Sediment dating analysis was conducted using the ^{210}Pb dating technique.

1.3 RESULTS AND DISCUSSION

1.3.1 *Extent of non-point source (NPS) pollution throughout an agricultural catchment*

The average concentrations of SS, turbidity, and TP of each stream under dry conditions were significantly lower than the concentrations of the water quality parameters during rain events and the transported sediment and associated nutrient concentrations generally increased with increasing discharge in the all of streams for all of the rain events as indicated in previous studies (Jain 2002, Wu et al. 2012). The exported TP and SS into the streams were influenced most among the water quality parameters by the rainfall (Fraser et al. 1999). The SS concentration in streams during rainfall in the Haean catchment was generally higher than the results of previous studies conducted in other main river systems in South Korea (Park et al.

2005, Kwak et al. 2008) and also at the same site in the past (Jung 2012). Highland agriculture in the catchment under high slopes is considered as one of the reasons that caused high annual SS loading to the streams in this region (Arnhold et al. 2014). The SS remained low at Site W with the lowest concentration during rainfall events because forested land use mitigated soil disturbance from the watershed of the Site W. The average EMCs of TN increased while the average EMCs of TP and SS decreased in 2010 compared to the EMCs in 2009 (Table 1.1).

Table 1.1 Event mean concentrations (EMC) of suspended solid (SS), total nitrogen (TN), and total phosphorous (TP) at an outlet stream during rain events in Haean catchment (unit: mg L^{-1})

Year	Event no.	SS	TN	TP
2009	1	2954	2.24	1.27
	2	1837	2.08	1.37
	3	1587	1.76	0.81
	4	3804	3.43	1.62
2010	5	1281	5.08	1.45
	6	304	3.90	0.49
	7	427	3.77	0.46
	8	661	3.54	0.71
	9	738	3.04	0.95
	10	332	3.16	0.46
	11	313	3.25	0.48

The decreased intensity of rainfall in 2010 seemed to mitigate the amount of SS and TP in runoff, which are usually exported together as attached forms on sediment derived from the agricultural fields (Kim et al. 2014). The government has driven construction of new facilities to contain turbid water generation in the catchment, which influenced on decreased soil loss from the catchment. BOD increased in the watershed for 2 years while COD decreased, which can be interpreted as biodegradable organic matter increasing in the catchment but non-biodegradable (recalcitrant) organic matter were produced less in 2010 relative to 2009. The EMC of TP at an outlet of the Haean catchment was much higher compared to other streams in other regions of Korea (Park et al. 2005, Kwak et al. 2008), which have similar summer monsoon rainfall characteristic such as rainfall intensity and periods. Also, compared to the results from locations in other countries, the EMCs of SS and TP were higher (Gentry et al. 2007, Hu and Huang 2014). These results imply that runoff into the stream through the Haean catchment transported significant amounts of suspended sediment with attached P into the Lake Soyang receiving reservoir.

The EMCs of SS and TP decreased for 2 years at Site N in which the land use had been dramatically changed from dry fields to orchard and ginseng fields. The decreased EMCs of TP and SS at Site N were assumed to be derived from decreased sediment and P exports as a function of land use changes. However, the other water quality parameters (BOD, COD, TN and NO_3^-) showed no clear discrepancies between 2009 and 2010. The results imply that migrating soil disturbance and erosion by land use changes efficiently reduced the P export (Ouyang et al. 2014) but EMCs of nitrate and TN increased minimally showing that land use changes did not mitigate those parameters because these pollutants are less related to soil erosion compared to TP and SS.

1.3.2 *Effects of a monsoonal climate and the release of materials from sediment to the water column in a reservoir*

The high POC values (4.0 mgC L^{-1} in the hypolimnion and 2.8 mgC L^{-1} in the metalimnion) in the reservoir emerged after heavy rainfall, stressing the relevance of POC loading during high flow conditions. The highest POC concentration in the reservoir is a result of intensive summer rainfall, which causes a large amount of particulate organic matter to enter the lake via storm runoff as shown in Lake Soyang (Kim et al. 2000) and other reservoirs (Aryal et al. 2014). The transported C was eventually deposited in the bottom sediment. The calculated C sedimentation rate in Lake Soyang (453 mg POC m^{-2} d^{-1}) was lower than the sedimentation rates in the other reservoirs, but higher than in natural lakes (Teodoru et al. 2013, Clow et al. 2015). The TP concentrations in the metalimnion (17.6 μgP L^{-1} at 30 m water depth and 19.5

μgP L^{-1} at 40 m water depth) were increased after summer monsoon rainfall. A previous study reported that the load of TP was highest (approximately, 1,200 tP yr^{-1}) in 2006 during the intensive rainfall of the summer monsoon season (Kim and Jung 2007). This input was increased by the disturbances in forested areas and agricultural practices with the overuse of P fertilizer and frequent soil disturbances (Park et al. 2010). The high amount of P load is also eventually deposited into the sediment in such reservoir systems. The input of Fe and Mn were also increased by an inflow of high amounts of Fe and Mn (137 μgFe L^{-1} and 25 μgMn L^{-1}, respectively). The high amounts of Fe, Mn, and S entered the lake along with high amounts of P adsorbed to these particles after rainfall. Hypolimnetic anoxia has emerged since the eutrophication period in 1980s in Lake Soyang (Fig. 1.8).

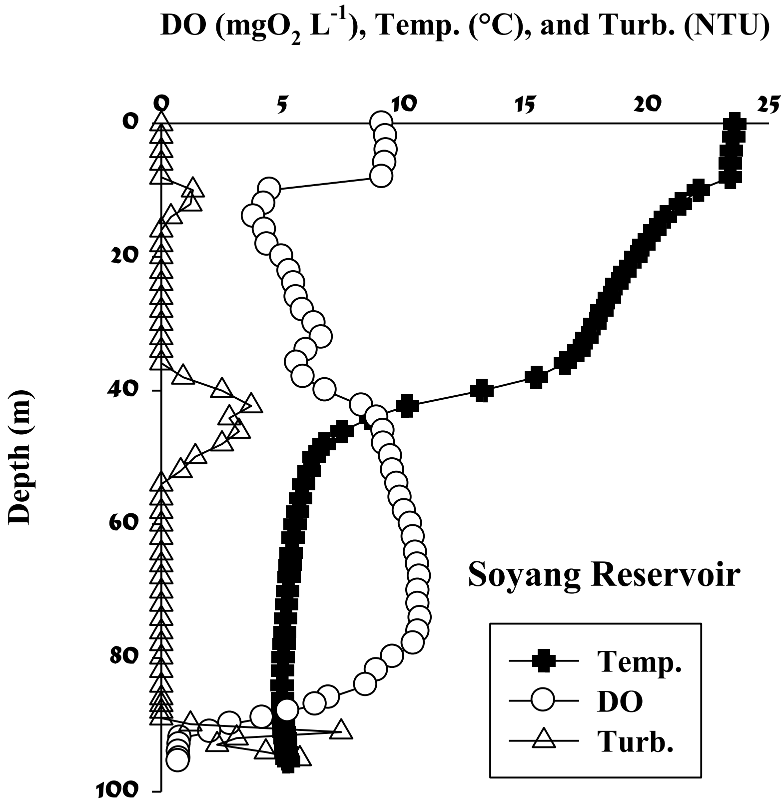

Figure1.8 Vertical profiles of dissolved oxygen (DO), temperature (Temp.), and turbidity (Turb.) in Soyang Reservoir during a stratification period

The oxidation redox potential (ORP) in sediment at site 1 was negative for the entire depth indicating anoxic conditions in the sediments. Under anoxic conditions, sulfate reduction is the main respiratory pathway as sulfate is used as the primary electron acceptor in decomposition processes (D'Hondt et al. 2002). The fact was well deflected in the observed high concentrations of TRIS (exceeded 20 mmol g^{-1}) in the upper layers of Lake Soyang sediment cores. Therefore, it appears that significant amounts of iron oxides are not reduced and P remains trapped in the sediment. High amounts of Fe in the sediment can act as P traps by strong adsorption. The decreased sulfate in the pore-water toward the top of the sediment and higher TRIS concentrations in this region imply the occurrence of sulfate reduction in the sediment, which leads to high amounts of reduced sulfur. The sedimentation of Fe, Mn, S and C and its interactions in the sediment seem to control the diffusion of nutrients from the sediment with the redox condition. Higher concentrations of DIP and ammonia were observed in pore water than in bottom water. This mobile P and N can diffuse to the water column as previously observed in eutrophic conditions (Reddy et al. 1996, Yang et al. 2015). However, despite the high concentrations of DIP and ammonia in the lower water column during stratification, the average concentration of DIP and ammonia remained constantly low after the monsoon season. We assumed that DIP can be resettled and ammonia can be oxidized when they contact the oxic layer around the time of the water mixing period (Beutel et al. 2008). In addition to that, the released N and P can be removed when the intermediate density current is discharged out of the dam through the outlet at the middle depth of the dam before the mixing period in the winter season. We found that heavy rainfall caused acute increases of C, P, Fe, and Mn in the lake by turbid density currents during the monsoon seasons. Such increased materials are eventually deposited to bottom sediments and control the diffusion process of mobile P and N at the interface between the bottom water and sediment under anoxic condition. This finding implies that sediment processes and internal loads are an important subject to monitor together with inflowing water quality change for effective reservoir management, especially in Asian monsoon climate areas.

1.3.3 *Potential of sediment core samples as a tool for historical archives*

The estimated sedimentation rate (0.2 cm yr^{-1}) of Soyang Reservoir by the Pb dating technique was much lower than observed in other reservoirs and seems to be similar to natural lakes (e. g. 6 cm yr–1 in the Danube Iron Gate Dam; Vukovic et al. 2014, 4 cm yr–1 in the Partoon Reservoir; Arnason and Fletcher 2003, between 2 to 7 cm yr–1 in the Conowingo reservoir; McLean et al. 1991, ranging from 0.01 to 0.32 cm yr–1 in Lake Superior; Evans et al. 1981).

The sedimentation rate also contrasts a previous estimate of 1.0 cm yr^{-1} in Lake Soyang (Cheong and Jung 2006). The limitations about ^{210}Pb dating have been reported in other reservoirs due to sediment disturbance by frequent water fluctuations and the relatively younger ages compared to natural lakes (Filstrup et al. 2010, Winston et al. 2014). To overcome the limitations of the Pb dating technique, we attempted to independently estimate sediment age with our sediment composition data. The reservoir has experienced different trophic states with specific events during each time period (Table 1.2).

Table 1.2 History of trophic state changes in Soyang Reservoir

Period	Trophic state	Year	Events (year)	References
1st	Oligo-	1973-1985	Dam construction completed (1973) Onset of Fish farms setup (1980)	
2nd	Eutro-	1986-1999	Massive blue green algae growth with SD only 0.7 m in 1990 Fish farm eliminations since 1998 and anabaena cells decreased in 3 year, 1996-1998	Kim and Jung 2007 Kim et al. 1999
3rd	Meso/ Oligo-	2000-2005	Phytoplankton species change (cyanobacteria to dinoflagellates and chrysophytes) Oligotrophication sign based on nutrient concentrations, phytoplankton species and transparency data. Increase in P load since 2000 from watershed	Kim's personal communication Kim and Jung 2007
4th	Meso/ Eutro-	2006-2012	After typhoon, Turbid water out released from the dam to the downstream for over 6 months in 2006 Frequent turbid water inflow from watershed after monsoon climate summer rainfall	Kim and Jung 2007

Since the dam construction in 1973, the reservoir had its last oligotrophic state from 1973 through 1985 (1st period). The reservoir had been eutrophic with frequent algal blooms during the late summer seasons in 1986 through 1999 (2nd period), after fish farming had started. This trophic state recovered into meso/eutrophic states from 2000 to 2005 (3rd period), after fish farm businesses were completely removed from the reservoir. However, the reservoir recently turned into a eutrophic state between 2006 and 2012 (4th period), since the reservoir water quality has been the worst observed in history due to massive turbid water inflow from the watershed in 2006. The chronological history reflected in sediment compositions of cores is presented in Figure 1.9.

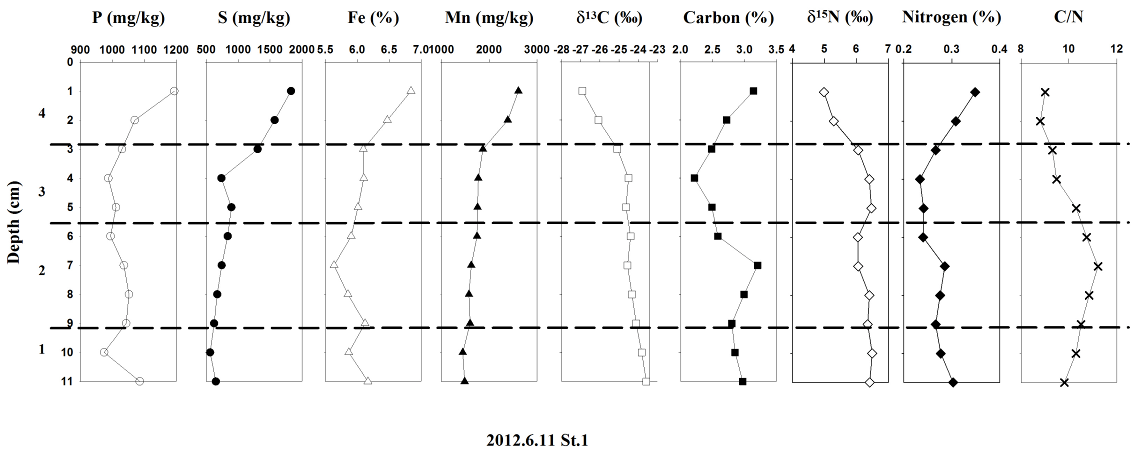

Figure 1.9 Profiles of P, S, Fe, Mn, C, N, $\delta^{13}C$, $\delta^{15}N$, and C/N ratio in core at site 1 (dash lines divide the reconstructed periods)

The elemental distributions clearly show the discrepancy between pre- and post-construction periods. The C/N ratio profile at site 1 was the primary evidence, which increased to 40.0 at a depth of 14 cm and they remained constant with an average ratio of 40.1 ±1.4 (n=10) below showing similar values from land-derived plants (Meyers 1994, Mayers and Ishiwatari 1993). On the other hand, the low C/N ratios observed in the upper region are similar to the values from lacustrine sediments (average 8.9; Murase and Sakamoto 2000, approximately 10; Koszelnik et al. 2008). In the second period, C and N increased, which results from the eutrophic condition caused by fish farming. During the 3rd and the 4th periods, the P, S, Fe, and Mn increased relative to the 1st and 2nd periods, as well as the C and N concentrations, which can be proof of increased exports from the watershed by increased agricultural activity and intensified rainfall characteristic in the watershed since the 2000s (Kim and Jung 2007). Decreased Chl *a* concentrations in the lake since the 2000s compared to the concentrations in

1990s led to less contributions of autochthonous organic matter than the contribution of allochthonous organic matter to the bottom sediment. The SS increased in the metalimnion after heavy rainfall, forming turbid current inflow and the SS remained high in the hypolimnion after the monsoon season with the maximum concentration of SS in 2 years (49.1 mg L^{-1} in July 2013). The turbid current emerged more often in the reservoir because of the increased agricultural area in the watershed and intensified rainfall characteristics since 2000 (Kim and Jung 2007). The turbid current inflow seemed to carry significant amounts of C sources from the watershed to the reservoir water and it led to increased contributions of allochthonous C into the reservoir sediment in the years since the 2000s.

1.4 CONCLUSIONS

A watershed of a reservoir (Soyang watershed) in South Korea was studied from an upland catchment (Haean catchment) to the bottom sediment of Soyang Reservoir. Three studies for this thesis were conducted to understand the interactions between each component in the watershed. First, we examined watershed activity effects on the stream water quality in the watershed by studying the pollution of agricultural NPS in the Haean catchment, which is a primary source of pollutants to Soyang Reservoir. The second study moved to the Soyang Reservoir to evaluate the water quality under monsoon climate characteristics and the role of the bottom sediment as an internal source of pollutants and nutrients to the water column. Finally, we reconstructed the history of trophic state changes in the reservoir and watershed activity changes in the watershed by interpreting the data from bottom sediment cores of the reservoir. The conclusions are summarized under three categories.

1) In the Haean catchment, significant amounts of pollutant exports entered into streams during the summer monsoon. Asian summer monsoonal rainfall enhanced the extent of agricultural

NPS pollution by flushing terrestrial pollutants in the catchment. EMCs of TP and SS were higher than findings of previous studies, which were conducted in South Korea and other overseas countries. Governmental driven land use changes were implemented for 2 years (2009–2010) as a way to reduce the soil erosion from the agricultural land and the policy led to conversion of large scales of land use (mostly dry fields and rice paddies to orchard and ginseng fields). The SS loads from the catchment into streams clearly decreased in 2010 as well as TP.

2) Heavy rainfall also caused dramatic increases of C, P, Fe, and Mn of the water in the reservoir by turbid density currents during monsoon seasons. The elements composed the bottom sediments in Soyang Reservoir. The increased organic matter and elements controlled the internal loads of PO_4^{3-}, NH_4^+, and S released from the sediment. However, the effects of diffused nutrients and toxic material were not significant because of the physical reservoir characteristics (deep water depth and an outflow from the middle layer) hampered the diffusion of materials into the entire reservoir water body. Regular investigations of sediment processes and internal loading with constant monitoring of inflow water quality are requisite for an effective management of reservoirs.

3) Sediment cores can be used as an archive, which includes the history of trophic states and watershed activity changes, through analyses of sediment dating and the composition of cores. The reconstructed sediment ages where highly correlated with the vertical profiles of elements in the sediment cores. Soyang Reservoir has received OM and nutrients through two sources, autochthonous and allochthonous source, since the dam construction. The composition of cores and the water quality parameter changes indicated that the main OM and pollutants sources have been changed from autochthonous matter to allochthonous matter.

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Chapter 2 IMPACTS OF LAND USE CHANGE AND SUMMER MONSOON CLIMATE ON NUTRIENTS AND SEDIMENT EXPORTS IN STREAM WATER QUALITY IN AN AGRICULTURAL CATCHMENT

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2.1 ABSTRACT

Agricultural non-point source (NPS) pollution is a major concern for water quality management in Soyang watershed in South Korea. Nutrients (phosphorus and nitrogen), organic matter, and sediment exports in streams were estimated in an agricultural catchment (Haean catchment) for 2 years. The stream water samples were taken in dry and rainy seasons to evaluate a monsoonal rainfall effect to pollutants exports in the streams. An influence of

land use changes on NPS pollution was assessed by conducting a land use census for 2 years, and comparing the NPS exports characteristic for the 2 years. Total phosphorus (TP), suspended solid (SS), biochemical oxygen demand (BOD), and chemical oxygen demand (COD) increased dramatically in rainy seasons for 2 years. Land uses were changed for the 2 years of study period. Especially, dry fields and rice paddies have been decreased distinctively while orchard (apple, grape, and peach) and ginseng crops have been increased throughout the catchment. The TP and SS loadings decreased in the streams in 2010 compared to the loadings in 2009 while the BOD and NO_3^- have been not changed significantly. In this study, monsoonal driven rainfalls increased exports of agricultural NPS pollutants into streams. Land use change (mostly crop and paddy fields to orchards and ginseng fields) mitigated TP and SS exports into the streams.

2.2 INTRODUCTION

Non-point source (NPS) pollution is the main cause of inland water deterioration and a priority issue for present water quality management worldwide (Rhee et al. 2012, Duncan 2014). NPS pollution is more difficult to control and to treat than pollution from point sources (PS) due to the complicated generation and formation (Berka et al. 2001, Shen et al. 2011), and concern for NPS pollution affecting lake water quality has continually increased (Qin et al. 2007, Gantidis et al. 2007). Better understanding nitrogen (N) and phosphorus (P) transport from agricultural NPS to surface waters is a major focus of scientific research and environmental policy (Hart et al. 2004, Vadas et al. 2005, Park et al. 2015). This is especially prevalent in agricultural areas where high amounts of N and P are the main NPS contamination factors into surface waters (Elçi and Selçuk 2013, Lou et al. 2015), which results in increased algal production and amplifies lake and reservoir eutrophication (Correll 1998, Ma et al. 2011). The NPS pollution contributes to excessive sediment, nutrients, and organic matter in streams during the summer rainy season under monsoonal climate conditions. Studies conducted in monsoonal climate regions have shown that mountainous areas with intensive highland agriculture induce high nutrient (especially N and P) loading into rivers, particularly during the summer monsoonal conditions (Park et al. 2010, Wang et al. 2011). Soil erosion is enormously induced on high land agricultural area with steep slopes in combination with intense rainfalls during rainy season (Jain 2002). High turbidity surface discharge due to large-scale soil erosion causes environmental deterioration that severely impacts to aquatic ecosystems (Lee et al. 2013). In recent years, studies have focused on finding practical and efficient agricultural practices that reduce agricultural NPS pollutant yields under the moniker of best management practices (BMPs) (Chiang et al. 2012, Dechim and Skhiri 2013). Efforts to identify the ideal BMP are still in progress (Yulianti et al. 1999, Gitau et al. 2008, Liu et al. 2013). Among the ways to manage NPS pollution, land use change is regarded as one of the most efficient factors, by directly influencing hydrologic processes at the catchment-scale (Johnes 1996, Sargaonkar 2006, You et al. 2012, Fučík et al. 2014, Ren et al. 2015). In general, land use change, such as dry field crops to orchard farms, can reduce soil erosion, which decreases fertilizer inputs and minimizes ecological disturbances in critical ecosystems.

In South Korea, the Ministry of Environment (MoE) has established comprehensive NPS pollution management measures for the four major rivers of the Han: the Nakdong, the Geum and the Yeongsan and the Sumjin rivers since 2004. The MoE has also designated the Lake Soyang watershed, which includes our study catchment, as a special management area (Jun 2015). These governmental policies and management directives have attempted to diminish turbidity levels in streams in South Korea. Consistent with these regulatory changes, the patterns in land use have been substantially altered in recent years, with the amount of land use for ginseng and orchard farming that causes less soil deteriorations compared to crop lands (Wang et al. 2001), continuously increasing.

Goal for this study is to scale the extent of NPS pollution in an agricultural catchment. We tried to assess the effect of exports from agricultural NPSs to streams in the catchment and also attempted to evaluate the land use change impact on nutrients and sediment exports by comparing 2 years in which the land use significantly changed in the catchment. To achieve the goals, the stream water qualities of the Haean catchment, located in the Lake Soyang watershed and a hot spot as nutrients, sediments, and organic matter sources into the lake, was monitored for 2 years (2009–2010). Event mean concentrations (EMCs) and biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solid (SS), total nitrogen (TN), and total phosphorus (TP) loading were calculated to evaluate the water quality in streams influenced by NPS. Principal component analysis (PCA) was also used to determine the factors contributing to NPS loading in the catchment. Land use re-classification processing along the stream areas (Seo et al. 2014) was conducted to assess land use change effects to NPS exports into the streams in the catchment.

2.3 Materials and methods

2.3.1 *Land use map survey*

We modified the land use dataset from Seo et al. (2014) to characterize the land use according to each stream basin. A plot-scale land use census was completed throughout the Haean catchment (61.52 km^2) in 2009 and 2010, and subsequently digitized into GIS. The investigation yielded more than 3,000 individual land use classifications with regard both to crop and non-crop areas. Land use polygons were classified into a categorical aggregation for simplicity and associated with ecological and physical traits. Ground observations, completed by the Research Institute of Gangwon Province (RIG) during the 2007 crop season, were used for qualitative validation of the 2009 and 2010 land use classification. A total 11 aggregated land use classifications were used to evaluate the land use change status for each stream watershed.

2.3.2 *Study site and sampling description*

The study area encompasses the Haean catchment located in Yanggu County, Gangwon Province, South Korea. The catchment is bowl-shaped and locally known as the ‘punch-bowl’; Bartsch et al 2013. It encompasses a mountainous headwater portion of the watershed of Lake Soyang, which supplies drinking water for the Seoul metropolitan area since construction in 1973 (Kim et al. 2000). The elevation of the Haean catchment ranges from 339 to 1,320 m and the area is surrounded by high elevation Precambrian Gneiss complex while the low elevation central portion is a highly weather Jurassic biotite granite intrusion (Kwon et al. 1990). The climate has a mean annual air temperature of 8.7 ˚C with winter temperatures as low as –27 ˚C and summer temperatures as high as 33 ˚C. The average annual precipitation determined by the Korea Meteorological Administration (KMA) is 1,400 mm yr^{-1} and over seventy percent of the annual precipitation falls during summer monsoon season, June to August, (Bartsch et al. 2013). The catchment is largely forested particularly at high elevation. The remaining area is comprised mostly of dry croplands and rice paddy agriculture (Seo et al. 2014). An important land use in the region is highland agriculture, which cultivates crops (potato, radish, and cabbage) in steep slopes, and the dominant nutrient sources are artificial fertilizers and livestock manure applications to cropland in the Haean catchment (Kettering et al. 2012). Highland agriculture in the Lake Soyang watershed has been shown to cause increases in nutrient loading into streams from non-point sources (NPSs) from sources such as the overuse of organic fertilizers, resulting in turbid water (Jung et al. 2009). The Haean catchment headwaters are one of the most problematic turbid water sources to Lake Soyang.

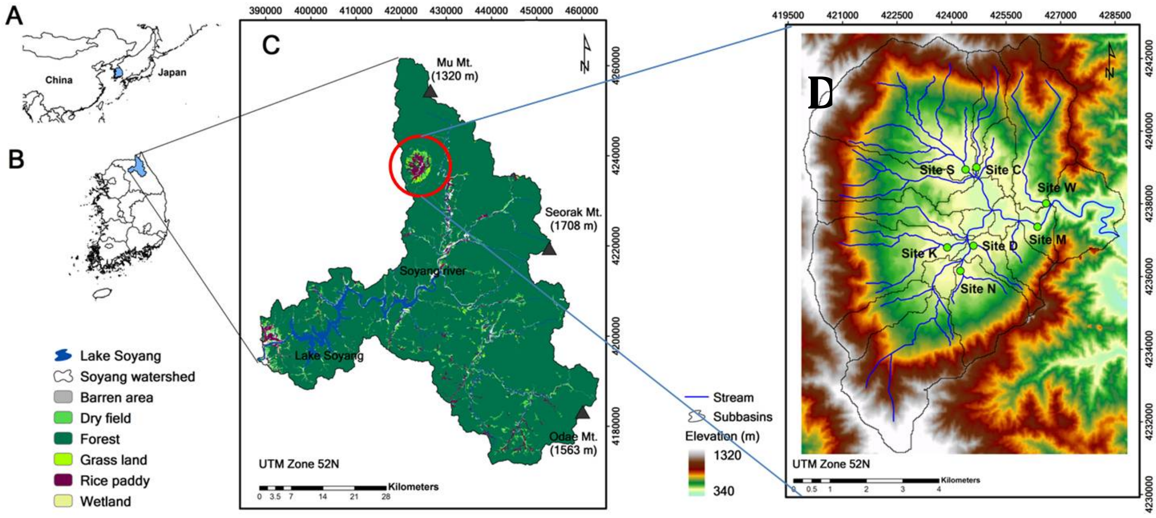


Figure 2.1 Study area and sites (maps of the Northeast Asia; A, the Korean Peninsula: B, Soyang watershed; C, and Haean catchment including study sites (green circles); D)

Seven streams were selected for water quality monitoring (Fig. 2.1) including: Naedong (Site N), Dunjunggol (Site D), Kunjigol (Site K), Sunghwang (Site S), Wolsan (Site W), Chungryongangol (Site C), which flow to the Mandae stream (Site M), an outlet of the Haean catchment continuing toward Inbuk stream and the Soyang River flowing into Lake Soyang. Water samples were collected at each site during rainfall periods and bi-monthly during dry conditions from June to December in 2009 and monthly in 2010. For 11 individual storm vents (4 times in 2009 and 7 times in 2010, respectively), at least 10 water samples were collected for each rainfall event (Table 2.1). However, samples were not collected at Site D during the 2nd storm event due to inaccessibility as a function of massive mudslides. Surface discharge data were also collected at each of the sites. Hourly precipitation data was obtained from the KMA.

Table 2.1 Dates, rainfall amounts, and rainfall intensities for each rain event

No. of event	Date	Total amount (mm)	Intensity (mm hr^{-1})	Intensity order
1	09' Jul 9^{th}–10^{th}	149.0	5.4	3
2	09' Jul 12^{th}–13^{th}	118.0	2.7	7
3	09' Jul 14^{th}–15^{th}	148.0	6.6	2
4	09' Aug 11^{th}–12^{th}	210.0	9.5	1
5	10' May 18^{th}–19^{th}	67.5	3.8	4
6	10' May 23^{rd}–25^{th}	43.0	1.5	8
7	10' Jul 2^{nd}–3^{rd}	36.5	1.3	10
8	10' Jul 16^{th}–19^{th}	91.5	1.3	9
9	10' Aug 7^{th}–8^{th}	56.5	1.2	11
10	10' Aug 25^{th}–27^{th}	117.0	2.7	6
11	10' Sep 2^{nd}–3^{rd}	77.5	2.8	5

2.3.3 *Laboratory analyses*

All water samples were stored in cool conditions (<4 ˚ C) and acidified prior to laboratory analysis. Water samples were filtered through Whatman GF/C glass fiber filters (pore size 1.0 μm) to measure the concentrations of SS and dissolved N and P. Unfiltered water samples were analyzed for TP and TN and were preserved by acidifying with H_2SO_4 to pH < 2. TP was analyzed using the ascorbic acid method after persulfate digestion. Total nitrogen was measured using the cadmium reduction method after digestion with potassium persulfate. BOD was calculated by determining the difference in dissolved oxygen (DO) concentration between in-situ conditions and after 5 days of incubation at 20˚C using a DO meter (YSI 58 Dissolved Oxygen Meter, USA, YSI incorporated).The $KMnO_4$ method was used for COD analysis. Turbidity was measured using a nephelometer (Hach). All of the analysis methods for water samples were completed according to references in Standard Methods 20th Ed. (APHA 2012). We used an electronic flow meter (Flo-Mate^{TM} 2000 Flow Meter, USA, Marsh-MacBirney) to estimate discharge with the velocity-area method, which is commonly used to measure discharge in open channels (Shope et al. 2013). Using this method, the flow velocity and cross sectional area are measured separately for each stream in the catchment (Buchanan and Somers 1968). Stream discharge during both wet and dry conditions were measured at least 10 times at each of the stream monitoring locations and rating curves were developed to describe the relationship between discharge and water level for each stream. When water samples were collected at each monitoring location, discharge was estimated using a stage/discharge rating curve.

Detailed description and equations about flow measurement method are shown below (Equation 2-1 and 2-2).

2.3.4 *Calculation for discharges, event mean concentration (EMC), and pollutant loading*

Surface water discharge

Equation 2-1

$$\boldsymbol{Q_1 = (H_{i+1} + H_i)\frac{W_i}{2}V_i}$$

where W_i is the distance to measurement points along the transect, V_i is stream velocity, H_i is water depth, and i is the subarea dimension, which is typically 20–25 measurements across the stream width.

Equation 2-2

$$\boldsymbol{Q = \int Q_i = \int A_i V_i}$$

where V_i is stream velocity and A_i is the integrated stream area.

EMC (event mean concentration) Pollutant export equations or EMC values are fundamental and effective approaches used in water quality assessment for examining changes in stream chemistry during rainfall events (Lin 2004, Hu and Huang 2014). EMC is the total loading divided by the total discharge volume for a storm event. EMC is defined as;

Equation 2-3

$$\boldsymbol{EMC = \frac{M}{V} = \frac{\int C(t)Q(t)}{\int Q(t)}}$$

where C(t) and Q(t) are the concentration of a solute and runoff measured during a storm event, M is the mass, and V is the discharge volume, respectively. The EMC results in a flow-weighted average and does not simply represent a time average of the solute concentration.

Constituent loading Loading of nutrients to receiving waters is estimated by the product of EMC and surface water discharge. The EMC values are expressed as milligrams per liter (mg L^{-1}) and can be used to calculate the pollutant load. Annual mean loading of pollutants was estimated as the total loading multiplied by the ratio of annual rainfall to total rain fall for the storm event. The annual total load of pollutants per area (km^2) for each sub-catchment was estimated as the annual total loading divided by area of each catchment.

2.3.5 *Principal component analysis (PCA)*

PCA analysis was used as multivariate statistical technique to identify the most influential factors that contribute to NPS pollution effects in the catchment. The EMC data of TP, TN, NO_3^-, BOD, COD, SS, and rainfall related factors (rainfall intensity (RI), amount (RA) and stream discharge) were used for the PCA analysis as explanatory variables. The PCA analysis produces a new variable set including information on the water quality data set. The analysis provides the principal components as number of parameters used, their eigenvalues, and proportions.

2.4 RESULTS

2.4.1 *Precipitation variations*

More than half of the annual precipitation is concentrated in the summer season (May to Sep.) based on 10 years of data (2002–2011) within the Haean catchment. In both study years (2009–2010), over 70 % of annual precipitation amount occurred during each of the summer monsoon seasons (73 % in 2009 and 81 % in 2010, respectively; Fig. 2.2). The precipitation volume and rainfall intensity differed among studied rain event periods (Table 2.1 and Figure 2.2). The maximum intensity was 9.5 mm hr^{-1} during the 4^{th} rain event in 2009 and overall, the intensity was stronger and the volume of rainfall for each event was greater in 2009 relative to 2010 (Table 2.1). In case of the 2^{nd} event in 2009 and the 10^{th} event in 2010, the intensities and the amounts of precipitation between the two events were similar (2.7 mm hr^{-1} with total 118.0 mm for the 2^{nd} event and 2.7 mm hr^{-1} with total 117.0 mm for the 10^{th} event, respectively; Table 2.1).

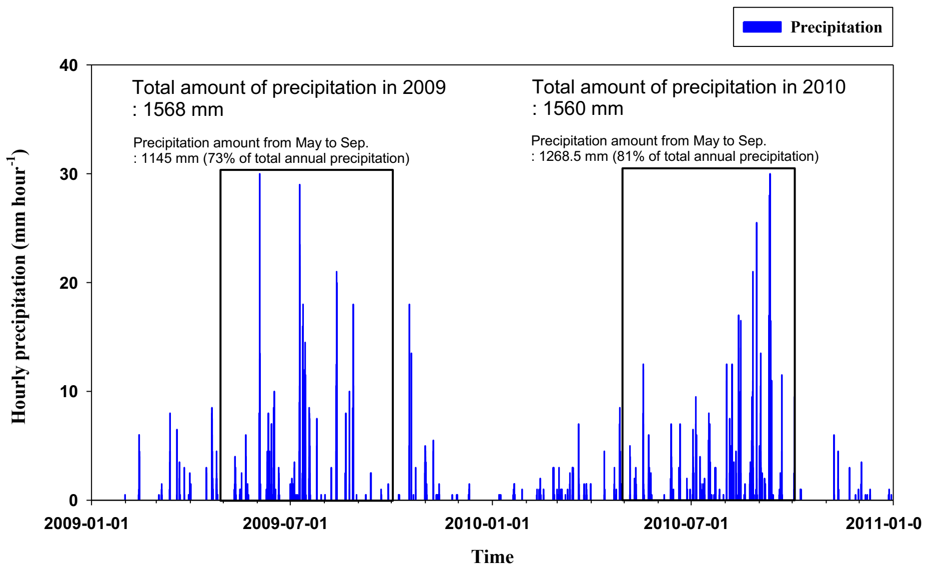


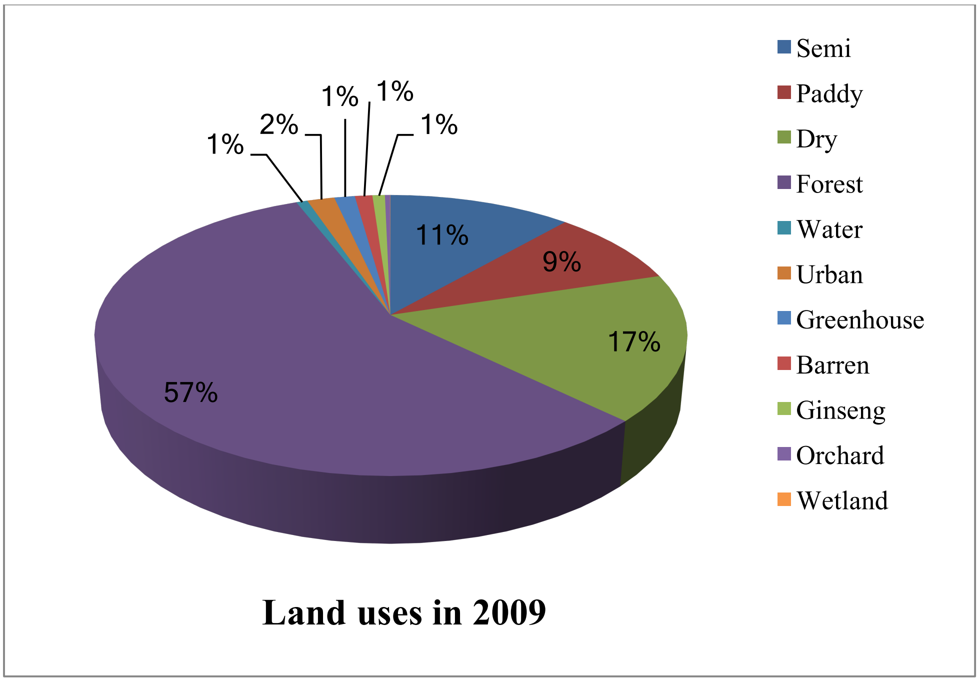
Figure 2.2 Variations of hourly precipitation for 2 years (2009–2010)

2.4.2 *Land use changes*

For the 2 years between 2009 and 2010, significant land use changes were found in dry fields (mostly white radish and potato), rice paddy fields, orchards (mostly apple, grape, and peach), and ginseng crops throughout the catchment (Table 2.2 and Fig 2.3). Dry and rice paddy fields decreased from 16.97 % (10.67 km^2) to 12.65 % (7.95 km^2) and from 8.71 % (5.47 km^2) to 8.24 % (5.18 km^2), respectively. On the other hand, more profitable orchards and ginseng farms increased from 0.32 % (0.20 km^2) to 1.51 % (0.95 km^2) and from 0.79 % (0.49 km^2) to 2.57 % (1.59 km^2) %, respectively in the catchment for the same 2 years (Table 2). Semi grid, which includes fallow land, also increased in the catchment from 11.53 % (7.24 km^2) to 14.43 % (9.07 km^2). Previous studies have shown (Seo et al. 2014) that the spatial footprint of ginseng farming has increased the most from 0.69 % (0.03 km^2) to 9.16 % (0.36 km^2) of the watershed in the region of Site N, among all of the watersheds of the study streams and that orchards also increased from 0.01 % to 0.82 % in the same watershed (Table 2.2 and Fig.2.4).

Table 2.2 Percentages of main land uses of Haean catchment in 2009 and 2010

Site		Semi	Paddy	Dry	Ginseng	Orchard
M	09’	12.7	9.9	19.1	0.9	0.4
	10’	15.8	9.4	14.4	2.7	1.7
W	09’	9.2	4.2	9.5	0.1	0.0
	10’	12.1	4.2	5.5	2.5	1.0
K	09’	9.7	14.1	15.7	0.7	0.0
	10’	13.4	12.2	11.2	1.5	1.8
D	09’	22.2	19.3	29.6	1.0	0.0
	10’	26.6	17.9	24.6	4.8	0.1
N	09’	18.3	7.1	24.9	0.7	0.0
	10’	21.9	6.8	18.9	9.2	0.8
C	09’	9.8	6.7	21.2	0.0	0.2
	10’	11.5	6.7	18.6	3.5	0.4
S	09’	10.7	10.6	16.7	1.2	0.1
	10’	12.7	10.0	13.4	1.9	2.7
Total	09’	11.5	8.7	17.0	0.8	0.3
	10’	14.4	8.2	12.6	2.5	1.5



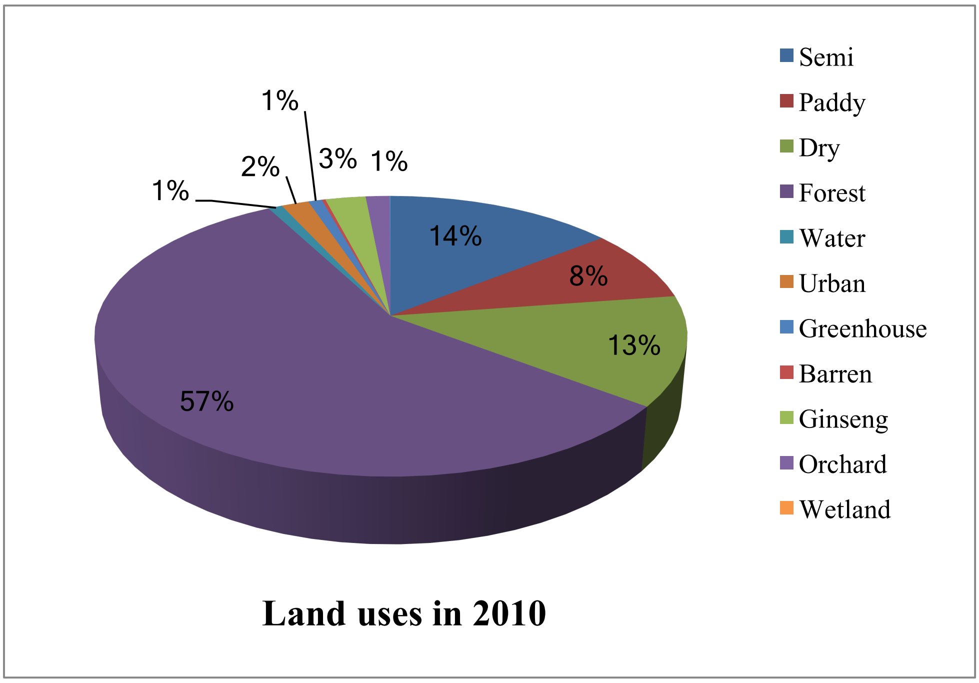
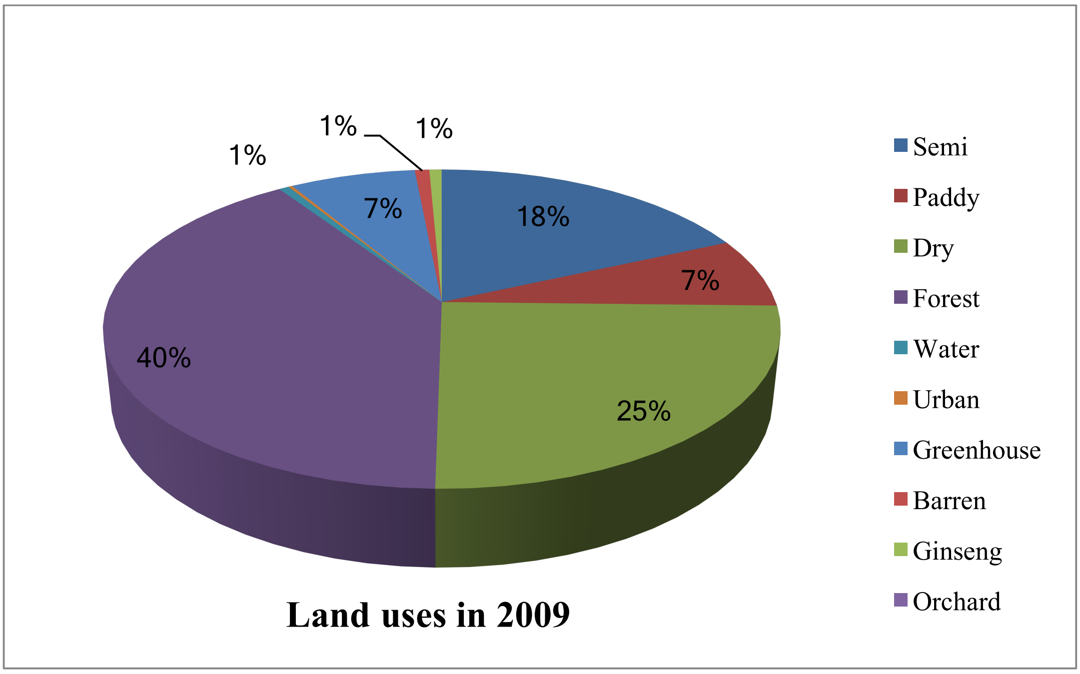


Figure 2.3 Land use changes in Haean catchment for 2 years (2009–2010)



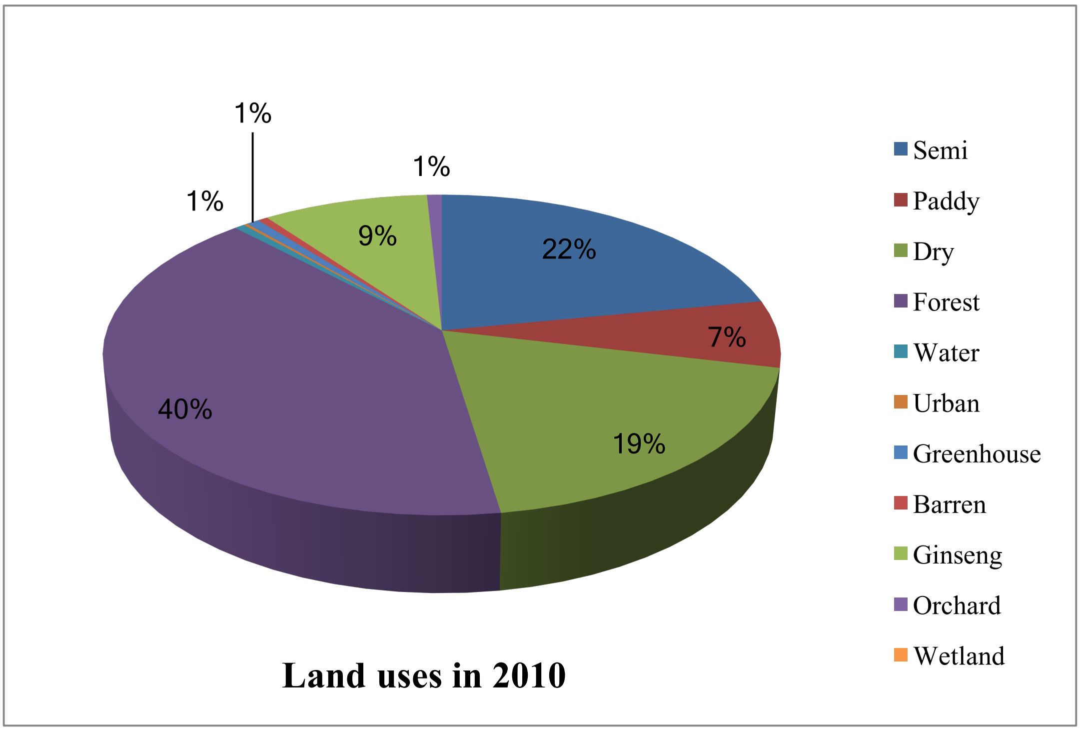


Figure 2.4 Land use changes in a watershed of Site N for 2 years (2009–2010)

2.4.3 *Variations of water quality parameters*

For this study, we sampled each of the stream sites during non-monsoon periods monthly and 11 times during storm events, respectively. During dry (non-monsoon) period, no significant variations of TN, NO_3^-, COD, and BOD were evident in either of the years, whereas TP and

SS varied widely at all of the sampling sites. At Site N, the average values of TN, NO_3^-, and BOD were 5.1 ±0.7 (n=44), 4.5 ±0.6 (n=41) and 1.0 ±0.6 (n=48), respectively while the annual averages of SS and TP were 84.2 ±302.1 (n=48) and 78.1 ±125.2 (n=47) with wider ranges of changes (Fig.2.5).

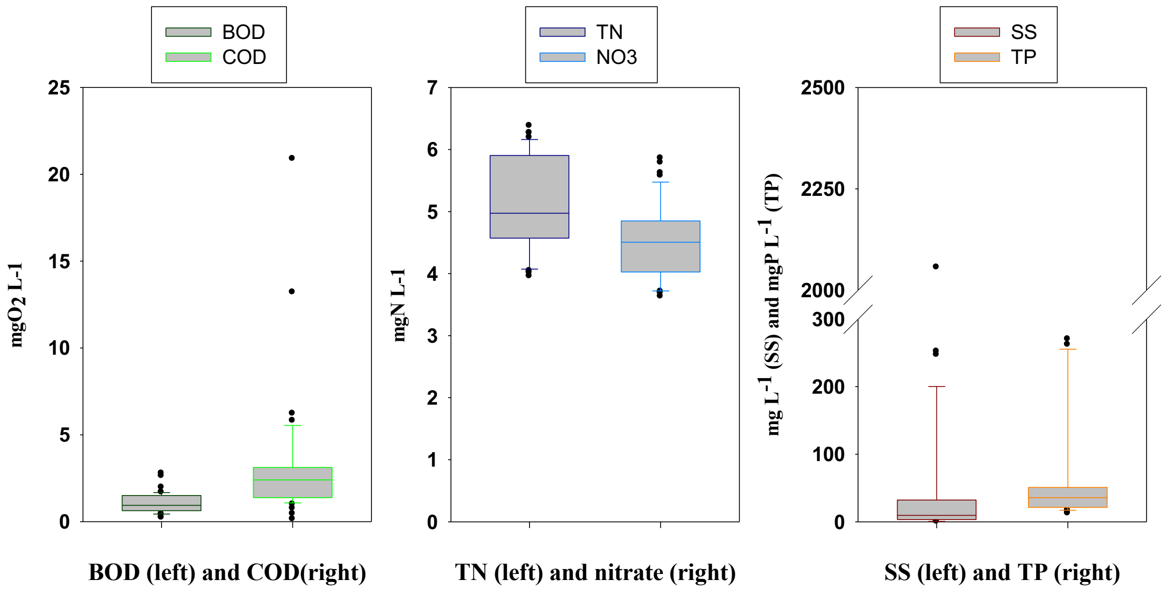


Figure 2.5 Average concentrations of biochemical oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (TN), nitrate (NO_3^-), suspended solid (SS), and total phosphorus (TP) at Site N during dry seasons for 2 years (2009–2010)

Throughout the rainy season, the concentrations of pollutants varied during all of the rainfall events. For the 1st precipitation event in 2009, the average concentrations of SS, TN, and TP at Site M (the outlet of the Haean catchment) were 2,934 (range 288–12,115) mg L^{-1}, 2.8 (range 1.8–3.9) mgN L^{-1}, and 1.2 (range 0.1–3.2) mgP L^{-1}, respectively (Fig. 2.6). The average concentrations of BOD and COD were 1.3 (range 0.1–2.9) $mgO_2\ L^{-1}$ and 15.4 (range 6.2–23.3) $mgO_2\ L^{-1}$, respectively during the same event (Fig. 2.6). Similar variations were found at Site N, in which the average concentrations of SS, TN, and TP were 3,187 (range 400–11,440) mg L^{-1}, 2.9 (range 1.6–4.5) mgN L^{-1}, and 1.4 (range 0.4–3.2) mgP L^{-1} for the same event, respectively (Fig. 2.7). The other studied streams showed similar patterns of concentrations for most of the parameters with the exception of TP, which remained below 2 mgP L^{-1} at the other sites. The average concentrations of SS, TN, and TP at Site D, in which the watershed area is smallest (1.45 km^2), were 2,641 (range 81–13,410) mg L^{-1}, 2.7 (range 1.6–5.7) mgN L^{-1}, and 1.0 (range 0.1–2.8) mgP L^{-1}. In Site C, which has the second smallest watershed area (2.01 km^2) among all of the study sites, the concentrations were 1,794 (35–6,688) mg L^{-1}, 2.1 (1.7–3.3) mgN L^{-1}, and 1.0 (0.1–3.6) mgP L^{-1}, respectively for the 1st event in 2009.

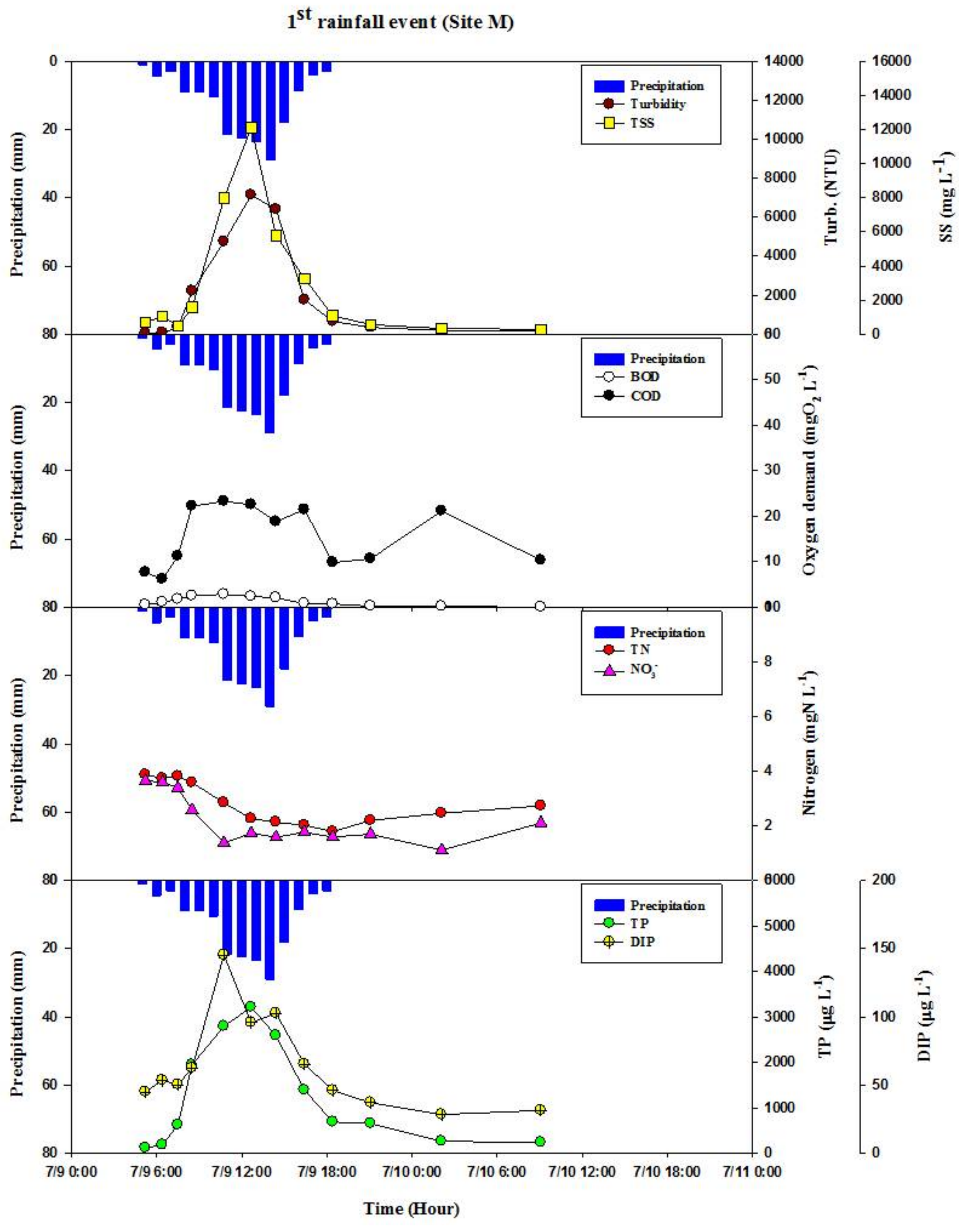


Figure 2.6 Variations of water quality parameters (turbidity, TN, nitrate, TP, DIP, and precipitation) at Site M during the 1st rain event

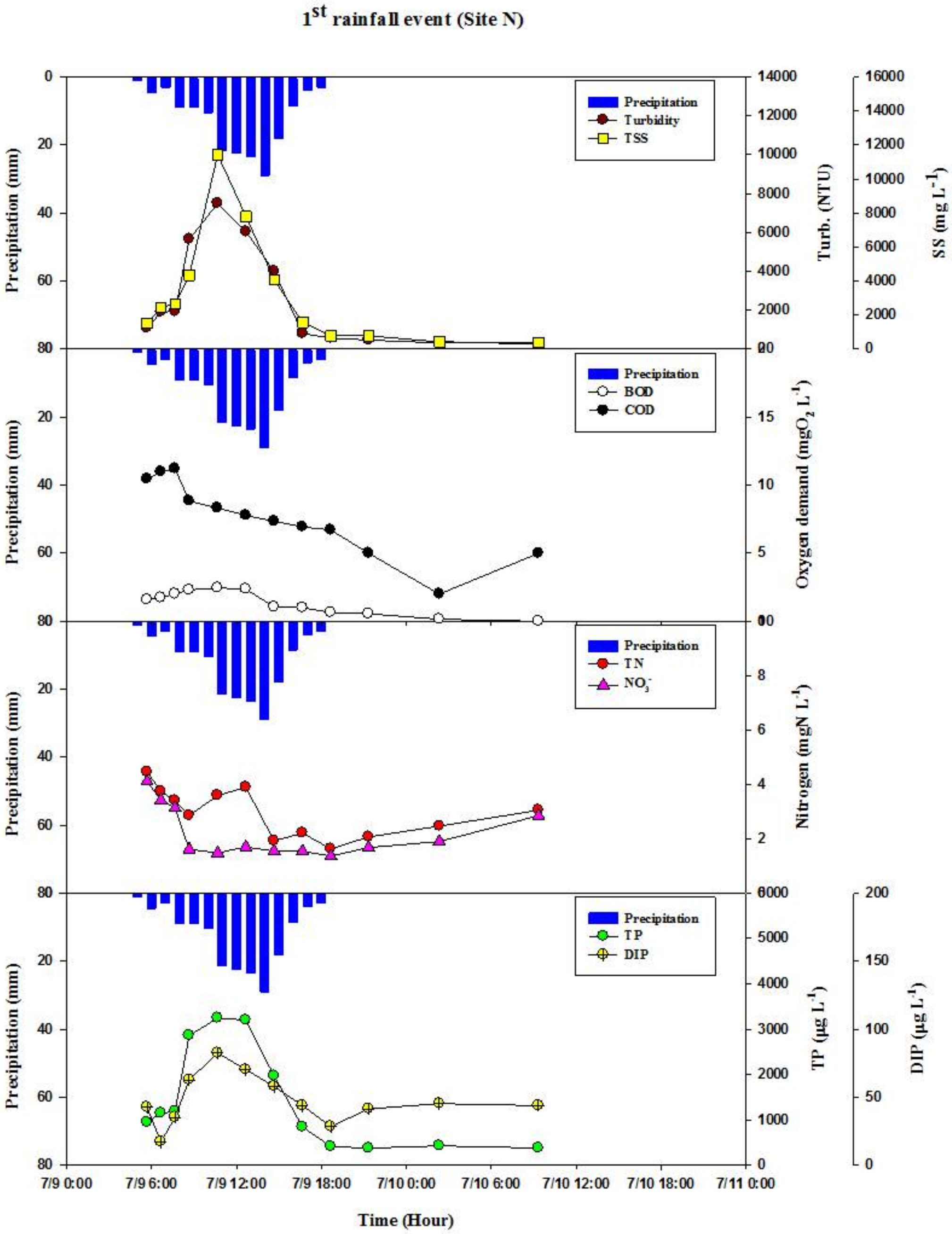


Figure 2.7 Variations of water quality parameters (turbidity, TN, nitrate, TP, DIP, and precipitation) at Site N during the 1st rain event

The maximum concentration of SS at Site K was 18,150 mg L^{-1} for the 1st rain event and was the highest concentration of SS among the measured SS concentrations in all of the study streams in the catchment in 2009. The average TP concentration for the 1st rain event at the Site W was 0.9 mgP L^{-1}, which is the lowest concentration for the event in 2009. For the fourth event in 2009, the average concentrations of SS, TN, and TP peaked in all of the streams, with the exception of Site W. The average concentrations of SS, TN, and TP at the Site W were 2,796 (156–8,155) mg L^{-1}, 2.4 (1.1–3.7) mgN L^{-1}, and 1.3 (0.1–4.6) mgP L^{-1}, respectively. The 5th rainfall event with the most intense precipitation caused the maximum average concentrations of the SS, TN, and TP, as well as BOD and COD at all study sites in 2010. The average concentrations of SS, TN, and TP at Site M were 1,073 (60–3,795) mg L^{-1}, 5.0 (3.3–7.2) mgN L^{-1}, and 1.3 (0.3–5.2) mgP L^{-1}, respectively. BOD and COD were 9.6 (3.0–16.5) mgO_2 L^{-1} and 20.6 (2.2–55.2) mgO_2 L^{-1}, respectively during the 5th event. The patterns of variations for the each parameter showed similar variations during storm events between 2009 and 2010. Especially, TP, SS, and Turbidity increased with increasing discharge and steadily decreased after rainfall cessation for both 2009 and 2010 years. However the variation in patterns of N concentrations (TN and NO_3^-) differed during each event and no consistent patterns were observed for either of the years.

2.4.4 *EMC and pollutant loading*

EMC (event mean concentration) The EMCs of SS, TN, and TP at Site M were 3,804 mg L^{-1}, 3.4 mgN L^{-1}, and 1.6 mgP L^{-1}, respectively for the 4th rain event in 2009 (Table 2.3). The EMC of SS was higher at each of the study sites during the 4th storm event relative to the other rain events in 2009. At Site K, the highest EMC of SS (8,763 mg L^{-1}) was recorded for the 4th rain event in 2009. At site S, which has a greater watershed area than the other sites, the EMC of SS (2,971 mg L^{-1}) was lower than the smaller streams, in which the EMCs of SS were 3,787 mg L^{-1} at Site D and 4,872 mg L^{-1} at Site C, respectively, for the 4th event. The EMCs of TN (2.5 mgN L^{-1}) and TP (1.6 mgP L^{-1}) were lower at Site W than the EMCs of TN and TP at site K (3.5 mgN L^{-1} and 2.5 mgP L^{-1}, respectively) with similar watershed area for the same event. The EMC of BOD was highest at all study sites for the first rainfall event (5th rain event) in

2010. The EMC of BOD at site M was 9.8 $mgO_2\ L^{-1}$ at the same time. Comparing the results of EMCs between all of the stream sites between 2009 and 2010, EMCs of SS and TP remained lower at all sites in 2010 while EMCs of TN and BOD increased over the 2 consecutive years. Of particular importance, an average EMC of SS at all of the streams drastically plunged in 2010, compared to the average EMC of SS in 2009 (Table 2.3).

Table 2.3 Event mean concentrations (EMCs) at Site M during rain events (unit: mg L^{-1})

Event No.	BOD	COD	SS	TN	NO_3^-	TP
1	1.0	16.15	2954	2.24	1.67	1.27
2	2.3	16.77	1837	2.08	1.56	1.37
3	2.0	16.56	1587	1.76	1.53	0.81
4	8.7	24.76	3804	3.43	1.37	1.62
5	9.8	20.92	1281	5.08	2.52	1.45
6	4.0	10.97	304	3.90	2.78	0.49
7	4.6	13.19	427	3.77	2.68	0.46
8	5.1	16.40	661	3.54	2.48	0.71
9	2.1	6.36	738	3.04	1.76	0.95
10	3.2	8.96	332	3.16	2.05	0.46
11	2.8	6.80	313	3.25	1.80	0.48

Areal pollutant loading throughout stream watersheds in the catchment Overall, the total areal loads of SS and TP in 2009 were higher relative to 2010 (Table 2.4). The areal loads of SS and TP at Site M were 1,148,377 kg km^{-2} and 558 kgP km^{-2}, respectively in 2009 and 169,526 kg km^{-2} and 209 kgP km^{-2}, respectively in 2010. The total loads of SS and TP at Site D were the lowest among the study sites with total SS and TP loads of 762,641 kg km^{-2} and 379 kgP km^{-2}, respectively, in 2009 and 138,284 kg km^{-2} and 157 kgP km^{-2}, respectively, in 2010. Site K transported the most SS, N, and P into Site M among all of the streams in the catchment. The loads of SS, TN, and TP were lower at Site W than the amount of loads at Site N, although the area of Site W watershed was bigger than the watershed area of Site N. The calculated annual load per total watershed area, based on the rainfall ratio between the 2 years indicated that loads of all parameters were higher in 2009 than in 2010 (Table 2.4).

Table 2.4 Areal loadings of pollutants (BOD, COD, SS, TN, and TP) at study sites during rain events (unit: kg km^{-2} yr^{-1})

Site		BOD	COD	SS	TN	TP
M	09’	1496	8246	1148377	1056	558
	10’	1250	3529	169526	1072	209
W	09’	1404	7384	901661	643	446
	10’	613	2472	103351	566	106
K	09’	1425	6430	2377372	931	629
	10’	893	3195	153741	968	163
D	09’	1320	4430	762641	654	379
	10’	701	2269	138284	585	157
N	09’	1768	6404	2172759	1397	850
	10’	981	3055	258560	979	185
C	09’	2386	15281	1873577	1170	1100
	10’	1218	3819	233318	1263	238
S	09’	1450	4267	481667	580	320
	10’	500	1435	73204	563	96
Annual loads	09’	28219	131568	24380657	16134	10741
	10’	19616	63021	3601173	19109	3676

2.4.5 *Statistical analysis - principal components analysis (PCA)*

For this study, the first two principal components (PC1 and PC2) showed eigenvalues higher than 1 (2.04 and 1.48, respectively) from the PCA analysis with the data set (Table 2.5). When eigenvalues are higher than 1, the corresponding components are considered as significant. The two components explained more than 70 % of total variance of our data set (Table 2.5). Therefore, PC1 and PC2 were the only datasets used for further interpretation. PC1 was comprised of EMC of SS, COD, and TP as well as rainfall indices (rainfall intensity (RI) and rainfall amount (RA)) while PC2 incorporated contributions from TN, NO_3^-, and BOD (Fig. 2.8). Therefore, PC 1 can be regarded as a factor representing high loading of TP, SS, and rainfall parameters and PC2 can be defined as the component that represents negative nitrogen parameters and BOD loadings. The events in 2009 were all located in the upper right section with values higher than the PC1 axis and the events in 2010 were located in the lower left section with values less than 0. The final 3 events (from 9^{th} to 11^{th} event) all located in the upper left quadrant indicating lower values in the PC1 axis and higher values in the PC 2 axis (Fig. 2.8).

Table 2.5 Results of principal component analysis with water quality parameters (SS, TP, TN, NO_3^-, BOD, COD, rainfall intensity, and rainfall amount)

	PC 1	**PC 2**
Eigenvalue	2.04	1.48
Proportion	0.46	0.24
Cumulative portion	0.46	0.71
	Loadings	
Parameters	PC 1	PC 2
SS	0.41	0.03
TP	0.42	–0.19
TN	–0.03	–0.63
NO_3^-	–0.24	–0.44
BOD	0.26	–0.45
COD	0.36	–0.26

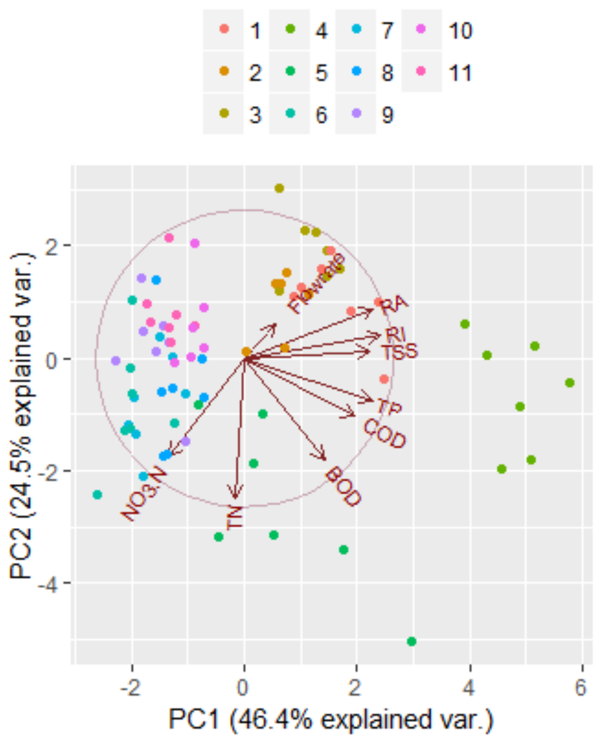


Figure 2.8 Loadings of two principal components from water quality parameters during rain events

2.5 Discussion

2.5.1 *Characteristics of agricultural NPS pollution in the catchment*

The average concentration of SS and TP of each stream under dry conditions was much lower than during rain events (Table 2.6), suggesting that primary transport processes are rainfall/runoff flushing of terrestrial sources (Su et al. 2016, Cho et al. 2016). In general, the average concentrations of BOD in all of the study streams in the Haean catchment during dry conditions was within the management guidelines as suggested by the Korean MoE (Table 2.7). However, the average concentration of TN in all of the study streams was higher than the criteria of TN for lake water quality (Table 2.6 and 2.7).

Table 2.6 Average concentrations (with standard deviations) of BOD, COD, SS, TN, and TP during dry seasons

Site		BOD	COD	SS	TN	TP
M	avg.	1.4	3.1	22.8	4.9	65.3
	s.d.	0.5	1.9	42.8	0.9	67.2
W	Avg.	0.9	2.9	16.5	2.8	29.9
	s.d.	0.5	3.3	71.5	0.8	88.3
K	Avg.	1.1	2.5	23.9	4.4	47.2
	s.d.	0.6	1.8	51.2	0.7	59.2
D	Avg.	1.0	3.0	13.6	4.0	29.1
	s.d.	0.6	2.5	21.6	0.8	35.9
N	Avg.	1.0	3.0	84.2	5.1	78.1
	s.d.	0.6	3.3	302.2	0.7	125.2
C	Avg.	2.0	4.3	19.2	3.3	61.5
	s.d.	1.4	3.1	67.1	0.9	82.4
S	Avg.	1.2	2.6	36.8	4.4	55.0
	s.d.	0.8	1.7	112.5	1.0	113.8

Table 2.7 Classification of water quality levels by Korean standards

Notch	For streams		For lakes	
	BOD	SS	TP	TN
1	≤ 1	≤ 25	≤ 0.01	≤ 0.2
2	≤ 3	≤ 25	≤ 0.03	≤ 0.4
3	≤ 6	≤ 25	≤ 0.05	≤ 0.6
4	≤ 8	≤ 100	≤ 0.10	≤ 1.0
5	≤ 10	No trash	≤ 0.15	≤ 1.5

The fertilizer seemed to cause the high N concentration in the streams as reported in many studies in agricultural areas (Bao et al. 2006, Giri and Qiu 2016). Of particular importance, SS and TP concentrations were much higher (with wider variability) than the Korean water quality standard during dry periods at many locations (Table 2.6 and Table 2.7). It appears that government-driven treatment facility construction to reduce turbidity in surface water, which is observed since 2009, ironically increased soil disturbance over the catchment. In terms of nutrients and sediment concentrations in stream water during precipitation events, the quality throughout stream sites in the Haean catchment were generally lower than water quality results from previous studies, which were conducted in the other main river systems in Korea and also at the same stream as Site M (Kim et al. 2007a, Jung 2012). Three sites, located in the forest area of Gum River watershed in Korea, displayed lower SS, TN, and TP concentrations than the Haean sites during storm events (Kim et al. 2007a). Two streams located in the Lake Soyang watershed (Jawoon and Naerin streams) displayed lower SS and TP concentrations compared to the monitoring locations of this study, although TN was similar (Jung et al. 2009). The concentration of TP at Site N was higher than the TP concentration at other monitoring locations, which seems the result of the government driven construction in the watershed of Site N. The watershed of Site N was identified as the primary subject area for turbid water control therefore it seemed that attached-P onto soil is exported into streams during the construction period. Site D and C extended over a relatively smaller area of the watershed than the remaining watershed areas in the catchment and showed lower average concentrations of SS, TN, and TP than those in the rest of the monitoring sites during rain events. During the 4th event, which produced the highest volume and intensity of rainfall during the study period, all parameters peaked with the highest concentrations at all steams except for Site N, clearly showing the rainfall impact on pollutant exports (Randall et al. 2001, Delpa et al. 2011). However, the rainfall effect seems mitigated by the land use at Site W, of which the watershed is dominated by forest. The forest land use mitigates the amount of exports from the watershed (Beaulac and Reckhow 1982, Poor and McDonnell 2007).

During all storm events over the 2 years of 2009 and 2010, the average EMCs of SS, TN, TP, and BOD were all the lowest at Site W among the monitoring locations, indicating that forest land use exports less nutrients and soil into streams during runoff (Zhuang et al. 2015). There was no clear difference among EMCs of pollutants based on the stream watershed sizes but the EMCs of TP and SS remained lower at Site W than the EMCs at Site K, which had a similar watershed area as Site W. These results again indicate that forested land use can potentially mitigate soil erosion and phosphorus exports (Peterjohn et al. 1984, Wang et al. 2014, Yao et al. 2016). Comparing the average EMCs of pollutants at the outlet site (Site M) between 2009 and 2010, the average EMC of TN increased while the average EMCs of TP and SS decreased. We hypothesize that the decreased intensity of rainfall in 2010, reducing soil erosion processes, is one of the possible reasons for the decreased SS and TP, which are usually exported concurrently from agricultural fields (Kim et al. 2014). Additionally, the government-driven construction of new facilities to diminish turbid water generation in the catchment seemed to decrease soil loss from the catchment. However, the extent of SS export is still higher than the export from other stream sites (Table 2.8), therefore consistent soil management protecting erosion, such as reducing soil inverting and mountainous soil disturbance for new crop land, should be implemented (Baumhardt et al. 2015).

Table 2.8 Event mean concentrations (EMCs) of BOD, COD, SS, TN, and TP of streams in South Korea (literature reviews)

Site	Area (km^2)	Primary land use (%)	BOD	COD	SS	TN	TP	Sources
Imsil stream	-	Forest (over 70 %)	2.7	6.9	75.9	2.7	0.19	Kwak et al. 2008
Seomjin River			2.6	5.1	46.5	2.3	0.13	
3 sites in Seomjin River	60.28	Forest	3.11-5.74	3.4-12.7	2.1-30.0	0.9-2.9	0.02-0.13	Park et al. 2005
		Paddy	8.2-15.5	15.6-33.4		3.2-7.2	0.21-.42	
		Dry field	4.6-11.8	6.7-17.6		2.3-3.7	0.03-0.44	
Sutong	3.38	Forest (99.5)	-	-	-	0.9	0.28	Kim et al. 2007
Sansuchon	2.85	Forest (94.2)	-	-	-	0.9	0.16	
Daegokchon	4.97	Forest (82.3 %) Crop & rice paddy (14.8 %)	-	-	-	2.1	0.62	
Sinheung	27.37	Forest (44.8 %) Rice paddy (35.9 %)	-	-	-	4.9	1.36	
2 sites in Sangju basin	0.47	Paddy and forest (58.6 %)	26.0	-	11.1	-	-	Choi et al. 2011
	0.54	Paddy and forest (55.5 %)	22.6	-	17.6	-	-	
Up & down streams in Kokseong River	4.29	Forest (100 %)	0.6	1.5	1.7	0.03	0.48	Yang 2006
	30.78	Forest (71.9 %) Paddy (12.4 %)	2.9	4.8	63.5	0.18	1.67	
Jawoon stream	-	Forest (85.6 %) Agricultural area (9.6 %)	1.8		207	3.94	0.27	Jung et al. 2009
Soyang River 2004	-	Mostly forest	1.4	8.9	199	1.6	0.20	Kim and Jung 2007
Soyang River 2005			0.8	4.2	303	2.1	0.103	
Soyang River 2006			1.7	10.1	531	2.4	0.244	
Mandae stream 2004	(Same site as the Site M in this study)		1.32	11.8	436	2.8	0.363	Jung 2012
Mandae stream 2006			1.57	8.97	387	2.68	0.338	
Site M 2009	This study		3.5	18.6	2545	2.4	1.27	This study
Site M 2010			4.5	11.9	579	3.7	0.71	

The highest EMCs of BOD in all of the sites during the 5^{th} event can be explained by a "first flush" effect (Kim et al. 2007b, Nguyen et al. 2010). The antecedent non-rainfall period was the longest at that time allowing for accumulation of biodegradable OM sources on the soil (Guggenberger et al. 1998, McLaughlin and Kaplan 2013). Perhaps, the most interesting results were found in the variability of BOD and COD, which display inverse relationships over the studied 2 years. BOD increased in the watershed, which can be interpreted as elevated biodegradable organic matter (i.e. manure) within the catchment (Haynes and Naidu 1998). On the other hand, we hypothesized that non-biodegradable (recalcitrant) organic matter (OM) was decreased in 2010 relative to 2009, based on the decreased EMC of COD. The results suggest that lower OM is exported from the forest area, which usually consists of forest detritus, leaf litter, and woody debris that containing lignin and cellulose substance, due to less intensive rainfall in 2010. In comparison with EMCs investigated in previous studies in Korea and overseas, the EMCs for SS and TP were much higher than the other localities, regardless of rainfall intensity and land use distribution (Table 2.8 and Table 2.9). The EMC of TP at Site M in this study was much higher compared to streams in other regions, which displayed similar summer monsoonal rainfall characteristics such as rainfall intensity and periods in Korea (Park et al. 2005, Kim et al. 2007, Kwak et al. 2008, Choi et al. 2011, Yang 2006, Jung et al. 2009, Kim and Jung 2007, Jung 2012; Table 2.8). Also comparing to results from locations in other countries, the EMCs were higher (Hu and Huang 2014, Sharma et al. 2012, Gentry et al. 2007, Harper 1998, McKergow et al. 2003; Table 2.9). These results imply that the runoff into streams throughout the Haean catchment transported a significant amount of suspended sediment with attached P into the receiving reservoir, Lake Soyang. The effects of turbid water inflow are well studied in the Soyang reservoir. The turbid water inflow deteriorated water transparency and the high amount of P, which is the primary limiting factor in most inland waters of Korea, also prompted eutrophic conditions in the reservoir (Kim and Jung 2007).

Table 2.9 Event mean concentrations (EMCs) of BOD, COD, SS, TN, and TP in streams in oversea countries (literature reviews)

Site		Watershed area (km^2)	Primary land use (%)	BOD	COD	SS	TN	TP	Sources
Siheshui watershed	China	131	Agriculture and forest	3.14	5.75	58.3	3.52	0.26	Hu and Huang 2014
River Yamuna	India	Agricultural runoff samples		21.8	73.5	77.6	15.3		Sharma et al. 2012
Embarras River (1997-2003)		481	Agriculture (91 %)					0.14-0.35	
Lake Fork watershed (1998-2003)	USA	365	Agriculture (91 %)					0.11-0.21	Gentry et al. 2007
Big Ditch watershed (2001-2003)		101	Agriculture (86 %)					0.19-0.38	
Florida	USA	Runoff samples	Agriculture	3.8		55.3	2.32	0.34	Harper 1998
North Willyung catchment	Australia	5.9	Cattle			9.9 Med	2.51 Med	0.48 Med	McKergow et al. 2003

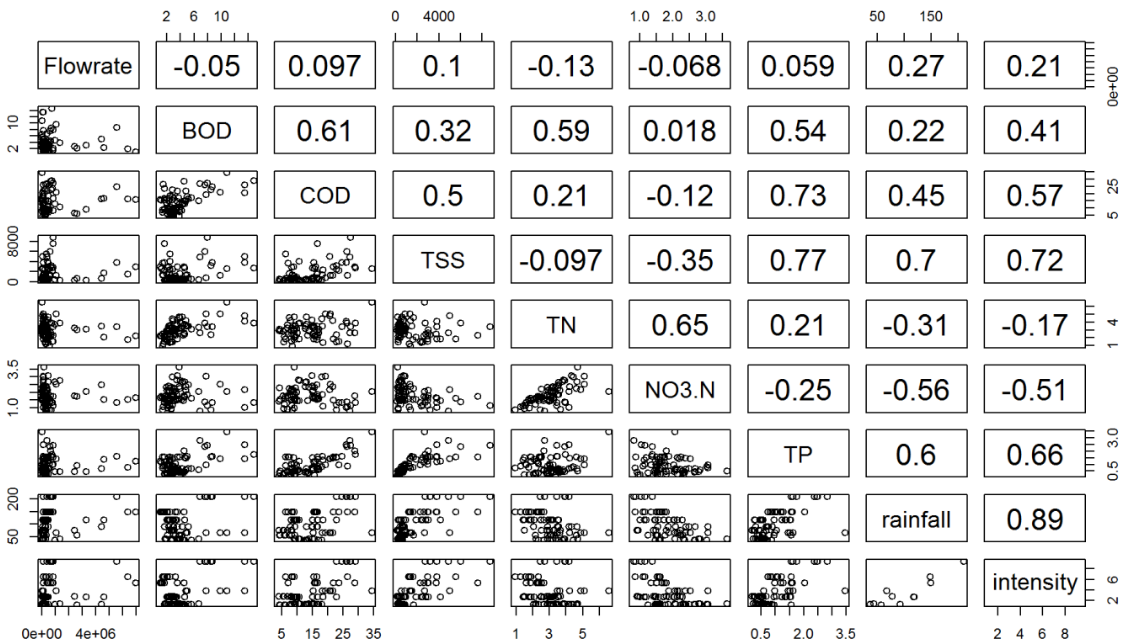


Figure 2.9 Scatter plots and correlation coefficients among water quality parameters at all study sites during rain events for 2 years (2009–2010)

The relationship in EMCs of TN and NO_3^- at all monitoring locations were relatively well correlated with a correlation coefficient of 0.65 (figure 2.9). However the NO_3^- and TN relationship at Site N was not evident with a lower correlation coefficient (0.37; Figure 2.10) and the patterns showed high temporal variations of TN and NO_3^- in some of the investigated rain events (Figure 2.11). It appears that there was a huge loss of organic N from Site N and the high correlation coefficient between TN and BOD, which also can explain biodegradable organic matter amounts such as manure and organic fertilizer, supports this assumption (Figure 2.10). However, the patterns differed temporally, which can perhaps be attributed to the effect of different time scales of organic fertilizer application.

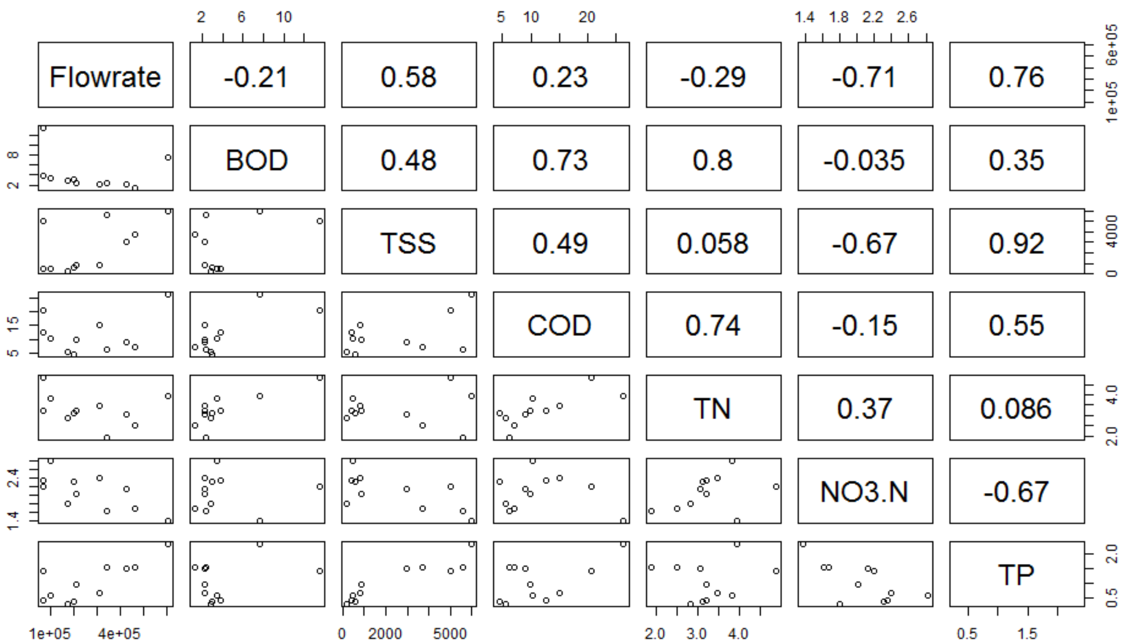


Figure 2.10 Scatter plots and correlation coefficients among water quality parameters at Site N during rain events for 2 years (2009–2010)

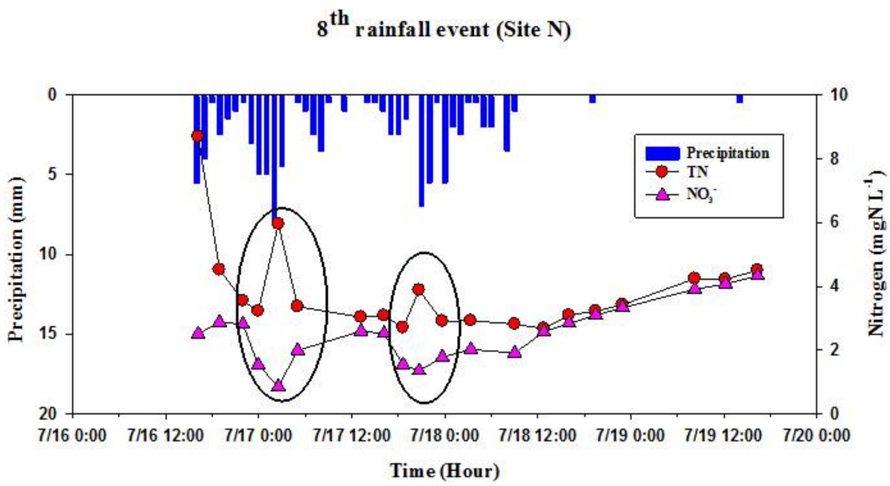


Figure 2.11 Variations of TN and nitrate concentrations at Site N during 8th rain event

2.5.2 *Monsoonal climate effects on the watershed*

Similar results were reported in other monsoonal climate areas (Jain 2002, Wu et al. 2012). Especially, the losses of TP and SS into the streams were influenced most by the rainfall among the water quality parameters (Fraser et al. 1999) and the losses of TP and SS is generated mostly during the summer monsoon season in Korea (Chun et al. 2010, Park et al. 2010). In combination with crop cultivation under high slopes in the area, the effect of monsoonal rainfall is amplified, producing higher annual SS loading relative to other SS loss estimations in Korea and other countries (Montgomery 2007, Arnhold et al. 2014). Comparing the export patterns of EMCs according to differences in the storm event intensities, the exports rates of all of the investigated pollutants were consistent with rainfall intensities that displayed high correlation coefficients (Fig. 2.9). This is commonly observed in studies that focused on agricultural NPS pollution exports, especially in monsoonal climate areas. However, the EMCs of TN and NO_3^- were not strongly correlated with the rain factors (Figure 2.9). It appears that the variations of N parameters during storm events depend on a variety of factors, including fertilizer application period, manure production, and N loss to the air through denitrification processes, compared to the other investigated parameters (Jenkinson 2001).

The results of our PCA analysis showed the relationship of monsoonal rainfall on SS and TP exports to streams. The PC1, which explained 46.4% of variance and is positively influenced by TP, SS, and rainfall factors (Table 2.5), displays a positive relationship with the relatively intense rain events (all events in 2009 and also the 5th event in 2010) (Fig 2.8).

2.5.3 *Land use change effect*

To reflect the increase in ginseng farming in the study area, ginseng was most commonly observed in the Naedong watershed (Site N). The fact that a project to reduce stream turbidity has been focused in the area around Naedong stream area explains the increase in ginseng cultivation in this area. Comparing the EMCs of SS and TP between 2009 and 2010, the EMCs drastically decreased at Site N and also at the main outlet stream. More specifically between the second and the 10th rainfall event, in which the amounts and the intensities of rainfalls were similar (Table 2.1), the EMCs of TP and SS at Site N decreased significantly, which suggests that the land use change influenced sediment and P exports in the site (Table 2.10).

Table 2.10 Comparisons with EMCs of pollutants in between the 2nd and the 10th event

Site	BOD	COD	SS	TN	NO_3^-	TP
M	+40.5	-46.6	-81.9	+51.7	+31.5	-66.4
W	–12.3	–50.7	–89.8	+26.8	–10.8	–80.2
K	–17.1	–24.3	–94.7	+53.2	+46.5	–76.8
N	+6.3	+9.2	–70.3	+5.1	–5.2	–36.6
C	+10.6	–56.5	–79.4	+79.2	+22.3	–63.0
S	–48.9	–37.5	–88.1	+41.6	+32.9	–65.5

We also examined the relationship between areal pollutant exports per rainfall amounts for each year at Site N to identify the land use effects on pollutant export with offsetting the rainfall amount effect between 2 years. BOD was decreased from 755 ±488 (n=4) kg km^{-2} mm^{-1} to 374 ±57 (n=7) kg km^{-2} mm^{-1} while SS decreased dramatically from 434,954 ±260,085 (n=4) km^{-2}

mm^{-1} in 2009 to 32,571 ±31,067 (n=7) km^{-2} mm^{-1} in 2010 (Fig.2.12). The effect of the land use change over the entire watershed also showed a relationship between each rain event (from the 1st to the 11th events) and areal loadings of SS and TP per rainfall amounts at Site M for 2 years (Fig 2.13). SS and TP clearly decreased in 2010, while the other water quality parameters (BOD, COD, TN and NO_3^-) showed no clear differentiation between 2009 and 2010. The results imply that mitigating soil disturbance and erosion through land use changes, efficiently reduces P export (Ouyang et al. 2014). However, the EMCs of NO_3^- and TN increased minimally, showing that land use change did not mitigate those parameters because these pollutants are less related to soil erosion processes relative to TP and SS.

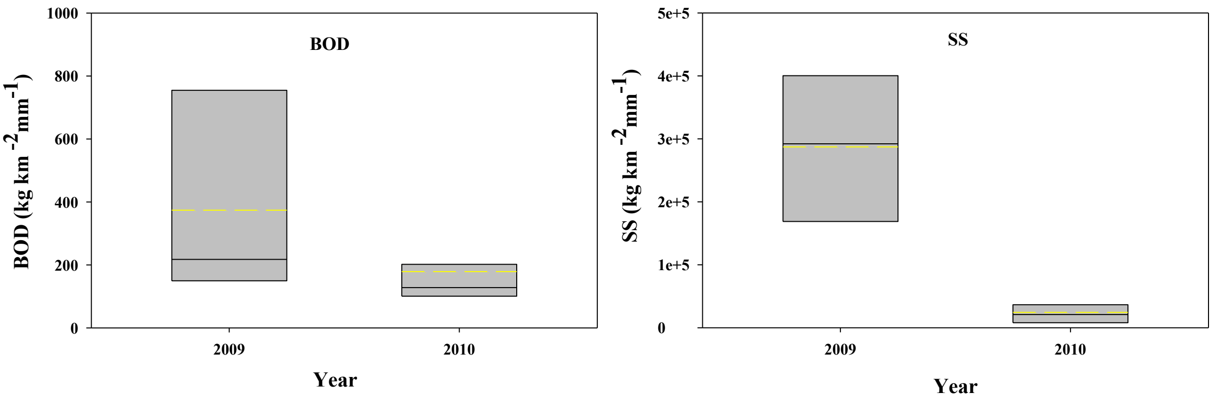


Figure 2.12 Areal loading averages of BOD and SS per rainfall amounts in 2009 and 2010

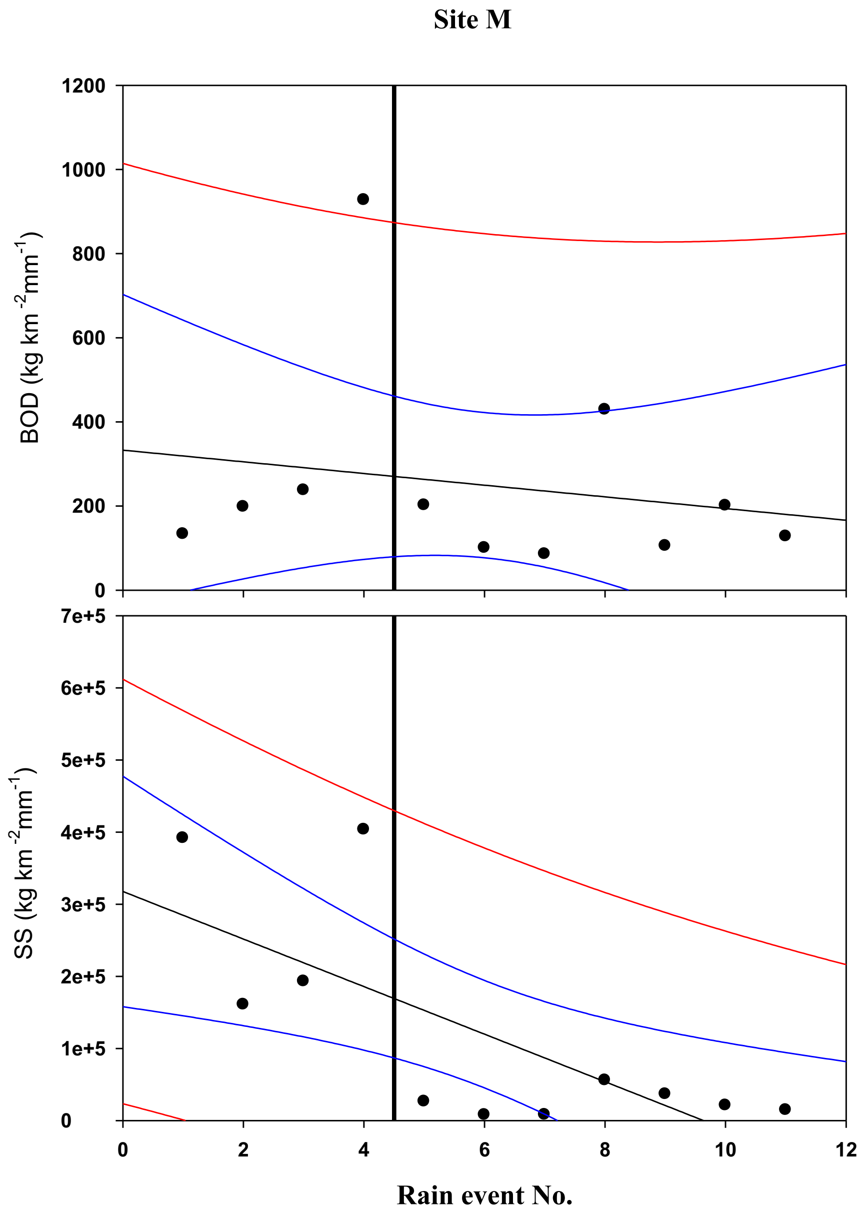


Figure 2.13 Variations of areal loadings of BOD and SS per rainfall amounts during rain events for 2 years

2.6 CONCLUSIONS

The Haean catchment is located in an upstream area of the Lake Soyang watershed that supplies metropolitan drinking water. Following rain events, the Haean catchment discharges turbid water containing elevated nutrient concentrations resulting from non-point sources. The mean concentrations of SS, TN and TP at Site M (the catchment outlet stream) were much higher than observed in other streams in Korea and locations overseas, indicating that the streams in the headwater catchment transport elevated amounts of sediment and nutrient to downstream areas. During the dry season, these headwaters do not appear to impose a substantial impact on water quality; however, monsoonal rainfall events increased the NPS discharge impacts on stream water quality. A government implemented project altered land use in the catchment dramatically since 2000s. As result of this project, many turbid water abatement facilities were constructed and less detrimental land use practices have been recommended, with many of these best management practices (BMP) initiated within the past few years. We compared 2 events (the 2^{nd} and the 10^{th} storm events), in which the rainfall amounts and intensities were similar, to evaluate the land use change impact to pollutant loads in the catchment and the results indicated that the land use change resulted in reduced amounts of sediment and TP transports to the stream sites. However, BOD and TN increased, which can be expected as the parameters are less related to soil erosion than TP and SS. BOD and TN are more related to other management factors, such as the annual spatial changes in manure application over the catchment and the temporal variability of fertilizer applications. In the future, more specific studies on manure and fertilizer applications are suggested to identify the role these processes have on headlands water quality and transport.

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Chapter 3 POTENTIAL EFFECTS OF SEDIMENT PROCESSES ON WATER QUALITY OF AN ARTIFICIAL RESERVOIR IN THE ASIAN MONSOON REGION

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3.1 ABSTRACT

Sediment processes in lakes may affect water chemistry through the internal loading of phosphorus, ammonia, and sulfides released under anoxic conditions. Lake Soyang is a deep warm monomictic reservoir with a dendritic shape, located in the Asian summer monsoon region, South Korea. During summer, the lake is stratified and receives a large nutrient input via storm runoff, which forms a turbid intermediate layer with high concentrations of suspended particles. The lake water, the main inflowing stream (the Soyang River), bottom sediment, and porewater of the lake sediments were studied over a 2-year period (2012–2013). After intensive monsoon rain events, particulate organic carbon (POC), total phosphorus (TP), and turbidity were high in the inflowing water (C: 1.21 mg L^{-1} in June 2013) and in the metalimnion (2.8 mg L^{-1}, 17.6 μg L^{-1}, and 58.5 NTU, respectively in July 2013). Higher concentrations of iron (Fe) and manganese (Mn) were also associated with the turbid intermediate layer (37 and 8 μg L^{-1}, respectively in July 2013). During the summer stratification period, oxygen started to deplete in the hypoliminion (down to 0.5 mg L^{-1} in September 2013), and sediment became anoxic, showing negative oxidation redox potential (ORP) in core samples. Diffusion of dissolved inorganic P and ammonia from sediment to the water column can be substantial, considering the concentration difference between the porewater and hypolimnetic water. Fe and Mn were abundant in the sediment porewater at the dam site, implying inorganic nutrients and minerals are well transported along the 60 km long lake axis by the density current of storm runoff. Sulfate and reduced sulfur were larger in the porewater of the top sediment than in the lower layer of the sediment core (below 10 cm). The results show that substantial amounts of inorganic nutrients and minerals are supplied to the lake by storm runoffs during monsoon and distributed through the lake by a density current, controlling the material cycle and flux at the sediment surface.

Key words: artificial reservoir, Lake Soyang, monsoon, porewater, sediment

3.2 INTRODUCTION

Lake sediments are frequently studied to understand and determine changes of water quality and internal processes occurring within lakes (De Boer 1994, Marce et al. 2006, Mushtaq et al. 2015). Lake sediments are used to derive historic changes of catchment processes such as previous changes in land use and agricultural activities (Morellón et al. 2011, Giguet-Covex et al. 2014) and also impact on water quality through internal loads of nutrients and toxic materials (Perkins and Underwood 2001, Liu et al. 2013). Artificial lakes are increasingly created for agricultural and hydroelectric purposes worldwide, especially in many Asian countries (WCD 2000, Gupta et al. 2012), including South Korea in the monsoon climate area (An and Jones 2000, Bae et al. 2008).

Reservoirs constructed in the middle reach of a river system generally have a higher ratio of watershed area to reservoir surface area than natural lakes of comparable size, resulting in relatively larger inputs of carbon and nutrients (Knoll et al. 2013). Nutrients and eroded soils from agricultural non-point sources are major problems for impounded water quality management in many places (Heathcote et al. 2013, Michalak et al. 2013). Typically non-point source pollution increases when intensive cultivation is combined with monsoon rainfall events, resulting in large amounts of pollutants transported by heavy runoff to receiving water bodies (Hu and Huang 2014).

Phosphorus (P) is typically limiting nutrient in freshwater and causes eutrophication by promoting massive algal growth (Correll 1999, Wetzel 2001, Xu et al. 2015). P is easily adsorbed onto soil particles in the watershed and mobilized through soil erosion and enters lakes or reservoirs via storm runoffs or inflowing streams (Ekholm and Lehtoranta 2012). After entering lakes, P can be released from the sediment to the water column, especially under anoxic conditions, enhancing eutrophication in lakes (Søndergaard et al. 2003, Kangura et al. 2013, Martins et al. 2014, Nikolai and Dzialowski 2014, Kowalczewska-Madura et al. 2015, Tang et al. 2015). Additionally, toxic materials such as ammonia (NH_4^+) and dissolved sulfides (S^{2-}) are released under anoxic conditions, depending on the concentrations of nitrogen (N), sulfur (S), and decomposable organic matter (Besser et al. 1998, Holmer and Storkholm 2001), and can harm the aquatic ecosystem (Wang and Chapman 1999). Thus, the internal load from lake sediment processes is considered an important factor in lake water quality management.

Previous Lake Soyang studies investigated its trophic state, phytoplankton–zooplankton successions, and C dynamics (Kim et al. 1985, 2000, 2001, Lee et al. 2013), but we found no study that focused on the interaction between lake water quality and sediment processes in artificial reservoir systems located in the monsoon climate. In this study, the effects of internal sediment processes on the water quality was studied in a deep, stratified reservoir (Lake Soyang, South Korea) by measuring the vertical and horizontal distribution of nutrient contents in the sediment along the main axis from the dam site to the tributary inlet site. We also assessed the external input of nutrients via monsoon runoff of the main inflowing river. The objectives of this study were to (1) assess the effects of inorganic nutrient input from intensive rainfalls on the lake sediment process, and (2) evaluate the potential effects of sediment processes by determining the distribution of elements in the bottom sediment and porewater of the lake sediments.

3.3 Study site

Lake Soyang was constructed in 1973 on the North Han River system for electrical power generation and flood control and today serves as an important drinking water resource for the Seoul metropolitan area (Jo and Park 2010, Bartsch et al. 2014). It is the largest and deepest reservoir in South Korea, with a maximum depth of 120 m, a main axis length of 60 km (Kim et al. 2001), a mean width of the lake of only 0.5 km, and a typical dendritic shape (Fig. 3.1). The watershed (total area 2,703 km^2; WAMIS 2003) of Lake Soyang is scarcely populated, mostly covered by forest (>85% of the watershed). It also includes small areas of cropland with increasingly intensive agricultural activities (Jung et al. 2012), and agricultural soil erosion has become a major source of suspended solids the lake (Shope et al. 2013). The Soyang River is the main inflowing stream to Lake Soyang, and most of the nutrients and organic matter are exported from the watershed during the summer monsoon season (May–Aug). The mean annual precipitation in the watershed is 1100 mm (WAMIS 2003), more than half of which occurs in summer, a season of episodic heavy rains (Hwang et al. 2003, Park et al. 2010). The trophic state of Lake Soyang has varied over time. Although it was oligotrophic at the beginning of impoundment, it has become eutrophic following the input of nutrients from fish farming (Kim et al. 2001). The water quality and trophic state are currently improving, however (Seo et al. 2014), presumably due to the removal of fish farms.

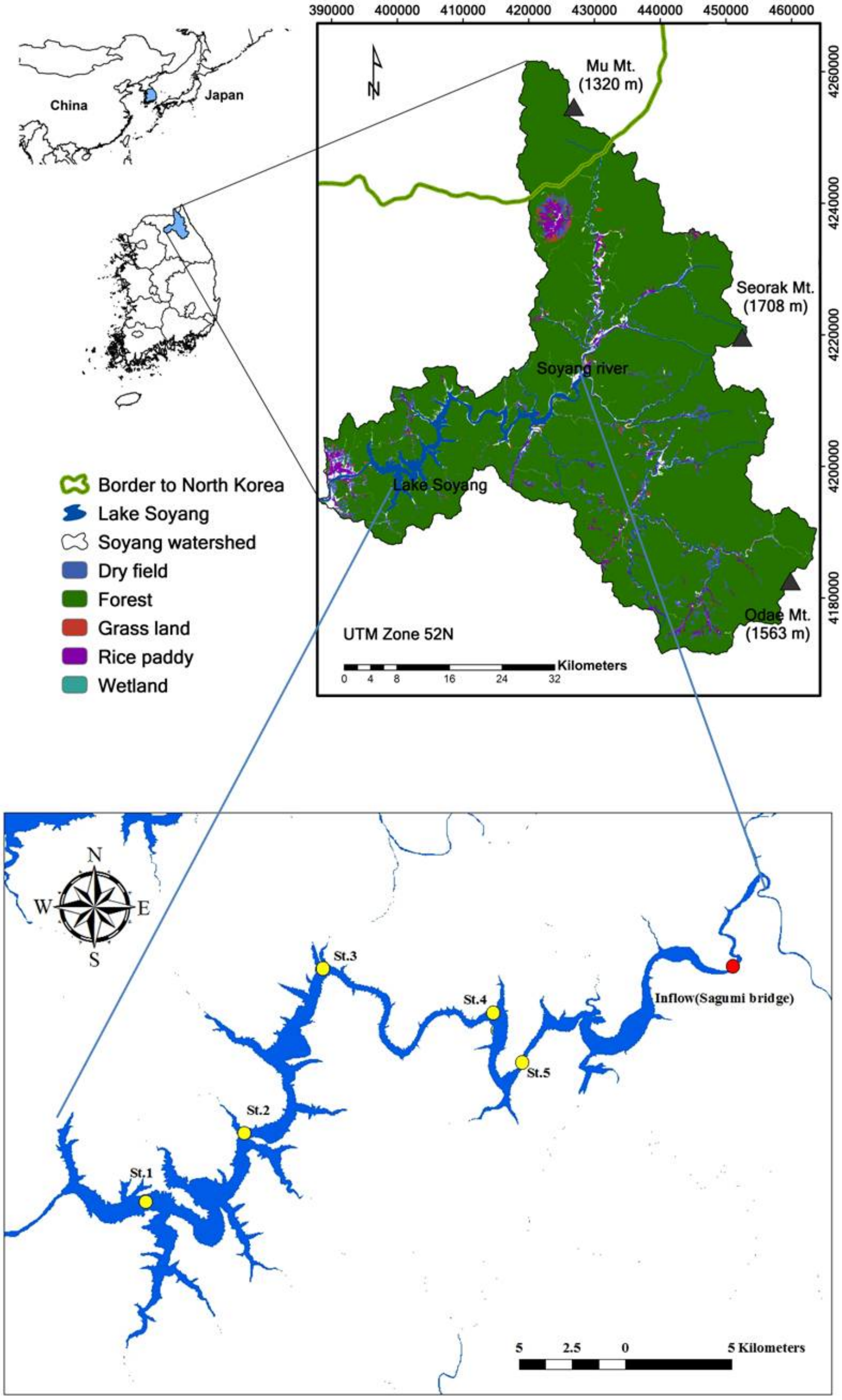

Figure 3.1 Lake Soyang watershed in South Korea (up) and study sites (down)

3.4 METHODS

Five sampling sites (St. 1–5 (yellow circles); Fig. 3.1) were selected along the main axis from the dam site (St. 1) to the upstream inlet site (St. 5) for collecting water and sediment. Lake water samples were collected once a month in 2012 and 2013 at St. 1 at depths of 0, 2, and 5 m, and at 10 m intervals below 10 m to the bottom. Water samples were also collected in the Soyang River on a monthly basis (inflow; Fig. 3.1). Core or grab-type sediment samples were collected with a gravity corer (UWITEC, Mondsee, Austria) and a grab sampler (Wild Co., USA) at each site before and after the summer monsoon period in both 2012 and 2013. Porewater samples were extracted by centrifugation from the sliced sediment core samples. Dissolved oxygen (DO), temperature, and turbidity were measured on site with a portable multi parameter probe (Hydrolab Quanta, Loveland, USA). On 2 additional occasions, vertical profiles of these parameters were measured at a 1 m depth resolution for detailed information. Water samples were filtered with glass fiber filters (Whatmann GF/F) for dissolved total P, organic carbon, nitrate (NO_3^-), sulfate (SO_4^{2-}), and other major and trace elements. Before filtration, total P (TP) of water samples was analyzed by the ascorbic method after persulfate digestion (APHA 2012). Filtered water samples were used to measure dissolved organic carbon (DOC) using a TOC analyzer (Shimadzu TOC 5000, Kyoto, Japan). Particulate organic C (POC) was measured by combusting the dried glass fiber filters using a Yanaco MT-5 CHN analyzer. NO_3^-, SO_4^{2-}, and chloride ion (Cl^-) concentrations in the porewater samples were determined by the ion chromatography method (Metrohm modular IC system 762, Herisau, Switzerland). Iron (Fe) and manganese (Mn) concentrations in water samples were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 3200XL, Perkin Elmer, Waltham, MA, USA).

Sediment core samples were sliced with a customized core cutter device at 1, 2, or 5 cm intervals according to the visual identification of layers. Sliced samples were freeze-dried, and the contents of TP, Fe, total reduced inorganic sulfur (TRIS), and other elements, including aluminum (Al), calcium (Ca), potassium (K), and sulfur (S) were determined. Fe was analyzed after HCL extraction using the phenanthroline assay (Tamura et al. 1974) to differentiate ferric

(Fe^{3+}) and ferrous (Fe^{2+}) iron in the sediment samples. TRIS species (S_2^{2-}, S^{2-}, and S^0) were extracted from sediment samples following chromium reduction (Canfield et al. 1986) and trapped as H_2S in NaOH solution. Reduced S concentration was measured by the methylene blue assay method (Williams 1979) using a UV-VIS-photometer. Further elements in the sediment samples were measured by ICP-OES method after 1 N HCl extraction.

3.5 RESULTS

3.5.1 *Seasonal changes in water quality parameters of lake and inflowing stream*

Vertical stratification The vertical variations of temperature, DO, and turbidity were measured on a monthly basis at the dam site (St. 1) in 2012 and 2013. The temperature varied between 5 and 30 °C, typical for a warm monomictic lake. The profiles of temperature in summer clearly showed a stable stratification in both years. DO was depleted at the hypolimnion, and the metalimnetic oxygen minimum was observed occasionally between 10 and 20 m depth during the stratification period. DO (as O_2) decreased to <4 mg L^{-1} in the bottom layer after the onset of stratification for both years. The DO depletion lasted until the end of September, with DO values <2.5 mg L^{-1} in 2012 and 2013 (Fig. 3.2 and 3.3).

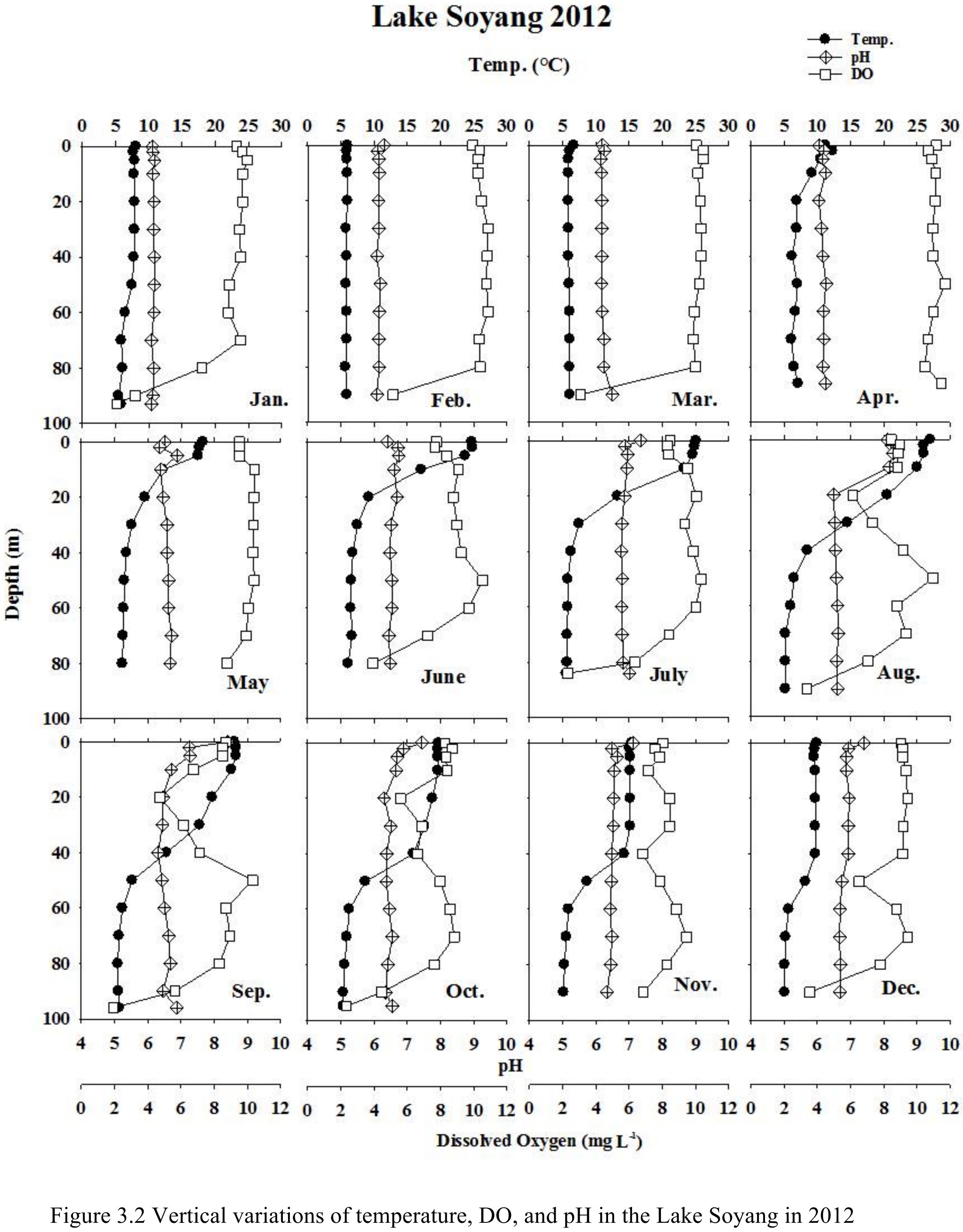

Figure 3.2 Vertical variations of temperature, DO, and pH in the Lake Soyang in 2012

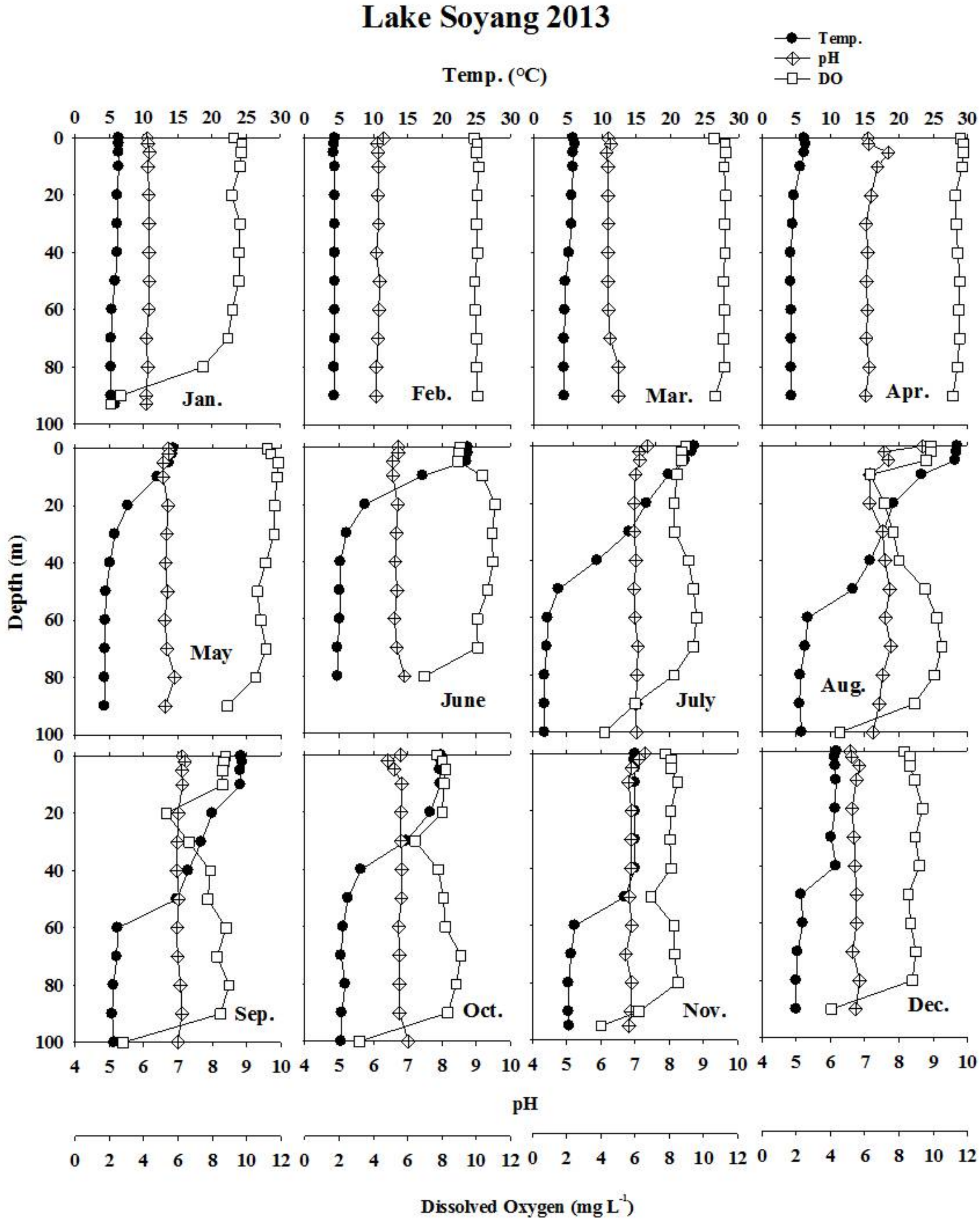

Figure 3.3 Vertical variations of temperature, DO, and pH in the Lake Soyang in 2013

The thermocline disappeared in winter, and the lake water was entirely mixed until the next stratification period. Turbidities were higher in the metalimnion (20–50 m depth) than in the other water layers in both summer monsoon seasons (Fig. 3.4). Based on average turbidity values, however, the turbidity of water in the metalimnion was different between the 2 survey years; the mean turbidity was only 1.1 ± 0.3 NTU in 2012 but was 15.9 ±11.7 NTU in 2013. The maximum turbidity of 58.5 NTU was observed at 30 m depth in July 2013 following intensive rainfalls. Turbidity varied in the same pattern as POC and TP (Fig. 3.4 and 3.5).

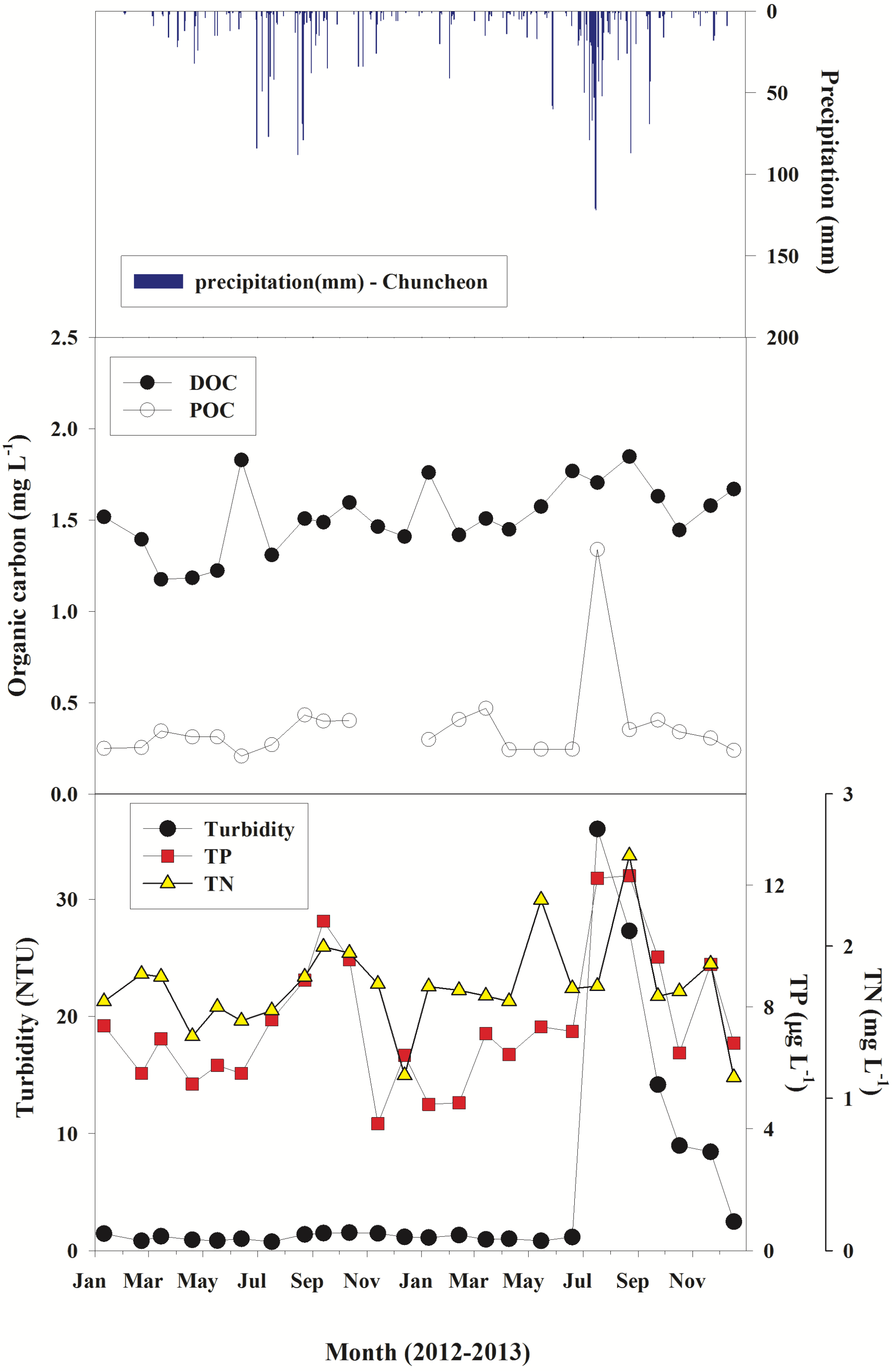

Figure 3.4 Records of daily precipitation in Lake Soyang watershed and seasonal variations of DOC, POC, turbidity, TN, and TP in a metalimnion (20−50m) of the lake for 2 study years (2012−2013)

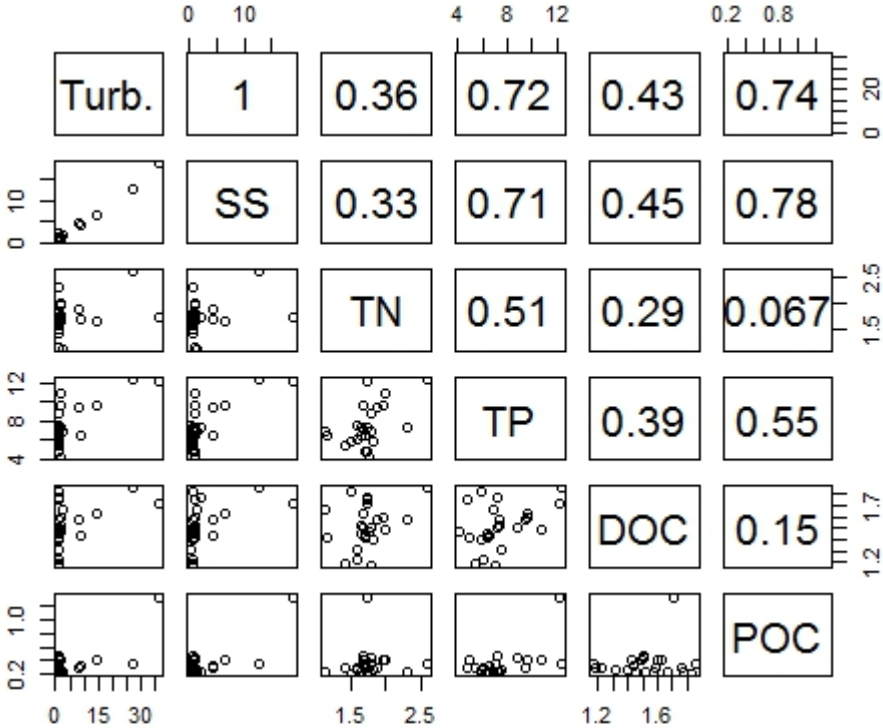

Figure 3.5 Scatter plots with correlation coefficient values among water quality parameters in the metalimnion in 2012−2013

Water chemistry During our study period, the median POC in the inflowing water was 0.5 mg L^{-1}. The maximum concentration of POC in the Soyang River reached 2.1 mg L^{-1} after heavy rainfall in 2012. POC remained <1.0 mg L^{-1} in most other monthly observations (range 0.04–0.96 mg L^{-1}) but was notably higher during the monsoon season (2.1 and 1.2 mg L^{-1} in Jul 2012 and 2013, respectively). Two different forms of organic C were also measured in the lake at St. 1 on a monthly basis during the study period. POC and DOC were uniform in the whole lake water and at all depths except during the summer season, when they reached a metalimnetic maximum, as did turbidity. The POC profile showed the highest value at the hypolimnion (4.0 mg L^{-1}), but it also showed a peak at the metalimnion (2.8 mg L^{-1}) in July after heavy precipitation of >430 mm within 8 days (8–15 Jul 2013; Fig. 3.4; Korean Meteorological Administration website; www.kma.go.kr). DOC, however, showed a smaller seasonal variation varying between 1.1 and 1.9 mg L^{-1}.

TP variation was associated with the variation of turbidity in both years. The annual averages of TP and TN were similar in both years (P: 7.7 ± 2.7 and 7.5 ± 2.5 μg L^{-1}; N: 1.6 ± 0.2 and 1.8 ± 0.5 mg L^{-1} in 2012 and 2013, respectively). TP in the metalimnion was much higher than in the other layers after monsoon rainfalls in July and August 2013 (17.6 μg L^{-1} at 30 m water depth; 19.5 μg L^{-1} at 40 m water depth, respectively; Fig. 3.4).

Fe and Mn of the inflow stream and reservoir water were determined for summer season in 2013. Concentrations of Fe and Mn in the inflowing water were >20 and 2 μg L^{-1}, respectively. Fe and Mn concentrations showed 2 peaks, one in the metalimnion (17 ± 14 and 5 ± 3 μg L^{-1}, respectively) and another in the hypolimnion (197 and 8585 μg L^{-1}, respectively) in July 2013 after heavy rainfall (Fig. 3.6). The concentrations of Fe and Mn were highest in the hypolimnion during the oxygen depletion phase after the onset of stratification (Fig. 3.3 and 3.6).

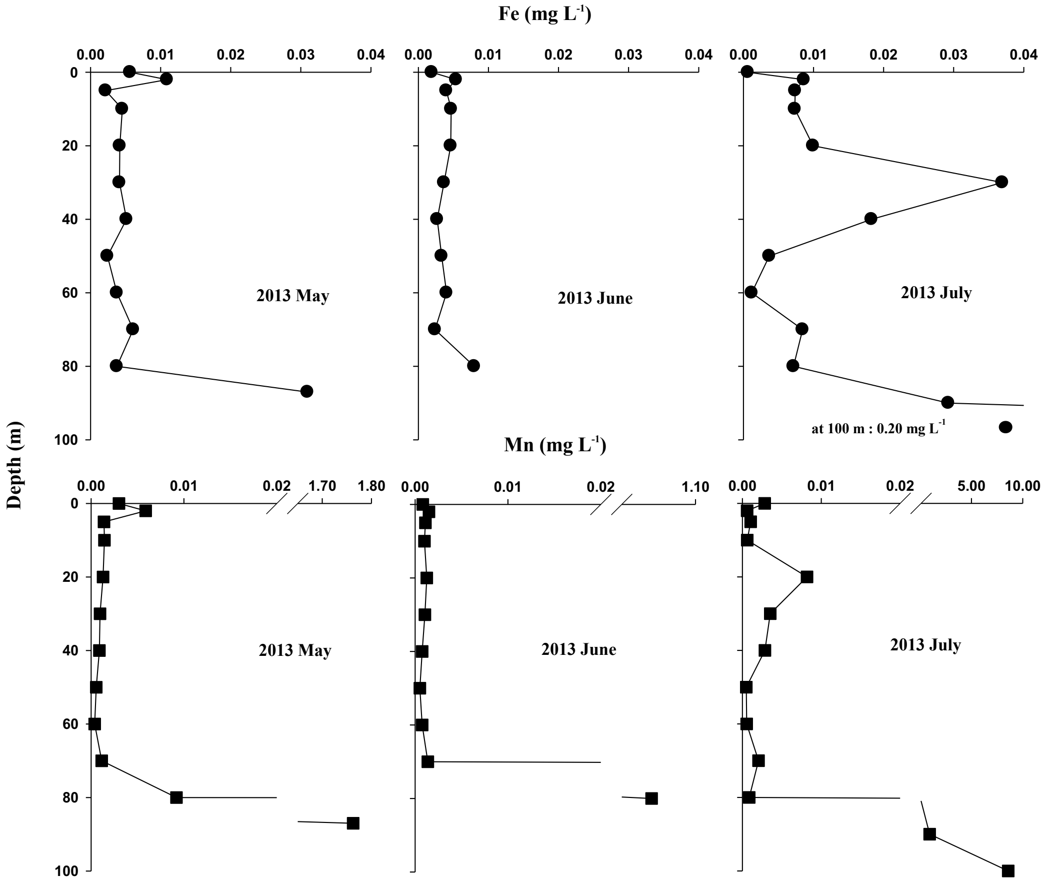

Figure 3.6 Distributions of Fe and Mn in Lake Soyang water during monsoon season in 2013

3.5.2 *Porewater and sediment analysis*

Porewater chemistry Oxidation redox potential (ORP) and pH and were measured with electrodes in core sediment samples at St. 1 in May and St. 5 in June. The pH remained virtually constant over depth, varying between 6.4 and 6.7 at St. 1 and 6.6 and 6.9 at St. 5; sediment pH was similar to the bottom water (6.6 and 6.9, respectively; data not shown). ORP indicated completely anaerobic conditions in the sediment samples. ORP decreased toward the bottom of sediment and was lower than −100 mV below 10 cm depth in both core samples (St. 1 and 5; data not shown). Dissolved inorganic phosphorus (DIP) and NH_4^+ concentrations of the porewater were measured at 2 cm resolution to determine the distribution of mobile forms of P and N. Both P and N showed an almost identical depth profile, with a maximum at 4 cm depth (23.0 and 251.5 μg L^{-1}, respectively) and decreased at the sediment surface (15.9 and 150.6 μg L^{-1}, respectively, at 2 cm depth). P and N increased again, however, deeper in the core (19.5 ± 5.0 and 201.1 ± 71.3 μg L^{-1}, respectively; Fig. 3.7). Concurrently, the P and N concentrations of DIP and NH_4^+ in the lake bottom water were 0.9 and 16 μg L^{-1}, respectively (data not shown), much lower than the uppermost porewater of the sediment. Hence, large concentration gradients exist between the sediment porewater and the overlying bottom water. NO_3-N^- was depleted in all sediment samples from St. 1 to St. 5 (<0.2 mg L^{-1}; Fig. 3.8). Concentrations of SO_4^{2-} showed sharp gradients between 0 and 4 cm depth, with S ranging from 3.3 to 0.7 mg L^{-1} and remaining constantly low in deeper zones. Furthermore, the concentrations of SO_4^{2-} were lower (2.2 ± 1.2 to 1.1 ± 0.6 mg L^{-1}) in the top sediment porewater (below 3 cm) at St. 1 after the monsoon than concentrations before the monsoon period. Chloride concentrations were on average 3.7 ± 0.8 and 3.0 ± 0.3 mg L^{-1} in the samples before and after the monsoon period, respectively. Dissolved concentrations of Fe and Mn were higher below 20 cm depth compared to the concentrations in the other depths in porewater of St. 1 sediment (Fig. 3.9).

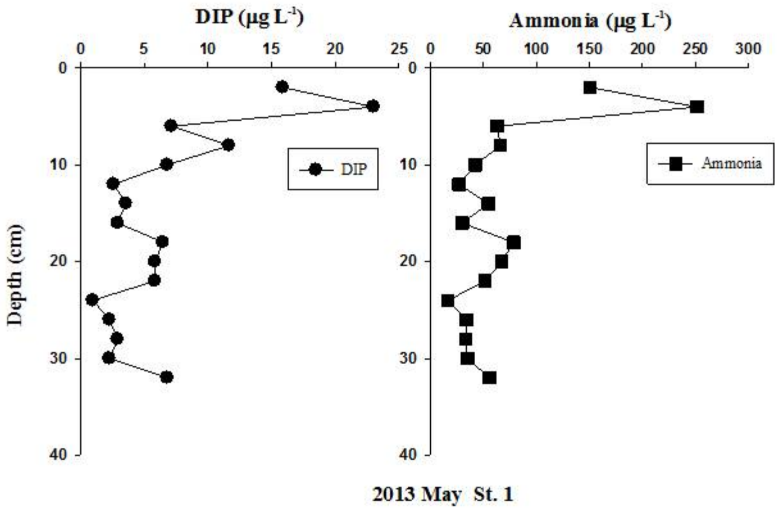

Figure 3.7 Distributions of DIP and ammonia in porewater samples of the core at St. 1 in 2013

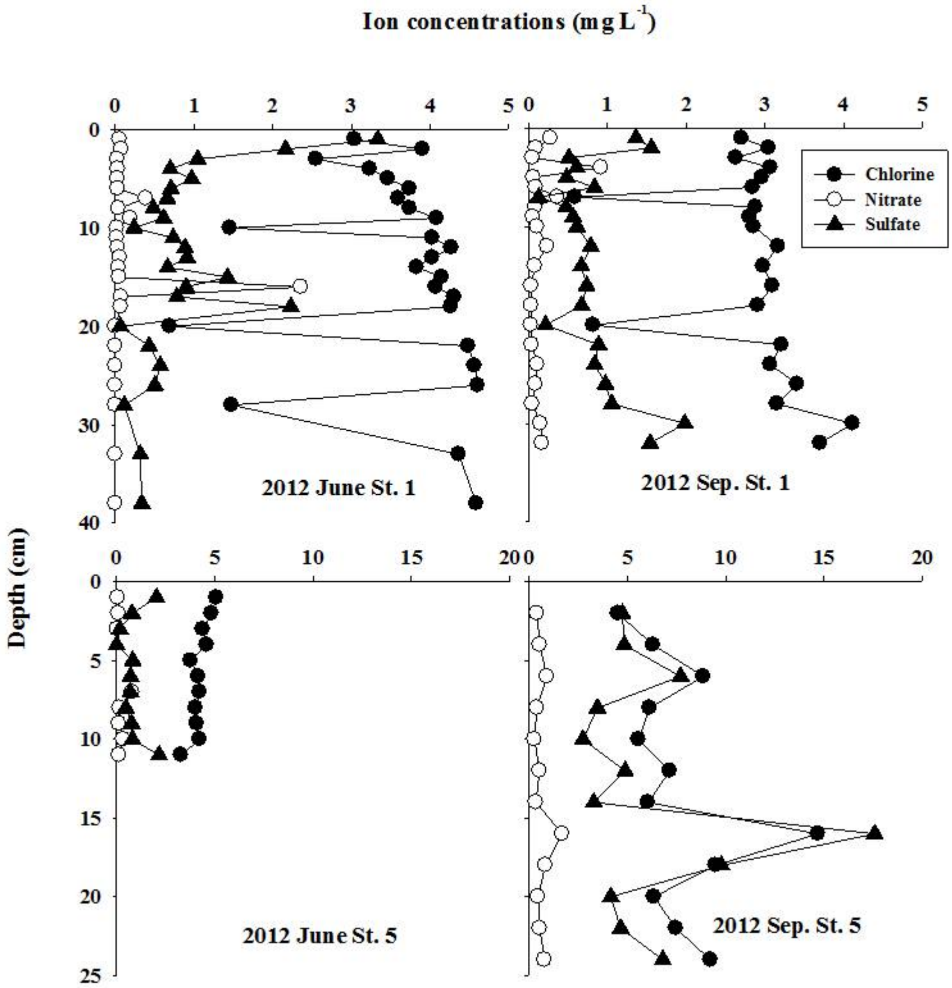

Figure 3.8 Distributions of chloride, nitrate, and sulfate ions in porewater of sediments samples at St. 1 and St. 5 in 2012

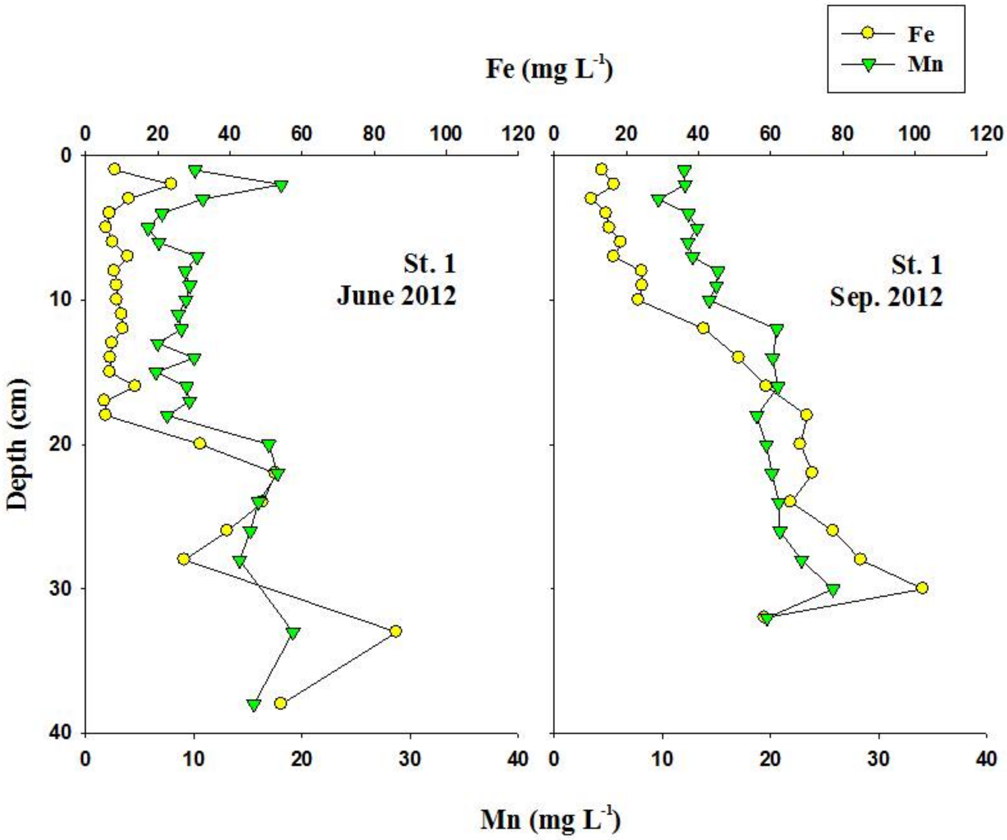

Figure 3.9 Vertical profiles of Fe and Mn in porewater at St. 1 before and after monsoon season in 2012

Sediment chemistry The average TP for all depths in the sediment core at St. 1 was 1.6 ± 0.1 mg g^{-1}. The amount of P decreased from the top to the bottom layers of the sediment. A strong gradient of TRIS existed between the top surface of the sediment and 4 cm depth, with concentrations decreasing sharply from 23.0 to 3.6 mmol g^{-1}. Below 4 cm, TRIS concentrations further decreased and leveled off at an average concentration of 1.0 ± 0.1 mmol g^{-1} below 8 cm. TRIS exceeded 20 mmol g^{-1} in the top sediment samples at St. 1 before and after the monsoon in 2012. TRIS in the deeper layers, especially below 10 cm, of the sediments was <5 mmol g^{-1} (Fig. 3.10). The vertical distributions of TRIS in the sediment from St. 2 to St. 5 were different from St. 1 (Fig. 3.10); the concentrations of TRIS were <5 mmol g^{-1} over the entire depth down to 30 cm.

Solid phase Fe was determined as 2 forms (Fe^{2+} and Fe^{3+}) in sediment cores from St. 1 to St. 5 in 2012 (Fig. 3.11). St. 1 had the highest Fe contents of the 5 sampling sites, and the concentrations continuously decreased along the lake axis from the dam (St. 1) toward the upstream site (St. 5). More than 80% of Fe was in the ferric form at all depths and at all sites. Accordingly, the ratio of Fe2+ to Fe3+ was approximately constant from St. 1 to St. 5, despite substantial concentrations of TRIS and the differences in TRIS observed between the sites.

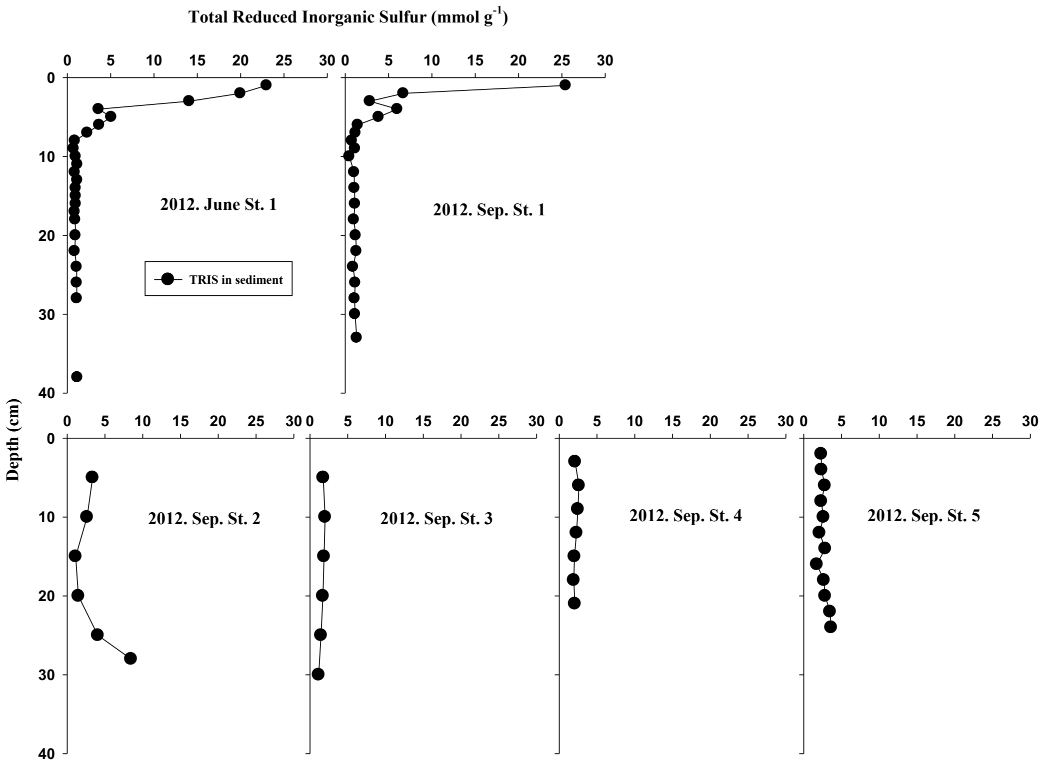

Figure 3.10 Vertical profiles of TRIS in sediment samples from St.1 to St. 5 before and after monsoon season in 2012

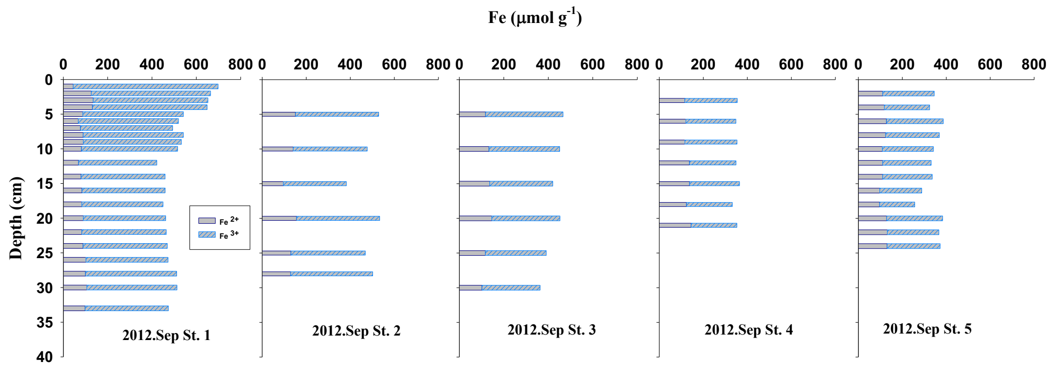

Figure 3.11 Fractions and amounts of Fe^{2+} and Fe^{3+} in sediments samples from St. 1 to St. 5 in 2012

3.6 DISCUSSION

3.6.1 *Material input from the watershed during the summer monsoon season*

The median value of POC in the inflowing stream was much lower than the worldwide median value of POC in rivers (2.0 mg L^{-1}); however, the highest POC values emerged after heavy rainfall in each year, stressing the relevance of POC loading during high flow. The ratio of DOC to POC was <1:1 in the metalimnion of the lake, much lower than data collected from other eutrophic lakes (6:1; Wetzel 2001). This low value indicates that intensive summer rainfalls cause a large amount of particulate organic matter to enter the lake via storm runoffs, which leads to higher POC concentrations in the lake, as reported earlier in Lake Soyang (Kim et al. 2000, 2009) and other reservoirs (Aryal et al. 2014). Moreover, a high amount of coarse woody debris (CWD), which is not included in POC measurements because of its large size (>2 mm), was observed floating on the surface of the lake during filed surveys after monsoon rainfalls. CWD may provide a high contribution to the C load of the lake water and of the sediment over the long term (Wipfli et al. 2007, Seo et al. 2008); therefore, also quantifying CWD input to the lake water body would be useful. Nevertheless, the observed POC concentrations compared well with previous measurements made at St. 1 (highest concentrations 2.4 mg L^{-1} in 1996: Kim et al. 2000; and ~3 mg L^{-1} in 2008: Kim et al. 2009), and the seasonal and vertical variations coincided with the results of previous studies on POC distribution in this particular reservoir (Kim et al. 2000, 2009). We therefore calculated a C sedimentation rate based on the annual average of POC concentration in this study and a previously reported C settling velocity in the same reservoir (POC 0.9 m d^{-1} in 2009; Kim 2009, unpublished data), yielding a POC sedimentation of 453 mg m^{-2} d^{-1}. This result is similar to the C sedimentation rates in the other reservoirs but higher than in natural lakes (Teodoru et al. 2013, Clow et al. 2015).

The ratios of DOC to POC varied over depths and seasons, possibly because of changes in stratification. High input of POC and TP caused by intensive rainfalls is a regular annual occurrence during the monsoon period in Lake Soyang (Kim et al. 1995, 2000). A previous study investigated the annual variation of input TP load into Lake Soyang for 16 years (1991–2006), and the P load was highest (~1200 t yr^{-1}) in 2006 during an intensive rainfall of the summer monsoon season (Kim and Jung 2007). This input is presumably amplified by the disturbances in forested areas and agricultural practices of overusing P fertilizer and frequent soil disturbances (Park et al. 2010). Consequently, a high load of P is deposited into the sediment in reservoir systems (Tang et al. 2015), a common occurrence in lake waters surrounded by intensively managed agricultural regions like Lake Soyang (Carpenter 2005). Interestingly, Fe and Mn concentrations were also high in the metalimnion during the summer monsoon, caused by an inflow of high amounts of Fe and Mn (137 and 25 μg L^{-1}, respectively), as already observed at an adjacent site during the summer monsoon in a previous study (Hong et al. 1989). Previous studies have attributed these high amounts of Fe, Mn, and S to input of particulate matter from the watershed, along with high amounts of P adsorbed to these particles (Stewart and Tiessen 1987, Gleyzes et al. 2002); therefore, The observed high concentrations of Fe and Mn in the hypolimnion seem to have resulted from diffusive fluxes from the sediment under anoxic condition (Graham et al. 2012).

3.6.2 *Stratification and formation of anoxia*

The metalimnetic DO depletion (3.8 mg L^{-1} at 14 m in Sep 2013) observed in this study was presumably driven by the density current induced by flooding from the monsoon rainfall (Kim and Cho 1989, Lee et al. 2013), which supplied a large amount of labile C from the watershed. A hypolimnetic anoxia was formed after the eutrophication period in the 1980s in Lake Soyang (Kim and Cho 1989), and, accordingly, the ORP in sediment cores from St. 1 were negative for the entire depth, comparable to values in anoxic sediments in Japanese lakes (Bibi et al. 2007). Under these conditions, oxidized Fe, Mn, and S phases can be favorable electron acceptors (Gambrell et al. 1983). Sulfate reduction is an important respiratory pathway in anoxic sediments (D'Hondt et al. 2002), which explains the observed high concentrations of TRIS in the upper layers of Lake Soyang sediment cores. We therefore presume that anoxic conditions happen frequently, but significant amounts of unreduced Fe oxides seem to be present that may thus still trap P to some extent.

3.6.3 *Processes in the sediment*

The mean TP in the sediment at St. 1 was higher than in other shallower reservoirs of South Korea (Kim et al. 2003) and in other eutrophic lakes of China (Zhang et al. 2008). The higher concentrations of DIP and NH_4^+ in porewater than in bottom water can result in internal loading by diffusion, as proposed earlier in a hypereutrophic lake and reservoirs (Reddy et al. 1996, Wang and Liang 2015, Yang et al. 2015). A substantial amount of NH_4^+ seems to be released from the sediment into the overlying lake water, evidenced by the highest NH_4^+ concentration just above the sediment. But rapid decrease of NH_4^+ concentration toward upper layer of the hypolimnion implies rapid oxidation of NH_4^+ in oxic conditions. NO_3^- showed the opposite distribution of NH_4^+, decreasing drastically under oxygen depletion (hypolimnetic DO of 1.9 mg L^{-1}) just below the boundary of the oxic and anoxic layers (e.g., Sep 2012; Fig. 3.12).

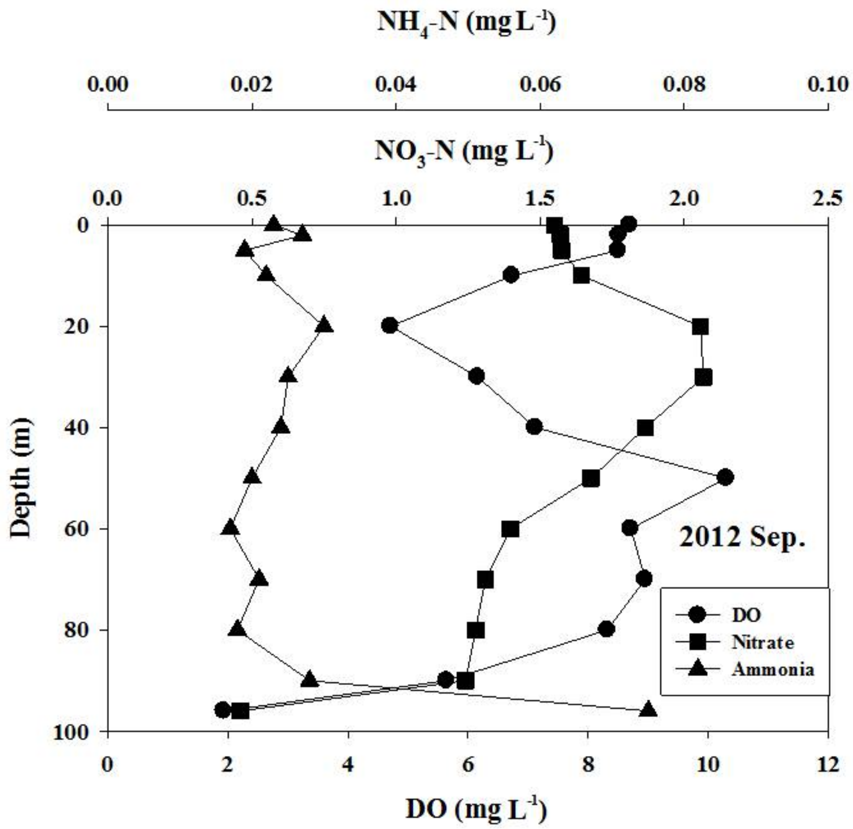

Figure 3.12 Vertical profiles of DO, nitrate, and ammonia in water columns in September 2012

Despite the high concentrations of DIP and NH_4^+ in the bottom water layer during stratification, however, the average concentration of DIP and NH_4^+ remained constantly low after the monsoon season (Sep 2012 to Dec 2013), when the onset of strong oxygen depletion was observed in the hypolimnion. DIP concentration in the epilimnion was 1.8 ± 1.2 μg L^{-1}, and the NH_4^+ concentration was 0.018 ± 0.008 mg L^{-1}, which is significantly lower than in the hypolimnion. We therefore assume that DIP and NH_4^+ do not reach the epilimnion after being released from the bottom sediment. The maximum lake depth of 120 m could be mainly responsible; in other words, DIP can be resettled and NH_4^+ can be oxidized when they enter the oxic layer on the way to the epilimnion. Although not measured in this study, turbulence energy in Lake Soyang is thought to be low because it is located in the midst of a high, mountainous area and well sheltered from wind action at the lake surface. Additionally, the removal of nutrients by the intermediate density current discharged from the dam through the outlet at the middle depth of the dam could also explain why nutrients from the sediment cannot easily reach the epilimnion (Fig. 3.2 and 3.3). The major transport mechanism of nutrients from the sediment to the epilimnion is thought to be the winter turnover circulation in January and February.

The high abundance of Fe and Mn was considered to be delivered by input from the lake watershed (especially agricultural areas) after monsoon rainfall, based on the high concentrations of Fe and Mn in the metalimnion of the lake after precipitation (Fig. 3.5). Previous studies noted that Fe, Mn, and Al can originate from soil particles, which also carry high amounts of P (SanClements et al. 2009). A horizontal concentration gradient of Fe was observed from the inlet to the outlet, which implies that finer particles can be transported far to the dam area, and an especially high amount of Fe and P is included in this fine particle fraction compared to coarse particles more associated with Mg and K (Delfino et al. 1969, Zan et al. 2011). High amounts of Fe in the sediment commonly act as P traps through strong adsorption (Wang et al. 2005, Doncheva 2010).

The Fe^{2+} to Fe^{3+} ratio was interestingly similar over the whole sediment depth, but the underlying reasons could not be elucidated in this study. We hypothesized, however, that the presence of a sulfate reduction reaction of sulfide with Fe oxide surfaces may lead to a passivation, impeding further reduction. Sulfate in the porewater sharply decreased in the top sediment, and TRIS concentrations were higher in the same depth. This finding supports the occurrence of SO_4^{2-} reduction in the sediment, leading to high amounts of reduced S trapping available cations as insoluble sulfides (Wersin et al. 1991, Burton et al. 2006, Yu et al. 2015). In the case of Lake Soyang, formation of Fe sulfides is likely due to a constant and high supply of Fe by inflow from the watershed (Hong et al. 1989). Additionally, a previous study revealed that TRIS in lake sediments mostly consisted of FeS and FeS_2 (Canfield et al. 1986). To form

Fe sulfides, ferric Fe becomes reduced by sulfide (Wan et al. 2014). After formation of sulfides their interaction with Fe and other metals controls and modifies mobilization of phosphate (PO_4^{3-}), NH_4^+, and hydrogen sulfide. Internal loads from sediments seem to be driven by not only anoxic conditions, but also by sedimentations of Fe, Mn, S, and C (Gächter and Müller 2003).

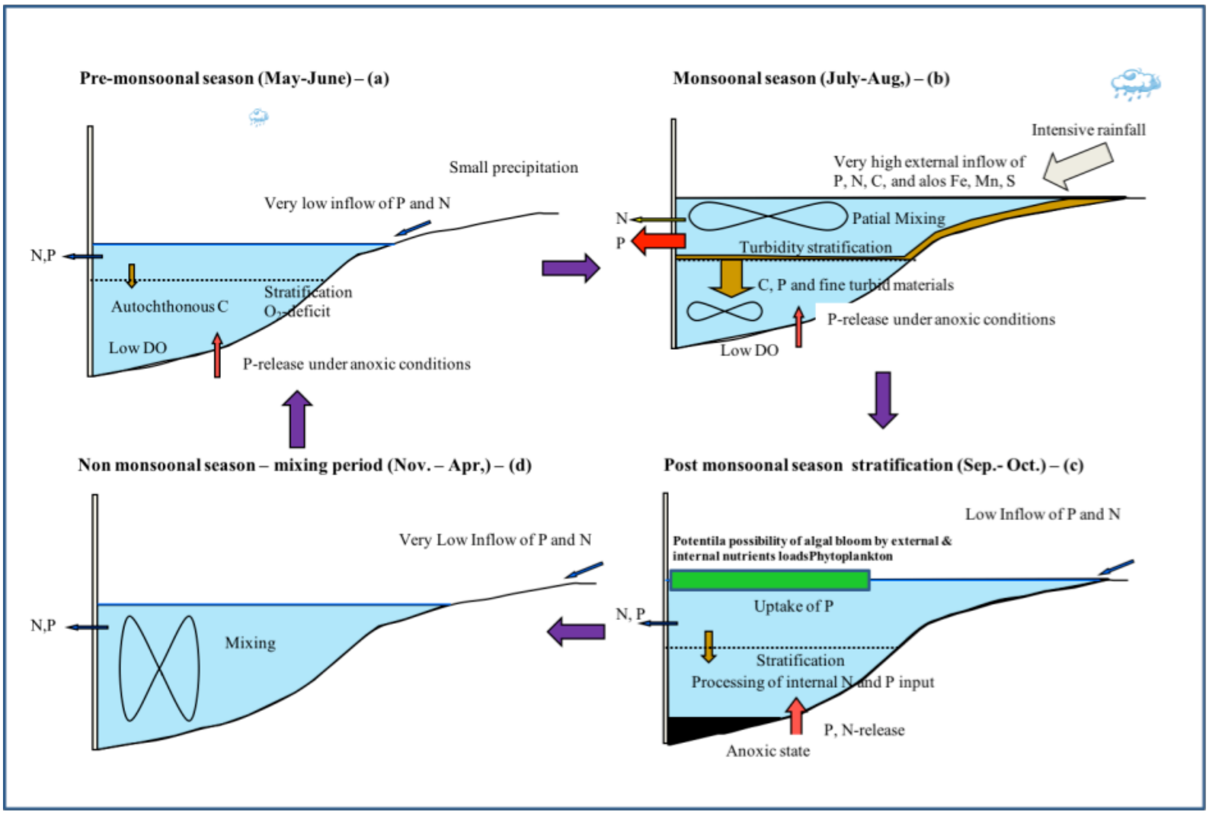

Figure 3.13 Seasonal changes of processes in the Soyang Reservoir under summer monsoon climate

Based on our findings, we established a conceptual model of the hypothesized seasonal variation of biogeochemical and hydrological processes in the Soyang reservoir located in the monsoon area (Fig. 3.13). In the pre-monsoon season (Fig. 3.13a), the reservoir begins to stratify and receives only low amounts of C, N, and P from the watershed because of low precipitation and few agricultural activities in the watershed. DO is thus still available for decomposition in the hypolimnion. During the monsoon season (Fig. 3.13b), a significant amount of suspended materials carrying substantial amounts of labile C, N, P, and other biogeochemically important elements (Fe, Mn) are added to the water body by intensive rain events and concomitant mobilization in the watershed. A turbidity layer establishes at a depth of 30–50 m. After the monsoon season (Fig. 3.13c), decomposition of the large pulse of allochthonous organic matter, especially in its particulate form, starts and leads to strong oxygen depletion. Under these conditions, PO_4^{3-} is released upon dissolution of solid phase electron acceptors (Fe (III), Mn (IV)) to which PO_4^{3-} is bound in the sediment. Finally, during the winter season, the reservoir water is mixed entirely, and ferrous Fe and Mn reoxidize, reestablishing conditions for sequestration of PO_4^{3-} at the sediment–water interface (Fig. 3.13d). The situation may differ under conditions of high discharge when a much larger fraction of the suspended material becomes dissipated in the entire water body, releasing a pulse of biogeochemically reactive substances into the entire water body. Nevertheless, we assume that our conceptual model represents many big artificial reservoirs located in the summer monsoon region (An and Park 2002, Wang et al. 2012).

Overall, heavy rainfalls caused acute increases of C, P, Fe, and Mn in the lake via turbid density currents during monsoon seasons. This increased availability of easily decomposable organic matter controlled the internal loads of PO_4^{3-}, NH_4^+, and reduced S released from the sediment because electron acceptors are consumed under anoxic conditions in the sediment. Our study has implications for reservoir management in monsoon climate regions. Sediment processes and internal loads must be constantly checked while monitoring inflowing water quality for effective reservoir management because the input of the nutrients with eroded soil from the agricultural watershed is consistently high from overuse of fertilizer and frequent soil disturbance.

3.7 ACKNOWLEDGEMENTS

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Chapter 4 REFLECTED CHANGES OF WATERSHED ACTIVITIES IN SEDIMENT COMPOSTION OF RESERVOIR SYSTEM UNDER MONSOON CLIMATE

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4.1 Abstract

Reservoirs are located in watersheds as experiencing a variety of activity changes, such as land use changes, soil disturbance for agricultural purposes, and deforestation, within the watersheds. In order to reconstruct the effects of changes in land use for reservoir water quality under monsoon climate, the chemical composition of sediments (carbon (C), nitrogen (N), phosphorus (P), iron (Fe), manganese (Mn), sulfur (S), and isotopes of C and N) and water quality parameters (suspended solid (SS), chlorophyll *a* (Chl *a*), and Secchi disk (SD) depth) were studied. Sediment cores were taken along a transect from the inlet to the dam of Soyang Reservoir and water samples were collected in the deepest part of the reservoir. Additionally,

water quality data from previous studies were used to track historical water quality changes of the reservoir water. The changes of a trophic state and of an activity in the watershed were well preserved in bottom sediment cores in the Soyang Reservoir. Until the late 1990s, C and N deposition was mainly autochthonous along with eutrophication driven by fish farming. The terrestrial input has clearly increased after fish-farm business was terminated as indicated by an increase in soil-borne elements (Fe, Mn, S, and P) as well as terrestrial C. Such increase coincides with an increase in loads of nutrients and SS following changes in land use in parts of the upper catchment (agricultural land expansion and application of external soils for improving crop land quality). Recently, the increased agricultural activity in the Soyang Reservoir watershed has the greatest effect on the water quality of the Soyang Reservoir under monsoon climate and the effect was well preserved in the bottom sediment of the reservoir.

4.2 INTRODUCTION

Artificial reservoirs have been constructed for multiple reasons (agriculture, hydroelectric power generations) worldwide, and also in many Asian countries (WCD 2000, An and Jones 2000, Gupta et al. 2012). Reservoirs commonly receive higher amounts of sediment and nutrients from their watershed since the reservoirs interact with a much larger watershed area than natural lakes (Thornton 1990, Kennedy 2001). Reservoirs were often constructed in rivers and the run-on-the-river reservoirs contact a much larger area of terrestrial watershed compared to natural lakes because of the long, narrow, and dendrictic shape (Chapman 1996). Additionally, many reservoirs lack of well fostered wetland area, which filters runoffs from watersheds, due to frequent fluctuations in water levels (Wetzel 2001). Therefore, water quality in reservoirs is more sensitive to watershed activity such as land use change. Rainfall increased the potential effect of watershed activity to reservoir by flushing process. In monsoon climate countries, the monsoonal rainfall can be a main factor for the exports of pollutants to the downstream water body (Kim et al. 2000, Park et al. 2010). Bottom sediment in reservoirs contains important information when assessing aquatic environments and record chronological information regarding changes of environmental factors, anthropogenic activities, and trophic states in watersheds (Szarlowicz and Kubica 2014). The Bottom sediments in reservoirs mostly provide a higher temporal resolution compared to sediments of natural lakes due to higher sedimentation rates (Wetzel 2001). Based on many existing studies, the ^{210}Pb dating technique is currently considered as a reliable indicator to estimate sediments ages in lacustrine systems (Arnaud et al. 2006, Tošić et al. 2012). However, reservoirs are spatiotemporally more dynamic compared to similar sized natural lakes (cf. irregular outflow, high water level fluctuations and relatively short residence times depending on the reservoir management) (Filstrup et al. 2009, Tang et al. 2014). The ^{210}Pb dating technique is thus commonly applied to natural lakes but much less to artificial reservoirs and here additional analyses to support sediment age estimations may be necessary to obtain precise paleolimnological reconstructions. Carbon (C) stable isotopes have thereby been recognized as a powerful tool to trace organic matter (OM) sources in many environments because the $\delta^{13}C$ ratio varies distinctively for various C sources, phytoplankton, C3, C4 plants, and soils (Deines 1980, Kendall et al. 2001, Ogrinc et al. 2005). Nitrogen (N) stable isotopes can further serve as indicator to reflect processes in the watershed, such as land use change, (Filstrup et al. 2010). Moreover, the C/N ratio can help to distinguish sources of OM, i.e. from terrestrial soils or lacustrine sediments, also in combination with C and N stable isotopes (Usui et al. 2006, Tue et al. 2011, Zhao et al. 2015).

In this study, we have therefore studied the bottom sediments of a reservoir located in the monsoon climate zone of South Korea and receiving water from a catchment that is partially heavily used for agricultural purposes. We hypothesized sediment incorporates the chronological information of land use changes and trophic states variations.

4.3 Materials and methods

4.3.1 *Study site*

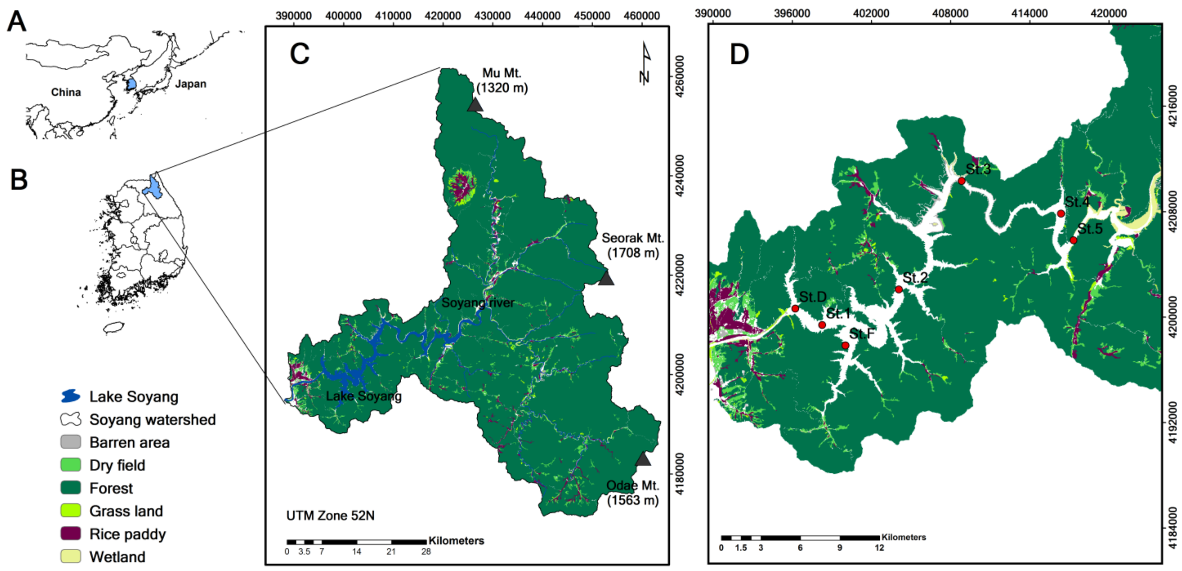

Figure 4.1 Study sites. (A: South Korea (Blue colored) in North East Asia B: Soyang watershed (Blue colored) in Korea Peninsula, C: Land uses in Soyang watershed, and D: Sampling points in Soyang reservoir)

Soyang Reservoir is the largest and the deepest artificial reservoir in South Korea with a maximum depth of 120 m and a capacity of water of 2.9 billion cubic meters (Water Management Information System website; www.wamis.go.kr). The mean residence time is about 275 days (Kim et al. 2001). The reservoir was constructed for multiple purposes, such as water supply in the dry season, flood control, and power generation, in 1973 on the North Han River system located in central region of the Korean peninsula (Fig. 4.1). The main inflowing river, Soyang River, contributes 90 % of the water supply (Kim et al. 2000). The reservoir is warm-monomictic, and has a vertical mixing period in the winter season. However, the area of an inflow inlet is frozen due to its shallower depth (less than 20 m) compared to its depth in front of dam. The reservoir has a typical dendritic shape with a mean width of 750 m and a length of main stem of about 60 km, which limits horizontal water mixing by wind, (Kim et al.

2000). The area of the watershed is 2,703 km^2 (www.wamis.go.kr) and most of the watershed is covered by forest (about 90 %). The watershed also includes small areas of cropland (about 5 %) where agricultural activities have increased and intensified recently (Fig. 4.1, Park et al. 2010, Jung et al. 2012, Kim et al. 2014). The watershed of Soyang Reservoir is scarcely populated and soil erosion by the agricultural expansion is a major source of SS to the reservoir water (Shope et al. 2013) causing a turbid density current in the middle layer of the reservoir (Kim and Kim 2006). The mean annual precipitation in the watershed is 1,100 mm (www.wamis.go.kr) and more than half of it falls during the summer monsoon season (June to Aug.), including frequent and intensive rain events (Hwang et al. 2003, Park et al. 2010, Kettering et al. 2012). In certain years (cf. in 1999 and 2006), typhoons or strong winds accompanying intensive rainfalls induced large amounts of woody debris and SS from the watershed into the reservoir (Kim et al. 2000, Jung 2012). The trophic state of Soyang Reservoir varied over time. The reservoir had been in an oligotrophic state at the beginning of impoundment but it has turned to a meso-/eutrophic state following the input of nutrients from fish farming and from agricultural areas after monsoon rainfalls (Cho et al. 1991, Kim et al. 2001). However, the water quality and trophic state are currently improving (Seo et al. 2014), presumably due to the cessation of fish farming. The reservoir plays an important role as a supply of drinking water for the Seoul metropolitan area (Jo et al. 2010, Bartsch et al. 2014).

4.3.2 *Methods*

Procedures for field works A site adjacent to the dam, which is the deepest part of the reservoir (St. D; Fig. 4.1) was chosen for water samples to determine SS, Chl. *a*, and SD. Water samples were collected by a horizontal Van Dorn water sampler (KC, Silkeborg, Denmark) from the several depths (0, 2, 5, 10, and 10 m intervals to the bottom). Collected samples were stored below 4℃ before Chl. *a* and SS analyses. SD depth was measured monthly in two consecutive years from a boat using a standard Secchi disk (diameter 30 cm). Sediment samples were collected using a gravity corer (UWITEC, Mondsee, Austria) along distance transect from the dam site to the area the main inflow. Initially five sampling sites (St. 1 to 5; Fig. 4.1) were selected for the sediment samples in 2012 and 2013 and additional sediment samples were collected from a former fish farm area (St. F) in 2013 (Fig. 4.1). Sediment traps, constructed of stainless material, were deployed 5 times from July to October in 2013 at St. D near the dam (Fig. 4.1) and were installed at 3 depths (20, 50, and 80 m depth) at the site. Sedimentation rates of C and N in the water columns of the reservoir were calculated based on the trap experiment data.

Procedures for pre-treatment and analyses Water samples were filtrated through GF/C filters and the filters were subsequently stored frozen until analysis of Chl. *a* by the Lorenzen method (APHA 2012). SS amounts in water samples were calculated by measuring the differences in weight of GF/F filters before filtration and dried filter paper (1hr, 105℃) after filtration of water samples (APHA 2012). Sediment core samples were segmented using a customized core cutter device at 1, 2, or 5 cm intervals according to visual identification of layers. Grain size distributions of the sediments were analyzed using a Mastersizer 2000 (Malvern, UK) after sonication. Grain size distributions are displayed as D 10 (size of 10^{th} % diameter), D 50 (size of 50^{th} % diameter) and D 90 (size of 90^{th} % diameter) values representing the cumulative percentile value of the particles in the sediment sample that are finer than the corresponding D grain size. C, N, $\delta^{13}C$ and, $\delta^{15}N$ were analyzed in sediment samples after freeze-drying. Relative C and N isotope abundances were measured with an elemental analyzer in dual-element analysis mode (Carlo Erba 1108, Milano, Italy) coupled to an isotope ratio mass spectrometer (delta S Finnigan MAT, Bremen, Germany) thorough a ConFlo III opensplit interface (Finnigan MAT). Relative isotope abundances are denoted using the common δ notation, calculated as follows:

Equation 4-1

$$\delta^{13}\mathrm{C} \text{ or } \delta^{15}\mathrm{N} = \left(\frac{\mathbf{R}_{\mathrm{sample}}}{\mathbf{R}_{\mathrm{standard}}} - 1\right) \times 1000\ ‰$$

in which $\boldsymbol{R}_{\mathrm{sample}}$ and $\boldsymbol{R}_{\mathrm{standard}}$ are the ratios of the heavy isotope to the light isotope of the samples and the respective standards. Standard gases (N and CO_2, respectively) were calibrated against international standards (N in air and Pee Dee Belemnite (PDB), respectively) by use of the reference substances N1 and N2 for the nitrogen isotopes and Australian National University (ANU) sucrose and NBS 19 for the C isotopes. The further elemental composition (P, S, Fe, Mn, Ca, Cd, Cu, and Pb) were detected by energy-dispersive X-ray fluorescence (XRF) spectrometry (ZSX Primus II, Rigaku, Japan), mixing 0.5 g of milled sediment powder with 50 mg of XRF pelleting agent (Licowax 21 C, APC Solutions SA). This mixture was pressed to a 13 mm pellet for subsequent analysis. One sediment core (obtained at St. 1 in Sep. 2012) was used for sediment dating using ^{210}Pb. We applied the constant rate of supply (CRS) model to the measured ^{210}Pb activity, which assumes a constant unsupported ^{210}Pb flux to the sediment allowing for temporal variation of the deposition rate. The sediment accumulation rate was then calculated (Appleby and Oldfield, 1978) as follows:

Equation 4-2

$$\mathrm{t} = \lambda^{-1} \times \ln\left(\frac{\mathrm{A}_{\infty}}{\mathrm{A}_{\mathrm{x}}}\right)$$

where t is the time in years, λ is the ^{210}Pb decay rate constant (0.031 yr^{-1}), and A_∞ is the integrated value for ^{210}Pb activity from bottom to surface, A_x is the integrated activity from bottom to depth x.

4.4 RESULTS AND DISCUSSION

4.4.1 *Sediment age*

The ^{210}Pb activity in the core taken at St.1 decreased from the top sediment until a depth of 12 cm (Fig. 4.2) below which the activity reached a constant value with some fluctuations with depth (40.3 ±13.3 Bq kg^{-1}, n=10). Estimation of the sediment age using Equation 4.2 predicts that the dam construction in 1973 is located at a depth of 8 cm (dotted-line; Fig. 4.2) and the calculated average sedimentation rate was 0.2 cm yr^{-1} with a range of 0.15 to 0.22 cm yr^{-1} in different depths.

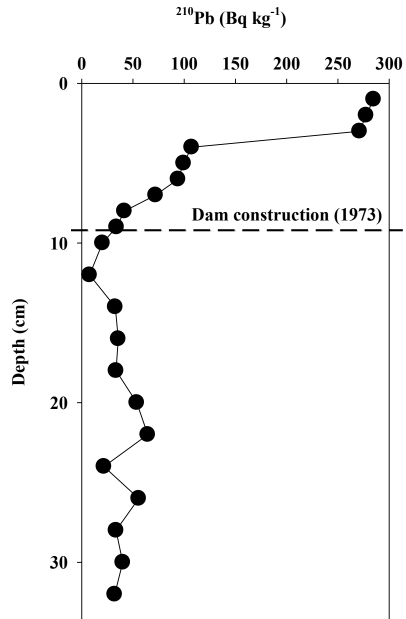

Figure 4.2 Profile of ^{210}Pb activity in a core at St. 1 (dotted-line indicates the temporal point of dam construction in 1973 calculated by the constant rate of supply (CRS) model)

The estimated sedimentation rate was much lower than observed in other reservoirs (e. g. 6 cm yr^{-1} in the Danube Iron Gate Dam; Vukovic et al. 2014, 4 cm yr^{-1} in the Partoon Reservoir; Arnason and Fletcher 2003, between 2 to 7 cm yr^{-1} in the Conowingo reservoir; McLean et al. 1991) and seems to be similar to natural lakes (e. g. ranging from 0.01 to 0.32 cm yr^{-1} in Lake Superior; Evans et al. 1981). It also contrasts a previous estimate of 1.0 cm yr^{-1} for the downstream part of Lake Soyang (Cheong and Jung 2006), which was calculated based on the discrimination of sediment features such as water content, lithologic structure, and organic matter contents. Similar discrepancies between ^{210}Pb dating technique observations and sediment stratigraphy were made in other reservoirs and were attributed to sediment disturbance by frequent water fluctuations and the relatively younger ages compared to natural lakes (Shotbolt et al. 2005, Filstrup et al. 2010, Winston et al. 2014). We therefore attempted to independently estimate sediment age from our sediment composition data.

The C/N ratios in the top sediment layers (0–10 cm) were constant with an average ratio of 9.4 ±0.7 (n=10) at St. 1 (Fig. 4.3). The ratios increased at a depth of 14 cm below which they remained constant with an average ratio of 40.1 ±1.4 (n=10). This value is characteristic for land-derived plants (Meyers 1994, Meyers and Ishiwatari 1993). Inversely, the low C/N ratios observed in the upper part are common in lacustrine sediments (average 8.9; Murase and Sakamoto 2000, approximately 10; Koszelnik et al. 2008).

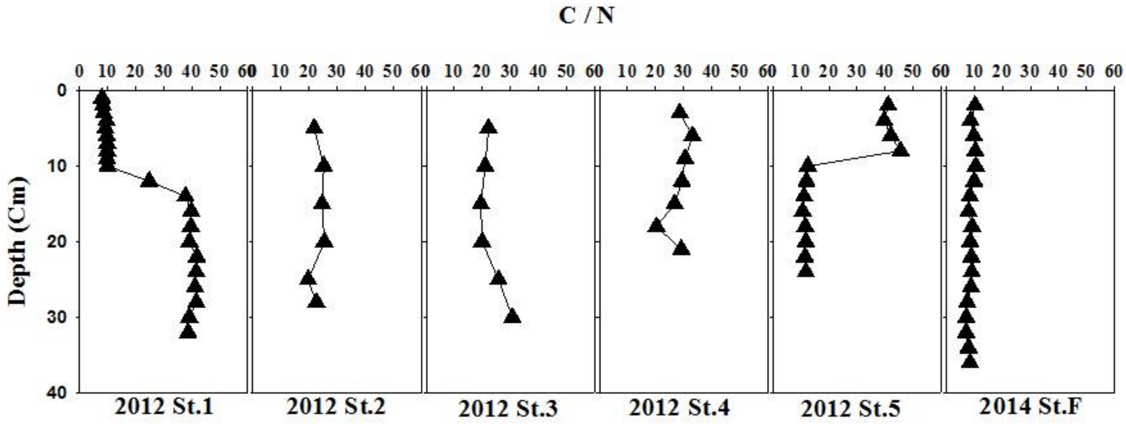

Figure 4.3 Vertical profiles of C/N ratios in cores from St. 1 to 5 and St. F.

This pattern is reflected also by the vertical distribution of the C contents at St.1 which is identical to the C/N ratio (Fig. 4.3 and 4.4). The C contents were constant down to a depth of 10 cm with a mean value of 2.7 ±0.4 % (n=10) and sharply increased to a constant value of 14.8 ±1.4 % (n=10) below 14 cm depth. The C content decreased again slightly below 20 cm.

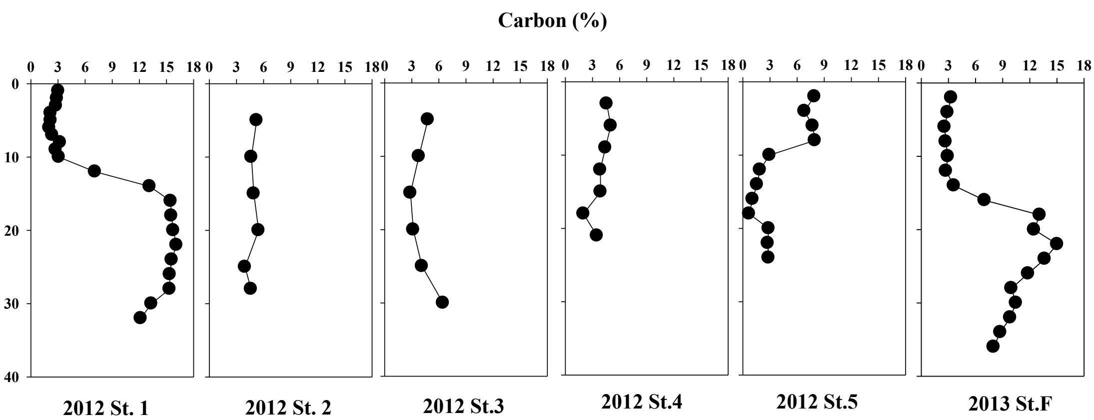

Figure 4.4 Vertical profiles of C contents in cores from St. 1 to 5 and St. F

Similar trends were observed in the vertical distribution of the C isotope signature (Fig. 4.5). $\delta^{13}C$ values displayed some variation from the surface to 12 cm depth ranging between –26.3 and –23.7 ‰. Below the 12 cm depth, the $\delta^{13}C$ values remained constant with an average value of –25.0 ±0.1 ‰ (n=10). The values of $\delta^{15}N$ were distinctly higher above a depth of 12 cm than below that depth with much more variability between 4.7 ‰ at the top surface and 6.5 ‰ at 12 cm depth (Fig. 4.6). A strong decrease in $\delta^{15}N$ values occurred in the bottom part below 12 cm depth to values of 4.0 ‰ at 28 cm depth (Fig. 4.6).

The vertical distributions of P, S, Fe, and Mn showed much variability above a depth of 13 cm while the concentrations leveled off to constant values below that depth with average concentrations of 1,101 ±31.4 mgP kg^{-1} (n=11), 897 ±38.6 mgS kg^{-1} (n=11), 1,258 ±43.8 mgMn kg^{-1} (n=11), and 51 ±0.3 gFe kg^{-1} (n=11), respectively (Fig. 4.7).

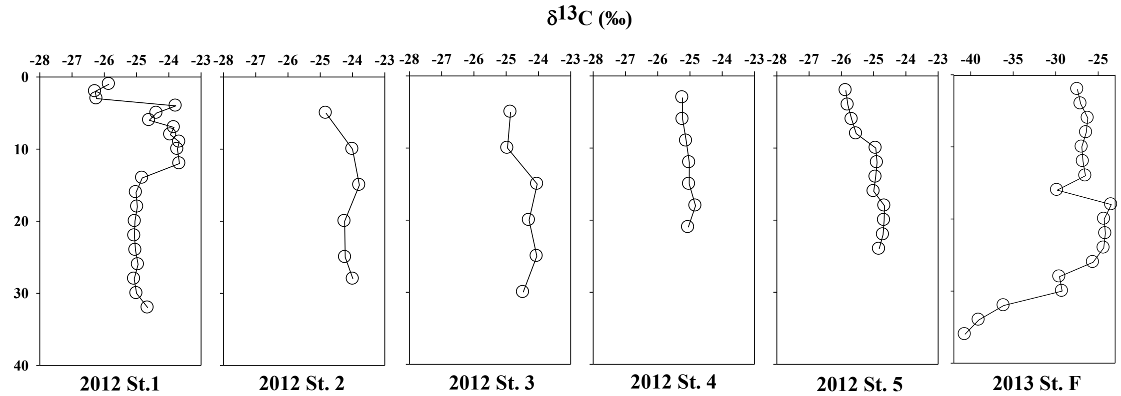

Figure 4.5 Vertical profiles of $\delta^{13}C$ in cores from St. 1 to 5 and St. F

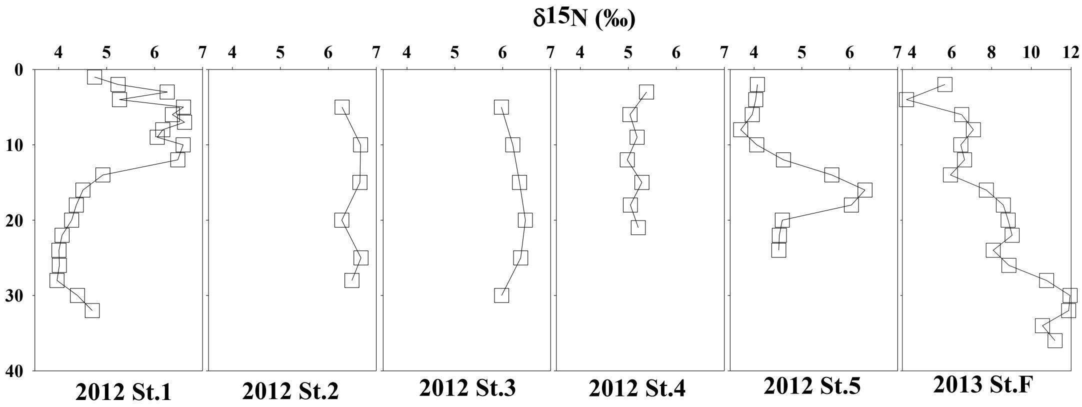

Figure 4.6 Vertical profiles of $\delta^{15}N$ in cores from St. 1 to 5 and St. F

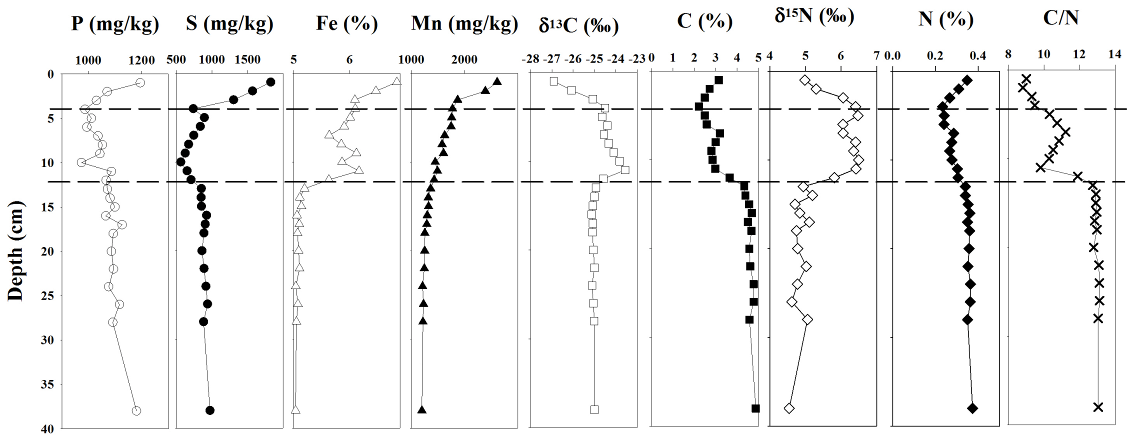

Figure 4.7 Vertical profiles of P, S, Fe, Mn, C/N ratio, C, N, and its isotopes in core at St. 1 (dotted-lines indicates presumed dam construction point (lower line) and an assumed boundary line between before and after agricultural lands expansion starting point (upper line))

A similar splitting of the sediment as indicated by the biogeochemical signatures is displayed by the vertical grain size distribution (Fig. 4.8). The D 90 value at St. 1 had a minimum of 15 µm above 12 cm which increased again towards the sediment-water interface. Below 12 cm, the D 90 value matched a grain size corresponding to the sand fraction (>63 µm). Such a splitting in grain-size distribution of Soyang Reservoir sediments has already been described earlier to distinguish between the pre- and post construction phase (Khim et al. 2005, Cheong and Jung 2006).

Considering the features of the vertical distributions of all these parameters, a clear boundary line can be identified at a depth of 13 cm in the core from St. 1, which we attribute to the starting point of flooding of the reservoir in 1973 after the dam construction with an adjusted average sedimentation rate of 0.3 cm yr^{-1} (lower dotted line; Fig. 4.8).

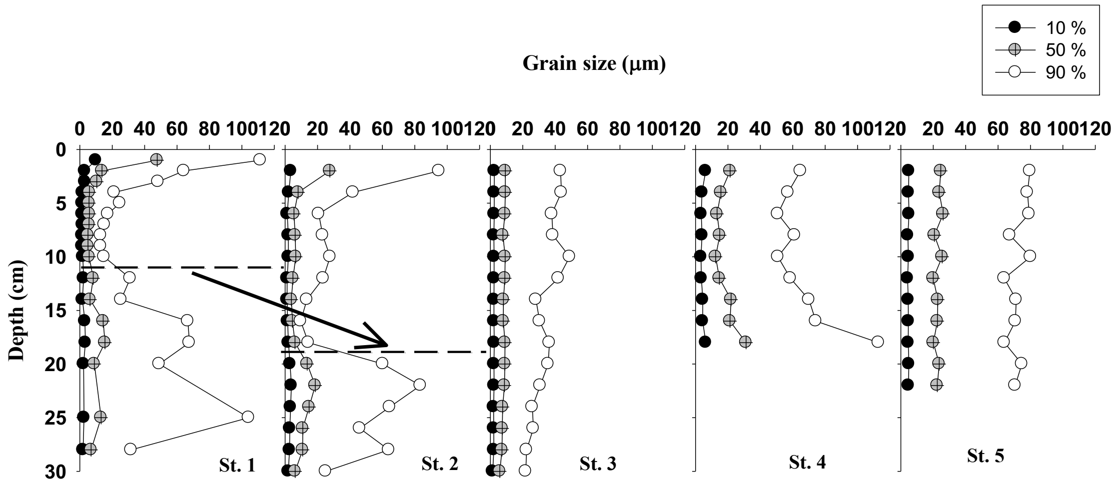

Figure 4.8 Vertical profiles of D 10, D 50, and D 90 values of grain size distributions from cores at St.1 to 5

4.4.2 *Lateral differences in Sediment composition*

The grain sizes at St. 1 and St. 2 had a similar depth distribution (Fig. 4.8). However, the increase of the D 90 value with depth that is also slightly visible for the D 50 value is shifted towards a greater depth at St.2 (about 18 cm; Fig. 4.8) and disappeared at St.3 to 5. D90 values at St.5 are uniform and generally higher compared to depths below 2 cm at St. 1 and 2. We therefore interpret this shift in grain size to be due to higher sedimentation rates closer to the inlet of the reservoir which is a common phenomenon in run-of-the-river reservoirs and has also been described in a previous study in Soyang Reservoir (Khim et al. 2005, Thothong et al. 2011). Cheong and Jung in 2006 found that the sedimentation rate near St. 5 was about 20 times higher than close to the dam in the Soyang Reservoir (Cheong and Jung 2006). The increase of the D 90 values at the top layers of St. 1 and St. 2 presumably reflects a recent change in the deposition pattern and will be discussed below.

C contents are displaying a gradient reversal from St. 1 to St. 5 (Fig. 4.4). A strong gradient existed at St. 1 with low values (3%) at the top 10 cm that increased to 15 % below 16 cm depth. C contents were vertically uniform at St. 2 to St.4 with averages of 4.8 ±0.5 % (n=6), 4.2 ±1.3 % (n=6), and 3.9 ±1.0 % (n=7), respectively, while a sharp decrease was observed at St. 5 at a depth of 10 cm from 7.6 ±0.5 % (n=4) to 2.1 ±0.9 % (n=8) (Fig. 4.4). Apparently, C contents in the top sediment layers decreased from St. 5 to St. 1 (Fig. 4.4). Hence not only sedimentation rates seem to increase towards the inlet of the reservoir but also the amount of deposited carbon changes. Grain size distributions suggest that coarser material was deposited at the inlet area (St.5) containing a high amount of C while finer material carrying a relatively smaller amount of C traveled along the reservoir water to become deposited further downstream (Fig. 4.8).

Surprisingly, the top sediment layers at St. 1 and 2 are enriched in larger particles, which seems contradictory to a particle-size fractionation effect along the reservoir. However, in the last years a turbid current has developed in the reservoirs following heavy rainfalls along with changes in land use in the upper catchment. The turbidity current is known as significant source of allochthonous carbon (Kim and Jung 2007, Lee et al. 2012), nutrients (Jung 2012), and other elements such as Fe and Mn (Hong et al. 1989) transferred from the watershed to the reservoir water. We assume that the materials were deposited closer to the outlet of the dam.

It has been demonstrated that C export from the watershed significantly contributes to the total C input to the Soyang Reservoir during the monsoon period (Namkung et al. 2001, Kim et al. 2000, Jung 2012). C export from the mountainous area in the watershed has even increased recently following a process of agricultural land expansion in the mountainous area (Kim and

Jung 2007). This trend is reflected by the observation that sedimentation rates of both PON and POC were highest in all lake depths after heavy rainfall in the summer season (311 mgN m^{-2} d^{-1}, 3,446 mgC m^{-2} d^{-1} in the trap at 20 m depth, 536 mgN m^{-2} d^{-1}, 5,010 mgC m^{-2} d^{-1} in the trap at 50 m depth, and 380 mgN m^{-2} d^{-1}, 3,841 mgC m^{-2} d^{-1} in 80 m depth, respectively; Table 4.1). The increase in C contents in the sediment core at St. 5 (Fig. 4.4) suggests that C exports have increased lately which we attribute to a change in land use since the 2000s. Such land-use change increase is reported to drive soil erosion and to increase loads of SS in the inflowing stream (Kim and Jung 2007, Seo et al. 2013).

C/N ratios in the top sediment layers (above 8 cm) were decreasing from the inlet (>40) to the dam area (<10) indicating a shift from a terrestrial to a limnetic carbon source with increasing distance from the inlet. This observation is supported by the average value of $\delta^{13}C$ in the top sediment (0–8 cm) at St. 5 (–25.7 ±0.1 ‰ (n=4), Fig. 4.5) which is similar to the $\delta^{13}C$ values of topsoil in Soyang watershed (Table 4.2). Similar $\delta^{13}C$ values were determined in the top sediment at St. 1 as shown above. Contrary to site 5, these values could be only found in a few centimeters of the core surface due to the lower sedimentation rate at St. 1 compared to St. 5.

Table 4.1 Sedimentation rates of PON and POC in three layers of Soyang Reservoir

(PON: mgN m^{-2} d^{-1}, POC: mgC m^{-2} d^{-1})

Times (dates)	**At 20 m**		**At 50 m**		**At 80 m**	
	PON	POC	PON	POC	PON	POC
1st (July 4th–16th)	88	920	38	344	72	593
2nd (July 16th–26th)	311	3446	536	5010	380	3841
3rd (July 26th–Aug. 2nd)	36	320	136	1150	113	957
4th (Aug. 22nd –Sep. 23rd)	20	165	72	586	66	546
5th (Sep. 23rd –Oct. 17th)	-	-	50	355	51	368

Table 4.2 Average values of $\delta^{13}C$ and $\delta^{15}N$ in various sources in Soyang reservoir and the watershed environment – literature reviews and referring personal data (s.d.: standard deviation)

source	year	$\delta^{13}C$	s.d.	$\delta^{15}N$	s.d.	references
soil	2007	–23.4	0.8			Lee et al. 2012
leaf litter	2007	–24.9	1.5			Lee et al. 2012
phytoplankton (diatom)	2007-2009	–32.0	2.5			Lee et al. 2012
phytoplankton (blue green algae)	2007-2009	–22.6	1.7			Lee et al. 2012
zooplankton (pre monsoon)	2007-2009			6.6	2	Lee et al. 2012
zooplankton (post monsoon)	2007-2009			4.3	1.5	Lee et al. 2012
watershed topsoil	2012	–26.4	0.9			Jung's data (n=81) unpublished
watershed topsoil	2012			3.2	1.5	Jung's data (n=81) unpublished

4.4.3 *Sediments matching changes in Soyang Reservoir water quality*

From a limnological point of view the Soyang reservoir history can be divided into 4 periods according to changes in the trophic state of the reservoir, which is well documented by variations of water quality parameters, i.e. Secchi disk (SD) depth, Chl. *a*, and SS (Table 4.3).

Table 4.3 History of trophic state changes and important events in Soyang Reservoir since the dam construction in 1976 - literature reviews

Period	Trophic state	Year	Events (ref.)
1st	Oligo-	1973-1985	Dam construction completed (1973) Onset of Fish farms setup (1980) Emerging turbid water in entire depth caused by intensive monsoon rainfall (1984)(Kim et al. 1989)
2nd	Eutro-	1986-1999	Fish farm expansion, The first advert of bluegreen algae (Anabena spp. in 1986; Cho et al. 1991, Lee et al. 1998) Blue green algal bloom during late summer (Sep.) in 1986-1989 (Kim et al. 1989) Hypolimnetic oxygen deficit since 1987 (Hong et al. 1989, Kim et al. 1989) Massive bluegreen algae growth with SD only 0.7 m in 1990 (Jung 2012, Kim and Jung 2007) Most C loads in 1990 in 15 years, 1986-2000, (42421 tC y^{-1}; Namgung et al. 2001) Cyanobacterial bloom in 1992, 1995 (Pack et al. 1998) Meso-eutrophic state based of TSI (trophic state index) in 1993 (Kim et al. 2001) Increased turbid water input with allochthonous C from the reservoir watershed in 1996 (Kim et al. 2000) Fish farm eliminations since 1998 and anabaena cells decreased in 3 year, 1996-1998 (Kim et al. 1999) Massive turbid water entered after intensive rainfall in summer in1999
3rd	Meso/ Oligo-	2000-2005	Phytoplankton species change (cyanobacteria to dinoflagellates and chrysophytes) Oligotrophication sign based on nutrient concentrations, phytoplankton species and transparency data. Increase in P load since 2000 from watershed (Kim and Jung 2007, Jung 2012)
4th	Meso/ Eutro-	2006-2012	After typhoon, Turbid water out released from the dam to the downstream for over 6 months in 2006 (Kim and Jung 2007) Frequent turbid water inflow from watershed after monsoon climate summer rainfall

The dam construction had been completed in 1973 and the reservoir has been impounded after the construction. The reservoir had remained in an oligotrophic state during the 1st period (1973–1985) before fish-farm business had started. The reservoir had then experienced eutrophication with frequent blue green algal blooms and the lowest SD values after summer rainfall in the 1980s and early 1990s (SD was as low as 0.7 m in 1989 during an algal bloom; Kim et al. 1989, Kim et al. 2001, Jung 2012). The trophic state has changed into meso/eutrophic conditions during the 3rd period (2000-2005) after the fish-farm business was banned in the reservoir followed by an increase in transparency of reservoir water. SDs were 5.1 ±1.8 m (n=12) in 2012 and 4.5 ±2.2 m (n=12) in 2013 respectively (data not shown).

The reservoir history is also reflected by the distributions of elements in the sediment. As outlined above clear changes in element composition followed the dam construction. However, the element composition does not match the periods distinguished by the history of water quality data (Fig. 4.7). Rather, a remarkable increase in the concentrations of all studied elements occurs in the top sediment layers above 4 cm depth (upper dotted-line; Fig. 4.7), where P, S, Fe, and Mn even reached their maximum values. This concentration increase seems to reflect the increased export of soil material from the watershed following an expansion of agricultural activity since the 2000s (Kim and Jung 2007). Soil disturbances by an increasing use of agricultural machinery since the late 1990s as well as the practice to apply external soil material to improve soil quality in the upper catchments facilitated soil erosion along with the expansion of agriculturally used areas in this watershed (Park et al. 2010, Jung 2012, Jun 2015). $\delta^{13}C$ values (– 25.9 to –26.3 ‰) as well as $\delta^{15}N$ values (4.7 to 5.2 ‰) are corresponding to values measured in top soils in the watershed ($\delta^{13}C$ = –26.4 ±0.9 ‰ (n=81); Jung, unpublished data, $\delta^{15}N$ = 3.2 ±1.5 ‰ (n=81); Meusburger et al. 2013 in Table 4.2).

The change in the composition of the youngest sediment layers is also reflected by a recent change in reservoir water quality data, which severely deteriorated since 2006 along with massive inflow of turbid water (Kim and Jung 2007, Park et al. 2010, Jung 2012). In both of the years studied, the SS concentration increased in the metalimnion after heavy rainfalls following turbid current inflow and it remained high in the hypolimnion after the monsoon season in 2013 reaching the maximum SS concentration within the 2 years (49.1 mg L^{-1} in July; Fig. 4.9).

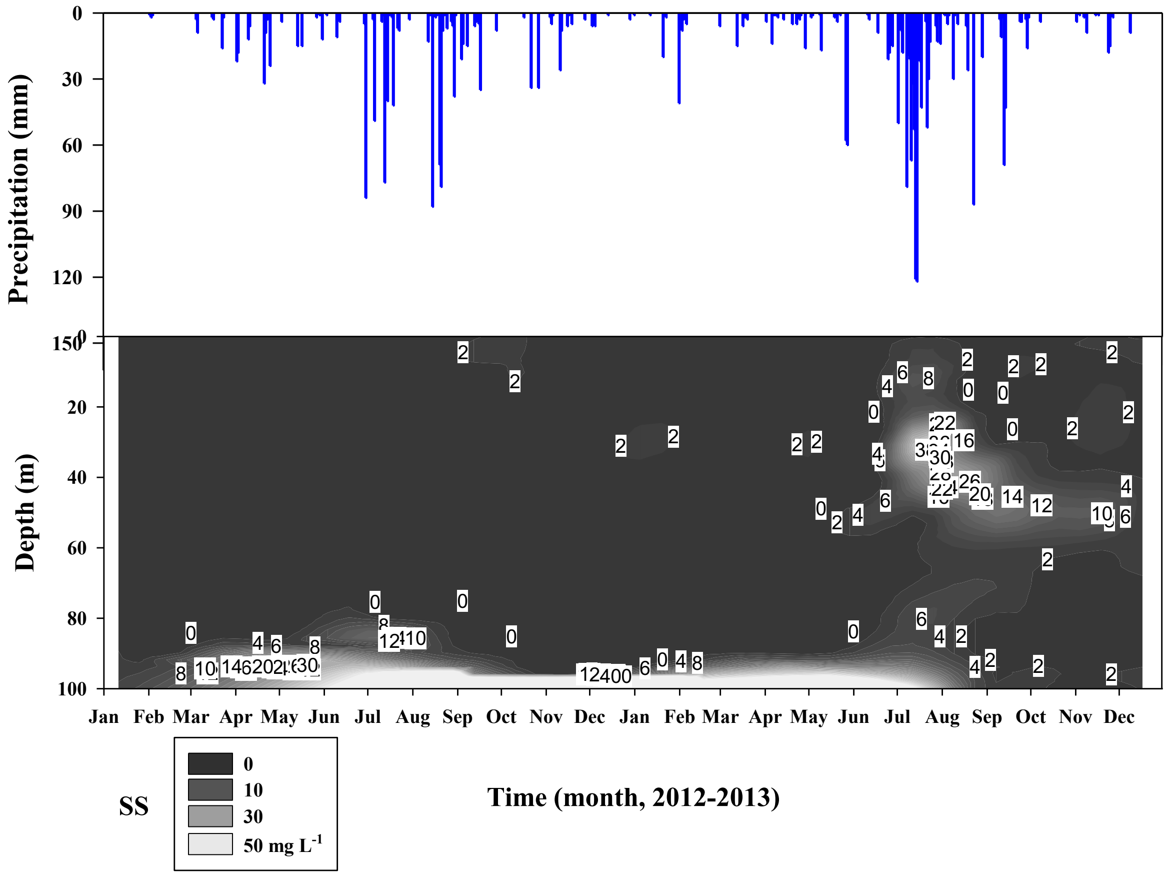

Figure 4.9 Variations of precipitation amounts in Soyang Reservoir watershed (Chuncheon Si) and suspended solids (SS) distributions of Soyang Reservoir for 2 years

Development of a dense population of cyanobacteria during the autumn season (Aug.-Sep.) became an annual characteristic in the reservoir (Kim et al. 1999, Choi et al. 2001, Srivastava et al. 2015). It is regarded to be fuelled by the inflowing turbid water from the watershed contributing to nutrient supply to phytoplankton before becoming released from the reservoir or deposited in the bottom sediment (Lee et al. 2012). However, based on its average Chl *a* concentrations in the epilimnion for 2012 and 2013 (3.4 ±2.3 μg L^{-1} (n=60) in 2012 and 2.8

±2.6 μg L^{-1} (n=60) in 2013, respectively) the trophic state of the reservoir would be regarded to be oligotrophic (Wetzel 2001). Surprisingly, The Chl *a* concentrations in the lake water has drastically decreased compared to the concentrations in the 1990s implying less contribution of autochthonous organic matter relative to allochthonous organic matter to deposition of the bottom sediment.

In contrast to St. 1, signals of autochthonous eutrophication are clearly visible in the sediment core from Station F, which reflects a fjord isolated from the main inflow and being strongly affected by fish farming. Therefore, the biogeochemical signals in the core strongly differ from those in the main body of the reservoir. Similar to the core from St. 1 a strong gradient in C content was visible increasing from 3.0 ±0.4 % (n=7) in the top layers to 10.9 ±2.5 % (n=11) below 14 cm (Fig. 4.4). It appears that only autochthonous carbon contributed to the bottom sediment at St. F compared to St. 1 even though the distance between two sites is only about 3 km (Fig. 4.1). In contrast to St. 1 also the N content in the sediment from station F increased below 14 cm (Fig. 4.10) making the vertical distributions of C/N ratios remarkably constant and indicative of algal sources. This assumption is supported by the vertical C and N isotope distributions which were completely different between the two sites (Fig. 4.5 and 4.6). $\delta^{13}C$ values at St. F drastically decreased with depth from –25.6 to –40.1 ‰ below 26 cm showing an opposite trend compared to St. 1. Massive algal blooms had been frequently observed during the period of fish farming (Lee et al. 1998) which resulted in the deposition of phytoplankton depleted in $\delta^{13}C$ compared to terrestrial plants (Hamilton and Lewis Jr. 1992, De Junet et al. 2009). $\delta^{15}N$ signals increased gradually downward from the surface (5.7 ‰) to the bottom (11.2 ‰) of the core from St. F (Fig. 4.6), Such an an increase has been attributed to eutrophication in reservoirs and lakes (Filstrup et al. 2009, Winston et al. 2014). Indeed, the values of $\delta^{15}N$ found in bottom sediment at St. F were similar with the value of $\delta^{15}N$ from fertilizer sources (10–25; Teranes and Bernasconi 2000).

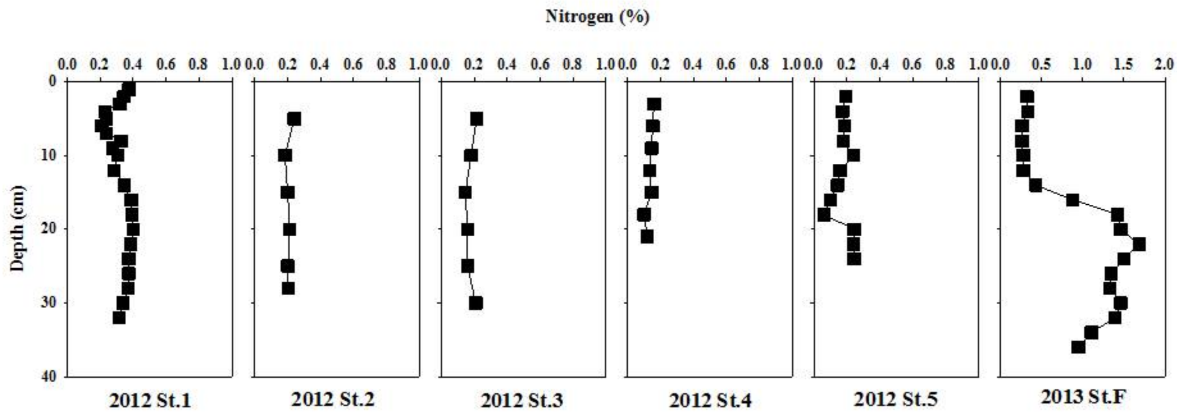

Figure 4.10 Vertical profiles of N contents in cores from St. 1 to 5 and St. F

4.4.4 *Indicators for a growing influence of external watershed-based processes on sediment composition and future water quality.*

Our data are clearly demonstrating the influence of the catchment on sediment composition and sediment quality in Soyang Reservoir. As a consequence, changes in agricultural activity in the watershed starting in the early 2000s have severely affected the chemical composition of the sediments as reflected by an increase in concentration of catchment borne elements in the top sediment layers. The change in agricultural activity in the Soyang watershed consists mostly of cultivation of former forested slope toes in the agriculturally heavily used upstream catchment (Haean catchment). The catchment is known as a hot spot of agricultural non-point pollution (Kettering et al. 2012, Shope et al. 2013). The steep slopes in the catchment promote loss of soil material and fertilizers during rainy seasons (Lee 2008) which is amplified by an increase in heavy storm events in South Korea (about 90 mm / decade for 30 years, 1973-2007; Choi et al. 2008). In the receiving Soyang river, which is the main inflowing stream to Soyang Reservoir concentrations of nutrients, C, Fe, Mn, and turbidity have therefore increased compared to the period before 1995 (Hong et al. 1989, Kim and Jung 2007, Park et al. 2010, Jung 2012). Nutrient concentrations are showing a trend of increasing concentrations in an inflowing river of the reservoir since 1995 (Fig. 4.11).

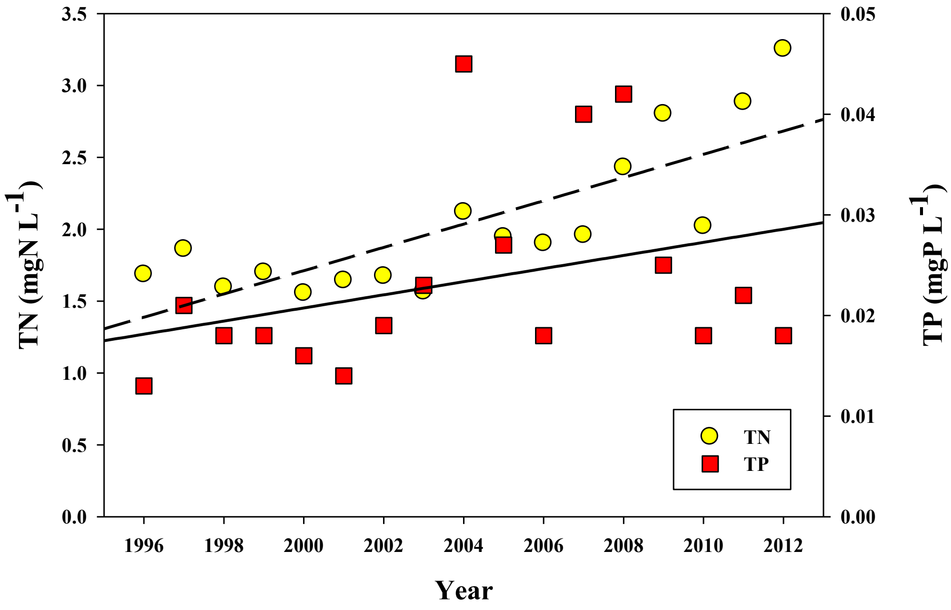

Figure 4.11 Annual variations of TN and TP concentrations in a main inflow stream to Soyang Reservoir (Soyang River) since 1996 (source: www.water.nier.go.kr)

Recently studies focusing on bottom sediment have been conducted with diverse aspects. **Schroeder et al. 2016** looked into diatom assemblages in a core to match the assemblages to chronological history of the watershed and **Cardoso-Silva et al. 2016** studied vertical distributions of heavy metals in cores of a reservoir in Brazil to assess the heavy metal pollution by anthropogenic sources in the watershed. In some studies, Pb contamination was also evaluated by analyzing the vertical profiles of Pb concentrations in sediment cores at reservoirs in China (Zhang et al. 2016) and in South Korea (Lee et al. 2013). In a similar way with this study, some studies have used sediment cores to reconstruct the trophic state change (Fontana et al. 2014) and agricultural intensification (Ni et al. 2015), however it seems that studies, which related in reservoir water process (by water quality monitoring) and watershed activity concurrently, are still limited.

To date, the effect of altered land use in the upper catchment on water quality is only partially visible and future changes are to be expected. The accumulation of redox active substances (Fe, S) in the sediment may impact on nutrient mobility as well as formation of more reduced hypolimnetic water composition during stratification (e. g. sulphide formation). Moreover, already now the accumulation of carbon in the sediments close to the inlet appears to trigger methanogenesis and ebullition of methane. All together, our data are suggesting that Soyang Reservoir is undergoing a regime shift following a change in watershed activities.

4.5 Acknowledgement

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Contribution to the studies

Manuscript 1 (Chapter 2)

Authors: Kiyong Kim, Bomchul Kim, Jaesung Eum, Bumsuk Seo, Christopher L. Shope, Klaus H. Knorr and Stefan Peiffer

Title: Impacts of land use change and summer monsoon climate on nutrients and sediment exports to stream water quality in an agricultural catchment

Journal: Water Research

Status: ready to submit

Own and author contributions statement:

Own contribution: concept and study design 50%, data acquisition 50%, analyses of samples 50%, data analyses and figures 90%, discussion of results 70%, manuscript writing 70%

K. Kim, B. Kim, S. Peiffer, and C. L. Shope designed the research

K. Kim, J. Eum, and B. Seo performed the field research and analyzed the data.

Samples were analyzed in the **Kangwon National University**, South Korea

K. Kim, C. L. Shope, B. Seo, S. Peiffer, and B. Kim interpreted and discussed results.

Figures and tables were created by **K. Kim**

K. Kim wrote the first draft of the manuscript.

The manuscript was revised and finished by **K. Kim, C. L. Shope, S. Peiffer, and B. Kim**

Manuscript 2 (Chapter 3)

Authors: Kiyong Kim, Bomchul Kim, Klaus H. Knorr, Jaesung Eum, Youngsoon Choi, Sungmin Jung, and Stefan Peiffer

Title: Potential effects of sediment processes on water quality of an artificial reservoir in the Asian monsoon region

Journal: Inland Waters

Status: accepted (31st December 2015)

Own and author contributions statement:

Own contribution: concept and study design 60%, data acquisition 70%, analyses of samples 70%, data analyses and figures 80%, discussion of results 60%, manuscript writing 70%

K. Kim, B. Kim, K. H. Knorr, and S. Peiffer designed the research

K. Kim, J. Eum, Y. Choi, and S. Jung performed the field research and analyzed the data.

Samples were analyzed at the **Hydrology department in University of Bayreuth**, Germany and in the **Kangwon National University**, South Korea

K. Kim, B. Kim, K. H. Knorr, and S. Peiffer interpreted and discussed results.

Figures and tables were created by **K. Kim and S. Peiffer**

K. Kim wrote the first draft of the manuscript.

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Manuscript 3 (Chapter 4)

Authors: Kiyong Kim, Klaus H. Knorr, Bomchul Kim, Manfred Freichen, and Stefan Peiffer

Title: Reflected Changes of watershed activities in sediment composition of reservoir system under monsoon climate

Journal: Journal of Soils and Sediments

Status: ready to submit

Own and author contributions statement:

Own contribution: concept and study design 60%, data acquisition 70%, analyses of samples 60%, data analyses and figures 80%, discussion of results 60%, manuscript writing 60%

K. Kim, B. Kim, K. H. Knorr, and S. Peiffer designed the research

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Samples were analyzed at the **Hydrology department in University of Bayreuth**, Germany, **Leibniz Institute for Applied Geophysics**, Germany, and in the **Kangwon National University**, South Korea

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(Eidesstattliche) Versicherungen and Erklärungen

(§ 8 S. 2 Nr. 6 PromO)

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